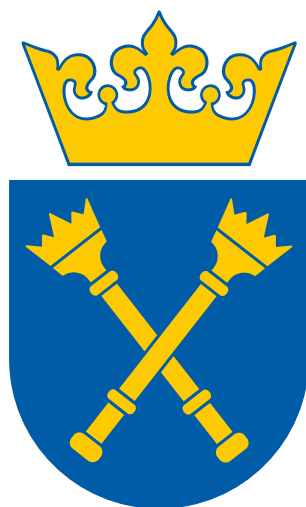


Nanoscale redox processes on surfaces of transition metal oxides: towards memristive and organic applications



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This dissertation is submitted for the degree of
Doctor of Philosophy

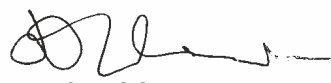
Oświadczenie

Ja niżej podpisany Dominik Wrana (nr indeksu: 1042939) doktorant Wydziału Fizyki, Astronomii i Informatyki Stosowanej Uniwersytetu Jagiellońskiego oświadczam, że przedłożona przeze mnie rozprawa doktorska pt. *„Nanoscale redox processes on surfaces of transition metal oxides: towards memristive and organic applications”* jest oryginalna i przedstawia wyniki badań wykonanych przeze mnie osobiście, pod kierunkiem prof. dr. hab. Franciszka Kroka. Pracę napisałem samodzielnie.

Oświadczam, że moja rozprawa doktorska została opracowana zgodnie z Ustawą o prawie autorskim i prawach pokrewnych z dnia 4 lutego 1994 r. (Dziennik Ustaw 1994 nr 24 poz. 83 wraz z późniejszymi zmianami).

Jestem świadom, że niezgodność niniejszego oświadczenia z prawdą ujawniona w dowolnym czasie, niezależnie od skutków prawnych wynikających z ww. ustawy, może spowodować unieważnienie stopnia nabytego na podstawie tej rozprawy.

Kraków, dnia 01.06.18



podpis doktoranta

*Władca wszechrzeczy nie ulęknie się osoby
ani nie będzie zważał na wielkość.
On bowiem stworzył małego i wielkiego
i jednakowo o wszystkich się troszczy,
ale możliwym grozi surowe badanie.
Do was więc zwracam się, władcy,
byście się nauczyli mądrości i nie upadli.*

Mdr 6, 7-9

*For the Lord of all does not cower before anyone,
he does not stand in awe of greatness,
since he himself has made small and great
and provides for all alike;
but a searching trial awaits those who wield power.
So, monarchs, my words are meant for you,
so that you may learn wisdom and not fall into error;*

Wisdom 6: 7-9

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To my daughter Ola, for teaching me responsibility and for being such an adorable dumpling.

To my wife Anna, I owe you everything.

Abstract

Transition metal oxides are playing an increasing and critical role as functional components in various fields of energy conversion and storage, in electronics: displays, sensors, memories and in (photo)catalysis. The reason behind their versatility is the fact their electrical, optical, magnetic and catalytic properties depend sensitively on their defect structure and oxygen non-stoichiometry, which is governed by the redox processes.

This dissertation is devoted to understanding of the underlying processes of reduction-oxidation happening at the nanoscale. To provide an insight into a broader class of transition metal oxides, two prototypical oxides were chosen for investigations: rutile titanium dioxide TiO_2 and perovskite strontium titanate SrTiO_3 . Within the scope of this work all significant means of reduction were examined: thermal, sputtering-induced and via doping. In order to investigate redox processes only, all experimental procedures were performed under ultra-high vacuum conditions.

Main results are recalled in five papers, published in peer-reviewed international journals.

It has been found that reduction and oxidation of TiO_2 and SrTiO_3 is in most cases limited to the surface region only, leaving crystal bulk unaffected. Depending on the reduction degree structural changes are induced, regarding at first point and extended defects, then a surface layer and finally ending in a new suboxide phases formation. Such transformations can be reversed at the very initial stage via oxidation, which was proved to hinder the work function and conductivity of the $\text{SrTiO}_3(100)$ surface even for as low exposure as a few Langmuirs.

Key findings from this thesis comprise the discovery of so-called extremely low oxygen partial pressure (ELOP) mechanism of transition metal oxide decomposition and then a controlled formation of suboxides, on the example of conductive TiO nanowires emerged on the surface of $\text{SrTiO}_3(100)$, which hold a high technological potential.

So far, conductivity and work function maps of reduced transition metal oxide surfaces had been regarded highly inhomogeneous, however here it was proved possible to create an uniformly conductive reconstruction on the surface of Nb-doped TiO_2 , due to the thermal reduction.

Finally, redox processes at the surface of $\text{TiO}_2(110)$ were discovered responsible for the different growth modes of a model *para*-hexaphenyl molecule and via them a control over thin film morphologies towards optoelectronic applications could be gained.

Streszczenie

Tlenki metali przejściowych odgrywają kluczową, coraz poważniejszą rolę w przemyśle. Są stosowane w wielu dziedzinach, takich jak przetwarzanie i magazynowanie energii, w produkcji wyświetlaczy, sensorów, pamięci w komputerach oraz w (foto)katalizie. Przyczyną takiej różnorodności jest możliwość kształtowania ich właściwości elektrycznych, magnetycznych, optycznych oraz katalitycznych poprzez kontrolę stopnia zdefektowania, dzięki reakcjom redukcji-utleniania.

Niniejsza praca doktorska jest poświęcona zrozumieniu działania procesów redukcji-utleniania w skali atomowej. W celu przedstawienia efektów, które mogą być przeniesione na szeroką gamę tlenków metali przejściowych, do badań wybrano dwa reprezentatywne tlenki: tytanian strontu w strukturze perowskitu (SrTiO_3) oraz ditlenek tytanu w strukturze rutylu (TiO_2). W ramach pracy skupiono się na najważniejszych metodach redukcji, czyli redukcji termicznej, indukowanej wiązką jonową oraz redukcji poprzez domieszkowanie. W celu zapewnienia jak najczystszych warunków eksperymentalnych oraz by ograniczyć wpływ czynników zewnętrznych, większość prac przeprowadzono w warunkach ultra-wysokiej próżni. Rezultaty badań są przedstawione w postaci cyklu pięciu artykułów opublikowanych w międzynarodowych czasopismach naukowych.

W toku prac zaobserwowano, iż procesy redukcji i utleniania w tlenkach takich jak TiO_2 i SrTiO_3 następują preferencyjnie na ich powierzchniach, pozostawiając niezaburzone wnętrze kryształu. Postępująca redukcja wpływa początkowo na wzrost defektów punktowych i rozciąglonych, następnie następują transformacje powierzchni, doprowadzając w dalszej perspektywie do powstania nowych zredukowanych faz krystalicznych. Początkowe stadia transformacji powierzchni mogą zostać odwrócone poprzez proces utleniania, co wykazano na przykładzie zredukowanej powierzchni $\text{SrTiO}_3(100)$, gdzie ekspozycja kilku langmuirów tlenu natychmiastowo obniżyła przewodnictwo i zmieniła pracę wyjścia.

Jednym z kluczowych odkryć tej pracy jest opisany efekt ekstremalnie niskich ciśnień parcyjnych tlenu (ang. *Extremely low oxygen partial pressure* - ELOP), powodujący dekompozycję kryształu tlenku metalu przejściowego i powstanie nowych zredukowanych faz. Zostało to przedstawione na przykładzie wytworzenia przewodzących nanodrutów z TiO na powierzchni $\text{SrTiO}_3(100)$, dzięki obecności materiału obniżającego ciśnienie parcyjne tlenu.

Do tej pory przewodnictwo oraz praca wyjścia na powierzchniach tlenków metali przejściowych były uważane za wysoce niejednorodne. W niniejszej pracy udało się jednakowoż uzyskać jednorodnie przewodzącą powierzchnię, dzięki redukcji termicznej domieszkowanego niobem ditlenku tytanu.

Procesy redukcji-utleniania okazały się także kluczowe w zrozumieniu wzrostu cienkich warstw organicznych na powierzchniach $\text{TiO}_2(110)$. Okazało się, że morfologia powstałej warstwy molekuł *para*-heksafenyłu może być kontrolowana poprzez stopień niestechiometrii podłoża.

Reasumując, dzięki результатам przedstawionym w niniejszej pracy udało się pogłębić zrozumienie procesów redukcji i utleniania tlenków metali przejściowych. Ponieważ skala zastosowań materiałów takich jak TiO_2 czy SrTiO_3 jest porażająca, może to w konsekwencji pomóc w polepszeniu wydajności w zastosowaniach elektronicznych czy katalitycznych.

Abbreviations

TMO	Transition Metal Oxide
UHV	Ultra High Vacuum
RT	Room Temperature
VCM	Valence Change Mechanism
RS	Resistive Switching
LRS	Low Resistance State
HRS	High Resistance State
ReRAM	Resistive Random Access Memory
ELOP	Extremely Low Oxygen partial Pressure
STM	Scanning Tunneling Microscopy
AFM	Atomic Force Microscopy
C-AFM	Contact Atomic Force Microscopy
NC-AFM	Non-Contact Atomic Force Microscopy
LC-AFM	Local-Conductivity Atomic Force Microscopy
TM-AFM	Tapping-Mode Atomic Force Microscopy
KPFM	Kelvin Probe Force Microscopy
CPD	Contact Potential Difference
6P	<i>Para</i> -hexaphenyl / <i>Para</i> -sexiphenyl
2DEG	Two-Dimensional Electron Gas
XPS	X-ray Photoelectron Spectroscopy
LEED	Low Energy Electron Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
HAADF	High-Angle Annular Dark-Field
EELS	Electron Energy Loss Spectroscopy
EDX	Energy-Dispersive X-ray spectroscopy

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Chapter 1

Preface

1.1 Thesis structure and overview

This dissertation presents research conducted on the properties of transition metal oxide surfaces and shows ways to tune them with use of nanoscale redox processes, towards potential memristive and optoelectronic applications. Main results are recalled in five scientific papers published in international peer-reviewed journals.

Thesis is divided into four parts:

- Chapter 1 - **Preface**

In this chapter a thesis scope and composition are presented.

- Chapter 2 - **Introduction**

Chapter provides a general overview of the literature on the transition metal oxides, redox processes, most important applications and chosen experimental methods.

- Chapter 3 - **Results**

This chapter contains preprints of five published papers on nanoscale redox processes on surfaces of TiO_2 and SrTiO_3 single crystals. Chapter begins with a general overview, which helps to understand most important ideas behind this research. Before each article a short summary and highlights are provided.

- Appendices A and B - **Experimental details and supplementary information**

In the appendix A most important details of experimental procedures and setups used in the showcased research are depicted. Appendix B contains additional information on the papers not included in this thesis and conference contributions presented by the Author.

Papers included in the thesis:

1. **In Situ Study of Redox Processes on the Surface of SrTiO₃ Single Crystals**
Dominik Wrana, Christian Rodenbücher, Wojciech Bełza, Kristof Szot and Franciszek Krok
Applied Surface Science, 2018, 432 A,
Reference no. [1]. Cited through the text as [STO_Redox]
2. **Stability and Decomposition of Perovskite-Type Titanates upon High-Temperature Reduction**
Christian Rodenbücher, Paul Meuffels, Wolfgang Speier, Martin Ermrich, **Dominik Wrana**, Franciszek Krok and Kristof Szot
Physica Status Solidi (RRL) - Rapid Research Letters, 2017, 11(9)
This research was featured on the cover of the Physica Status Solidi journal.
Reference no. [2]. Cited through the text as [STO_Decom]
3. **Bottom-up process of self-formation of highly conductive titanium oxide (TiO) nanowires on reduced SrTiO₃**
Dominik Wrana, Christian Rodenbücher, Benedykt R. Jany, Oleksandr Kryshtal, Grzegorz Cempura, Adam Kruk, Paulina Indyka, Krzysztof Szot and Franciszek Krok
Nanoscale, 2018
Reference no. [3]. Cited through the text as [STO_TiO]
4. **Tuning the Surface Structure and Conductivity of Niobium-Doped Rutile TiO₂ Single Crystals via Thermal Reduction**
Dominik Wrana, Christian Rodenbücher, Mariusz Krawiec, Benedykt R. Jany, Jakub Rysz, Martin Ermrich, Kristof Szot and Franciszek Krok
Physical Chemistry Chemical Physics, 2017, 19,
This research was highlighted on the cover of the Physical Chemistry Chemical Physics journal.
Reference no. [4]. Cited through the text as [TiO2_Nb]
5. **Growth of para-Hexaphenyl Thin Films on Flat, Atomically Clean versus Air-Passivated TiO₂(110) Surfaces**
Dominik Wrana, Markus Kratzer, Konrad Szajna, Marek Nikiel, Benedykt R. Jany, Marcin Korzekwa, Christian Teichert and Franciszek Krok
Journal of Physical Chemistry C, 2015, 119 (29),
Reference no. [5]. Cited through the text as [TiO2_6P]

Presented thesis has a form of series of publications, which share a common denominator, but touch on the different aspects of nanoscale redox processes on transition metal oxides surfaces: TiO_2 and SrTiO_3 . To help the reader to follow up the idea behind the thesis, here a graphical representation of all five papers is revoked (Fig. 1.1). Publications are presented in the clockwise order, beginning from the research on reduction-oxidation processes on the SrTiO_3 surface.

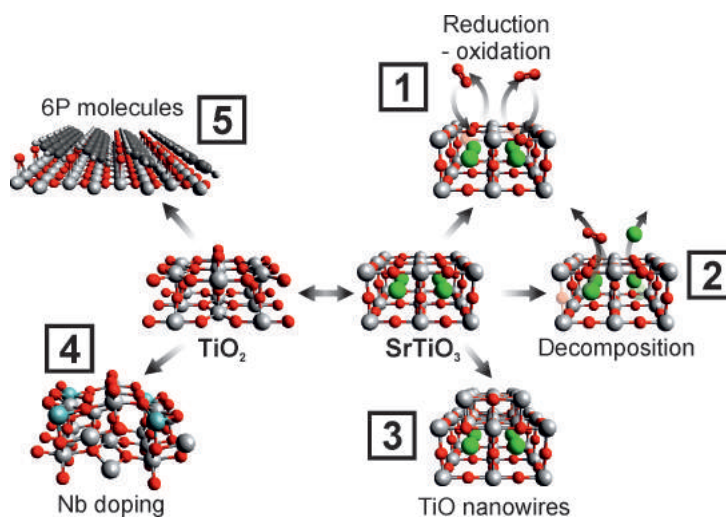


Figure 1.1. Graphical representation of the thesis composition.

1.1.1 Contribution to the papers

According to enclosed forms, the personal contribution of Author (DW) is as following:

1. Paper 1: SrTiO_3 - reduction-oxidation

DW was the first and leading author of the paper, as well as the corresponding author. Author has planned and designed research, including novel method of the *in situ*, *in operando* work function tracking upon oxidation. All experimental results were collected by DW, excluding 4-point resistivity measurements and XPS spectra. Thesis author prepared all images, after thorough analysis and described them in the text, having written the whole text. DW carried on the peer-reviewing process.

2. Paper 2: SrTiO_3 - decomposition

DW made a substantial contribution to this paper, being however a co-author. Thesis author has participated in the manuscript preparation and in the peer-reviewing process. DW has contributed to the data analysis and interpretation. Additionally, author cooperated in the experimental realization of the SrTiO_3 decomposition. This paper, even without the main role of DW in the publishing process, constitutes an important link between papers 1 and 3 and serves as the introduction to the ELOP mechanism.

3. Paper 3: SrTiO_3 - TiO nanowires

DW was the first and leading author of the paper, as well as the corresponding author. Thesis author has designed the research and introduced the concept of the ELOP mechanism. DW has prepared dozens samples with TiO nanowires formed on SrTiO_3 and made

a substantial majority of experimental results. All STM, NC-AFM, LC-AFM, TM-AFM, LEED and SEM images were collected by DW. DW contribution involved carrying on analysis and interpretation of results, literature overview and manuscript writing. Thesis author has guided the communication within all co-authors and peer-reviewing process.

4. Paper 4: TiO₂ - Nb doping

DW was the first, leading author of the paper and the corresponding author. Design of the research and majority of experimental results were obtained by the author, including: undoped and Nb-doped TiO₂(110) crystals preparation in the UHV system, annealing to various temperatures, *in situ* STM, LC-AFM, KPFM and LEED measurements. SIMS profiling was done with the presence of DW. Author has performed analysis, drawn conclusions and prepared a manuscript, after thorough literature study. DW handled peer-reviewing process and designed the showcasing graphic for the PCCP cover.

5. Paper 5: TiO₂ - 6P molecules

DW was the first and leading author of the paper (journal policy did not allow to be a corresponding author without a PhD). All experimental procedures were conducted by DW, in order: TiO₂ crystal mounting and handling into UHV system, cycles of cleaning, characterization of TiO₂(110) surfaces by means of STM, NC-AFM and LEED, deposition of submonolayer coverages of 6P molecules on *as prepared* surfaces, characterization of morphology of formed 6P structures: islands and nanowires - *in situ* and also *ex situ* with use of NC-AFM, TM-AFM and SEM respectively. All images were prepared by DW as well as whole text was written. DW has also supervised the peer-reviewing process.

1.1.2 Funding

During the course of PhD studies, author has received numerous stipends and grants, both internal and state. Funding, apart from covering costs of research on site, enabled for the participation in international conferences (with over 10 oral talks presented by DW on international conferences, listed in the Appendix B) and many scientific visits in leading research centers such as Montanuniversität Leoben in Austria, Università degli Studi di Genova in Italy and Forschungszentrum Jülich in Germany (stays for over eight months). Amongst funding sources the support from the Polish National Science Center, covering expenses of this research, is hereby acknowledged:

Number	Role	Name
2016/21/N/ST5/01313	PI	PRELUDIUM: Reduction in SrTiO ₃ and TiO ₂ single crystal oxides: sputtering and annealing impact on electronic and structural properties
2017/24/T/ST5/00427	PI	ETIUDA: Nanoscale electronic and chemical properties of semiconductor surfaces and its influence on growth of organic nanostructures

Chapter 2

Introduction

The rapid progress in the fields of energy conversion, organic electronics as well as the information storage and computing is not only fueled by purely technological improvements but rather by scientific discoveries of new materials and methods. Advances in the chemical synthesis and material sciences has opened countless possibilities for the design of new compounds, allowing also for tuning their properties in many ways. In the recent years, the huge amount of attention has been attracted by the class of materials called transition metal oxides (TMOs), mostly due to the availability, interesting physical and chemical properties but most importantly, their tunability.

Transition metal oxides exhibit manifold properties comprising resistive switching [6], high temperature superconductivity [7], piezoelectricity [8], ferroelectricity [9], magnetism [10], thermoelectricity [11], multiferroicity [12], as well as applications in neuromorphic computing [13], optoelectronics [14] and (photo)catalysis [15].

A specific quality which makes TMOs so versatile is the ease to control their properties by changing a cation's reduction state. Typically, transition metal cations are multivalent, therefore can exist in several different valence states, making oxides with different electronic properties and crystal structures. As an example, titanium oxide phases varies from titanium dioxide TiO_2 , through so-called Magnéli phases ($\text{Ti}_n\text{O}_{2n-1}$, $4 < n < 7$), monoclinic Ti_3O_5 , corundum-type Ti_2O_3 , titanium monoxide (TiO) and finally titanium suboxides Ti_2O and Ti_3O . Each of them has different density of electronic states, building up another fascinating feature about titania, which lies in its conductivity span from wide band-gap semiconducting to metallic [16, 17]. Structural transformations as well as insulator-to-metal transitions are possible by tuning the lattice oxygen content (O/Ti stoichiometry), which is controllable by the reduction-oxidation processes. Mentioned changes can happen in the whole bulk but can be also limited to a specific volume of a crystal. Commonly, reduction or oxidation processes are more effective in a surface region and also in the defective regions of the crystal, such as extended defects.

This thesis is dedicated to present ways to utilize redox processes in order to change structural and electronic properties of transition metal oxides. Unlike most literature studies to date, not only one specific property of a material was studied, but the system was approached holistically, taking care of a crystal structure, chemical composition and electronic properties. Presented dissertation contains results from basic studies performed on transition metal oxide crystals,

Table 2.1. Comparison of TiO_2 and SrTiO_3 physical properties [18–20].

Property	SrTiO_3	TiO_2 (rutile)
Atomic density [g/cm^3]	5.12	4.23
Melting point [$^\circ\text{C}$]	2080	1843
Dielectric constant [ϵ_0]	240	85
Thermal conductivity [$\text{W}/\text{m K}$]	12	11.7
Refractive index	2.31-2.38	2.61

focusing on binary and ternary oxides. However, as many applications come into view, the surface properties, governing the efficiency in many technological aspects, were examined with the utmost care in this thesis.

2.1 Transition metal oxides

Transition metal oxides are composed of one (binary oxides), two (ternary oxides) or more cations of transition metals bound to oxygen. They are widely used in the industry, most notably for their catalytic and optoelectronic properties.

Within the scope of this thesis three transition metal oxide materials are intensively investigated: titanium monoxide (TiO), titanium dioxide (TiO_2) and strontium titanate (SrTiO_3), each of them having different physical and chemical properties, which will be introduced in details in next paragraphs. Before this, here some basic properties of two core materials TiO_2 and SrTiO_3 are recalled (Table 2.1). One of the most important feature of both oxides, which is particularly important with regard to redox processes, is the high melting point, allowing to use high temperature annealing under reducing or oxidizing conditions. As for the technological applications, substantial dielectric constants and also colossal refractive indices are of great relevance.

2.1.1 Binary oxides

With the exception of noble gasses, oxygen forms at least one binary oxide with other elements. Compounds with a metal cation bound to the oxygen are called binary oxides. Alkali metals form oxides where bonding mechanism is ionic, whereas for elements with a higher oxidation state (such as Ti) have a covalent nature. In any given period in the periodic table of elements, bonding in binary oxides progresses from ionic to covalent. At the same time their acid-base character goes from strongly basic, through amphoteric (can react both as an acid and as a base, e.g. TiO_2 [21]) to strongly acidic. It helps to understand the huge variety of possible chemical reactions with oxides, as well as different electronic and structural properties. Variety of electronic properties, with an example of Ti, can be also understood in terms of the electron occupancy. Neutral atomic states of Ti are described by the s and d-shell occupancies: Ti: $4s^2 3d^2$. It is known that for strongly correlated systems, the removal of a neutral O atom reduces

the average ionic charge below 4+. [22]. Hence, TiO is a metallic d^2 oxide, Ti_2O_3 is a narrow band semiconductor d^1 oxide and TiO_2 is a d^0 insulator oxide.

Now representatives of two classes of binary oxides will be introduced: dioxides (TiO_2) and monoxides (TiO).

Titanium dioxide TiO_2

Titanium dioxide (especially rutile and its (110) surface) is one of the most studied metal oxides, mostly due to its substantial technological value. In recent years, titanium dioxide has attracted much attention due to its catalytic and photocatalytic properties which lead to a variety of applications [23]. Numerous reviews exist on the subjects of: heterogeneous photochemistry, self-cleaning coatings, dye sensitization, solar energy conversion, photocatalytic water splitting - hydrogen production as well as photochemical air and water treatments. Especially huge interest has started since Fujishima's and Honda's first reports in the early 1970s of the UV-induced redox chemistry on TiO_2 [24]. Wide range of applications is connected to the different structural-related properties of a titanium dioxide. The utilized morphology ranges from nanoparticles of various shape and size, porous films, polycrystalline materials to single crystal structures. As for the crystal structure, titanium dioxide occurs in nature in form of rutile, anatase and brookite minerals. The most abundant and most widely investigated of them is tetragonal rutile, which is chemically stable. This crystal structure is shown in Fig. 2.1. The rutile unit cell consists of two titanium atoms and four oxygen atoms in a tetragonal geometric structure (D_{4h}^{14} - $P4_2/mnm$) with lattice constants $a = 0.4584$ and $c = 0.2953$ [25]. Each Ti atom is surrounded by six O atoms in a distorted octahedral configuration (TiO_6).

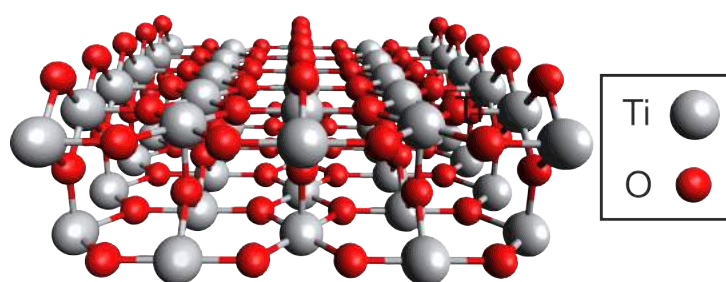


Figure 2.1. Rutile TiO_2 crystal structure, with a (110) surface and a 1×1 reconstruction.

The most stable low-index rutile surface is nonpolar $\text{TiO}_2(110)$, which is the most studied of titania surfaces as well [26]. Exceptional stability is regarded to be founded in the fact that to form this surface the least number of bonds (and the longest) in the crystal structure need to be broken [27], which results in the lowest degree of the coordinative unsaturation [28]. The top-most layer of $\text{TiO}_2(110)$ is charge neutral, containing twice as many oxygen anions O^{2-} as titanium cations Ti^{4+} .

The surface contains both Ti and O atoms with two different kinds of coordination. In the surface plane, asymmetry is induced by atomic rows going in the $[001]$ direction. Five-fold coordinated (5f) Ti atoms alternate with rows of six-fold coordinated (6f) Ti atoms separated by

rows of (O_s) oxygen atoms (see Fig. 2.2 a. Ti_{6f} atoms are bound to two-fold bridging oxygen atoms (O_b), which stick out from the surface. The unit cell of the (1×1) reconstruction is $a = 0.649$ nm and $b = 0.296$ [15]. In the STM picture (Fig. 2.2, empty states), bright rows are assigned to 5-coordinated Ti^{4+} atoms and dark ones are identified as bridging oxygen rows [20].

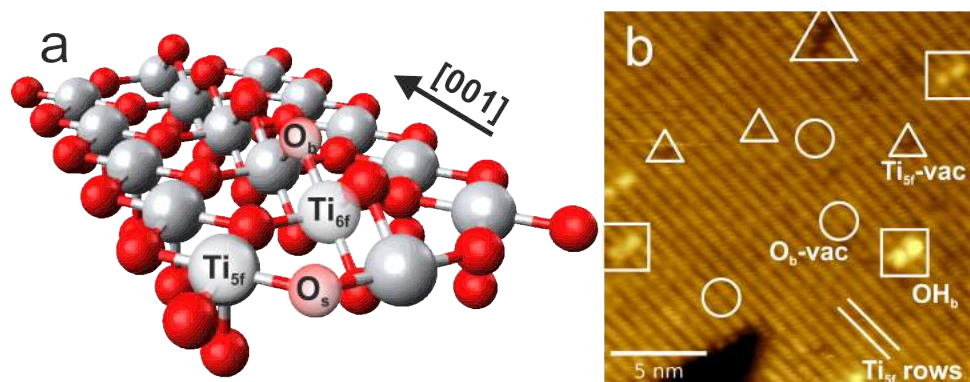


Figure 2.2. $TiO_2(110)$ surface structure. a) Identification of differently coordinated titanium and oxygen atoms, b) STM empty states image of the $TiO_2(110)$ surface showing most abundant surface defects: oxygen vacancies (circles), surface hydroxyl groups (squares) and titanium vacancies (triangles).

Defects in oxides: TiO_2 Few words need to be written here about a defect structure in oxides. Generally point defects are most abundantly present in transition metal oxide crystals - more frequently vacancies (Schottky disorder) than interstitials (Frenkel disorder) - see Fig. 2.3. Such defects occur in isolation due to the increase of entropy in the crystal (intrinsic point defects), mostly at the stage of a crystal growth and preparation (where redox processes play a key role). During crystal growth the high-temperature distribution of point defects are frozen when cooled fast, but in fact point defects would also be present in an ideal crystal at RT. Zero-dimensional defects may be also formed to balance the presence of an aliovalent cation impurity (extrinsic point defects) - as it is for the case of Ti interstitials in the Nb-doped TiO_2 crystal [TiO_2_Nb]. In general, defect concentration in oxides can be calculated as a function of temperature and oxygen partial pressure p_{O_2} . Equilibrium defect concentration vs. p_{O_2} is typically illustrated in a so-called Brouwer diagram, where concentrations under simplified limiting cases of dominating defects are plotted. Such diagram for Nb-doped TiO_2 is presented in the section 2.2.3.

Not only 0D features are present in oxides, defects may agglomerate and propagate throughout the crystal, making extended defects. Amongst one-dimensional defects the most noteworthy class regards dislocations: edge, screw or a dislocation loop. An edge dislocation can be imagined as the end of an extra half plane introduced midway through the perfect crystal matrix, whereas in a screw dislocation atoms are arranged in a helical pattern which is normal to the direction of the distortion (as illustrated in Fig. 2.3).

A single dislocation is described by the direction and by the Burgers vector, which represents the magnitude and direction of a lattice distortion induced by the dislocation presence. Generally, a dislocation line cannot end inside of a crystal but at the surface - inner or outer. The exception

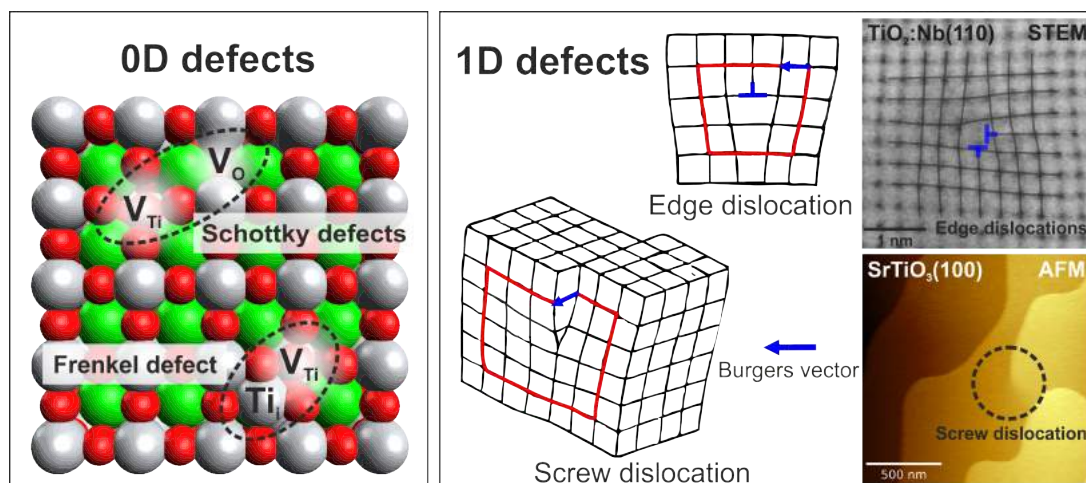


Figure 2.3. 0D and 1D defects comparison. Point defects: Schottky and Frenkel defects. Extended defects: edge and screw dislocations, exemplified additionally on the BF-STEM image of the reduced $\text{TiO}_2\text{:Nb}(110)$ and AFM topography image of the reduced $\text{SrTiO}_3(100)$ surface.

is a node, where three or four dislocation lines meet. Dislocations can perform movements (gliding, pinning, climbing) inside a crystal, which is governed by the electric, thermal and stress gradients [29]. Typical number of dislocations on a rutile TiO_2 surface is in order of 10^5 per cm^2 TiO_2 [30] to 10^7 per cm^2 [31], depending on the growth process. Typically, in a cut and polished single crystals dislocations form a hierarchical tree, with the higher density the closer to the surface. Such order is easily visible for instance on a cleaved plane of a reduced TiO_2 [32]. In transition metal oxides dislocations can be also induced with use of a plastic strain engineering, giving rise to the density up as high as 10^{10} per cm^2 for the case of SrTiO_3 [33].

Regarding properties, dislocations are less chemically stable than the matrix, therefore are preferentially etched, making easily detectable etch pits [31]. Since some d^0 Ti states are reduced to d^1 close to the dislocation cores in TiO_2 and SrTiO_3 , a surplus of electrons is created, making them more conductive than the matrix [34, 35]. In the classical picture, oxygen vacancies are created at the dislocation having positive charge which are then screened by electrons in a space charge layer around the dislocation. Noteworthy, dislocations get easily reduced when subject to the thermal reduction [34], which is a property widely investigated in the thesis [STO_Redox] [STO_TiO][TiO2_Nb].

Oxide crystals host also higher dimensional defects: 2D and 3D. A typical 2D defects are outer or inner surfaces (e.g. at voids in the crystal), stacking faults, grain boundaries and shear planes. 3D defects are constituted by voids themselves, pores and new phases (precipitates).

Let's return for a moment to the titanium dioxide crystal and a situation of a typical surface investigation. Point defects are common on the surface of $\text{TiO}_2(110)$: the most abundant are oxygen vacancies ($\text{O}_b\text{-vac}$) and surface hydroxyls (OH_b), both identified in Figure 2.2 b. These defects appear as bright features in the STM, with OH_b having much brighter contrast. Rarely, dark features assigned as titanium vacancies ($\text{Ti}_{5f}\text{-vac}$) are present. Defects on the TiO_2 surface are often desirable, and play a key role in various catalytical processes. Oxygen vacancies act as

trapping centers for electrons and are then negatively charged, being preferential sites for a water adsorption [36, 37].

As for its macroscopic properties, stoichiometric rutile TiO_2 is a transparent yellowish insulating crystal which becomes blue and finally dark blue upon reduction [25]. Stoichiometric TiO_2 has a wide bandgap of 3.1 eV, which makes it translucent for a visible light, however reduction induces band gap narrowing, due to the emergence of Ti 3d (related to Ti^{3+} interstitials) states 0.76 eV below the conduction band [20, 38]. That makes TiO_2 a perfect material for a band-gap engineering towards making efficient catalytic devices and solar cells [39]. Defects presence affects not only optical properties but primarily electronic, namely charge carriers concentration and electric transport. In the undoped TiO_2 two representatives of donor type defects occur: predominantly oxygen vacancies and minority of them are titanium interstitials. As a rule of thumb introduction of oxygen vacancies and titanium interstitials acts as a n-type doping of a crystal, whereas least abundant titanium vacancies induces p-type behavior.

The reason making TiO_2 so promising application-wise is the ease of introducing defects via self-doping of oxygen vacancies or other metals doping. Oxygen vacancies can be created either via sputtering or heating, when the TiO_2 crystal is heated above 500 K [40], whereas cations with a oxidation state greater than 4+ (n-type doping) or below (p-type doping) can be introduced during crystal growth or via ion implementation. More detailed description on this subject is provided in the section 2.2.1.

Titanium monoxide TiO

As it was previously stated, there are many stable titanium oxide phases, with a reduced titanium oxidation state. When the oxygen nonstoichiometry ratio O/Ti is close to 1 and therefore dominant valence state is Ti^{2+} , a titanium monoxide crystal is formed. It has an exceptionally stable structure - depending on the stoichiometry, different crystal structures have been found which are all closely related to the NaCl structure. Two most prominent of them is monoclinic α -TiO and cubic γ -TiO phases. Cubic rock-salt phase of a TiO(100) crystal is depicted in Fig. 2.4.

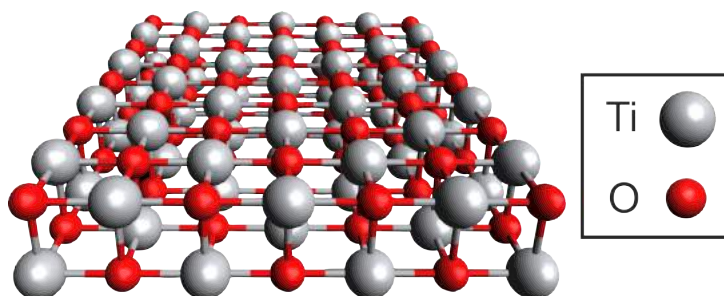


Figure 2.4. Titanium monoxide $\text{TiO}(100)$ crystal in a cubic rock salt structure.

Due to the presence of vast structural vacancies, TiO has a broad region of chemical and structural homogeneity from $\text{TiO}_{0.80}$ to $\text{TiO}_{1.25}$ and behaves as a typical d-metal [41, 17]. Among all titanium oxides, the highest bulk conductivity, of $1000 \text{ S}\cdot\text{cm}^{-1}$ was reported for TiO [42]. While being metallic, TiO exhibits also weak paramagnetism [42].

Titanium monoxide does not form as abundant minerals as TiO_2 , only a rarely spotted mineral named Hongquiite, which has a crystal structure close to the structure of TiC , found in the platinum ores in Hongqui in China [43]. Pure TiO fabrication is based mostly on costly top-down techniques, such as laser irradiation [44, 45], ion [46] or electron [47] beam bombardment of other compounds, TiO_2 especially. Other methods involving reduction at extremely high temperatures as 2000°C have been reported [48]. Mentioned methods lack in control over either crystal structure or sizes of fabricated particles. A new method, called extremely low oxygen partial pressure (ELOP) has been introduced as a result of the presented PhD work, to overcome many of those limitations [STO_TiO].

To date, very little research has been devoted to the surface properties of TiO . Only LEED investigations confirming cubic surface reconstruction of a $\text{TiO}(100)$ could be found [46]. Real space imaging of the surface, defects species and concentration as well as conductivity had been unknown until they were just studied in a research constituting this thesis [STO_TiO].

Recently, a huge effort is put to explore titanium monoxide superconducting properties. It has been found that, the superconductive transition temperature T_c raises from below 1.3 K for TiO with 15% vacancy concentration, through 5.5 K for stoichiometric rock-salt TiO to 7.4 K for thin TiO films[49–51]. TiO finds an application also in the energy storage, where addition of nanospheres was found beneficial for lithium-sulfur batteries efficiency [52]. Recent works have also proposed a memristor-like device specifically based on TiO , which would be forming-free (one preparation step would not be necessary) [53].

2.1.2 Ternary oxides

Having two cation metals in their structure, ternary oxides can undergo plenty of structural transformations, while the stoichiometry of an oxide changes by varying the relative concentrations of the two components and their oxidation states. This opens manifold new possibilities in the material design, since each particular oxide has different properties.

Within the broad class of ternary oxides the most commonly investigated structures are perovskites, with the formula of ABO_3 . Substantial stability of perovskites is caused by the disproportion of cation sizes: element "A" has a much larger ionic radius than "B". In the ideally symmetric case, perovskite adopts a cubic cell: the "A" cation sits in the center (0,0,0), type "B" cation occupies the body-centered positions (e.g. $1/2, 1/2, 1/2$), whereas oxygen sits at face-centered positions ($1/2, 1/2, 0$) - see Fig. 2.5. At the $\langle 001 \rangle$ surfaces ABO_3 crystals commonly have two distinct terminations: AO or BO_2 , which have different chemical and electronic properties. For instance, a huge variability of the work function depending on the termination is reported [54]. Perovskites are naturally present around us: a perovskite mineral

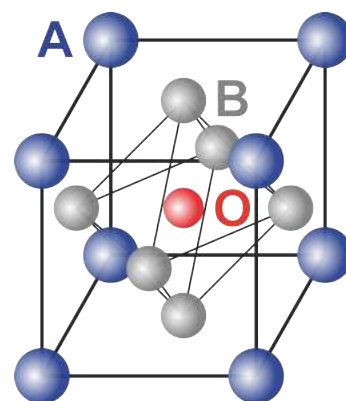


Figure 2.5. ABO_3 perovskite crystal structure.

bridgmanite ((MgFe)SiO₃) is considered the most abundant mineral on Earth, constituting up to 38% of its volume.

Ternary perovskites find a great variety of applications as piezoelectric and ferroelectric materials [55]. Perovskites are also commonly used in the solar cell technology, methylammonium lead halides especially, having reached efficiency greater than 25% for the tandem design [56]. Moreover, there are many approaches to use also perovskite heterostructures based on transition metal oxides, such as LaVO₃/SrTiO₃ [57].

SrTiO₃

The most studied crystal and regarded as a representative of all perovskite oxides is strontium titanate, having a cubic structure in RT, hence being dielectric. SrTiO₃ crystal structure can be regarded as a system of TiO₆ octahedra (which makes it in many ways similar to TiO₂) with Sr atoms being placed between them. Another useful perspective is to view it as an arrangement of alternating planes of SrO and TiO₂ in <100> directions (see Fig. 2.6). Bonding within the SrTiO₃ crystal is mixed covalent-ionic, with Ti⁴⁺-O²⁻ bonds within octahedron being covalent and Sr²⁺-O²⁻ mainly ionic [58]. At room temperature SrTiO₃ crystal structure is cubic. A distortion from cubic to lower symmetries occurs if the temperature is lowered or if a foreigner cation/dopant is introduced in the lattice (e.g. by an ion implantation) [59].

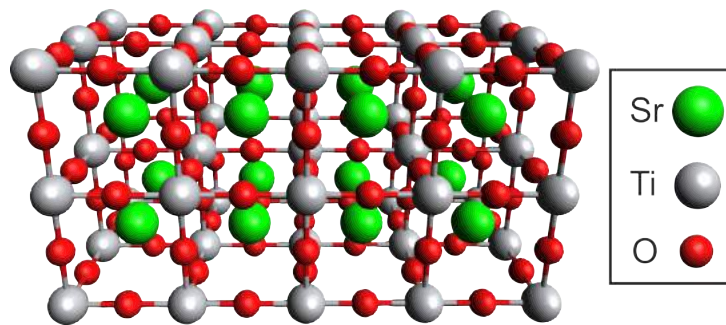


Figure 2.6. Crystal structure of a strontium titanate SrTiO₃(100).

SrTiO₃ is an excellent substrate for an epitaxial growth of high-temperature superconductors (e.g. cuprates such as Y-Ba-Cu-O [60], for the lanthanum aluminate-strontium titanate heterostructures design and 2DEG gas investigation LaAlO₃/SrTiO₃ [61]) or other oxide-based thin films (e.g ferromagnetic oxides [62]. Moreover, STO finds many applications also as a prototypical resistive switching material [63]. Strontium titanate, similarly to TiO₂, shows a VCM (valence change mechanism - see section 2.3.1) underlying mechanism of resistive switching, connected with the oxygen vacancies movement [64]. Moreover, perovskite transition metal oxides are often regarded most suitable materials for the uncovering of exotic electronic properties. Up to now, one of the questions remaining open in the search of topological exotic states has been whether a 2D polar metal can exist. Recently however, a realization of a room temperature two-dimensional polar metal of the tri-layer superlattices BaTiO₃/SrTiO₃/LaTiO₃ has been presented [65].

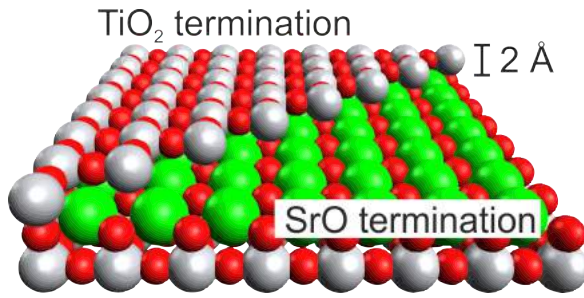


Figure 2.7. TiO_2 and SrO terminations of $\text{SrTiO}_3(100)$.

oxide films and perovskite heteroepitaxial layers [66]. Moreover, high-mobility two-dimensional electron gas (2DEG) between grown LaAlO_3 and SrTiO_3 substrate is formed for the TiO_2 termination only [61].

Defects in SrTiO_3 It is important to provide here some basics of defects concentration in strontium titanate. In an undoped SrTiO_3 three kinds of vacancies can in principle exist: oxygen, strontium and titanium. At very low oxygen partial pressures, oxygen vacancies (which are counterbalanced by conduction electrons) are predominant [67]. Oxygen vacancy formation becomes much more efficient at higher temperatures, above 500°C . The formation of strontium vacancies becomes relevant at temperatures above 1500°C , whereas the formation of a titanium vacancy is rather unlikely due to the high formation energy [68]. Conductivity of a SrTiO_3 crystal evolves accordingly to the changes of vacancy concentrations. For the high enough temperatures ($> 1000^\circ\text{C}$) conductivity changes from n-type at reducing conditions (governed by the concentration by oxygen vacancies) to p-type under oxidizing conditions (driven by the increased Sr vacancy concentration). It is suggested that the oxygen vacancy is a trapping site for a polaron, remaining in a $1+$ charge state and provides one electron to the conduction band, which results in the n-type behavior in SrTiO_3 [69], however this picture is still under debate since other research propose that both electrons freed at the oxygen vacancy form polarons, which are mobile at elevated temperatures [69]. Not only oxygen vacancies play a role in governing macroscopic properties of SrTiO_3 , but also cation defects. Pristine SrTiO_3 has no ferroelectric properties, however for the non-stoichiometric case Ti-Sr antisite defects induce pronounce spontaneous ferroelectric polarization, which can be further tuned by the Sr/Ti ratio variation [70].

As it was already mentioned in the section 2.1.1, strontium titanate hosts also higher dimensional defects such as dislocations. As they get preferentially reduced over the crystal matrix and gain metallic conductivity, their impact on the observed electronic properties is crucial [35]. This can be visualized by the nonhomogeneous conductivity and work function maps of a reduced and oxidized SrTiO_3 surfaces [STO_Redox]. Another important feature, which may help to understand the TiO nanowires formation due to reduction presented in [STO_TiO] is the fact that dislocation cores adopt TiO rock-salt structure [71].

As mentioned, at RT SrTiO_3 crystallizes in the cubic perovskite phase with two distinct surface terminations of the $\langle 100 \rangle$ plane: TiO_2 and SrO (as visualized in Fig. 2.7. For the untreated single crystal, regions with different terminations are randomly distributed, yet under certain conditions one of them is promoted. Precise control over surface termination turned out to be crucial for the growth of thin

Recently a thorough study on the dislocation impact on SrTiO_3 and TiO_2 has been published by Szot et al. [29], where more details on this topic can be found.

2.2 Redox processes

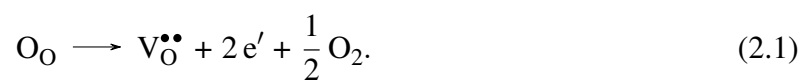
Reduction-oxidation (redox) processes involve all reactions where an oxidation state of atoms changes. It needs the transfer of electrons between species present in the system. When reduction occurs, the electron is gained (oxidation state decreases) and otherwise for oxidation. Redox processes happen all around us and may be treated as desirable (e.g. cellular respiration) or adverse (e.g. corrosion of metals). Focusing on the field of nanotechnology, redox reactions are widely investigated for bio applications (e.g. redox protein design [72]), interfaces and molecular redox films [73] but are most crucial for the transition oxide materials. In their case, vast majority of structural, chemical and physical properties are governed by the oxygen concentration and, subsequently, by the cation oxidation state. In this section, three important effects affecting the oxidation state are described: reduction, oxidation and doping.

2.2.1 Reduction

In general, reduction in an oxide crystal is connected with a decreasing cation oxidation state. It can be realized either by a oxygen excorporation from a matrix or by (either extrinsic or intrinsic) doping. For an oxygen removal a certain amount of energy has to be transferred from the environment, which can be supplied by external stimuli: thermal [74], [STO_Redox] electrical (electrodegradation, electroforming) [75] or ballistic (sputtering) [76], [TiO2_Nb]

Two most common channels of the energy dissipation at oxide surfaces are thermal (annealing) and ballistic (ion beam sputtering). They constitute important ways of sample treatment in nanotechnology, especially when it comes to either tune surface properties or to pattern a material. In fact, the most frequently used procedure of an *in situ* UHV cleaning, in order to obtain flat atomic terraces, consists of subsequent cycles of sputtering and annealing [20].

Generally, during reduction oxygen is emitted from the oxide crystal lattice leaving behind oxygen vacancies and d-electrons, which can be described as follows (Eq. 2.1) [77].



In turn, this leads to a change in the cation oxidation state. It will be exemplified by the titanium oxide situation. Titanium, being a transition metal with a partly filled d-band, can exist in several oxidation states (4+, 3+, 2+, 0). When the oxygen vacancy is formed, remaining two electrons, which were previously involved in the Ti-O ionic bonding, are relocated onto two surrounding titanium atoms, changing their oxidation state from 4+ to 3+ and contributing also to the conductivity increase. Such point defects are randomly distributed in the crystal.

This picture is in force for the initial stages of reduction of a (nearly) stoichiometric crystal. However, it fails for larger departures from stoichiometry. Point defect disorder in TiO_2 and

SrTiO_3 is only valid for relatively low concentrations of defects, which allows the solution of point defects in the crystal to be analyzed in terms of non-interacting defects. This assumption, which is typical of classical statistical physics with randomly distributed defects, fails at concentrations of defects (oxygen vacancies) higher than $x = 0.01\%$ for TiO_{2-x} [78] and $x = 0.1\%$ for SrTiO_{3-x} [79, 31]. For a higher reduction of a crystal, defects cannot be considered in terms of a Schottky disorder [74].

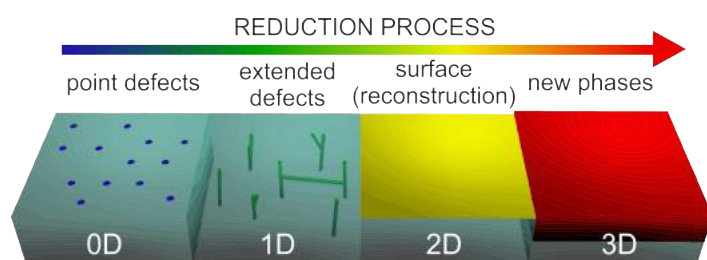


Figure 2.8. Scheme of the reduction process impact on the transition metal oxide.

Therefore, not only uniformly distributed point defects but also vacancy agglomerations leading to phase transformations are to be expected as result of reduction in particular in the surface and subsurface region. It can be viewed as a transformation of a 0D defect system, through 1D, 2D and finally to new 3D crystallographic phases (see this

idea illustrated in Fig. 2.8). As it is postulated, with increasing oxygen depletion at first a linear arrangement of vacancies e.g. Magyari-Köpe defects occurs [80], which can lead to the evolution of a quasi-homogeneous distribution of filamentary structures interacting with existing crystal dislocations as seen by LC-AFM as conducting spots on the surface [32]. Then a formation of Wadsley defects and subsequently crystallographic shear planes within the crystal occurs [81, 82], in which adjacent regions of the crystal are displaced with respect to each other with half a lattice unit in the $\langle 011 \rangle$ direction. Finally, after prolonged reduction, new titanium suboxides such as Magnèli phases can evolve [74], which have been found to have as good electrical conductivity as carbon [83, 84]. Considering the Ti-O system many different suboxides are stable phases, so structural transformations are definitive [20]. Concluding, the fascinating titania characteristics lie in its structural diversity and conductivity span from semiconducting to metallic by tuning the lattice oxygen content (O/Ti nonstoichiometry) [16, 17]

Thermal reduction

Annealing of a transition metal oxide can result in severe O/Ti stoichiometry evolution. Direction of this change is governed by the chemical gradient of the oxygen concentration between the bulk and surface region. When a crystal is placed in the oxygen-depleted environment, vacuum for instance, oxygen diffusion from bulk to surface is triggered. Otherwise holds for oxygen-rich atmosphere annealing. Numerous studies show that oxygen diffusion can be initialized in temperatures as low as 500°C for the case of TiO_2 [85]. Oxygen (oxygen vacancy) mobility is dominant over cation diffusion, which occurs for higher temperature annealing [86]. Literature indicates that Ti cation self-diffusion in TiO_2 is realized by an interstitial-type mechanism with both trivalent and tetravalent interstitial titanium ions contribution [86].

Thermally-induced reduction does not happen homogeneously over the whole crystal. It is widely acknowledged that surface gets reduced faster than a bulk, when subject to the low oxygen partial pressure annealing [74]. At the actual surface of $\text{TiO}_2(110)$, annealing under moderate reducing conditions leads to the reconstruction transformation, from (1×1) to (2×1) , which is Ti-enriched [87]. For a stronger reduction, changes in the O/Ti can be tracked with use of thermogravimetric analysis (TGA), where mass loss due to the oxygen effusion from the sample is measured. When TiO_2 is annealed under very low oxygen partial pressure ($p_{\text{O}_2} = 10^{-20}$ mbar) oxygen diffuses towards surface and flows out of crystal, reaching 1% of a crystal mass loss after 24h at 1000°C [74]. As a result, Magnéli phases are formed, with the highest oxygen nonstoichiometry at the surface [74]. Similar process of thermal reduction under heavily reducing conditions is presented in Fig. 2.9 for the case of Nb-doped TiO_2 (0.5% dopant content), where a typical dependence of a TiO_2 mass loss on time and temperature of vacuum annealing is plotted (adapted from [TiO2_Nb]). Apparently, crystal cannot be treated as stoichiometric after 3 h annealing at 800°C , when oxygen defects concentration exceeds classical limit of 0.01% and new phases are expected, all the more so since non-stoichiometry is concentrated in (sub)surface region. Such severe reduction processes have a pronounce kinetical nature and cannot be treated as purely thermodynamic, since equilibrium could be reached only when the oxygen concentration gradient is removed. For the case of extremely low oxygen partial pressures such would be achieved if a whole TiO_2 crystal is reduced and highly non-stoichiometric oxides are formed and finally situation could end up with almost pure metallic titanium remaining, namely when the oxygen activity inside the crystal is the same as in the surrounding atmosphere.

During thermal reduction of $\text{SrTiO}_3(100)$, its surface accordingly undergoes several structural changes. The termination evolves from mixed TiO_2/SrO towards TiO_2 . At the nanoscale, annealing in ultra-high-vacuum (UHV, $p_{\text{O}_2} < 10^{-10}$ mbar) conditions causes a restoration of

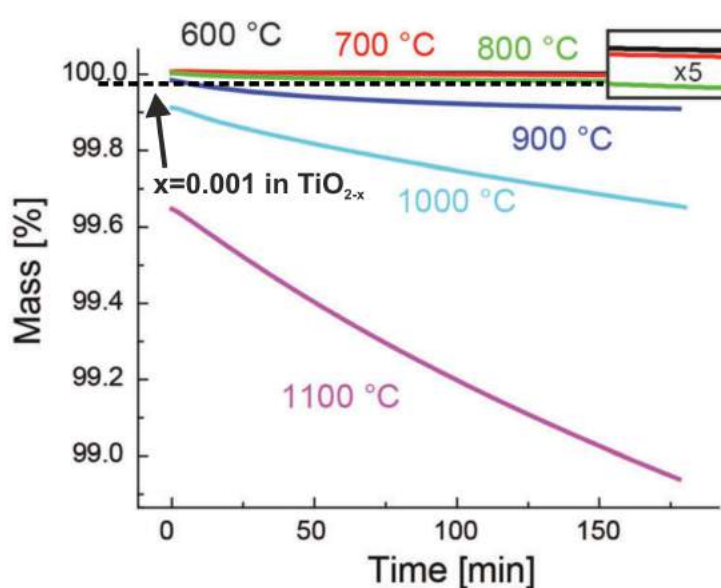


Figure 2.9. $\text{TiO}_2(110):\text{Nb}$ mass loss due to the thermal reduction measured by means of thermogravimetric analysis (TGA). Adapted from [TiO2_Nb].

the long-range atomic order of the (1×1) pattern. However, above annealing temperatures of 900°C , a complex reconstruction of $(\sqrt{13} \times \sqrt{13})R33.7^\circ$ and subsequently $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ appears [STO_Redox], [STO_TiO]. Simultaneously, the chemical composition changes and the surface becomes Ti-rich [STO_Redox], [STO_TiO]. For higher temperatures of reduction (also true for the oxidation) SrTiO_3 crystal undergoes severe crystallographic transformation. This restructuring of the surface region is caused by a dramatic redistribution of material and the formation of nonperovskite phases at elevated temperatures, such as Sr-enriched Ruddlesden-Popper phases [88] for oxidizing conditions and various forms of titanium oxides under reduction [89], [STO_TiO].

Reduction-induced phase transformations are accompanied by the changes in the optoelectronic properties. Annealing of a transition metal oxide crystal under reducing conditions commonly leads to dramatic changes in conductivity. Bringing up the example of SrTiO_3 , even the moderate reduction at 750°C under low oxygen partial pressure ($p_{\text{O}_2} = 10^{-9}$ mbar) results in 10 orders of magnitude drop in resistivity and a gain of metallic behavior of conductivity [35]. This behavior cannot be however understood in terms of homogeneous reduction of a crystal. Given the temperature of 750°C , the total oxygen loss would be much below the limit of 0.01%. Therefore, it is expected that reduction of a crystal is initiated at the filamentary 1D defects, which are assigned as dislocations [35]. In a such scenario, dislocations get easily reduced [34], forming metallic network inside a crystal which is responsible of macroscopic conductivity behavior [35]. Congruent observations have been made for the case of TiO_2 thermal reduction, where conductivity proved to be nonhomogeneous after reduction, with filaments having several orders of magnitude lower resistivity than matrix [74].

Sputtering-induced reduction

Another mean of nanoscale reduction of transition metal oxide surfaces is provided by the ion beam sputtering. It is crucial to understand the influence of ion beam irradiation since it constitutes the widest used way of cleaning the oxide surfaces, such as TiO_2 and SrTiO_3 . Namely, for the case of the atomically flat surface preparation in the UHV, it is necessary to remove top layers of the sample, which are affected by an interaction with air and where easy-diffusive species agglomerate.

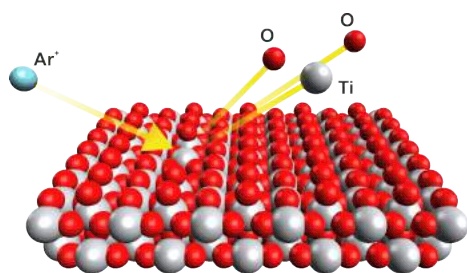


Figure 2.10. Reduction of the TiO_2 crystal induced by the preferential sputtering of oxygen.

The common *in situ* cleaning procedure consists of several cycles of a noble ion beam (Ar^+ , Xe^+ , Ne^+ , Kr^+) bombardment and annealing in vacuum (at 700 – 800°C) until the atomically flat surface is reached [20].

Reduction effect of a transition metal oxide sputtering is related to the uneven sputtering yields for cations and oxygen. Generally, oxygen is preferentially sputtered over a transition metal [90]. For the case of TiO_2 , O/Ti sputtered ratio is approx. 1.3 [91], hence for each ten titanium atoms removed, thirteen oxygen vacancies

are formed. It is schematically drawn in Figure 2.10. From the other perspective, ion beam sputtering results in the preferential removing of oxygen from TiO_6 octahedra and the reduction of the cation oxidation state from Ti^{4+} to Ti^{3+} and Ti^{2+} [76]. Concentration of accordingly created point defects rises and subsequently surface region cannot be treated as a rutile TiO_2 . As a result of prolonged sputtering, a thick conducting layer can be formed at the surface, with a structure resembling Ti_2O_3 [76]. Similar effects were observed for the case of SrTiO_3 , where Ar bombardment resulted in the formation of a metallic oxygen-depleted and Ti-enriched layer at the surface [92]. Thus, by the ion beam sputtering, an insulator-to-metal transition of the surface region of transition metal oxide can be triggered and emergence of a quasi-electron gas can be observed.

Likewise, sputtering is commonly utilized as a mean of a surface nanopatterning. By this top-down technique various nanoscale patterns can be created, such as checkerboard, ripples, pillars or dots, depending on experimental conditions such as incidence angle or temperature [93, 94]. For a polar incidence angle other than normal, anisotropic ripple patterns on oxide surfaces develops. For the case of TiO_2 tunable periodicity and height of such structures can be achieved [95, 96] and then utilized as a substrate for a thin films growth [97–99]. It has been additionally shown that mild sputtering of an atomically flat $\text{TiO}_2(110)$ surface results in the dramatic change in the molecular films morphology [TiO2_6P]. The best efficiency of formation is realized by a grazing incidence $\approx 80^\circ$ off normal. In principle, starting from the normal incidence ion beam irradiation and increasing the angle, sputtering yield (number of atoms sputtered per one ion projectile) increases [100]. It is connected to the fact that the ion energy is deposited closer to the surface and surface atoms receive enough energy to be ejected. However, when angle of incidence is grazing, ion beam is reflected from the surface and energy dissipation decreases greatly. In addition to such basic presumptions an atomic structure and crystallography should be imposed, especially for the cases of oxide surfaces. It can be assumed that the higher sputtering yield at step edges is the main process responsible for the nanoripple formation at the titanium dioxide surface [95].

It is important to elaborate here on the redox processes happening at the oxide surface during cycles of cleaning, especially since the lion share of literature studies are based on such, as well as part of this thesis [TiO2_6P]. As it was already mentioned, sputtering results in the reduction of a surface layer, correlated with the increase of oxygen vacancy concentration. Under typical ion beam fluences (10^{15} - 10^{16} per cm^2) surface gets amorphised and the long-range atomic order disappears (see Fig. 2.11). On

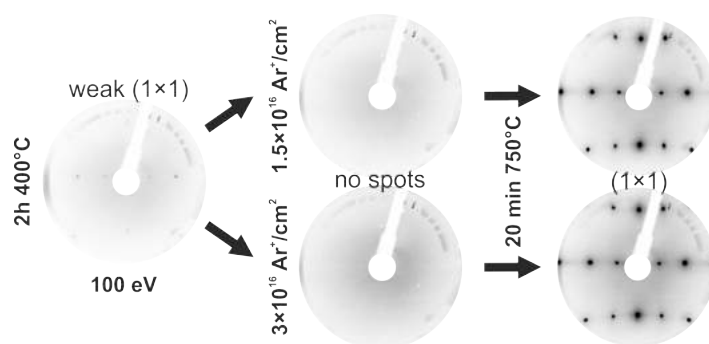


Figure 2.11. Influence of the UHV sputtering-annealing cycle on the $\text{TiO}_2(110)$ surface reconstruction as measured by LEED.

On

the other hand, annealing activates the out-of-plane diffusion of Ti and O [20], which acts in the opposite direction, towards restoring of stoichiometry and atomic arrangement. While TiO_2 is annealed, oxygen atoms diffuse from bulk to surface, filling some vacancies, but above certain threshold temperature (about 800°C , as described in the section 2.2.1) flows greatly from the sample, whereas Ti atoms diffuse to bulk via interstitalcy mechanism [101, 96], however overall stoichiometry is not fully recovered. It is postulated that mostly Ti cations movement causes the partial re-oxidation of the surface [90], which was beforehand reduced by sputtering.

Surface reduction exemplified on the evolution of the sputtered-annealed rutile $\text{TiO}_2(110)$ surface is shown in Fig. 2.12. STM images a - c depict $\text{TiO}_2(110)$ surface after increasing number of sputtering-annealing cycles. Apparently, stoichiometry after cleaning is not recovered, which can be deduced from the rising concentration of surface defects. In addition to point defects: titanium and oxygen vacancies and OH groups, described in the section 2.1.1 a new class of 1D surface defects can be spotted. Observed lines along $[001]$ directions corresponds to the Ti_2O_3 [102] or Ti_2O_3 [103] adatom strands, which are the building blocks for the (2×1) reconstruction. The roughly estimated concentration of all defects is given in the upper right corner of an image, showing the increasing non-stoichiometry of the surface. For comparison, situation after heavy reduction is shown in d), realized by the prolonged UHV annealing at 1000°C - surface structure cannot be resolved anymore. It can be thus concluded that even a standard cleaning procedure can result in severe reduction of the TiO_2 surface, and a great care should be taken to monitor the surface quality.

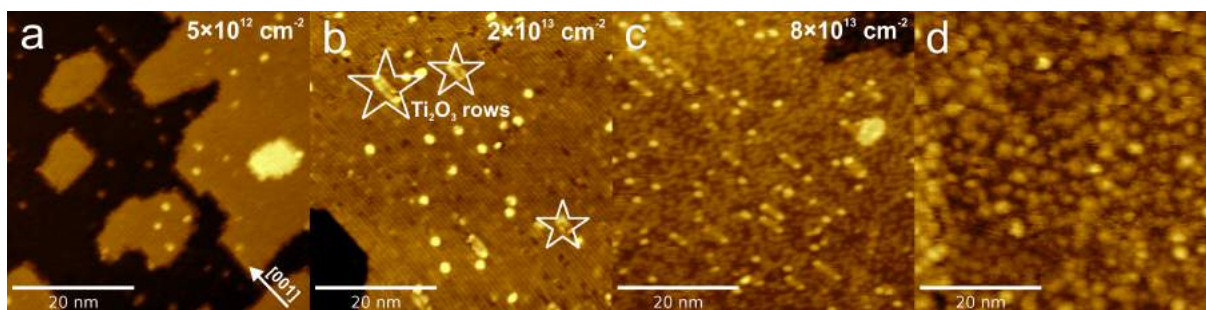


Figure 2.12. Different stages of the reduction of the $\text{TiO}_2(110)(1\times 1)$ surface (STM empty states, $50\times 50\text{ nm}^2$). a) - c) images of a $\text{TiO}_2(110)$ after increasing number of sputtering-annealing (1 keV Ar^+ low fluence sputtering, 780°C annealing) cycles, d) $\text{TiO}_2(110)$ surface after 2h of 1000°C UHV annealing.

2.2.2 Oxidation

Oxidation can be simply understood as a reverse process to reduction. For the case of transition metal oxides it is connected with the restoring of the cation oxidation state, e.g. from $3+$ to $4+$. It is most commonly associated with re-filling of oxygen vacancies. Since in stoichiometric TiO_2 and SrTiO_3 cations have highest valence state, (re-)oxidation occurs when an already reduced material is exposed to a higher oxygen partial pressure or there is an internal oxygen movement inside a crystal (self-healing). It has been already shown that oxygen self-diffusion coefficients increase with increasing non-stoichiometry [104].

While in vacuum, oxygen vacancies, which are common defects of the oxide surfaces can be refilled upon exposure to the oxygen partial pressure or also by the tip-induced oxidation, when strong electric fields between a negatively biased STM tip and a sample causes oxygen atoms movement [40]. By the oxidation one can also control the surface reconstruction. The re-oxidation of slightly reduced $\text{TiO}_2(110)$ surfaces by an exposure to an oxygen pressure of 2×10^{-7} mbar in the temperature range 200-730°C results in the re-growth of TiO_2 overlayers by a diffusion of Ti^{n+} interstitials from the bulk [105]. At a slightly reduced crystal with a (2×1) reconstructed surface the (1×1) islands nucleate within the (2×1) layer and grow laterally. As the (1×1) reconstruction reach a critical size, which is temperature dependent, a new (2×1) layer begins to nucleate on top of it and grow. Such reaction is cyclic and several layers of titanium dioxide can be grown in this way [105].

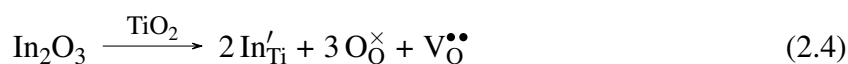
Oxidation is commonly employed to change electronic properties of reduced transition metal oxides. Re-oxidation, realized by supplying 10^6 L dose of oxygen at RT, of the moderately reduced $\text{TiO}_2(110)$ surface results in conductivity hindering by over two orders of magnitude [32]. Since only surface layer is affected by a such reoxidation, this process can be reversed by tip-induced reduction, allowing for the conductivity nanopatterning, which is of great importance for the resistive switching phenomena study [32].

Similar conclusions about re-oxidation can be drawn for the case of reduced SrTiO_3 single crystals [35], where a metallic behavior changes to semiconducting after ambient conditions exposure. As it has been recently shown, even a several Langmuirs dose of oxygen dramatically changes the conductivity and work function of reduced STO surfaces [STO_Redox].

2.2.3 Doping

Reduction of a transition metal oxide material can be viewed as a self-doping with oxygen vacancies. However, oxidation state may additionally be tuned by the introduction of extrinsic defects due to doping of other aliovalent transition metals. Since Ti is tetravalent, doping of TiO_2 or SrTiO_3 with cations with higher valence (such as pentavalent Nb^{5+} and Ta^{5+} or hexavalent W^{6+}) would increase the concentration of electrons, as shown in Eq. 2.2, using the Kröger-Vink notation (where a negative charge is indicated by the prime symbol (A'), whereas a positive charge by a dot ($B^\bullet$)) [106]. Electrons are trapped at Ti^{4+} lattice sites to form Ti^{3+} species as shown in Eq. 2.3. This constitutes an idea of a donor doping, which improves the electrical conductivity of TiO_2 even many orders of magnitude [107]. Meanwhile, when the Ti^{4+} site of TiO_2 is isomorphously substituted by a lower valence cation (e.g. trivalent Ga^{3+} , In^{3+} , and Al^{3+}), an $\text{V}_\text{O}^{\bullet\bullet}$ is generated without forming Ti^{3+} species (Eq. 2.4) [108]. This is referred to as acceptor doping, which can decrease the electron concentration of n-type oxides (Eq. 2.5) [108].





It was shown that donor doping (e.g. of Ta^{5+} and Nb^{5+}) enhances greatly the photocatalytic activity of a rutile TiO_2 . Conversely, acceptor doping of lower valence cations such as In^{3+} and Ga^{3+} decreases photocatalytic activity for O_2 evolution by water oxidation [109], however the mechanisms of doping influence are still under debate.

Electronic properties of a doped oxide are not only affected by the dopant concentration but moreover by the external oxygen partial pressure, hence redox processes. Here a detailed description of the influence of reduction-oxidation conditions on the electronic conductance, exemplified on the case of Nb donor doped TiO_2 , is presented. According to the point defect chemistry model, the concentration of defects in the donor-doped TiO_2 can be calculated based on thermodynamic equilibrium considerations implying the conservation of mass and charge [106]. The defect concentration of an oxide varies with oxygen partial pressure in the surrounding and temperature. Assuming a constant temperature, four different regions can be distinguished [77, 110, 111]. A schematic illustration of the Brouwer diagram showing the defect concentrations as function of the oxygen partial pressure is given in Fig. 2.13.

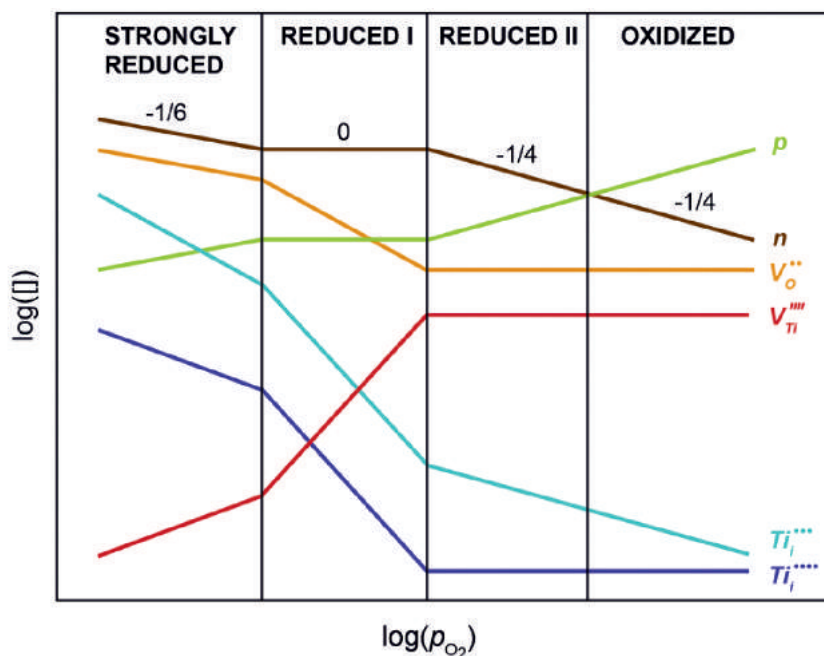


Figure 2.13. Schematic illustration of defect concentrations in $\text{TiO}_2\text{:Nb}$ as function of oxygen partial pressure according to Sheppard [110]. The slope of the electron concentration in the specific regimes is indicated.

Under strongly reducing conditions, the concentration of intrinsic defects significantly exceeds the concentration of extrinsic defects related to the influence of donors. Hence, the major defects under those strongly reducing conditions are oxygen vacancies, similarly as in undoped TiO_2 (at even more reducing conditions, titanium interstitials will be the dominant defects) [112].

Hence, the charge neutrality condition yields $n=2[V_O^{\bullet\bullet}]$ resulting in an electron concentration derived from the law of mass action presented in Eq. 2.6.

$$n_{sr} \propto (p_{O_2})^{-1/6} \quad (2.6)$$

For the moderate reducing conditions (reduced regime I), the charge introduced by the Nb donor substituting Ti is compensated by electrons. The electron concentration is thus equal to the donor concentration $n=[Nb_{Ti}^{\bullet}]$. In this so-called plateau region, the electron concentration does not depend on the oxygen partial pressure:

$$n_{rI} \propto const. \quad (2.7)$$

In the reduced regime II (for increased oxygen partial pressure), the concentration of oxygen vacancies is decreased due to the higher oxygen partial pressure and the donor charge is compensated by titanium vacancies $[Nb_{Ti}^{\bullet}]=4[V_{Ti}^{''''}]$. Using the law of mass action, the electron concentration yields

$$n_{rII} \propto (p_{O_2})^{-1/4}. \quad (2.8)$$

Under oxidizing conditions, the defect disorder is again governed by the intrinsic defects with oxygen vacancies and titanium vacancies being the majority defects. The charge neutrality equation thus yields $[V_O^{\bullet\bullet}]=2[V_{Ti}^{''''}]$ resulting in p-type conductivity while the electron concentrations keeps the proportionality

$$n_{rII} \propto (p_{O_2})^{-1/4}. \quad (2.9)$$

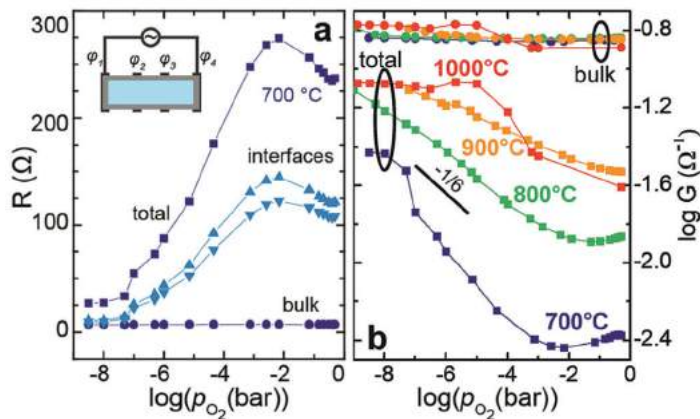


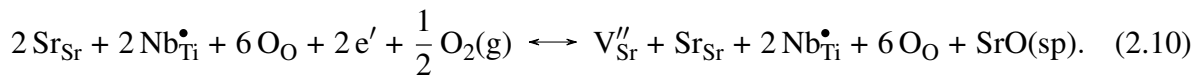
Figure 2.14. Four-point electrical measurement of a Nb-doped TiO₂(110) crystal annealed at a) 700°C and b) 700°C to 1000°C, under variable oxygen partial pressures p_{O_2} . Adapted from [TiO₂_Nb].

This general rule would be now exemplified in a real situation. As can be seen at a plot in the Fig 2.14, adapted from the [TiO₂_Nb], the measured four-point conductance reflecting the bulk properties of Nb-doped TiO₂ did not vary significantly with the oxygen partial pressure and temperature. Since the conductance is proportional to the electronic charge carriers, it can be concluded that the vacuum annealing takes place in the regime “reduced I” and hence an influence of titanium interstitials or titanium vacancies is not expected.

For the surface region instead, the situation is different. Here, a strong dependence

of the conductance on oxygen partial pressure and temperature is observed. This indicates that the surface layer of the Verneuil-grown $\text{TiO}_2\text{:Nb}$ crystals investigated in this study cannot be treated as an ideal crystal and its properties may be influenced by space charges, segregation effects, or extended defects such as linear vacancy clusters or dislocations.

Similar considerations based on the point-defect chemistry can be also written for the case of the Nb doping of a strontium titanate. There is however one crucial difference: a donor doping of SrTiO_3 adds a third cation to the system, which makes a charge compensation mechanism more difficult. Under reducing conditions, this charge is compensated for by the free electrons generation leading to metallic conductivity. Meanwhile, the compensation mechanism under oxidizing conditions results in the formation of strontium vacancies and the segregation of SrO as a secondary phase (sp), which can be written in a complex formula [68]:



2.3 Applications

In this section the most common and crucial applications of transition metal oxides will be presented as well as influence of redox processes on key phenomena governing their applicability.

2.3.1 Resistive switching

Rapidly growing computing performance creates an urgent need for developing new classes of memories, which should be fast, non-volatile and reliable. Non-volatile memory (NVM) is a memory which is capable of retrieving stored information after power is turned off, which saves a great amount of energy. Up to now the most common used NVM class has been NAND flash memories, however their main drawback are slow response times. In the recent years, redox-based resistive random access memory (ReRAM) has been considered as a promising candidate for the next generation of memories, due to its simple device architecture, excellent retention endurance and fast switching (timescales as short as 100 picoseconds for set/reset times in oxide-based ReRAMs have been reported so far [113]). ReRAM devices are further divided into three classes with respect to the redox-related process standing behind switching: electrochemical metallization mechanism (ECM), thermochemical mechanism (TCM) and the key mechanism for transition metal oxides - valence change mechanism (VCM).

A resistive switching device is a two-terminal resistor device, whose resistance state can be changed between high resistance state (HRS) and low resistance state (LRS) by the use of the external voltage (see Figure 2.15a). Commonly, differences between conductivity in LRS and HRS states are several orders of magnitude, which prevents false assignment of a state.

Historically, experimental observations of a similar phenomena in thin oxide films dates back to 1965 [114]. In theory, a conception of the circuit element called ‘memristor’ (memory-resistor)

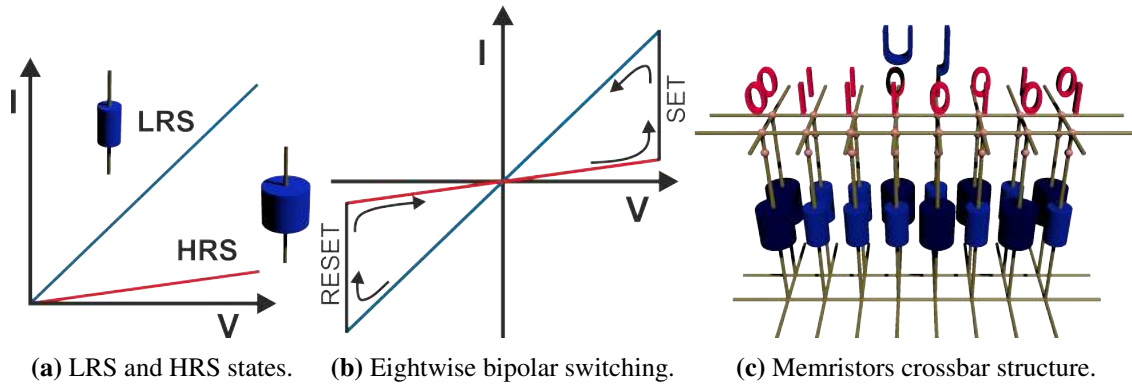


Figure 2.15. Resistive switching.

was first developed from fundamental symmetry arguments in 1971 by Leon Chua [115]. It was postulated to complement the resistor, inductor and capacitor and change their resistance state according to the time integral of applied current or voltage. The first experimental realization of a memristor was announced in 2008 by researchers from HP Labs [116], however this claim was questioned [117] and nowadays researchers are rather in the position that discovered materials have memristive or resistive switching properties, however being not a actual memristor.

In bipolar ReRAMs, the switching direction depends on the polarity of the applied voltage. Fig. 2.15b depicts the schematically simplified I — V curves of the bipolar resistive switching (actual curves for oxide-based devices are non-linear). The switching from HRS to LRS is called the SET process, while the switching from LRS to HRS is called RESET process. For a device being initially in the HRS, a certain threshold voltage V_{SET} causes a transition to the LRS. This resistance state is maintained until the opposite voltage V_{RESET} is applied, causing reset to the HRS. In the SET process, a current compliance (CC) is often used to avoid permanent breakdown. In most situations, a forming voltage larger than the SET voltage is initially needed for the pristine device to trigger the resistive switching behaviors for the subsequent cycles. Voltages between V_{RESET} and V_{SET} are used for a reading of a device state: if a device is in HRS, digital 0 can be assigned, otherwise 1 could be recorded for LRS. Following this reasoning, a single ReRAM memory cell could be built. By arrangement of cells in a ordered structure, information can be written, read and erased. A model of working memristive device is presented in Figure 2.15c. An abbreviation of the Jagiellonian University (UJ) is here stored in a prototypical ReRAM crossbar structure.

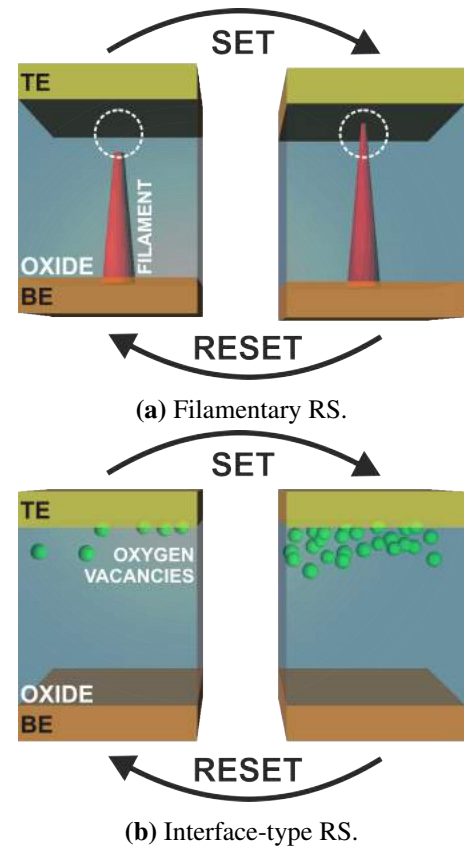


Figure 2.16. Postulated mechanisms of the resistive switching in oxides.

The actual resistive switching mechanism in oxides is still under debate. The proposed mechanisms of resistive switching can be divided according to the conduction mode in LRS: the filament type and the interface type [6, 118] (see the Fig. 2.16). Interfacial-type switching occurs in the spatially extended area at the oxide-electrode interface. There, oxygen vacancies are distributed that controls the conductivity of the metal–insulator–metal (MIM) structure. In the filamentary resistive switching, current in LRS flows through the confined local path in the insulating matrix while current in HRS flows through the films homogeneously. A distinct feature of the filament-type switching is that the resistance in LRS is independent on device area while the conductivity in HRS increases when the cell size decreases, as reported e.g. in MnO_x thin films [119].

Nanoscale investigations of TiO_2 -based memristive devices have shown that the switching process is localized in many cases in filamentary structures consisting of a secondary phase [120], which evolve during the forming process. There are many ways of introducing them, such as using electric field (electroforming) [120] or by the thermal induction [74], though all of them fall under the process of a local reduction. Conductive paths formation in the oxide crystal are dominantly driven by reduction-oxidation processes governing the oxygen motion [121], however cation mobility in various oxide phases, such as TaO_x or TiO_x is postulated [122]. Locally, an insulator-to-metal transition occurs, leading to the valence change of the Ti d-electron, from d^0 , through d^2 to d^3 , which can participate in conduction [123]. Resistive switching in oxides, most notably TiO_2 , Nb_2O_5 , HfO_2 and TaO_x , are most widely realized in thin films, with metallic top and bottom electrodes and often buffer layers. Additionally, resistive switching in single oxide crystals and synthesized nanorod arrays are reported [124].

2.3.2 Optoelectronic applications

Oxides are commonly investigated as materials for various organic and optoelectronic applications. For light emitting/absorbing applications one of the electrodes needs to be semitransparent in order to observe light emission from the organic layer [125]. The transparency and (at least weak) conductivity properties are not commonly coexistent, however a wide class of oxides fulfill those criteria. The most widely used transparent (band gap of 4 eV) conducting oxide is indium tin oxide (ITO), due to its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film [126]. Another important class of materials is transition metal oxides, such as ZnO or TiO_2 . Since there are plentiful of organic and optoelectronic applications of transition metal oxides, in this section one chosen system will be introduced in detail, namely *para*-hexaphenyl molecules on TiO_2 .

Titanium dioxide is the semiconductor of choice for the photoelectrode, in the fields of sensitized photochemistry and photoelectrochemistry [127]. It is a widely available, low-cost, nontoxic and biocompatible material, which is nominally transparent, but optical properties can be controlled by reduction and oxidation, as described in the section 2.2. TiO_2 has become especially important for dye-sensitized solar cells (DSSC), where a current generation is caused by the injection of photoexcited electrons into conduction band, from adsorbed photosensitive dye

molecules [128]. In addition to DSSC, organic light emitting diodes (OLED) and organic thin film transistors (OTFT) applications based on TiO_2 surface has been postulated and demonstrated [129]. Since performance of organic devices drastically depends on the molecule-surface interface, numerous studies have been conducted on the adsorption and growth of molecular films. The commonly investigated model molecule, which represents the broader class of rod-like molecules, for adsorption and thin film growth on TiO_2 is *para*-hexaphenyl.

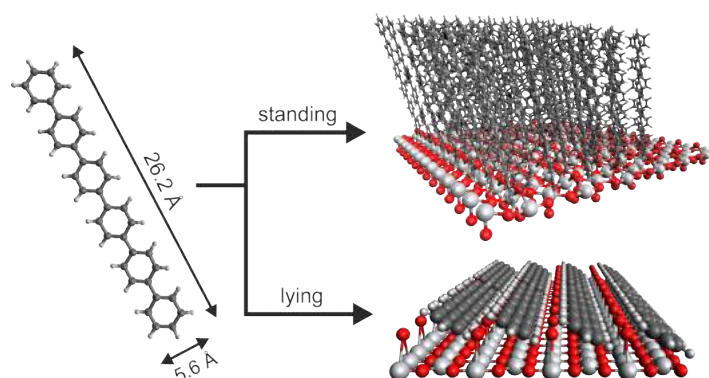


Figure 2.17. A single *para*-hexaphenyl (6P) molecule with two possible configurations, lying and standing, on the surface of $\text{TiO}_2(110)$.

Para-hexaphenyl (6P, p6P, P6P *para*-sexiphenyl) is a rod-like conjugated molecule, widely investigated as a representative of p-oligophenyls (see Figure 2.17). 6P consists of six phenyl rings connected with single bonding. Due to single bonds of the molecule, it possesses a certain flexibility while in the gas phase [130]. In a bulk cry-

stal molecules adopt a planar configuration in the herringbone structure. Its high-energy gap (3.1 eV) between the highest occupied molecular orbital and the lowest unoccupied molecular orbital and consequently the blue electroluminescence emission recommends 6P for multicolor OLED displays [130] and also for lasing nano-fibers [131].

In a crystal phase, 6P molecules interact with each other by π -orbitals. As a rule of thumb, charge transport is always best in directions with the maximum π/π overlap. Hence, for OLED applications, the π -system should be oriented parallel to the substrate and the top electrode (see Fig. 2.18a). For rod- or plate-like molecules, this usually requires a flat-lying configuration. Technically, there are two approaches for the RGB (red-green-blue) architecture color dots for color (O)LED display:

- different active layers for different color pixels: e.g. molecules emitting blue light, red light and green light,
- large area blue electroluminescence devices covered by appropriate dye layers, which convert blue light into other emission colors.

Para-hexaphenyl is suitable for both external energy conversion devices. It has high electroluminescence quantum yield and has an emission maximum situated at 425 nm [132], thus it can be easily used as a blue light source.

In an organic thin film transistor (OTFT) application, the conjugated molecules should be oriented in an upright orientation (Fig. 2.18b). This facilitates an isotropic electric transport from source to drain parallel to the gate electrode. For holes, the requirements on molecular

orientation are unchanged, as only the direction but not the path of the charge transport changes [129]. Both parallel and perpendicular (lying and upright standing) orientations of a molecule are achievable for the case of $\text{TiO}_2(110)$ substrate [TiO2_6P]. For the atomically flat reconstructed surface, 6P molecules are lying down, constituting wetting layer and nanowires, whereas for the reduced surface (induced by a low fluence ion beam sputtering) molecules are upright standing, forming nanoislands [133] [TiO2_6P]. It has been additionally proven that ambient air passivation induces upright standing growth of molecules, which agglomerate into dendritic islands [TiO2_6P].

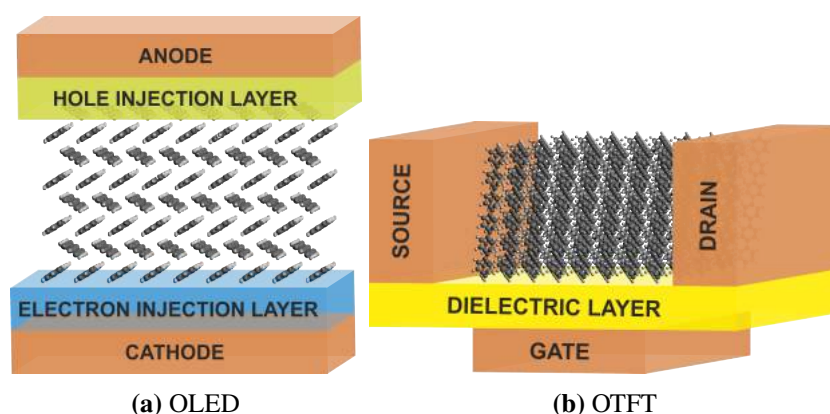
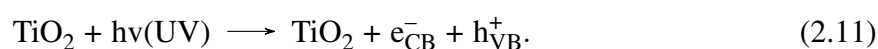


Figure 2.18. Device architectures for two possible applications of 6P molecules on transition metal oxide surfaces: a) Organic Light Emitting Diode (OLED) and b) Organic Thin Film Transistor (OTFT).

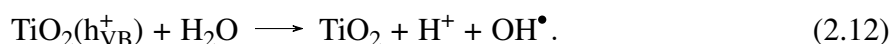
2.3.3 Photocatalysis

Beyond doubt, oxides such as TiO_2 are especially significant with respect to catalysis, with their catalytic activity associated with the partly filled d-bands. Transition metal oxides exhibit a number of properties that are further conducive to catalytic applications, including thermal and mechanical stability needed to survive severe reaction conditions. Performance of catalytic reactions are often enhanced due to the photo irradiation, in a process called heterogeneous photocatalysis, where an oxide (mostly in a form of nanocrystals) acts as a catalyst in a reaction taking place in a liquid or gas. Due to the wide bandgaps (e.g for TiO_2 3.0 eV - 3.2 eV and SrTiO_3 3.2 eV - 3.4 eV, depending on the literature source), in order to create an electron-hole pair, which is further used in a specific reaction, an ultraviolet irradiation is needed. Thus, when the photon energy is high enough, an electron-hole pair is created in the crystal according to the simple equation (see also Fig. 2.19):



They both can be regarded as intrinsic electronic defects, in addition to intrinsic point defects introduced in the section 2.1.1. Such disorder implies elevation of electrons into higher energy levels creating vacant states in lower energy bands, which are named holes. The photogenerated holes in the valence band diffuse to the oxide surface and react with the adsorbed water molecules

to produce hydroxyl radicals $\text{OH}^\bullet$, which is a very strong oxidizing agent (with a standard redox potential of +2.8V):



Hydroxyl radicals and photogenerated holes oxidize organic molecules on the surface, i.e. photo-generated holes are trapped on the surface defects with low electron density and then can react with methanol to produce CO_2 and protons. Meanwhile, electrons created in the conduction band are trapped on the surface Ti^{4+} sites and lead to the reduction of Ti^{4+} to Ti^{3+} . This surface bound Ti^{3+} and electrons participate in the reduction processes at the surface. Typical reaction is the reduction of an oxygen molecule to produce activated oxygen species, such as superoxide radical anions:

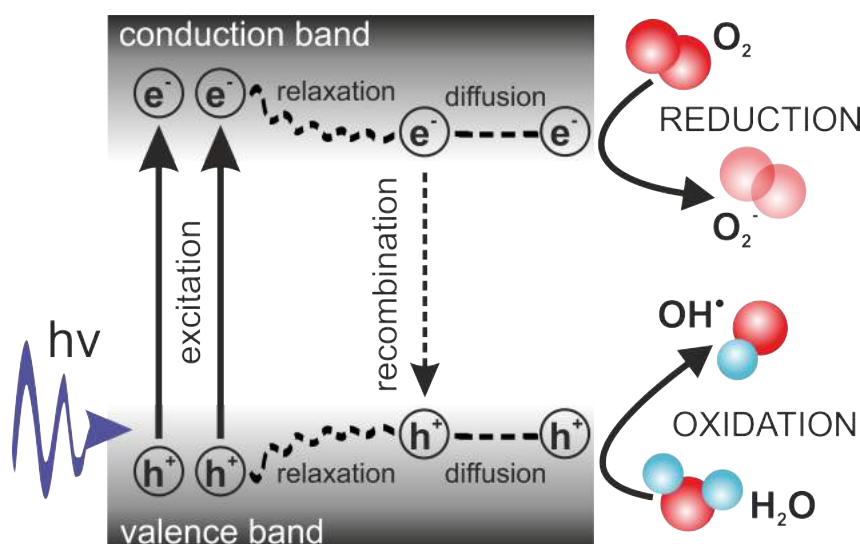
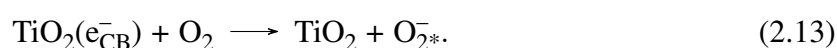
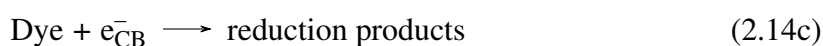
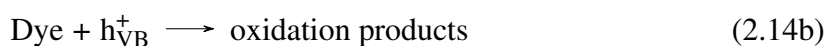


Figure 2.19. Scheme of the photocatalysis process on the oxide surface after UV irradiation.

It is generally acknowledged that the photocatalytic performance of TiO_2 samples can be influenced by their physico-chemical properties, especially crystalline phases, exposed crystal facets and density of surface and bulk defects, which is a function of the reduction state [134]. The photocatalytic performance can be enhanced by the intentional defects creation via nanoscale redox processes. Presence of reductant point defects on a surface of TiO_2 such as oxygen vacancies or titanium interstitials shifts band-edges of both valence and conduction bands, improving the reducing efficiency of electrons in the conduction band [135]. Also, defect states occur in the forbidden band, which can enhance the optical absorption. It has been discovered that the defective TiO_2 materials exhibit superior performance over pristine TiO_2 for CO_2 photoreduction [136, 137]. It is not only TiO_2 finding an application in the photochemistry, but also a broader class of transition metal oxides. For example, perovskite oxides are widely investigated for the potential use as catalysts in fuel cells and metal-air batteries [138, 139]

An interesting application of transition metal oxides (TiO_2 especially) is dyes degradation. The discharge of many hazardous dyes from textile industry in waste water is one of the main causes for serious environmental problems that affected the aquatic medium and therefore a human health, due to the toxicity and the carcinogenic effect of these materials [140, 141]. One of the ways to effectively decompose dangerous organic substrates as dyes is to use TiO_2 for the heterogeneous photodecomposition. The relevant reactions at the semiconductor surface causing the degradation of dyes can be simply expressed as in Eq. 2.14 [141]. Performance of the dyes photodegradation can be also enhanced with doping (metals like Pt or Mg or self-doping), reaching efficiencies over 90% [142].



Another, quite unusual application of a titanium dioxide photocatalytic properties is in a coating of paving blocks (so-called Noxer blocks) to lower the pollution levels in crowded cities such as Osaka or London. By using the active superoxide ions and hydroxyl radicals formed due to sunlight irradiation, it was found possible to efficiently oxidize hazardous nitrogen dioxide NO_2 and nitrogen monoxide NO from air, to form nitrate ions and therefore greatly reduce photochemical smog [143].

The last important application of transition metal oxides in (photo)catalysis is the electrochemical water splitting, which has been considered as an inevitable, foreseeable, and ultimate route to produce ultrapure hydrogen from plentiful water [144]. Compressed hydrogen is the most vibrant, neat, environmentally benign fuel, moreover possessing very high specific energy density - $141.65 \text{ MJ} \cdot \text{kg}^{-1}$, which is over 3 times higher than diesel or gasoline [145, 146]. Conversion of water to hydrogen gas by photocatalytic water splitting needs an efficient catalyst, like a perovskite oxide (e.g. sodium tantalite [147]) and most commonly titanium dioxide [148]. Since stoichiometric TiO_2 is not active for a water absorption at room temperature [149], defects such as oxygen vacancies need to be induced by the redox processes mentioned before. Thermodynamically, the water splitting potential is equal 1.23 V only, much smaller than the potential corresponding to the TiO_2 band gap (3.1 V). Therefore, instead of using UV light (which constitutes only 5% of solar light), infrared irradiation with a wavelength of 1000 nm would suffice, assuming that the overpotentials for the oxygen and hydrogen evolutions are successfully removed and the electronic structure of the oxide aligns perfectly with the water redox potentials [150]. Thus, in order to enhance efficiency of water splitting devices it would be beneficial to narrow the TiO_2 band gap. Recently, it has been successfully realized by the heavy thermal or chemical reduction of an oxide (mostly nanoparticles), resulting in the opaque color of a so-called black TiO_2 [151]. This redox-driven procedure was found greatly beneficial for the various applications in the photocatalysis, fuel cells, sensing and energy storage [150].

2.4 Methods

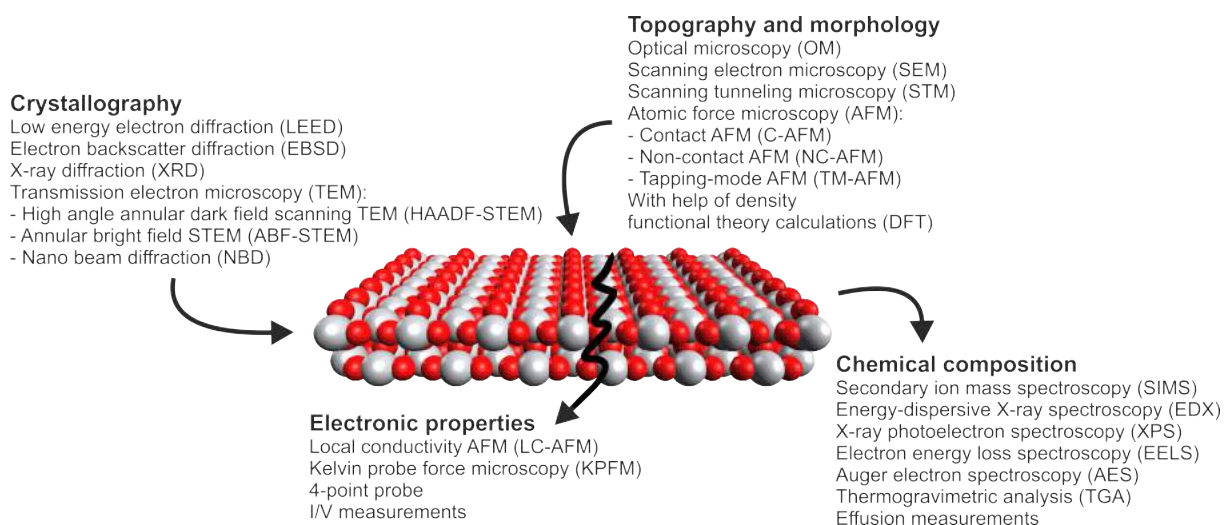


Figure 2.20. Overview of methods used in the research presented in the thesis.

In this section, an overview of experimental methods used in the thesis is presented. So far, many literature studies were related to the topic of redox processes on the surface of transition metal oxides, however a vast majority of them regarded only one specific aspect or property. In order to present as complete picture as possible, in this research a variety of methods have been employed, to investigate both surface and bulk features, including topography and morphology, crystallography, electronic properties and chemical composition. The full list of methods utilized is presented in Fig. 2.20. The better part of them are *in situ* techniques, which enabled for a direct measurements of *as prepared* (oxidized / reduced) samples. Amongst them KPFM and LC-AFM provided also *in operando* observation of re-oxidation of SrTiO_3 surface, which is described in detail in the paper [STO_Redox]. Most of techniques employed are commonly known and well established, hence to avoid lengthy introduction and to maintain consistency of this dissertation, a brief descriptions of four are written: STM, KPFM, LC-AFM, and a 4-point probe.

2.4.1 Scanning Probe Microscopy (SPM)

A class of techniques utilizing a physical probe scanning the specimen is called Scanning Probe Microscopy (SPM). A general principle of operation is to raster scan the tip over a given surface area and to collect data, obtained typically as a two-dimensional grid of points.

SPM techniques enables for direct and indirect measurements of many physical quantities, such as piezoresponse, thermal conductivity, magnetic and electronic properties. At most cases such property is mapped over the surface and simultaneously surface topography is acquired, which enables for identification of surface features and their properties. Many of SPM techniques can reach atomic or even orbital resolution of surfaces. Great majority of SPM techniques enables also for a manipulation at the nanoscale, e.g. a lithography to build a field-effect transistor [152]

or formation of gold atomic chains at the surface [153]. The inherent feature of all SPM methods is that they allow direct investigations only of a surface and a few atomic layers beneath.

SPM techniques are often regarded as a step forward from the optical microscopy, which is unable to image the specimen with the lateral resolution better than several hundreds nm. In fact, combining the SPM and optical microscopy enabled to overcome the diffraction limit. In the so-called Near-field Scanning Optical Microscope (SNOM, by usage of a nanoscopic tip and employing the evanescent waves, the resolution better than 20 nm was achieved [154].

Scanning Tunneling Microscopy (STM)

Historically, the first SPM was the scanning tunneling microscope (STM), developed in 1982 at the IBM Research Lab in Zurich by Gerd Binnig and Heinrich Rohrer [155]. It was also the first technology to be recognized as having surface atomic resolution capability.

A schematic view of an STM is presented in Figure 2.21. The main part of the microscope is the conducting probe. Probes are usually made of metals such as platinum-iridium alloy or gold, however the most common choice is tungsten. Due to the geometry there is a strong likelihood that the apex is terminated with a single atom, enabling for atomic resolution. An equally important part of the STM microscope is the positioning system, consisting usually of two separate systems: x, y, z piezoelectric scanner for the coarse moving and a piezoelectric tube for the fine control.

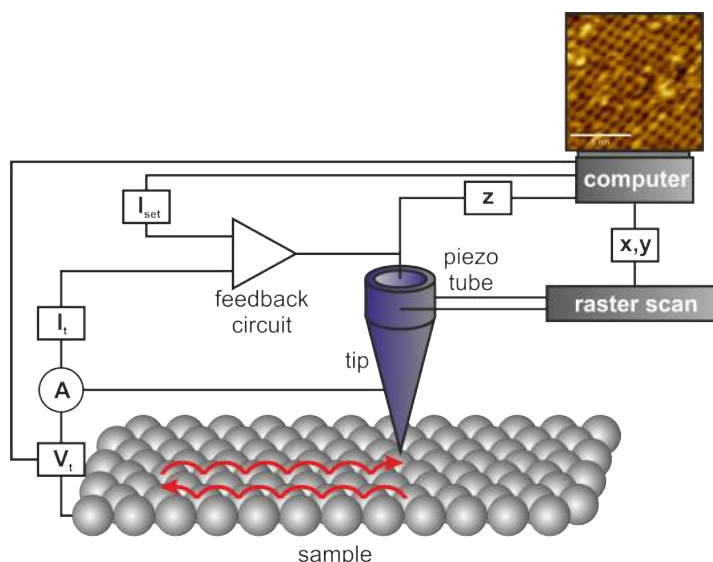


Figure 2.21. Schematic of the STM microscope.

The tube controls the lateral and depth position of the tip which it is attached to. The piezoelectric tube is made of ferroelectric ceramics which deform by several nm if a certain voltage is applied to the electrodes. An operation principle is straightforward: the tunneling current flowing between a tip and a sample, due to the applied voltage. A user of a microscope can set this bias voltage V_{bias} and then the corresponding tunneling current I_{set} is measured. Typical voltages are in the range of -3 V to +3 V and the quantum current is ranging from tens of nA down to the single pA. Measured current value is processed by the feedback loop which keeps the one specific quantity constant depending on the mode. Figure 2.21 depicts the so-called constant current mode (CCM). The scanner controlling circuit maintains previously set current value I_{set} via feedback loop. Z scanner movement represents surface topography (assuming constant local density of states). STM also enables local density of states (LDOS) imaging in

a so-called scanning tunneling spectroscopy (STS) mode. Voltage bias is then modulated with an amplitude dV and the corresponding modulation of tunneling current dI is measured. dI/dV represents LDOS of the tip and the sample. In addition to imaging and spectroscopy, STM enables also for the nanoscale manipulation on the surface. Moving complex objects such as gold islands on MoS_2 [156] or single atoms [157] can be performed. It is also possible to initialize chemical reactions using the probe tip, e.g. remove bonds on the hydrogenated silicon surface [158] or enhance Raman signal (tip enhanced Raman spectroscopy, TERS) [159].

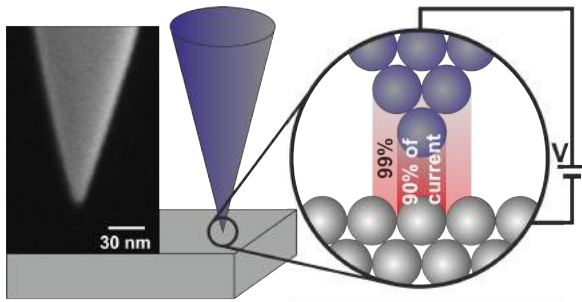


Figure 2.22. Zoom on the STM tip apex.

Let us now devote the rest of this section to the brief description of the quantum processes of the tip-surface interaction. The concept of quantum tunneling itself appears to be counter-intuitive - classically, in a macroscopic world, when an object approaches a barrier, it cannot pass through. Here, vacuum between the surface and the tip corresponds to the finite potential barrier which is few $\text{\AA}$ thick (let x be the thickness of the barrier). When the electron energy E is smaller than the barrier height, $U(z) > E$, classically electron is trapped. However, in the quantum picture solutions exist, allowing an electron to propagate, but its wave function becomes a decaying wave:

$$\psi_n(z) = \psi_n(0)e^{-\kappa z}, \quad (2.15)$$

where

$$\kappa = \frac{\sqrt{2m(U - E)}}{\hbar}. \quad (2.16)$$

In scanning tunneling microscopy a voltage bias V_{bias} is applied between the tip and the sample. If surface filled electronic states are imaged, voltage bias is negative and electrons are tunneling from sample to the tip. Accordingly, in the opposite situation empty states are imaged. Probability that the electron from the very edge of the sample ($z = 0$) can be found in the tip (right edge of the barrier, $z = x$) is proportional to the squared wave function:

$$P \propto |\psi_n(0)|^2 e^{-2\kappa x}. \quad (2.17)$$

In a case of applied voltage bias V_{bias} , only electronic states which lie within $e V_{\text{bias}}$ range are excited. Thus, only the electrons that are near the Fermi level E_F can participate in tunneling. In other words, tunneling occurs only when there are occupied states in the sample within the $e V_{\text{bias}}$ range from the Fermi level and there are empty states at the corresponding energy in the tip at the same time. Finally, the tunneling current I is proportional to the probability of electrons tunneling through the potential barrier:

$$I \propto \sum_{E_f - eV}^{E_f} |\psi_n(0)|^2 e^{-2\kappa x}. \quad (2.18)$$

Using the definition of local density of states near certain energy E (interval $\varepsilon \rightarrow 0$):

$$\rho_s(z, E) = \frac{1}{\varepsilon} \sum_{E-\varepsilon}^E |\psi_n(z)|^2 \quad (2.19)$$

one can rewrite the upper formula in terms of LDOS:

$$I \propto V \rho_s(0, E_F) e^{-2\kappa x}, \quad (2.20)$$

where $\rho_s(0, E_F)$ is the local density of states near the Fermi level of the sample surface.

It is apparent, based on presented simple calculations, that a tunneling current is exponentially dependent on the tip-surface distance. For the typical barrier heights (tip-sample distance) of a few Å, tunneling current changes by an order of magnitude, when distance changes by 1 Å. Thus, most of the current flows through the last atom at the very tip (approximately 90%) and therefore an atomic resolution can be achieved - see Figure 2.22. SEM image presented on the left hand side shows a PtIr tip, etched with use of gallium focused ion beam (FIB). Such procedure results in mechanically stable tips, with a very sharp apex, allowing for reproducible measurements, as presented in the thesis.

Atomic Force Microscopy (AFM)

In 1986, four years after STM, the atomic force microscopy (AFM) was developed [160]. This invention allowed to identify and measure many interactions at the nanoscale. The manner of using these interactions to obtain an image is generally called a mode.

KPFM and LC-AFM methods, widely used in this thesis, are two different AFM modes, therefore it is justified to begin with the basic introduction. AFM is a class of methods of scanning probe microscopy, where imaging is realized by sensing various atomic forces between a tip (attached to a cantilever) and a sample surface. Amongst them are van der Waals forces, capillary forces, electrostatic forces, chemical bonding, Casimir forces, magnetic forces etc. A few elements of tip-sample interaction can be distinguished: electrostatic long-range interaction (which can be nulled by applying external bias in the KPFM mode), Van der Waals attractive forces acting on a scale of tens of nanometers, short-range chemical interactions and Pauli repulsion at subnanometer range, due to overlapping electron orbitals. The mathematical formula, which provides a basic estimation of a tip-surface interaction, taking into account van der Waals forces and Pauli repulsion, is given by the Lennard-Jones potential for the inter-particle interaction V_{LJ} [161] (there are also extensions having regard to the electrostatic interaction, e.g. Coulomb-Buckingham potential [162]):

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2.21)$$

where ϵ is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, while r stands for the distance between the particles (here, between an AFM tip and a surface).

The van der Waals force is caused by fluctuations in the electric dipole moment of atoms and their mutual polarization. For two atoms at the distance z , the value of this interaction is proportional to $1/z^6$, hence the second term in the Eq. 2.21. For the macroscopic probe and sample, van der Waals interaction strength can be estimated using Hamaker approach [163]. For a spherical tip (with a radius R) at the distance z above flat surface, the van der Waals potential is as follows [164]:

$$V_{\text{vdW}} = -\frac{A_H R}{6z}, \quad (2.22)$$

where A_H stands for a material Hamaker constant, which is typically in order of 1 eV in vacuum [165], and can be calculated with a formula (ρ_1 and ρ_2 are number densities of two kinds of particles and C is the coefficient of particle-particle pairwise interaction): $A_H = \pi^2 \times C \times \rho_1 \times \rho_2$. The van der Waals interaction is large and dominant at the moderate tip-sample distances. Typically, nanoscale topography resolution is driven by the van der Waals interaction, whereas atomic resolution is provided by the contact forces (Pauli repulsion $\approx 1/z^{12}$ and short-range chemical interactions).

The most interesting feature of AFM is the ability to sense forces as low as nN and pN by macroscopic means of detection. When the tip is brought in the vicinity of the sample, forces between the tip and the surface result in a deflection of the whole cantilever. A deflection extent is proportional to the tip-sample interaction and is ruled by the Hooke's law. The two most common ways to determine deflection are: laser beam deflection detection and the use of piezoresistive cantilevers, which act as a strain gauge.

As for the interaction regimes and therefore, tip-sample distance, three AFM modes can be distinguished: contact, non-contact and tapping modes. In Figure 2.23 those modes are schematically marked, with comparison to the STM tunneling current regime [165].

Contact mode AFM operates in a static mode. The soft cantilever is dragged across the surface of the sample and the tip-sample interaction (short-range, repulsive) is measured indirectly from the deflection of the cantilever. By applying additional bias, galvanic current can be detected, which is a foundation of LC-AFM mode, described in details in the next section.

The non-contact (NC-AFM) mode is an example of a dynamic mode AFM. The tip does not contact a sample surface, as the whole cantilever is set into oscillations with an amplitude in order of a few nm. The oscillations frequency is either the resonant frequency of the cantilever (the frequency modulation mode, FM-AFM [166]) or slightly above (the amplitude modulation mode, AM-AFM [167]). The interaction value (and therefore a topography) is measured as a change in the resonant frequency Δf (FM-AFM) or in the oscillation amplitude (AM-AFM). Highest resolution measurements are obtained in UHV employing the FM-AFM, where the minimum detectable force is inverse proportional to the figure-of-merit called quality factor Q [168]. In NC-AFM cantilever is short and stiff, causing the eigenfrequency to be in order of

hundreds thousand Hz and a quality factor $f/\Delta f \approx 10000 - 300000$ [168]. An useful extension to non-contact AFM is KPFM, where by applying additional loop the workfunction of a material can be measured.

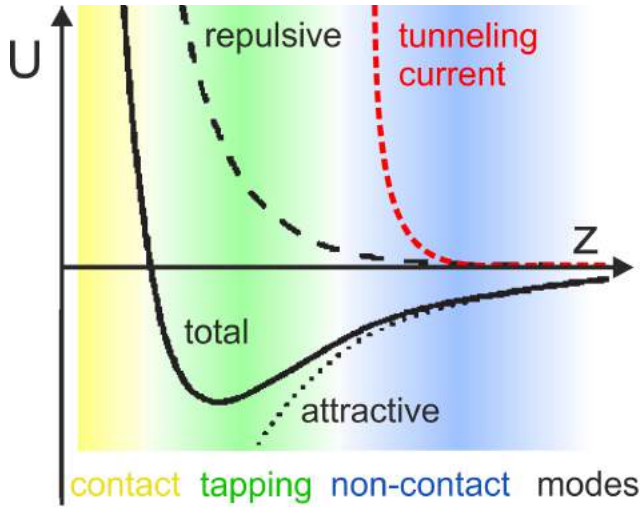


Figure 2.23. Regimes of the Lennard-Jones potential in contact, non-contact and tapping AFM modes. In addition the STM tunneling current dependence over distance is plotted.

In the tapping-mode (also called intermittent contact mode) the tip touches the surface of the specimen intermittently. This is most useful for ambient measurements, when the sample has a soft surface, e.g. for polymer or biological samples [169]. Due to the substantial damping caused by the interaction with ambient air, achievable Q factors are in order of 1000 [170], which is the reason for the amplitude-modulation interaction sensing in a tapping-mode. Cantilever is still set into oscillations and the dominant interaction is attractive, however at the closest distance range tip touches the sample and feels repulsive tip-sample interaction.

Kelvin Probe Force Microscopy (KPFM)

Kelvin Probe Force Microscopy (KPFM, sometimes referred as Scanning Kelvin Probe Microscopy SKPM) is an extension of a dynamic non-contact AFM mode. A concept of the KPFM technique stems back to the original work of Lord Kelvin, who in 1898 observed that plates of copper and zinc mounted on insulating shafts created charge when brought into electrical contact and then moved apart [171]. This discovery can be explained in terms of the work function (ϕ , representing the energy between Fermi level and the vacuum level) difference of these two materials. Many experiments based on the idea of Lord Kelvin were performed, in order to evaluate work functions of various materials, e.g. tungsten [172]. In the SPM realization, KPFM, one electrode (with a work function of ϕ_{tip}) is realized by the metallic tip of a cantilever and the second one is sample surface (ϕ_{sample}). Then the contact potential difference would be as follows:

$$V_{CPD} = \frac{\phi_{sample}}{e} - \frac{\phi_{tip}}{e}. \quad (2.23)$$

KPFM mode operation is imposed on the FM-AFM by applying additional AC voltage component and a feedback loop. KPFM images the surface potential by tuning sample bias voltage (V_{bias}) to minimize the electrostatic interaction between the tip and the sample while the total interaction between the tip and the sample, the detuning δf , is kept constant. The electrostatic interaction is induced by a difference of work functions of the tip and the sample.

Based on the vibrating capacitor model (vibrating tip over the sample surface) [173] the electrostatic force between the tip and the sample can be written as:

$$F_{el} = \frac{1}{2} \frac{\partial C}{\partial z} (V_{bias} - V_{CPD})^2, \quad (2.24)$$

where $\partial C/\partial z$ stands for the tip-sample capacitance gradient. In order to provide precise measurements, V_{bias} between tip and sample has two components $V_{bias} = V_{DC} + V_{AC} \sin(\omega t)$: an offset V_{DC} and a AC component (with the frequency ω of hundreds to thousands Hz).

The equation 2.24 can be then expressed as:

$$F_{el}^{DC} = -\frac{1}{2} \frac{\partial C}{\partial z} (V_{DC} - V_{CPD})^2 \quad (2.25a)$$

$$F_{el}^{\omega} = -\frac{\partial C}{\partial z} (V_{DC} - V_{CPD}) V_{AC} \sin(\omega t) \quad (2.25b)$$

$$F_{el}^{2\omega} = \frac{1}{4} \frac{\partial C}{\partial z} V_{AC}^2 (\cos(2\omega t) - 1). \quad (2.25c)$$

The second component (F_{el}^{ω}) is proportional to the modulation frequency ω and can be measured using a lock-in technique. Utilizing Kelvin feedback loop, this electrostatic component is minimized and the DC voltage V_{DC} needed for this compensation is equal to the contact potential difference V_{CPD} . This way, the relative tip-sample work function can be mapped in the FM-KPFM mode, reaching even an atomic precision [174]. Also for the transition metal oxides, atomic resolution of the charge distribution at the surface of $\text{TiO}_2(110)$ was measured in a so-called local potential difference mapping (LCPD) [175].

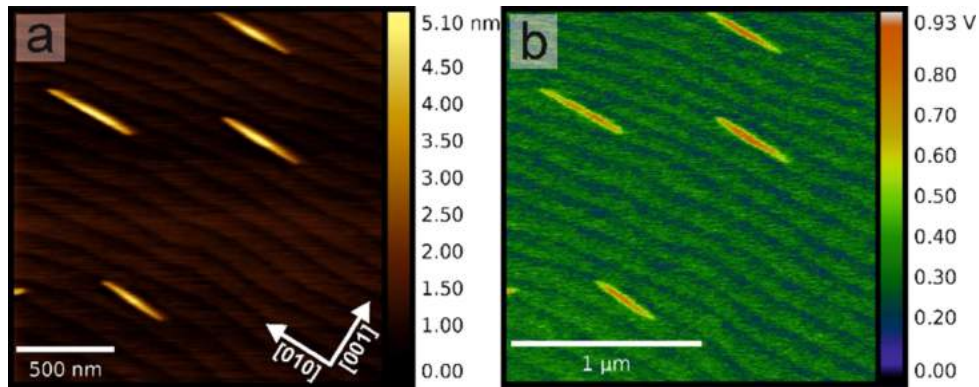


Figure 2.24. KPFM characterization of a new TiO oxide phase formed on $\text{SrTiO}_3(100)$ upon thermal reduction. a - topography map, b - KPFM surface potential map.

KPFM can be also used as a tool for a new 3D phases determination. When a $\text{SrTiO}_3(100)$ crystal is heavily reduced, to the temperatures exceeding 1000°C , new crystallographic phases are formed, what is one of the main results of this thesis [STO_TiO], [STO_Decom]. Strontium titanate decomposes: strontium effuses, leaving behind titanium monoxide nanowires emerged on the surface. The difference in chemical composition of the TiO nanowires initial growth stage, compared to the STO surface is clearly presented in Figure 2.24. The measured work function difference is as high as 0.65 eV, which represents different electronic states in SrTiO_3

and TiO. One can see that the contact potential difference variation within one terrace is below 20 meV. However, there is strong influence of the terrace edges, lowering the potential by about 70 meV. Two effects can contribute to the apparent decrease of the work function near edges: difference in chemical composition and also electrical dipole moment emergence. The first effect is related to the fact that two surface terminations of SrTiO₃: TiO₂ and SrO have different surface potential. Values extracted from KPFM and XPEEM measurements are as follows: $\Delta\text{CPD}(\text{TiO}_2) - \Delta\text{CPD}(\text{SrO}) \approx 70 \text{ meV}$ [176] which is exactly the value obtained from presented measurements. This might suggest that even if terraces are made of reconstructed TiO₂, surface near edges may be enriched in Sr/SrO.

Local Conductivity Atomic Force Microscopy (LC-AFM)

Local conductivity AFM (LC-AFM, sometimes referred as C-AFM) is an extension to a contact mode AFM, where a tip-surface system is polarized due to the application of an external bias. By a detection of current flowing to or from the sample upon applied voltage (which is typically lower than the bias in STM, in the range of 10-100 mV) conductivity can be directly evaluated and compared to the simultaneously measured contact AFM topography and friction maps. In order to detect a current flow, the cantilever needs to be metallic, which is realized either by using solid metal tips, or more commonly by an additional coating - e.g. 20 nm of PtIr alloy. For the case of frequently used (also in the research presented in the thesis) PPP-CONTPT Nanosensors cantilevers, silicon tips are coated with a grain-like PtIr layer, where individual grains have a radius of $\approx 10 \text{ nm}$ (see in Figure 2.25). Such kinds of tips can be still ultra-sharp, with the tip radius of 10-20 nm [177] providing potential of atomic resolution. Estimated tip contact area is in order of 1 nm^2 , which proved to be enough for a current mapping with a true atomic resolution, which was recently demonstrated by the Rodenbücher et al. (with a co-authorship of the thesis author) [178].

LC-AFM is well suited for the resistivity switching phenomena observation. Current vs. voltage behavior can be directly observed, while tip acts as a mobile electrode. Due to the high electric fields induced by the polarized tip, local switching at the scale of single nm can be obtained [179]. The possibility of switching of individual conductive filaments has been demonstrated for both SrTiO₃ and TiO₂ oxide materials [32, 35].

LC-AFM finds also an application in various fields, ranging from characterization of thin molecular layers (e.g. pentacene thin films [180]), investigation of tunneling behavior across 2D materials (tunneling through thin hexagonal

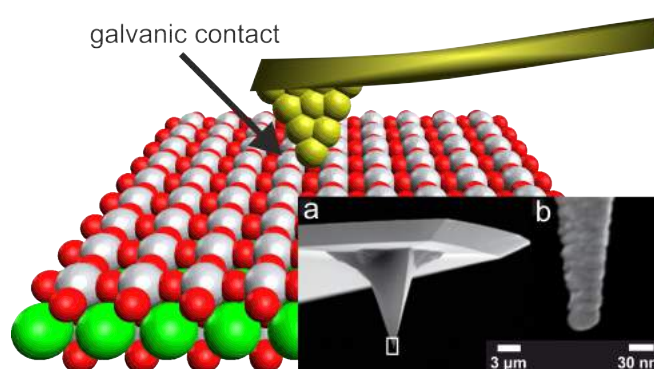


Figure 2.25. Contact-mode AFM. a, b - SEM images of a Pt/Ir coated LC-AFM silicon tip.

boron nitride film [181]) and finally determining domain wall conductivity of perovskite materials (e.g. BiFeO_3 [182]).

2.4.2 Macroscopic 4-point probe

In order to get macroscopic insight into electrical transport properties of the macroscopic sample, 4-point method (also known as four-terminal sensing, 4T) is often used. The easiest way to perform conductivity measurements is to connect two probes to the sample with set bias and measure voltage drop. However, this way the resistance of the sample cannot be estimated correctly because of the influence of the contact resistance. In order to overcome this issue, two further inner probes are added - a total of four electrodes are placed at the sample (in line in the Valdes geometry). Two outer electrodes supply current, while potential drop is measured by the inner ones [183]. This way, a measurement is virtually current-free, thus the precise estimation of the resistivity of a crystal can be provided, by the ratio between the measured voltage and current, according to the Ohm's law.

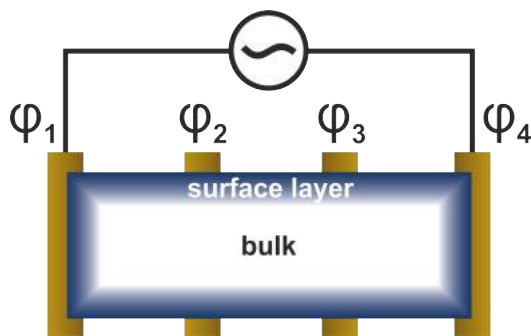


Figure 2.26. Scheme of the 4-point probe electrical setup in the Valdes geometry.

The experimental realization utilized in the thesis is presented in Figure 2.26 [TiO₂_Nb], [STO_Redox]. Four electrodes were deposited by Pt paste on an oxide crystal - the choice of platinum was driven by the chemical inertness and stability up to high annealing temperatures. An AC voltage with a small amplitude was applied to the outer electrodes and the potential at all electrodes was recorded by electrometers using lock-in technique. This way a potential sample degradation or stoichiometry polarization due to the ionic conductivity could be avoided.

Chapter 3

Results

3.1 Overview

This thesis is meant to provide a novel insight into the understanding of nanoscale redox processes on surfaces of transition metal oxides. In recent years a considerable interest has been generated on this topic, mostly due to the high technological relevance in photocatalytics, organic and memristive applications (which are described in much detail in the section 2.3). However, a lot of attention has generated also a lot of chaos. Namely, there is no consensus within a community about the exact nature of processes happening on the surfaces of transition metal oxides. For instance, the actual mechanism of the resistive switching in TiO_2 and SrTiO_3 is under debate (filamentary vs. interface-type) which is correlated with a still open question of a oxygen diffusion along dislocations - is it enhanced [29, 184] or not [185, 186]? More unresolved issues concern the surface composition of most common surface structures: for instance of (2×1) reconstruction of $\text{TiO}_2(110)$ [187] or $(\sqrt{5} \times \sqrt{5} \text{ R } 26.6^\circ)$ of SrTiO_3 [188, 189]. Problems lie mostly in difficulties in simulation (DFT, *ab initio*) of such oxides, due to the bonding complexity, a significant share of van der Waals interactions and finally in the complicated experimental steps needed for the preparation and investigation of transition metal oxides. Another source of discrepancy would be not optimal and uncontrolled experimental conditions, e.g. using of DC current direct heating instead of AC, which was recently proved to introduce stoichiometry gradients inside an oxide sample [75].

All of this is revoked in order to underline the importance and necessity of a careful and thorough studies of transition metal oxide surfaces, in hope of answering some of raised questions and doubts. Presented thesis is devoted to investigate two important oxides: TiO_2 (papers [TiO2_6P], [TiO2_Nb]) and SrTiO_3 ([STO_Redox], [STO_Decom], [STO_TiO]), which are representatives of broader classes of binary oxides and perovskites, respectively. Therefore, all findings can also help to understand other members of transition metal oxide family, for instance hafnium oxide HfO_2 or barium titanate BaTiO_3 . Nanoscale redox processes studied in this thesis involve those already mentioned in section 2.2: thermal reduction ([TiO2_Nb], [STO_Redox], [STO_Decom], [STO_TiO]), sputtering-induced reduction ([TiO2_6P]), oxidation ([STO_Redox], [STO_TiO]) and doping ([TiO2_Nb]). Such processes are by nature interdisciplinary, touching on manifold chemical and physical properties, making research challenging but important in many ways.

Since the performance of oxides are governed by the oxygen activity, it is justified and crucial to begin with the understanding of the reduction-oxidation processes influence on basic properties. Strontium titanate SrTiO_3 , a prototypical ternary oxide has been chosen for investigations, since it is widely acknowledged as a model perovskite material and is itself extensively used as a substrate for oxide films growth, making its surface properties in terms of atomic structure, conductivity and Fermi energy of a great importance [STO_Redox]. Presented approach considered SrTiO_3 system holistically, taking care of bulk properties and, with the greatest accuracy, surface features.

The goal of the experimental research presented in [STO_Redox] was to describe reduction-oxidation processes of $\text{SrTiO}_3(100)$ single crystals in the purest experimental conditions of

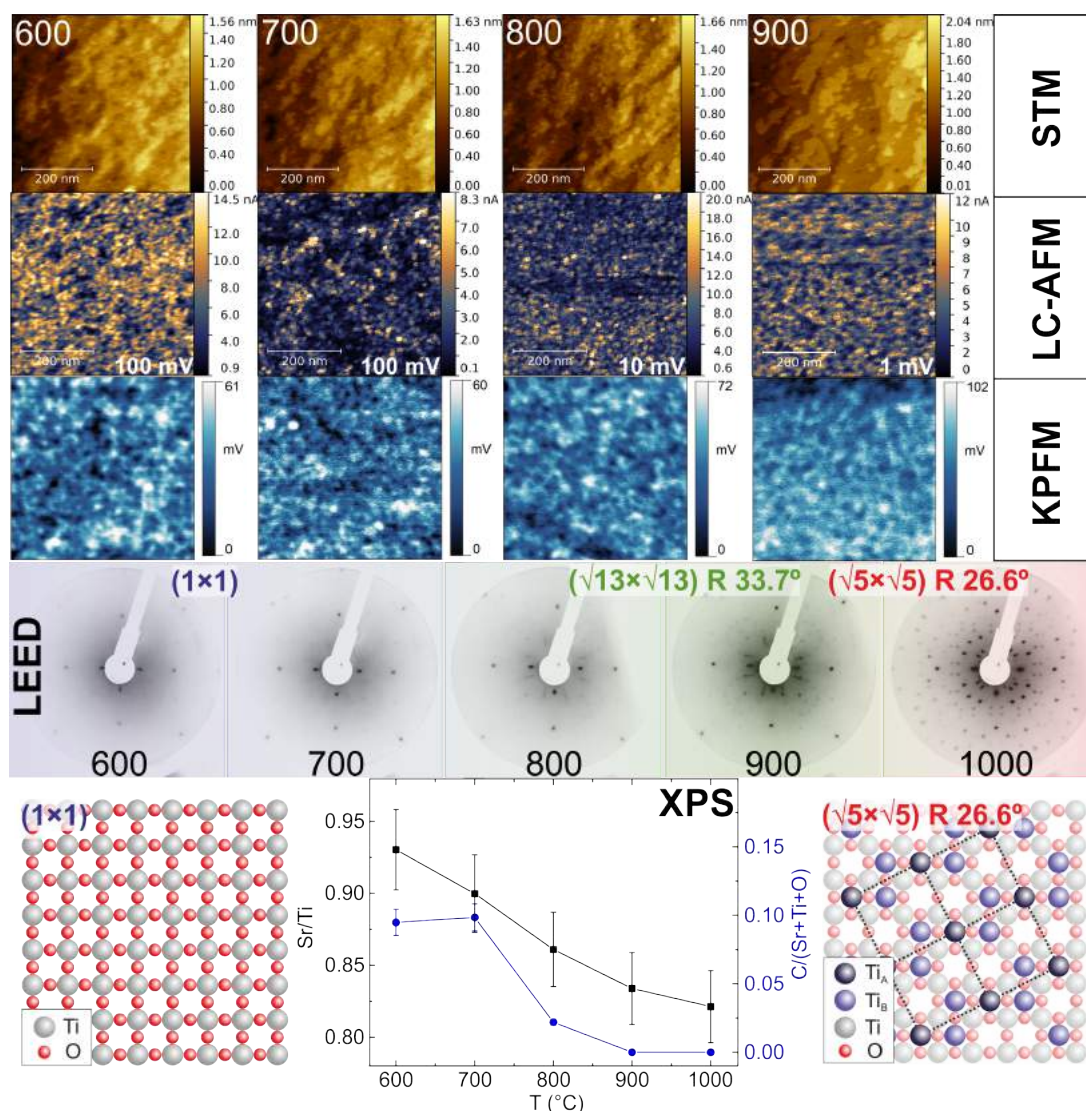


Figure 3.1. Comparison of AFM, LC-AFM (biases indicated in the bottom-right corners) and KPFM maps of thermally reduced SrTiO_3 to temperatures ranging from 600°C to 900°C. SPM results can be directly correlated with LEED measurements and further compared with the XPS Sr/Ti stoichiometry evolution, which supported two reconstruction models. In addition, disappearance of surface carbon contamination after 800°C reduction is presented.

the ultra-high vacuum (UHV). By comparing bulk reduction and oxidation with local properties change upon the same conditions a comprehensive insight linking macro and nanoscale is provided: combined surface reconstruction, determined by means of Low Energy Electron Diffraction (LEED) with topography and local current (LC-AFM). Additionally, surface potential mapping was provided by Kelvin Probe Force Microscopy (KPFM). Surface stoichiometry evolution was measured with X-ray Photoelectron Spectroscopy (XPS) (see Fig. 3.1). Due to this multidirectional approach we have observed unknown phenomena, such as macroscopic resistance of the crystal being indifferent to oxidation in contrary to nanoscale surface conductivity [STO_Redox]. It has been found that Sr/Ti cations segregation results in surface phase transition upon reduction, from common (1×1) reconstruction to complex $(\sqrt{13} \times \sqrt{13} \text{ R } 33.7^\circ)$ and $(\sqrt{5} \times \sqrt{5} \text{ R } 26.6^\circ)$. All results from surface-sensitive techniques after *in situ* reduction are

shown in Fig. 3.1. In this paper, the literature inconsistency was solved, proving that latter reconstructions are Ti-enriched (based on XPS results), which proved the validity of a model postulated for a different perovskite BaTiO_3 [188] and refute the initial proposal of Kubo and Nozoye [189]. In addition, the surface carbon content was studied, proving that it is not safe to study SrTiO_3 single crystals without thermal reduction to at least 800°C , cause results can be biased due to the surface carbon contamination.

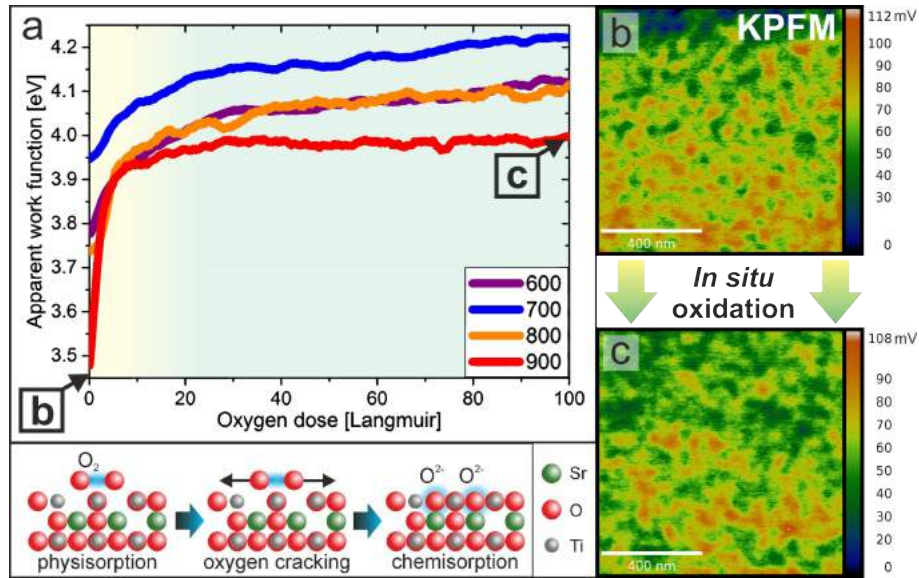


Figure 3.2. Reoxidation of a reduced $\text{SrTiO}_3(100)$ surface and its impact on the work function. a - Measured increase of a surface work function due to the *in situ* oxygen exposure from 0 to 100 L after different reduction temperatures. KPFM surface potential maps are shown in b – before oxidation and c – after oxidation (values are shifted to have zero potential at lowest value). Below the scheme is a proposed model of oxygen interaction with the reduced $\text{STO}(100)$ surface: molecular oxygen lands on the surface, splits into atoms, and chemisorbs at active sites such as surface oxygen vacancies.

At the surface, annealing upon low oxygen partial pressures intensifies initial surface electronic structure inhomogeneity (second and third rows in Fig. 3.1), which is most likely related to dislocation networks [35]. Current-voltage curves measured at the exits of dislocations, visible on local current mapping as conductive spots, change their characteristic to Ohmic after $800\text{--}900^\circ\text{C}$ reduction indicating an insulator-to-metal transition. Key results from [STO_Redox] constitute precise local work function measurements, with reference to the $\text{Au}(111)$ standard. Surface potential maps are similarly heterogeneous both after reduction and *in situ* oxidation (Fig. 3.2). The mean work function however is increased by 0.55 eV upon oxidation, preserving the heterogeneous lateral distribution. Regarding conductivity, inhomogeneity is substantially increased and only small spots remain conducting presumably at the exits of dislocations confirming that they are hard to oxidize.

Concluding, it has been shown that the surface properties of the reduced STO are very sensitive to oxidation which may have implications for a number of technological applications ranging from sensing and resistive switching to preparation of substrates for thin film growth [STO_Redox].

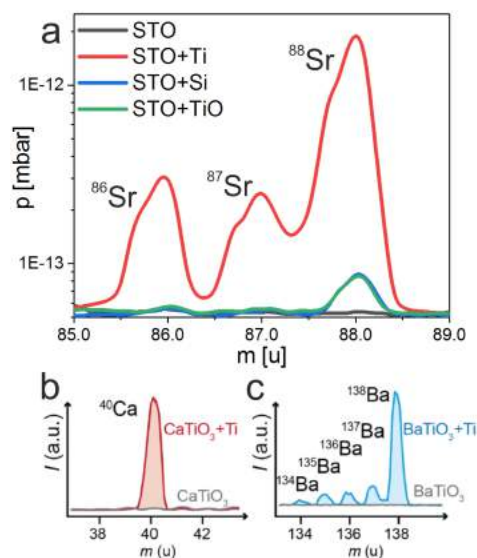


Figure 3.3. Decomposition of perovskite oxides (a - SrTiO_3 , b - CaTiO_3 and c - BaTiO_3), due to the oxygen getter presence, in terms of a strontium (calcium, barium) effusion measured by the mass spectrometry.

In the paper [STO_Decom] we investigate the influence of the oxygen partial pressure during thermal reduction by performing annealing experiments under standard vacuum conditions as well as under extremely low oxygen partial pressures, established by using an oxygen getter. The key output of this research is the discovery of perovskite oxides decomposition due to the presence of standard materials used in the UHV: titanium, titanium oxide or silicon.

We have found in particular that under standard vacuum conditions, SrTiO_3 is macroscopically stable. However, as soon as the oxygen activity is lowered by the employment of the oxygen getter (Ti, TiO and Si - not presented in the main text, here presented in Fig. 3.3 a), decomposition takes place, resulting in the sublimation of gaseous Sr, which was detected with use of a mass spectrometry. The same situation regards other ternary oxides: perovskite titanates CaTiO_3 and BaTiO_3 , which are technologically highly relevant materials (see Fig. 3.3 b and c). We suppose that similar observations can be made on the broader class of transition metal oxide materials.

Decomposition takes place from the surface towards bulk, and as a consequence of the Sr depletion, a Ti-rich nanocrystalline layer is formed. Observed layer is several μm thick and had

Having investigated the moderate reduction and oxidation impact on the surface of SrTiO_3 , it was justified to explore further this topic and observe processes happening at extreme conditions. The next paper is devoted to the investigation of a heavy reduction influence on the stability of perovskite oxides [STO_Decom]. Numerous research activities involved annealing oxides such as SrTiO_3 , e.g. in order to build superconducting heterostructures [61], achieve flat atomic surfaces [190] or towards sensing applications [191]. The invariant basis for such investigations was assumption that perovskite oxides are stable at temperatures below 1200°C under standard vacuum conditions [191], and the result of vacuum annealing (reduction) of a crystal would not have significantly different properties. We have dared to ask a question whether such "typical" preparations is harmful to the oxide stoichiometry and to what extend chemical segregation effects take place.

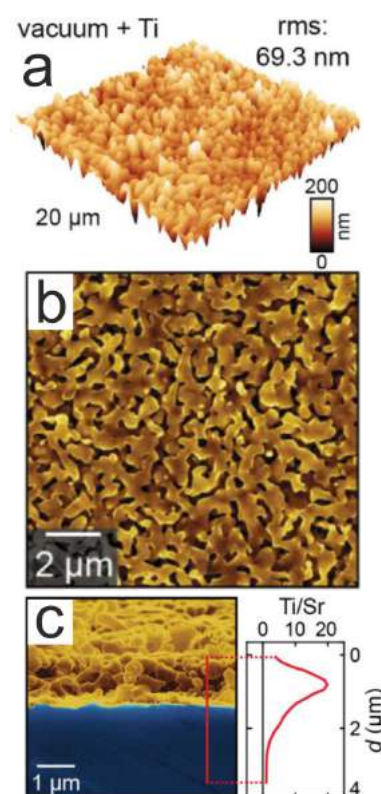


Figure 3.4. Resulting SrTiO_3 morphology after incongruent sublimation of Sr; a - AFM 3D view, b - SEM top view, c - Ti enrichment of a porous layer investigated by EDX.

a rather porous structure (see Fig. 3.4), in contrary to the ordered TiO crystalline nanowires array, which is described in paper [STO_TiO], although the same basic principle stands behind both structures formation. With use of thermodynamic calculations we proved that the decomposition at a very low oxygen activity is driven by the incongruent sublimation since the vapour pressure of gaseous Sr is significantly higher than that of the other gaseous species such as Ti or TiO.

As demonstrated, SrTiO_3 decomposes upon vacuum annealing in the vicinity of a material with a high oxygen affinity. Therefore one has to pay much attention which metals are used when performing vacuum annealing. Primarily, the use of oxygen getters should be avoided when the properties of the pure oxide materials are of interest, in order to prevent an unintentional surface decomposition. On the other hand, a dedicated application of oxygen getters could be exploited as an easy method for producing oxide surfaces with tailored properties for various technological applications.

Thermal reduction (and oxidation) impact on surface properties of single crystalline $\text{SrTiO}_3(100)$ surfaces was already investigated in the paper [STO_Redox], however it was not unintentional to confine the temperature range for most research to 900°C . At temperatures above we have sometimes observed the formation of a new, unexpected crystallographic phase. After careful checking to exclude any contaminations influence, we found out that a rock-salt TiO nanowires emerge and such formation is triggered by the incongruent sublimation of strontium (enabled with use of a silicon oxygen getter), which we have explored in [STO_Decom].

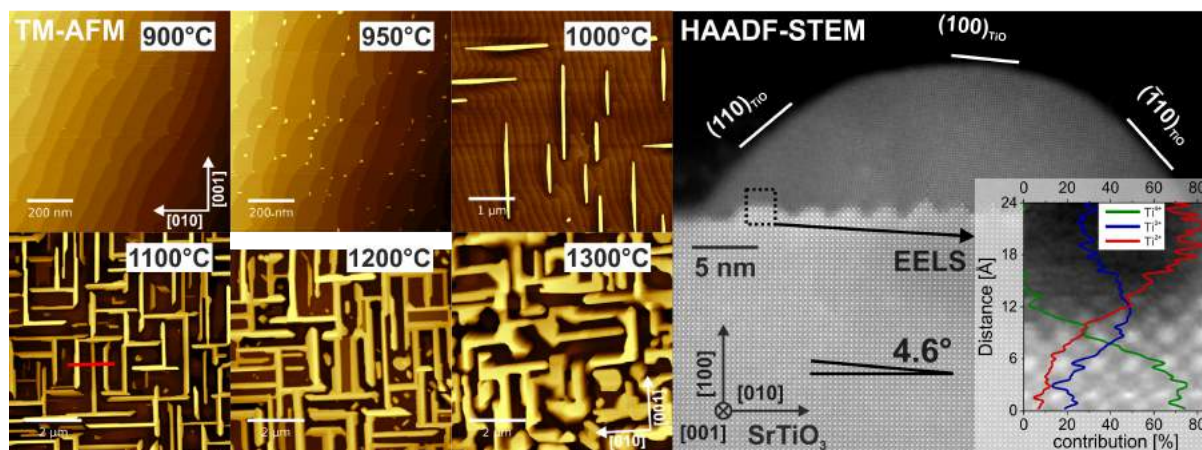


Figure 3.5. TiO nanowires formation on the surface of SrTiO_3 . On the left the evolution of a TiO morphology after thermal annealing is presented. Right hand side presents the transmission electron microscopy (HAADF-STEM, EELS) results on the crystallography and on the Ti oxidation state change across the TiO/STO interface.

In the research presented in [STO_TiO], we have considered the TiO/ SrTiO_3 system globally, taking care of bulk, subsurface and, with greatest concern, surface and interface properties of both materials. Combining surface resolving techniques such as STM, AFM (both in contact and tapping modes), LEED and SEM (with EDX and EBSD) and finally atomically resolved HAADF STEM imaging (utilizing EELS and EDX techniques) it was proven possible to determine the crystallographic structure of TiO nanowires, the Ti valence state, Sr/Ti/O stoichiometry in the system as well as surface reconstruction and conductivity.

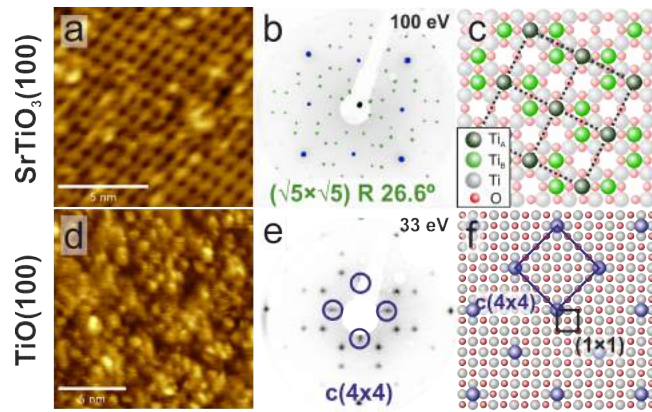


Figure 3.6. Comparison of surface reconstructions of $\text{SrTiO}_3(100)$ - $(\sqrt{5} \times \sqrt{5} \text{ R } 26.6^\circ)$ and $\text{TiO}(100)$ - $c(4 \times 4)$; a, d - STM images, b, e - LEED patterns, c, f - proposed models.

vable with use of an additional oxygen getter, and temperatures in the range of 1000°C enables SrTiO_3 single crystals to decompose and as a result a network of TiO nanowires can be formed. The whole evolution of such network is presented in Fig. 3.5. The nanowires' density, sizes and heights can be easily controlled by varying the temperature of reduction, for the given oxygen partial pressure. As unquestionably proven by means of transmission electron microscopy, TiO crystallizes in the defect-free rock-salt structure with an atomically sharp interface, where a transition between stoichiometric Ti^{4+} and Ti^{2+} happens over two lattice cells (see HAADF-STEM and EELS data in Fig. 3.5).

As a side, but still important result, a new $c(4 \times 4)$ reconstruction on $\text{TiO}(100)$ surface has been recognized and a model of such surface was given (Fig. 3.6). Metallic conductivity of a material placed on top of a nominal insulator may seem surprising, but in this paper we have observed such behavior. TiO nanowires are proved to have an excellent Ohmic-like conductivity, which is additionally preserved after an oxidation (see Fig. 3.7). This feature is explained in terms of a connection between a TiO nanowire array and a dislocation matrix, which provides a metallic current paths throughout the crystal. Based on such findings, a potential growth model is introduced and described in much detail in the supplementary information. It is suggested that actual formation of nanowires is initialized at dislocation exits, where Sr and O atoms are preferentially removed and via the crystallographic shearing of TiO_6 octahedra TiO nanophase develops.

In addition to performed measurements, an atomistic growth model of TiO nanophase was developed, considering the controlled decomposition of SrTiO_3 , but also the crystallographic shearing and surface diffusion.

In particular, in this research we have developed and described a mechanism called Extremely low oxygen partial pressure (ELOP), based on the process of incongruent sublimation of strontium, mentioned firstly in [STO_Decom]. We proved here that pressures less than 10^{-20} mbar, achievable

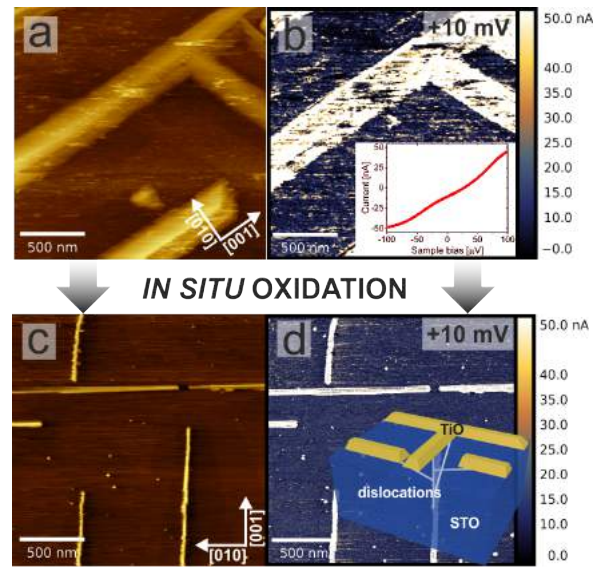


Figure 3.7. LC-AFM maps of conductivity of TiO nanowires on SrTiO_3 , before and after *in situ* oxidation. Insets show Ohmic behavior of TiO (top) and proposed connection to the dislocation network (down).

As already stated in the introduction, the rule of thumb of the oxidation and reduction impact on the work function is quite straightforward. Transition metal oxide reduction induces formation of d-electrons, due to the cation valence state change towards lower values, and should be observed as a work function decrease. Oxidation hinders conductivity as potential charge carriers are involved in the oxygen-metal bond formation and subsequently the work function increases. Unfortunately, devil is in the details and this general rule is not always in effect, especially when it comes to the structural changes due to reduction-oxidation, like new phases formation introduced in [STO_TiO]. Another example of a structural change affecting electronic properties is studied in the paper [TiO2_Nb], where a new reduction-induced surface reconstruction happened to dramatically change the observed conductivity and work function.

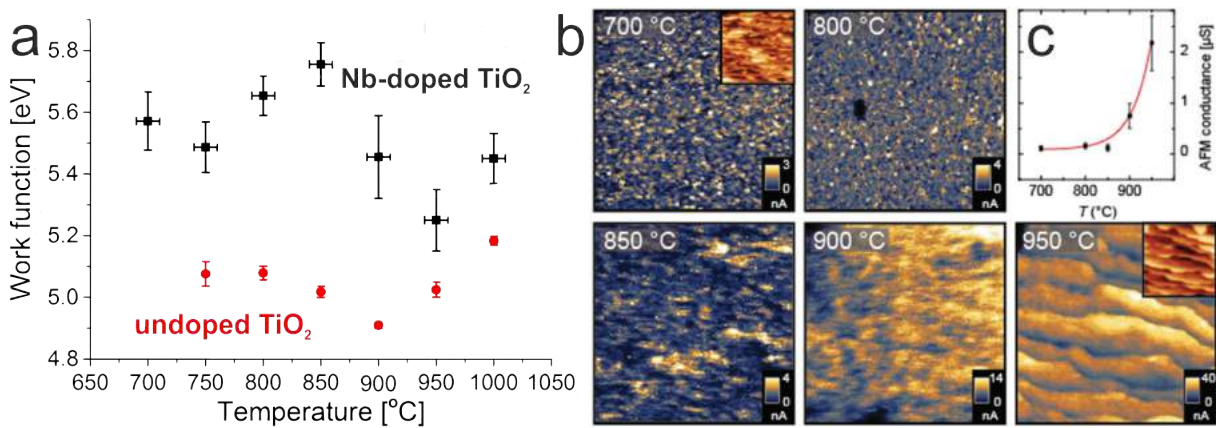


Figure 3.8. Thermal reduction impact on the electronic properties of undoped and Nb-doped TiO₂(110). a - work function evolution versus temperature of reduction, b - LC-AFM conductivity maps showing the advancing homogenization of resistivity, c - exponential increase of a measured conductivity with temperature.

We choose to investigate simultaneously the influence of thermal reduction and donor doping of TiO₂(110), since they are both widely investigated in the literature [77, 107, 192], however neglecting the ongoing structural changes on the surface. We aimed to fill this gap. In this case, 0.5% Nb-doped crystals underwent thermal reduction under UHV conditions and both structural transformations were tracked as well as macroscopic and nanoscale conductivity and work function. After each reduction step the KPFM tip was calibrated against Au(111) sample to exclude tip influence and obtain the non-biased, actual work function. Work function dependence on the thermal reduction for Nb-doped TiO₂(110) in comparison to the undoped crystal is plotted in Figure 3.8a. The measured values are in good agreement with the literature, since the work function of TiO₂(110) rutile falls in the range of 5.1–5.5 eV [193]. Surprisingly, in the case of the TiO₂:Nb(110) surface, the mean work function is higher compared to the undoped TiO₂(110) surface. This difference is related to the structural changes on the surface. From SIMS measurements in the literature it is known that there are concentration gradients emerging upon reduction [194] and such positively charged surface layer can be made responsible for the apparent increase of the work function of Nb-doped TiO₂ over undoped crystals.

However, the second unexpected trait of the work function dependence of Nb-doped TiO₂ on the reduction temperature is its non-monotonic behavior. In this case it was proved by other

surface-sensitive techniques (STM, LC-AFM, LEED) that the surface undergoes reconstruction evolution, from (1×1) to the new (4×2) reconstruction, which is Nb-enriched as suggested by SIMS measurements and backed by DFT calculations [TiO₂_Nb]. The new row-like reconstruction seen by STM and LC-AFM is presented in Fig. 3.9a and b, whereas the increase of Nb concentration is seen in the SIMS depth profile in c. DFT calculations suggest that Nb substitutes Ti atoms at the surface, driving them to go interstitial, as illustrated in Fig. 3.9 d- f. Therefore, one can expect that the emergence and evolution of this new reconstruction, which is partially composed of Nb atoms, lowers the work function, imposing on the general effect. Apparently, the highest work function is measured after annealing at 850°C, when the new structure begins to form, whereas the lowest work function is measured for the temperature of 950°C, when the (4×2) rows domain reaches its maximum area coverage. Furthermore, it stands in agreement with conductivity measurements – more d-electrons, which are attributed to the pentavalent Nb atoms in the (4×2) surface, lowers the surface work function and also contributes to the substantial increase of conductivity (see Fig. 3.9 b and c).

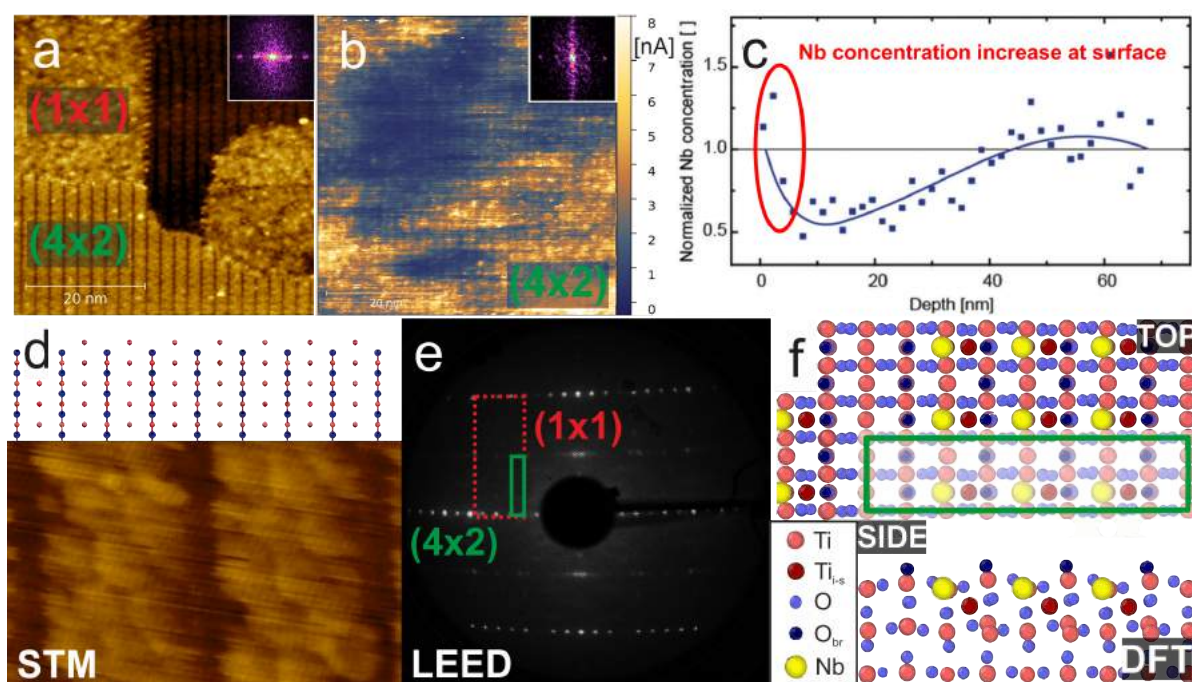


Figure 3.9. Ongoing surface transformation of a Nb-doped TiO₂(110) due to the thermal reduction. a, b - STM and LC-AFM maps, respectively, of a new $c(4 \times 2)$ reconstruction, c - increase of a relative Nb concentration at the surface, as proven by SIMS, d, e - STM and LEED results of a $c(4 \times 2)$, f - DFT calculations showing the Nb (yellow) substitution on the surface of TiO₂.

From the LC-AFM measurements a conclusion of exponential increase in conductivity can be drawn, while the lateral current distribution tend to be more and more homogeneous with the reduction temperature. Such effect is potentially of a great importance in the application of titania surfaces as electrodes, where the goal is to have a good, homogeneously conducting surface. It was already presented in numerous occasions that undoped rutile TiO₂(110) crystals (SrTiO₃ as well) are characterized by the highly inhomogeneous conductivity maps over whole

range of reduction degrees [32, 35]. We show here, that small doping of Nb does not affect the bulk crystal structure but enhances greatly the electronic performance of the surface.

So far, we have investigated the redox processes impact on SrTiO_3 and the influence of thermal reduction and doping on TiO_2 , taking utmost care of structural changes happening in the oxide crystal structure. Now, we would like to present directly the consequence of redox processes on the development of organic thin films. As it was already presented in the section 2.3.2, transition metal oxides, TiO_2 especially, frequently find applications in the design of organic electronics devices. We know already from this thesis (but it is not the common knowledge), that typical material preparation techniques such as annealing or sputtering can dramatically change structural and electronic properties of surfaces, which are substrates for organic film growth. In order to provide an insight into such topic the we have chosen the typical molecule-substrate system, which have both been widely investigated [128, 195, 196].

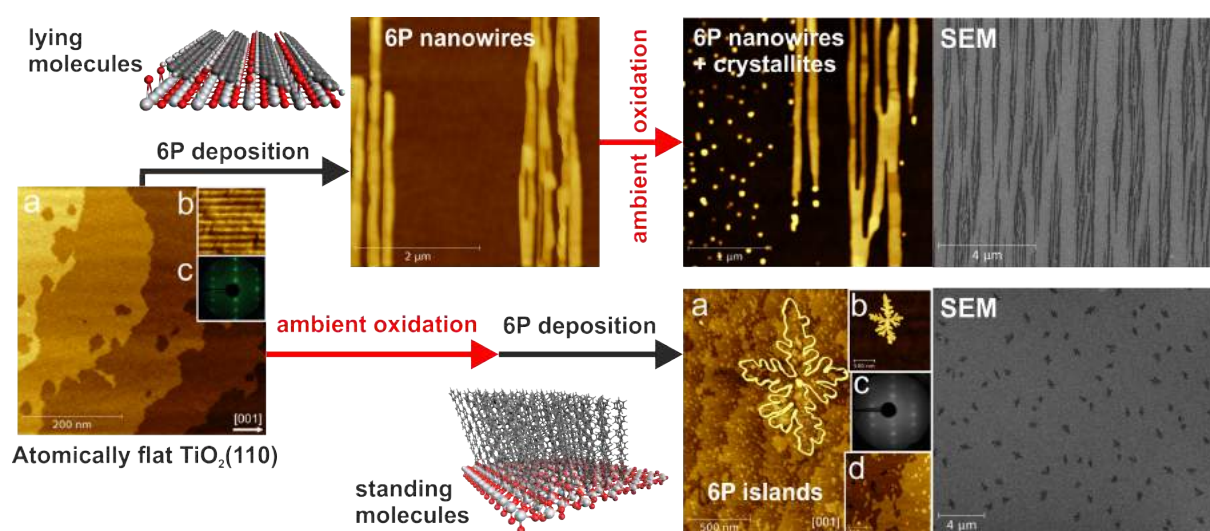


Figure 3.10. Control over 6P molecular thin film growth on the surfaces of $\text{TiO}_2(110)$. 6P deposition *in situ* on the atomically flat surface result in the molecular nanowires formation and a wetting layer, which then can dewet due to the ambient passivation. When a deposition is conducted after passivation, randomly distributed dendritic islands with standing molecular orientation are formed.

Goal of this research was to describe and understand growth process of a model rod-like parahexaphenyl (6P) molecule on a differently treated surfaces of $\text{TiO}_2(110)$ [**TiO2_6P**]. Before, 6P growth on TiO_2 was observed separately on atomically flat or amorphised surfaces, *ex situ* in the ambient air conditions only. Presented paper contains also results of the first direct observation of changes between molecular films morphologies, while kept in the ultrahigh vacuum (UHV) and air. We have found that 6P on flat $\text{TiO}_2(110)$ surface (achieved by use of sputtering-annealing cycles) forms a nanoneedle structure growing on a complete wetting layer of molecules in a lying orientation with respect to the substrate (compare Fig. 3.10).

When exposed to air after deposition, the wetting layer decomposes, making small islands in between nanoneedles. Up to this study, such structures had unknown origin. To have a complete view, we have also investigated the reverse process of the air influence on the molecular films growth when a surface is exposed before deposition. Resulting morphology was utterly

different (see Fig. 3.10). Randomly distributed dendritic islands, composed of upright standing molecules emerged as a consequence. By that, it was proved possible to control a single molecule orientation in a film, towards different optoelectronic properties (OLED, OTFT, section 2.3.2).

In the paper we have also explained in a detailed manner the formation principles of all observed molecular structures: wetting layer (2D), nanowires (1D), crystallites and islands (3D).

Ambient air exposure of the deposited molecular film, affected mostly the 6P layer itself. We have asked a question what would be the influence of an oxide surface reduction induced by the ion-beam sputtering, on the result of the molecular deposition. Therefore, in addition to the air exposure influence, we have also performed experiments regarding the 6P growth on ion beam irradiated $\text{TiO}_2(110)$ substrates. The intention was to determine which effect plays a dominant role in the molecular growth (namely the lying-to-standing orientation transition): nonstoichiometry or atomic scale roughness. It was assumed that the surface O/Ti nonstoichiometry caused by the ion-beam sputtering is partially restored by the annealing (which was described in the section 2.2.1, while roughness, recognized as a topography trait, in terms of RMS, is invariant in the first approximation.

Results of specially designed experiments, which allowed us to detangle those effects, show that local surface chemistry have a severe influence on the molecular films morphology while an increasing roughness forces molecules to stand up (see Fig. 3.11).

3.1.1 Significance of results

Here a several significant aspects of the results presented in this dissertation are briefly recalled. We focus only on those issues, which have not been sufficiently covered and highlighted in the introduction, overview or in the publications.

It is worth mention here, that discussed papers are being widely acknowledged in the scientific community, which is supported by over 20 citations so far (as for July 2018). Another measure of acclaim could be provided by the fact that two papers ([STO_Decom], [TiO2_Nb]) have been highlighted on outer cover pages of the Physica status solidi - Rapid Research Letters (PSS-RRL) and Physical Chemistry Chemical Physics (PCCP) journals respectively.

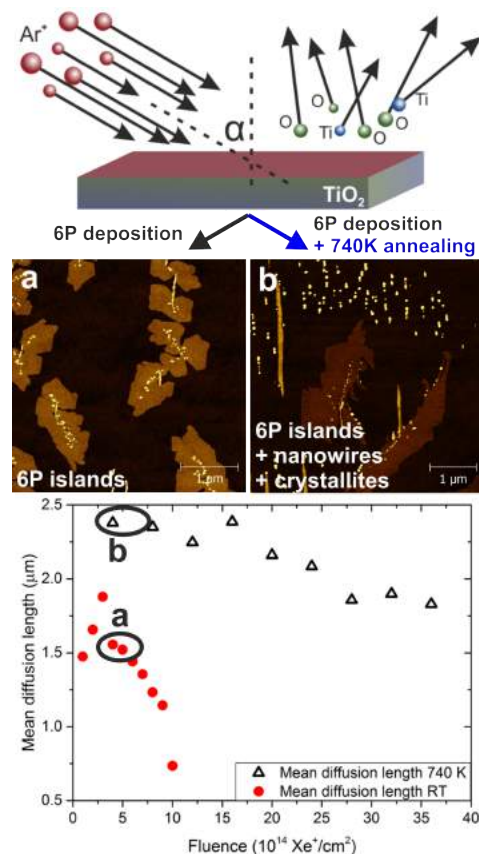


Figure 3.11. Influence of the ion-beam sputtering on the formed 6P molecular structures and mean diffusion lengths. a - 6P deposition on sputtered TiO_2 , b - 6P deposition on the sputtered-annealed surface.

Scientifically, we believe that most of studied phenomena regarding reduction-oxidation processes on surfaces of SrTiO_3 and TiO_2 concern the most generic effects and could be therefore generalized to a broader class of binary and ternary oxides.

New way of TiO formation (and possible Ti)

By utilizing the ELOP mechanism a possibility to control the formation of conductive crystalline TiO nanowires was demonstrated, which is an important result itself [STO_TiO]. However, this finding not only determines the properties and growth of TiO nanowires on strontium titanate, but presents a much more general mechanism of the incongruent sublimation implementation for the formation of new oxide phases, as it has been shown for the case of CaTiO_3 , BaTiO_3 [STO_Decom]. The developed method is a promising technique for fabrication of defined conductive nanostructures on perovskites for diverse applications in nanotechnology.

Titanium is expensive, although it is not rare and titanium dioxide is a ubiquitous component of such mundane articles as toothpaste, paper or plastics. Despite the fact that titanium-enriched ores are abundant in the Earth crust [197], metallic titanium is about six times as expensive as a stainless steel. It is supposed that the production of Ti via reduction of TiO_2 or other titanium oxides with an ELOP process ([STO_TiO]) would be more efficient than commonly used Kroll process [198], which in addition to high cost leaves high concentration of impurities. For less severe reduction, ELOP method may also help to produce black TiO_2 (TiO_{2-x}) materials without using hydrogen, and at lower temperatures [150].

TiO surface characterization

To date, no research studied directly the surface of cubic rock-salt TiO (the only measurement to knowledge of the Thesis author compromised a LEED pattern observation [199]). In [STO_TiO], in addition to a LEED pattern of a well-defined single crystalline TiO structures, STM study was performed. Based on this study a new $c(4 \times 4)$ reconstruction has been discovered and described.

***In situ in operando* oxygen dosing and work function evaluation**

In the study on the reduction-oxidation influence on the surface of SrTiO_3 a new experimental technique has been designed, namely the *in situ in operando* oxygen dosing and work function measurements with use of a Kelvin Probe Force Microscopy (KPFM) [STO_Redox]. Such approach can be utilized in many applications, e.g. organic or biological samples stability, in addition to the study of redox processes.

KPFM and LC-AFM techniques improvements

In this thesis KPFM and LC-AFM methods have been intensively employed. As a consequence several improvements of those techniques have been made. First extension to the KPFM would be a work function absolute value measurement, realized by the calibration with respect to the

gold Au(111) standard [TiO2_Nb], [STO_Redox]. It may help to provide a direct observation of surface work function at the nanoscale changes, in place of tracking only relative differences, which is so far common.

Another improvement is the possibility of simultaneously measure work function and conductivity at the same area of the sample, with use of LC-AFM and KPFM techniques. A soft, contact-mode conducting cantilever is set into oscillations to a higher harmonic, which enables to use it in the non-contact mode and perform KPFM investigations. This technique is described in detail in the dedicated paper with a co-authorship of a thesis author [200].

A way to control molecular orientation on oxide surfaces using redox processes

As a consequence of the detailed study of a *para*-hexaphenyl growth on TiO₂(110) surfaces a way to control the molecular orientation on oxide surfaces is postulated [TiO2_6P]. We show that the *in situ* deposition of 6P on atomically flat (sputtered-annealed) surface result in the lying molecular orientation, whereas ion-beam sputtering or ambient oxidation cause transformation to the upright-standing configuration. Preliminary studies show also that for the annealed-only TiO₂ surfaces, molecules tend to lie down as well, so the sputtering step during cleaning procedure may not be necessary.

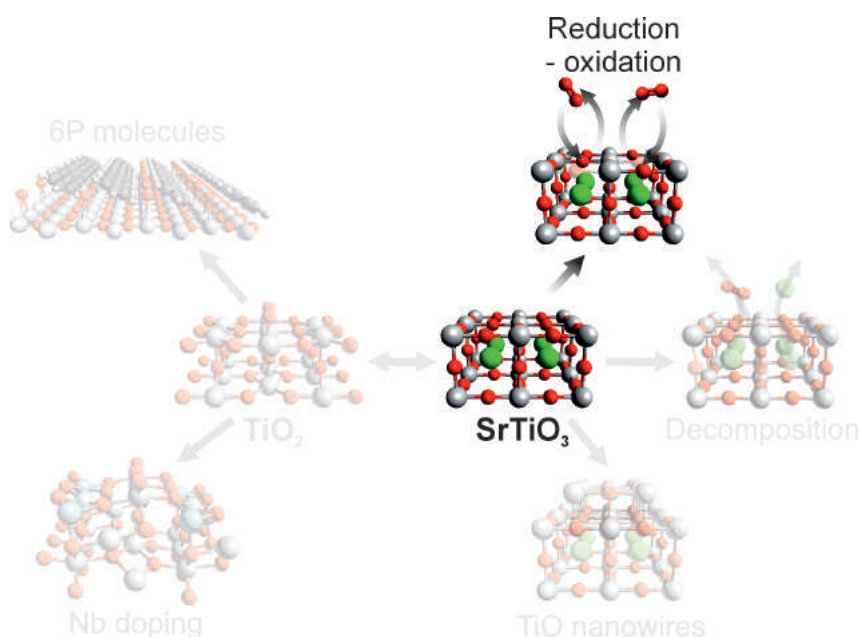
Pointing up the necessity of a careful material selection for oxide preparation

A lot of effort has been dedicated to explore the oxygen getters influence on the reduction of perovskite oxides. We have shown that some of the typical materials used in the vacuum research (titanium, silicon) cause a dramatic reduction of an oxygen partial pressure and as a result induce structural transformations and finally a complete decomposition of a crystal [STO_Decom], [STO_TiO]. Therefore, materials for sample holders, heaters, manipulators should be selected with utmost care, bearing in mind that in most cases they may affect the preparation and therefore, results. We propose using non-gettering materials for the purest and most precise experiments, for example using platinum when it comes to the high temperature annealing.

Formation of a highly and homogeneously conductive TiO₂ by doping and reduction

In the paper [TiO2_Nb] an important observation has been made, namely the formation of the homogeneously conductive layer as a consequence of a thermal reduction of a slightly Nb donor-doped TiO₂. Since for most applications the best case would be to have an oxide with the highly and homogeneously conductive surface, we propose a way to produce such, which is potentially of a high technological relevance.

3.2 In Situ Study of Redox Processes on the Surface of SrTiO₃ Single Crystals



The first paper building up this thesis ([**STO_Redox**]) is devoted to the investigation of the actual impact of thermal reduction and oxidation on the properties of the strontium titanate surface. Therefore, this research serves as a foundation for more detailed considerations presented in the following articles. A step-by-step study of the UHV annealing influence on the surface reconstruction, chemical composition, electronic conductivity and work function is presented. Finally, the paper contains results of the *in situ* reoxidation of reduced SrTiO₃(100) surfaces, showing fast and dramatic change in the local work function and metal-to-insulator transition of the surface conductivity.

Highlights

1. Reduction of SrTiO₃ crystal to 900°C results in macroscopic insulator-to-metal transition,
2. Surface undergoes transformation towards Ti-enriched reconstructions,
3. Reduction preserves conductivity and work function inhomogeneous lateral distributions,
4. Oxidation reverses insulator-to-metal transition at the nanoscale,
5. Oxidation impact is saturated after 10 L of oxygen dose, whereas work function increases as high as 0.5 eV.



Full Length Article

In situ study of redox processes on the surface of SrTiO₃ single crystalsD. Wrana^{a,*}, C. Rodenbücher^b, W. Bełza^a, K. Szot^{b,c}, F. Krok^a^a Marian Smoluchowski Institute of Physics, Jagiellonian University, 30-348 Krakow, Poland^b Forschungszentrum Jülich GmbH, Peter Grünberg Institute (PGI-7), 52425 Jülich, Germany^c A. Chelkowski Institute of Physics, University of Silesia, 40-007 Katowice, Poland

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ABSTRACT

In this paper, we report on surface transformations under high-temperature (up to 1000 °C) annealing of SrTiO₃(100) single crystals under reducing conditions and *in situ* oxidation. We compare macroscale electrical measurements with nanoscale investigations of as-reduced and oxidized surfaces. On the nanoscale, annealing in ultra-high-vacuum (UHV) conditions causes a restoration of the long-range atomic order of the (1 × 1) pattern. However, above annealing temperatures of 900 °C, a complex reconstruction of ($\sqrt{13} \times \sqrt{13}$)R 33.7° and subsequently ($\sqrt{5} \times \sqrt{5}$)R 26.6° appears. The surface becomes Ti-rich and residual carbon desorbs. Electrical surface conductivity increases with the annealing temperature, revealing an inhomogeneous spot-like structure on the nanoscale. Mapping of the surface potential also reveals comparable spatial variations, marking exits of dislocations. The estimated surface work function is increased upon reoxidation by 0.55 eV in the case of annealing at 900 °C, when ($\sqrt{13} \times \sqrt{13}$)R 33.7° dominates. Our results show that in contrast to the macroscopic resistance of the crystal, the nanoscale surface conductivity and surface potential are significantly influenced by redox processes at room temperature.

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1. Introduction

An increasing amount of effort is today being put into finding new materials to replace silicon in electronic applications, as its performance is reaching its limit. Some of the most promising candidates are oxides due to their stability, transparency, electronic structure, and last but not least, their low cost. Although most oxides are initially insulating, redox reactions provide a simple and effective way to tune the electronic and chemical properties of oxides for a variety of applications ranging from fuel cell fabrication [1] and the supercapacitor industry [2] to the photocatalytic inactivation of *E. coli* bacteria [3]. Even if the consequences of redox processes are seen on the macroscale, it is crucial to understand processes occurring under oxidizing and reducing conditions on the nanometer scale.

To investigate surface reduction and oxidation we focused on the widely used model material strontium titanate (SrTiO₃, STO). STO crystallizes in the cubic perovskite phase with two distinct surface terminations on the (100) plane: TiO₂ and SrO. For the untreated single crystal, regions with different terminations are randomly distributed, yet under certain conditions one of them is

promoted. Precise control over surface termination is crucial for the growth of thin oxide films and perovskite heteroepitaxial layers [4]. Moreover, high-mobility two-dimensional electron gas (2DEG) between grown LaAlO₃ and SrTiO₃ substrate is formed for the TiO₂ termination only [5]. The creation of such a termination in most cases involves using buffered acid etching and subsequent annealing under reducing conditions [6] [7]. To create a SrO-terminated surface, annealing in an oxygen-rich atmosphere is required [8]. Oxygen activity during crystal preparation thus plays an important role in the tailoring of surface properties. In addition to the termination, STO(100) surfaces can relax in various distinguishable reconstructions [9], depending on the annealing temperature and the partial pressure of oxygen [10]. Ultimately, non-stoichiometric phases evolve under annealing at higher temperatures. Crystal annealing under oxidizing conditions usually results in SrO-rich structures appearing [11], whereas various TiO_x phases evolve under oxygen-depleted conditions [12].

This paper aims to explore the relation between the macroscale and nanoscale properties of SrTiO₃ upon reduction and oxidation. Since it is a very broad and complex topic, we opted for thermally driven reduction under well-defined reducing vacuum conditions and surface response to a low dose of oxygen. The experimental conditions we used for the redox process are of great significance for the basic studies as well as for the growth of thin oxide films, for example using the pulsed laser deposition (PLD) technique

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and electrochemistry, especially for the fabrication of redox-based memristive devices [13]. In our research, the macroscopic behavior of a reduced and reoxidized crystal is provided by four-point electrical measurements. To gain a comprehensive understanding of the nanoscale properties of the STO(100) surface upon reduction and oxidation, we used a low-energy electron diffraction (LEED) technique for a reconstruction identification, X-ray photoelectron spectroscopy (XPS) for stoichiometry analysis, contact mode atomic force microscopy (C-AFM) with current signal for surface topography and surface conductivity, and non-contact atomic force microscopy (NC-AFM) with a Kelvin loop for characterizing the topography and surface potential.

In our study, we were able to demonstrate how during reduction the surface reconstruction changes from (1×1) through $(\sqrt{13} \times \sqrt{13})R 33.7^\circ$ to $(\sqrt{5} \times \sqrt{5})R 26.6^\circ$, accompanied by significant changes in Ti/Sr stoichiometry, causing the surface to become Ti-enriched. At a transition temperature of 800–900 °C, the surface becomes metallic, with conductivity a few orders of magnitude better than for annealing at 600 °C. However, we observed distinct local variations in current and local work function maps, marking exits of dislocations. The reduced STO(100) surface reacts instantly with oxygen, even for partial pressures of 10^{-8} mbar. Oxygen atoms are chemisorbed at surface active sites and change the charge state of Ti from +3 to +4, thus lowering the conductivity and increasing the work function by 0.55 eV for reduction at 900 °C, when $(\sqrt{13} \times \sqrt{13})R 33.7^\circ$ reconstruction dominates.

We are able to show that controlled reduction and oxidation of the SrTiO₃(100) surface provides an easy way of tuning both substrate work function and conductivity, which is of great technological importance for the growth of thin oxide films and for the development of resistive switching devices.

2. Materials and methods

SrTiO₃(100) *epi*-ready single crystals provided by Shinkosha and Crystec were used for the investigation. The experiments were carried out under ultrahigh vacuum (UHV) conditions with a base pressure of 2×10^{-10} mbar (maintained using turbomolecular, ion, and Ti-sublimation pumps). STO samples were introduced into the UHV system after cleansing in isopropanol and ethanol using an ultrasonic bath and they were subsequently outgassed to 300 °C to remove water. Unlike many other investigations, no chemical etching was involved during crystal preparation. The cleaning method applied ensures that the surface is clean without any residual contamination from the acids or solvents. Crystals were nominally undoped, with low levels of contamination, which was additionally checked by means of secondary ion mass spectrometry (SIMS). Intrinsic bulk dopants, such as Ca, Na, Si, C, Nb, and K, were below the ppb regime.

The macroscopic resistance of the crystals was measured using a four-probe technique. Four electrodes were deposited on a single crystal ($8 \times 3 \times 0.5$ mm³) using Pt paste and connected to Pt wires. The sample was placed into an evacuated quartz tube (with base pressure $<10^{-6}$ mbar) surrounded by a tube furnace. The outer electrodes were connected to an AC voltage source and the potential of all electrodes was measured by electrometers using the lock-in technique. This ensured that a potential degradation of the sample, which can be expected for DC voltage due to ionic conductivity, was avoided. In situ oxidation of the crystal was performed by supplying pure oxygen into the vacuum chamber via a needle valve.

For nanoscale investigations, crystals ($10 \times 3 \times 0.5$ mm³ in size) were mounted onto an AC current heater. The use of an alternating current served to ensure that the reduction and temperature was uniform for all sample crystals. Annealing was performed at up to 1000 °C; the sample was kept at each indicated temperature for

30 min and cooled down slowly at a cooling rate of about 50 K/min. The temperature was recorded using a calibrated digital pyrometer, with an estimated systematic error of 20 °C. Estimated oxygen partial pressure during the reduction process was in the order of 1×10^{-10} mbar.

The resulting surface properties were examined in situ using scanning probe techniques, performed at room temperature with an Omicron RT STM/AFM device. Atomic force microscopy (AFM), either in contact mode (C-AFM) or non-contact mode (NC-AFM), with conductive Pt-coated cantilevers, was used for the study. Additionally, we used a low-energy electron diffraction (LEED) system with a multichannel plate detector to examine the surface reconstruction. In contact AFM mode, we measured surface topography as well as local conductivity (LC-AFM). Due to the microscope amplifier limits, the minimum current measured was in the order of 100 fA, whereas the maximum current was set at 50 nA (almost in the 6 orders of magnitude range). When operating in frequency modulation (FM) non-contact mode, the contact potential difference (CPD) signal in Kelvin probe force microscopy mode (KPFM) together with the topography signal was acquired. In FM-KPFM, the sample was biased with a 600 Hz AC component and modulation amplitude of $V_{ac} = 500$ meV for the CPD measurement. In order to obtain reliable information about the work function of the SrTiO₃(100) surfaces measured, the AFM tip was calibrated against a reconstructed Au(111) surface for absolute work function measurements. Since the work function of Au(111) is known to be 5.31 eV, the real work function of reduced or oxidized STO could be resolved, regardless of the state of the tip.

Oxidation experiments were performed in situ while the sample was scanned using FM-KPFM mode at a rate of 1 line/sec, oxygen (10 ppm impurity) was dosed into the SPM chamber. Oxygen partial pressure was set to 5×10^{-8} mbar, which corresponds to 100 langmuir (L) over 30 min of exposure.

XPS analysis was performed using a Physical Electronics PHI 5600 spectrometer with an Al K α monochromatic X-ray source. The spectra were measured at a take-off angle of 45° resulting in an information depth of 6 nm. The measurements of the core lines Sr3d, Ti2p, O1s, and C1s were conducted in the temperature range of up to 1000 °C in situ and in operando under controlled UHV conditions.

3. Results and discussion

3.1. Macroscopic reduction

The results of electrical four-point measurements of reduction and oxidation of a bulk STO(100) single crystal are presented in Fig. 1. The setup of the four electrodes provides information on the interface and bulk-related potential drops (see schematic representation in the inset of Fig. 1b). Additionally, the total resistivity of the crystal is plotted. Fig. 1a presents *in situ* resistivity changes for a STO(100) crystal annealed at 900 °C under reducing conditions. Resistivity decreases significantly for the first 30–40 min, meaning this time was used for the optimization of the crystal reduction process. After reaching a minimum, it begins to increase again – presumably due to segregation effects. The resistivity of a reduced crystal cooled down to room temperature was recorded (Fig. 1b) in order to determine macroscopic electrical behavior. After maintaining the sample at 900 °C for 18 h the resistance increased to approx. 300 Ω . The temperature dependence was then recorded during cooling to room temperature, revealing metallic behavior. The final RT resistivity measured for the reduced sample at 900 °C was $\rho = 0.65$ Ω cm, which is comparable to values presented in the literature [14]. It was also shown that after cooling down to RT, the exposure of the reduced STO crystal to the O₂ atmosphere (of

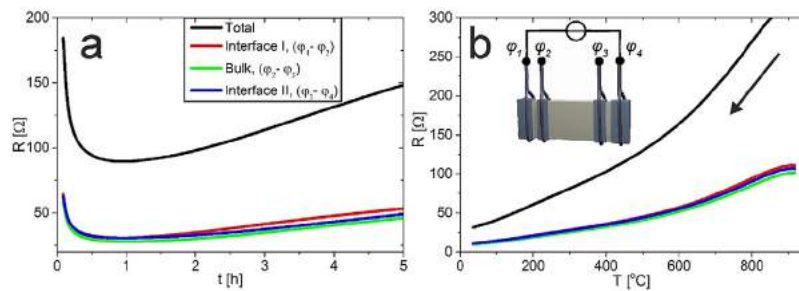


Fig. 1. Four-point resistivity measurements of the thermally reduced SrTiO₃(100) single crystal. Schematic representation of experimental setup is shown in the inset. (a) Resistance dependence over time for reduction at 900 °C. There is an abrupt drop in resistivity after about half an hour. (b) Resistivity changes during cooling from 950 °C to room temperature, thus indicating the metallic behavior of a reduced STO crystal.

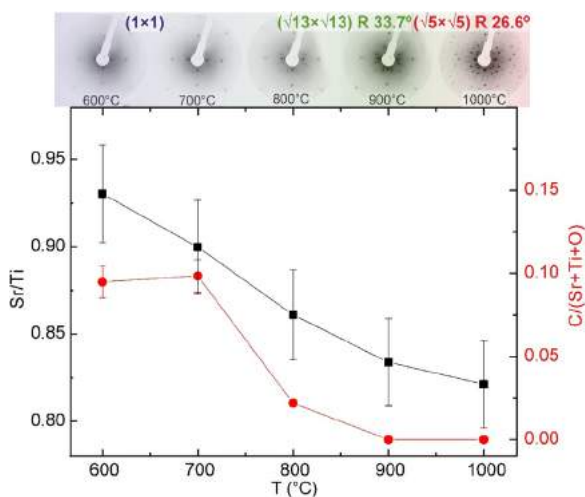


Fig. 2. Surface reconstruction evolution. Top: LEED patterns of SrTiO₃(100) surface recorded after annealing at different temperatures (200 eV energy beam). Initially the dominant reconstruction is (1 × 1), then at 800 °C to 900 °C more complex ($\sqrt{13} \times \sqrt{13}$)R 33.7° appears and finally for the highest reduction regime ($\sqrt{5} \times \sqrt{5}$)R 26.6°. Below: XPS Sr3d to Ti2p peak ratio for SrTiO₃(100) single crystal annealed at temperatures of 600 °C to 1000 °C with corresponding C1 s content for each temperature.

200 mbar for 16,000 s, which is equivalent to 2×10^{12} L) did not change the macroscopic crystal resistivity.

3.2. Surface reconstruction

In Fig. 2, the evolution of LEED patterns for the SrTiO₃(100) surface upon annealing is shown. The LEED patterns (for 200 eV beam energy) were measured at room temperature after annealing the samples to the temperatures indicated. For annealing at up to 700 °C, the surface adopts the (1 × 1) reconstruction. At 800 °C, a new complex pattern appears. The new ($\sqrt{13} \times \sqrt{13}$)R 33.7° (referred to as $\sqrt{13}$ hereinafter) structure develops until 1000 °C is reached and a ($\sqrt{5} \times \sqrt{5}$)R 26.6° ($\sqrt{5}$) pattern is observed. The $\sqrt{13}$ surface is likely to be enriched in TiO₂, as it is formed by means of TiO₅ polyhedra tiling [15]. This is in agreement with our XPS measurements, since there is considerable Ti enrichment (see Sr/Ti ratio in Fig. 2).

The carbon concentration of the reduced STO(100) was evaluated at the same time as the cations. The carbon is assumed to originate from strontium carbonate dissociation at elevated temperatures under vacuum conditions. For low annealing temperatures, its content amounts to, at most, 10 % of the surface layer and decreases to 4 % for 800 °C. Above 900 °C, the C1 s peak disappears completely, thus demonstrating that the surface is free of carbon-related contaminants.

3.3. Surface conductance

Real-space mapping of the surface was performed using the LC-AFM mode (Fig. 3, left column). Even at the lowest annealing temperature, flat regions of about 50 nm were found. Surface roughness decreases with increasing annealing temperature and at 900 °C the monatomic terraces with a width of 100 nm are easily resolved. The transition from (1 × 1) to $\sqrt{13}$ does not affect the step-like behavior. However, electrical conductivity, which was recorded simultaneously with topography, exhibits an inhomogeneous structure and does not appear to be directly related to terrace development (Fig. 3, center column). Spots (e.g. filament ends) with dimensions <10 nm and a current measured orders of magnitude higher are scattered randomly on the surface. Their density does not change upon a reduction in temperature, but there is a significant increase in the conductivity of the individual spots (see the decreasing bias for successive temperatures while maintaining a similar current flow). There is an apparent increase by about 2–3 orders of magnitude between crystal reduced at 600 °C and at 900 °C, although it is difficult to provide exact values since the images had to be recorded with different sample voltages.

KPFM surface potential maps for each annealing temperature are presented in Fig. 3 in the right-hand column. A similar level of inhomogeneity as seen in the current maps is present, with a dispersion of about 60–100 meV. The average diameter of the regions of higher surface potential is 45.5(5.1) nm (measured using 2D autocorrelation).

In Fig. 4a and e, representative I/V curves of conductive spots acquired on the reduced STO before and after oxidation are shown. For the as-annealed STO surface, an abrupt change towards higher conductivity is seen at 800 °C, whereas the I/V curve shows predominantly ohmic behavior at 900 °C. The corresponding average AFM conductance of conductive spots at 800 °C is 0.6(2) μS, whereas at 900 °C it is 6.3(1.1) μS – one order of magnitude higher. The surface oxygen exposure causes a decrease in the average conductivity, even for a dose as small as 100 L (Fig. 4e). Samples treated previously under low-temperature annealing (600–700 °C) maintain the same I/V curve behavior but with much less current (see Fig. 4e inset). For high temperatures, however, a change from ohmic to rectifying behavior occurs. This is possibly related to a metal-to-insulator transition on the surface, which results in the formation of an energy barrier between the metallic tip and the semiconducting surface. The topography of the surface annealed to 900 °C (Fig. 4b and f: before and after oxidation, respectively) is unchanged, whereas conductivity mapping reveals that most of the conducting areas switch off upon oxidation (Fig. 4c and g). Some spots are more resistant to oxygen incorporation, while others become completely insulating. The density of the remaining spots is in the range of 10^{11} per cm².

Very intense oxidation (exposure to ambient air, not shown) of an SrTiO₃(100) surface reduced at 900 °C causes nearly all the spots

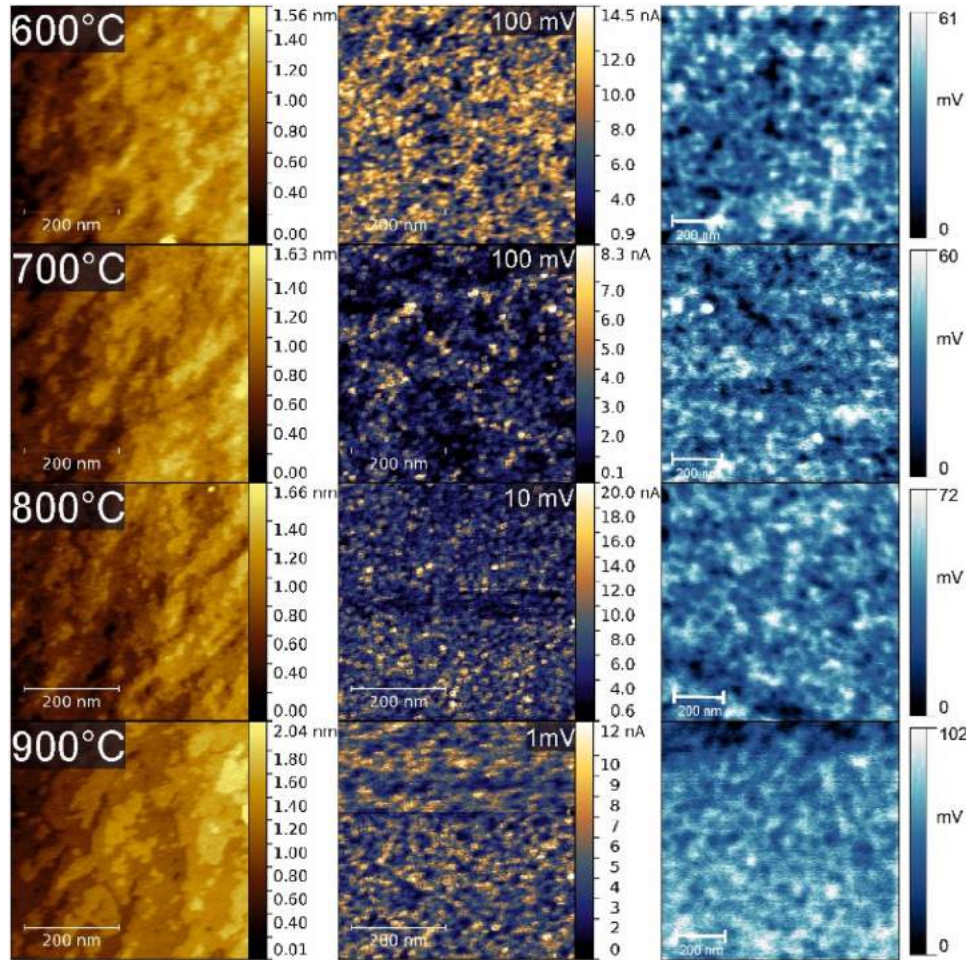


Fig. 3. Contact-mode AFM topography (left) with simultaneously acquired current maps (center) images ($500 \times 500 \text{ nm}^2$) of $\text{SrTiO}_3(100)$ annealed at temperatures from 600°C (top) to 900°C (bottom). The sample bias was independently set for each image (top right corner) to prevent current values exceeding the preamplifier range of the microscope. Additionally, each current map also contains a set of I/V curves recorded on the corresponding STO surface. Right-hand column contains typical KPFM surface potential maps of annealed $\text{STO}(100)$ ($1 \times 1 \mu\text{m}^2$).

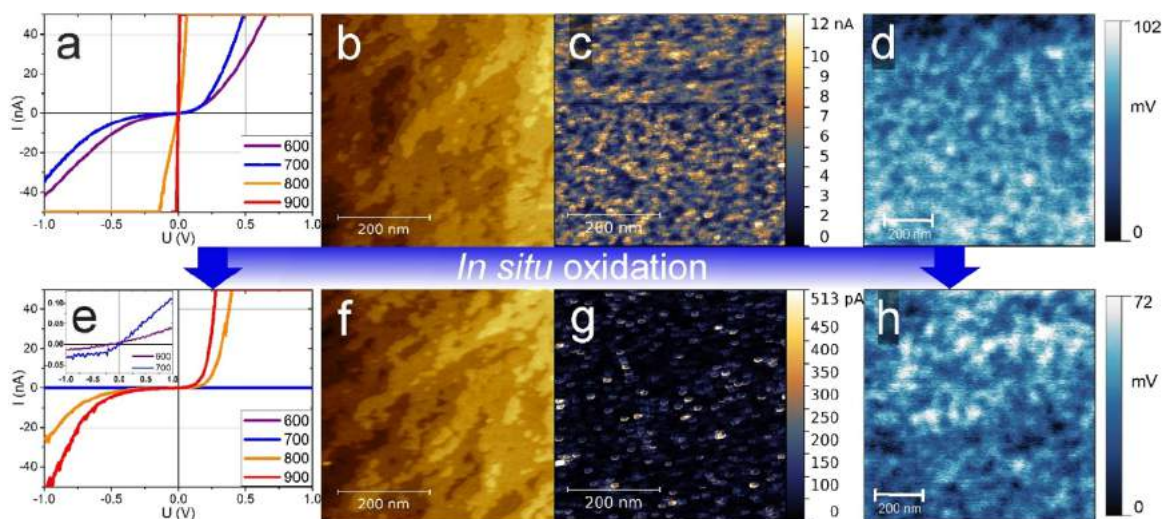


Fig. 4. State of electrical conductivity before (top row) and after (bottom row) oxidation of the reduced $\text{SrTiO}_3(100)$ surface. (a) I/V curves of conductive spots at different annealing temperatures; (b) and (c) LC-AFM topography and current map for STO annealed at 900°C ($500 \times 500 \text{ nm}^2$, sample bias of 1 mV); (d) CPD map for STO annealed at 900°C ($1 \times 1 \mu\text{m}^2$, rescaled to the lowest value); (e) I/V curves of conductive spots after 100 L oxidation at different annealing temperatures. Inset zooms in on curves at 900°C and 700°C ; (f) and (g) LC-AFM topography and current map for STO annealed at 900°C after 100 L oxidation (sample bias of 10 mV); (h) CPD map for STO annealed at 900°C after 100 L oxidation ($1 \times 1 \mu\text{m}^2$, rescaled to the lowest value).

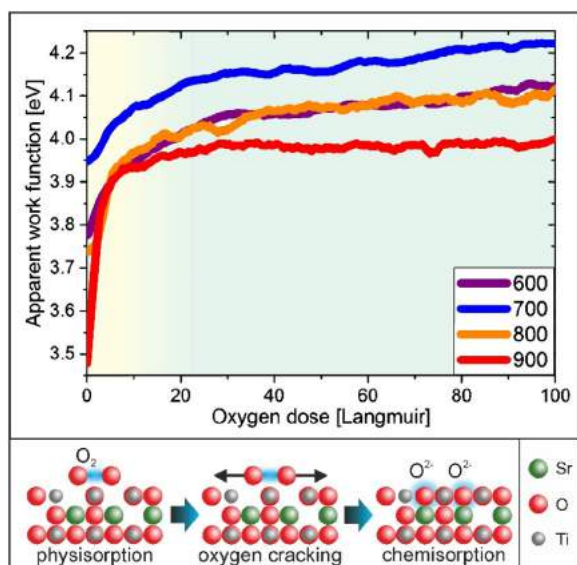


Fig. 5. Measured increase of surface work function due to oxygen exposure from 0 to 100 L under different annealing temperatures. Below the scheme is a proposed model of oxygen interaction with the reduced STO(100) surface: molecular oxygen lands on the surface, splits into atoms, and chemisorbs at active sites such as surface oxygen vacancies.

to switch off, leaving some still highly conductive with a density of 3×10^{10} per cm^2 marking the exits of switchable dislocations [16].

3.4. Surface potential

In order to investigate the dependence of the surface potential on the annealing temperature, NC-AFM measurements were performed with a Kelvin loop (KPFM). CPD maps (Fig. 3) revealed significant lateral variations where the average size of individual areas of increased surface potential for all images was 45.5(5.1) nm. The mean values of the apparent work function (applying the calibration procedure described in the Materials and Methods section) were evaluated for each annealing temperature. It was found that the work function was variable over the annealing temperature. For the initial reduction at 600 °C, a value of 3.775(74) eV was recorded. This then increases slightly before decreasing linearly to a minimum value of 3.478(64) eV. The surface work function can be adjusted – even an extremely small level of exposure to oxygen (100 L) with a low partial pressure of 5×10^{-8} mbar is sufficient to increase the work function significantly. Fig. 5 depicts the development of the local work function recorded during in situ oxygen exposure for surfaces annealed at temperatures from 600 °C to 900 °C. Increases for lower temperatures are in the order of 0.25 eV, whereas for higher temperatures, especially 900 °C, the difference in work function, between the reduced and the oxidized surfaces, is twice as high. The energy difference of 0.55 eV suggests the formation of chemical bonds between oxygen and the reduced STO (see Fig. 5 scheme). Together with a substantial change in the average work function value, no changes were observed in lateral structure after oxidation (Fig. 4d and h). Fig. 4d and e show surface potential maps for STO(100) annealed at 900 °C before and after oxidation, respectively. Oxidation preserves heterogeneity, with the same average size of regions and increased potential of 53(7) nm.

When the sample was measured after 24 h in UHV conditions, without oxygen exposure, the work function of the previously oxidized surface (reduced at 900 °C) decreased by almost 0.1 eV. This value does not change thereafter, however, thus indicating the equilibrium state of the oxygen near the surface.

4. Discussion

The influence of redox reactions on electronic properties was primarily investigated for a bulk crystal. For annealing at low oxygen partial pressure, oxygen vacancies were created resulting in an increased d-electron density in the range of 10^{15} to 10^{18} per cm^3 [14]. Our macroscopic measurements confirm the electrical behavior of the reduced STO sample for temperatures from 900 °C down to RT. According to theory, we would expect macroscopic resistance to decrease with reduction time. This is indeed proven by a four-point electrical characterization of STO(100) reduced at 900 °C (Fig. 1a). The subsequent increase in macroscopic resistivity is presumably related to Sr/Ti phase separation [12]. For later nanoscale investigations, we selected 30 min of annealing for each temperature to ensure we were in the monotonic regime of reduction. When the sample cools down from 950 °C to room temperature, macroscopic resistivity decreases, which indicates the metallic behavior of a reduced STO crystal (Fig. 1b).

On the nanoscale, the surface undergoes structural transitions. Observed LEED (Fig. 2) pattern changes are consistent with the findings of Kubo and Nozoye with respect to a new STO reconstruction appearance after annealing under reducing conditions [7]. Upon annealing under UHV conditions, the surface phase transformation from (1×1) through $(\sqrt{13} \times \sqrt{13})R 33.7^\circ$ to $(\sqrt{5} \times \sqrt{5})R 26.6^\circ$ occurs and the first transition temperature lies between 800 °C and 900 °C, while the second transition temperature is 1000 °C. Moreover, the reconstruction of the surface layer not only results in a change in the cation–anion distance but also leads to a change in the surface lattice dynamics. $\sqrt{13}$ and $\sqrt{5}$ reconstructions are assumed to be related to the nonstoichiometric layers of Sr and Ti cations on the surface, with a significant oxygen deficiency [12,17–19]. Surprisingly, a similar transition from (1×1) to $(\sqrt{13} \times \sqrt{13})R 33.7^\circ$ reconstruction was observed during annealing under oxidizing conditions [20]. However, this may be due to the use of a different preparation procedure (HF etching). In our study, the only instance we found in which the $\sqrt{13}$ reconstruction forms was under annealing at 800 °C with significant Ti-enrichment, which is consistent with its proposed origin of a polyhedral tiling of TiO_2 [15]. There are two alternative explanations for the reconstruction origins of $\sqrt{5}$: 1) it forms on a TiO_2 -terminated surface as a Sr-adlayer [7], [12] or 2) as a Ti-rich layer on TiO_2 termination [17]. XPS measurements (Fig. 2) reveal that the $\sqrt{5}$ reconstruction is Ti-enriched, indicating that scenario 2 is more realistic.

LC-AFM investigations show that the reduction of STO crystals under vacuum conditions leads to the inhomogeneous distribution of the in-plane conductance of the reduced surface layer (filaments of increased conductivity are observed). The concentration of the filaments (in the range of 10^{11} per cm^2) after oxidation of the STO is similar to the concentration of filaments measured on the reduced STO crystal after *ex situ* LC-AFM measurements [21]. However, *in situ* measurements of the reduced STO crystal are presented for the first time. For the annealing temperature of 900 °C, the I/V curves recorded are predominantly of an ohmic character. The oxidation (100 L O_2 exposure) switches off the conductance between conductive filaments. A similar effect was observed for the reduced $\text{TiO}_2(110)$ surface [22]. This correlation and observed reconstruction evolution might suggest that in the case of STO crystals reduced at 900 °C, a TiO_2 -enriched layer emerges in the surface region with properties similar to the reduced TiO_2 crystal surface.

In situ local CPD measurements show an increase of the apparent work function upon oxidation. The work function increases after oxygen exposure (of 0.25 eV) is constant for the temperatures below the transition and double at 900 °C, when the surface adopts $\sqrt{13}$ reconstruction (0.55 eV). Slower dynamics and values for CPD response to oxygen after annealing at lower temperatures might be attributed to a different surface reduction state

and reconstruction transformation, but might also be influenced by carbon contamination, as revealed by XPS. We thus mainly focus on contamination-free annealing at 900 °C, when a sharp increase (for the first 10 langmuirs) in the apparent work function was measured. It was shown that TiO₂-rich SrTiO₃(100) termination enhances oxygen evolving activity [23]; at a temperature of 900 °C, we observe an increasing Ti-content on the surface. Oxygen vacancies are also created, since a higher annealing temperature and new reconstruction may cause a higher reduction state of surface cations, especially Ti, as was shown in [12]. We know from point defect chemistry that oxygen vacancies are created at the very surface, contributing to valence states changes (e.g. Ti⁴⁺ to Ti³⁺) and the release of d-electrons, which we observe as increased conductivity [24]. Different scenarios are proposed for the actual preferential surface site for oxygen vacancy [25].

However, the structure of a few nm spots of electrical conductive and heterogeneous surface potential maps of reduced surfaces suggests that vacancies are not only scattered individually at the surface. Inhomogeneity might be related to vacancy clusters but is more probably linked to crystal extended defects. It was shown previously that there is a significant number of dislocations in SrTiO₃ single crystals, which can be reduced preferentially, resulting in the formation of structurally fixed oxygen vacancies [16,26]. Models predict that this is associated with the generation of a space-charge zone resulting in enhanced electronic conductivity along the dislocation [27]. Dislocations could thus be regarded as the electronic filaments that we see in LC-AFM mapping.

Dislocations and the bulk crystal also react differently upon annealing: due to the lower formation energy of oxygen vacancies at dislocation cores they are assumed to be reduced more easily [26]. Since dislocations are formed during crystal growth and processing, their average density at the surface, estimated to be around 10⁹–10¹⁰ per cm², is insensitive to annealing at moderate temperatures [28], which is confirmed by the rather stable density of the conductive spots recorded by our LC-AFM investigation (Fig. 3).

In this paper, we present for the first time the results of *in situ* surface oxidation recorded live. The observed work function increase of about 0.55 eV (Fig. 5, red line) between as-annealed and oxidized surfaces of STO might ultimately be a result of the oxygen interacting with the reduced surface and dislocations. It can be assumed that initially molecular oxygen adsorbs on the surface, electrons are transferred and O–O bonds dissociate, oxygen atoms then diffuse on the surface to fill active vacancy sites, and the Fermi level changes [29]. The present CPD measurements do not allow us to distinguish or separate the two paths of chemisorption or physisorption in the present incubation time. The average size of individual areas of increased surface potential is measured at 45.5(5.1) nm. This value represents the upper limit of the actual size, since there is a contribution from tip geometry and sample-tip separation [30]. However, the value is in agreement with theoretical calculations of the size of a space-charge zone around the dislocation core [26]. As can be seen in Fig. 4, the average conductivity of the surface at 900 °C decreases after oxidation, but the inhomogeneous structure of the conductive spots remains. The same situation applies to surface potential mapping, which indicates that the dislocations maintain their electronic conductivity and thus provide a filamentary network for current flow in the surface region.

In order to confirm that the phenomena observed in the investigation are the result of ongoing reduction steps, we estimated the contribution of weakly bonded oxygen. Physisorbed oxygen contributes to, at most, a 0.1 eV increase in the work function, as we recorded the CPD signal just after oxidation and after 24 h of being stored under UHV conditions. The observed surface potential differences of more than 0.3 eV can thus be attributed to surface

redox processes: interaction with surface reconstruction (mostly homogeneous) and with dislocations (heterogeneous).

5. Conclusions

In summary, we present a systematic study of redox processes on STO(100) single crystals for bulk and surface regions. The macroscopic bulk of the crystal reaches maximum conductivity after 0.5 h of reduction at 900 °C. For longer annealing periods, it decreases again – possibly due to segregation effects. Once a crystal is cooled down under vacuum conditions, the macroscopic conductivity is not affected by reoxidation.

The reduced surface undergoes transformations in reconstruction and becomes Ti-rich. On the nanoscale, this is associated with characteristic local variations in surface conductivity and surface potential, which are also influenced by the presence of reduced cores of dislocation exits.

In contrast to the bulk, reoxidation at room temperature has a huge impact on the surface properties with decreasing conductivity and increasing potential. After oxidation, the inhomogeneity of the surface is increased and only small spots remain conductive, most likely at the exits of dislocations.

In this paper, we have shown that the surface properties of reduced STO are very sensitive to oxidation at RT. This may have implications for a number of technological applications ranging from sensing to the preparation of substrates for thin film growth, since the performance of thin oxide films grown on SrTiO₃ might be significantly increased by matching with the substrate Fermi energy level.

Acknowledgments

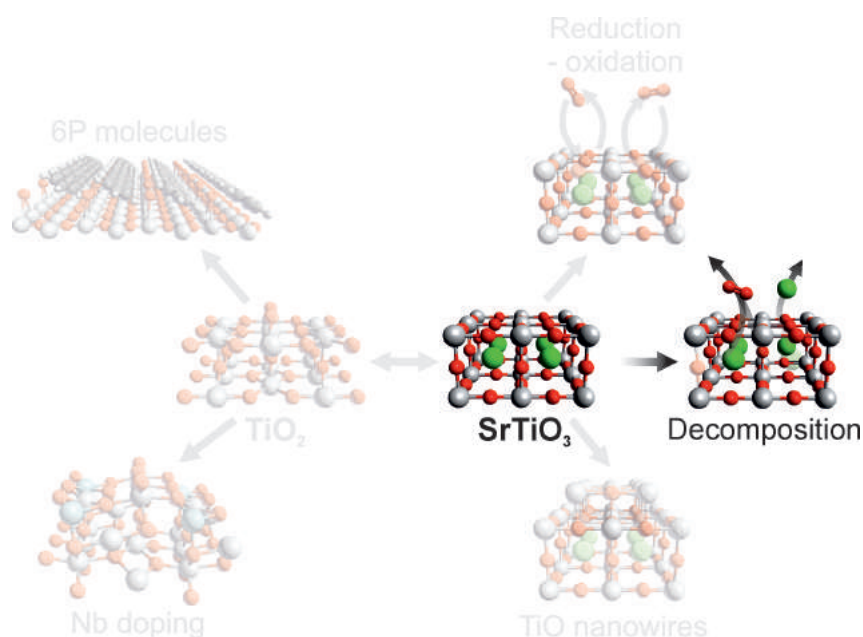
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3.3 Stability and Decomposition of Perovskite-Type Titanates upon High-Temperature Reduction



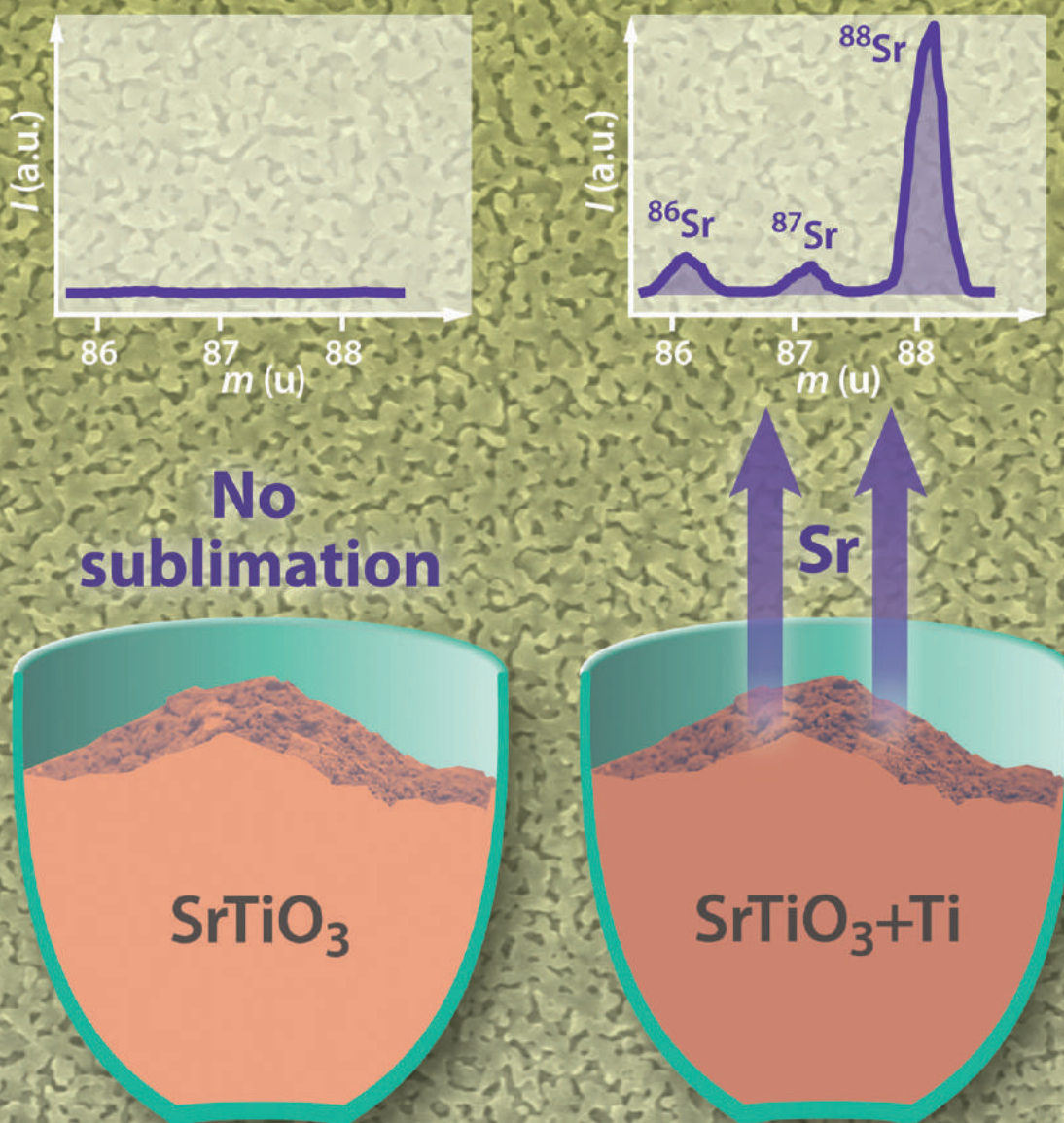
Following study is dedicated to explore the boundary conditions for the perovskite oxide stability [STO_Decom]. On the example of SrTiO_3 (but also confirmed for BaTiO_3 and CaTiO_3) we have presented that the use of an external getter, such as metallic titanium, enables for the oxide decomposition via incongruent sublimation of strontium. As a result, surface becomes porous and heavily non-stoichiometric with an excess of Ti. Such an effect have a potential technological relevance, but also can be adverse when unintentional. Paper preprint is preceded by a cover image of the PSS-RRL journal and followed by the supplementary information.

Highlights

1. Under standard vacuum conditions, SrTiO_3 is macroscopically stable,
2. Presence of external getter triggers incongruent sublimation of Sr and SrTiO_3 decomposition during reduction,
3. Oxygen partial pressure is lowered to below 10^{-10} mbar,
4. Ti-rich phases are formed after decomposition,
5. Decomposition procedure is applicable to different perovskites (e.g. BaTiO_3 , CaTiO_3).

Stability and Decomposition of Perovskite-Type Titanates upon High-Temperature Reduction

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Stability and Decomposition of Perovskite-Type Titanates upon High-Temperature Reduction

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Controlling the properties of the surface region of ternary perovskite-type titanates is of high importance in the field of future energy and information technologies. A common method to modify the surface of perovskite oxides such as SrTiO_3 is annealing under vacuum conditions. Here we show that the local oxygen partial pressure near to the surface plays a crucial role during annealing. While the oxide is found to be macroscopically stable during high-temperature reduction under standard vacuum conditions and only segregation effects on the nanoscale seem to take place, surface decomposition due to incongruent sublimation occurs as soon as an oxygen getter such as Ti is positioned close to the oxide. In consequence, owing to the high volatility of Sr-containing species at very low oxygen pressures, a Sr-depleted TiO_x surface layer is formed. This effect might reveal an alternative possibility to tailor composition and structure of perovskite-type titanate surfaces.

Ternary alkaline earth titanates with perovskite structure offer a wide variety of properties that can be exploited for future energy and information technologies. Among the titanate family, SrTiO_3 has attracted enormous attention in recent years as a prototype memristive oxide.^[1,2] Since its electronic properties can be controlled by disorder, the introduction of oxygen vacancies leads to self-doping related to a valence change of the Ti ion, resulting finally in an insulator-metal transition.^[3,4] Simultaneously, a non-stoichiometry is introduced by the oxygen vacancies raising the

question of the stability of the oxide, in particular with respect to applications e.g., in memristive or electrochemical cells. It has been reported that SrTiO_3 can compensate even large oxygen deficiencies and globally maintain the perovskite structure or at least a cubic structure close to perovskite.^[5] On the other hand, chemical reorganization or phase separation is well known to be easily achieved at perovskite surfaces by thermal treatment.^[6–8] Surface properties and stability can differ from those of the bulk because atomic rearrangements by relaxation, rumpling, and reconstruction have to be expected.^[9] In the following, we focus on stoichiometry changes of the very surface of SrTiO_3 upon thermal reduction. It has been reported that annealing under reducing conditions leads to the evolution of a Ti-rich surface with new reconstruction^[10–15] and eventually Ti_2O_3 or TiO islands can form on

the surface.^[16–18] In general, two different channels changing the chemical composition of the surface have to be taken into account, namely segregation and sublimation.^[19] Segregation takes place if thermodynamic driving forces exist between the surface and the bulk region. Experimentally, the evolution of a Ti-rich surface layer due to the redistribution of Sr within the near surface region under reducing conditions has been confirmed by depth profiling.^[20] Such effects might result from the establishment of a new Schottky equilibrium^[17] inside the bulk upon thermal reduction. Surface decomposition due to sublimation effects can arise in case the sublimation rates of the different species constituting the oxide differ considerably from each other, viz. we are dealing with decomposition owing to incongruent dissociative sublimation/vaporization.^[21] Commonly, effects of this kind have to be taken into consideration during SrTiO_3 crystal growth experiments at extremely high temperatures ($>1300^\circ\text{C}$).^[22]

In the present paper, we intend to investigate whether incongruent sublimation could lead to the decomposition of SrTiO_3 surfaces at lower temperatures ($<1000^\circ\text{C}$) and very low oxygen pressures under vacuum conditions. We follow the approach of lowering the local oxygen partial pressure by positioning an oxygen getter such as Ti close to the material. We present a study of the reduction of SrTiO_3 under vacuum conditions, with or without using an oxygen getter and demonstrate that surface decomposition due to incongruent sublimation can indeed occur owing to the high sublimation rate of Sr-containing species at very low oxygen pressures. In

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consequence, the surface disintegrates so that a surface layer consisting of Ti suboxides is left behind.

Powders of SrTiO_3 (made by grinding SrTiO_3 single crystals (MaTeck)) were annealed in an alumina crucible surrounded by Mo heating elements. The annealing experiments were conducted in a vacuum chamber with a base pressure $<10^{-6}$ mbar and an oxygen partial pressure $<10^{-11}$ mbar, maintained by turbomolecular pumping. To significantly lower the local oxygen partial pressure, the crystal powder was mixed with the oxygen getter Ti at a ratio of approx. 50 wt.% (cf. Supporting Information). Evolution of gaseous species was monitored by a quadrupole mass spectrometer (Balzers QMG 112 and MKS e-Vision 2) measuring the corresponding ion currents, I . In a second experiment, single crystals of SrTiO_3 (Shinkosha) were annealed after placing them on top of a layer of Ti powder inside the crucible. The morphology and topography of the single crystals after annealing were analyzed by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX, Hitachi SU 8000) and atomic force microscopy (AFM, Jeol JSPM 4210).

In **Figure 1**, the setup of the powder annealing experiments is illustrated. Two powders, pure SrTiO_3 and a mixture of SrTiO_3 and Ti, were annealed under identical conditions up to temperatures of approx. 1000 °C. While for the pure material gaseous Sr could not be detected (probably below the detection limit), significant signals stemming from the isotopes ^{86}Sr , ^{87}Sr , and ^{88}Sr reflecting their natural abundance were observed for the mixture (cf. full spectra in the Supporting Information). Other gaseous species such as Ti, TiO, or SrO were not detected. This confirms that at low oxygen partial pressure Sr sublimation from SrTiO_3 takes place. To analyze this effect in more detail, we investigated the temperature dependence of the Sr(g) evolution rate. We increased the temperature from 450 to 1030 °C in steps of approx. 50 °C with an annealing time of 40 min each. As shown in **Figure 1b**, significant evolution of Sr(g) from the SrTiO_3/Ti powder mixture started at a temperature as low as 650 °C. With increasing temperature, the amount of gaseous Sr evolving further increased (the non-monotonous behavior with the kink around 800 °C might be explained by taking into account that the Ti powder was gradually consumed by oxidation in course of time). After annealing, we performed an X-ray diffraction analysis of the powders revealing that the original Ti powder has changed most probably from $\alpha\text{-Ti}$ to $\text{TiO}_{0.176}$ (cf. Supporting Information).

We repeated this annealing experiment for a mixture of SrTiO_3 and TiO powders and we also observed Sr(g) evolution, however, with lower yield than for the SrTiO_3/Ti mixture (cf. Supporting Information). Mixtures of SrTiO_3 and TiO_2 as well as SrTiO_3 and Ti_4O_7 did not result in a measurable Sr(g) evolution upon annealing showing that the oxygen partial pressure established by the oxygen getters has indeed a subtle influence on the sublimation rate.

We extended our investigations to the two other technologically relevant perovskites CaTiO_3 and BaTiO_3 . Again, we performed annealing experiments under vacuum conditions on pure powders and on mixtures of the respective perovskite and Ti powder. As in the case of SrTiO_3 , we only observed significant evolution of gaseous alkaline earth metals when the oxygen activity was lowered by the addition of an oxygen getter (see **Figure 2**), illustrating that the preferred alkaline earth metal

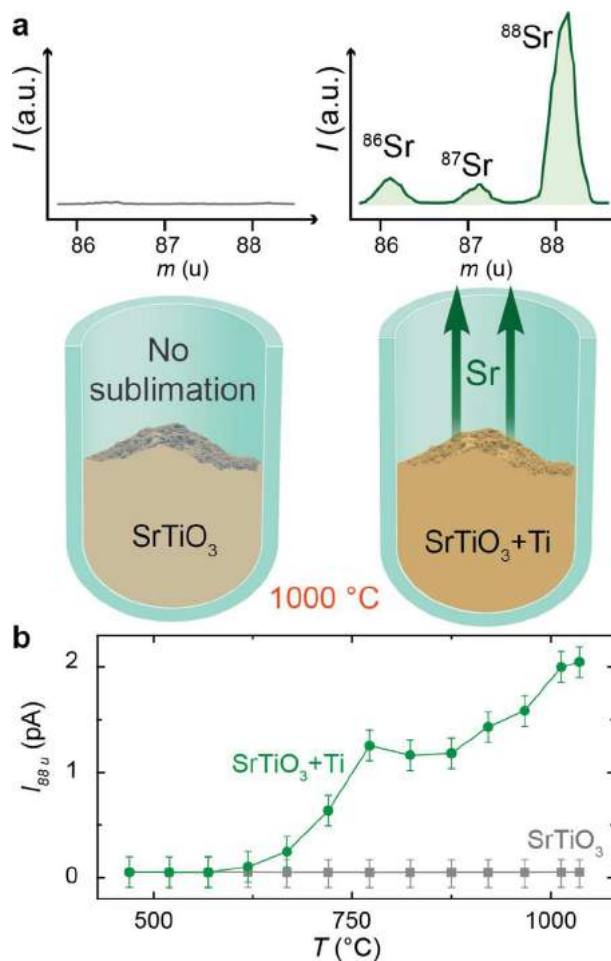


Figure 1. (a) Evolution of Sr(g) while annealing pure SrTiO_3 powder and a SrTiO_3/Ti powder mixture at 1000 °C under vacuum conditions as revealed by mass spectrometry. (b) Evolution of Sr(g) (ion current at 88 u) while ramping up the annealing temperature.

sublimation during annealing is typical for perovskite-type titanates at low oxygen partial pressures.

Next, we analyze how the surface of single crystals transforms when preferred Sr sublimation takes place. We annealed two pieces of a SrTiO_3 single crystal for 5 h at 1000 °C. One sample was annealed under standard vacuum conditions, while the other one

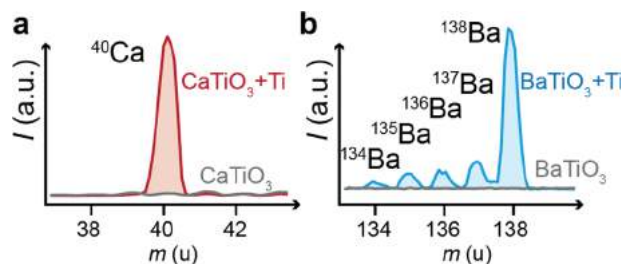


Figure 2. Alkaline earth metal evolution from CaTiO_3/Ti (a) and BaTiO_3/Ti (b) powder mixtures during vacuum annealing at 1000 °C revealed by mass spectrometry.

was positioned on top of a layer of Ti powder. After annealing, the surface of the samples were analyzed by AFM (Figure 3a). It can be seen that the vacuum-annealed sample had still a flat surface (roughness value rms below 1 nm) while the surface of the sample annealed in the vicinity of the Ti oxygen getter had changed significantly owing to the Sr loss (rms = 69.3 nm). In consequence, a porous structure consisting of crystallites on the nanoscale as illustrated by the SEM top view in Figure 3b has evolved. We performed a SEM/EDX cross section analysis by cleaving the crystal (Figure 3c) which revealed that the porous region had a thickness of more than 1 μm and was highly depleted of Sr indicating that a layer of titanium suboxides had evolved.

The observed surface disintegration must be the result of incongruent sublimation – because the reducing agent Ti is not capable to “thermodynamically” decompose the more stable compound SrTiO_3 . Our findings indicate that the sublimation rate of Sr is much higher than those of Ti containing species at very low oxygen pressures. According to the Hertz–Knudsen equation, the maximum sublimation rates of species from a compound are in a first approximation proportional to the equilibrium vapor pressures of these species over the compound. Thus, as soon as the equilibrium vapor phase over SrTiO_3 cannot be preserved – vaporization either under vacuum conditions or under flowing carrier gases – the preferential loss of Sr will lead to a progressing surface disintegration at very low oxygen pressures.

To support our interpretation of the experimental findings, we performed thermodynamic calculations to determine the equilibrium vapor phase composition over solid SrTiO_3 . In the calculation, the oxides were treated as ideal crystals and the possible influence of extended defects on the sublimation kinetics/thermodynamics was not taken into account. Figure 4 depicts the equilibrium vapor pressure of various species over solid SrTiO_3 at 1000 °C in reducing atmospheres ($\text{H}_2(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})$ -mixtures), plotted versus the self-adjusting equilibrium oxygen pressure. The pressures were calculated by means of a Gibbs free energy minimization procedure, following the well-known SOLGASMIX

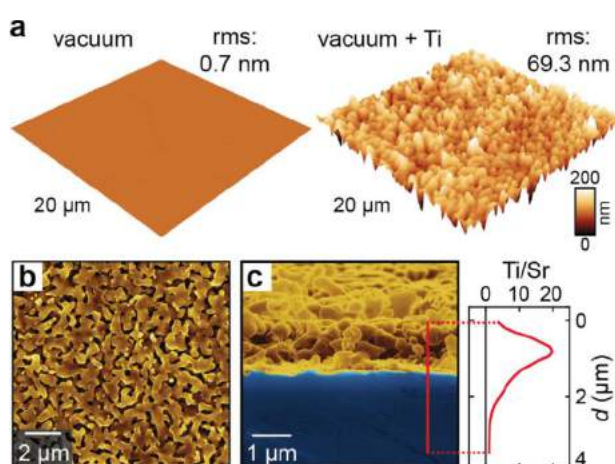


Figure 3. (a) AFM measurements on SrTiO_3 single crystals heated for 5 h at 1000 °C under vacuum conditions without (left) and with the oxygen getter Ti placed near to the crystal (right). (b) SEM top view and (c) colorized SEM cross section with EDX line scan (along red line) of the crystal heated with the oxygen getter Ti placed in the vicinity.

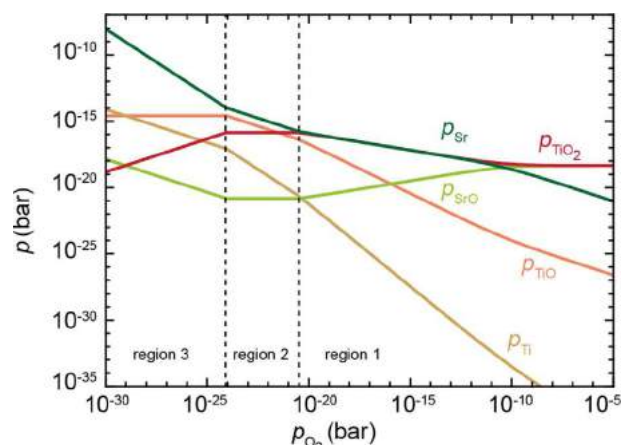
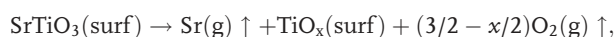


Figure 4. Calculated equilibrium vapor pressures over SrTiO_3 at 1000 °C as function of oxygen pressure in reducing $\text{H}_2(\text{g})/\text{O}_2(\text{g})/\text{H}_2\text{O}(\text{g})$ atmospheres.

approach^[23] (cf. Supporting Information). While for high oxygen partial pressures (region 1 of Figure 4) an almost congruent sublimation can be expected, this is not the case when the oxygen pressure is below about 10^{-20} bar. Due to the strong dissociation of $\text{SrO}(\text{g})$, the amount of Sr-containing species in the equilibrium vapor phase over solid SrTiO_3 cannot be compensated by an equivalent amount of gaseous Ti-containing species (the dissociation reaction of $\text{SrO}(\text{g})$ is much more favorable compared to the dissociation of $\text{TiO}_2(\text{g})$ and $\text{TiO}(\text{g})$). Hence, aside from solid SrTiO_3 , small amounts of solid TiO_2 (region 2 in Figure 4) or TiO (region 3 in Figure 4) remain after establishment of the equilibrium. Thus, if the appropriate conditions (elevated temperature, extremely low oxygen activity) can be maintained near to the surface of SrTiO_3 by positioning an oxygen getter in close vicinity, Sr(g) will finally become the dominant species in the adjacent vapor phase. In case the ongoing vaporization cannot be hindered (open systems), one will thus always be faced with a progressing surface decomposition owing to incongruent sublimation. Qualitatively, this can be summarized into the following formal reaction:



where “surf” denotes the surface and “ $\text{TiO}_x(\text{surf})$ ” the sub-stoichiometric titanium oxides which are stable at certain low oxygen pressures.

In summary, we have confirmed that incongruent sublimation from perovskite titanate surfaces occurs at very low oxygen partial pressures. Although under standard vacuum conditions such a low oxygen partial pressure will not be established and the perovskite can be regarded as macroscopically stable upon reduction, we have demonstrated that a getter with a high oxygen affinity can easily be used in order to achieve conditions where incongruent sublimation sets in leading to a decomposition of the perovskite surface. This implies that great care has to be taken when comparing thermal reduction treatments on ternary perovskite-type titanates performed in different vacuum systems. The local oxygen partial pressure can differ significantly from the expectation not only depending on ionizing measurement

devices^[24] but also on the materials used in the system, e.g., when Ti or Si is employed as getter material, overlayer or substrate^[25–27] the possibility of incongruent sublimation should be kept in mind. Sublimation effects may also play a role when local reduction at sufficient high temperature is performed by ion beams since O tends to be preferentially sputtered, or by electron irradiation or X-rays (radiolytic damage). On the other hand, the controlled admixture of oxygen getters during thermal reduction could allow for a tailored surface patterning of perovskite crystals by the formation of titanium oxides opening up pathways for various technological applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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We would like to thank J. Friedrich, M. Gerst, C. Makowicka, S. Masberg, and T. Pössinger for their support. This work was supported in part by the Deutsche Forschungsgemeinschaft (SFB 917 “Nanoswitches”).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

incongruent sublimation, reduction, surface decomposition, titanates, vaporization

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3.3.1 Supplementary Information: Stability and Decomposition of Perovskite-Type Titanates upon High-Temperature Reduction

Supporting information to

Stability and decomposition of perovskite-type titanates upon high-temperature reduction

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I. Full mass spectra

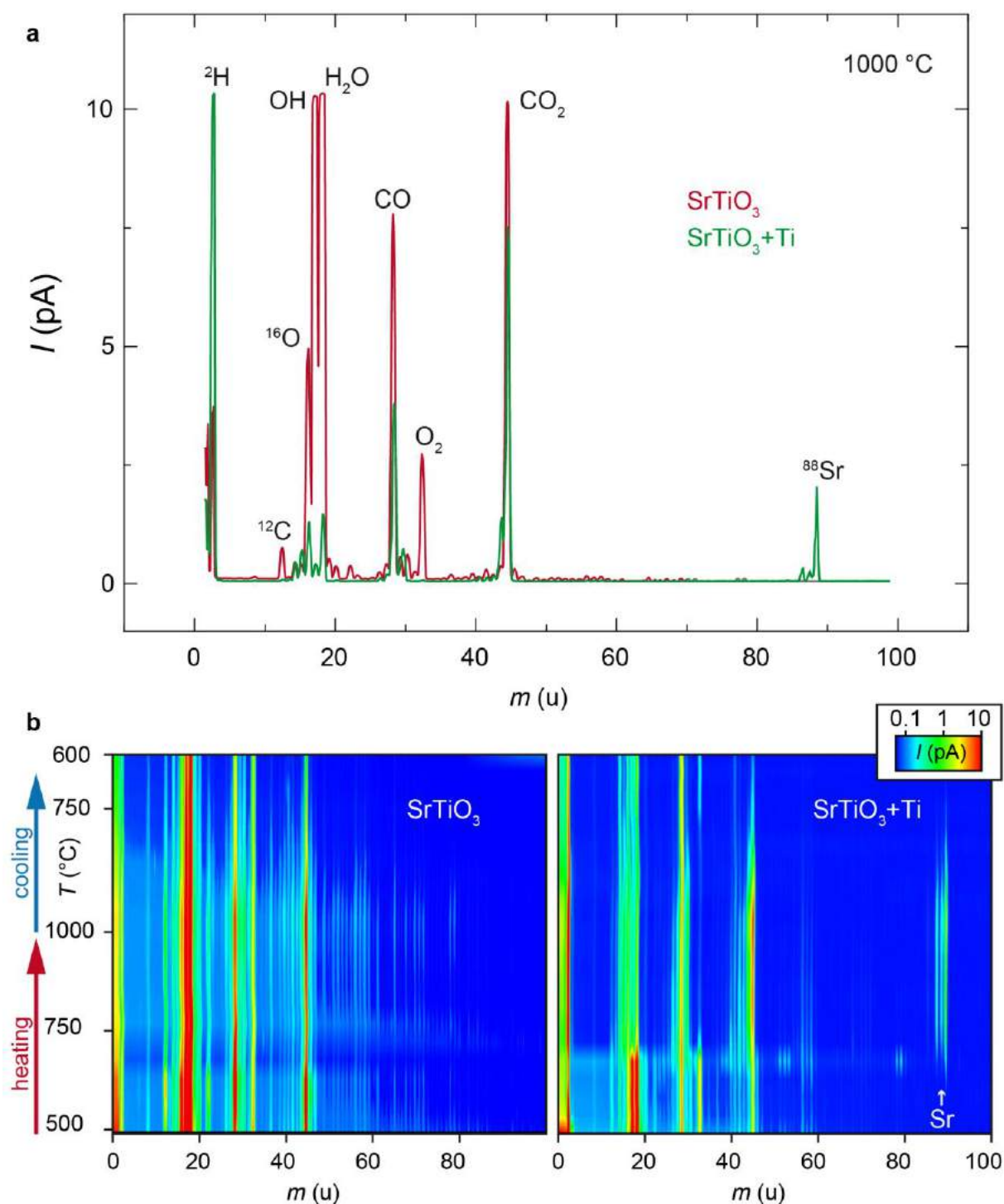


Figure S1. a) Mass spectra obtained while annealing pure SrTiO_3 powder (red) and a SrTiO_3/Ti powder mixture (green) at 1000°C under vacuum conditions. b) Temperature evolution of mass spectra during heating and subsequent cooling as logarithmic false colour plot.

To illustrate the influence of the admixture of Ti powder on the reduction of SrTiO_3 we plot the full mass spectra in Fig. S1a obtained during vacuum annealing. The spectra were measured after ramping up the temperature of the crucible containing the powder to 1000°C . At first, it can clearly be seen that $\text{Sr}(\text{g})$ evolution was only detected during the annealing of the SrTiO_3/Ti powder mixture as already

described in the main text. Furthermore, the high oxygen affinity of Ti significantly influenced the residual gas composition in the vacuum chamber. During annealing of pure SrTiO_3 , oxygen was present in the residual gas atmosphere; however, it could not be detected while the SrTiO_3/Ti powder mixture was annealed. Additionally, the amount of water in the residual gas atmosphere was significantly reduced resulting in an increase of the amount of hydrogen. These measurements confirm that using the oxygen getter Ti a low oxygen partial pressure was established, which can be expected to be even lower adjacent to the surface of the SrTiO_3 crystallites in the powder mixture than at the mass spectrometer positioned 5cm above the crucible. This can also be seen regarding the comparison of mass spectra as function of temperature presented in Fig. S1b (corresponding to the measurements in Fig. 1b in the main text). Here, it gets obvious that as soon as temperatures above 700 °C had been reached the water amount in the residual gas atmosphere decreased and Sr sublimation started.

II. Comparison of reducing agents

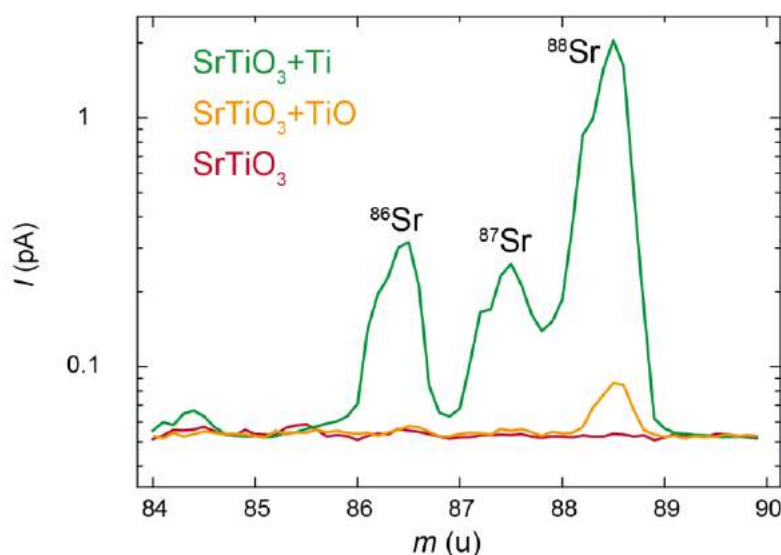


Figure S2 Evolution of Sr(g) while annealing pure SrTiO_3 powder, a SrTiO_3/Ti and a $\text{SrTiO}_3/\text{TiO}$ powder mixture at 1000 °C under vacuum conditions.

The low oxygen partial pressure which is necessary for the incongruent sublimation of Sr from SrTiO_3 to occur cannot only be established by Ti powder but also by other oxygen getters. This is shown in the mass spectra in Fig. S2. We found that also powders of TiO admixed to SrTiO_3 were able to establish the conditions for preferred Sr sublimation. An ion current signal stemming from the Sr isotope with mass 88 u could still be resolved, but the yield was much lower than for the admixture of Ti; this is reasonable since TiO is a weaker reducing agent than Ti. In contrary, the admixture of powders TiO_2 or Ti_4O_7 did not result in a measureable Sr(g) evolution upon annealing showing that the oxygen affinity of the admixed powder is decisive for the establishment of the appropriate oxygen partial pressure needed for incongruent sublimation to occur.

III. XRD analysis

In order to investigate the structural changes occurring in the powder mixture of SrTiO_3 and Ti during annealing under vacuum conditions, XRD (X-ray diffraction) was performed. The powder was measured in transmission mode and Rietveld refinement was applied for qualitative phase analysis. For reference, a not annealed SrTiO_3/Ti mixture was measured and compared to the powder mixture after 5 h of vacuum annealing at 1000 °C. Fig. S3 depicts the measured diagram. The diagram obtained before annealing (blue) can be assigned by the cubic SrTiO_3 structure (PDF #1-81-9665, green dashed lines) with Pm3m symmetry and the hexagonal $\alpha\text{-Ti}$ structure (PDF #4-7-9759, purple dashed lines) with P63/mmc symmetry. In the diagram obtained after annealing (red), the peaks of the SrTiO_3 structure can still be found but the peaks of the original $\alpha\text{-Ti}$ structure are not present anymore. Instead, new peaks at lower reflection angles can be found (yellow dashed lines) which however cannot be assigned unambiguously. They represent a lattice with higher lattice parameters as calculated by the Rietveld refinement (the lattice volume increases about 2.2%). These new peaks either reflect a hexagonal $\alpha\text{-Ti}$ structure (PDF #4-8-4973) or the hexagonal $\text{TiO}_{0.176}$ structure (PDF #1-82-7490). Since Ti acts as a getter for oxygen, we think that most probably the original $\alpha\text{-Ti}$ got oxidized and has formed $\text{TiO}_{0.176}$ in course of the annealing treatment.

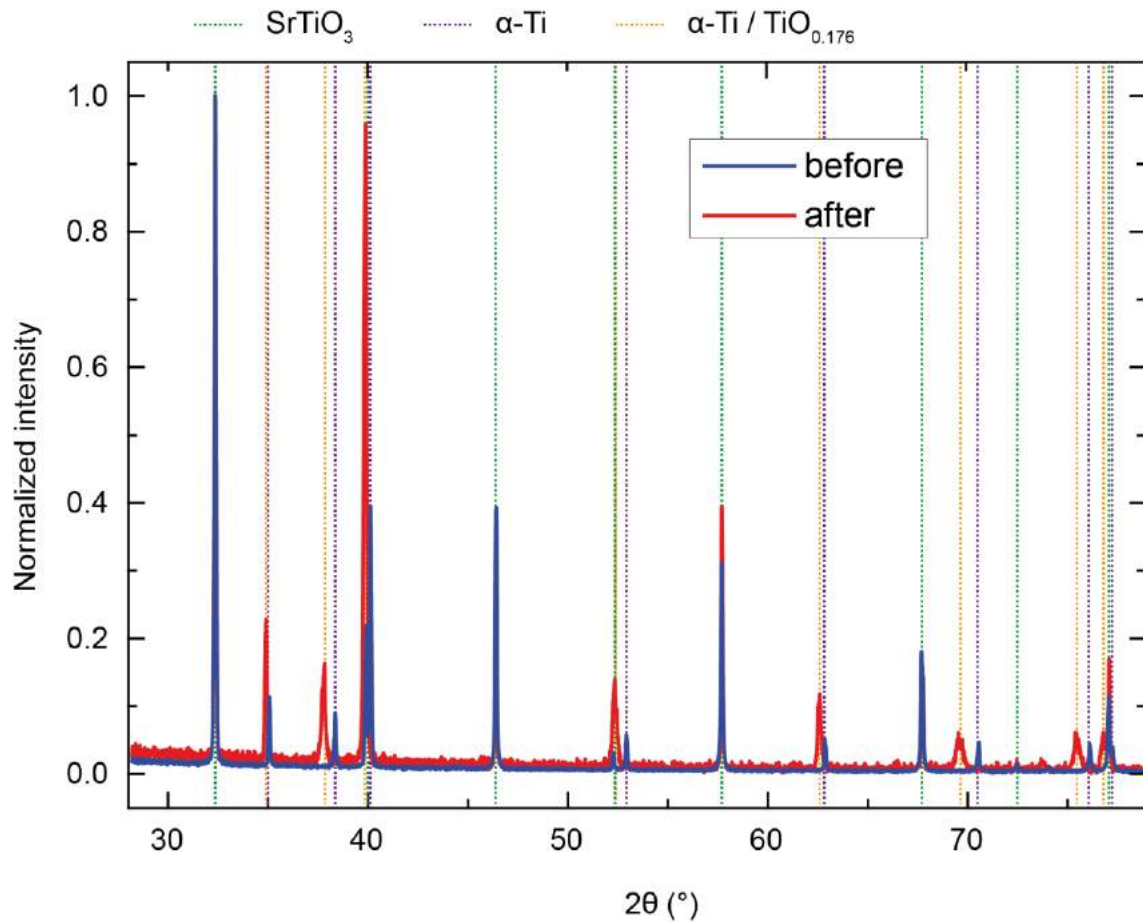


Figure S3 XRD spectra of SrTiO_3/Ti mixtures obtained before and after annealing under vacuum conditions for 5 h at 1000 °C.

IV. Particle size analysis

To determine the particle size of the powders used for the sublimation experiments, the size distribution was measured using the light scattering method. The powders were dispersed in liquid and the measurements were performed on a Malvern Mastersizer setup. Fig. S4 depicts the histograms of the Ti powder and of the SrTiO₃ powder, which was obtained by grinding a SrTiO₃ single crystal. It can be seen, that both powders had particle sizes in the micrometre range with Ti having slightly higher particle size than SrTiO₃. The mass median diameter were $D_{Ti}(v,0.5) = 111 \mu\text{m}$ for Ti and $D_{STO}(v,0.5) = 30 \mu\text{m}$ for SrTiO₃.

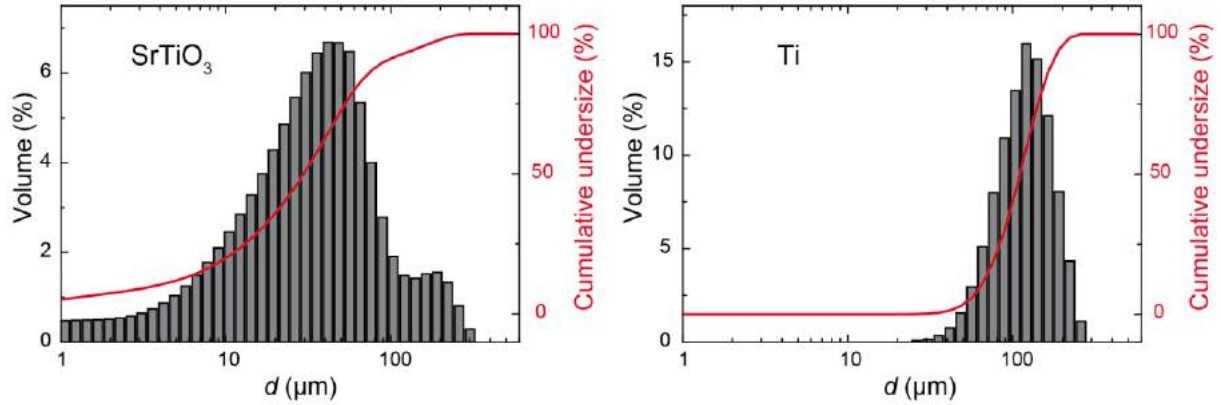
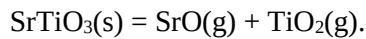


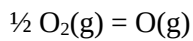
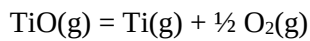
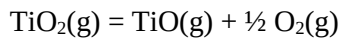
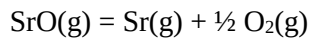
Figure S4 Histograms of the particle size analysis obtained by the light scattering method.

V. Vapour pressure calculations

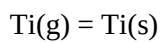
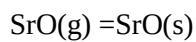
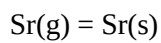
Thermodynamic calculations were performed to determine the equilibrium vapour phase composition over solid SrTiO₃. The vaporization of strontium titanate can formally be described to proceed by the partial dissociation reaction

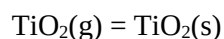
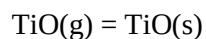


Additionally, dissociation reactions in the gas phase



and re-condensation reactions

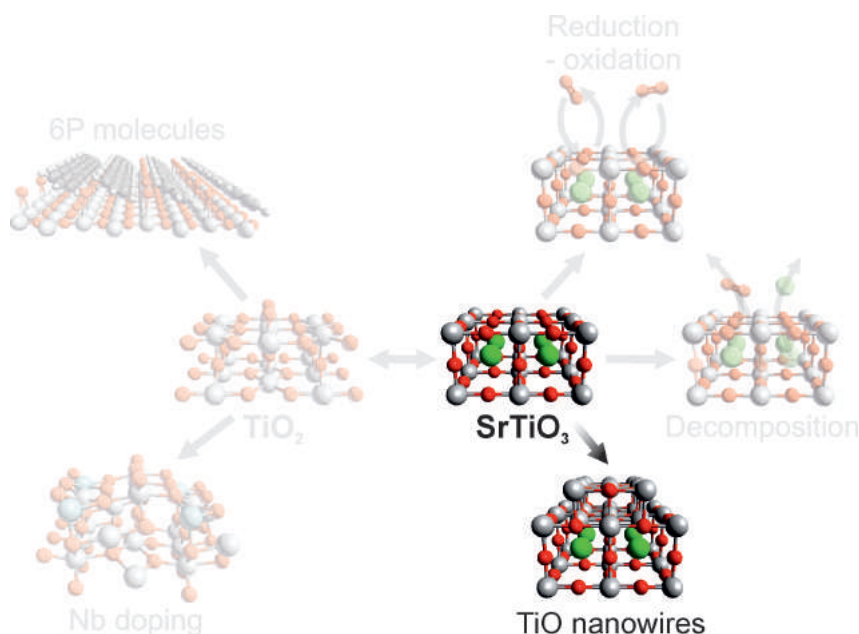




have to be taken into account.

Based on this, the pressures were calculated by means of a Gibbs free energy minimization procedure under the constraint of mass conservation and at a fixed total pressure of 1 bar, following the well-known SOLGASMIX approach (G. Eriksson, *Chemica Scripta* 8, 100–103 (1975)). To establish a reducing environment, $\text{H}_2\text{(g)}$ and $\text{H}_2\text{O(g)}$ were additionally considered as constituents of the gas phase. The standard Gibbs' free energies of the various species were calculated by means of the software HSC Chemistry (A. Roine, HSC Chemistry® for Windows, Version 5.1 (Outokumpu Research Oy, 2002)). After having specified the reaction system, initial input amounts of $\text{SrTiO}_3\text{(s)}$, $\text{H}_2\text{(g)}$ and $\text{O}_2\text{(g)}$ were given to start the minimization procedure for every data point. The Gibbs free energy minimization were performed using the Optimization[NLPSolve] command of the math software MAPLE (Maple 18, Maplesoft, a division of Waterloo Maple Inc., Waterloo, Ontario).

3.4 Bottom-up process of self-formation of highly conductive titanium oxide (TiO) nanowires on reduced SrTiO₃



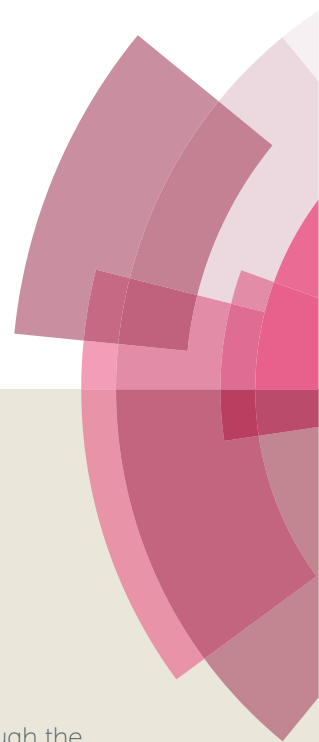
This research is aimed to present an important application of a transition metal oxide instability induced by the extremely low oxygen partial pressure [STO_TiO]. A novel way of crystalline TiO nanowire formation on the surface of SrTiO₃ is presented, where a recipe how to control size and density of nanowire array is provided. We show that TiO crystals are virtually defect-free and have interesting interface properties. Noteworthy, nanowires have persistent metallic conductivity, which is related to the connection to the dislocation network in the SrTiO₃ matrix. A detailed explanation of a growth of nanowires, in terms of incongruent sublimation, crystallographic shearing and diffusion is hereby postulated. Publication preprint (it is accepted manuscript version) is followed by a supporting information.

Highlights

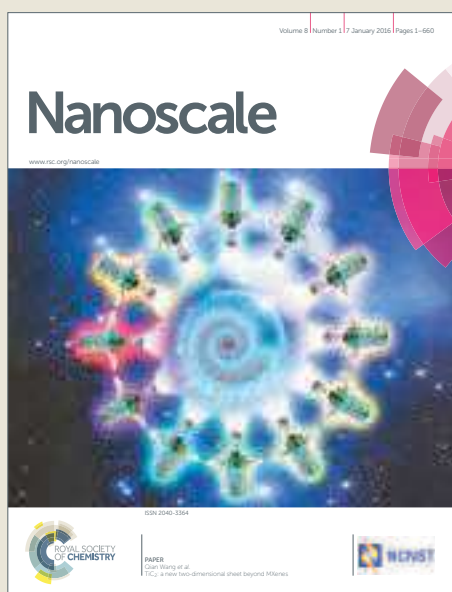
1. Controllable formation of crystalline TiO nanowires on SrTiO₃ is reported,
2. Extremely Low Oxygen Partial Pressure (ELOP) mechanism is responsible for Sr and O effusion,
3. Size, density and height of nanowires can be tuned by the reduction temperature,
4. Nanowires have excellent, metallic conductivity, which remains after oxidation,
5. Growth of TiO nanowires is enhanced by the dislocation presence and explained in terms of crystallographic shearing.

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Bottom-up process of self-formation of highly conductive titanium oxide (TiO) nanowires on reduced SrTiO₃

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Reduced titanium oxide structures are regarded as promising materials for various catalytic and optoelectronic applications. There is thus an urgent need for developing methods of a controllable formation of crystalline nanostructures with tunable oxygen nonstoichiometry. We introduce the Extremely Low Oxygen Partial Pressure (ELOP) method, employing an oxygen getter in close vicinity to the oxide during thermal reduction in vacuum, as an effective bottom-up method for the production of nanowires arranged in a nanoscale metallic network on a SrTiO₃ perovskite surface. We demonstrate that the TiO nanowires crystallize in a highly ordered cubic phase, where single nanowires are aligned along the main crystallographic directions of the SrTiO₃ substrate. The dimensions of the nanostructures are easily tunable from single nanometers up to mesoscopic range by varying the temperature of reduction. The interface between TiO and SrTiO₃ (metal and insulator) was found to be atomically sharp providing the unique possibility of the investigation of electronic states, especially since the high conductivity of the TiO nanostructures is maintained after room temperature oxidation. According to the growth model we propose, TiO nanowires formation is possible due to the incongruent sublimation of strontium and crystallographic shearing, triggered by the extremely low oxygen partial pressure (ELOP). The controlled formation of conductive nanowires on a perovskite surface holds technological potential for the implementation in memristive devices, organic electronics, or for catalytic applications and provides insight in the mechanism of nanoscale phase transformations in metal oxides. We believe the ELOP mechanism of suboxide formation is suitable for the formation of reduced suboxides on other perovskite oxides and for the broader class of transition metal oxides.

1. Introduction

Crystalline, polycrystalline, and amorphous oxides with a tailored nonstoichiometry in the oxygen sublattice are recently of a wide interest in all fields of material sciences. Among many others, particular attention is currently focused on the fabrication and investigation of titanium suboxides, where electronic properties are greatly enhanced due to the n-type self-doping induced by the formation of oxygen vacancies. Substoichiometric titanium oxides TiO_x are known to have high electrical conductivity^{1,2} and are often used as substrates for organic light emitting diodes (OLEDs) and organic thin film transistors (OTFTs) due to the easy energy-level alignment³. The vast majority of photocatalysts is based on reduced titanium oxides, e.g. so-called black TiO₂ materials⁴. Most

recently, the scientific community has focused also on a widely known, yet not sufficiently investigated, titanium monoxide (TiO). Superconductivity of TiO films was reported independently by two groups^{5,6} and just recently improved for core-shell TiO nanoparticles⁷. Moreover, the addition of TiO turned out to be a great enhancement in the performance and cathode selectivity in solar cells and beneficial for lithium-sulfur batteries efficiency^{8,9}. Also, as a future material in electrochemical energy storage, the utilization of metal oxides is frequently discussed¹⁰. Titanium monoxide finds application also as a support for organic films¹¹ and for memristive devices¹². Up to now, TiO fabrication in nanotechnology is mostly based on costly top-down techniques, relying on a laser^{13,14,15}, ion¹⁶ or electron beam induced formation¹⁷ or needs an enormously high temperature of 2000°C¹⁸. Importantly, these techniques do not provide precise control over the sizes of formed nanostructures. A new way of controllable and scalable manufacturing of crystalline titanium monoxide is thus needed and we, in this research, introduce an alternative pathway how these expectations could be met.

We report on a bottom-up method of crystalline TiO formation on the strontium titanate (SrTiO₃) surface, based on a thermally-induced crystal reduction. Although SrTiO₃ is regarded stable at temperatures employed, our method of Extremely Low Oxygen partial Pressure (ELOP) enables the

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Electronic Supplementary Information (ESI) available.

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creation of new phases. SrTiO₃ itself as a perovskite is especially important as substrate for the growth of functional thin films e.g. for high temperature superconductivity in FeSe/SrTiO₃ or LaAlO₃/SrTiO₃ layers^{19,20} and finds many applications also as a resistive switching material^{21,22}. It is known for decades that annealing of SrTiO₃ under different experimental conditions results in the formation of various suboxides, ranging from Sr-rich phases (oxidizing conditions) to Ti-enriched structures (reducing)^{23,24} and eventually to TiO nanostructures^{25,26}. When the reduced SrTiO₃(100) which is additionally sputtered by an Ar⁺ ion beam, other nonstoichiometric oxides may form, e.g. Ti₄O₃ ordered triline nanostructures²⁷. Here, we present a thorough study of formation of TiO nanowires under extremely reducing conditions revealing also their evolution with temperature, conductivity, as well as surface and interface properties, which makes the resulting TiO arrays promising for various applications. Moreover, a recipe how to control the formation of TiO nanowires is given, together with the detailed explanation of the growth mechanism. We show that sizes, spacing and height of TiO nanowires in a network are temperature dependent and can be therefore tuned. We prove that the necessary condition for the nanowires formation is achieving extremely low oxygen partial pressure pO₂ below 10⁻¹⁵ mbar, which turns out to be accessible locally under standard vacuum conditions by employing an oxygen getter. Importantly, our approach is low-cost and easily scalable – networks of TiO nanowires can be grown on microscopic samples as well as on big crystals. In addition, the method may be applied to SrTiO₃ films grown on different substrates and for other transition metal oxides.

2. Experimental

2.1. Sample preparation

Verneuil-grown SrTiO₃(100) epi-ready one side polished single crystals were annealed in an ultra-high vacuum (UHV) system by an AC current method, to temperatures ranging from 800 °C to 1300 °C, measured by a digital pyrometer. The base pressure of the system during heating was in the order of 1 × 10⁻⁹ mbar. Crystals were annealed on a pure silicon crystal, which reduced the oxygen partial pressure in the close proximity by orders of magnitude (details in the main text). Subsequent cooling was performed with a rate of 50K/min.

2.2. Scanning probe methods

Reduced samples were investigated by use of various scanning probe techniques. *In situ* investigations included Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), also in local conductivity mode (LC-AFM, C-AFM), all using an Omicron RT STM/AFM microscope, in the same UHV system as sample preparation. Samples were also investigated *ex situ* using Tapping Mode AFM (TM-AFM) Agilent 5500 microscope.

2.3. Electron-based methods

Reduced STO surfaces were examined *in situ* with use of Low Energy Electron Diffraction (LEED) with a multichannel plate detector. Samples were also investigated *ex situ* using a field-emission Scanning Electron Microscope (SEM) FEI Quanta 3D FEG. For Transmission Electron Microscopy (TEM) measurements, thin lamella were cut using the gallium Focused Ion Beam (FIB) gun. The chemical mapping of nanowires (Energy-dispersive X-ray spectroscopy, EDX) as well as Nano Beam Diffraction (NBD) measurements were carried out in FEI Tecnai Osiris 200 kV Transmission Electron Microscope equipped with Super-X EDX detector setup. All HAADF STEM and EELS investigations were performed on Titan Cubed G2 60-300 microscope, equipped with X-FEG Schottky high brightness source with a monochromator. Spatially resolved information on the oxidation state of Ti cations was obtained by STEM-EELS using a Gatan Image Filter Quantum 693 spectrometer. EELS spectra were acquired in a diffraction mode with 0.01 sec exposure time (in the spectral imaging mode), 0.1 eV per pixel energy dispersion, and 1 eV energy resolution of the zero-loss peak. To fit the spectra, the EELSMODEL software package was used (software package available at www.eelsmodel.ua.ac.be (Verbeeck & Van Aert, 2004)), where a power-law background was combined with three Ti-L2,3 edge reference spectra components: Ti²⁺ Ti³⁺ and Ti⁴⁺.

2.4. Mass spectrometry

Evolution of gaseous species was monitored by a Balzers QMG112 quadrupole mass spectrometer. Grinded SrTiO₃ samples were admixed with pure silicon and annealed in an alumina crucible in the vacuum system with a base pressure below 10⁻⁶ mbar.

3. Results and discussion

3.1. Temperature evolution

Thermal reduction is a widely known way to dope oxide materials with electrons. For the case of SrTiO₃, oxygen atoms are removed from the octahedra, which contributes to lowering the valence state of the transition metal ion to 3+ and subsequently 2+. Additionally, structural changes at the surface^{28,29} may be induced, however under “standard” vacuum conditions the terraced surface structure remains³⁰. Here we show that one hour high-temperature UHV annealing (at additionally reduced oxygen partial pressure) results in the emergence of a new oxide phase (Figure 1 a)). Up to 900°C, SrTiO₃(100) has single terminated terraces with well-developed, sharp edges. Then small TiO crystallites of dozens of nanometers in diameter and several nanometers in height are formed. When the annealing temperature is higher, structures grow in size and begin to be aligned along the main crystallographic substrate directions [001] and [010]

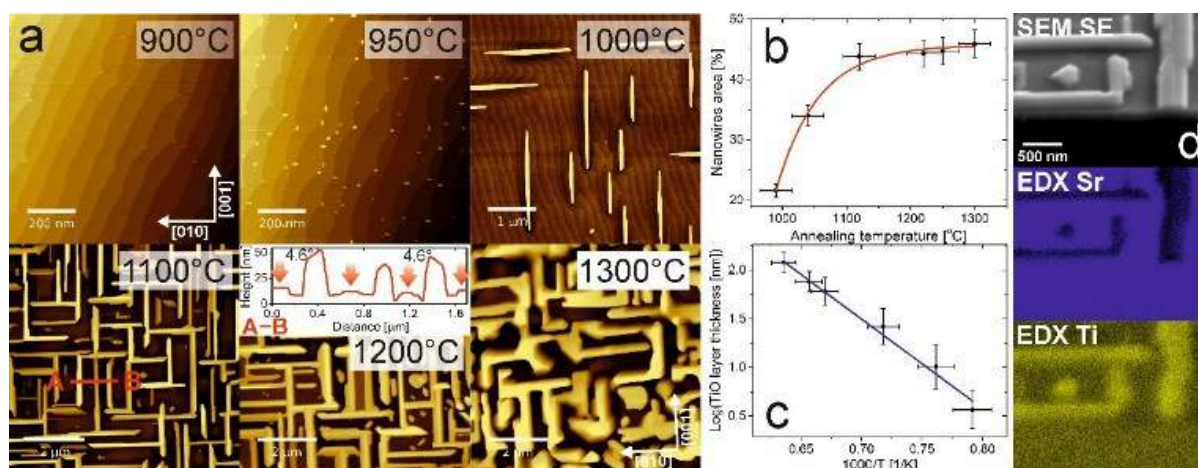


Fig. 1 Evolution of TiO nanowires network on SrTiO₃(100) surface due to the thermal reduction. a) TM-AFM room temperature images of resulting surface morphology. Temperatures are indicated in the upper right corner of each image. Inset: height profile across nanowires; b) Nanowires projected area dependence on annealing temperature; c) Arrhenius plot of the TiO layer thickness. d) EDX characterization of a cleaved nanowire sample with a Sr and Ti concentration maps.

(occasionally nanowires with the 45° angle are observed). A network of micrometer-long oriented nanowires is created and gets denser and higher with the increasing annealing temperature, though for a stable homogeneous temperature a macroscale uniform nanowire network is formed (see Supporting Information). The top plane of the nanowires is apparently tilted by 4.6 degrees with respect to the STO substrate surface as revealed by AFM inspection (see inset for 1200°C map). The actual projected area of the nanowires is plotted in Figure 1 b). It reaches a saturation of 45% at an annealing temperature of 1200°C. Noteworthy, the matrix superstructure is maintained. Since the structures do not flatten with temperature and the surface area of TiO increases, the resulting morphology holds potential for catalytic applications.

From the plot containing TiO thickness dependence over annealing temperature (Figure 1 c) the activation energy for titanium monoxide structures formation $E_{\text{TiO}} = 0.75(10)$ eV is estimated. For comparison, a calculated activation energy for oxygen vacancy migration in SrTiO₃ accounts for 0.7 eV³¹, whereas strontium is considered immobile with 3.7 eV activation energy. Hence, the structures formation could be related to the oxygen vacancies migration (leading to the decomposition described later). Recently, the oxygen vacancy

clustering was observed, along {001} directions, which are here the preferred directions of the nanowires growth³². From EDX measurements of a cleaved plane one can conclude that nanowires are uniformly depleted in Sr and simultaneously enriched in Ti (see Figure 1 d).

3.2. Surface structure

Presuming the crystal is strongly reduced, structural transitions of the surface are expected. Upon annealing under low oxygen partial pressure, the surface reconstruction is known to change from (1×1) through (√13×√13)R33.7° to the ultimate (√5×√5)R26.6° (Sqrt5) structure. Regarding the value of the transition temperature for the formation of the Sqrt5 reconstruction a considerable variation can be found in literature - from 830°C³³ through 1000°C²⁸ to 1200°C³⁴ (this discrepancy will be explained in the 3.5 paragraph). Some other reconstructions may be formed at the surface sputtered by an ion beam, e.g. Ti₄O₃ triline ordering²⁷ or nanolines³⁵. Noteworthy, the Sqrt5 reconstruction formation on the reduced SrTiO₃ was reported also by Newell et al., where additional structures, presumed to be TiO-related, were reported at certain areas²⁵. Here we present a straight correlation of a reduced SrTiO₃ Sqrt5 reconstruction and TiO

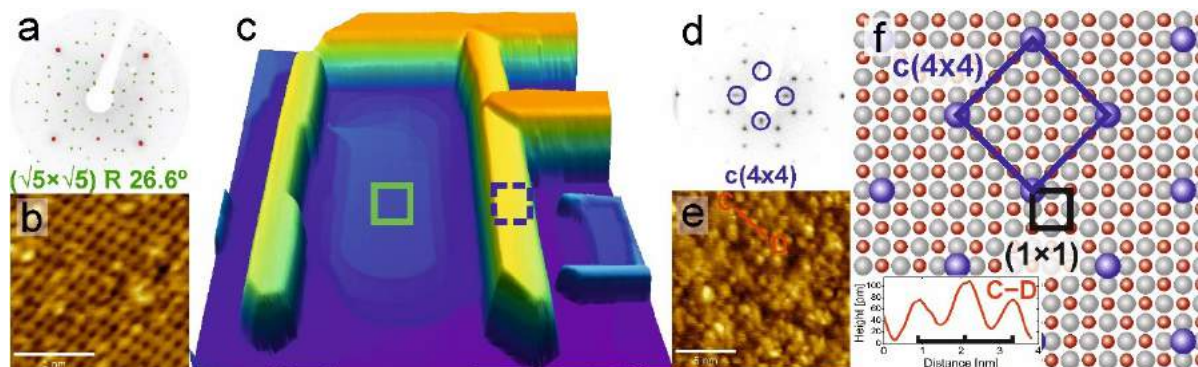


Fig. 2 Surface structure of nanowires and the surface between them. a) LEED pattern of a reduced SrTiO₃ crystal ($E_{\text{beam}} = 100$ eV). (1×1) and (√5×√5)R26.6° reconstructions are marked in red and green respectively; b) Corresponding STM image of a (√5×√5)R26.6° reconstruction; c) 3D view of a TiO nanowire matrix formed on SrTiO₃(100); d) LEED pattern of the same reduced SrTiO₃ crystal, with new c(4×4) reconstruction marked in blue ($E_{\text{beam}} = 33$ eV); e) Corresponding STM image of a c(4×4) reconstruction recorded at the top surface of the nanowire; f) Model of a c(4×4) superstructure superimposed on a TiO (1×1) surface.

nanowires, with direct observation of both surface structures.

A detailed analysis of the surface morphology is presented in Figure 2, for both TiO nanowires and SrTiO₃ substrate. A representative nanowire region is shown as height-coloured 3D AFM topography map in Figure 2 c). The surface of the area between nanowires adopts ($\sqrt{5}\times\sqrt{5}$)R26.6° reconstruction, proved by global LEED pattern (Figure 2 a)) and locally by means of STM imaging (Figure 2 b)). Bright features in the STM image correspond to the titanium atoms protruding from the surface³⁶ and the degree of defectiveness is comparable to the Sqrt5 reconstructions previously observed^{34,36}. No other STO nanostructures were recognized, e.g. no c(4x2) nor nanolines as seen by Castell were observed³⁵. This discrepancy can be explained by the different experimental conditions they applied e.g. Nb-doped, HF etched and Ar sputtered samples were used, in contrary to undoped, nonsputtered STO in the present experiments, with purposely reduced oxygen partial pressure. Interestingly, even the surface of the TiO nanowires is periodic. Figure 2 e) presents a STM map of a single terrace on top of the nanowire. A reconstruction tilted by 45 degrees with respect to the main crystallographic directions of STO is recognizable. The nearest-neighbours periodicity evaluated from height profiling (C-D, inset in Figure 2 f) equals $x = 1.194(82)$ nm. The same reconstruction is present for LEED patterns obtained with a low energy of 33 eV (Figure 2 d)). A proposed model of this new c(4x4) reconstruction is presented in Figure 2 f). Since features which build up c(4x4) appear as bright contrast in STM, atoms coloured in blue may be either oxygen vacancies or titanium adatoms, with the latter more possible, by comparison to the Sqrt5 reconstruction interpretation³⁶. We believe that this reconstruction may be

similar to the c(4x4) structure formed on the reduced BaTiO₃ via TiO clustering³⁷ and thus be interesting for future catalytic applications. Since unit cell of c(4x4) is simple but relatively large and TiO nanowires are conductive, this reconstruction may be further interesting for the molecular films growth.

3.3. Crystallography

Determining the actual surface structure is important, however the charge transfer efficiency and its mobility is greatly affected also by the interior structure and interface properties between nanowires and substrate. According to the literature, there are four TiO phases: α , β , γ and the recently found ϵ -TiO^{38,39}. Here, TiO nanowires adopt cubic rock salt γ -TiO structure as proved by STEM (Figure 3, no filtering applied). A single nanowire, cut perpendicularly to its long axis, and parallel to the [001] direction of STO, is presented in Figure 3 a). HAADF STEM imaging along (001) zone axis reveals that nanowires are made of crystalline TiO with a lattice unit cell of 4.18 Å which stands in an excellent agreement with literature value (PDF: #89-3660). Moreover, the STO substrate adopts perovskite structure with easily distinguishable Sr and Ti + O columns and a lattice parameter of 3.9 Å. To compensate strain induced by lattices misfit a complex zig-zag interface was formed (see also inset in Figure 3a) and additionally the TiO crystal structure was tilted by 4.6 degrees (also seen by EBSD analysis – see Supporting Information). This tilt accounts for strain relaxation and together with the apparent zig-zag structure of the TiO/SrTiO₃ interface is explained in the section 3.5. High crystallographic order of both TiO and STO is additionally proven by nano diffraction

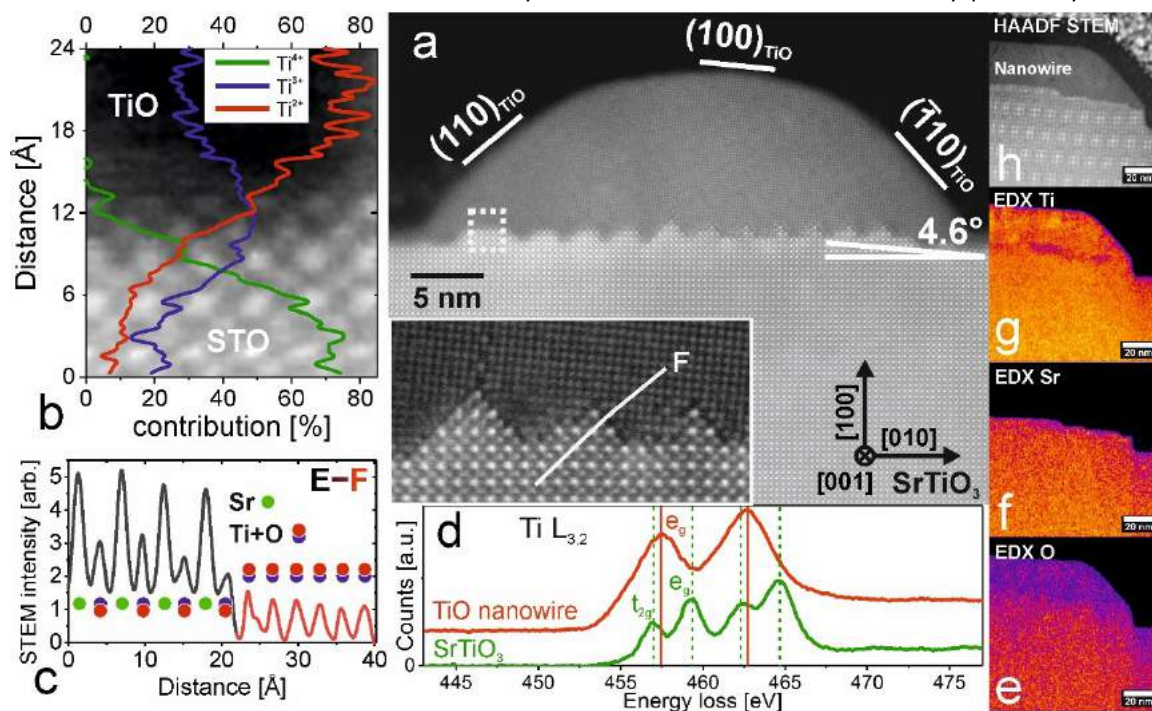


Fig. 3 Crystallographic structure of a single TiO nanowire. a) HAADF STEM image of a TiO nanowire grown on SrTiO₃(100) surface (for raw images see Supporting Information). TiO and SrTiO₃ crystallographic directions are shown. Inset: magnified interface area showing the sharp zig-zag structure. b) Ti valence state at the TiO/SrTiO₃ interface (dashed box from a)) measured by EELS. Ti⁴⁺, Ti³⁺ and Ti²⁺ concentrations are plotted. c) Intensity profile across the STO (black) and TiO (red) interface (E-F line from a) inset). d) Ti L-edge spectra measured on the STO matrix and TiO nanowire by EELS. e) – h) EDX elements mapping performed on a different TiO nanowire grown on SrTiO₃; e) EDX map of O concentration; f) EDX Sr concentration from the same area; g) EDX Ti concentration; h) HAADF STEM image of a TiO nanowire.

patterns (see Supporting Information). Unlike previous observations²⁶, presented TiO nanostructures and the SrTiO₃ substrate seem to be virtually free of defects. E-F line profile across the TiO/SrTiO₃ interface reveals a sharp transition, within one unit cell, from strontium titanate, with columns of Sr and Ti+O to titanium monoxide with Ti+O atoms only (Figure 3 c). Atomic number Z-contrast in HAADF STEM imaging is clearly visible, since Sr (mass of 88 u) contributes to much higher intensity than Ti and O (mass of 48 and 16 u, respectively)⁴⁰. To have a deeper insight into the valence state at the interface, where for many oxide heterostructures exotic electronic states are localized^{20,41}, EELS study, from the area marked in dashed white box, was performed (Figure 3 b). Comparing the energy loss fine structure of Ti L-edge with reference spectra enables tracking the actual evolution of the cation (here Ti) valence state at the TiO/SrTiO₃ interface⁴². In the presented case, Ti⁴⁺ oxidation state corresponds to the titanium in octahedral coordination in SrTiO₃, whereas Ti²⁺ are octahedrally coordinated atoms in the TiO rock-salt structure. Ti L-edge spectra from the nanowire region and STO matrix are presented on Fig 3 d), reflecting the changes in the near-edge structures of the Ti-L_{2,3} edges due to increasing Ti valence and the effects of the crystal field. Two L₃ and L₂ peaks separated by 5 eV visible for the case of TiO can be attributed to the spin-orbit splitting of Ti 2p core hole¹⁵, whereas the SrTiO₃ spectrum clearly shows further splitting of L_{2,3} peaks followed by a chemical shift, corresponding to pure Ti⁴⁺ valence state. It can be explained based on molecular orbital theory⁴³. Ti 2p core levels can be excited either to 3e_g or 2t_{2g} state, with the latter occupied for the case of TiO, resulting in two peaks instead of four for SrTiO₃ (more detailed spectra and study is presented in Supporting Information). From the line profile of the actual valence state (Fig. 3b) it is apparent that both Ti⁴⁺ and Ti²⁺ intensities change rapidly at the interface, by 60% within one unit cell. Even though the crystallographic structures of TiO and SrTiO₃ have 6% lattice misfit, the interface is atomically sharp, probably due to the substantial content of Ti³⁺ contributing to interface stabilization. This sharp TiO/SrTiO₃ interface may contribute to enhanced conductivity and magnetic properties, as it is postulated for polar/non-polar interfaces⁴⁴. Chemical composition of the wider area is provided with the use of EDX mapping (Figure 3 e) – h). Importantly, there is no Sr diffusion into the nanowire, meaning the phase separation is definitive.

3.4. Conductivity

The resulting structure of the TiO nanowires could be employed as an array of nanoscale metallic electrodes e.g. for optimizing the performance of solar cells, organic devices and also for catalytic applications. To prove excellent conductivity properties of nanowires, nanoscale current mapping was performed, *in situ* after reduction, using the LC-AFM method, allowing for a measurement of the conductivity independently from the measurement of the topography. Local current mapping (Figure 4 b)) indicates that the electric conductivity

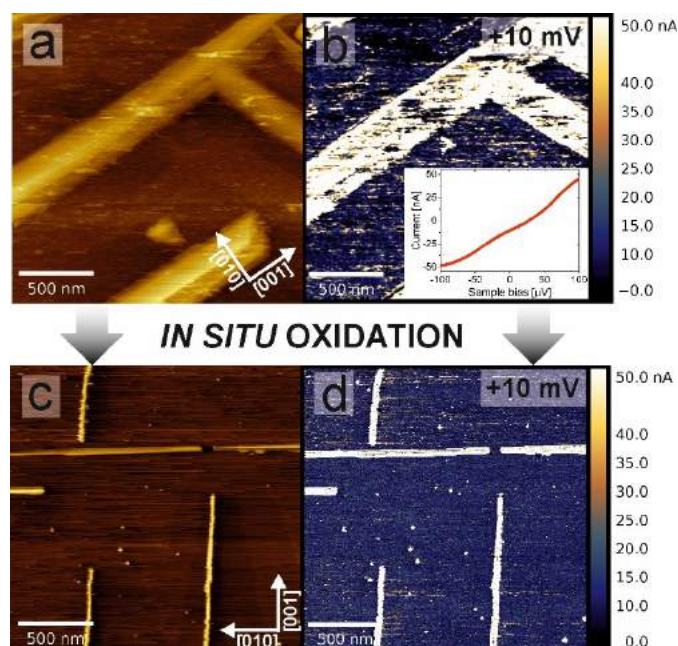


Fig. 4 Conductivity of the TiO nanowires array. a) LC-AFM topography of TiO nanowires grown on reduced SrTiO₃; b) Corresponding current map collected with +10 mV tip bias. Inset: I/V curve collected at one point on the nanowire's surface; c), d) Topography and current of TiO nanowires on SrTiO₃ after *in situ* oxidation. 100 Langmuir of pure O₂ were dosed into the microscope chamber and the excellent conductivity properties of the nanowires remained.

of the nanowires is at least 3 orders of magnitude higher than that of the STO surface between them. From LC-AFM I/V curve (the inset to Figure 4 b)), which shows an ohmic behaviour, one can estimate the conductance of the whole system (tip + contact + TiO nanowire + interface + STO bulk) to be $G_{\text{LC-AFM}} = 500 \mu\text{S}$, which is two orders of magnitude higher than for the case of reduced Nb-doped TiO₂⁴⁵, a commonly used conducting substrate. Current maps prove that the high conductivity of the nanowires is not dependent whether they are separated from each other (reduction temperatures around 1000°C) or connected in the network (for higher temperatures of reduction). Moreover, conductivity properties remain virtually unchanged after oxidation, as we have demonstrated by dosing 100 Langmuir of pure O₂ *in situ* to the microscope chamber. The resulting current map of oxidized surface is shown in Figure 4 d). For comparison, we have proven recently that even a few Langmuir of oxygen are sufficient to switch off the conductive SrTiO_3 surface of the reduced SrTiO₃²⁸. Apparently, even a higher dose does not affect the electronic properties of the TiO structures, which is a crucial information for using TiO arrays in real systems, operating under ambient conditions.

3.5. Growth mechanism

The intriguing issue is the origin of the high conductivity of nanowires placed on nominally semiconducting/insulating substrate. In reality, even in the purest SrTiO₃ crystals available on the market dislocations are present, coming from the growth limitations as well as from applied polishing and cutting procedures. When reduced, dislocations act as

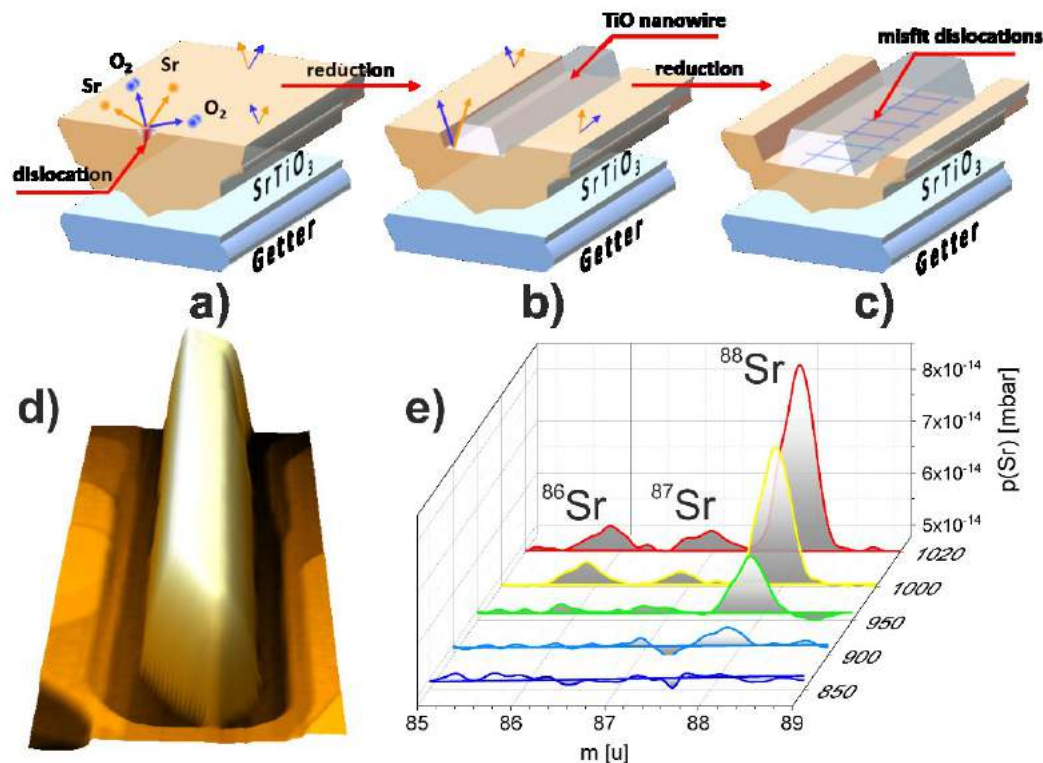


Fig. 5 Macroscopic view on the growth of TiO nanowires on SrTiO₃ at extremely low oxygen partial pressure (ELOP). a) Due to the lowered oxygen partial pressure, SrTiO₃ decomposition starts preferentially at dislocations; b) With prolonged reduction, due to the crystallographic shearing and surface diffusion, TiO nanowire network develops; c) After a certain thickness is reached, strain relaxes and dislocations in the TiO are formed; d) 3D view of the actual depression around nanowire grown at 1100°C (TM-AFM image); e) Strontium effusion from the SrTiO₃/Si sandwich during reduction to different temperatures under extremely low oxygen partial pressure, detected by a mass spectrometer.

electrically conducting paths^{21,46,47}. In the present case it is most likely that TiO nanowires are pinned to the dislocations in the STO crystal (see also Supporting Information). Hence, electric current flowing from nanowires uses low resistance paths of reduced dislocations and the total conductance is very high. Dislocation cores of reduced crystals have up to 3 orders of magnitude less resistivity than STO surface⁴⁷, which stands in a perfect agreement with our measurements of nanowire/surface conductivity. Since dislocations are easy to reduce but they are not as good in oxygen transport⁴⁸, crystal oxidation does not affect the conductance of the nanowires significantly, especially when the dislocation exits are additionally protected by a layer of TiO. This conclusion is further supported by the observation of structures formed at the edges of a crystal which was mechanically cut and thus ordered dislocations were introduced by the applied stress. There, a 1D linear structure of nanowires, which grew parallel to the cut edge evolved (see Supporting Information). It was already proved that dislocations formed due to the plastic strain engineering have enhanced electronic properties with respect to the crystal matrix⁴⁹. In the presented case it could open up the opportunity to create desired TiO nanowire patterns. Moreover, a possibility of creating dislocation bands via indentation, in both <001> and <011> crystallographic directions^{50,51}, allows for the precise designation of a nanowire growth site, with submicrometre precision.

The creation of a new TiO phase out of a SrTiO₃ single crystal requires a particular explanation. High annealing

temperatures alone are not sufficient for the triggering of the SrTiO₃ decomposition since in many literature studies SrTiO₃ proved up to be stable even upon 1200°C annealing³⁴. We address this issue and present a mechanism we call ELOP (Extremely Low Oxygen partial Pressure). Our recent study revealed that the use of getter materials such as Ti or TiO during reduction of perovskite crystals lowers significantly the oxygen partial pressure to values of 10⁻¹⁵ to 10⁻²⁵ mbar, even if the base pressure of the vacuum system was much higher⁵². This triggers the incongruent sublimation of strontium from the crystal. In the present case we have used a SrTiO₃/Si crystals sandwich, where the latter acted as a heater and as an oxygen getter simultaneously (see Figure 5 a)). The use of an external getter proved to be the necessary condition for the formation of Ti-rich phases. When the STO crystal was annealed under exactly the same experimental conditions, but without silicon, no nanowires emerged. The influence of Si on macroscopic sublimation of SrTiO₃ was checked by a separate experiment where a mass spectrometer was used to detect Sr coming from an annealed STO/Si admixture. The presence of silicon caused STO to decompose via incongruent sublimation (Figure 5 e)) due to the enforced global oxygen deficiency. Importantly, no silicon was incorporated into the STO sample, as proven by EDX measurements. It is worth noticing that substantial Sr effusion started when the annealing temperature reached 950°C, which is consistent with the observation of TiO nanowires starting to emerge at the same temperatures (Fig. 1).

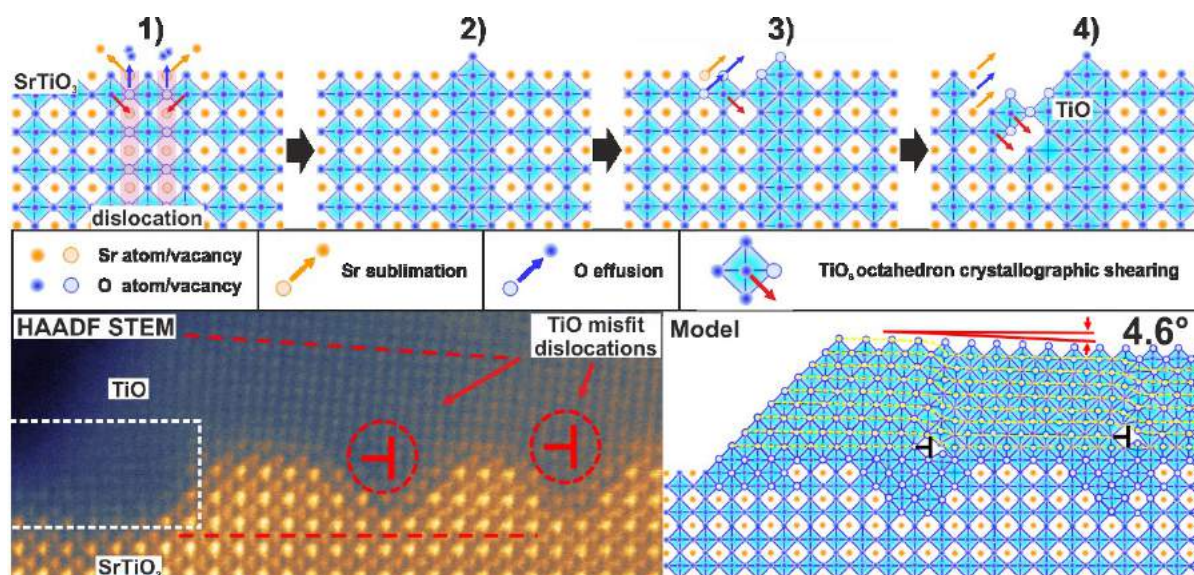


Fig. 6 Schematic model of the SrTiO_3 decomposition and initial stages of the TiO nanowires formation: 1) Due to the heavy reducing conditions (lowered oxygen partial pressure and high temperature) Sr and O effuses from the surface and the process starts preferentially at dislocation exits, 2) Due to the crystallographic shearing of TiO_6 octahedra, new TiO phase is formed, 3), 4) Process continues in the vicinity of a new phase and results in nanowire formation along $\langle 001 \rangle$ directions. Bottom: HAADF STEM image of a TiO nanowire formed on SrTiO_3 . Dislocations formed due to the strain relaxation are marked. Ball-and-stick model on the right hand side depicts actual TiO/STO interface from the HAADF STEM image.

To illustrate the first stages of the TiO nanowires growth we developed an empirical model shown in Fig. 6 (more detailed description in the Supporting Information). We assume that the formation of the nanowires can preferentially start on dislocation exits since it was reported that during reduction its cores adopt TiO nanophase⁵³. At first, during annealing, the Si getter triggers the reduction and subsequent decomposition, which happens over the whole surface, but is initiated first at the dislocation exits, due to the lowered enthalpy of formation of O vacancies (Fig. 5 a)⁴⁸. SrTiO_3 decomposes locally and gaseous Sr and O_2 species are released, leaving TiO_6 octahedra with oxygen vacancies under the extremely low oxygen partial pressure established by the Si getter. Then, a Ti-enriched phase may form due to crystallographic shearing mechanism, a typical process for the transformation of TiO_2 into Magnéli phases, (which additionally have high electrical conductivity)^{2,54}. Point defects (here oxygen vacancies) accumulate and form planar defects, e.g. Wadsley defects, which could then be annihilated via a crystallographic shearing, resulting in the evolution of a new TiO phase⁵⁵. Due to the locally lowered oxygen partial pressure (higher oxygen vacancy concentration) induced by the presence of TiO, the SrTiO_3 crystal decomposes further and the process continues, with more material being absorbed to the nanowire (Fig. 6 3) and 4)). In addition to crystallographic shearing, diffusion of TiO on the surface is anticipated as a movement of a Ti-O pair, which was found to have a lower energy barrier for the case of in-channel and cross-channel diffusion in TiO_2 ⁵⁶. This scenario is further proven by depressions around nanowires, as seen e.g. in Figure 1 a (inset, marked by red arrows) and in Figure 5 d showing a 3D view of a single nanowire. The closest vicinity of nanowires is always lowered, due to the finite diffusion length of Ti-O adspecies and the limited radius of crystallographic shearing. TiO nanowires grow, although the 6% misfit between TiO and STO

lattices results eventually in the relaxation in form of dislocations formed in the TiO crystal, close to the interface (see Fig. 6 bottom row). When the TiO layer is thin enough, approx. below 10 atomic layers, the crystal is aligned accordingly to the STO substrate (see dashed box) although stress accumulates. Then, edge dislocations in the $\langle 001 \rangle$ directions are formed (see also Fig. 5 c) and eventually an observed microscopic tilt of 4.6° appears. Formation of dislocations at the TiO/STO interface explains additionally the zig-zag shape of an interface. It is known that in oxides cation vacancies are formed preferentially in the close proximity to the dislocations (e.g. for the case of MgSiO_3 ⁵⁷). Also for the case of the MgO-Mg system, dislocations proved to be easy paths for Mg sublimation⁵⁸. In our case misfit dislocations can act as pipes for the Sr and O diffusion from the STO layer at the interface, enabling for the transformation to rocksalt TiO and formation of the observed zig-zag intrusions.

We expect that the same growth mechanism is being applicable to other perovskites and analogous binary oxide structures can be created. In the study of Kolpak et al. some structures resembling nanowires, called there “precipitates”, are formed for the case of BaTiO_3 UHV annealing⁵⁹. On the basis of presented research it is much likely those structures to be TiO nanowires. Hence, the ELOP mechanism of the incongruent sublimation can be employed for growth of various oxide nanostructures (depending on the actual equilibrium vapour pressures in the system)⁵². Moreover, we believe that unintentional lowering of the oxygen partial pressure by gettering materials present in the close vicinity of the sample (e.g. sample holder, clamps) is the cause of the huge discrepancies of transition temperatures of surface reconstruction mentioned in the chapter 3.2.

4. Conclusions

In conclusion, we have developed a way of forming a crystalline TiO matrix on the surface of SrTiO₃(100), an archetypal perovskite oxide. Our ELOP (Extremely Low Oxygen Partial Pressure) method bases on a crystal reduction under very low oxygen partial pressures, realized by use of an oxygen getter. With this, one can produce a large-scale array of titanium monoxide nanowires, with an excellent metallic conductivity, even after oxidation, on account to the connection with the dislocation network. We demonstrate that TiO and reduced SrTiO₃ crystal structures are almost defect-free, with an atomically sharp zig-zag interface between them. To relate the observed electrical properties to the microstructure and chemistry on the nanoscale. using a combined TEM - EELS technique, we have succeeded in tracking the structural changes in TiO/STO interface at the atomic scale. Due to the abrupt Ti valence state transition, exotic electronic states are expected. The actual formation of TiO nanowires is caused by the incongruent effusion of Sr, further decomposition of SrTiO₃ and the crystallographic shearing of TiO₆ octahedra. We propose a method of nanopatterning the crystal surface with TiO nanowires, taking advantage of their connection with the dislocation network. The use of plastic strain engineering and indentation allows for controlling the formed TiO nanowires network orientation and spacing. We finally believe that our ELOP method may be utilized in the broad class of oxide crystals and therefore improve efficiency of various catalytic and electronic devices. In addition to the intentional fabrication of suboxide structures on surfaces of transition metal oxides, our findings may also help to understand huge discrepancies between literature studies on the thermal reduction process, as it was demonstrated for the case of SrTiO₃(100) surface reconstruction evolution. Therefore, we suggest materials for sample holders, heaters, manipulators should be selected with an utmost care, bearing in mind that in most cases they may affect the preparation procedure and as a consequence, experimental results.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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3.4.1 Supplementary Information: Bottom-up process of self-formation of highly conductive titanium oxide (TiO) nanowires on reduced SrTiO₃

SUPPORTING INFORMATION

Bottom-up process of self-formation of highly conductive titanium oxide (TiO) nanowires on reduced SrTiO₃

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1. Atomically resolved images of nanowires from Transmission Electron Microscopy (TEM)

Here we present a few high-resolution examples of TiO nanowires formed on SrTiO₃(100), imaged by means of atomically resolved transmission electron microscopy, in the scanning mode (STEM). Figure S1 shows the raw HAADF-STEM image from Figure 3 in the main text, to prove no defects were hidden by insets. Crystallographic structure seems to be nearly perfect (within the focal length of the imaging mode). No dislocations in the SrTiO₃ matrix are visible, which may be explained by the fact the lamella has the thickness of about 40 nm, which constitutes only approx. 1/100 of the nanowire length. Figure S2 presents the HAADF (a) and ABF (b) images of another nanowire. The same zig-zag interface structure is visible, as well as the relative 4.6° tilt angle of SrTiO₃ and TiO crystal structures.

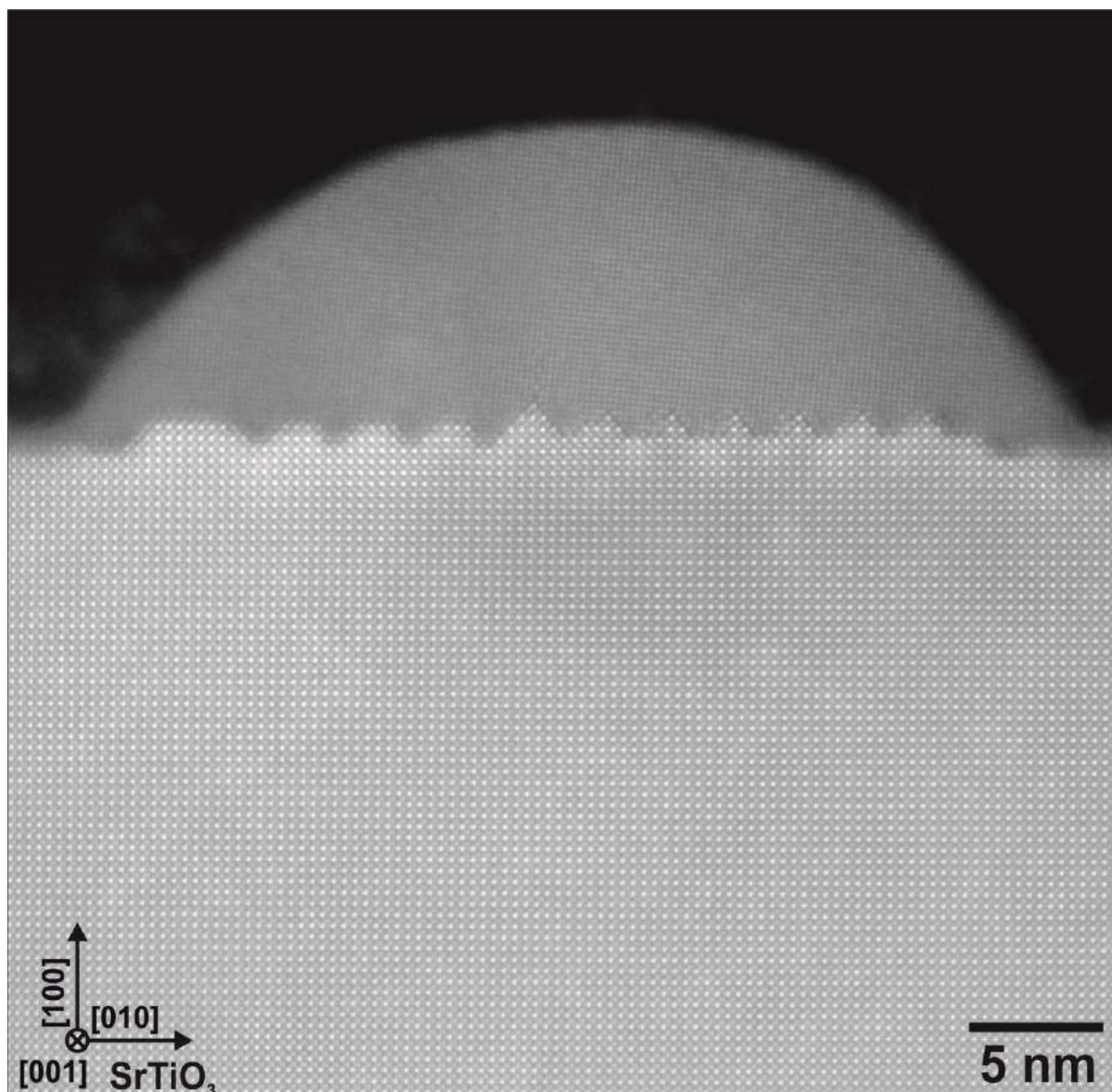


Figure S1. Atomically resolved HAADF-STEM image of a single TiO nanowire grown on SrTiO₃ surface (the same area which is displayed in Figure 3 in the main text).

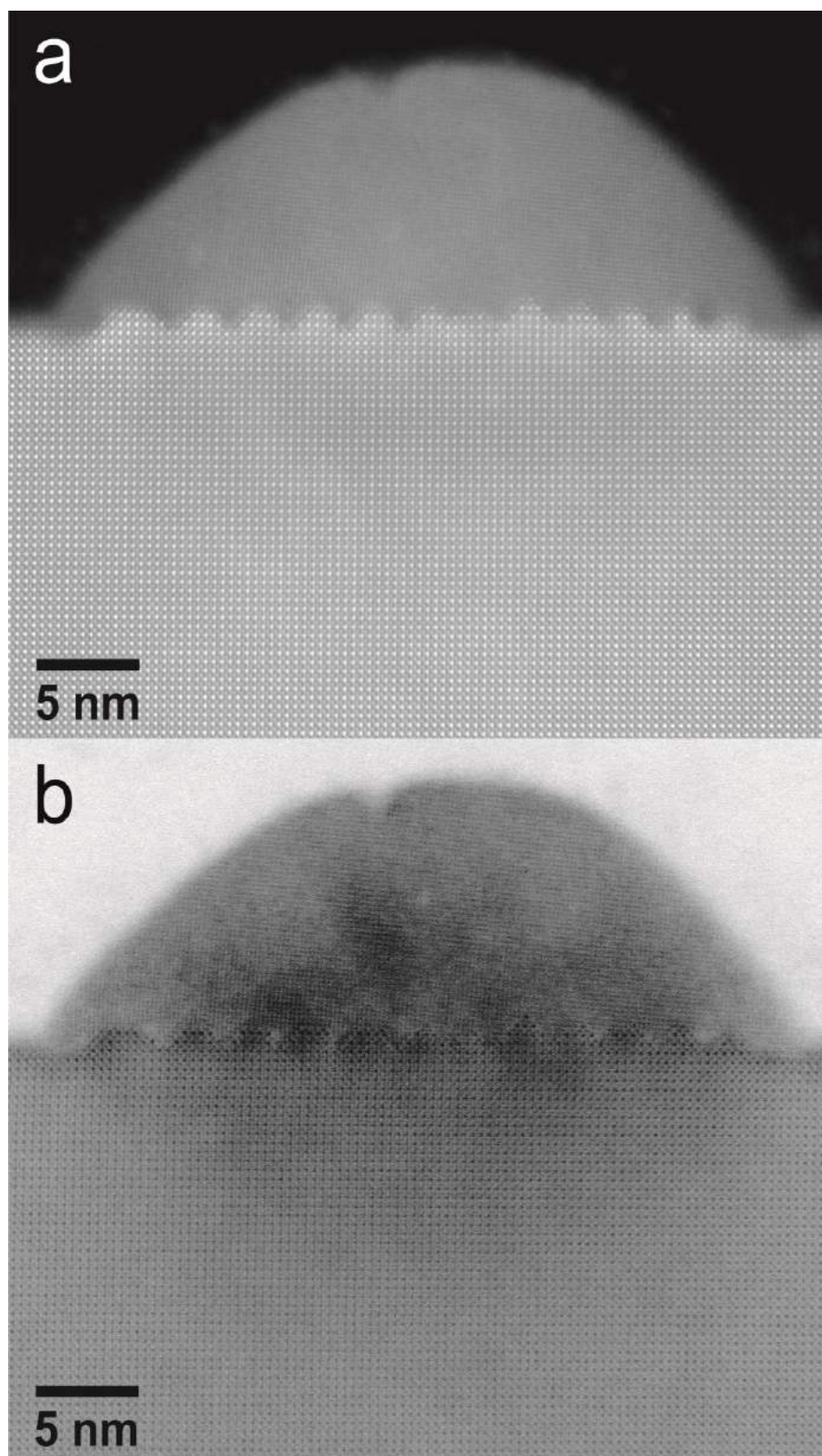


Figure S2. Atomically resolved STEM images of a single TiO nanowire grown on SrTiO₃ surface, taken at the [001] incidence. a) High Angle Annular Dark Field (HAADF-STEM) image. b) Annular Bright Field (ABF-STEM) image of the same island.

Figure S3 presents diffraction patterns collected by means of Nano Beam Diffraction technique in TEM. Smallest condenser aperture was used to obtain diffraction from areas of about 5 nm in

diameter. Three distinguishable patterns were acquired: 1 – SrTiO₃ matrix underneath the nanowire, 2 – TiO nanowire, 3 – TiO/STO interface. Simulated diffraction patterns of perovskite SrTiO₃(001) and rock-salt TiO(001) crystal structures fitted perfectly to the acquired spots, proving that ELOP mechanism resulted in the formation of perfect TiO nanowires, maintaining the high crystallinity of the SrTiO₃ substrate. From the pattern collected at the TiO/STO interface the mutual angle of 4.6° was established.

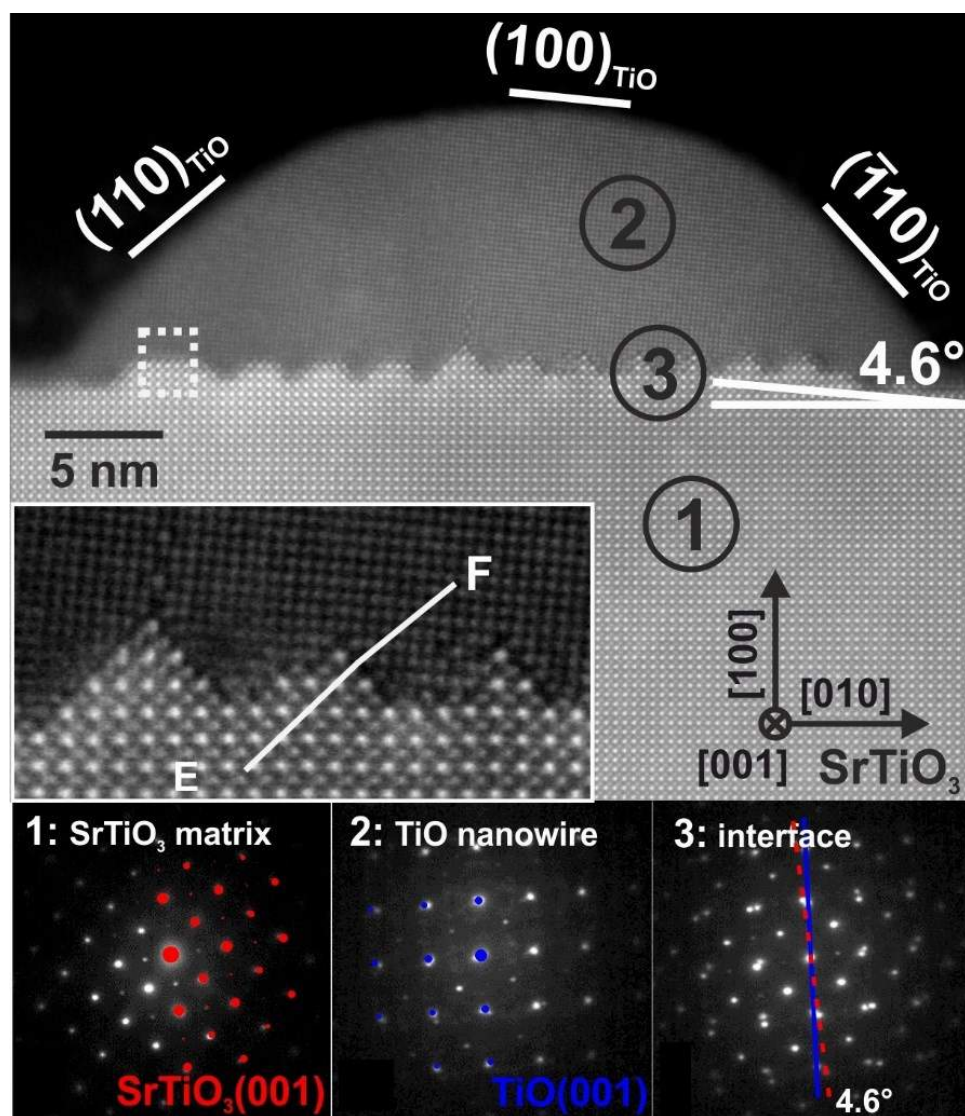


Figure S3. Nano-Beam Diffraction (NBD) patterns from three regions: 1 – SrTiO₃ matrix, 2 – TiO nanowire, 3 – interface. Theoretical diffraction patterns of SrTiO₃ and TiO are fitted, in red and blue respectively

2. Crystallographic texture of TiO nanowires on SrTiO₃

The crystallographic texture of reduced SrTiO₃ samples were characterized additionally via the Electron Backscatter Diffraction method (EBSD) in a SEM system equipped with the EDAX TSL DigiView camera. The aim of this investigation was to prove that all the formed nanowires have the same crystallographic structure, since TEM measurements allow only for a selective and limited characterization. The EBSD diffraction patterns were collected at a 70° sample tilt at 5 keV beam energy. The diffraction patterns were automatically indexed by EDAX TSL OIM DC 7.2.1 software, according to the perovskite phase of SrTiO₃ and the cubic rock-salt phase of TiO. The collected EBSD data were subject to clean-up algorithm procedures to ensure that reliable data were displayed, only data with CI>0.1 are shown.

Figure S4 shows the results of the phase identification. Image Quality (IQ) as well as Phase map show inarguably that all the nanowires adopt different crystallographic structure than SrTiO₃ surface betwixt and between them. Inverse Pole Figure (IPF) map shown in Fig. S4 c proves that all of them aligned along main crystallographic directions ([001], [010] of SrTiO₃) have the same TiO rock salt structure. The tilt angle from the STO surface normal is about 4.6°, which stands in agreement with TEM images as well as TM-AFM investigations presented in the main text. IPF map of the STO surface proves that no structural transformations affect areas between nanowires and globally the surface has still the perovskite symmetry and the (100) orientation.

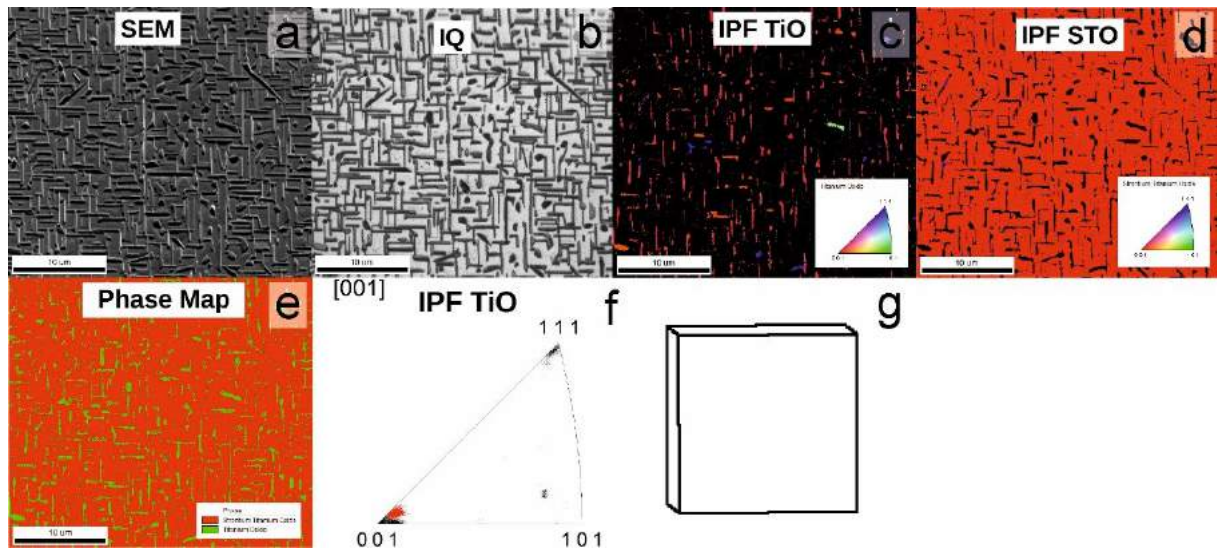


Figure S4. Crystallographic texture of TiO nanowires grown on SrTiO₃(100). a) Secondary electrons (SE) SEM image of a nanowire matrix, b) Image Quality (IQ) map of the same region, c) Inverse Pole Figure (IPF) map of TiO, obtained from EBSD, d) IPF map of STO, showing that the only STO orientation is still (100), e) Phase map with TiO nanowires marked in green and SrTiO₃ surface in red. f) IPF plot of TiO, showing that predominant orientation of nanowires is (001) with 4.6° tilt from the STO surface normal (marked in red), g) Schematic representation of TiO crystallographic orientation with respect to the STO substrate.

3. Chemical imaging contrast

Most common imaging mode in the electron microscopy utilizes secondary electrons emitted from the surface, detected by use of the Everhart-Thornley detector. It allows for an effective measurements of surface topography, with hindered chemical contrast.

In contrary, backscatter electrons (BSE) mode is a powerful tool for the chemical analysis of the surface. The fraction of backscattered electrons is proportional to the atomic number Z of the elements in the material. Since we deal with three-elements system (Ti, Sr, O) where two cations have substantially different atomic numbers ($Z_{\text{Sr}} = 38$, $Z_{\text{Ti}} = 22$), one can distinguish between areas of different Ti/Sr ratio. Figure S5 presents the comparison of topographical (SE) and chemical (BSE) imaging of the network of TiO nanowires grown on SrTiO₃. Clearly nanowires have darker contrast in BSE, meaning the average Z number is lower. One can also estimate the TiO nanowires height from the BSE image, since there is a strong dependence of the probability of the backscattering electron on the depth. Table presented in Figure S5 contains the calculated BSE emission yields, using the CASINO software¹. Assuming that areas between nanowires are pure STO (TiO thickness = 0 nm) and comparing the BSE intensities of nanowires and STO, the estimated average height of TiO is approx. 50 nm, which is in a good agreement with the measured height of nanowires at this region (by means of TM-AFM).

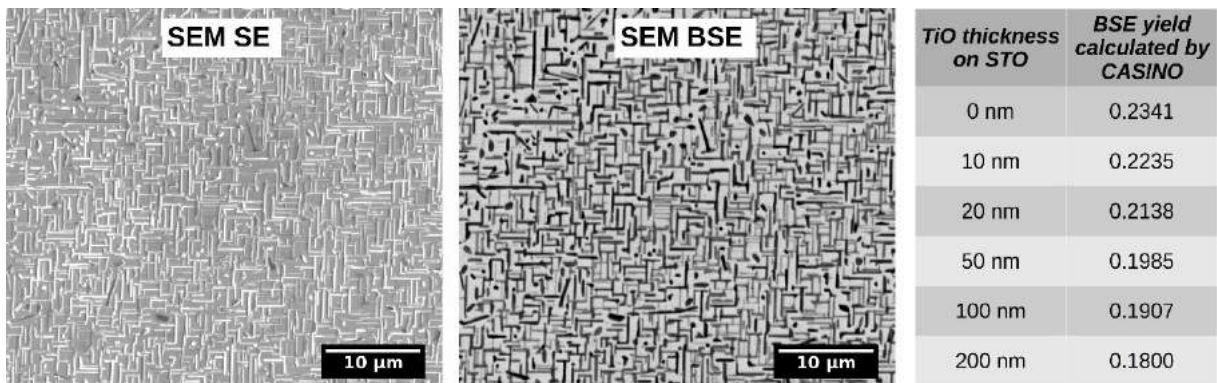


Figure S5. Comparison of Secondary Electrons (SE) and Backscattered Electrons (BSE) imaging contrast of TiO nanowires on SrTiO₃, collected at 5keV electron energy. Table contains calculated (by the CASINO software) BSE emission yields of a thin TiO layer on SrTiO₃.

4. EELS spectra of TiO/SrTiO₃ interface

To determine actual chemical and valence composition at the interface between TiO nanowires and SrTiO₃ substrate, Electron Energy Loss Spectroscopy (EELS) scans in the STEM mode were performed. Energy loss near-edge structure (ELNES) provided information about the Ti and O electronic states and also geometrical structure. Although in both TiO and SrTiO₃ structures Ti atoms are surrounded by O atoms in the octahedral configuration, profound differences are expected due to the different bonding and therefore splitting of EELS spectra. Figure S6 shows line profile of a Ti L-edge across the TiO/SrTiO₃ interface. Sharp transition of a Ti ELNES spectrum is clearly visible. Titanium atoms in the TiO rocksalt structure have 2+ valence state, which is seen as two L₂ and L₃

peaks due to the Ti 2p spin-orbit splitting. For the case of Ti^{4+} in the SrTiO_3 interaction with a crystal field results in the removal of the degeneracy of Ti 2p levels and thus to the further splitting of $L_{2,3}$ into t_{2g} and e_g states. Moreover higher oxidation state of Ti in the STO region is also evident in the Ti- $L_{2,3}$ edge onset shift towards higher energy loss.

It is noteworthy that the shift of the TM onset value of the energy loss and the change in white-line intensity ratio (L_3/L_2) are two essential indicators of valence state modification. The EELS peak features of the O-K edges are more related to the geometry of the metal–oxygen bonding rather than the oxidation state, to which the transition metal is more sensitive [2][3].

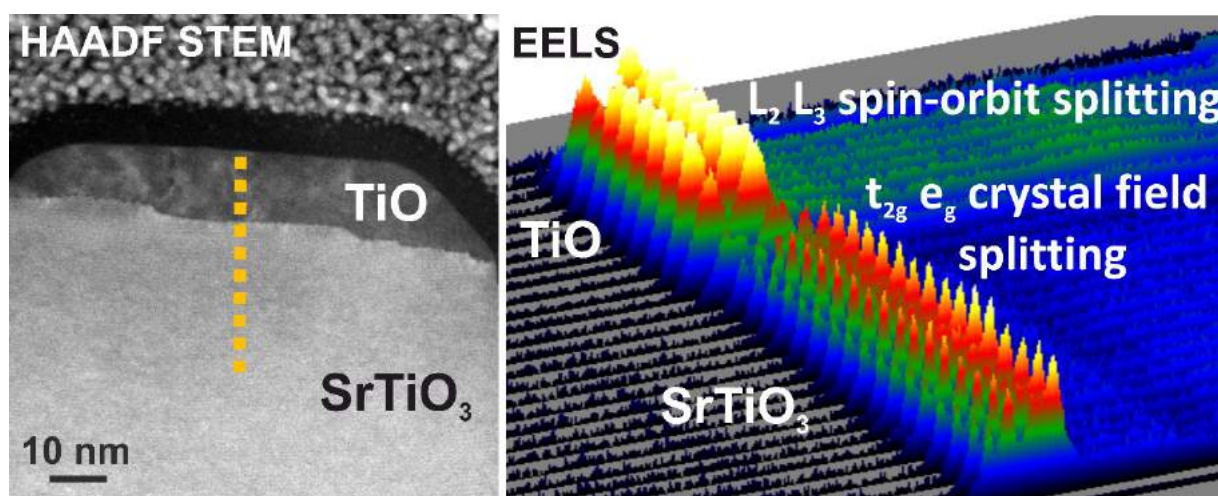


Figure S6. EELS line profile across the TiO/STO interface. Fine structure resolved at the ELNES Ti- $L_{2,3}$ edge shows evolution from Ti^{2+} at the nanowire to Ti^{4+} in the SrTiO_3 matrix.

More precise measurements reveal that the transition from Ti 2+ to 4+ valence state occurs within two unit cells (Fig S7). Additionally, Ti L-edge and O K-edge ELNES spectra are shown in a) and b) respectively. Ti spectra show clearly the two splitting processes mentioned before. In addition, positions of Ti L-edge peaks are in good agreement with the literature [4] indicating energy shifts attributed to changes of Ti oxidation state. Unaffected O-K position serves as a marker tool providing better control over the acquisition experiment assuring any drift of the spectrum is cancelled and observed effects of the Ti- $L_{2,3}$ range spectrum shifts are real. This is crucial while taking the average of the signal for many pixels (binning in the vertical direction) when it might happen that the spectrum is broaden due to the uncorrected drift. Significant differences in the oxygen K-edge for TiO and SrTiO_3 structures are visible in Fig. S7 b).

For the case of strontium titanate, a number of peaks can be attributed (A, B, C, D, E), coming from the titanium-oxygen interactions. The O K-edge in STO shows two intense peaks A and C with the suggestion of a less intense shoulder B, following by the peak D and less intense peak E.

In the simplest form, O K-edges represent electron transitions of the O 1s core level to the unoccupied p-like states [5]. It has been suggested that the peak A in TiO and A, B, C peak series in STO are due to oxygen 2p-metal 3d hybridization [6], and the main D peak in the O K-edge is thought to arise from hybridization of oxygen p-states with the TM 4s/d-states and continuum like states [7]. Peak E arises from higher lying energy states which can be most conveniently described in a scattering picture as resulting from scattering events in the first oxygen shell [4] being sensitive to the medium range order within the structure and so reveal any differences in the packing arrangements of oxygen anions. Here (see Fig. S7 b), peak A corresponds to the transitions into unoccupied Ti 3d (t_{2g})–O 2p whereas less intense B peak represents the unoccupied Ti 3d (e_g)–O 2p bands. Reduced intensity of a peak B may come from the geometrical reasons and reflect directionality of a Ti-O bonding at a specific oxygen site, from which EELS spectrum was acquired [8][9][10]. Here it seems that the high intensity of peak A and low intensity of peak B is more governed by the little or no change in symmetry rather than by the exchange splitting in the t_{2g} - e_g ligand field [6].

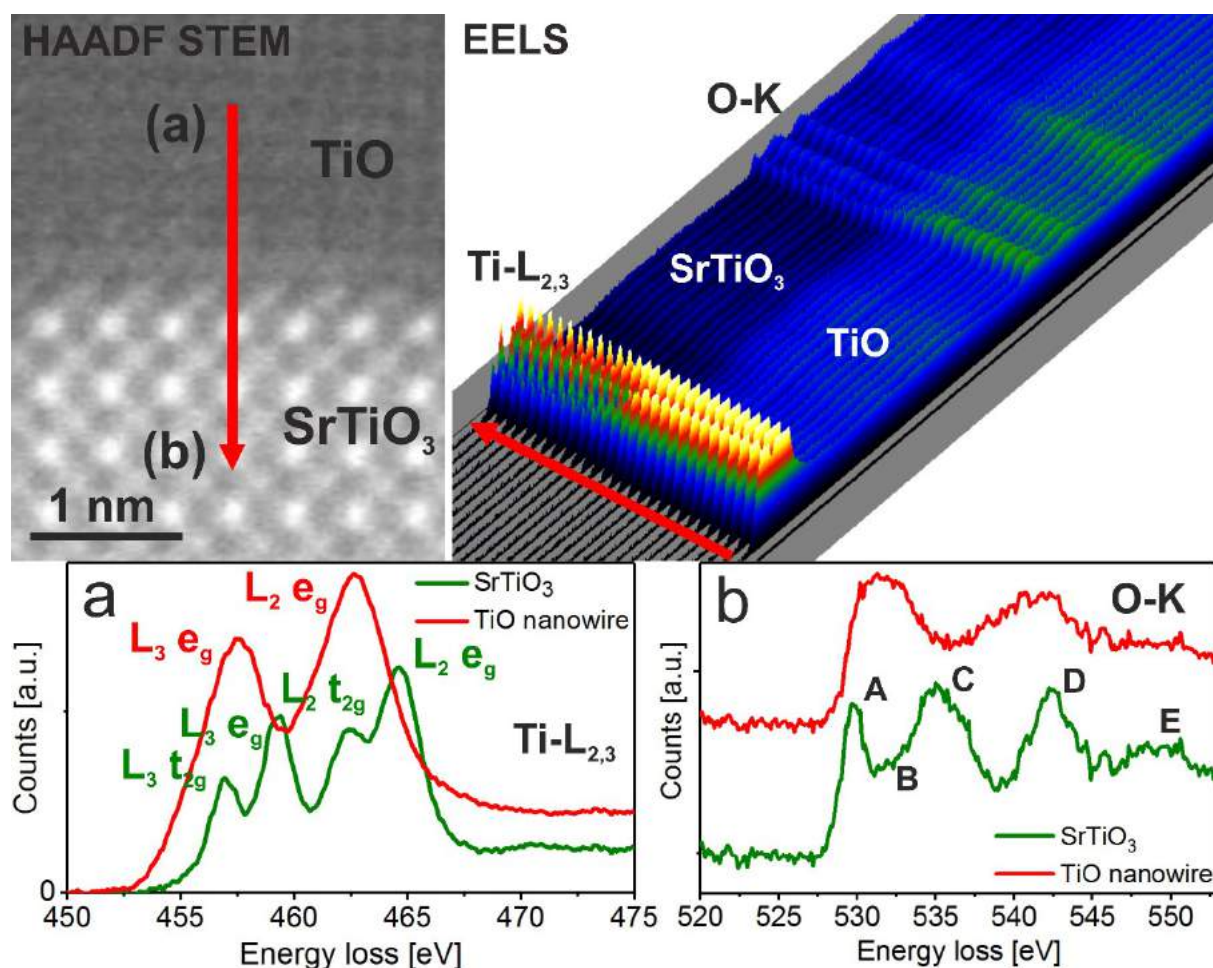


Figure S7. EELS profile at the TiO/STO interface, with the atomic precision. a) Ti L-edge ELNES acquired at the TiO nanowire and SrTiO₃ are compared. b) ELNES spectra of the O K-edge at the TiO and STO respectively.

5. Scalability of TiO nanowire networks

Utilizing the ELOP mechanism, one can produce TiO nanowire arrays covering macroscopic samples homogeneously. Maintaining stable reducing conditions (oxygen partial pressure, temperature of annealing) enables for the fabrication of macroscopic films of TiO with high surface area, for catalytic and energy storage applications. Figure S8 shows the uniform TiO nanowire network formed on the surface of SrTiO₃. The area covered by nanowires are even larger, however, the lower magnifications do not allow for a proper identification.

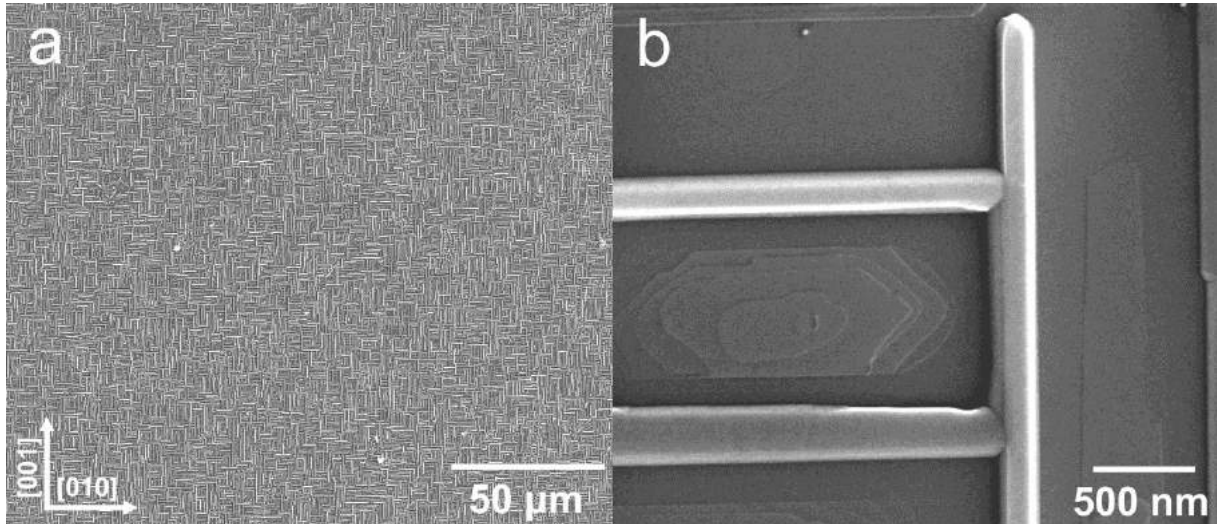


Figure S8. SEM images of a macroscopic TiO nanowire network formed on the surface of SrTiO₃. Structure has a high long range order (a), 200 x 200 μm², maintaining the perfect crystallinity at the nanoscale (b), 2.5 x 2.5 μm².

6. Ways to control nanowires formation

Having presented in the main text of this paper that by the temperature control one can tune the dimensions of the formed TiO nanowires, the main challenge would be to influence the growth at the local scale. Fortunately, the formation of nanowires is correlated with the extended defects in the SrTiO₃ matrix. Such defects as dislocations tend often to accumulate into linear agglomerates, oriented along main crystallographic directions. If our growth model is valid, there should be also linear agglomerations of nanowires. To check this experimentally, SrTiO₃(100) single crystal surface had been etched for a short time and then an image from optical microscope was collected (Fig. S9 a). It is known that dislocation exits are preferentially etched and pyramidal etch pits are formed [11]. Therefore, apparent lines of etch pits, aligned along main crystallographic directions correspond to the lines of dislocations in STO single crystals. As it was postulated in the main text, dislocations are preferred sites for TiO nanowires growth. It is indeed true and such a structure is presented in Figure S9 b, where a cross-like feature in the nanowire network is observed. The direct proof of the connection between nanowires and dislocations is shown in Figure S9 c, where for the thick enough lamella a feature resembling dislocation with an exit in the TiO nanowire was found.

It is known for decades that the plastic deformation induces a dislocation formation and when the strain is exerted on crystal surface in a linear manner, the resulting dislocations will be also agglomerated linearly. The single crystal cutting is just a procedure that generate tremendous stress in the vicinity of the cut line, which relaxes and ensues high density of dislocations. The TiO nanowire network formed at the edge of STO is presented in Figure S10. Nanowires, which hitherto have equal probability of be aligned along [010] or [001] directions now are all oriented parallel to the cut edge. It can be directly observed on SEM (Figure S10 b)) and TM-AFM (Figure S10 c)) maps. It provides an opportunity to control the formation of nanowires in terms of their orientation and spacing (nanowire network is now much denser). Summarizing, by the plastic strain engineering one can tailor the metallic nanowires on the perovskite surface.

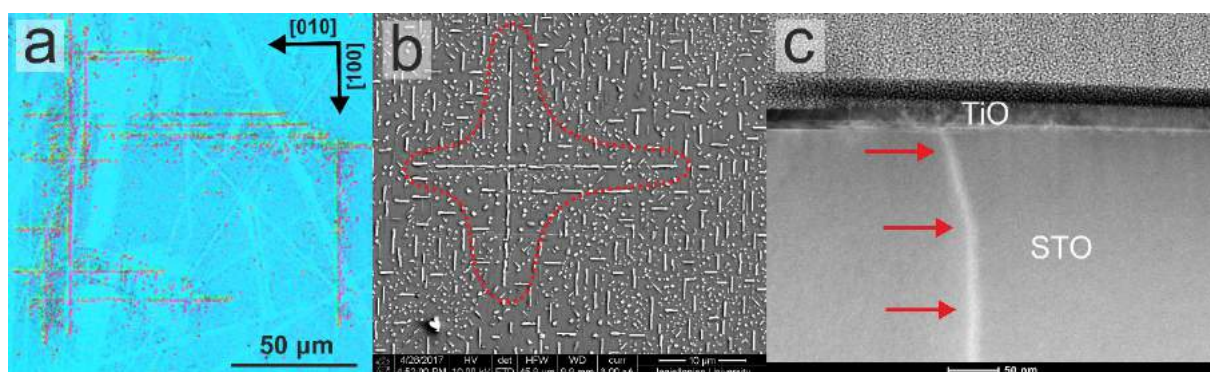


Figure S9. Dislocations impact on TiO nanowires formation. a) Optical image of a SrTiO₃(100) surface after etching, showing bands of etch-pits. b) SEM image of a region with cross-like arrangement of nanowires (marked in red), c) HRTEM image of a single TiO nanowire with a dislocation pinned to it.

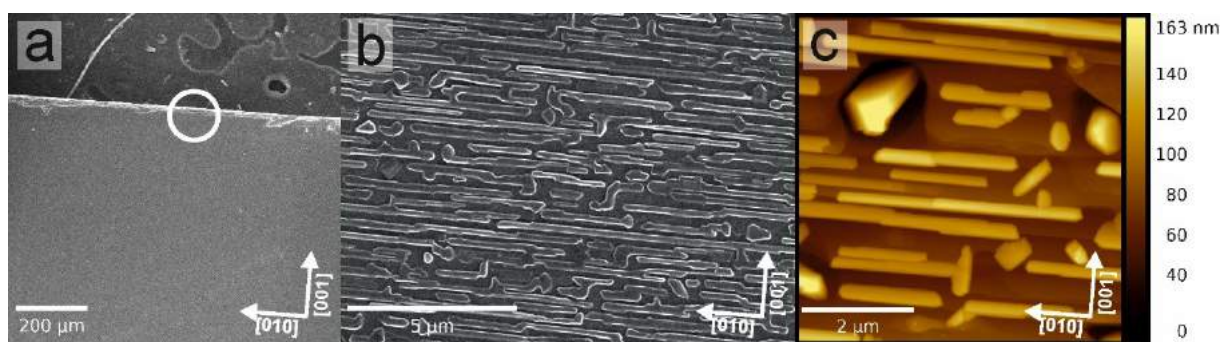


Figure S10. Stress influence on TiO nanowires formation. a) SEM image of a reduced SrTiO₃(100) [010] crystal edge, b) SEM image of a zoomed edge area, showing that nearly all of the nanowires are aligned along of the cut direction, c) TM-AFM image of the same area, illustrating that not only all nanowires are grown along horizontal direction but also terrace steps are aligned.

7. TiO nanowires growth model

Here we show a graphical representation of our proposed model regarding initial stages of the TiO nanowires formation on the surface of SrTiO_3 due to the thermal reduction. We postulate the transformation of SrTiO_3 into network of ordered TiO nanowires is governed by two key processes: incongruent sublimation of strontium and crystallographic shearing. In Figure S11 a side view of the $\text{SrTiO}_3(100)$ surface region (blue and yellow atoms stand for oxygen and strontium respectively) is presented.

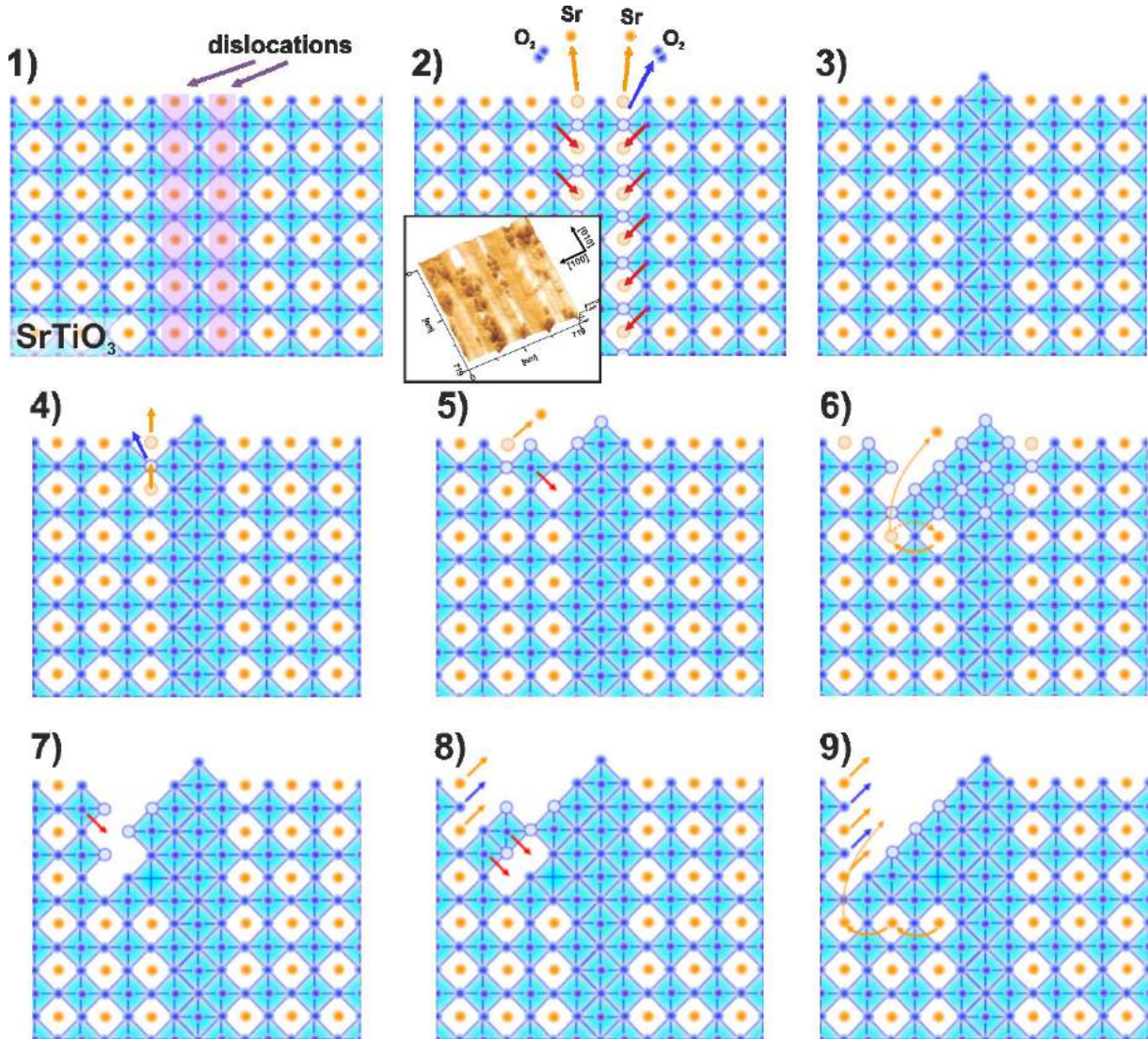


Figure S11. A model explaining the preferred formation of TiO nanowires on the surface of $\text{SrTiO}_3(100)$, due to the incongruent sublimation of Sr and crystal decomposition.

1. In the first stage of high-temperature UHV reduction of $\text{SrTiO}_3(100)$ crystals an arrangement of reduced edge dislocations is generated. They form of bands along of the $\langle 100 \rangle$ directions (see Fig. S9 a), where a distribution of etch pits on the surface of the reduced SrTiO_3 crystal is presented).

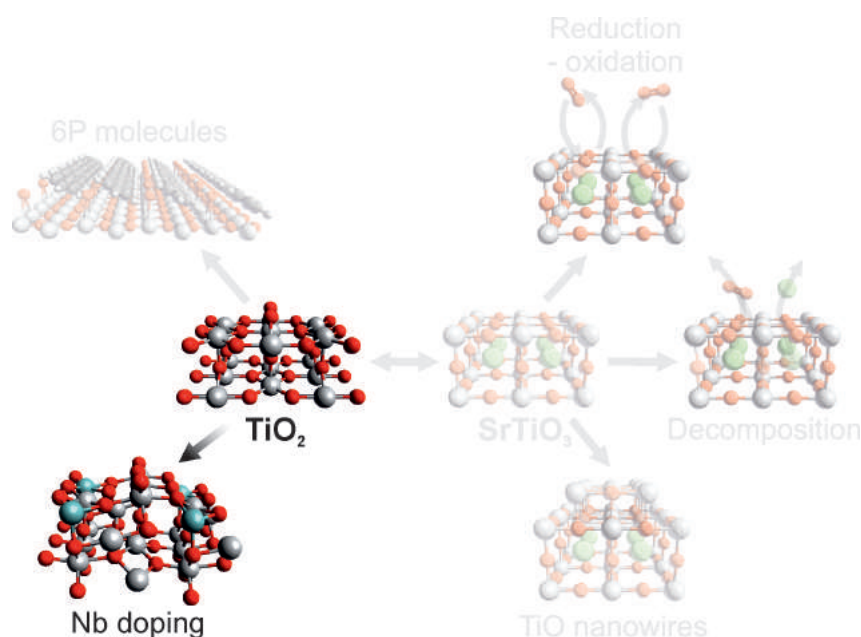
2. Under extremely low oxygen partial pressure (utilizing ELOP mechanism with use of the external getter - Si crystal in the experimental realization described in the main text) two processes start along of the dislocations cores: at first a selective sublimation of Sr and removing of O. An effect of such selective decomposition of the crystal close to the dislocation exits is manifested on the topography of the strongly reduced surface layer of SrTiO_3 , where after heavy thermal reduction pits of tens of nanometers are present (see AFM inset). The easy sublimation of Sr along dislocations on the surface layer of SrTiO_3 , should be similar to the sublimation of Mg close to the exit of dislocations in MgO [12], This process can be classified as a thermal generation of etch pits. After local depletion of Sr and O a second process takes place, namely a phase transformation of the $\text{Sr}_0\text{TiO}_{3-1}$ via crystallographic shearing, into anatase TiO_2 and then into TiO with rock salt structure. Notice: it would be difficult to define the sequence of mentioned transformation. It could be that the very strong reduction conditions lead directly in one step to the creation of TiO. Such embedded rocksalt TiO structures were already observed at dislocations cores in SrTiO_3 by Buban et al [13].
3. After shearing a TiO nanowire germs with a width of a few lattice constants are created (their crystallographic orientation is $\langle 100 \rangle$). The third stage of the out-of-plane conversion of the SrTiO_3 surface layer into TiO is presumably limited to the length of the first segment of dislocations in the hierarchic tree - in our case the depth of the nanowires would be about a few nm.
4. The next phase of the growth of TiO nanowires needs an interplay of the three “sinks for oxygen”: ultrahigh vacuum itself, external getter (here Si) and local getters on the surface of SrTiO_3 (here: TiO nanowires edges). We have presented that the annealing of the SrTiO_3 in the proximity of TiO leads to the sublimation of Sr [14]. Therefore along of the edge of the TiO nanowires Sr would be much easier removed.
5. After sublimation of Sr atoms close to the edge of a TiO nanowire a row of TiO_{6-x} octahedra is created, which would be subsequently absorbed to existing nanowires using mentioned shearing mechanism. This process causes the in-plane growth of the nanowires. Noteworthy, this kind of transformation of SrTiO_3 into titanium suboxides differs than classical growth mechanisms, which would be determined by a free diffusion of Ti and O. In this case, the shearing would be a more plausible mechanism than the interstitial diffusion of metallic Ti.
6. Images 6-9 present a progress in the in-plane and out-of-plane growth of the TiO nanowires. In principle steps are similar to those, described in points 3-5, with the additional interface mechanism (see Figure 6 and 9). Both figures show a diffusion process of Sr (or SrO) parallel to the interface between nanowires and SrTiO_3 crystal. After reaching of the free surface SrO will be incongruently evaporated. This process of conversion of TiO nanowires into the interior of the SrTiO_3 crystal along of the interface would only effectively work for a short

distance of a few lattice constants. However, since the surface far away from the existing nanowires is also decomposed (due to the ELOP mechanism) causing the Ti(O) enrichment of the surface, nanowires are also expected to absorb material supported by the surface diffusion. This may be proved by a simple observation of TiO nanowires being much higher than the SrTiO₃ surface between them. Finally, when nanowires are thick enough, edge dislocations are generated in the TiO crystal, due to the lattices misfit. Those misfit dislocations most likely play an important role in the formation of zig-zag TiO/STO interface, acting as easy diffusion pathways for Sr or SrO [15][16].

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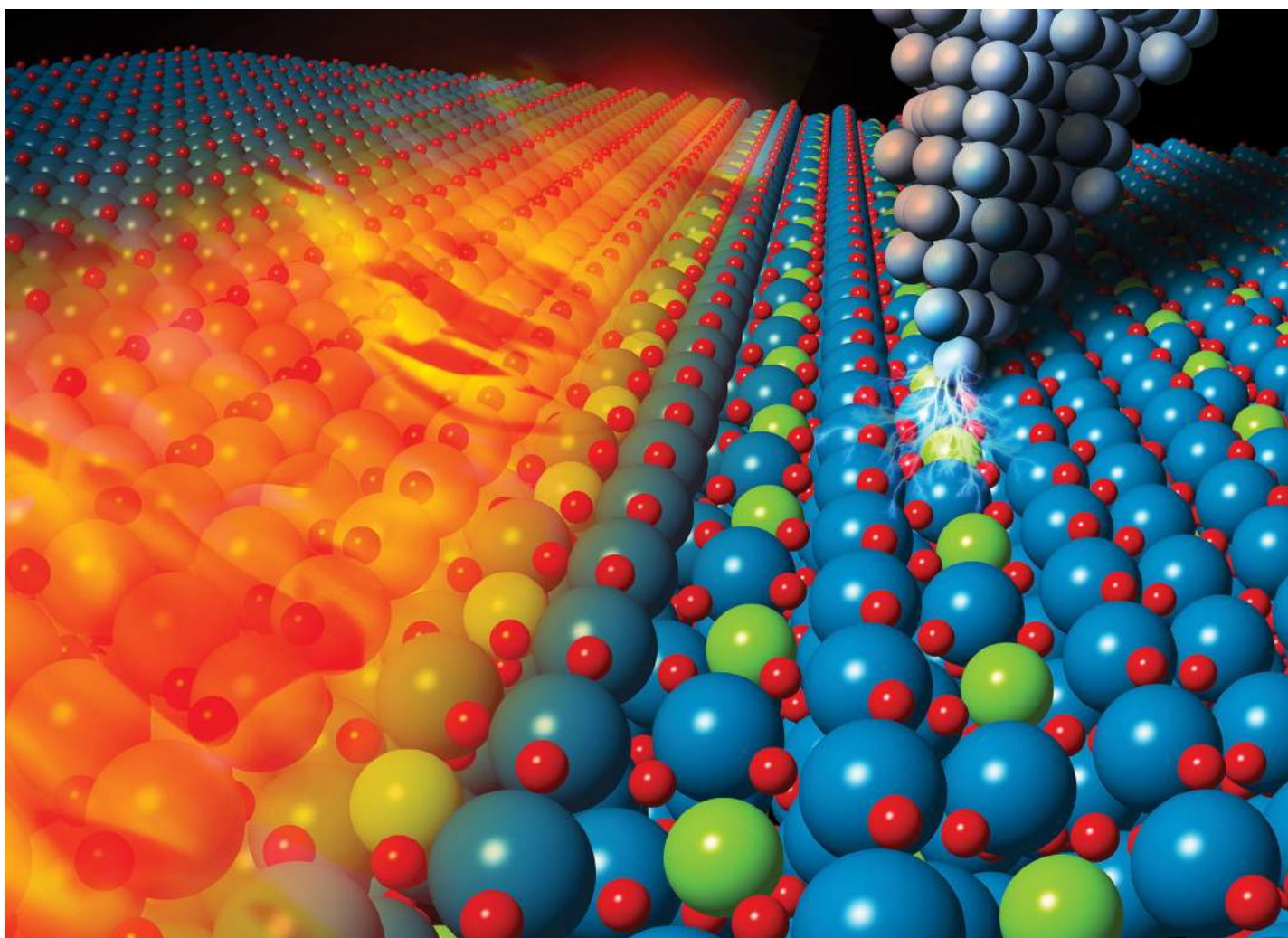
3.5 Tuning the Surface Structure and Conductivity of Niobium-Doped Rutile TiO_2 Single Crystals via Thermal Reduction



Here, a influence of a donor-doping on the structural and electronic properties of thermally reduced TiO_2 is studied [**TiO2_Nb**]. Conductivity and work function evolution versus the temperature of annealing are tracked and correlated with the surface reconstruction and composition changes. The electronic phenomena are explained in terms of Nb substitution at the surface, forming the new $c(4 \times 2)$ reconstruction. In addition, we show that conductivity becomes more homogeneous with the reduction degree, unlike the undoped TiO_2 . Paper preprint is preceded by the cover image of the PCCP journal.

Highlights

1. Impact of thermal reduction is limited to the subsurface region of Nb-doped $\text{TiO}_2(110)$,
2. A new $c(4 \times 2)$ reconstruction is formed by the Ti-to-Nb substitution, although deeper subsurface region is Nb-depleted,
3. Conductivity rises by three orders of magnitude and becomes homogeneous,
4. Surface transformations are reflected by the work function evolution.



Showcasing collaborative research between the Institute of Physics, Jagiellonian University, Poland and Forschungszentrum Jülich Germany.

Tuning the surface structure and conductivity of niobium-doped rutile TiO_2 single crystals via thermal reduction

Donor doping of titanium dioxide (TiO_2) is a common way of adjusting its properties, especially in order to enhance photocatalytic activity or performance of organic devices. We present that the electronic properties of Nb-doped TiO_2 crystal surfaces can be significantly modified not only by the dopant concentration but rather by thermal reduction. The surface conductivity increases by orders of magnitude after the reduction procedure and a new surface superstructure is formed while additionally the surface work function is changed. Tuning the parameters of thermal reduction allows for a dedicated tailoring of the electronic surface properties.

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Tuning the surface structure and conductivity of niobium-doped rutile TiO₂ single crystals via thermal reduction

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We report on the systematic exploration of electronic and structural changes of Nb-doped rutile TiO₂(110) single crystal surfaces due to the thermoreduction under ultra-high vacuum conditions (without sputtering), with comparison to undoped TiO₂(110) crystals. It has been found that the surface of the doped sample undergoes a previously unknown transition during reduction above 850 °C, as provided by LEED, STM and LC-AFM. This transition involves a change from heterogeneous conductivity (due to the presence of conducting filaments) to homogeneous conductivity, connected with a new (4 × 2) reconstruction of rows parallel to the [001] direction. DFT calculations suggest substitution of Ti by Nb atoms in the first atomic layer. Due to the strong reducing conditions during annealing, oxygen is released from the crystal and Nb diffuses from the subsurface into the bulk, agglomerating however on the surface, as shown by SIMS depth profiling. We present that 0.5% Nb doping significantly influences the reduction process and in turn the structural properties of the surface by supporting the evolution of the new reconstruction. It is shown that the thermal treatment of TiO₂:Nb under low oxygen partial pressure gives an opportunity to tune the electrical conductivity and work function of the surface.

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1. Introduction

Titanium dioxide is one of the most widely investigated semiconductors nowadays.¹ Due to the low cost, corrosion resistance and stability, TiO₂ is not only scientifically studied, but also used in many industrial sectors, often in the doped form. Given the visible light transparency, TiO₂ is often used as an electrode material for solar cells² or as a tunable substrate for the controlled adsorption of functional organic molecules.^{3,4} The photocatalytic activity of low-index titanium dioxide surfaces finds application, among many others, in water purification, removal of air pollutants and self-cleaning coatings.⁵ It was also found that doping with Nb can increase the photocatalytic activity significantly.⁶ Despite the high lifetime of TiO₂-based devices, the energy conversion in fuel cells is in the range of a few percent, which may be improved by doping. It was shown

that annealing of Nb-doped titania results in the emergence of concentration gradients which enhances charge separation and prevents charge carrier trapping on the surface.^{7,8} Recently, there has also been wide research interest in so called black TiO₂ nanomaterials which are formed *via* reduction in various hydrogen-rich gaseous atmospheres,⁹ which is thought as a breakthrough for effective water splitting.

In the last few decades, TiO₂ has also attracted much attention as a prototypical memristive material¹⁰ that can be used to build high-efficient memory and logic cells based on the resistive switching effect.¹¹ Here, the underlying mechanism is a local redox process by the valence change of the transition metal as has been found in a broad class of binary and ternary oxides,^{12–16} which may be altered *via* doping.^{16,17} Nanoscale investigations of memristive devices have shown that the switching process is localized in many cases to filamentary structures consisting of a secondary phase^{18,19} evolving during the formation process.

For many reasons listed above much effort has been exerted to investigate bulk Nb-doped TiO₂ systems^{7,8,20} or nanoparticles.²¹ Furthermore, TiO₂:Nb can be used as a conducting substrate for the growth of functional thin films and the knowledge about the influence of external gradients on the properties of the surface is needed to tailor the interface between film and substrate in a controlled way. However, there is still a lack of understanding of

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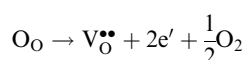
the actual surface properties of Nb-doped titania and the possibility to control them *via* oxygen activity. Therefore, the main aim of the present study is to describe the influence of the reduction process on the surface structure of Nb-doped TiO₂ as well as on its electronic properties.

In order to get an insight into the fundamental processes taking place during redox processes we investigate the influence of thermal reduction on the transformation of the surface layer of Nb-doped rutile TiO₂ single crystals kept in the cleanest environment of ultra-high vacuum (UHV).

Hence, our paper contains a systematic study of reduction-induced changes, divided into sections containing information about the crystallographic structure, reconstruction, chemical composition, electronic structure and transport properties of the surface at the nanoscale.

1.1 Rutile TiO₂

Stoichiometric TiO₂ is classified as a poor semiconductor/insulator with a wide bandgap of 3.2 eV and high electrical resistance. However, electronic states and conductivity can be easily tuned *via* donor metal doping lowering the bandgap which allows for the use of doped TiO₂ as an efficient photocatalyst.⁶ Another way of manipulating the electronic properties of oxides is *via* thermal reduction, which comes down to doping with oxygen vacancies.²² Under reducing conditions, oxygen is emitted from the titanium dioxide crystal lattice leaving behind oxygen vacancies and d-electrons, which can be described as follows:²³



Since in the Ti–O system many different suboxides exist as stable phases,²⁴ not only uniformly distributed point defects but also vacancy agglomerations leading to phase transformations are to be expected as a result of reduction, in particular, in the surface and subsurface region. It can be assumed that, with increasing oxygen depletion, at first a linear arrangement of vacancies, *e.g.* Magyari-Köpe defects, occurs,²⁵ which then lead to the evolution of a quasi-homogeneous distribution of filamentary structures, interacting with existing crystal dislocations as seen by LC-AFM as conducting spots on the surface.¹⁵ The next step of ongoing reduction would then be the formation of Wadsley planes²⁶ and finally, after prolonged reduction, new titanium suboxides such as Magnéli phases can evolve.^{10,27,28}

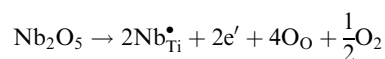
Using scanning probe techniques, the TiO₂(110) surface, which is the thermodynamically most stable one, has been investigated intensively.¹ The surface exhibits a (1 × 1) reconstruction which turns into a (2 × 1) reconstruction upon reduction due to oxygen loss from the surface. More complex reconstructions of (nx1) type have been found on the facets of the crystal such as on the (100) or (011) surface.

1.2 Nb-Doped TiO₂

Due to the high relevance of rutile TiO₂ surfaces in catalysis and photovoltaics, numerous works have been presented regarding element doping and their diffusion in TiO₂: *e.g.* nitrogen²⁹

and iron,³⁰ or the most important n-type dopant-niobium.⁸ Up to now, there has been considerable interest in investigating the properties of titanium dioxide enriched in Nb, especially regarding polycrystalline structures such as nanodots or nanotubes for (photo)catalytic applications, solar cells and energy storage applications.^{21,31–37} Recently, Nb-doped anatase thin films (TNO) have attracted wide attention as they have sufficient potential to replace indium tin oxide (ITO) transparent electrodes.^{38,39} Research on pressure-induced phase transitions⁴⁰ and bolometric properties⁴¹ was also performed. Natural rutile mineral is often enriched in niobium and tantalum as well (even in lunar rutile minerals collected by the Apollo 12 mission where a 6.4% content of Nb₂O₅ was found).⁴²

When pentavalent Nb is incorporated into TiO₂, a Nb_xTi_{1–x}O₂ solid solution is formed within the solubility range (approx. 20%).⁴³ Nb substitutes Ti cations in the lattice, providing additional electrons in the conduction band.⁴⁴ According to point defect chemistry, the additional charge of the Nb⁵⁺ dopant is compensated either by titanium vacancies under oxidizing conditions or by a valence change of the transition metal from Ti⁴⁺ to Ti³⁺ leading to the generation of free d-electrons under reducing conditions:^{23,45}



Hence the donor doping leads to an insulator–metal transition. In the low *p*_{O₂} regime, the bulk conductivity does not depend on the oxygen partial pressure (so-called plateau region) and metallic behaviour is expected.⁴³ It was presented recently that 3% Nb incorporation into polycrystalline rutile TiO₂ results in 6 orders of magnitude increase in conductivity.⁴⁶ Interestingly, the change from high to low conductivity for polycrystalline Nb-doped anatase is reversible *via* oxidation and reduction.³⁸ When it comes to dielectric properties, TiO₂ ceramics with 4% Nb content possess giant permittivity, which can be attributed to the high Ti³⁺ to Ti⁴⁺ ratio.⁴⁷

Despite the significant impact on the electronic properties, as little as 1% Nb does not change the structural properties of a bulk crystal even with the substantial charge injection done by Nb.⁴⁸ For doping levels below 15% the formed structure is rutile,⁴⁹ and the lattice parameter deformation is negligible. Furthermore, the interatomic spacing difference between metal atoms in pure rutile TiO₂ and NbO₂ is less than 0.05% in the *c* direction.⁵⁰ Also for Nb-doped TiO₂ in anatase structure, differences in *a* and *c* lattice parameters for a doping level of 1% are below 0.05%.

Regarding Nb behaviour on the surface, Y. Gao *et al.*⁵¹ concluded that Nb substitutes Ti at their sites and adopts a 4+ oxidation state in the surface lattice which leads to half-filled dangling bond surface states and a nonbonding bulk band localized on the Nb ions. Other works suggest that Nb surface cations may preferentially have 5+ oxidation state.⁴⁸

Here we present a complementary study of the influence of Nb doping in TiO₂(110) single crystals simultaneously on the surface reconstruction, electronic structure and chemical composition of both surface and bulk regions. Since upon prolonged reduction a phase transformation into titanium suboxides takes

place, we aim to investigate the initial steps of this transformation which is limited to the surface. That way we show how reduction processes (as a function of temperature) lead to a change of the properties of the surface. Due to the procedure applied in our research we are investigating real reduction–oxidation processes of a kinetic nature rather than thermodynamically equilibrium processes.

2. Experimental

In situ parts of the experiment were carried out in two similar UHV systems. Each of them consisted of chambers interconnected by a magnetically coupled linear transfer arm allowing for sample preparation, analysis and imaging. The base pressures of systems used were below 2×10^{-10} mbar (starting from ambient conditions and maintained by use of the turbomolecular, ion and sublimation pumps). The oxygen partial pressure estimated from the residual gas analyser (RGA) was below 10^{-13} mbar.

We used two kinds of epi-polished rutile samples: undoped $\text{TiO}_2(110)$ and Nb-doped $\text{TiO}_2(110)$ provided by the Shinkosha company. The Nb doping level was nominally of 0.5 wt% for all doped crystals used. We have also checked this doping level with the Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method. The measured Nb atomic concentration was 0.48 ± 0.01 wt% and that of Ti 59.1 ± 0.4 wt%. Other measured elements (e.g. Ca, Si, Mg, Mn, K) were either in the abundance of ppm level or below the sensitivity of the ICP-OES method. Therefore, the effect of significant intrinsic contaminations can be excluded for the investigated crystals.

Nb-doped and undoped samples were introduced into the ultra-high vacuum (UHV) system after cleansing with isopropanol using an ultrasonic bath and outgassed overnight. Titanium dioxide crystals (size of $10 \times 3 \times 0.5$ mm³) were mounted onto a heater (either silicon or ceramic). The use of an alternating current or ceramic heater isolated from the crystal ensured uniform reduction and temperature along the samples. Annealing was performed up to 1000 °C. The temperature was recorded by use of a digital pyrometer, with an estimated systematic error of 30 °C. We have additionally measured the oxygen partial pressure dependence on the temperature of the heater, without a sample, and we have found that there was almost no change of O_2 pressure in the vicinity of the holder.

The resulting surface quality was examined *in situ*, after cooling down to room temperature, using scanning probe techniques in UHV, performed at room temperature, namely Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM), either in contact mode (C-AFM) and in non-contact mode (NC-AFM).

In AFM contact mode we have measured surface topography as well as local conductivity (LC-AFM) using conductive Pt–Si and Pt–Ir cantilevers.¹² When operating in the non-contact mode, the contact potential difference (CPD) signal in Kelvin Probe Force Microscopy mode (KPFM), together with topography, was acquired.⁷³ The crystals' surface reconstruction was checked additionally by means of Low Energy Electron Diffraction (LEED).

The bulk oxygen loss of the $\text{TiO}_2\text{:Nb}(110)$ single crystal upon annealing under reducing conditions was determined by thermogravimetric analysis (TGA). The sample was placed in an Al_2O_3 oven and stored in an atmosphere of 4% H_2 in Ar, to generate reducing conditions. The rate of annealing was $30^\circ\text{C min}^{-1}$. The sample was kept at each temperature for 3 hours, with a step of 100 °C, beginning from 500 °C to 1100 °C. The TOF-SIMS5 apparatus (ION-TOF GmbH) working in dual beam mode was used to analyse the chemical composition by depth profiling. The sample was sputtered with a low energy (500 eV or 1 keV) O_2 ion beam rastered over a $300 \times 300 \mu\text{m}^2$ area. A pulsed bismuth ion beam (energy 30 keV) scanned over $100 \times 100 \mu\text{m}^2$ was used to probe the central region of the sputtered crater. Secondary ions induced by primary Bi_1^+ ions were analysed using a time-of-flight mass spectrometer. The profile of the normalized Nb concentration was evaluated as the count ratio ($\text{Nb}/(\text{Nb} + \text{Ti} + 2\text{O})$) for the sample annealed at 1000 °C divided by the same ratio for the as-received $\text{TiO}_2\text{:Nb}$ sample.

The macroscopic electronic transport properties were investigated using the four-point method in Valdes geometry. Four electrodes were deposited by using Pt paste on a crystal of $7 \times 3 \times 0.5$ mm³. An AC voltage was applied to the outer electrodes and the potential at all electrodes was recorded by electrometers using the lock-in technique. This way the potential sample degradation or stoichiometry polarization due to ionic conductivity could be avoided. The experiments were conducted inside a vacuum tube furnace and the oxygen partial pressure was controlled by introducing pure oxygen into the vacuum.

In order to investigate the crystallographic changes occurring in the Nb-doped TiO_2 during annealing under heavily reducing conditions (p_{O_2} of 10^{-20} mbar), XRD (X-ray diffraction) was performed using a STOE STADI diffractometer. The powdered single crystal was measured in transmission mode and Rietveld refinement was applied for qualitative phase analysis.

Density functional theory (DFT) calculations were performed within the generalized gradient approximation (GGA) to density functional, as implemented in the Vienna ab initio simulation package (VASP).^{52,53} The Perdew–Burke–Ernzerhof (PBE)⁵⁴ functional was used to describe the correlation–exchange interaction. The core electrons were treated by the projector augmented wave (PAW) method.⁵⁵ The plane wave basis set was restricted by an energy cutoff of 340 eV. The Brillouin zone of the $\text{TiO}_2(110)$ (4×2) system was sampled by a $3 \times 12 \times 1$ Monkhorst–Pack k -points grid including the gamma point.⁵⁶ The total energy convergence criterion was chosen to be 10^{-6} eV. The system was modelled by four layers, and all the atomic positions, except the bottom layer, were fully relaxed by a conjugate gradient method until the maximum force in any direction was less than $0.01 \text{ eV } \text{\AA}^{-1}$.

3. Results and discussion

In the following sections we will present experimental results of the thermally induced changes in Nb-doped single-crystals $\text{TiO}_2(110)$, starting from bulk properties towards surface at the nanoscale.

3.1 Mass loss

In order to monitor the oxygen loss taking place simultaneously with the reduction thermogravimetric measurements were performed (Fig. 1a). In this experiment the sample was kept under Ar/H₂ flow providing stable reducing conditions ($p_{\text{O}_2} \approx 10^{-20}$ mbar). It can be seen that the mass of the TiO₂:Nb crystal decreased with time and temperature. In particular, above 800 °C a significant mass loss indicating the exorporation of oxygen was observed. The stoichiometry range of $x = 0.0001$ in TiO_{2-x} was reached after reduction at 700 °C (for 3 hours), which is similar to the TGA spectrum observed for undoped TiO₂.¹² Regarding the mass loss at higher temperatures, even after 3 h of reduction the mass was not stable showing that the reduction persisted and that no thermodynamic equilibrium could be reached. This shows that at high temperature a continuous transformation into titanium suboxides takes place.¹³ In order to demonstrate this, we performed long-time reduction of the single crystal powder under heavily reducing conditions. As measured by X-ray Diffraction (XRD), new crystallographic phases emerged for the Nb-doped TiO₂ sample reduced for 36 hours in H₂ as presented in Fig. 1b. The material transformed completely from a rutile structure to Magnéli-type phases such as Ti₈O₁₅ or Ti₉O₁₇ (no (110) diffraction spots are present), which is similar to the reduction process of undoped TiO₂.¹⁰ Knowing that heavy reduction of TiO₂:Nb leads to the formation of new phases we limit ourselves to initial stages and its impact on the surface properties of single crystals. Using surface resolving techniques we will show that these initial stages of reduction are related to a modification of surface reconstruction and conductivity that is in the present case additionally affected by Nb.

3.2 Macroscopic electronic transport

The electronic transport on the macroscale was measured by the four-point technique. The sample was kept at different temperatures and the oxygen pressure was altered starting from reducing to oxidizing conditions. As shown exemplarily for 700 °C in Fig. 2a, the dependence of the bulk resistance extracted from the potential drop between the inner electrodes differs significantly from the interface resistance extracted from

the potential drop between inner and outer electrodes as illustrated in the inset of Fig. 2a. This way the bulk resistance $R_b = (\varphi_2 - \varphi_3)/I$, the total resistance $R_t = (\varphi_1 - \varphi_4)/I$ and the two interface resistances $R_{i1} = (\varphi_1 - \varphi_2)/I$ and $R_{i2} = (\varphi_3 - \varphi_4)/I$ can be extracted. While the bulk resistance is nearly constant as a function of oxygen pressure as expected from point defect chemistry for doped TiO₂, the interface resistance increases significantly upon oxidation and hence contributes a major part to the total resistance. This indicates the existence of a metastable surface layer that can be easily oxidized in contrast to the bulk being in the plateau region of the Brouwer diagram⁵⁷ (called the reduced regime I). In this regime, the charge introduced by the Nb donor substituting Ti is compensated by electrons. The electron concentration is thus equal to the donor concentration $n = [\text{Nb}_{\text{Ti}}^\bullet]$, regardless of the oxygen partial pressure, and thus the influence of titanium interstitials or titanium vacancies is not expected. 4-Point measurements indicate however that reduction of Nb-doped TiO₂ single crystals takes place separately in the bulk region, following the defect chemistry and surface, where the bulk defect chemistry cannot be applied. When increasing the temperature and

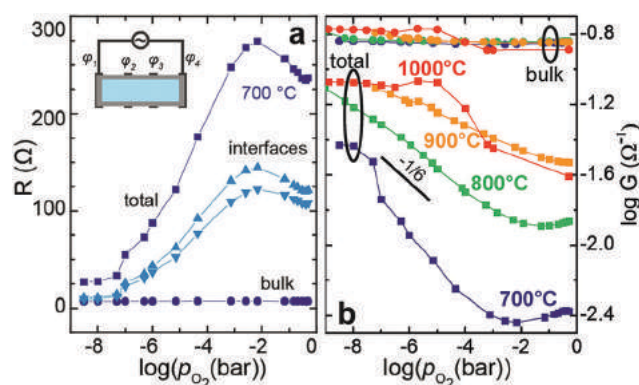


Fig. 2 Four-point measurements as a function of O₂ partial pressure. (a) Partial resistance of the sample at 700 °C obtained by analysis of the potential drops as illustrated in the inset. (b) A logarithmic plot of total (squares) and bulk (circles) sample conductivity measured at different annealing temperatures.

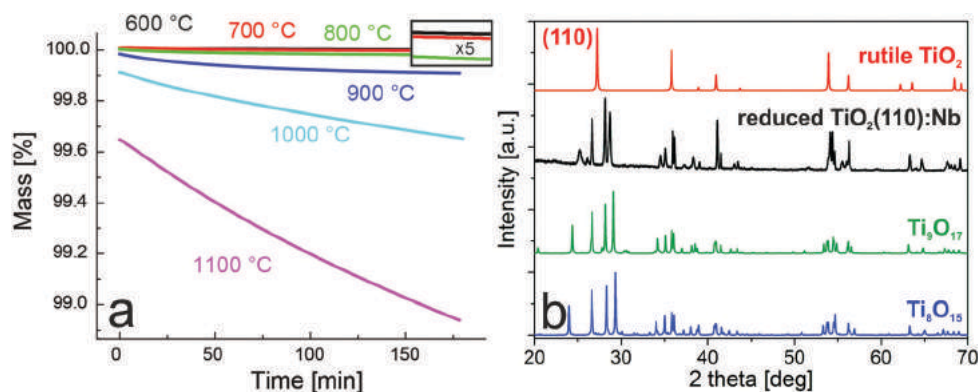


Fig. 1 (a) TiO₂:Nb(110) mass loss due to the thermoreduction of a crystal as measured by TGA. The crystal was kept for 3 h at the indicated temperatures, ranging from 600 °C to 1100 °C. (b) XRD pattern of TiO₂:Nb(110) reduced for 36 h (black), showing the formation of the phases Ti₈O₁₅ and Ti₉O₁₇ (green and blue respectively). Rutile TiO₂ is shown in red, with the (110) spot highlighted.

performing the oxidation starting from UHV conditions at each temperature, the total conductivity reflecting the conductivity of the surface layer changes (Fig. 2b). It increases significantly up to 900 °C and then stays almost constant, while the bulk value shows only minor variations with temperature and pressure. This additionally illustrates that reduction-induced transformations take place in the surface layer, which is to be also concluded from the surface-sensitive measurements discussed below (Sections 3.4–3.6).

3.3 Chemical composition

In order to determine the influence of thermal reduction on the stoichiometry of the surface layer, the Nb distribution in particular, we performed SIMS depth profile measurements of the crystal before and after reduction at 1000 °C. For Ti and TiO, the measured ion fluxes are beyond the detection limit so we chose the isotope $^{47}\text{Ti}^+$, which had a sufficiently low flux. The oxygen concentration measured was 30–40 times less than that of Ti because the projectile we used was positively charged and the cross section for O^+ ion formation was very low. The raw depth profiles of $^{47}\text{Ti}^+$, O^+ and Nb^+ are presented in Fig. 3b. From the intensities we evaluated the depth profile of Nb concentration for the reduced $\text{TiO}_2\text{:Nb}$ sample, according to the formula $c_{\text{Nb}} = \frac{I_{\text{Nb}}}{I_{\text{Ti}} + 2I_{\text{O}} + I_{\text{Nb}}}$. To exclude all possible sources of errors this measure was subsequently normalized to the concentration from the as-received one, since SIMS depth profiling was performed using the same experimental conditions for both samples, and finally plotted in Fig. 3a. Previous investigations of niobium doping prove that in thin films grown from $\text{TiO}_2\text{:Nb}$ niobium appears in two ways: the uniformly distributed substitution in the crystal or *via* creation of Nb_2O_5 phases.⁵⁸ Nb atoms' out-of-plane diffusion is thought to act *via* the interstacy mechanism which is similar to the Ti self-diffusion in undoped TiO_2 .⁵⁹ In our case of single-crystal $\text{TiO}_2\text{:Nb}$ before and after annealing likewise, the Nb concentration was uniform in the bulk and no big crystals of niobium oxides were grown (based on SIMS mapping).

Extensive studies regarding the Nb segregation in the TiO_2 sample were performed by the group of Nowotny,⁵⁵ on both poly- and monocrystalline samples annealed in either oxidizing or reducing conditions. The rule of thumb is that annealing in

an oxidizing atmosphere leads to Nb surface enrichment while annealing in reducing conditions results in Nb depletion in the surface region,⁶⁰ but much less substantial (e.g. for polycrystalline $\text{TiO}_2\text{:Nb(110)}$ (0.18% Nb) 10 hours of annealing at 1000 °C caused an increase of the Nb concentration by 230% when annealed in 1 bar of O_2 and only 11% depletion when annealed in low oxygen partial pressure of $p(\text{O}_2) = 10^{-10}$ mbar).⁵⁸ The same situation of Nb enrichment in an oxygen atmosphere applies also for single crystals.⁶¹ In the present study, we investigate the changes of the Nb concentration of the surface region of single crystals after annealing under UHV conditions. The base pressure in the UHV chamber during annealing was in the range of 10^{-9} mbar and the oxygen partial pressure was below approx. $p(\text{O}_2) = 10^{-11}$ mbar. Therefore, we see a certain depletion of Nb on the surface, yet not as high as for non-vacuum gaseous reducing conditions.

Fig. 3a presents the relative Nb in-depth concentration variations. One of the limitations of the SIMS technique is non-equilibrium sputtering of the sample at the very beginning, and hence the signal coming from first nanometers may be fraught with higher uncertainty. In order to overcome this problem the relative intensity of the Nb signal coming from the sample annealed at 1000 °C is here compared with the same signal acquired for the as-received one. Although the subsurface layer is depleted in Nb up to 40 nm, the very surface region seems to have an increased Nb content. Other surface-resolving measurements introduced in Sections 3.4–3.6 strengthen the claim of Nb enrichment at the very surface. In the deeper regions, the Nb concentration slightly increased, reaching a plateau (above 50 nm), where the doping level was comparable to that of the as-received sample. Most probably the reduced subsurface adopts one of the Nb-doped Magnéli-type phases (e.g. Nb-doped Ti_8O_{15}), which has the (4×2) reconstruction.⁷ This low-dimensional surface structure exerts an additional driving force for niobium segregation, since it has different electronic and chemical properties. In fact, rutile TiO_2 grain boundaries have been observed to be the preferred sites for Nb segregation.⁶²

3.4 Surface reconstruction

The main goal of this research was to correlate the bulk properties (oxygen loss, Nb segregation and macroscopic conductivity) with

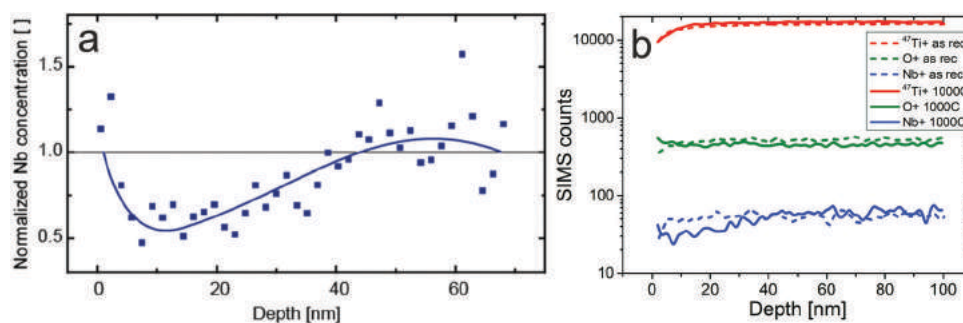


Fig. 3 (a) Nb content after annealing at 1000 °C (normalized to the Nb content of the as-received sample) as measured by SIMS depth profiling. The solid line serves as a guide for the eye. (b) Raw SIMS depth profiles of $^{47}\text{Ti}^+$ (red), O^+ (green), Nb^+ (blue) of the as-received Nb-doped TiO_2 (dashed) and 1000 °C annealed Nb-doped TiO_2 (solid).

nanoscale surface traits. In Fig. 4, the comparison of reduction-induced STM topography changes of a pure rutile $\text{TiO}_2(110)$ vs. $\text{TiO}_2\text{:Nb}(110)$, together with the corresponding LEED pattern, is presented. STM surface topography consists of atomically flat terraces of width in the range of hundreds of nanometres and with a monatomic step height of 3.2 Å. The terrace layer is composed of alternating atomic rows of oxygen and titanium, which are oriented along the [001] crystallographic direction and are separated by 0.65 nm. Although oxygen atoms protrude from the surface of $\text{TiO}_2(110)$, bright rows visible on empty states (positive sample bias) represent titanium atoms being topologically below the rows of oxygen atoms.⁶³ At higher temperatures step edges become better defined and compact. Using LEED a (1×1) surface pattern for annealing temperatures up to 850 °C was found. Due to oxygen loss from the crystal, a

(2×1) reconstruction is formed at higher temperatures, which stands in agreement with previous results.¹

The situation is different when it comes to the Nb-doped sample. Topography (STM) combined with surface crystallography (LEED) is provided for four representative annealing temperatures (Fig. 4, bottom part). Large-scale STM images show hundreds of nanometer wide terraces with the same step height as for pure $\text{TiO}_2(110)$. However, these terraces appearing at the temperatures from 850 °C have a row-like structure as can be seen in the magnified images (insets). The rows have a period of 2.6 nm, which is exactly 4 times more than those coming from the (1×1) reconstruction (called “ (4×2) rows” in the rest of the text). They can be connected with a complex LEED pattern coming up accordingly at the same temperature (see Fig. 4 insets). Up to a temperature of 800 °C the surface has an

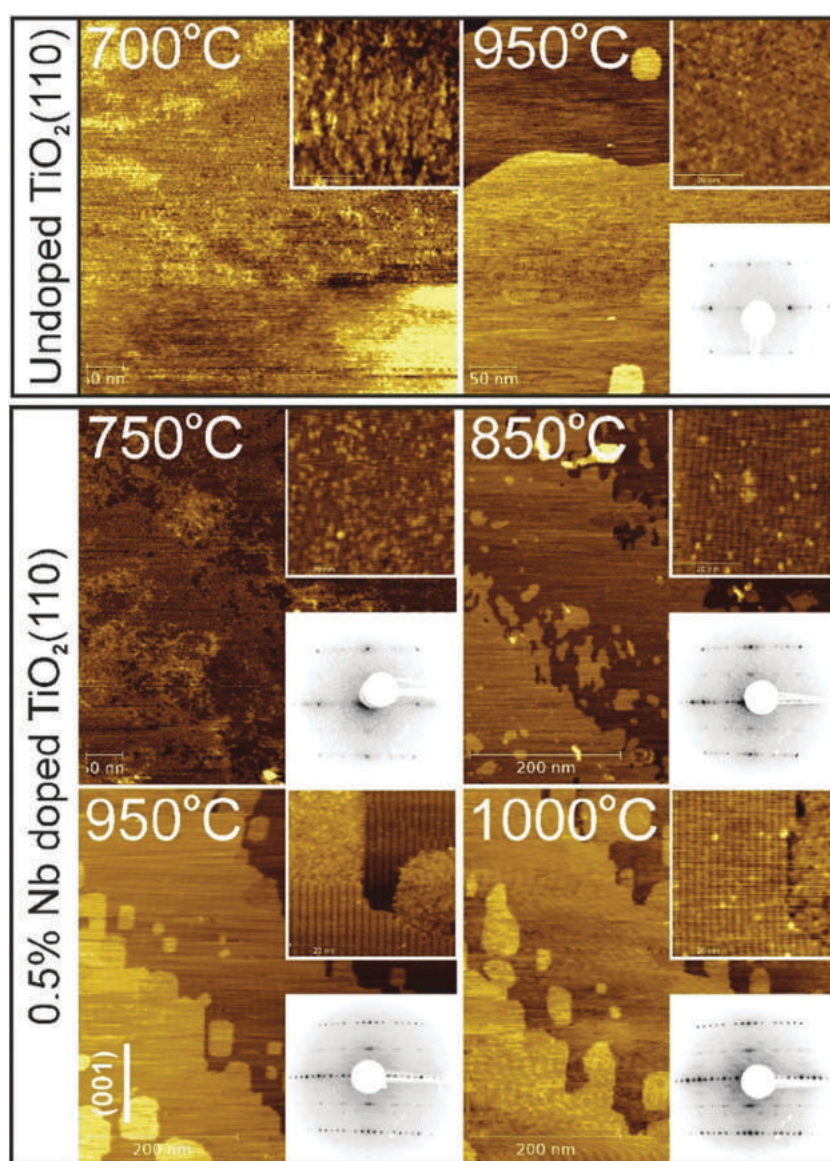


Fig. 4 RT STM topography images ($500 \times 500 \text{ nm}^2$, empty states, +1.5 V sample bias) of undoped and Nb-doped $\text{TiO}_2(110)$ surfaces thermally reduced at the indicated temperatures, respectively. Areas of uniform colour are monatomic terraces. Upper right corners of the insets: high-resolution images of STM topography ($50 \times 50 \text{ nm}^2$). Bottom right corners of the insets: the corresponding LEED patterns (electron beam energy of 70 eV).

ordinary (1×1) reconstruction which is influenced by defects (LEED pattern background). At 800–850 °C there is a further pattern of (4×2) reconstruction visible in addition to the (1×1) reconstruction. At 950–1000 °C even more features can be seen in the LEED pattern reflecting possibly the evolution of an additional reconstruction $(4 \times 2)/(n \times 8)$. Regarding the surface coverage, the (4×2) row-type domain reaches its maximum at 950 °C (of about 80–90% surface area) as provided by STM and LC-AFM (see below) measurements. The remaining surface area has a (1×1) reconstruction structure and periodicity; however bright features are seen in the STM map, indicating the presence of defects such as oxygen vacancies.

In Fig. 5, a detailed investigation of the (4×2) rows structure of the reduced $\text{TiO}_2\text{:Nb(110)}$ by means of high-resolution STM (a) and LC-AFM (b) images is shown. The rows with a period of 2.6 nm are clearly visible, both as the higher density of empty states (STM) and the increase in local conductivity (LC-AFM). In the STM image the highly defective (1×1) domain can also be identified. The dark rows of the (1×1) domain propagate as dark rows in the (4×2) rows structure (see white marks in Fig. 5a). Therefore, we conclude that the dark rows in

those two structures correspond to bridging oxygen atoms. Zoomed areas 1 and 2 support the hypothesis that the (4×2) domain has fourfold translational symmetry. Two grain boundaries found in area 1 have a certain mismatch which corresponds to $1/4$ (4×2) periodicity shift (see two line profiles drawn on different domains). Regarding the step edge, the (4×2) domain behaves according to the $\text{TiO}_2(110)$ (1×1) reconstruction, where neighbouring terraces have additional 0.5 lattice shift¹ (the smallest terrace has a width of 0.5 oxygen rows periodicity). In the area 2 measured shift between terraces equals exactly 1.5 times the periodicity of (1×1) ($1.5 \times 6.5 \text{ \AA} = 9.7 \text{ \AA}$). Due to the commensurability of (4×2) and (1×1) reconstructions it is likely that the observed domain emergence is a surficial feature.

For the pure $\text{TiO}_2(110)$ bright rows in empty states maps represent Ti cations on the surface. Since Nb atoms appear either in 4+ or in 5+ oxidation state, bright spots in empty states STM may be also associated with Nb either replacing the Ti atoms or arranged as adatoms. Such a case was already observed by Sasahara *et al.*⁶⁴ in a UHV STM investigation of the $\text{TiO}_2\text{:Nb(110)}$ surface after the sputtering and annealing process, where single niobium atoms were observed on the surface.

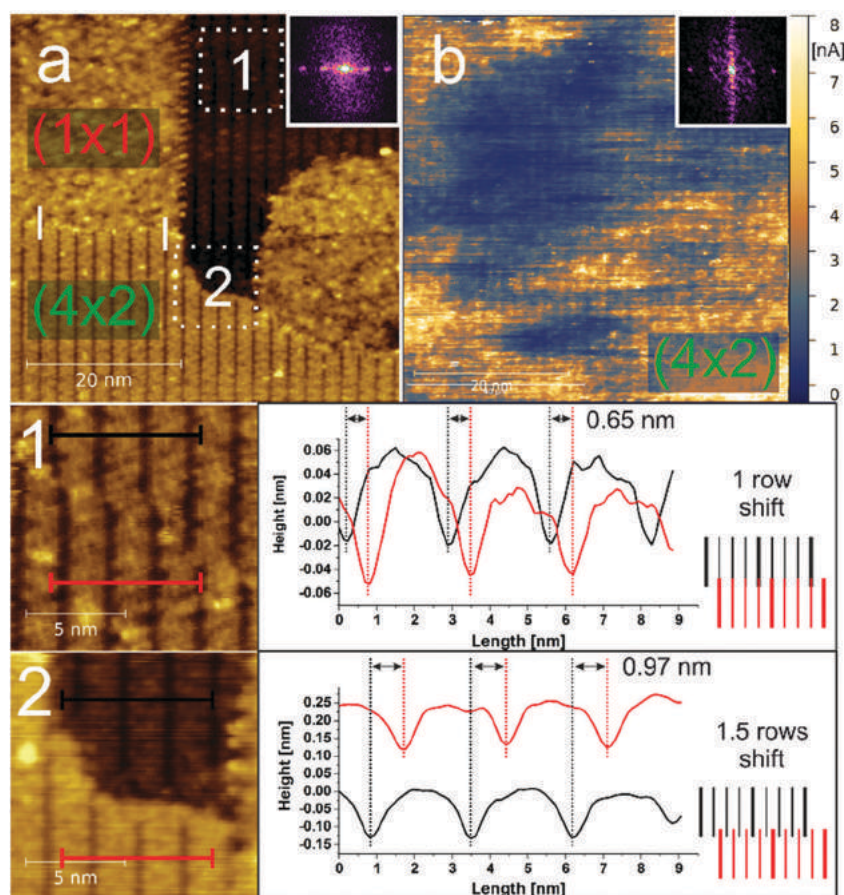


Fig. 5 High resolution images of the (4×2) rows structure: (a) STM topography of $\text{TiO}_2\text{:Nb(110)}$ annealed to 950 °C ($50 \times 50 \text{ nm}^2$, sample bias of +1.5 V), (b) LC-AFM current map of the $\text{TiO}_2\text{:Nb(110)}$ sample annealed beforehand to 1000 °C ($50 \times 50 \text{ nm}^2$, sample bias of +0.4 V, colour scale adjusted to show individual rows). In the insets – 2D Fourier transforms indicating periodicity in the STM and current maps. At the bottom two zoomed areas from (a) are presented: 1 showing the domain boundary together with the corresponding profiles of each (4×2) domain; 2 presenting propagation of (4×2) through monoatomic steps and certain shift additionally determined by line profiles.

Nb atoms tended to gather in certain areas of different charge state (such as Ti deficiencies) and form structures which can be treated as initial stages of periodic rows seen in our measurements.

In the LC-AFM current map the modulation with the (4×2) periodicity is apparent as proven by Fourier analysis (see the inset in Fig. 5b); however it is supported by a non-uniform background. This indicates that the (4×2) reconstruction is only a surface feature and may suggest inhomogeneity of electronic density of states underneath the surface layer.

Fig. 6 presents our understanding of the reconstruction of the reduced Nb-doped $\text{TiO}_2(110)$. On the left hand side the simple ball-and-stick surface model depicts the (1×1) reconstruction, from which the new (4×2) domain emerges. Titanium and oxygen are shown as pink and blue balls respectively. On average, (4×2) rows have higher contrast than both titanium atoms and defects in the (1×1) reconstruction, which are mainly oxygen vacancies. They are also bigger in size; thus one possible explanation would be that they come from segregated dopants, Nb in this case. On the other hand it could be possible that the Nb dopant acts as a kind of catalyst for the evolution of a new arrangement of Ti and O atoms within the rows. For both cases the (4×2) reconstruction seen in the LEED pattern fits the presented model, where the bright atoms row is altered with one empty position. The observed domains of the (4×2) reconstruction are stable against STM and LC-AFM tip interactions, whereas for single Nb adatoms it has been reported that even a mild STM tip interaction caused Nb atoms to diffuse on the surface.⁶⁴ This shows that during reduction a distinct rearrangement on the surface took place leading to the evolution of a new stable surface structure.

The atomic structure, deduced from STM, LC-AFM and LEED (Fig. 2), seems to be confirmed by the DFT calculations (Fig. 6, right). Indeed, Nb atoms prefer to substitute Ti atoms in the middle of terraces between oxygen rows, rather than adsorb on the surface. However, a simple substitution of Ti atoms cannot explain the asymmetry in the STM topography with respect to the O rows. In fact, the situation is more complicated. Namely, Nb atoms tend to occupy the middle terrace Ti positions expelling the residing Ti atoms, which take inter-site positions. On the other hand, the inter-site Ti atoms prevent Nb atoms from occupying precisely the Ti sites. The resulting atomic structure is asymmetrical with respect to the O rows, as it is evident in Fig. 6. Assuming that a high STM signal is due to Nb, such an atomic structure explains the STM topography. Note that the inter-site

Ti atoms play a very important role in this regard; without them it is impossible to explain the STM topography, as Nb atoms would occupy the middle-terrace symmetric Ti positions. The zig-zag structure of (4×2) rows may in this case come from the different position of buried inter-site Ti atoms (left or right with respect to the Nb atom). Moreover, such local arrangement of Nb and Ti atoms seems to be preferable also in the presence of O vacancies.

3.5 Local work function

To determine reduction-induced changes of the surface local work function, we performed CPD measurements by KPFM on the undoped and Nb-doped $\text{TiO}_2(110)$ versus the annealing temperature. For each data point two separate measurements were performed, using the same NC-AFM cantilever, under the same experimental conditions: on $\text{TiO}_2\text{:Nb}$ and, for the calibration, on the Au(111) surface.⁶⁵ Therefore, we can present absolute values of the effective work function on the surface, related to the literature estimation of the Au(111) surface work function – 5.31 eV, whereas the work function of $\text{TiO}_2(110)$ rutile falls in the range of 5.1–5.5 eV^{66,67} (for nanotubes a work function of even 4.9 eV was reported⁶⁸). These huge reported variations can be understood since CPD is very sensitive to the surface conditions and most of the measurements described in the literature were performed on diversely prepared samples with unknown final reduction states.⁶⁹ This can be even more clearly understood, as there is even a 2 eV difference between the experimental results and simulations performed on the ideal crystal structure of $\text{TiO}_2(110)$.⁷⁰ Furthermore we have to take into account that the surface potential as mapped by KPFM can be influenced by inhomogeneities in the surface conductivity that could be related to filamentary conductance (*cf.* Section 3.6) paths causing the evolution of space-charge zones and variations in the density of electronic states. Hence, the measured effective work function is a surface property and may differ from the real work function of the bulk material.

In Fig. 7, the effective surface work function (ϕ) is presented as a function of the annealing temperature of both undoped and Nb-doped $\text{TiO}_2(110)$. For pure rutile $\text{TiO}_2(110)$, CPD maps reveal a uniform chemical potential over the whole surface with a variation of approx. 2 percent. Upon reduction however, the mean work function relative to Au(111) shows some changes. After the 850 °C reduction step, the average ϕ had decreased

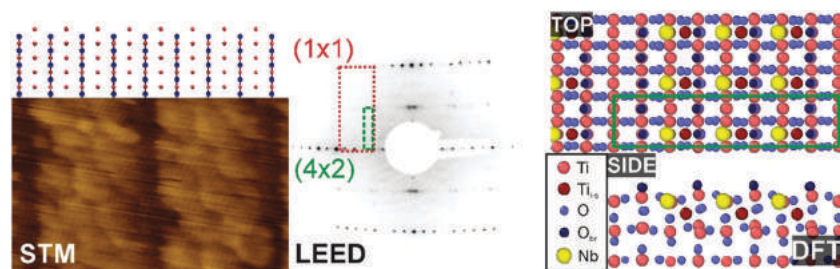


Fig. 6 DFT surface model (right) for the annealed Nb-doped $\text{TiO}_2(110)$ surface, compared to the RT STM map (left) and LEED (middle) pattern acquired after sample annealing at 950 °C. In the ball-and-stick model Ti atoms are shown in pink, Ti interstitials in brown, O bulk atoms in light blue, bridging O atoms in dark blue, and Nb atoms in yellow. The red dashed box represents the (1×1) unit cell, whereas the green box stands for $c(4 \times 2)$.

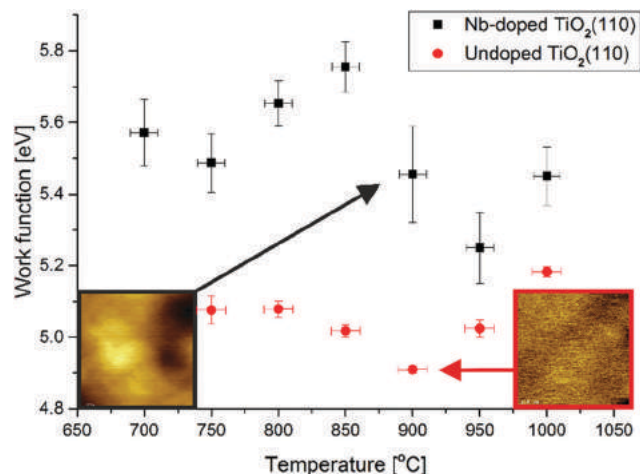


Fig. 7 Dependence of the effective surface work function (ϕ) measured (at room temperature) by KPFM on the annealed surfaces of undoped $\text{TiO}_2(110)$ (red dots) and Nb-doped $\text{TiO}_2(110)$ (black squares). CPD maps ($500 \times 500 \text{ nm}^2$) for both undoped and doped $\text{TiO}_2(110)$ surfaces acquired after annealing to 900°C are presented in framed boxes, red and black, respectively. CPD variation within one map is below 80 mV .

and reached a minimum after reduction at 900°C . This is correlated with the (1×1) to (2×1) reconstruction transition observed in STM and LEED measurements. After annealing at even higher temperatures, the work function is characteristic for reduced crystals having a large amount of oxygen vacancies.⁶⁴ However, since the reduction level increases with the temperature of annealing but the measured effective work function is not monotonic, it is likely that the surface structure change has a dominant influence on the work function measured on the surface.

Surprisingly, in the case of the $\text{TiO}_2\text{:Nb}(110)$ surface the mean work function is higher compared to the undoped

$\text{TiO}_2(110)$ surface, and is also reduction dependent with clearly resolved extrema. From SIMS measurements we know that there are concentration gradients emerging upon reduction.⁷ It was reported that a Magnéli-type (sub)surface layer is formed due to oxygen depletion.⁷¹ This positively charged surface layer can be made responsible for the apparent increase of the work function of Nb-doped TiO_2 over undoped crystals. Additionally, we can expect that also the evolution of the new reconstruction, which is partially composed of Nb atoms (as suggested by DFT calculations), lowers the work function, which will impose the general effect. The highest ϕ is measured after annealing at 850°C , when the new structure begins to form, whereas the lowest work function is measured for the temperature of 950°C , when the (4×2) rows domain reaches its maximum area coverage. Furthermore, it stands in agreement with conductivity measurements – more d-electrons which are attributed to the new surface structure lower the surface work function. The influence of surface transitions on electronic properties is substantial: the difference between ϕ_{MAX} and ϕ_{MIN} is two times higher than for the case of reduced undoped $\text{TiO}_2(110)$.

3.6 Surface conductivity

The surface conductivity of the $\text{TiO}_2\text{:Nb}(110)$ surface was measured by the use of LC-AFM, which can be regarded as a mapping of the distribution of d-electrons. It evolves significantly with the reduction temperature (Fig. 8). The surface of the as-received Nb-doped crystal is insulating, which may be attributed to oxidation processes in the surface layer as has also been found for $\text{SrTiO}_3\text{:Nb}$.^{16,72} Upon reduction the average surface conductivity increases. For the reduction regime from 700°C to 800°C , the maps consist of randomly distributed spots of high conductivity, separated by less conductive areas. The measured difference in the conductivity is at least 3 orders of magnitude. After reduction

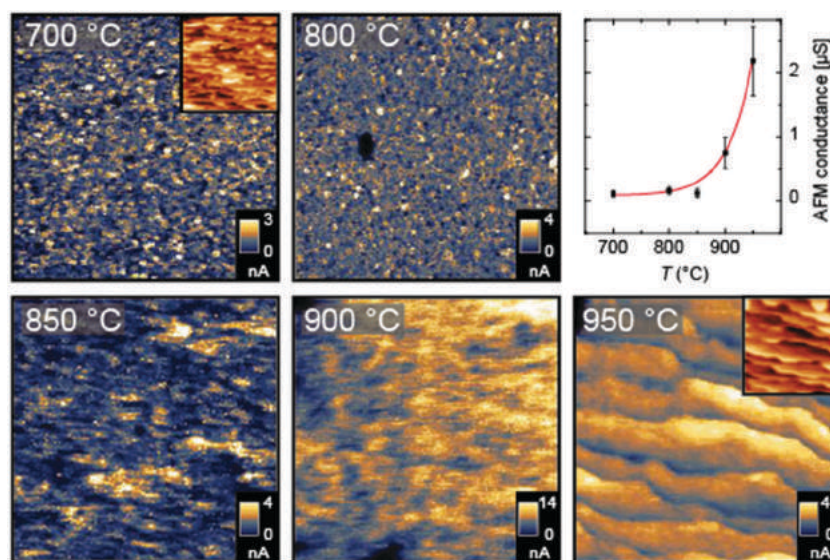


Fig. 8 RT LC-AFM local current maps of the $\text{TiO}_2\text{:Nb}(110)$ surface after heating up to the 700 – 950°C range (applied sample bias of 10 mV , false colour scale – some spots are beyond the colour scale). Topography maps shown additionally for 700°C and 950°C . Upper right corner: average AFM conductance (current measured for each point, divided by the sample bias) dependence on the reduction temperature.

at 850 °C the surface became more homogeneous in terms of conductance, after 900 °C it was almost uniform, while at 950 °C the influence of terraces is apparent (see the actual topographic terrace structure in the inset). The conductivity at the vicinity of step edges is higher on the ascending terrace and lower on the descending terrace (see the conductivity map for 950 °C). This suggests a growth-like behaviour of in-plane diffusion: atoms diffuse on the surface, and stick to the kinks which resemble diffusion barriers for them.

We thus state that there is a transition from grain-like conductivity, which may indicate an arrangement of filamentary current paths,¹⁵ to planar terrace-like conductivity at about 850 °C, which is connected with the evolution of the 2D layer of the Nb-rich (4×2) reconstruction. The surface layer of $\text{TiO}_2\text{:Nb}$, which was found to be initially insulating presumably due to oxidation, gains inhomogeneous, filamentary conductivity due to the local reduction by formation of oxygen vacancies, which then may agglomerate to linear filamentary structures seen in surface projection as conductive spots. However, not only the spatial distribution of conductive paths changes with reduction but also surface resistivity. The average conductivity extracted from the current maps measured at room temperature after each reduction step *versus* the reduction temperature is presented in the upper right corner of Fig. 8. Data points obtained for the high-temperature reduction reveal an exponential increase with the reduction temperature. It reflects temperature-induced changes of the electronic transport in the surface layer due to surface transformations. The exponential increase of surface conductivity of the donor-doped sample upon reduction is in contrast to the bulk conductivity of an electron compensated oxide, which is not expected to change significantly with decreasing oxygen partial pressure. This shows that the surface layer of oxides has significantly different electronic properties than the bulk, which we initially stated from 4-point probe measurements (Section 3.2) and now uphold after resolving the nanoscale surface structure.

4. Conclusions

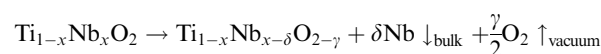
In our study, we presented a thorough picture of the thermo-reduction impact on the physical and chemical properties of the surface layer of Nb-doped rutile $\text{TiO}_2(110)$ in comparison with undoped single crystals. We found out that long annealing under extremely low oxygen partial pressure causes decomposition of doped rutile TiO_2 and formation of new suboxides, such as Magnéli-type phases Ti_8O_{15} and Ti_9O_{17} . Therefore to investigate the impact of Nb doping on the surface of rutile TiO_2 and on surface properties we limited ourselves to initial stages of reduction. Macroscopic four-point electrical measurements indicate that the surface layer itself cannot be treated as an ideal $\text{TiO}_2\text{:Nb}$ crystal but can be oxidized and reduced more easily than expected. On doped $\text{TiO}_2(110)$ the mean surface conductivity rapidly increases and oxygen is released from the crystal leading to the creation of oxygen vacancies upon annealing under reducing conditions. However, n-type doping of Nb atoms induces structural transitions of the surface, which are absent in

the case of undoped TiO_2 crystals. In particular, we have observed a transition in surface reconstruction after 850 °C reduction, connected with the evolution of a new row-like (4×2) surface reconstruction as provided by STM and LEED measurements. Additionally, at the same (1×1)-to-(4×2) transition the effective surface work function measured by means of KPFM has a maximum.

Additionally, high resolution current maps reveal the same pattern, indicating the spatial arrangement of d-electrons in row-like structures. By comparing current maps with STM topography, we could assign features with higher conductivity to higher electron state density. In the presented model of the (4×2) reconstructed surface of $\text{TiO}_{2-x}\text{:Nb}(110)$ we correlate lower empty states density spots with oxygen positions, which is additionally supported by the modulation (decreasing) of the current measured over these sites. Assisted by DFT calculations we conclude that bright STM spots in-between are correlated with Nb atoms substituting Ti in the first atomic layer while repelled Ti atoms prefer to form interstitials.

Together with the surface reconstruction, the measured local conductivity undergoes an evolution from weak and spot-like at lower temperatures to a quasi-homogeneous state after reduction at the transition temperature of 850 °C. We correlated the observed nanoscale conductivity with the bulk, where one should expect increased conductivity due to the Nb donor doping, which is to be constant in the wide range of oxygen partial pressure under reducing conditions. However, we found that the as-received surface layer was insulating but then, upon thermal reduction, an exponential increase of conductivity was observed. Simultaneously with this, we observed exponential, thermally activated mass loss by TGA, showing that reduction of the crystal is of great relevance.

By SIMS depth profiling we proved that upon reduction an out-of-plane diffusion of the Nb dopant from the surface towards the bulk occurred in agreement with previous literature reports. We have also observed a certain increase of relative Nb concentration at the very surface which is attributed to the formation of a new (4×2) reconstruction. This shows that during reduction a complex surface transformation takes place involving oxygen loss and Nb diffusion which can be expressed as follows:



In summary, we have presented a way of tuning the electronic and structural properties of n-type doped TiO_2 substrates which are of great relevance for nanotechnology. Since the properties of nanoscale systems are significantly influenced by the surface quality, control of the surface allows one to tailor the interface properties of various devices like catalytic or memristive systems. The new homogeneously conducting (4×2) reconstruction on reduced Nb-doped $\text{TiO}_2(110)$ may also serve as a perfect template for growth of molecular films in organic electronics.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

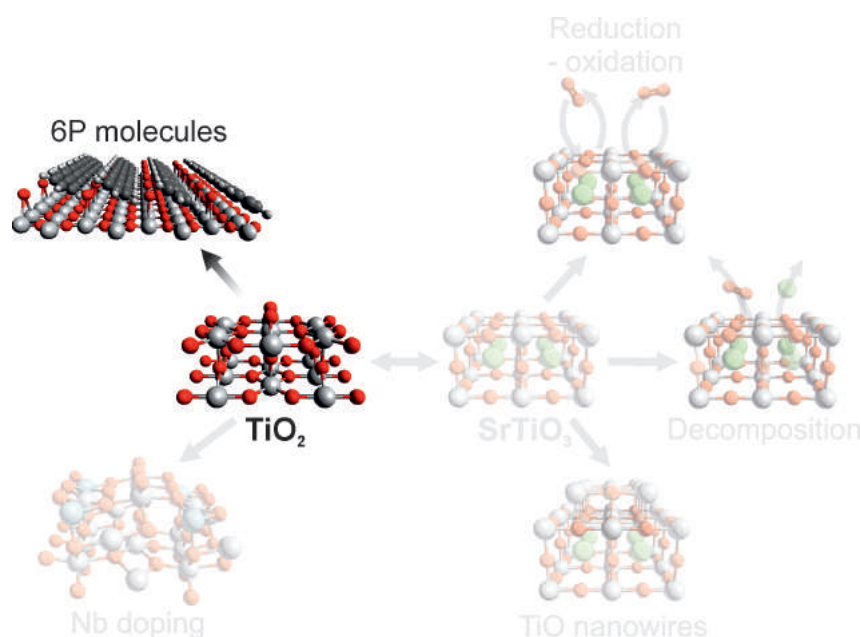
The support by the Polish National Science Center (DEC-2015/19/B/ST5/01841) and the Deutsche Forschungsgemeinschaft (SFB 917 “Nanoswitches”) is acknowledged. Part of the research was carried out with the equipment purchased with financial support from the European Regional Development Fund in the framework of the Polish Innovation Economy Operational Program (Contract No. POIG.02.01.00-12-023/08). D.W. acknowledges additionally the support of the Polish National Science Center under the grant 2016/21/N/ST5/01313. We thank J. Friedrich, M. Kulpa, and V. Nischwitz for technical assistance and contribution of measurements. We would also like to acknowledge J. Kubacki and J. Szade for their support and P. Meuffels for fruitful discussions. In addition we would like to express our gratitude to P. Dabczynski for his support in the SIMS analysis.

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3.6 Growth of para-Hexaphenyl Thin Films on Flat, Atomically Clean versus Air-Passivated TiO₂(110) Surfaces



The last paper of this dissertation is dedicated to investigate the influence of an oxide surface properties (e.g. non-stoichiometry) on the formed molecular thin film morphology [TiO₂_6P]. The model system of a *para*-hexaphenyl (6P) molecule and TiO₂ oxide proved to be very sensitive to the initial conditions during deposition. Two molecular orientations of 6P are observed: lying (on a flat atomic surface) and standing (on a passivated or sputtered substrate). In this study, the formation mechanisms of all molecular features such as nanowires, crystallites and dendritic islands are explained in a detailed manner. Importantly, it is also proved possible to have a control over the density of molecular islands via tuning surface non-stoichiometry via the sputtering-annealing process.

Highlights

1. Different molecular structures of para-hexaphenyl (6P) molecules on three classes of TiO₂(110) surfaces: atomically flat, passivated and sputtered,
2. 6P molecule orientation and film morphology can be controlled from lying (nanowires) to standing (islands) through redox processes,
3. During *in situ* deposition a wetting layer is formed, which dewets due to air exposure and nano-crystallites are formed,
4. Lying-to-standing orientation transition is triggered by the slight changes in the surface roughness due to sputtering.

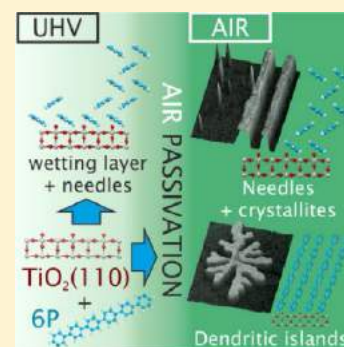
Growth of *para*-Hexaphenyl Thin Films on Flat, Atomically Clean versus Air-Passivated TiO₂(110) Surfaces

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ABSTRACT: We report on *para*-hexaphenyl (6P) ultrathin film growth on freshly prepared and air-passivated atomically flat rutile titanium dioxide single-crystal (110) surfaces. The surface morphology of the developed structures has been investigated in situ and ex situ by means of various scanning probe techniques and electron microscopy. In situ 6P deposition results in the formation of a wetting layer of lying molecules coexisting with bunches of tens of micrometers long needles oriented along the TiO₂[110] surface direction. The observed bunching of the 3–5 nm high needles is explained in terms of anisotropic diffusion paths along and perpendicular to the needles. Air exposure of the as-prepared films induces the formation of small features at the cost of the 6P wetting layer, whereas the needles stay unchanged. In contrast, 6P deposition on already air-passivated TiO₂(110) yields the formation of dendritic islands, composed of roughly upright-standing molecules. No 6P wetting layer forms on the air-passivated surface. In addition to air exposure, we have checked the impact of surface modification via ion beam bombardment. Growth of 6P on gradient ion-beam-modified titanium dioxide substrates kept at either room or elevated temperature reveals that a slight surface roughening is sufficient to switch the film from lying molecular orientation to upright-standing orientation. However, surface stoichiometry severely influences film properties like size, density, and shape of the 6P islands.



1. INTRODUCTION

A crucial issue in fabricating electronic devices is to control organic thin film growth and resulting morphology on semiconducting, insulating, or metallic substrates in order to optimize film structure and interface properties with respect to the device performance.¹ The application of such films for organic devices in terms of performance and durability has been intensively studied in the past. Within these studies, a main focus was device degradation because of operation under ambient conditions.^{2–5} Morphological optimization has been shown to be a viable way for improving device performance and stability.^{3,4} As pointed out by Kumar,³ there are at least three parameters available for tuning film properties: growth temperature, deposition rate, and substrate–molecule interaction. However, studies on (vapor-deposited) organic thin film growth are mostly focused on the effect of substrate temperature and deposition rate for given molecule–substrate combinations.^{6–18} Manipulating the molecule–substrate interaction has also been investigated in some detail. For example, ion-bombardment-induced surface roughening or rippling has been demonstrated to severely influence organic thin film morphology.^{19–21} Also, oxygen plasma treatment and surface functionalization,²² interface layers,²³ or photochemical modifications²⁴ can be effective. However, for some systems the molecule–substrate interaction can be noticeably changed by less aggressive methods. Two of them, most relevant for application, are ion-beam-induced modification of a substrate and especially air passivation, which cannot be avoided in real-world systems.

In this study, we systematically explore the influence of the ambient atmosphere on organic thin film morphology because of volitional air exposure of TiO₂(110) substrates pre- and postdeposition. Further, ion-beam-treated substrates with more stoichiometric and nonstoichiometric surface composition were prepared in order to differentiate between chemical and roughness induced morphological changes in the organic thin films.

As a model system, we chose *para*-hexaphenyl (6P) which is an important representative of the class of small, conjugated, semiconducting organic molecules such as other oligophenyls or pentacene. The high thermal²⁵ and chemical stability²⁶ of 6P guarantees that morphological changes are mediated by molecule–substrate interaction and not by chemical degradation of the molecule itself. 6P (C₃₆H₂₆) is a linear conjugated molecule consisting of six phenyl rings connected with single bonds through para carbon atoms. Because of the single bonds of the molecule, it possess a certain flexibility while in the gas phase.²⁷ In the crystal bulk, a planar flat configuration is adopted. Still, there can be a certain twist angle between neighboring rings,²⁸ although a molecule in the bulk, averaged over time and space, can be treated as planar. The wide band gap of 3.1 eV between highest occupied molecular orbital and lowest unoccupied molecular orbital^{29,30} makes *para*-hexaphenyl an

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interesting candidate for light-emitting devices.³¹ Often, rodlike molecules, 6P in particular, form a so-called herringbone structure in the bulk (equilibrium beta structure)³² where adjacent molecules are rotated alternately to left and right around their long molecular axis. The resulting crystal unit cell is monoclinic and belongs to the $P2_{1/a}$ space group.

So far, 6P has been tested as active material in organic thin film transistors (OTFT)³³ and organic light-emitting diodes (OLED).^{30,34–36} Its high photoluminescence quantum yield in the blue spectrum makes it attractive for various optoelectronic applications.^{27,37} Moreover, concepts using 6P nanoneedles as lasing nanofibers³⁸ or wave guides^{39,40} have been envisaged.

Depending on the substrate, 6P exhibits two different growth morphologies that determine device design. For anisotropic crystalline substrates such as Cu(110)⁷ or TiO₂(110)(1 × 1),¹³ the molecules are lying flat and form nanoneedles alongside them, which are oriented with respect to the surface anisotropy (i.e., atomic rows). On noncrystalline substrates or on surfaces with high defect density, the 6P molecules exhibit upright-standing island growth.¹⁶ Substrate-dependent growth is a result of a competition between molecule–substrate and molecule–molecule interactions. Within such kinds of organic molecular crystals, the bonding is primarily determined by van der Waals forces. The binding to the substrate is further influenced by the lattice matching, defect concentration, surface chemistry, and roughness.

2. EXPERIMENTAL SECTION

In situ parts of the experiment were carried out in an ultrahigh vacuum (UHV) system consisting of three chambers interconnected by a magnetically coupled linear transfer allowing for sample preparation, analysis, and imaging. The base pressure of the used system was below 2×10^{-10} mbar.

2.1. Substrate Preparation. Rutile TiO₂(110) epi-polished samples (MaTecK Company) were introduced into the UHV system after cleansing in isopropanol in an ultrasound bath and being outgassed overnight. The titanium dioxide crystal was mounted onto a silicon wafer piece to allow direct current heating through the silicon. Alternating sputtering and annealing cycles were applied in order to obtain a clean and atomically flat surface. Ion-beam bombardment was performed by using Ar⁺ projectiles, with an energy of 1 keV. The Ar⁺ beam with a spot size of ~ 1 mm was scanned over the sample. The corresponding ion-beam current (measured on the sample) was in the range of 1 μ A. Samples were heated by means of ac direct heating through the TiO₂/Si sandwich. The use of an alternating current allowed the electroreduction and temperature to be uniform along the sample crystals. (A more detailed analysis of the electroreduction influence on TiO₂ is provided in ref 41.) Annealing was performed up to 1050 K. The resulting surface quality was examined using scanning tunneling microscopy (STM) and atomic force microscopy (AFM). The crystal surface reconstruction was checked by low-energy electron diffraction (LEED).

2.2. *para*-Hexaphenyl Deposition. Submonolayer coverages of 6P were prepared by organic molecular beam epitaxy (OMBE) under UHV conditions at room temperature. Deposition experiments were carried out on two differently prepared TiO₂ surfaces: freshly prepared atomically flat, pristine TiO₂(110)(1 × 1) and identically prepared TiO₂(110)(1 × 1) surfaces that were additionally passivated in ambient air prior to deposition. After an hour of air exposure, samples were introduced back to the UHV chamber and heated up to 380 K

in order to remove the adsorbed water layer, then underwent exactly the same deposition procedure as the pristine substrates.

6P molecules were evaporated (in situ in the UHV system) from a Knudsen effusion cell heated up to 520 K. Prior to deposition, the source was calibrated using a quartz microbalance (QMB). The growth rate was estimated to be about 1 Å per minute (26 Å is the molecular equivalent of one monolayer (1 ML) of 6P molecules in the upright-standing orientation). Throughout the text, *para*-hexaphenyl coverages will be mostly specified with respect to the upright-standing 6P monolayers (molecule density in the 6P(001) plane = 4.4×10^{14} molecules/cm²).¹⁵

We also observe and discuss lying 6P configuration in a herringbone structure, with a lower molecular packing. The bulk 6P(203) unit cell mentioned in⁷ corresponds to a density of $\sim 6.6 \times 10^{13}$ molecules/cm². Also according to ref 7, a 30 nm film thickness corresponds to roughly 80 layers, which would give ~ 0.375 nm for the single layer. This is close to the densely packed flat-lying 6P layer described in ref 42. The explicit value stated there is 5.8×10^{13} molecules/cm².

Within this article, we will refer either to an upright-standing 6P(001) monolayer with a density of 4.4×10^{14} molecules/cm², denoted as ML (monolayer) or to a flat-lying 6P(203) monolayer with the assumed density of 6.6×10^{13} molecules/cm², denoted as LML (lying monolayer).

2.3. Characterization. The 6P thin films grown on TiO₂(110) were initially characterized in UHV directly after deposition and subsequently under ambient conditions. Just after deposition, samples were examined in situ by noncontact AFM (NC-AFM) using a Park Scientific Instruments VP2 device and then under ambient conditions ex situ by tapping-mode AFM (TM-AFM), using either an Agilent 5500 or an Asylum Research MFP-3D system. Additionally, scanning electron microscopy (SEM) imaging for examining larger areas was performed using an SEM FEI Quanta 3D FEG.

2.4. Ion-Beam-Induced Surface Nanomodification. Atomically flat TiO₂(110) has been irradiated with a Xe⁺ ion beam under normal incidence. A low flux of 1×10^{12} ions/cm² has been adjusted to ensure a linear sputtering regime. The substrate could be shadowed from the ion beam by the moveable transfer rod of the UHV system thus enabling a linear variation of the total ion fluence across the sample long axis ranging from zero to a few 10^{15} ions per square centimeter. This resulted in a substrate with a linear increase of the surface roughness from one side to the other. However, the ion bombardment also induces stoichiometric changes because of preferential oxygen sputtering, creating an oxygen-depleted titanium-rich surface layer.

The chemical balance of the TiO₂(110) surface was kept stoichiometric by holding the substrate at 740 K during ion irradiation. At this temperature, the excess Ti atoms diffuse into the bulk, recovering surface stoichiometry.⁴³

3. RESULTS AND DISCUSSION

3.1. Atomically Flat TiO₂(110) Surface. An STM topography image of clean, atomically flat TiO₂(110)(1 × 1) is presented in Figure 1. The surface is composed of wide terraces, over 100 nm in width, separated by monatomic steps with a height of about 3.2 Å. Step edges run along main crystallographic directions [001], [111], and [1 $\bar{1}$ 1]. High-resolution STM images (e.g., Figure 1b) reveal that the surface is anisotropic with atomic rows along the [001] direction. For Figure 1b, empty electronic states have been measured. Thus, the bright stripes correspond to fivefold-coordinated titanium surface atoms and dark ones to the

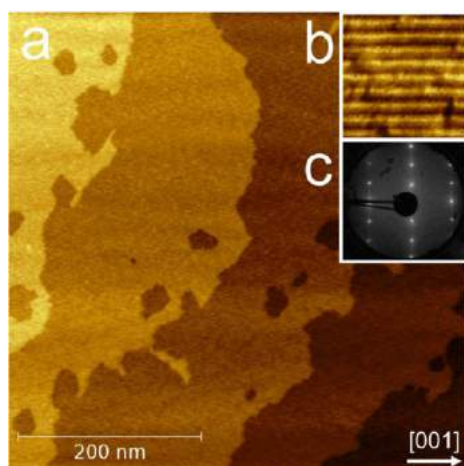


Figure 1. (a) Room-temperature UHV STM ($500 \times 500 \text{ nm}^2$) image of $\text{TiO}_2(110)(1 \times 1)$ (empty states). Atomically flat terraces of 100–200 nm width are visible. (b) Oxygen rows parallel to the $[001]$ direction ($5 \times 5 \text{ nm}^2$). (c) Corresponding sharp LEED pattern revealing the (1×1) surface reconstruction.

oxygen atoms in the bridge positions.^{44,45} The separation between the rows is 0.65 nm. The long-range anisotropy of the TiO_2 surface is also visible in the corresponding LEED pattern (Figure 1c). The sharp clear spots from the titanium dioxide (110) (1×1) reconstruction are clearly observable. Thus, the $\text{TiO}_2(110)(1 \times 1)$ surface provides an atomically anisotropic template for molecular growth.

3.1.1. In Situ Observations. To investigate the initial stages of the molecular growth, we focus on submonolayer thin films. We performed molecular deposition of 0.25 ML (1.7 LML) and 0.5 ML (3.4 LML) coverages on atomically flat $\text{TiO}_2(110)$ surfaces. The initial characterization of the thin film morphology was performed in situ, just after deposition.

In Figure 2a, an UHV NC-AFM topography image of the film structure developing after deposition of 0.25 ML 6P is shown. The surface is covered with μm long needles with their long axes perpendicular to the $[001]$ crystallographic direction of the titanium dioxide substrate. The height varies typically from 3 to 5 nm (Figure 2c). This is a consequence of the nonuniform height of these nanoneedles, which is presented in Figure 2d. Some of the needles exhibit a modular structure as was already observed previously.⁴⁶ The nanoneedles have abrupt terminations and a smooth surface structure in the vicinity of their endings (Figure 2e). The typical width of the needles varies from 100 to 200 nm.

Interestingly, the nanoneedles do not cover the substrate uniformly but they form by trend bundles separated by a few micrometers, whereas the typical TiO_2 terrace width is an order of magnitude less. Within one bunch, there are several parallel-aligned nanoneedles separated by 100–150 nm. The needle bunching is easily visible in Figure 2b, showing the film morphology after deposition of 0.5 ML, twice as much as has been deposited in Figure 2a. Apparently, the higher amount of 6P just increases the density of the nanoneedles. The length, width, and height of the nanoneedles as well as the spacing within the bunches are left unchanged.

Previous studies of the 6P growth on flat $\text{TiO}_2(110)$ revealed that the nanoneedles are composed of flat-lying *para*-hexaphenyl molecules with their long axes aligned parallel to the oxygen rows ($[001]$ direction) of the titanium dioxide substrate (Figure 3).^{13,46} Within the needle bulk, the molecules arrange in the so-

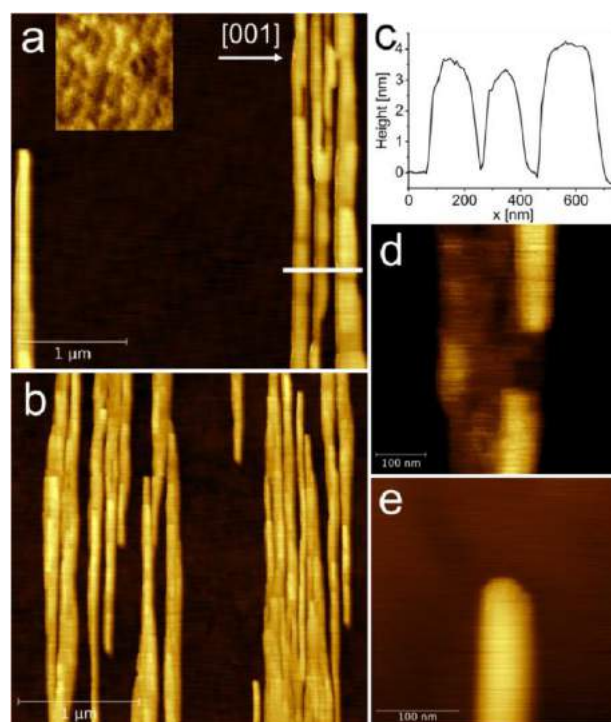


Figure 2. UHV NC-AFM images of *para*-hexaphenyl nanoneedles grown on an atomically flat $\text{TiO}_2(110)(1 \times 1)$ surface: (a) Coverage of 0.67 nm (0.25 ML of standing molecules monolayer equivalent); inset shows the actual terrace structure of a TiO_2 substrate. (b) Coverage of 1.23 nm (0.5 ML). (c) Line height profile across nanoneedles shown in a. (d) Details of the top of one of the nanoneedles (z scale adjusted). (e) Details of a single nanoneedle's ending.

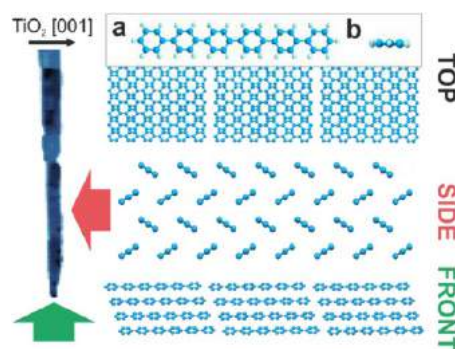


Figure 3. *Para*-hexaphenyl lying herringbone structure exemplified on a single nanoneedle grown on atomically flat $\text{TiO}_2(110)$. Top, front, and side magnified views on a crystalline molecular wire are presented. Insets: (a) View of a single 6P molecule's long axis, perpendicular to phenyl rings. (b) View of a single 6P molecule's short axis.

called herringbone structure.⁴⁷ X-ray diffraction studies revealed that on the $\text{TiO}_2(110)$ surface, the 6P $(20\bar{3})$ contact plane is adopted.⁴⁶

3.1.2. Ex Situ Measurements. After in situ NC-AFM imaging in UHV, the samples were exposed to ambient air, and the morphology was again imaged by means of TM-AFM (Figure 4). Interestingly, a number of new small features emerges in addition to the nanoneedles (compare with Figure 2a). For now, we will refer to these additional structures as crystallites, without actually knowing their internal structure. (Some studies suggest that they

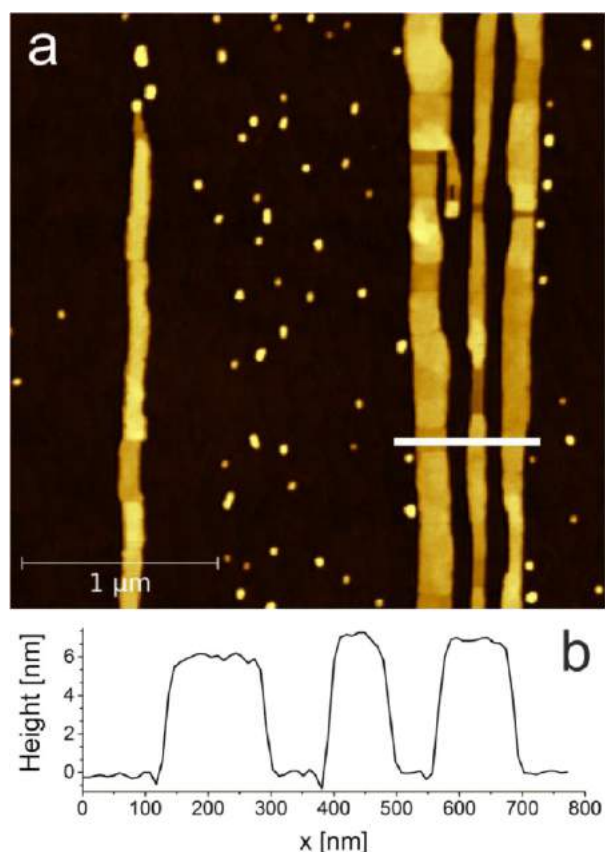


Figure 4. (a) Ambient conditions TM-AFM image ($3 \times 3 \mu\text{m}^2$) of the morphology of 0.25 ML 6P on $\text{TiO}_2(110)$ after air exposure; both nanoneedles and crystallites are visible. (b) Height profile along the white line indicated in a.

are mainly composed of lying molecules.)⁴² Their mean lateral size is approximately 50–100 nm, and they are between 5 and 10 nm high, which is about twice the height of the nanoneedles. In addition to the appearance of the crystallites, the nanoneedles imaged under ambient conditions also seem to have increased in height because of air exposure (Figure 4). The rise is in the order of 1–2 nm compared to the UHV measurements, whereas other

quantities such as length, width, and spacing between the needles are left unaltered.

Large-scale TM-AFM images of the morphology of 0.25 ML (1.7 LML) 6P/ TiO_2 after air exposure are presented in Figure 5. Areas closely adjacent to the nanoneedles are essentially crystallite-free, whereas at greater distances from the nanoneedles, the crystallite density is high. In Figure 5a, (for 0.25 ML 6P coverage) the white arrows indicate some areas between the nanoneedles that seem too narrow for crystallites to emerge. This is a generic behavior for low 6P coverages as the same observation is made for 0.5 ML coverage (Figure 5b).

Figure 6 reveals details of the actual surface morphology of the air exposed nanoneedles. They appear to have a terraced

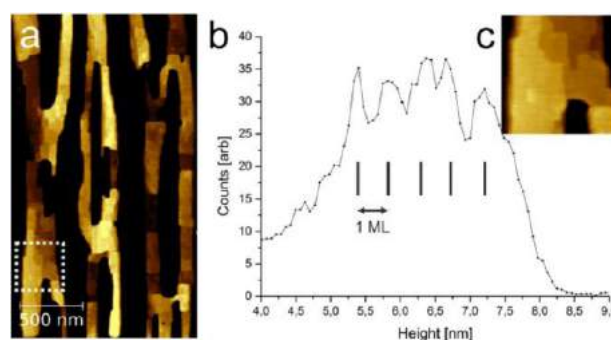


Figure 6. Ambient condition TM-AFM image of 0.25 ML coverage of 6P on $\text{TiO}_2(110)$: (a) View on the top of the nanoneedles. (b) Height histogram of nanoneedles from a) reveals a discretization by about 0.4 nm. (c) Monolayer terraces of the lying molecules imaged on top of the nanoneedles (zoom of the area marked by the dotted square in a).

structure with step heights of ~ 0.4 nm (as determined from the height histogram in Figure 6b), which is close to the height of a single bulk $(20\bar{3})$ layer (as for $\text{Cu}(110)2 \times 1\text{-O}^7$). There, the tilt angle of 6P's short axis with respect to $(20\bar{3})$ is in the range of $30\text{--}40^\circ$ corresponding to a single layer height of ~ 0.35 nm). Therefore, we assume that the single terraces consist of single layers of 6P molecules with their long axes oriented roughly parallel to the substrate and their short axes tilted by $30\text{--}40^\circ$. In Figure 6c, several monomolecular terraces on top of a nanoneedle are visible.

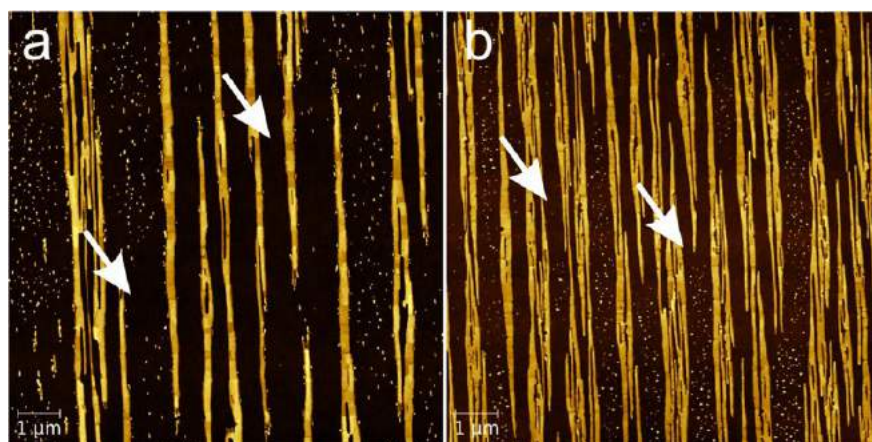


Figure 5. Ambient condition TM-AFM images: (a) ($10 \times 10 \mu\text{m}^2$) Coverage of 0.25 ML of 6P on $\text{TiO}_2(110)$. (b) ($10 \times 10 \mu\text{m}^2$) Coverage of 0.5 ML of 6P on $\text{TiO}_2(110)$. White arrows indicate the crystallite-free depletion zones.

The question immediately arising is whether the crystallites originate from nanoneedle degradation. Occasionally, as shown in Figure 4, some crystallites appear just at the endings of nanoneedles. In the case that the crystallite formation is due to air induced needle degradation, the process might proceed with residence time in air. To reveal the temporal evolution of the air exposed film, the 6P thin film morphologies after 10 min in air and after 10 h in air have been measured (Figure 7). Some sites

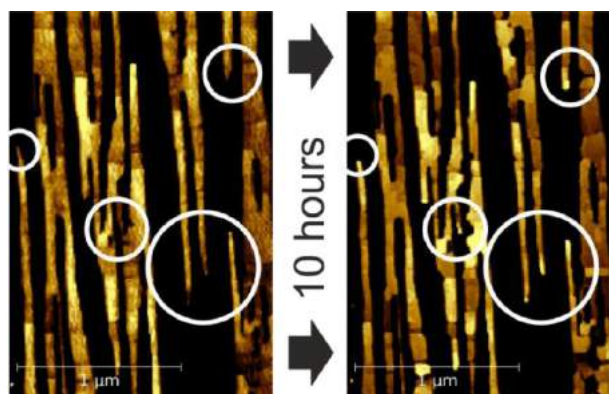


Figure 7. Ambient condition TM-AFM images (0.5 ML of 6P on $\text{TiO}_2(110)$) of the same area just after air exposure (left) and after 10 h (right). White circles mark some changes in the morphology of the needles.

are slightly altered with time (a few of them marked by white circles in Figure 7), whereas the number of nanoneedles stayed unchanged. A degradation initiating on topographical active sites such as kinks and nanoneedle endings is observable. Kinks in general deepen because molecules move and accumulate at the nanoneedles' endings. In general, the changes are minor, indicating that the material migration is extremely slow and does not provide enough molecular volume to contribute to crystallite formation. On top of that, the crystallites are already present after <10 min of air exposure, making needle decomposition as their origin unlikely.

Thus, a different mechanism is responsible for crystallite formation. Recently, Tumbek et al.⁴² have shown the formation of bimodal 6P islands on mica surfaces. It is well-known that during 6P vapor deposition on freshly cleaved mica nanoneedles form together with a wetting layer of lying molecules which covers the complete substrate surface. The authors suggest that this wetting layer dewets because of air contact when the vacuum chamber is vented which results in the formation of the small clusters.

We think that the same mechanism is active in the 6P/ $\text{TiO}_2(110)$ system. The observed crystallite formation is just a consequence of air-induced dewetting of a complete layer of lying 6P molecules present between the nanoneedles (Figure 8). During deposition, rodlike 6P molecules arrive randomly on the substrate and preferentially diffuse aligned with and along the atomic rows of the titanium dioxide surface (1D diffusion), leading to the formation of a complete wetting layer. A similar behavior has been suggested for 6P growth on the anisotropic $\text{Cu}(110)(2 \times 1)\text{-O}$ surface²¹ (oxygen row spacing is about 0.51 nm). On the atomically flat metal oxide, 6P forms a wetting layer of molecules with their long axes aligned parallel to the surface (one full layer of lying molecules, namely 1 LML). Additionally, the molecules are tilted sideways, lying edge-on on the substrate. The $\text{TiO}_2(110)(1 \times 1)$ surface is also anisotropic because of oxygen rows running in [001] direction with a spacing of 0.65 nm. The distance between molecules within the (203) 6P bulk plane is estimated to be 0.56 nm.⁷ The resulting lattice misfit leads to an accumulation of strain energy in the second layer (SL) of molecules. SL growth continues until it is almost filled (1.95 LML altogether for $\text{Cu}(110)(2 \times 1)\text{-O}$).⁴⁸ For TiO_2 , this situation might occur at a little bit lower coverage because of slightly higher lattice misfit. When a critical molecule density in the SL is reached, it triggers the nucleation of 3D bulklike nanoneedle germs.

Finally, in the present case, the deposition process on a flat $\text{TiO}_2(110)$ surface results in a surface partially covered with nanoneedles and one filled compact LML in the needle-free areas. Air (most presumably water) interaction causes lowering of the diffusion barrier. Molecules that are released from the

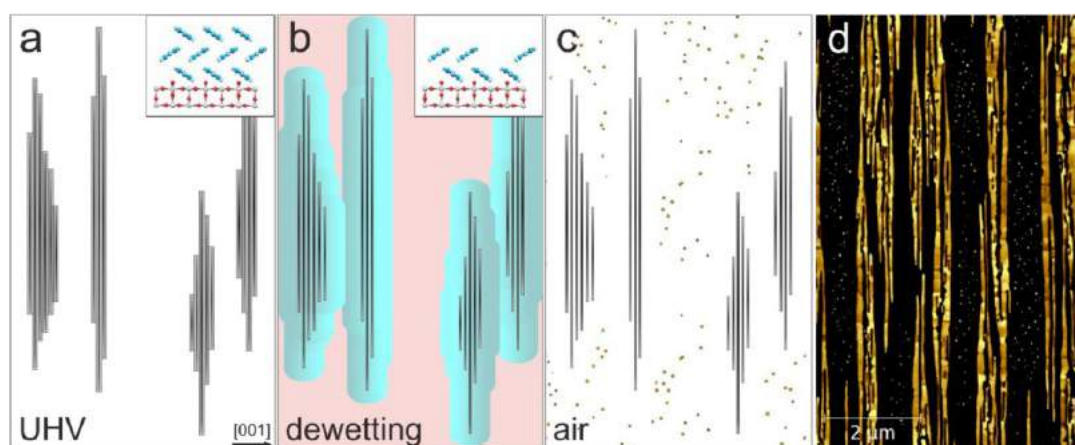


Figure 8. Wetting and dewetting concept: (a) Scheme of the film morphology just after deposition; NC-AFM measurements show the nanoneedle structure only (but the entire surface is covered by a wetting layer of lying molecules). Inset: side view of a lying herringbone structure (as in nanoneedles) on titanium dioxide(110)(1 $\times$ 1). (b) During air exposure: depletion zones around nanoneedles form (blue); pink areas provide material for crystallites to arise. Inset: wetting layer at its maximum thickness. (c) Scheme of the morphology as found by ex situ TM-AFM; crystallites emerge except for the depletion zone around nanoneedles. (d) Corresponding TM-AFM image of nanoneedles and crystallite structures; depleted areas of a certain width around the needles are visible.

wetting layer (WL) start to diffuse across the surface and nucleate at some active points, such as surface defects like step edges (heteronucleation), forming crystallites.

The broad height distribution of the small features suggests that the incorporation of molecules into the crystallites is too fast to allow an entire arrangement in either upright or flat-lying configuration. Otherwise, certain heights equal to those of the needles or any integer multiple of the 6P long axis length would be expected.

The assumption of a dewetting process as the origin of the small 6P crystallites on titanium dioxide is supported by the data in Table 1. There, an AFM-based quantitative estimation of the

Table 1. Differences in Molecular Coverage before and after Dewetting

sample	difference in coverage (nm)	crystallite height from WL (nm)	crystallite height measured (nm)	needle height from WL (nm)
0.25 ML	0.49(13)	6.26(42)	5.34(25)	1.81(49)
0.5 ML	0.419(17)	3.72(25)	3.91(19)	1.180(50)

amount of material in the WL is provided (statistical errors are presented in parentheses). The second column represents the difference of the measured visible volumes between in situ

(nanoneedles) and ex situ (nanoneedles + crystallites) averaged over the entire surface. Assuming similar molecular densities in the WL and the nanoneedles (there are small differences originating from the misfit between substrate lattice and bulk molecular structure), we obtain that the WL is ~ 0.4 nm thick. This result corresponds well with one monolayer of molecules packed with their long axes aligned parallel to the surface and tilted edge-on by $\sim 40^\circ$. Tilt angle and, subsequently, the molecular surface density are presumably higher than in a bulk crystal.

A semiquantitative cross check of the latter introduced dewetting mechanism can be done on the basis of a few assumptions. First, we assume that the molecular density in the WL, nanocrystals, and the needles is approximately the same. Second, we consider that the individual crystallites have uniform height (neglecting that the top of the crystallites will in general be slightly domed or faceted). We now calculate the average capture area of a crystallite by dividing the area covered by crystallites by the number of contained crystallites. Taking the capture area and dividing it by the average projected area (base area) of a nanocrystal yields the number of contained 6P layers. The resultant average crystal height for an estimated layer thickness of 0.4 nm are provided in Table 1. The resulting heights are in reasonable agreement with the measurements. In the last column, the calculated height increase of the nanoneedles because of the decomposition of the WL in their vicinity is

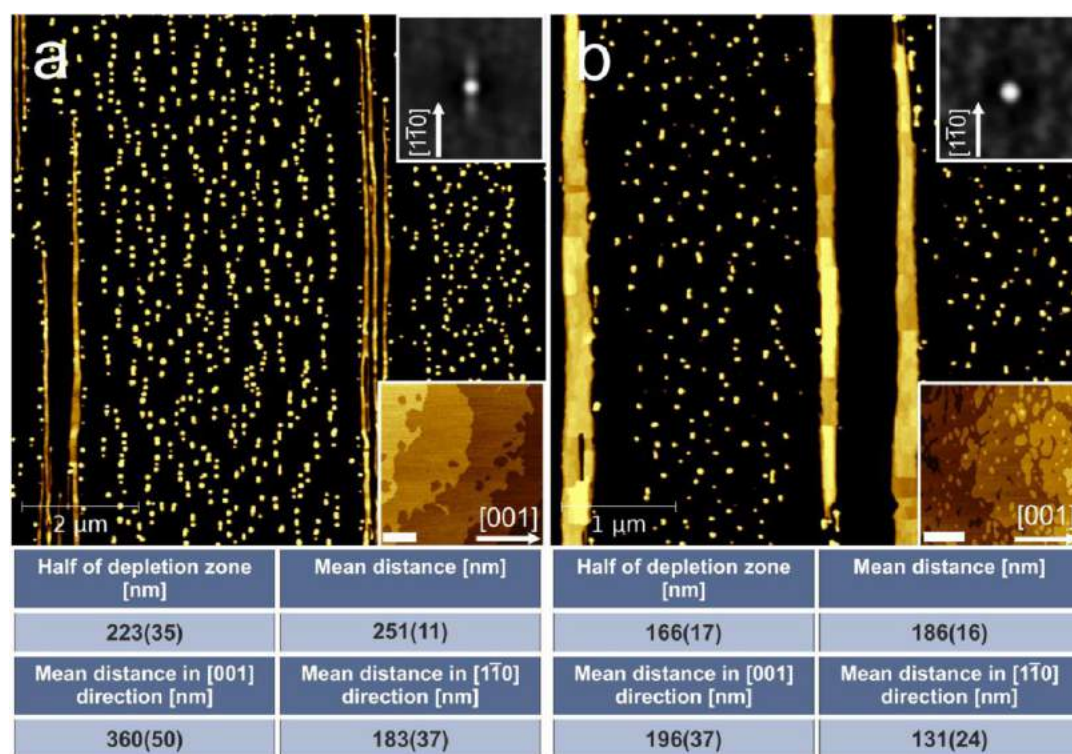


Figure 9. Influence of surface quality on crystallite arrangement for 0.25 ML (1.7 LML) 6P on two differently prepared $\text{TiO}_2(110)$ surfaces. Top row: (a) Ambient condition TM-AFM image ($10 \times 10 \mu\text{m}^2$) of the morphology of a *para*-hexaphenyl film deposited on atomically flat $\text{TiO}_2(110)$ with straight, compact step edges, mostly parallel to $[1\bar{1}0]$ direction. STM image of the $\text{TiO}_2(110)$ surface prior to the deposition presented in the lower right corner (white bars = 100 nm); Inset upper right corner: Corresponding central peak of 2D autocorrelation function from the area of crystallites. (b) Ambient conditions TM-AFM image ($5 \times 5 \mu\text{m}^2$) of the morphology of a *para*-hexaphenyl film deposited on atomically flat $\text{TiO}_2(110)$ with complex terrace structure. STM image of the $\text{TiO}_2(110)$ surface prior to the deposition presented below. Tables provide direct comparison between the half of average width of denuded zones and mean distances between crystallites for each sample. In addition, the mean distances between crystallites in both $[001]$ and $[1\bar{1}0]$ directions are presented.

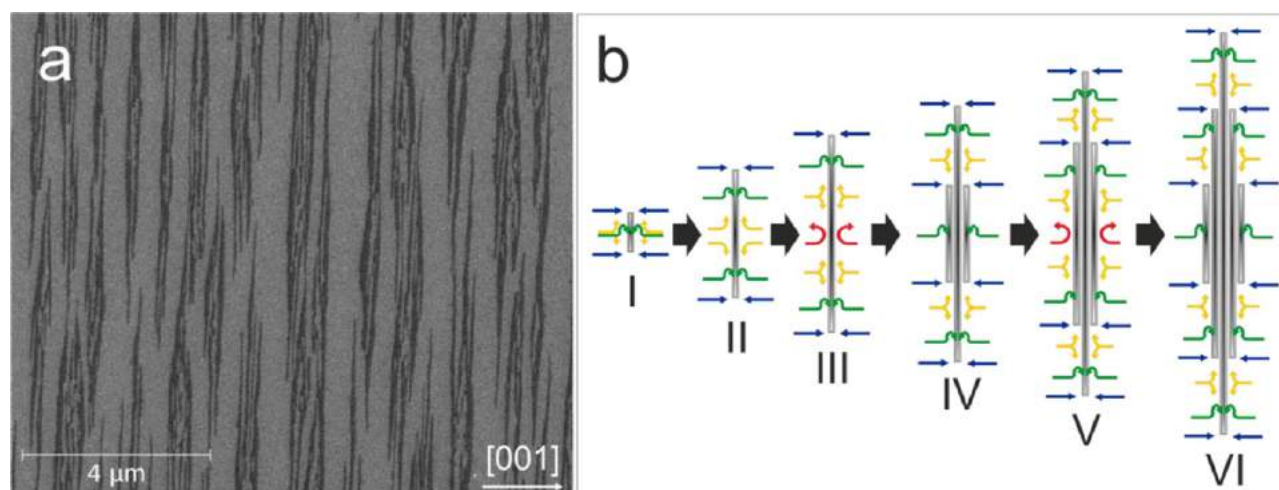


Figure 10. (a) SEM image ($12 \times 10 \mu\text{m}^2$) of *para*-hexaphenyl nanoneedle bundles (0.5 ML (3.4 LML) of 6P) on atomically flat $\text{TiO}_2(110)$. (b) Scheme of the nanoneedle bunching process. Arrows indicate 6P movement: blue, sticking to the end; green, climbing on the top; yellow, diffusion along nanoneedle; and red, being reflected from needle side wall.

presented. It is on the same order as the measured difference between in situ and ex situ approaches.

Dewetting as origin of the crystallite formation is thus further supported by the crystallite-free depletion (denuded) zones around the nanoneedles as shown in Figure 5. The proposed wetting/dewetting concept is illustrated in Figure 8b. The needles act as traps, absorbing the diffusing molecules from the air exposed wetting layer. The additional material unhitched from the wetting layer can explain the height increase of the air exposed needles. The average width of the depletion zone corresponds well to the average crystallite–crystallite distance (measured from 2D autocorrelation function (2DAC)⁴⁹) suggesting that both needle growth after exposure and crystallite formation are caused by the same mechanism.

3.1.3. Crystallite alignment. As already stated above, it is assumed that the crystallites nucleate at active surface sites. In the case of $\text{TiO}_2(110)$, such sites might be oxygen vacancies, OH groups, or Ti^{3+} ions.⁴⁵ Specifically, the monatomic steps separating the $\text{TiO}_2(110)$ terraces represent active sites, where preferential nucleation is expected.⁵⁰ However, the nanoneedles appear to be insensitive to the steps, just overgrowing the step edges undisturbed, irrespective of the step direction. Nevertheless, the small crystallites indeed preferentially nucleate at the step edges, sometimes forming linear arrangements roughly along the $[1\bar{1}0]$ direction. In Figure 9, the surface morphologies of two air-exposed TiO_2 samples with 0.25 ML (1.7 LML) 6P coverage are compared. In Figure 9a, the alignment along $[1\bar{1}0]$ of the crystallites is evident, whereas in Figure 9b, the distribution appears to be random. This is also reflected in the 2DAC of the corresponding images (insets, Figure 9a,b).

On closer inspection, one notices that the $\text{TiO}_2(110)$ substrate in Figure 9a has rather compact and straight step edges running preferentially in $[1\bar{1}0]$ direction, whereas the step edges in Figure 9b are much less compact and irregularly shaped (insets, bottom right of Figure 9a,b). Consequently, the crystallites in Figure 9b exhibit a more isotropic spatial distribution compared to those in Figure 9a. Furthermore, the crystallite density in Figure 9b is higher (note the different scales of Figure 9a,b) than in Figure 9a, and, therefore, also the typical crystallite spacing as well as the depletion zone width around the nanoneedles. (The corresponding average distances are provided in the bottom insets of Figure

9.) This is also a consequence of the more irregular step edges in Figure 9b. There, the specific step length per unit area is significantly higher as compared to that of the substrate in Figure 9a, therefore providing a higher density of active sites available for nucleation.

The apparent occurrence of 6P heteronucleation is a rather surprising result. Considering the high molecular density in the wetting layer and the small size of a critical nucleus of just about 7 molecules,⁴² mainly homonucleation would be expected. Consequently, a high number of very small crystallites randomly distributed (independent of the surface step structure) across the surface should occur. Obviously (Figure 9a), there is certain anisotropy and agglomeration of crystallites in the $[1\bar{1}0]$ direction.

However, one should bear in mind that there are some differences between nucleation during vapor deposition and nucleation because of air-induced dewetting. First, the contact with the ambient atmosphere, which abruptly increases the diffusivity, might also have an influence on the probability of nucleation. The presence of water molecules from the ambient, which are most likely responsible for the reduced diffusion barriers, might also hinder the formation of stable 6P nuclei shifting the system from homonucleation to heteronucleation. Second, there is no material supply from the gas phase constantly recovering the wetting layer. Once dewetting has started, the molecular density on the surface reduces drastically, allowing larger diffusion lengths. Finally, the titanium dioxide surface is highly reactive, with many active sites such as oxygen vacancies, hydroxyl groups, and step edges (Figure 9) that influence the formation of crystallites as has been observed.

3.1.4. Nanoneedle Bunching. One issue left to discuss is the observed bunching of the nanoneedles. The nanoneedles tend to assemble into bundles of several parallel needles separated by a few hundred nanometers, whereas the distance between the bundles can be several micrometers. Branching and truncation sites are visible, but in most cases, the individual needles stay separate. As visible in the SEM image in Figure 10a, the needles in the bundle's center are longest, whereas the exterior needles are usually noticeably shorter. Both the needle bunching as well as the needle length variation from bundle's center to rim can be explained in terms of anisotropic diffusion during nanoneedle

growth. An evolution scheme illustrating the development from a nucleus to a nanoneedle bundle is presented in Figure 10b. At a later stage of deposition, molecules land on the previously formed wetting layer, the structure of which mirrors the atomic scale anisotropy of the titanium dioxide substrate. One possible diffusion path for the molecules is perpendicular to the [001] direction, bringing material to the nanoneedles' endings. Another possibility is a perimetric diffusion lengthwise of the nanoneedle side until it finds a site to stick. When a 6P molecule attaches to a nanoneedle, it can diffuse upward and be incorporated on top. Such incorporation was suggested on the basis of DFT calculations.⁵¹ Most preferentially, the needles grow in height via upward diffusion at the ends as suggested in ref 52. The existence of different Ehrlich–Schwoebel barriers for the molecular movement on different crystal planes makes the nanoneedles grow preferentially perpendicular to the [001] direction of the substrate surface.⁵²

When a nanoneedle forms, molecules stack with their long axes perpendicular to the needles long axis, which means that the long side facets of the needle are mainly composed from 6P(001) planes exposing just the hydrogen-terminated ends of the molecules.⁵³ These hydrogen-terminated planes are only weakly interacting with the π systems of arriving molecules, making it unfavorable for the molecules to stick there. Therefore, a significant fraction of the impinging molecules is reflected at the needle side wall. This backflow of molecules from the needle side wall together with the continuous flux of molecules from the surrounding surface toward the needle causes a local increase in molecular density in the vicinity of the needle's side. The higher molecular density makes the nucleation of a new needle very likely. Once formed, the new needle continues growing as the primary nanoneedle does. However, the situation has changed because the needles now compete for the molecules. Molecules landing between the needles are adsorbed in equal shares by both. However, molecules coming left of the needle pair are adsorbed/reflected by the left needle, preventing the molecules from reaching the right needle and vice versa. Because the primary needle had a head start in growth, it will always be longer than the offspring. Now, it is easy to anticipate that the latter described process will create further needles that will always be shorter than the preceding ones, finally forming the generic structure of observed needle bunches as illustrated in Figure 10b.

3.2. 6P on Air-Passivated Crystalline Flat TiO₂(110). To examine the influence of air on the wetting layer formation, the clean, atomically flat TiO₂ substrates were exposed to ambient air prior to deposition. After 1 h in air, they were introduced back into UHV and heated up to 390 K to remove residual water contaminations. The resulting film morphology after deposition of submonolayer amounts of 6P (0.1 ML that is 0.67 LML) have been imaged in situ using NC-AFM and ex situ using TM-AFM and SEM (Figure 11).

Now, the film is composed of dendritic islands with lateral sizes between 500 and 1000 nm and uniform heights of about 2.8 nm. Similar 6P structures have been reported for amorphous substrates such as ion-bombarded mica^{15,42} or SiO₂^{16,54} and have been identified to be islands composed of roughly upright-standing molecules. This is quite surprising because crystalline substrates usually promote 6P needle formation with horizontal molecular orientation as for KCl,⁵⁵ freshly cleaved mica,⁵⁶ Ir(111),⁵⁷ and graphene.⁵⁸

Interestingly, the 6P morphology stays unaltered when exposed to air. A comparison of the in situ NC-AFM with ex situ TM-AFM and SEM measurements reveals neither changes

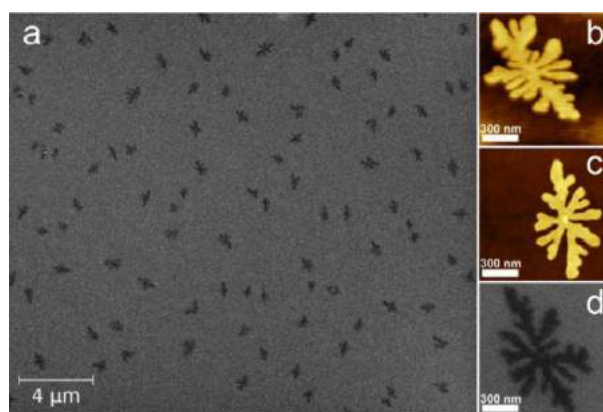


Figure 11. (a) SEM image ($25 \times 21.5 \mu\text{m}^2$) of dendritic islands (composed of upright-standing 6P) grown on air-passivated TiO₂(110). (b) NC-AFM image ($1 \times 1 \mu\text{m}^2$) of a single island in UHV. (c) TM-AFM image ($1 \times 1 \mu\text{m}^2$) of a single island under ambient conditions. (d) High-resolution SEM image ($1 \times 1 \mu\text{m}^2$) of a single island.

in the island shapes (Figure 11b,c) nor the formation of additional crystallites. The latter findings indicate that on air-passivated TiO₂(110) no wetting layer is formed. A comparison of the morphologies of the nonpassivated (needles) and passivated (islands) substrates also suggests that the formation of a wetting layer in the initial growth stage is necessary for the formation of needles.

Dendritic island shapes are often the result of diffusion-limited aggregation (DLA).⁵⁹ DLA growth requires a high diffusivity of the molecules across the substrate surface and a low diffusivity of the molecules along the island edges. Ideally, the growth proceeds in a hit and stick fashion. The low island density of just 0.27 islands per square micrometer, as revealed by the large scale SEM image in Figure 11a, suggests a high surface diffusivity with a mean diffusion length of about $1.9 \mu\text{m}$. However, for a quantitative proof of DLA, the fractal dimension d_f of the island shapes has to be evaluated. The theoretical value of d_f for pure 2D DLA growth is 1.71.⁵⁹

We evaluated d_f of the 6P islands by means of an advanced cube-counting method.⁶⁰ The mean value is $d_f \approx 1.29$, which is clearly too small for pure DLA. The value is much closer to the theoretical d_f of L systems ($d_f = 1.26$) as used to describe the growth shape of trees.⁶¹ Even DLA models considering the movement restrictions that are caused by the substrate lattice result in just slightly different dimensions. However, DLA models allowing sticking probabilities to be lower than 1 (which is the most reasonable assumption in this case) can result in smaller fractal dimensions.⁶² Therefore, we conclude that the island growth involves either significant edge diffusion and/or a certain detachment/reflection rate of the molecules. This is consistent with the observation of Tumbek et al.⁶³ who found attachment limitations to crucially influence 6P nucleation on moderately sputtered mica(001) surfaces. They argued that the attachment probability depends on the relative orientation of the approaching molecules with respect to the molecules at the island rim, causing an integral sticking probability smaller than unity.

Apparently, the air passivation significantly altered the TiO₂(110) surface with respect to the 6P growth. A more detailed look at the substrate and 6P islands is presented in Figure 12. It reveals a substrate essentially unchanged by air exposure or 6P deposition. The spots in the LEED pattern in

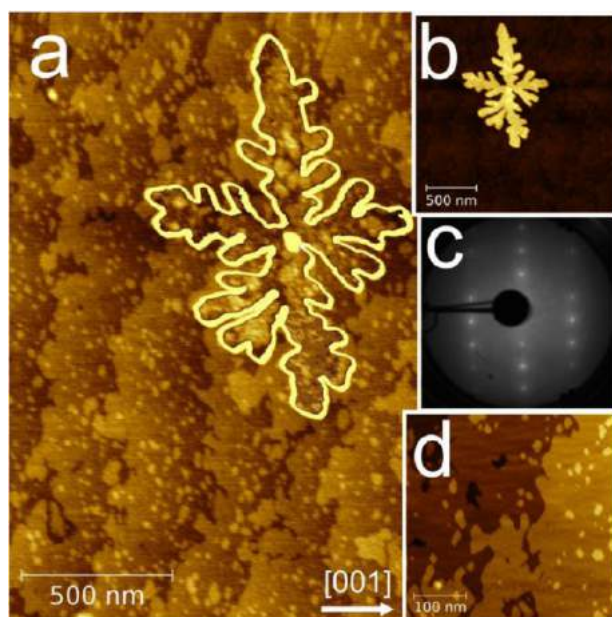


Figure 12. (a) TM-AFM image ($2 \times 2 \mu\text{m}^2$) of a single 6P island grown on air-passivated $\text{TiO}_2(110)$. Z scale is adjusted separately for the substrate and the island surface (island height $\approx 2.8 \text{ nm}$) in order to visualize the substrate step structure under the island. The island contour is visible as bright line. (b) Same TM-AFM image with linear z scale showing the complete island for comparison. (c) LEED pattern of an air-passivated surface. (d) STM image ($400 \times 400 \text{ nm}^2$) of the atomically flat titanium dioxide surface.

Figure 12b are slightly weaker and a little blurred compared to those of the fresh unexposed substrate but still clearly confirm the (1×1) $\text{TiO}_2(110)$ periodicity. Also, an STM image at higher resolution (inset Figure 12d) supports the claim that the local terrace structure is preserved. On a closer inspection, the terrace structure underneath the 6P islands can also be seen. In the TM-AFM image in Figure 12a, the height scales for the substrate and the island have been adjusted separately to illustrate that the substrate step edges run unaltered under the island. Indeed, this result is expected because the upright-standing molecules just interact weakly with the substrate via van der Waals interactions, which makes substrate modification unlikely. For the upright molecular orientation, the molecule–molecule interaction is significantly stronger than the substrate–molecule interaction. However, there is still sufficient influence of the substrate to cause a slight elongation of the island along the step edges as observed for many islands.

3.3. 6P Growth on Ion-Beam-Irradiated Surfaces. We have just established that air passivation of the rutile $\text{TiO}_2(110)$

surface strongly affects the subsequent growth of the rodlike 6P molecules. During exposure, air molecules presumably adsorb preferentially on active surface sites such as oxygen vacancies and step edges. The influence of step edges has been profoundly investigated for 6P growth on ion-beam-rippled TiO_2 surfaces.⁶⁴ There, the increased step density on the rippled titanium dioxide promotes 6P molecules to arrange into upright-standing islands. Furthermore, across the step edges the molecule–molecule interaction is reduced because of a relative shift of the molecules by the step height. This weaker binding across the steps causes detachment anisotropy during growth and in turn results in noticeable elongation of the island parallel to the step edges.^{64,65}

For the atomically flat titanium dioxide surfaces, air exposure passivates (saturates) active sites. On the one hand, this influences the local topography, and on the other hand, it also changes the local chemistry. Both substrate topography and chemistry may affect the 6P growth. To disentangle both effects, we have performed growth experiments on two substrates with a roughness gradient. One of the samples has been prepared by ion-beam irradiation while at room temperature, and the other has been kept at 740 K during bombardment. A TiO_2 substrate temperature of 740 K is sufficient to restore the surface stoichiometry but still basically preserves the roughness. Subsequently, the same amount (0.25 ML (1.7 LML)) of 6P has been deposited in situ at the same rate on both substrates without air exposure.

In Figures 13 and 14, SEM images of the resulting morphologies for areas exposed to different ion fluences are compared. (SEM images provide better statistical overview compared to AFM.) The not-bombarded region of the 740 K sample shown in Figure 13 exhibits the well-known needle structures already discussed in the previous sections. At already very small ion fluences ($4 \times 10^{14} \text{ ions/cm}^2$), 6P forms primarily islands characteristic of upright-standing molecular arrangements and only very few short needles. The needles vanish entirely at higher fluences. With increasing ion fluence, the island density increases, whereas simultaneously the mean island size decreases. In addition, despite the ion-bombardment-induced roughening, the islands still evince a certain elongation in the $\text{TiO}_2(110)$ $[1\bar{1}0]$ direction.

In Figure 14, the 6P morphologies arising on the substrate bombarded at room temperature are presented. A comparison with the morphologies obtained on the substrate prepared at 740 K yields some significant differences. On the room temperature prepared substrate, the 6P islands are more compact, and their density is higher. The shape anisotropy is much less pronounced. Apparently, a very small ion fluence of $1 \times 10^{14} \text{ ions/cm}^2$ is also sufficient to promote primarily island growth, as visible in Figure 14.

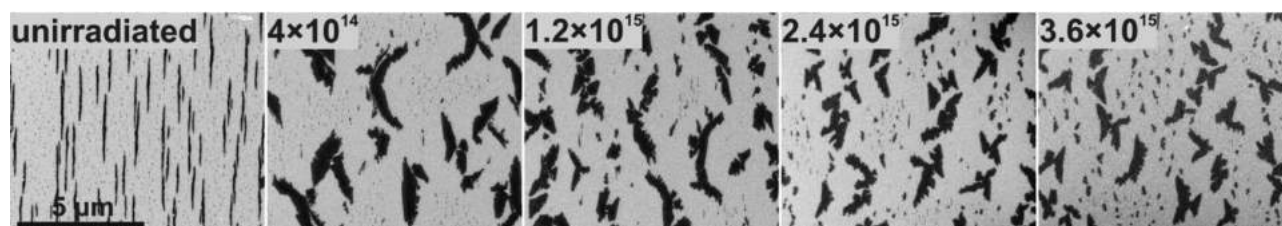


Figure 13. SEM images of a 6P (0.25 ML (1.7 LML)) molecular structure developed on $\text{TiO}_2(110)$ sputtered at 740 K with a Xe^+ ion beam under normal incidence. Fluences are given in the upper left corner of each image. Each image has a size of $12 \times 10 \mu\text{m}^2$.

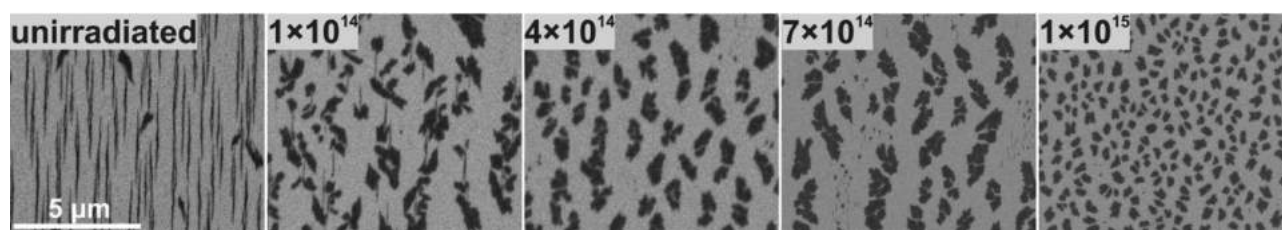


Figure 14. SEM images of a 6P (0.25 ML (1.7 LML)) molecular structure developed on TiO₂ sputtered at room temperature with a Xe⁺ ion beam under normal incidence. Fluences are given in the upper left corner of each image. Each image has a size of 12 × 10 μm².

The increasing island density with increasing ion fluence, which is evident for both samples is just a consequence of the roughness induced reduction of the molecular surface diffusivity. The more compact islands on the room temperature sample compared to the 740 K sample might be explained in terms of different ratios of island edge diffusion to surface diffusion. For the 740 K sample, the surface diffusion is still rather fast with respect to the diffusion along the island edges. Therefore, material supply from the surrounding is faster than the redistribution along the island edge, resulting in rather ragged island rims. In contrast, the 6P diffusion over the room temperature sample is slow compared to the edge diffusion, leaving sufficient time for transporting molecules along the island rim to favorable sites such as kinks and edges before the next molecule from the surrounding arrives. Therefore, a smoother island rim evolves, resulting in an overall more compact island shape. In Figure 15, the mean diffusion lengths derived from the

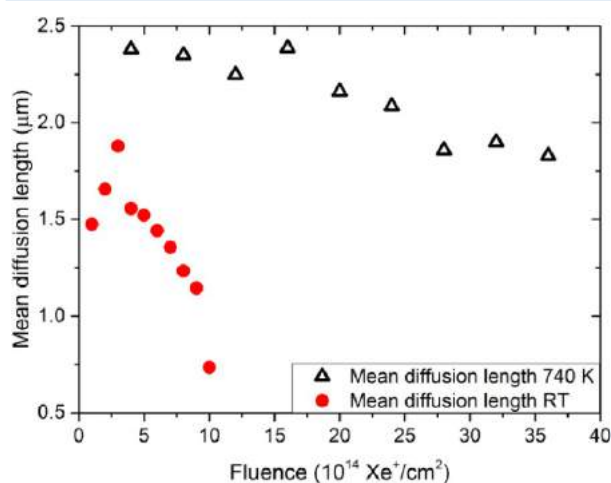


Figure 15. Mean diffusion lengths evaluated for the sample sputtered at normal incidence with Xe⁺ 2 keV ion beam at room temperature (red dots) and the sample sputtered at 740 K (black triangles).

island density in Figures 13 and 14 are plotted as a function of the ion beam fluence. Evidently, the mean diffusion length for the 740 K substrate is always significantly higher than that for the room temperature sample. Assuming that the 6P edge diffusion is independent of the substrate, it nicely reflects the variation in surface-to-edge diffusion ratio, which is assumed to cause the differences in island shape.

Previous studies which investigated in-plane (surface) and into-bulk diffusion of various TiO₂ components (Ti, O, TiO, etc.) revealed that those diffusion rates behave differently at room and elevated temperature.⁴³ Into-bulk diffusion, which compensates a titanium enrichment of the subsurface layer

(because of the preferential O sputtering), is activated at 620 K, providing a significant difference in stoichiometry between room temperature and 740 K irradiated samples. We further assume that the local roughness of both substrates, room temperature and 740 K, is comparable. In-plane diffusion recovery of the surface smoothness (local crystallographic order) after sputtering is already activated at lower temperatures.⁴³ Therefore, we expect that in the case of TiO₂(110) the surface chemistry/stoichiometry is a decisive factor for the resulting film morphology. However, because in both cases, 740 K and room temperature, the upright molecular configuration is already dominating at small ion fluences, it seems that slight disturbance is sufficient to switch the growth from flat-lying molecular orientation (needles) to upright orientation (islands). Still, the variations in island size, shape, and density apparently depend noticeably on the surface stoichiometry.

4. CONCLUSIONS

We have investigated the thin film growth morphology of the small organic *para*-hexaphenyl molecule on atomically flat TiO₂(110) surfaces. Special emphasis was put to the effect of air exposure of the substrates after and prior to 6P vapor deposition. On pristine TiO₂(110), 6P forms bunches of several micrometer long nanoneedles oriented with their long axis along the substrate's [110] direction. The oriented needle growth is attributed to alignment and anisotropic diffusion of 6P molecules along the TiO₂(110) oxygen rows in [001] direction, facilitating a parallel stacking of the 6P and thereby forming crystallites preferentially extending into the [110] direction.

The formation of needle bunches can be explained by an enhanced nucleation probability in the vicinity of already existing nanoneedles, caused by a locally increased molecule density. This increased molecule density arises from a tailback of molecules in front of the needles caused by the low sticking probability at the needles' sidewalls, which are presumably mainly composed of weakly interacting 6P(001) planes.

Exposing the as-prepared film to ambient conditions yields the spontaneous formation of 5–10 nm high features with diameters between 50 and 100 nm and an increase of the nanoneedle height by 1–2 nm. We find, on the basis of the corresponding volumes and the average feature spacing, that the features are formed by an air-induced decomposition of a monomolecular wetting layer existing between the needles.

When the substrate is passivated in air prior to deposition, 6P only forms dendritic islands with a uniform height of 2.8 nm characteristic for an upright-standing molecular arrangement. In this case, further air exposure does not alter the film morphology, indicating that no wetting layer is formed on the air-passivated TiO₂. Apparently, the formation of a wetting layer is a prerequisite for needle growth.

Further growth experiments on nonstoichiometric and stoichiometric ion-bombarded substrates suggest that the lying-to-standing orientation transition of the 6P film is already triggered by slight changes in the surface roughness. This finding is in agreement with the assumption that a compact 6P wetting layer is a prerequisite for needle formation (flat-lying molecular orientation). On a rough surface, the formation of a well-ordered wetting layer is hindered, finally resulting in island growth (upright molecular orientation).^{66,67}

The presented in-depth study of the 6P growth morphology on differently prepared TiO₂ (110) substrates revealed the origin of small crystallites coexisting with micrometer long needles. Additionally, a mechanism causing the formation of needle bunches has been proposed. Furthermore, from comprehensive experiments with pristine, air-passivated, and sputtered TiO₂ substrates, it was deduced that changes in the local surface chemistry have a severe influence on the size, shape, and density of the 6P islands even though simple roughening is sufficient to switch the basic growth morphology from needlelike to islandlike. Because our measurements have been conducted under UHV and ambient conditions, our results are important for basic surface science as well as for technical applications.

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Notes

The authors declare no competing financial interest.

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Appendix A

Experimental details

A.1 Ultra high vacuum system

Vast majority of experimental results presented in this dissertation were obtained at the home-made UHV system at the Institute of Physics, Jagiellonian University. Almost all STM, LC-AFM, KPFM, LEED, C-AFM images were collected using appropriate apparatus shown. Also *in situ* preparation steps and *in situ* measurements were conducted here. Following images depict this setup, with key components marked (A.1, A.2). Additionally a top-view of the Omicron RT STM/AFM microscope is provided (A.3)

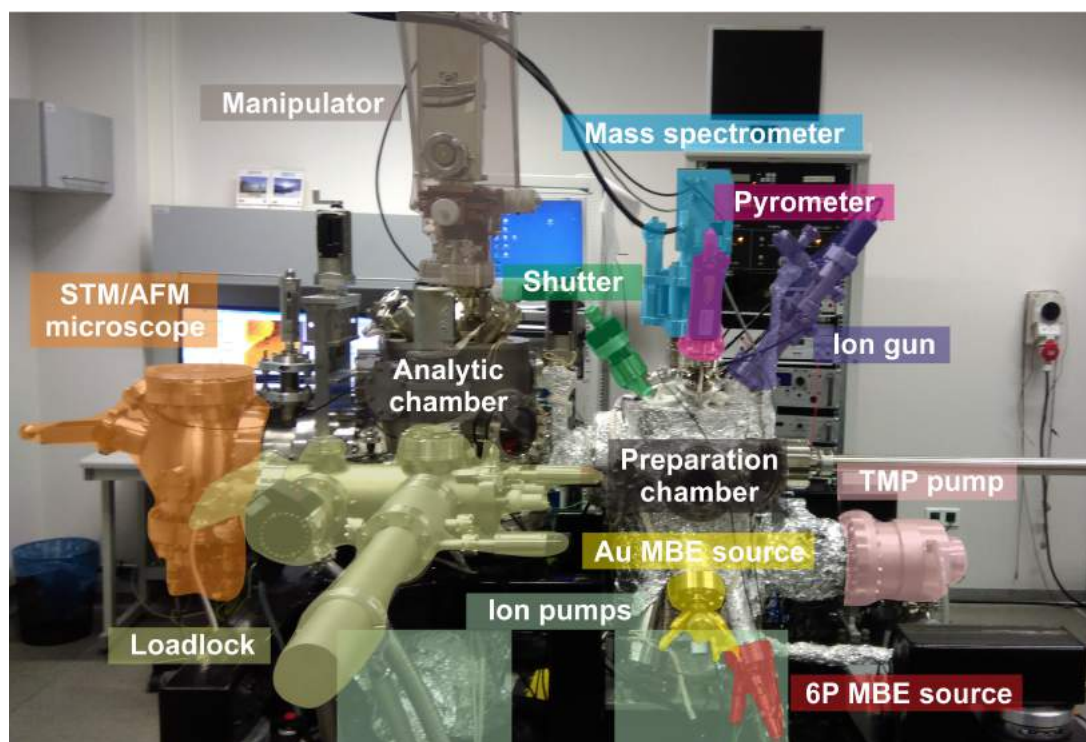


Figure A.1. The UHV system in Prof. Franciszek Krok's lab.

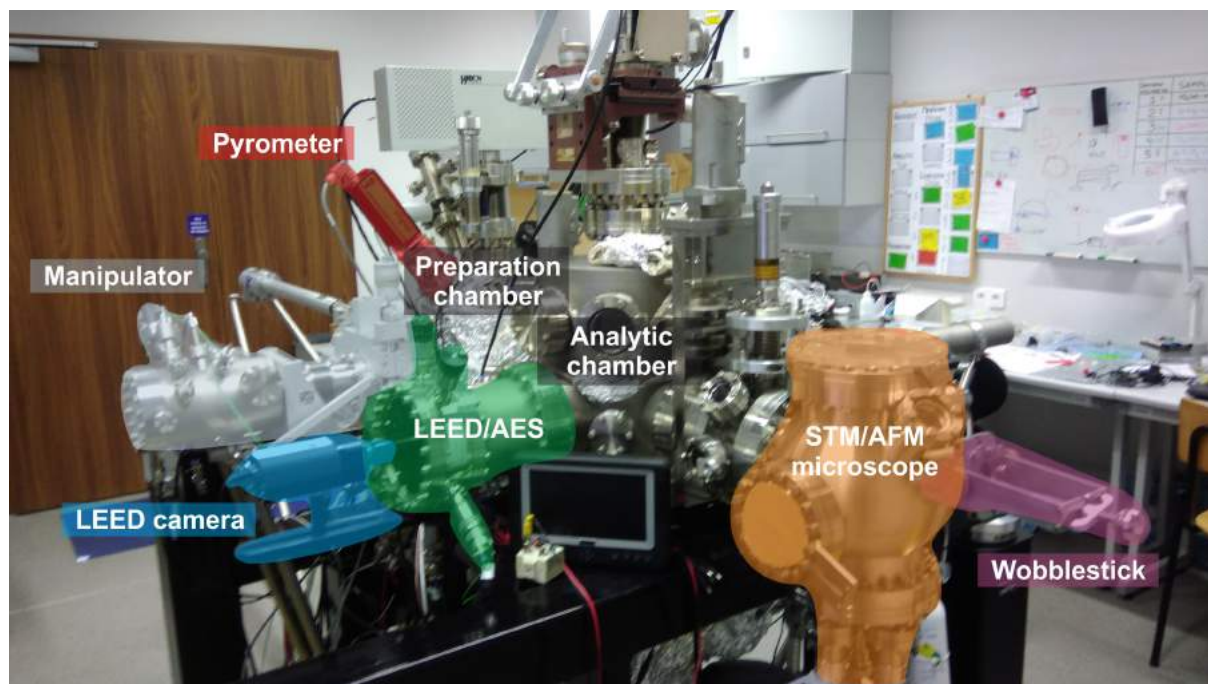


Figure A.2. The same UHV system from another perspective.

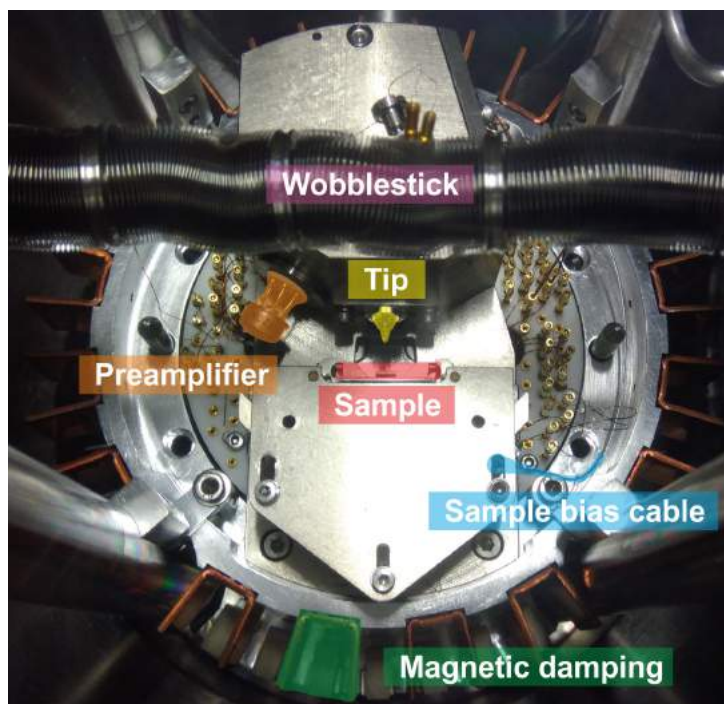


Figure A.3. Omicron RT STM/AFM microscope.

A.2 Oxide single crystals

In this section several pictures of TiO_2 and SrTiO_3 single crystals are presented, *as received* and after treatments described in the thesis. Each time thermal reduction was performed with the presence of the silicon getter (sandwich: oxide crystal + silicon) and the sample holder used for the most experiments was standard Omicron direct heating holder, where current flows through the crystal (see Fig. A.4).

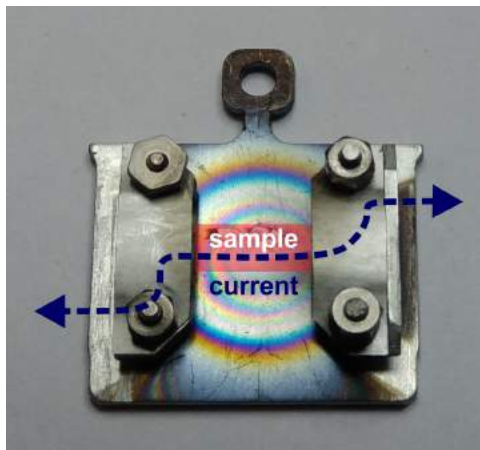


Figure A.4. Image of the Omicron AC direct heating holder, after heavy reduction of SrTiO_3 .

The great deal of experiments were performed on one-side polished crystals, since one exposed surface was sufficient for most investigations. To show however a transparency of used materials (and therefore a high purity of crystals), images of double-side polished SrTiO_3 and TiO_2 are shown (Fig. A.5).

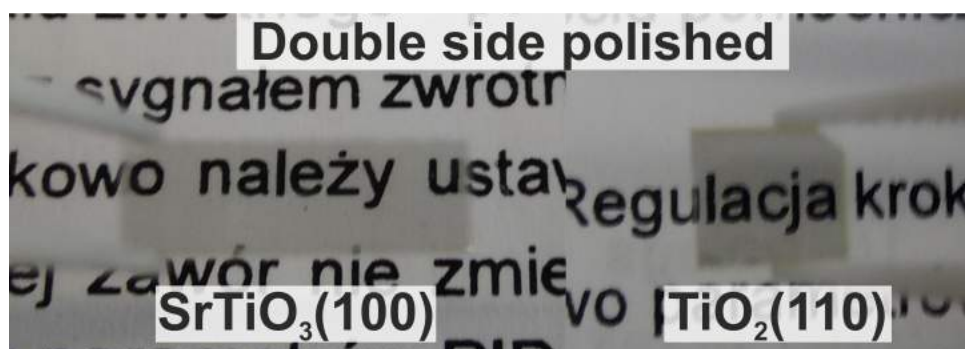


Figure A.5. Comparison of double-side epipolished $\text{SrTiO}_3(100)$ and $\text{TiO}_2(110)$ single crystals.

A.2.1 SrTiO_3

Thermal reduction was proven to change dramatically optical properties of crystals. Here representative images of $\text{SrTiO}_3(100)$ single crystals are presented - A.6. For the 1000°C reduction resulting crystal was nearly opaque. Transparency was lost completely for the case of 1100°C annealing.

1. $\text{SrTiO}_3(100)$ one side epi-polished
2. $\text{SrTiO}_3(100)$ reduced at 1000°C for 1h
3. $\text{SrTiO}_3(100)$ reduced at 1100°C for 1h

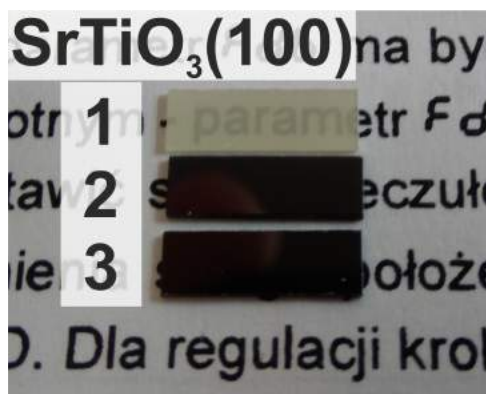


Figure A.6. $\text{SrTiO}_3(100)$ crystals: *as received* and after thermal reduction (see text).

A.2.2 TiO_2

TiO_2 crystals were used in this thesis for investigations of the Nb-doping influence and of the 6P molecule growth. Therefore following images show accordingly $\text{TiO}_2(110)$ single crystals: undoped (A.7) and Nb-doped (A.8), *as received* and after *in situ* treatments. Nb-doped crystals proved to be completely opaque, even with as low dopant concentration as 0.5%.

4. $\text{TiO}_2(110)$ one side epi-polished
5. $\text{TiO}_2(110)$ after 7 cycles of cleaning (sputtering + 750°C reduction) + 0.5 monolayers 6P
6. $\text{TiO}_2(110)$ after 1000°C reduction for 2h + 0.5 monolayers 6P

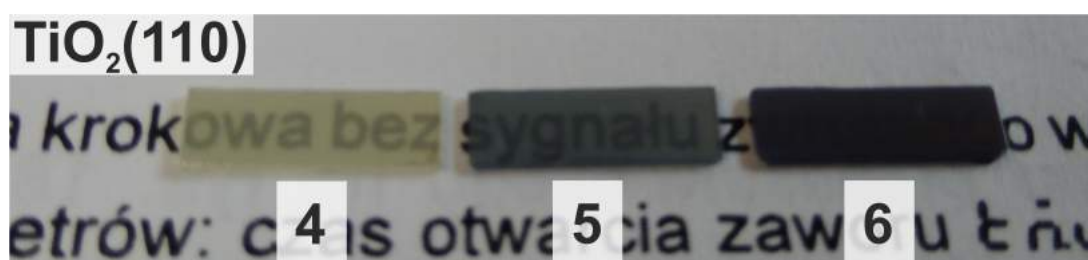


Figure A.7. $\text{TiO}_2(110)$ crystals: *as received* and after reduction (see text).

7. $\text{TiO}_2(110)$ 0.5% Nb-doped, one side epi-polished
8. $\text{TiO}_2(110)$ 0.5% Nb after 950°C reduction for 1h

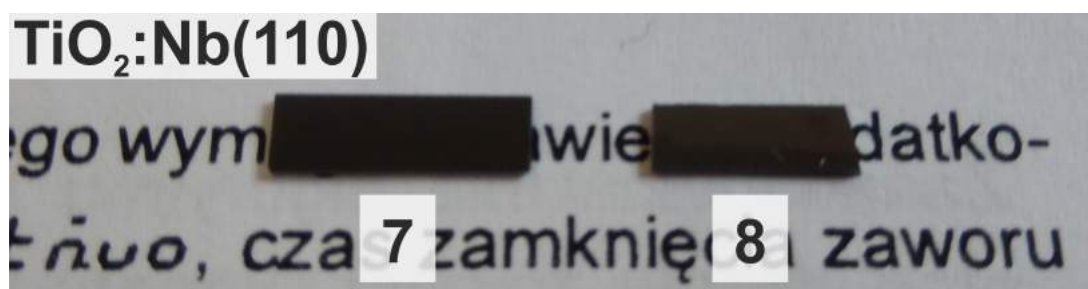


Figure A.8. Nb-doped $\text{TiO}_2(110)$ crystals: *as received* and after reduction (see text).

Appendix B

Miscellaneous

B.1 Other published papers

Other papers published during PhD studies, excluded from the Thesis (in the chronological order):

1. **Island shape anisotropy in organic thin film growth induced by ion-beam irradiated rippled surfaces**
Markus Kratzer, **Dominik Wrana**, Konrad Szajna, Franciszek Krok and Franciszek Krok
Physical Chemistry Chemical Physics, 2014, 16(47), [97]
2. **SEM studies of vacuum condition influence on thermally induced Au self-organization on Ge(001) surface**
Marek Nikiel, Benedykt R. Jany, **Dominik Wrana**, Konrad Szajna and Franciszek Krok
Surface and Coatings Technology, 2015, 277, [201]
3. **Energy dependence of nanopillars formation on InSb semiconductor surfaces under gallium FIB and noble gas ions beam irradiation**
Benedykt R. Jany, Konrad Szajna, Marek Nikiel, **Dominik Wrana**, Elżbieta Trynkiewicz, Roman Pędrys and Franciszek Krok
Applied Surface Science, 2015, 327, [93]
4. **Dynamics of thermally induced assembly of Au nanoislands from a thin Au layer on Ge(001)**
Marek Nikiel, Benedykt R. Jany, **Dominik Wrana**, Konrad Szajna, Arkadiusz Janas, Rafał Kozubski and Franciszek Krok
CrystEngComm, 2016, 18(30), [202]
5. **Influence of TiO₂(110) surface roughness on growth and stability of thin organic films**
Konrad Szajna, Markus Kratzer, **Dominik Wrana**, Carlo Mennucci, Benedykt R. Jany,

Francesco Buatier de Mongeot, Christian Teichert and Franciszek Krok
The Journal of Chemical Physics, 2016, 145(14), [98]

6. **Thermally controlled growth of surface nanostructures on ion-modified AIII-BV semiconductor crystals**

Elżbieta Trynkiewicz, Benedykt R. Jany, **Dominik Wrana** and Franciszek Krok
Applied Surface Science, 2018, 427, [94]

7. **Local surface conductivity of transition metal oxides mapped with true atomic resolution**

Christian Rodenbücher, Gustav Bihlmayer, Wolfgang Speier, Jerzy Kubacki, Marcin Wojtyniak, Maciej Rogala, **Dominik Wrana**, Franciszek Krok and Kristof Szot
Nanoscale, 2018, [178]

8. **Fabrication of ion bombardment induced rippled TiO₂ surfaces to influence subsequent organic thin film growth**

Markus Kratzer, Konrad Szajna, **Dominik Wrana**, Wojciech Belza, Franciszek Krok and Christian Teichert
Journal of Physics: Condensed Matter, 2018, [99]

9. **Electrical nanopatterning of TiO₂ single crystal surfaces in situ via local resistance and potential switching**

Christian Rodenbücher, **Dominik Wrana**, Paul Meuffels, Maciej Rogala, Franciszek Krok and Kristof Szot

This research was highlighted on the cover of the APL Materials journal.

APL Materials, 2018, [200]

B.2 Conference contributions

Here, a table containing conference contributions (oral - O and poster - P) presented by the Thesis author during PhD studies, is revoked:

Date	Place	Name		Title
06.2014	Vienna	JVC 15: Joint Vacuum Conference	O	Growth of para-hexaphenyl thin films on flat, atomically clean vs. air passivated $\text{TiO}_2(110)$ surface
09.2014	Krakow	The 17th International Workshop for Young Mathematicians "Discrete Mathematics"	O	The Motorway Problem from the Physicists Point of View
09.2014	Eisenerz	73 IUVESTA Workshop on Nanostructures on two-dimensional solids	O	Influence of Air Passivation on Para-Hexaphenyl Thin Films Growth on $\text{TiO}_2(110)$ Flat Surfaces
12.2014	Zakopane	VIII Seminarium: Badania prowadzone metodami skaningowej mikroskopii bliskich oddziaływań STM/AFM 2014	O	Struktury molekularne na atomowo płaskiej powierzchni $\text{TiO}_2(110)(1 \times 1)$: wpływ pasywacji na wzrost
06.2015	Trzebnica	7th International Workshop on Surface Physics: Molecular Nanostructures	O	Para-Hexaphenyl as a Molecular Sensor of $\text{TiO}_2(110)$ Surface Quality: Influence of Ion Beam Irradiation and Air Passivation of Substrate Surface
07.2015	Krakow	8th International Workshop on Nanoscale Pattern Formation at Surfaces	P	Control over formation of nanoscale molecular structures on flat $\text{TiO}_2(110)$: From highly anisotropic nanoneedles to dendritic islands
09.2015	Como	7th School on Organic Electronics: from Semiconductor to Biomolecular Interfaces	P	Para-Hexaphenyl as a Molecular Sensor of Surface Quality: Influence of Ion Beam Irradiation and Air Passivation of $\text{TiO}_2(110)$

Date	Place	Name		Title
09.2015	Krakow	Kryształki molekularne 2015	O	1D, 2D, 3D - nanodrut, warstwy, wyspy: kontrola wzrostu molekuł para-heksafenylu na powierzchni $\text{TiO}_2(110)$
06.2016	Katowice	Internano Poland 2016	O	Tuning The Electronic Properties Of Metal Oxide Surfaces By Thermal Reduction
09.2016	Grenoble	ECOSS 32 - European Conference on Surface Science	O	Thermal reduction of Nb-doped TiO_2 single crystals: surface properties and composition evolution
12.2016	Zakopane	IX Seminarium: Badania prowadzone metodami skaningowej mikroskopii bliskich oddziaływań STM/AFM 2016	O	Badanie procesów redukcji i utleniania w nanoskali na przykładzie SrTiO_3
04.2017	Krakow	XIV Katowicko-Krakowskie Seminarium Fizyka Fazy Skondensowanej	O	Procesy redox w nanoskali na przykładzie SrTiO_3 : powstanie krystalicznych przewodzących nanodrutów
05.2017	Lviv	OMEE - 5th International Conference on Oxide Materials for Electronic Engineering	O	An easy method for oriented conductive nanowires formation on $\text{SrTiO}_3(100)$
06.2017	Lodz	Doktoranckie Sympozjum Nanotechnologii NanoMat	O	Przewodzące struktury powstające na powierzchni tlenków metali wskutek termoredukcji
06.2017	Lodz	VIII Krajowa Konferencja Nanotechnologii	O	Wzrost krystalicznych przewodzących nanodrutów na powierzchni SrTiO_3
12.2017	Aachen	SFB 917: Doctoral Researcher Meeting 2017	O	Tailoring the surface properties of transition metal oxides via redox processes
02.2018	Bad Honnef	663. WE-Heraeus-Seminar: Dynamics and Structure Formation of Organic Molecules on Dielectric Surfaces	P	Controllable formation of molecular nanostructures on $\text{TiO}_2(110)$: from nanoneedles to dendritic islands
03.2018	Spa	SFB 917 Meeting 2018	P	Importance of Reduction-Induced Structural Changes in VCM Resistive Switching Oxides
07.2018	Brno	The International Conference on Nanoscience + Technology (ICN+T) 2018	O	Conductive titanium oxide (TiO) nanowires on $\text{SrTiO}_3(100)$: formation mechanism and properties