

Graphitization of SiC surfaces in Si flux

Doctoral thesis

Piotr Ciochoń

Faculty of Physics, Astronomy and Applied Computer Science

Jagiellonian University

supervised by:

prof. Jacek J. Kołodziej

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Wydział Fizyki, Astronomii i Informatyki Stosowanej
Uniwersytet Jagielloński

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“Wisdom comes from experience. Experience is often a result of lack of wisdom.”

— Terry Pratchett

Looking back at the years that led to me writing this thesis, one thing is clear: how beautifully meandering was the route towards this moment. From the first attempts as an undergraduate student to get funding for this project, which would be a new direction for my group, through the pain of (repeated) rejections, the joy of (smaller and larger) successes and (excruciating) struggles with the reality, to this moment, when the only thing that remains to be done is to show my deep appreciation to all the people, without whom I could not have made it.

“It’s still magic even if you know how it’s done.”

— Terry Pratchett, *A Hat Full of Sky*

I would like to thank everyone, who made it possible for me to discover the magic of science and use it to create this work: my supervisor, Jacek Kołodziej, who provided exceptional guidance and mentorship and whose brilliant suggestions helped me successfully complete the project, Natalia Olszowska, who introduced me to the field and helped me extensively along the way, Mariusz Garb, who provided outstanding technical support, Łukasz Bodek, who made large parts of this project possible thanks to our close collaboration, and many others, who have helped me in one way or another, including: Mikołaj Gołuński, Bartosz Such, Łukasz Zajac, Marek Kolmer, Mateusz Marzec, Johannes Binder, Dorota Kowalczyk, Miika Soikkeli.

“The future came and went in the mildly discouraging way that futures do.”

— Neil Gaiman, *Good Omens: The Nice and Accurate Prophecies of Agnes Nutter, Witch*

This journey took me six years to complete and, in the meantime, both me and the world have changed. I have experienced happiness and misery, I have made friends and I have lost friends, I have won and I have failed. However, there were a few people who were a constant reminder of the important things in my life and who made this moment possible: my beloved Ania, a brilliant scientist and my soulmate, who keeps on surprising and inspiring me in the best possible way, my mother Elżbieta, my father Krzysztof and my sister Agnieszka, who constantly supported and encouraged me during this adventure, my grandmother Czesława, who had always pushed me in the right direction, and the rest of my family. In these acknowledgements, I need to also honor the Dinosaurs (they know who I’m writing about), who have become my second family and provided (much needed) unconditional love and support. A big thank you to all my friends who have been there for me when I needed them, and with whom I could share my experiences. I’m also grateful to the fellow young scientists, who I was lucky to meet during Graphene Study 2017 and 2018 and European School on Nanosciences and Nanotechnologies 2019, and to my friends from the time I got to spend in Copenhagen and Seattle.

Abstract

Since its discovery in 2004, graphene has been considered as one of the materials of the future, potentially revolutionizing numerous industry sectors, from electronics to biomaterials. Despite its extraordinary physical and chemical properties, attempts to apply it in the industry were, to this date, largely unsuccessful. This is a consequence of inadequate production methods, which are often unscalable, lack repeatability and yield material of low quality, which requires further processing. Graphitization of the surfaces of silicon carbide, especially the Si-terminated (0001) surface, is one of the most promising methods, which could enable wafer-scale growth and processing of the material. The process is based on high-temperature treatment of the SiC wafer resulting in preferential sublimation of silicon atoms. Remaining carbon atoms spontaneously rearrange into the thermodynamically preferred graphene structure. However, because the process is not self-limiting, the process temperature needs to be relatively low, in order to avoid the formation of the thick layer of graphite on the surface. As a result, carbon atoms have insufficient mobility on the surface, and the resulting graphene is of low quality.

In this work, I propose and investigate a new graphene on SiC growth method, in which the effective Si loss from the surface is controlled by an external flux of Si atoms/molecules applied to the SiC surface. I show, that the graphitization of the surface can be fully inhibited, for the processing temperature of up to 1350°C, by using the Si flux of $1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. This makes it possible to increase the growth temperature of a monolayer graphene to around 1430°C, which is around 150°C higher than in UHV conditions. While the resulting surface is characterized by the lower degree of disorder at a nano-scale, homogeneity at a macro-scale remains low. I then show, that the process of SiC graphitization is reversible under Si flux, and that clean SiC can be restored from the previously graphitized surface, by prolonged annealing in the temperature slightly below the equilibrium temperature of the $\text{SiC} \rightleftharpoons \text{C}_{\text{graph}} + \text{Si}$ reaction. This allows me to design a new process flow, based on a very slow heating and cooling down of the SiC surface. The process consists of two steps: (1) growth of multi-layer graphene during slow annealing and (2) partial etch of the graphene layer until the desired thickness is reached, through the graphitization reaction reversal, occurring during the cooldown in the Si-rich conditions. Using this scheme, maximum process temperature used to grow few-layers graphene can be significantly increased, while using the same, relatively low Si flux. It is shown that this growth method allows for the synthesis of up to 5, ABC-stacked graphene layers. The samples are homogeneous and well-ordered both at the nano- and at the

macro-scale and a regular step structure is formed at the surfaces. Minimal step bunching is observed, with step heights on the order of 2nm, which makes the graphene properties isotropic.

The developed method is very promising, even though it is far from optimum yet. It allows for the synthesis of high-quality, isotropic material directly on an insulating substrate, which makes it a very good candidate for further development of the wafer-scale processes, possibly finding applications in the rapidly growing graphene industry.

Streszczenie

Grafen jest uważany za jeden z materiałów przyszłości, który może zrewolucjonizować liczne gałęzie przemysłu, od elektroniki po biomateriały. Pomimo wyjątkowych właściwości fizycznych i chemicznych, dotychczasowe próby wdrożenia tego materiału jako bazy do produkcji urządzeń elektronicznych się nie powiodły. Wynika to z niedopracowanych metod produkcyjnych, które są często nieskalowalne, charakteryzuje je niska powtarzalność, a wytworzony grafen jest niskiej jakości. Jedną z najbardziej obiecujących metod wytwarzania jest grafityzacja powierzchni węgla krzemu, zwłaszcza powierzchni (0001) o terminacji krzemowej, która może doprowadzić do opracowania metod produkcji w skali przemysłowej. Proces ten opiera się o wygrzewanie podłoża SiC w warunkach próżniowych, w wyniku czego następuje sublimacja bardziej lotnych atomów krzemu z powierzchni. Pozostałe na powierzchni atomy węgla ulegają następnie spontanicznej reorganizacji do preferowanej termodynamicznie struktury grafenu. Ponieważ proces nie jest samo-limitujący, w celu uniknięcia wytworzenia na powierzchni grubej warstwy grafitu, stosowane temperatury wygrzewania są stosunkowo niskie. Skutkuje to niską mobilnością atomów węgla na powierzchni i niską jakością wytworzonego grafenu.

W niniejszej pracy zaproponowałem i zbadałem nową metodę wytwarzania grafenu na powierzchni węgla krzemu. W celu obniżenia tempa utraty krzemu z powierzchni podczas wygrzewania, na powierzchnię skierowany jest strumień atomów/molekuł krzemu z zewnętrznego źródła. Zastosowanie strumienia krzemu o wielkości $1.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ pozwala na całkowite zahamowanie grafityzacji powierzchni aż do temperatury 1350°C , i podniesienie temperatury wzrostu monowarstwowego grafenu do 1430°C . Prowadzi to do wykształcenia warstwy grafenu na powierzchni, charakteryzującej się znacznie lepszym uporządkowaniem i niższą koncentracją defektów; przygotowane w ten sposób próbki są jednak niejednorodne w skali mikrometrów. W dalszej części pracy pokazuję, że grafityzacja węgla krzemu jest procesem odwracalnym, w atmosferze bogatej w krzem, a czysta powierzchnia SiC może zostać odbudowana z grafenu, przez długotrwałe wygrzewanie próbek w temperaturze niższej niż temperatura równowagi reakcji $\text{SiC} \rightleftharpoons \text{C}_{\text{graph}} + \text{Si}$. Na podstawie tego odkrycia, proponuję nową, dwuetapową metodę wytwarzania grafenu na SiC. W pierwszym etapie, podczas ogrzewania podłoża SiC, na powierzchni następuje wzrost wielowarstwowego grafenu, który w drugim etapie, podczas ochładzania próbki, jest częściowo zredukowany w strumieniu krzemu, przez odwrócenie kierunku reakcji. Wykorzystanie tej metody pozwala na zwiększenie temperatury syntezy grafenu kilkuwarstwowego, bez konieczności stosowania wyższego strumienia

atomów/molekuł krzemu. Zaproponowana metoda pozwala na wzrost grafenu o grubości do 5 warstw, ułożonych w strukturę typu ABC. Wytworzone w ten sposób próbki są jednorodne w skali mikrometrów, a na ich powierzchni wykształca się jednorodna struktura stopni atomowych. Maksymalna wysokość stopni wynosi 2nm, co świadczy o zminimalizowaniu szkodliwego zjawiska grupowania stopni (*step-bunching*), dzięki czemu właściwości uzyskanego grafenu są izotropowe.

Opracowana przeze mnie metoda pozwala na syntezę wysokiej jakości, izotropowego grafenu bezpośrednio na izolującym podłożu. Pomimo, że jej potencjał optymalizacyjny nie został jeszcze wyczerpany, jest bardzo obiecująca pod kątem przyszłych, przemysłowych zastosowań.

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Introduction

The discovery of graphene in 2004, by Andre Geim and Konstantin Novoselov, is considered to be a great example of scientific serendipity, leading to exceptional results. Two scientists, working at the University of Manchester, used to frequently hold “Friday night experiments”, which weren’t directly connected to their day-to-day work and focused on the more playful approach of trying out different scientific ideas [1]. During one of the sessions, they tried to repeatedly peel off ever thinner flakes from the graphite sample, reportedly using a regular Scotch tape. They soon realized, that this approach could lead to the isolation of a thinnest possible layer – with a thickness of a single atom. This unexpected discovery led to the Nobel Prize in 2010, just 6 years later, which was awarded “for groundbreaking experiments regarding the two-dimensional material graphene” [2].

This discovery sparked massive interest of the scientific community, because of the combination of unique properties of graphene (especially with regard to the electron transport), allowing for significant advances in the basic condensed matter physics, and the possible applications of the material in various industry sectors, potentially leading to disruptive innovations in the areas of, for example, electronics and spintronics. It was followed by the extensive research focused on isolating other two-dimensional materials, obtained from the vast number of different layered materials, especially transition metal dichalcogenides (TMDs) [3]. While mechanical exfoliation of the flakes of graphene and other 2D materials, performed in a manner similar to the very first experiments performed by Geim and Novoselov, is a technique which is easy to implement in various laboratories and yields high-quality material, it is unfeasible for industrial applications. This is because of its low repeatability and difficulties in upscaling production of the material. Therefore, there is an urgent need to develop large-scale growth techniques of graphene, in order to enable its wafer-scale processing and the application of standard, lithographic microfabrication techniques.

One of the most promising methods of wafer-scale production of graphene is graphitization of silicon carbide. The method relies on the surface decomposition of the compound in high temperatures, sublimation of Si atoms and rearrangement of the excess carbon into graphene structure. Formation of graphene using this approach has been observed as early as 1962 [4], but the extraordinary properties of the material became known only after the discovery of graphene isolated by mechanical exfoliation. Even though the method has been significantly improved over the years, it is still facing several problems and the mechanism of the process is far from understood.

The aim of this thesis is to describe a new approach to the ultra-high vacuum graphitization of Si-terminated (0001) surface of silicon carbide, in the flux of Si atoms emitted from an external source. This method can be used to study semi-equilibrium processes, occurring during material growth, and can be applied to the wafer-scale graphene synthesis.

The first chapter of the thesis will offer an introduction to the physics of graphene and the main production methods of the material, with special emphasis on the growth on SiC. The Si beam-assisted growth method will be described in detail in chapter two, along with the experimental methods used for the investigation of the properties of the synthesized graphene: low energy electron diffraction (LEED), angle-resolved photoelectron spectroscopy (ARPES), X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and atomic force microscopy (AFM). Chapter three will be devoted to the description of the SiC graphitization process dynamics and influence of the process parameters (temperature, time, silicon flux density) on the properties of the synthesized graphene. Chapter four will focus on the phenomena occurring in the semi-equilibrium conditions, especially on the reversibility of the SiC graphitization and on how these phenomena could be used to improve graphene quality. The results will be summarized in chapter five, along with the outlook for future studies and a discussion of the potential of the elaborated graphene growth method for future applications.

Chapter 1

Graphene and its properties

This chapter will offer an introduction to the physics and properties of graphene. After discussing the basics of the physical and electronic structure of the material, including the effects of different stacking arrangements of a few-layers graphene, it will move on to briefly summarize its most important properties and most widely used production methods. The second part of the chapter will be focused on the detailed description of graphene growth on SiC (0001) surface, which is the main focus of this work. The structure of the silicon carbide crystal and its (0001) surface will also be described to provide the necessary background to the process. At the end, mechanisms of graphitization of this surface will be discussed, which will serve as an introduction to the experimental studies presented in Chapter 2.

1.1 Introduction to graphene and its electronic structure

Graphene is a single layer of a common material, graphite, with a thickness of one atom. It is the first isolated two-dimensional material, consisting of carbon atoms arranged in a honeycomb lattice, as shown in a ball and stick model in Fig. 1a.

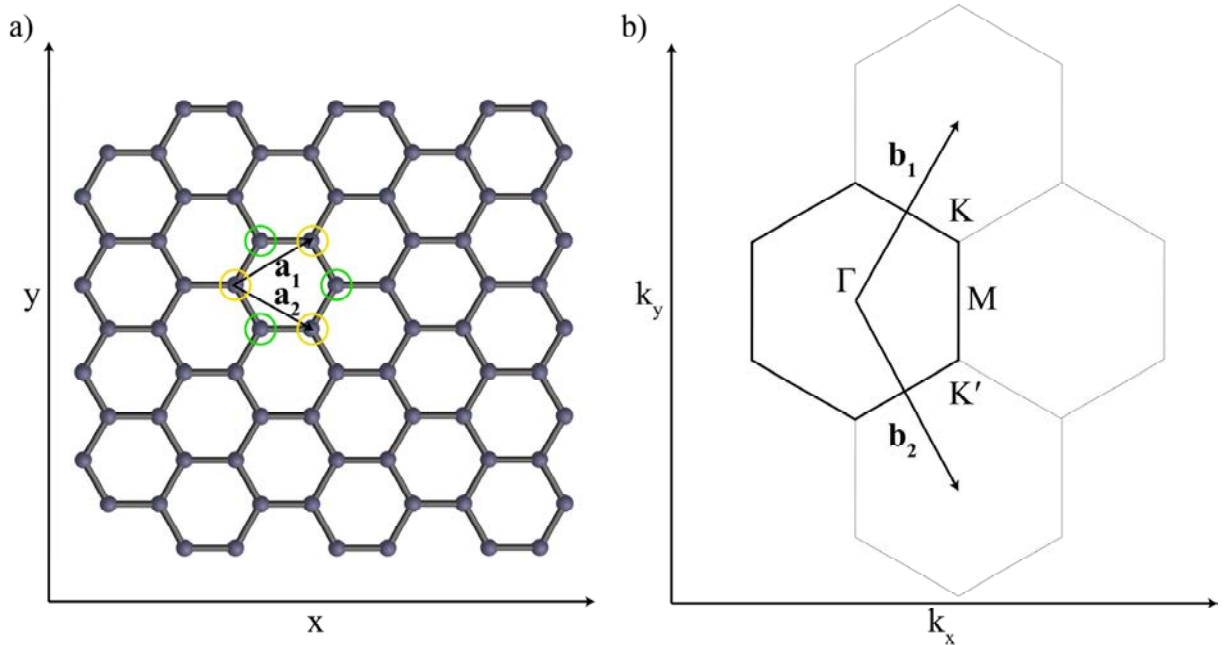


Figure 1: a) Atomic structure and basis vectors of the real lattice of graphene; b) reciprocal lattice of graphene, its basis vectors and high symmetry points.

The graphene lattice is hexagonal and its basis vectors are marked in Fig. 1a. The lattice can be understood as a superposition of two triangular, sub-lattices, rotated by 60° one relative to the other, marked by green and yellow circles. The basis vectors of the lattice are equal to:

$$\mathbf{a}_1 = \frac{a}{2}(3, \sqrt{3}), \mathbf{a}_2 = \frac{a}{2}(3, -\sqrt{3}). \quad (1)$$

with $a \approx 1.42 \text{ \AA}$. The reciprocal lattice of the material is also hexagonal, and its structure, with high symmetry points and basis vectors is shown in Fig. 1b. The basis vectors of the reciprocal lattice have the form of:

$$\mathbf{b}_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \mathbf{b}_2 = \frac{2\pi}{3a}(1, -\sqrt{3}). \quad (2)$$

Two high symmetry points in the reciprocal lattice are especially important regarding graphene properties: these are so called “Dirac points”, labelled as K and K’. They are located at the edges of the Brilluoin zone and their coordinates in the reciprocal lattice are equal to:

$$\mathbf{K} = \left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right), \mathbf{K}' = \left(\frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a}\right). \quad (3)$$

The electronic structure of the material has been calculated using tight-binding approach in the quasi-particle formalism [5] and the electron bands have the general form of:

$$E(\mathbf{k}) = \pm t\sqrt{3 + f(\mathbf{k})} - t'f(\mathbf{k}), \quad (4)$$

where the positive (+) branch represents the conduction band, while the negative (-) branch represents the valence band of the material and:

$$f(\mathbf{k}) = \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right). \quad (5)$$

The parameters t and t' in the model are the nearest-neighbor and next nearest-neighbor hopping energies, respectively. Calculated band structure of monolayer graphene, with $t=2.7\text{eV}$ and $t'=0.2t$ (which is the approximation, based on ab-initio studies [6] and cyclotron resonance experiments [7]) is shown in Fig. 2.

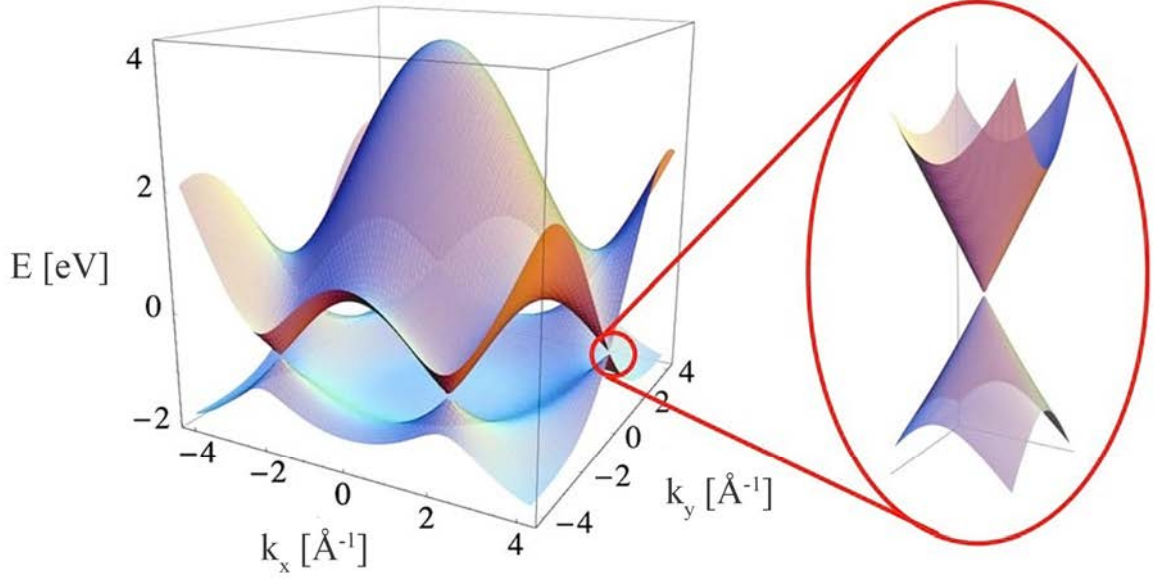


Figure 2: Calculated electronic structure of a monolayer graphene near the Fermi energy ($E=0\text{eV}$, adapted with permission from [8]).

Conduction and valence bands of graphene overlap exactly at the Fermi energy in the 6 Dirac points of the Brillouin zone, hence the material is often referred to as semi-metal, or “zero-bandgap” semiconductor. This is a highly unusual situation, making the classification of the material difficult, in terms commonly used in solid-state physics. Density of states per unit cell, computed from equation (2) can be approximated, near Fermi energy, as:

$$\rho(E) = \frac{2A}{\pi} \frac{|E|}{v_f^2}, \quad (6)$$

where E is the electron energy relative to the Fermi level, A is the unit cell area, given by:

$$A = 3\sqrt{3}a^2/2, \quad (7)$$

and v_f is the Fermi velocity given by:

$$v_f = \frac{3}{2}ta \simeq 1 \times 10^6 \text{ m/s}. \quad (8)$$

This shows the semi-metallic behavior of the material [9], since the density of states goes to zero, exactly at the Fermi energy of the material.

Electronic structure of the material, near Fermi energy, around one of the Dirac points is enlarged and shown in an inset in Fig. 2. By expanding equation (2) around the K point, one can obtain the dispersion relation relative to the K point:

$$E(\mathbf{q}) \approx \pm v_f |\mathbf{q}| + O[(q/K)^2], \quad (9)$$

where $\mathbf{q}$ is the electron momentum relative to the K point, v_f is Fermi velocity and O is the remainder term of the series. Obtained electron energy dispersion relation near the Fermi level is very different from other, more typical materials, for which we would expect a parabolic (or

a corrected parabolic) relationship. In case of graphene, electronic dispersion is linear with respect to the electron momentum. This description is similar to the ultrarelativistic particles, described by massless Dirac-Weyl equation [10]. The analogy shows, that electrons in graphene, when interacting with its periodic potential, can be seen as relativistic quasi-particles, as described by quantum electrodynamics (QED). Their effective cyclotron mass can be expressed as:

$$m^* = \frac{\sqrt{\pi}}{v_f} \sqrt{n}, \quad (10)$$

where n is electron density. The square-root dependence of the effective mass of electrons in graphene has been verified experimentally [11, 12], which proves their behavior as massless Dirac quasiparticles. This means that the material allows to study QED effects in a condensed matter system, leading to some calling graphene a “bench-top” QED system. Out of many interesting effects, only Klein tunneling has been experimentally verified so far [13].

1.2 Electronic structure of multi-layer graphene

Electronic structure of multi-layer graphene depends strongly on the stacking sequence of the consecutive graphene layers. There are three distinct stacking arrangements of multiple hexagonal layers, denoted as A, B, and C. In AA-type stacking, the $n+1$ th graphene layer, stacked above the n th layer in the z direction, has exactly the same position in x and y ; in AB-type stacking, the $n+1$ th layer is shifted, with respect to the n th one, by $1/2$ unit cell in x and y directions; in case of ABC-type stacking, the $n+1$ th layer is shifted in x and y directions, while $n+2$ th layer is shifted only in y direction, with respect to the n th layer, as shown in Fig. 3.

AA, ABA and ABC stackings are often referred to as hexagonal, Bernal and rhombohedral stacking. ABA stacking is the same stacking as in thermodynamically stable form of graphite [14]. There is some debate, regarding the maximum thickness of a multi-layer graphene, over which its properties become identical to a thin layer of graphite, but the general consensus is that the limit is equal to 10 layers. This is highlighted in the recently published ISO norm no. ISO/TS 80004-13:2017, describing the nomenclature used in the area of two-dimensional materials, which defines three types of graphene: monolayer graphene, bilayer graphene and few-layers graphene, with the thickness of 3-10 layers [15].

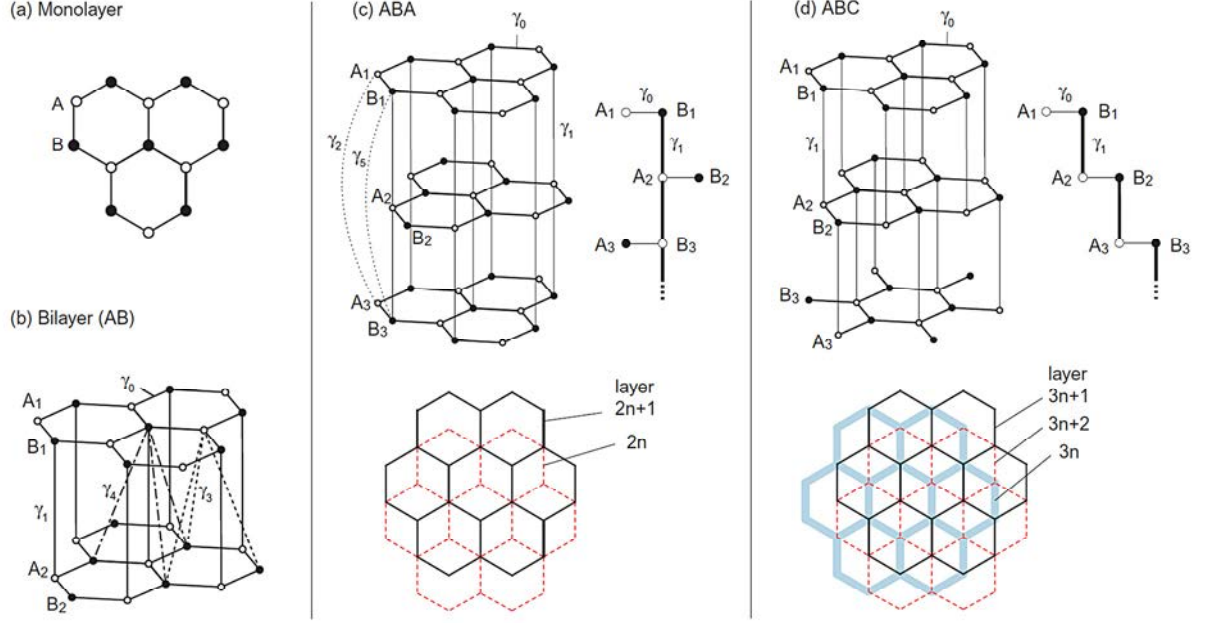


Figure 3: Different types of multi-layer graphene stacking (reprinted from: [16] under CC BY 3.0 license).

The analysis of the dispersion relations found in those types of graphene stacks has to include not only the nearest-neighbors hopping, found in monolayer graphene, but also interlayer hopping. In case of AB-stacked bilayer graphene, the approximate solution, taking into account only nearest-neighbor interlayer hopping ($t_{\perp}$), takes the form of:

$$E(k) = \pm v_f^2 k^2 / t_{\perp} \pm m t_{\perp} \quad (m = [0,1]). \quad (11)$$

When we take into account the presence of a potential V , which is half the shift in the electrochemical potential between the first and second graphene layer (which can be induced by the application of a potential bias, or by molecular doping of the outermost graphene layer), the relationship takes the form of:

$$E(k) = \pm(V^2 + v_f^2 k^2 + t_{\perp}^2 \pm \sqrt{4V^2 v_f^2 k^2 + t^2 v_f^2 k^2 + t_{\perp}^4 / 4}). \quad (12)$$

The dispersion relation for bilayer graphene is, in case of the absence of a potential V , parabolic, with two bands, originating either at Fermi energy, or at $E = \pm t$. When the potential is present, as is the case for most real samples of graphene, it makes the two layers non-equivalent (breaks their inversion symmetry), making the relationship more complex and leading to the band-gap opening at:

$$k^2 \approx 2V^2 / v_f^2. \quad (13)$$

The band structure of bilayer graphene, in case of $V=0$ and $V \neq 0$, is plotted in Fig. 4.

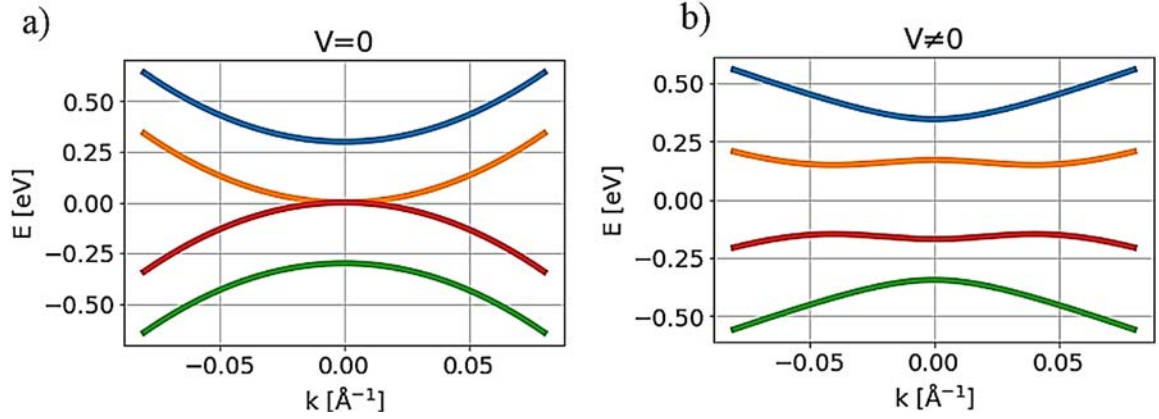
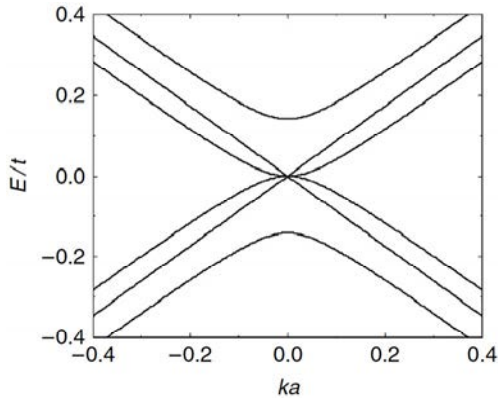
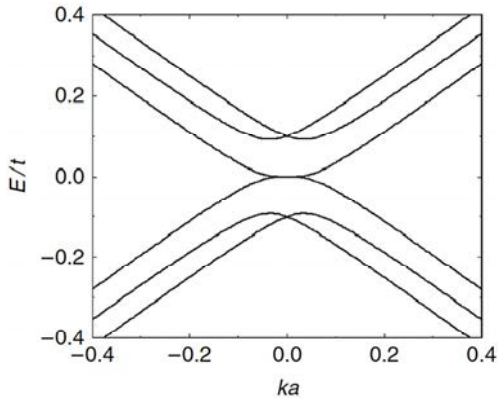
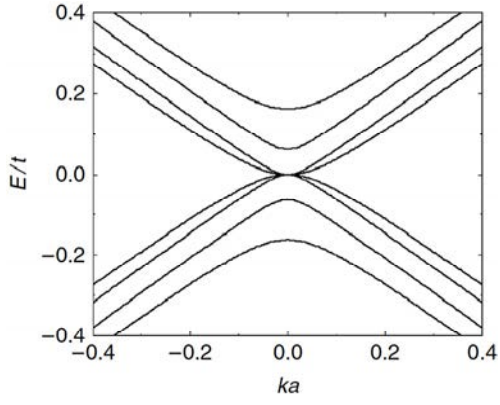
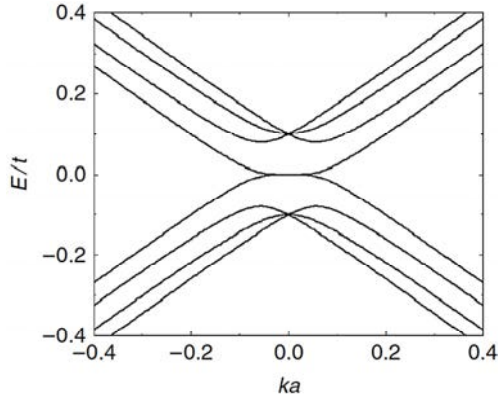


Figure 4: Calculated band structure around K point of the AB-stacked bilayer graphene for: a) $V=0$ and b) $V \neq 0$.

The bandgap in the AB-stacked bilayer graphene is also dependent on the external potential bias applied to graphene, which has been confirmed experimentally [17] and opening the material's bandgap is a widely studied topic, in hopes of eventually applying graphene for the logic electronics applications. Proposed approaches focus on either applying an electrical displacement field to the material, or inducing charge distribution asymmetry between the layers, through the molecular doping from various molecules adsorbed on the top layer [18]. These attempts have been partially successful and band-gap values of few hundred meV at room temperature were reported [19], however this is still not enough to achieve sufficient ON/OFF ratios for the graphene-based transistors to operate in logic applications.

Similar calculations have been done for differently stacked graphene multilayers and the corresponding band structures of tri- and tetra-layer graphene are summarized in Table 1 (k is a wavevector measured relative to the K point of the reciprocal lattice of graphene and a is the lattice constant of graphene).

Table 1: Electronic structure of AB- and ABC- stacked 3 and 4 layer graphene (adapted with permission from: [20]).

No. of graphene layers	AB-stacking	ABC-stacking
3		
4		

The type of graphene stacking has a strong influence on its optical and electrical conductivity, as well as for the position of “jumps” in the quantized Hall conductivity [20]. Stacked graphene layers, misaligned by specific angles, have sparked a significant research interest in the previous years. Specific misalignment angles result in the creation of graphene superlattices, similarly to the creation of *Moiré* patterns, some of which exhibit unique properties. In particular, bilayer graphene, with the second layer rotated by 1.1° with respect to the first layer, has shown insulating – and then, with an increase of the applied electric field – superconducting behavior, as a result of the flat electronic bands formed near the Fermi energy [21]. This opened up a new research area, investigating properties of superlattices, formed by stacks of twisted (misaligned) multi-layer graphene and other 2D materials.

1.3 Properties of graphene

Physical structure of graphene, resulting in a unique electronic structure described above, is responsible for the extraordinary properties of the material, leading many to call it “the material of the future” [22], or the “wonder material of the XXI century” [23]. Those properties can be broadly divided into categories of mechanical and thermal, electronic, and optical ones. The uniqueness of graphene largely stems from the fact that it combines vastly different properties, unachievable for other materials.

Mechanical properties of graphene result from the very high stability of the sp^2 bonds, forming hexagonal lattice, which can oppose different in-plane deformations [24]. Monolayer graphene has been described as “the strongest material ever measured” [25] and the value of its Young’s modulus, measured using nanoindentation via AFM tip and assuming the thickness of 0.335nm, was found to be equal to $E=1.0 (\pm 0.1) \text{TPa}$, while the value of its intrinsic strength was determined to be 130GPa. Graphene can be stretched elastically by around 20%, which is more than any other crystal [25]. It has been found that the mechanical properties of monolayer graphene can be significantly altered by out-of-plane ripples, which soften graphene’s in-plane stiffness, and by grain boundaries, which decrease its breaking strength [26]. Thermal conductivity of graphene was found to be between 1500 and 5000 $\text{W/m}\cdot\text{K}$ at RT [27, 28], which is above bulk graphite limit (2000 $\text{W/m}\cdot\text{K}$ [29]), and remained as high as 1400 $\text{W/m}\cdot\text{K}$ at the temperature of 500K.

In terms of electronic properties, the most striking feature characterizing graphene is an extremely high electron mobility, which was found to exceed $\mu=2.5\times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [30] and $\mu\approx 6\times 10^6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 4K [31] for exfoliated samples. Mobility was found to be weakly affected by the chemical doping [32] and electron transport remains ballistic at macroscopic, micrometer scale [33]. Quantum Hall effect in graphene was observed even at room temperature [34].

Even though mobility for exfoliated, suspended samples reaches extremely high values, in case of samples produced with other methods, it is usually much lower, due to the interaction with substrates and the presence of defects. For graphene on any substrate, mobilities over 20.000 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ were rarely found [35], although this changed during recent years, with the introduction of ultra-flat hexagonal boron nitride (hBN), as a substrate and encapsulating material for graphene [36], for which mobilities of $1.25\times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at RT were reported [37]. Because of the high mobility and small spin-orbit interaction, graphene is considered to be one of the key materials for spintronics. Spin coherence length of up to 1 μm at room

temperature has been demonstrated [38] and the material has been used to fabricate, for example, spin valves [39].

Optically, graphene is commonly considered to be a transparent material, as it absorbs around 2.3% of incoming light for photon energies above 0.5eV [40]. However, because it is just a monolayer of atoms, this absorption is actually very large, compared to its thickness [41]. Because of its band structure, optical interband transitions in graphene are expected to be frequency-independent and its photocarrier density, due to the large optical absorption, is higher than in traditional semiconductors [42]. Graphene is characterized by the presence of saturable adsorption [43] and other nonlinear optics phenomena, such as the optical nonlinear Kerr effect [44]. The nonlinear graphene parameters were predicted to be orders of magnitude stronger than in other materials [45]. However, after initial high expectations, some authors have concluded that graphene as “a rather ordinary nonlinear optical material” and found that its properties aren’t superior to currently used materials [46], even though this statement has been strongly opposed by others [47].

1.4 Graphene production methods

Historically, the first method of obtaining isolated graphene was mechanical exfoliation of graphite. This process, as mentioned earlier, is based on repeated peeling off graphite flakes with adhesive tape, until thinnest possible flakes are obtained. The flakes are then transferred to an insulating substrate, usually SiO₂, for further studies. This method is remarkably simple and yields material of a very high quality. Highest obtained single-layer graphene flakes reach millimeter size [48], and the areas of mono- and multi-layer graphene can be easily distinguished, using optical microscopy, when placed on the Si/SiO₂ wafer with the right oxide thickness [49]. This technique was a method of choice for basic research and fabrication of complex devices, however, characteristics of graphene on SiO₂ are far inferior to the expected intrinsic properties of the material [50, 51, 52, 53, 54]. It was the introduction of hexagonal boron nitride as atomically smooth substrate for graphene, free of dangling bonds, charge traps, characterized by similar lattice constant, large bandgap and large optical phonon modes [36], which allowed for full utilization of the electronic properties of graphene. However, mechanical exfoliation is still significantly limited as a production method. It is inherently unscalable, yield of monolayer graphene is usually rather low, and it requires transfer and precise positioning of graphene flakes for devices fabrication. This made it necessary to develop techniques more suitable for mass-scale production, automation, and wafer-scale processing of graphene.

The natural evolution of mechanical exfoliation was a higher-throughput approach, based on liquid phase methods. Exfoliation of bulk graphite is performed with help of sonication and in different solvents [55] and the following centrifugation can help separate larger agglomerates and graphite particles, from graphene platelets with controlled thickness [56]. Resulting graphene is in the form of dispersion and the platelets are often oxidized, forming graphene oxide (GO) [57], which can then be reduced back to graphene [58]. Graphene or graphene oxide dispersions can then be used to “print” graphene onto different substrates, to create polycrystalline films, or used as additives in composites [55, 59]. While many of the extraordinary properties of the material are lost, or weakened, because of the interfaces present between different graphene flakes, and the presence of impurities, as well as agglomerates and graphite particles, this method of production seems very well suited for certain applications, which focus on utilizing mostly mechanical and thermal properties of graphene.

The most widely used method to produce large-area films of graphene with uniform thickness is chemical vapor deposition (CVD). The process utilizes carbon-containing gas, which is decomposed on the surface of a metal catalyst, kept at an elevated temperature. Upon cooling, excess carbon atoms left on the substrate rearrange into graphene structure, as shown schematically in Fig. 5.

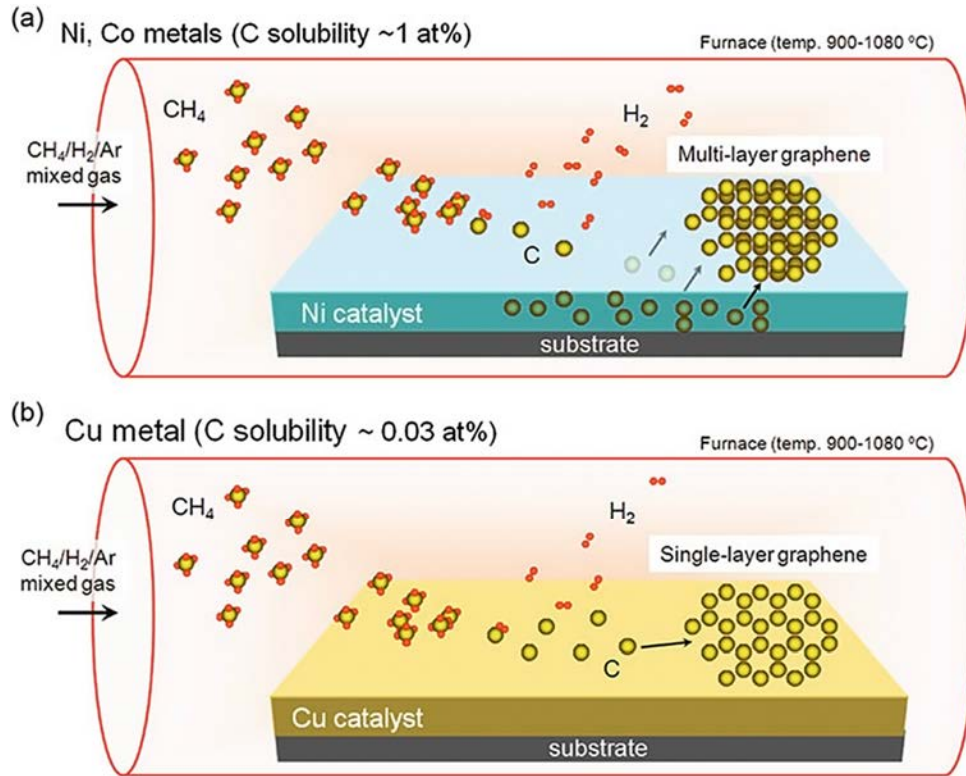


Figure 5: Growth mechanism of CVD graphene on two different metal catalysts (reprinted with permission from: [60]).

The most commonly used carbon source is methane gas (CH_4) and the used metal catalysts are usually either monocrystalline copper, Cu (111), or nickel, Ni (111), although many other materials, such as: cobalt, sapphire, or MgO [61, 62, 63], have been studied. The key to obtaining uniform coverage with monolayer graphene, is limiting the nucleation density of graphene on the catalyst surface, so that the whole layer grows in a single-grain form. Important technical factors to consider are: (1) using oxidized surfaces, (2) performing annealing of a catalyst in an inert atmosphere before graphene growth and (3) enclosing the catalyst foils to lower the precursor impingement flux during growth [64]. Growth of uniform, millimeter-sized single crystals of monolayer graphene has been demonstrated [65]. Despite recent advances, commercial CVD graphene is mostly available in a form of polycrystalline material, with grain sizes equal to several tens of micrometers. This significantly impedes electron transport in a macroscopic material, suppresses the magnetoresistance and enhances intervalley scattering, which limits the performance of the fabricated graphene devices [66].

Another challenge faced by this method, stems from the fact, that growth occurs on a metallic substrate, making it necessary to transfer graphene to an insulating surface, before it can be used to fabricate electronic devices. Many different techniques have been developed over the years, including wet, PMMA-assisted transfer, with the polymer layer serving as dissolvable carrier for graphene [67, 68], direct lithographic etching of the Cu catalyst, supporting graphene [69], dry transfer using thermal processing of PMMA [70], roll-to-roll processes [71], stamping method [72], or processes utilizing Van der Waal's forces and encapsulation in hBN [73]. Most of the currently used techniques, especially with regard to commercially available graphene, result in the degradation of the material's properties, via, for example, introduction of cracks, folds, PMMA residuals, or partial oxidation of the material [74]. Additionally, they introduce large uncertainty in the final values of the key parameters, making it difficult to implement CVD-grown graphene in an industrial setting.

This work focuses on the alternative growth method of epitaxial graphene, through a thermal decomposition of the surface of silicon carbide. It is one of the few methods that allow for wafer-scale growth and processing of graphene directly on a semi-insulating substrate, eliminating the need to transfer the material to another surface. Despite relatively high cost of the substrate, it is considered a promising route towards industrial applications of graphene in certain areas, for example high-frequency electronics, rugged electronics, or sensors.

The following sections will discuss the structure of bulk SiC, the process of graphitization of its (0001) surface and the properties of the grown graphene.

1.5 The structure of bulk SiC crystal and SiC (0001) surface

Silicon carbide is a wide-band semiconductor material, characterized by excellent mechanical and thermal properties, making it widely used as a specialty construction material, heat-resistant material, abrasive, or in the area of electronics, especially power electronics. The basic structural unit of silicon carbide is a covalently-bound tetrahedron, with 4 silicon (or carbon) atoms, coordinated around a central carbon (silicon) atom, forming Si-C bilayers. The material is characterized by the presence of one-dimensional polymorphism – polytypism. The polytypes are characterized by the different stacking sequence of the following tetrahedrally-bonded Si-C bilayers, which determine the crystal symmetry [75]. Over 250 SiC polytypes have been identified [76], existing in one of the three crystalline structures: cubic, hexagonal and rhombohedral [77]. In the crystal structure, Si (or C) atoms maintaining tetrahedral coordination can be positioned in the neighboring bilayers in one of the three inequivalent lattice points: A, B or C, leading to either zincblende (cubic) – or wurzite (hexagonal) – type bonding between the adjacent SiC bilayers. The common notation for different polytypes has the form of N “H/C/R” where N is the periodicity of the bilayer stacking, while the letter C represents cubic structure, H hexagonal structure and R rhombohedral structure. With the pure zincblende-type bonding between adjacent SiC bilayers, equivalent to ABCABC stacking of the material, cubic polytype 3C is formed, which is the only possible cubic crystal structure of the material. The other polytypes are a result of either purely wurzite-type bonding between the adjacent bilayers, or the mixture of the two, which, in turn, reduces the final crystal symmetry. The stacking arrangement of the SiC tetrahedra in the structure of 3 common polytypes is shown in Fig. 6.

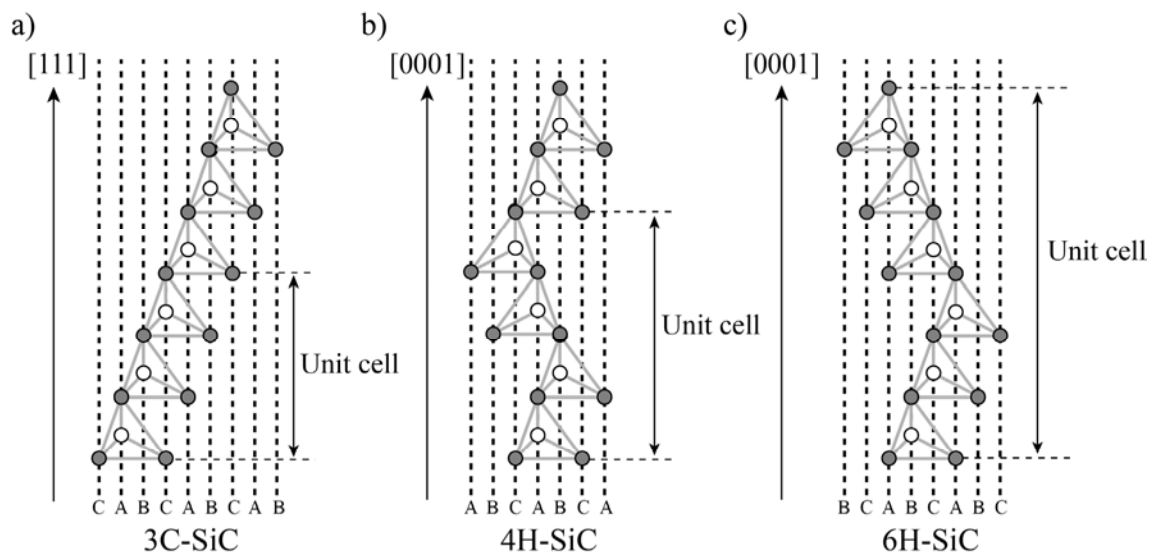


Figure 6: Three inequivalent lattice positions of a closely packed structure and the stacking arrangement of the SiC tetrahedra for: a) 3C, b) 4H, c) 6H polytype (adapted with permission from: [78]).

Different polytypes are characterized by different physical and chemical properties; for example, SiC bandgap can range from 2.3eV for 3C SiC to 3.3eV for 2H SiC. This work focuses on the 4H polytype, which is the polytype composed equally from cubic and hexagonal – type bonds. Its bandgap is equal to around 3.26eV at room temperature, with the intrinsic carrier density of $5 \times 10^{-9} \text{ cm}^{-3}$ [79]. Unit cell of 4H has the dimensions of: $a=b=3.081\text{\AA}$, $c=10.085\text{\AA}$, with the angles equal to: $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$, and is shown in Fig. 7.

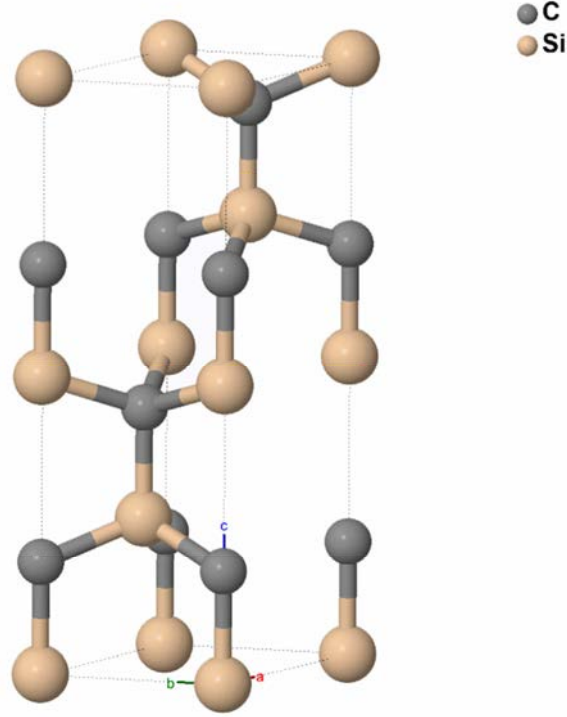


Figure 7: Unit cell of 4H SiC (created using the AFLOW library of crystallographic prototypes [80, 81]).

Most common SiC surfaces are so called “basal plane” surfaces, resulting from cutting the crystal perpendicular to the c -axis (perpendicular to the axis of the periodicity of SiC bilayers for a given polytype – i.e. along a single SiC bilayer, making it the surface layer). Two possible configurations are possible: either silicon atoms or carbon atoms are positioned at the surface after cutting the crystal. The first configuration is commonly referred to as a “Si-face” of a crystal and has the Bravais index of (0001), while the second one is referred to as “C-face” of the crystal and has the (opposite) Bravais index of (000 $\bar{1}$). It has to be noted, that the lack of mirror symmetry, with respect to the plane perpendicular to the c axis, makes the two faces and their properties fundamentally different – lower and upper faces of the crystal model shown in Fig. 6 are physically different surfaces.

In case of the Si-face of 4H polytype, 4 different configurations of the outermost SiC layer are possible, corresponding to the different position of the cutting plane in the stacking sequence (ABCBA, ABCB, ABC, or AB), or a number of identically oriented sub-surface SiC bilayers, as shown in Fig. 8.

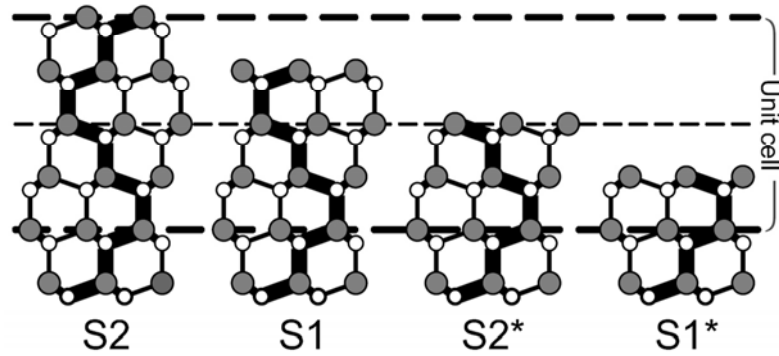


Figure 8: Four possible orientations of the topmost SiC bilayers for the Si-face of the 4H polytype of SiC; grey circles represent Si atoms and white circles C atoms (adapted with permission from: [82]).

The configurations are close to being energetically degenerate and a superposition of the different configurations gives rise to the macroscopic six-fold symmetry of the surface of the crystal, although micro-LEED measurements have shown the presence of the domains with a three-fold symmetry [83, 84]. Fig. 9a shows the (0001) surface projection (perpendicular to the *c* axis of the crystal) of the bulk SiC 4H lattice, in a ball and stick model, with marked surface projection of a crystal unit cell, and blurred sub-surface carbon atoms. Fig 9b shows the projection perpendicular to the *b* axis of the crystal, to show the configuration of surface and sub-surface atoms

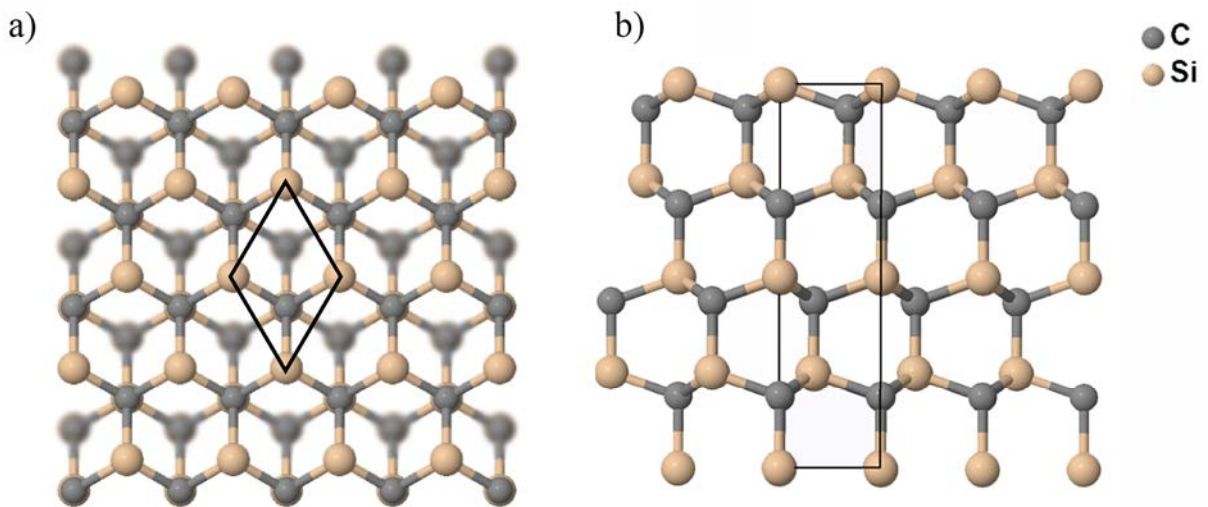


Figure 9 Projection of 4H crystal structure along: a) *c* axis (0001 surface projection), b) *b* axis, with marked projections of the bulk unit cell (created using the AFLOW library of crystallographic prototypes [80, 81]).

The unit cell has the space group $P6_3mc$ and a sketch of main symmetry elements is shown in Fig. 10.

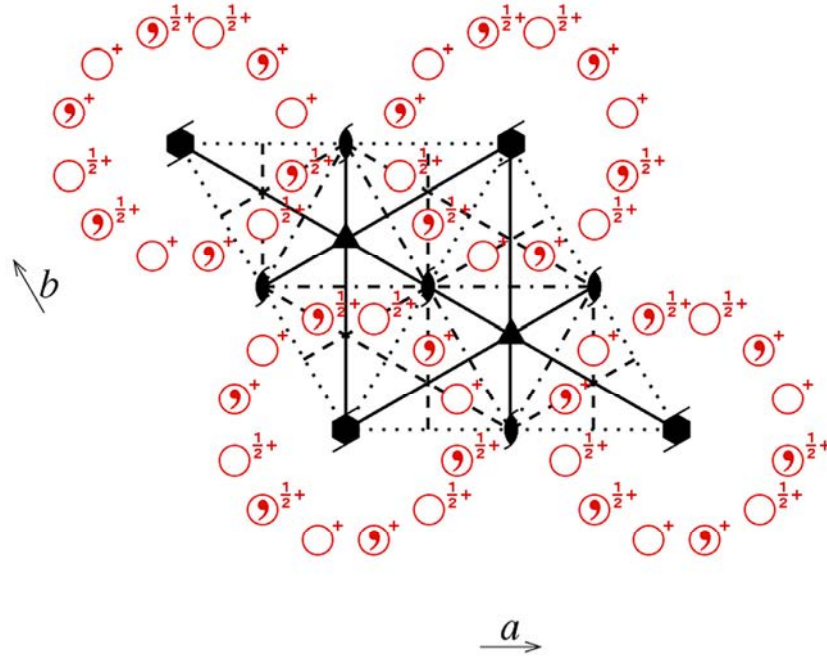


Figure 10: Main symmetry elements of the $P6_3mc$ space group [85].

In case of a two-dimensional surface, on top of which graphene will be formed, the space group $P6_3mc$ simplifies to the plane group $P6mm$. Fig 11 shows the sketch of the main symmetry elements of this group.

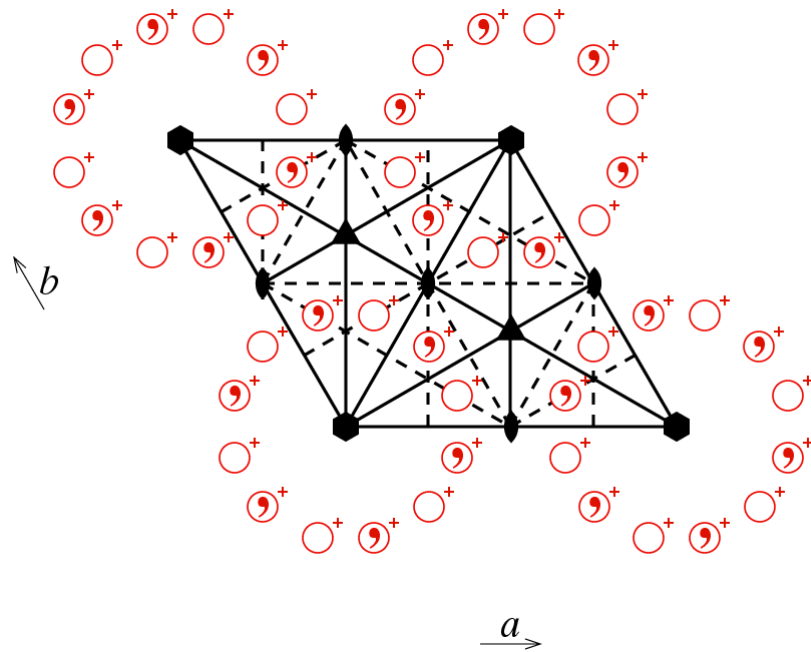


Figure 11: Main symmetry elements of the $P6mm$ plane group [86].

The length of the surface lattice vectors is equal to $3.081\text{\AA}$ (which is the same as the length of the a/b vector of the 3D lattice). The outermost Si or C atoms are bound covalently to the three atoms in the bulk crystal, but have one broken, free bond, referred to as the “dangling bond”. This energetically unfavorable configuration gives rise to several possible phenomena, such as saturation of the bonds by other atoms (for example hydrogen [87]), surface relaxation, and its reorganization into various possible surface reconstructions. This reorganization might cause the surface to have different symmetry than the bulk crystal. This is most often described using Wood’s notation in the general form of $(m \times n)R\ X^\circ$, where the surface unit cell is m and n times longer, then the surface projection of a bulk unit cell, in the two main crystallographic directions and is rotated with respect to it by X degrees.

The (0001) surface of SiC is, in general, characterized by the presence of three main reconstructions, depending on the preparation procedure. (3×3) reconstruction is formed on the surface in Si-rich conditions, in temperatures below 900°C . It is then transformed to $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase upon annealing at $950\text{--}1000^\circ\text{C}$, regardless of the Si presence, followed by the transformation into the complex $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction (often referred to as 6R3 reconstruction), formed in Si-deficient conditions at temperatures of around $1100\text{--}1200^\circ\text{C}$. The 6R3 reconstruction, which will be described in more detail in the following section, is the “buffer layer”, serving as a precursor and template for further graphene growth, which occurs, in the Si-deficient conditions, at temperatures above 1200°C . The structure of (3×3) reconstruction is the result of a Si adlayer, positioned on top of the SiC surface, with an additional, topmost Si adatom bound to the three Si atoms in the adlayer [88], while the $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructions forms as a result of a Si adatom, bound directly to three Si atoms in the topmost SiC bilayer [89]. The formation temperature of the different reconstructions can be shifted upwards, by increasing the concentration of gaseous Si at the surface. There exist many more surface phases, some of which are considered metastable, which are formed mostly at temperatures between the formation temperatures of (3×3) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ reconstructions. However, their structure and formation mechanisms have not been fully described.

1.6 Graphene on silicon carbide

Graphitization of silicon carbide is the process of the thermal decomposition of its surface. In vacuum, at temperatures above around 1100°C , silicon-carbon bonds at the surface break and Si atoms, which are, in these circumstances, much more volatile than C atoms, sublime to vacuum. Excess carbon atoms then spontaneously reorganize into the energetically favorable graphene structure [90]. The process has been described in reasonable detail as early as 1962

by Badami et. al. [4], although already in 1896 E. Acheson observed that overheating SiC leads to the formation of graphite on its surface [91].

To create a single layer of carbon atoms arranged in a honeycomb lattice, around three bilayers of SiC, must be depleted of silicon, through their thermal decomposition. This follows a purely stoichiometric argument – amount of carbon in a single graphene layer is equal to the amount of carbon in 3.139 SiC bilayers [92]. The first created carbon-rich layer is often referred to as the “buffer layer”, or a “zero-layer graphene”, and is a $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ (6R3) surface reconstruction of SiC. Carbon atoms in the buffer layer are ordered in an identical fashion as carbon atoms in graphene, but around 1/3 of them are still covalently bound to the silicon atoms of the substrate [93]. The buffer layer is insulating and serves as a “buffer” between bulk SiC and the following graphene layers. It is also responsible for the electrostatic n-type doping of the overlying graphene, shifting the Dirac point of the material by about 0.3-0.4eV below the Fermi level, in case of monolayer graphene.

Detailed structural and electronic properties of the buffer layer are still debated and different structural models are being investigated. The exact symmetry and conformation of the buffer layer is unknown and it’s been suggested that different symmetries might coexist and inter-convert at elevated temperatures [94]. In Fig. 12, a top-view scheme of a so-called CSG (covalently bound stretched graphene) model is shown, which is one of the simplest models of the layer, with exactly 30° rotation between the unit cell of the buffer layer and bulk SiC.

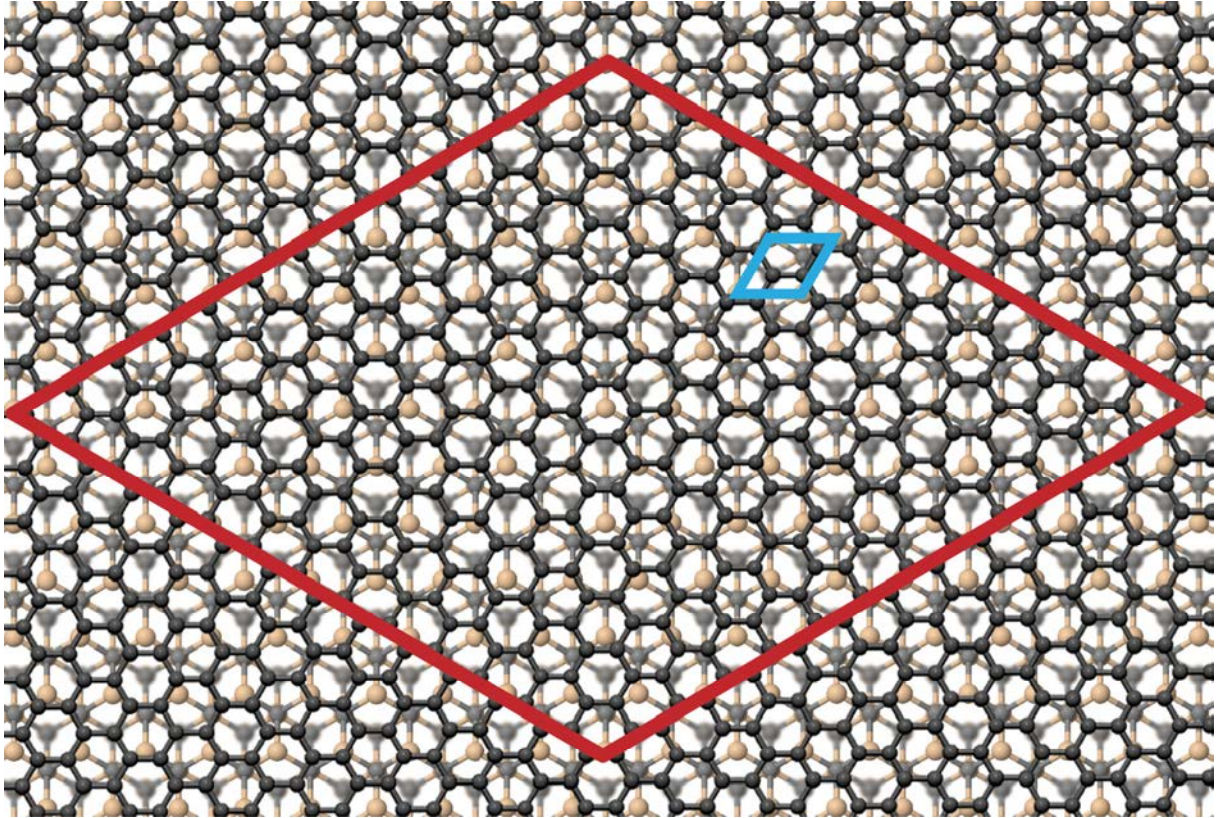


Figure 12: Top-view of the CSG model of the buffer layer (6R3 surface reconstruction) on the (0001) surface of SiC; color coding: black: carbon atoms in the buffer layer, grey: carbon atoms in bulk SiC, yellow: Si atoms in bulk SiC; the unit cell of the 6R3 reconstruction is marked in red and the surface-projected bulk unit cell is marked in blue (the same as shown in Fig. 9a; source: own work, based on the AFLOW library of crystallographic prototypes [80, 81]).

After the formation of a buffer layer, annealing at increased temperatures results in the growth of the “true”, decoupled graphene, bound to the substrate only by Van der Waal’s forces (which makes it different from the buffer layer, or “zero-layer” graphene).

Mechanism of the buffer layer and graphene formation on a reconstructed SiC (0001) surface is described as a process consisting of at least three distinct phenomena. Firstly, atomic terraces on a clean SiC (0001) surface undergo erosion, through the desorption of Si atoms, in a reverse step-flow mode – from the front of the terraces. Secondly, some terraces, with slightly less energetically stable configuration, with regard to the thermal decomposition, undergo erosion both from the front and from the back, breaking the lock-step erosion mode and resulting in the step-bunching on the surface. Thirdly, pits, originating most likely from surface point defects, are formed at the terraces, eroding them preferentially along the threefold symmetric $\{11\text{-}20\}$ planes. Some pits, with the depth of 1nm, equal to 4 SiC bilayers, are covered with graphene, while the shallower pits, with the depth of 0.5nm, equal to 2 SiC bilayers, remain graphene-free. Erosion rates of the terraces depend on the basal plane stacking sequence (see Fig. 8), with

the S2- and S2*-configured terraces having higher erosion rate than S1- and S1*-configured ones, which has been shown to induce step-bunching [95].

After these initial steps, the surface develops structures resembling elongated fingers, originating from the terrace edges, or from the edges of the deeper pits, having their height lowered by around 0.2 nm (which is the height of around 1 SiC bilayer), compared to the surface they originate from. Between the fingers, areas described as “depressed interdigitated regions” are formed, positioned around 1 nm (height of around 4 SiC bilayers) below the terrace they originate from. The terraces and fingers are covered in reconstructed SiC, while the depressed regions are covered with graphene, consistently with the stoichiometric assessment, that at least 3 SiC bilayers have to be decomposed to form a single graphene layer. A topographic AFM image, showing the aforementioned features, is shown in Fig. 13.

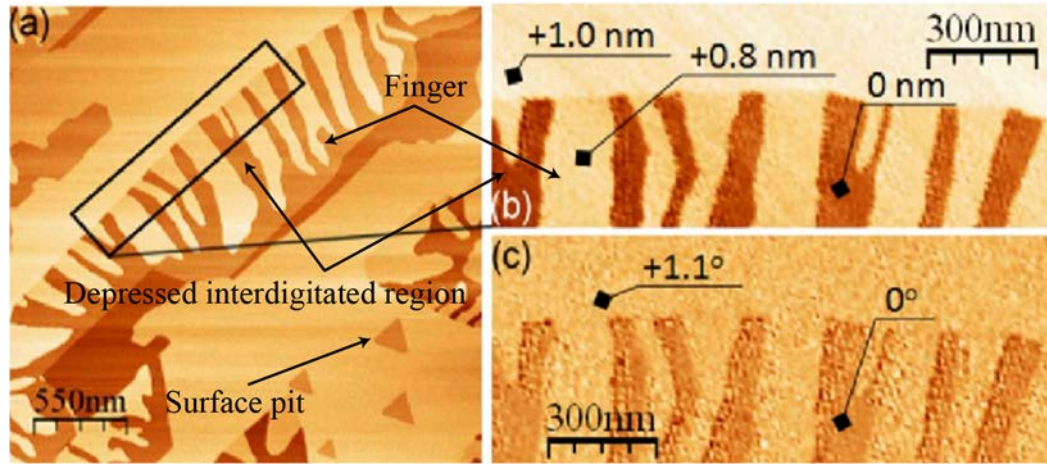


Figure 13: a) AFM image of the SiC (0001) surface during the growth of the first graphene layer; b) magnified area marked by an inset in Fig. 12a; c) phase data of the image shown in Fig. 12b (adapted with permission from: [96]).

After increasing annealing temperature or time, the surface becomes gradually more uniform, with graphene covering the whole terraces, leaving ungraphitized, elongated islands of reconstructed SiC, which are the remains of the abovementioned fingers. These islands hinder the development of continuous graphene film and are gradually eroded. These processes are schematically shown in Fig. 14.

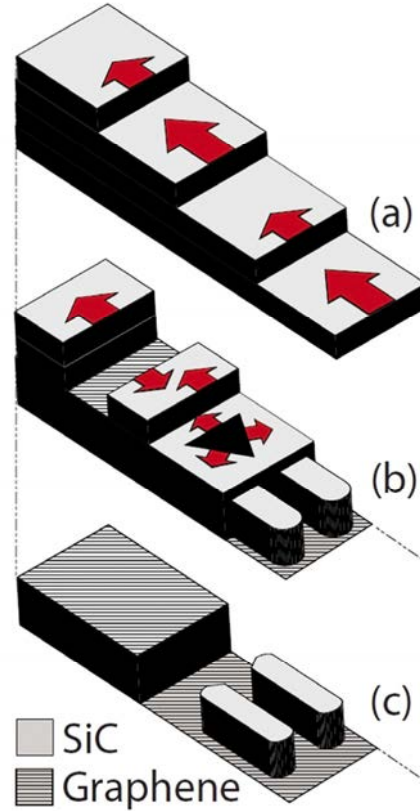


Figure 14: Graphene growth mechanisms on SiC (0001), showing: a) initial surface, with varying relative erosion rates of the terraces, represented by shorter or longer arrows; b) step bunching through an erosion of a terrace from two sides, fingers of reconstructed SiC originating in the second step-bunched terrace and the formation of pits; c) graphene-covered surface, with the islands of ungraphitized SiC, formed from the previously present fingers of reconstructed SiC (reprinted with permission from: [96]).

Atomistic graphene growth mechanisms are still investigated, but the general model is shown in Fig.15. HRTEM studies show that the graphene nucleates at step edges (1), consistently with the mechanisms described above, which is a consequence of a lower binding energy of Si atoms in step position and their preferential sublimation. Aggregating carbon atoms then form curved graphene layer, often consisting of several layers, covering step edges (2), and consequently growing over higher terrace (3), until coalescing with curved graphene formed around the next step edge (4). Graphene can sometimes continuously cover step edges, without the curved sub-surface layer, but it's often strained and defective.

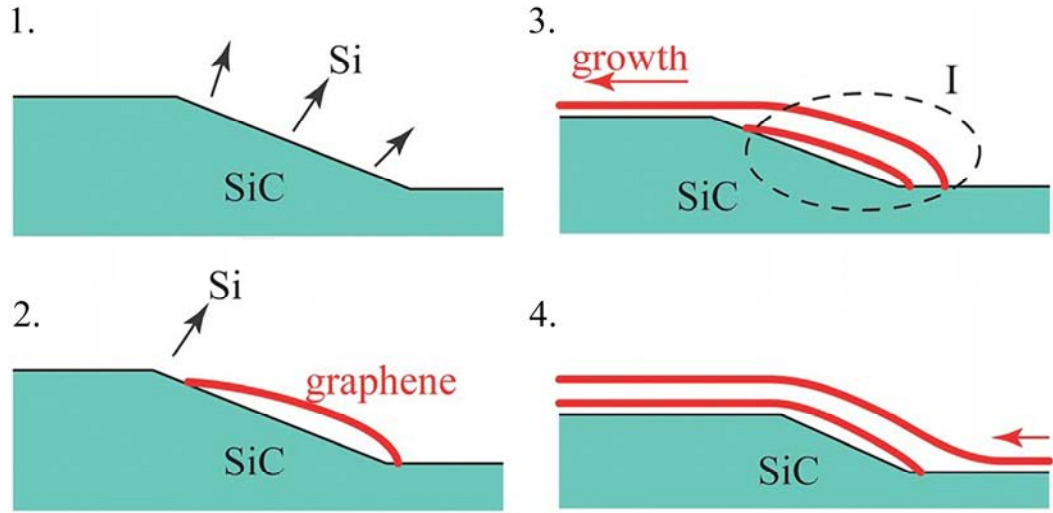


Figure 15: Growth model of graphene SiC (0001) (adapted with permission from: [97]).

The following graphene layers grow underneath the first graphene layer, according to the “bottom-up” growth model [98]. The carbon atoms from the newly decomposed SiC become the new buffer layer, while the previously present buffer layer is transformed into the first, decoupled graphene layer, on top of a newly grown material. This explains the observed low height difference between monolayer and bilayer graphene, equal to around 0.07nm, which is very close to the difference between SiC bilayer height (0.25nm) and epitaxial multi-layer graphene spacing (0.34nm), as shown schematically in Fig. 16.

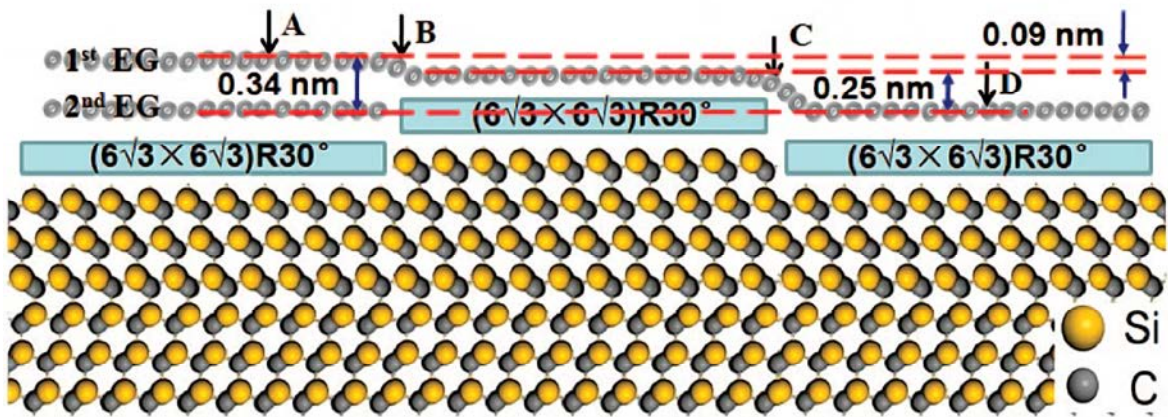


Figure 16: Bilayer – monolayer graphene boundary, with the apparent step height between the two equal to 0.09nm, in accordance to the bottom-up growth model; graphene layers are labelled EG, Si atoms are marked yellow, C atoms in grey and the buffer layer is shown as the blue rectangles (adapted with permission from: [98]).

After the creation of a second graphene layer, further growth is significantly slowed down [99]. This is attributed to the inhibition of Si removal from the surface, which, after the creation of the complete graphene layer, can escape through defects or terrace edges only [100]. Thickness of the graphene layer therefore increases with the concentration of defects in graphene and the

growth is not completely self-limiting. The process on the Si-face of silicon carbide is controllable up to the certain extent, while graphene growth on C-face is usually faster but much harder to control, leading to highly inhomogeneous surface and larger graphene coverage. Graphene grown on the C-face is also characterized by a rotational disorder. It has to be noted, that the C-face has a completely different atomic arrangement at the surface, and that the detailed discussion of the graphene growth on this surface is beyond the scope of this work.

1.7 Overcoming the limitations of SiC graphitization

In vacuum conditions, in order to avoid the formation of multi-layer graphene, SiC graphitization has to be conducted at relatively low temperatures, at which carbon atoms have limited mobility on the surface. This results in the high defect density and inhomogeneity of the grown material. Because the process is not self-limiting, as observed by low-energy electron microscopy, regions of variable thickness of graphene (1-6 monolayers) coexist on the surface [100], further deteriorating the properties of the macroscopic material. In order to improve the overall quality of graphene, it is necessary to increase process temperature, to enable higher mobility of carbon atoms of the surface, while at the same time limiting the effective sublimation rate of silicon atoms, to restrict the growth to maximum few graphene layers.

One of the proposed methods to achieve that is through placing the SiC substrate, during annealing, in a controlled atmosphere of a noble gas, such as argon. Because Si atoms leaving the sample have a finite probability of being reflected back to the surface, due to the collision with Ar atoms [101], the overall sublimation rate is reduced (alternatively, this can be understood as the increase of reaction enthalpy by a pressure-volume factor). This results in the possibility of significantly increasing process temperatures, while maintaining low graphene coverage of the surface. In case of Ar pressure equal to 1 bar (atmospheric pressure graphitization), the temperature can be increased as high as 2000°C [102], although usually lower temperatures of 1650-1700°C are used [101]. In these range of temperatures, carbon atoms have much higher mobility on surface and create higher-quality graphene layers, with relatively uniform thickness of 1-2 monolayers. Overall characteristics of the synthesized graphene are strongly dependent on the surface quality of the substrate. Other approaches developed in order to increase the processing temperature include: confinement controlled graphitization, where SiC sample is confined in a graphite enclosure, with Si leak to the atmosphere controlled via an aperture [103], capping the SiC sample with another SiC sample, to achieve relatively high partial pressure of sublimed Si near their surfaces, which has been used to produce high-quality graphene on the C-face of the compound [104], or by capping the

SiC with molybdenum plate during annealing, which was shown to induce heat accumulation at the surface, by reflecting thermal radiation, in addition to providing Si confinement [105].

Despite wide ongoing research, many phenomena, occurring during graphene growth via surface thermal decomposition of SiC, remain only partially understood and controlled. In particular, the formation of macro-steps, with the height of several tens of nanometers on the graphene covered SiC surface, via the step-bunching mechanism, and bilayer-patches near the step edges, are considered to be important issues hindering the development of future SiC/graphene-based electronics [106]. Several solutions to this problem have been studied, including tuning the heating rate of the SiC wafer [107], or using a polymer masks, serving as a source material for buffer layer formation [108].

In this work, I investigate an alternative approach to improving the process of the surface graphitization of SiC (0001). The approach is based on UHV annealing combined with exposing the surface during graphene growth to the atomic/molecular beam of Si from an external source. The beam serves as a way of effectively slowing down Si sublimation rate, however, it has several advantages over currently used methods, in particular atmospheric-pressure graphitization. Firstly, using even the purest available buffer gases at the atmospheric pressure results in the large exposition of the silicon carbide surface to unknown impurities during graphitization (of the order of 1000 L/s, in case of the buffer gas of 6N purity). In contrast, using high-purity (MBE compatible) sublimation source (using a monocrystalline Si filament) results in the beam equivalent pressure (BEP) in the range of 10^{-7} mbar and the BEP of the impurities in the range of 10^{-13} mbar in the worst-case scenario. This is possibly a significant improvement, especially in case of samples annealed for the prolonged time. Secondly, the areal density of the silicon beam can be adjusted freely, with high precision, and within a wide range of values, which creates the possibility to execute semi-equilibrium graphitization at high temperatures. This approach also allows for the co-deposition of other atoms on the graphitized surface, alongside the Si beam, which could lead to new strategies for graphene doping and intercalation. The flux of Si atoms incoming to the surface can also be spatially varied, by tilting the sample or placing a patterned aperture in front of it, creating a potentially useful tool for different applications [109]. While the preparation of ordered SiC (0001) surfaces via annealing in the Si flux is rather common and has been thoroughly described, utilizing such approach for SiC graphitization has not been studied so far. Somewhat similar ideas have been used only in course of few graphitization studies using disilane background gas [110, 111], which is, however, fundamentally different to using atomic/molecular Si beam.

Chapter 2

Experimental methods

This chapter will focus on the experimental methods used to study the structure and properties of graphene. Since graphene is the two-dimensional, surface material, surface-sensitive techniques must be applied for its analysis. Methods used in this work include spectroscopic: X-ray photoelectron spectroscopy (XPS), angle-resolved UV photoelectron spectroscopy (ARPES), diffraction: low energy electron diffraction (LEED) and microscopic techniques: atomic force microscopy (AFM), scanning tunneling microscopy (STM). After a brief introduction of the methods and their application to study epitaxial graphene on SiC (0001), experimental setup will be described. At the end of the chapter, the design of the new growth process, developed in this work, will be described, leading to the description of the obtained results in Chapter 3.

2.1 Photoelectron spectroscopy

Photoelectron spectroscopy is a broad term describing a set of spectroscopic techniques, based on the analysis of the energy and momentum of electrons, ejected from the studied material upon irradiation with photons (i.e. photoelectrons). Depending on the excitation energy of the photons, two variants used in this study can be distinguished: spectroscopy based on the high-energy X-ray photons, which excite core-level electrons and spectroscopy based on the low-energy UV photons, which excite valence-band electrons. If the angular distribution of the photoelectrons is measured, the technique can be described as angle-resolved. The main application of angle-resolved studies, in this case, is the study of the valence-band electronic structure of graphene and the term angle-resolved photoelectron spectroscopy (ARPES) will be used interchangeably with UV-ARPES (UV-based angle-resolved photoelectron spectroscopy). Angle-resolved variant can also be used with high-energy X-ray photons, in particular for increasing surface-sensitivity of the method, or for non-destructive studies of the distribution of certain elements along sample depth, but for most experiments described here, the simple, non-angle-resolved variant will be used. Since in the experiments, photoelectrons ejected from the sample are measured, an analysis chamber requires ultra-high vacuum conditions (pressure $p < 1 \times 10^{-10}$ mbar), to ensure no scattering between electrons and residual gas atoms. In both variants, a single hemispherical analyzer is used to separate electrons with respect to their energy and momentum.

Photoelectron spectroscopies are considered, in general, surface sensitive, mainly due to the low inelastic mean-free path λ_m of free electrons in solids. In case of XPS and the typically used energies of 100-1200eV, the mean free path has the value of around 5-20Å [112], while for the energies typically used in APRES experiments of 10-100 eV, the mean free path has the value of around 10-30 Å [113]. In case of two-dimensional materials, however, those mean free paths are several times larger than their sub-nanometer thickness. This means that any measured photoelectron signal will have the components associated with the studied graphene, underlying buffer layer and bulk SiC, as these form the first few atomic layers of the studied samples. In this case, however, both valence-band and core-band electron energies of graphene and other components are well separated, simplifying the experimental setup and data analysis and justifying the choice of non-angle-resolved XPS studies of the graphene samples.

2.1.1 X-ray photoelectron spectroscopy

In the simple variant, XPS experiment analyzes the distribution of the kinetic energies of the photoelectrons emitted from the sample upon irradiation with X-ray photons. The scheme of an experiment is shown in Fig. 12:

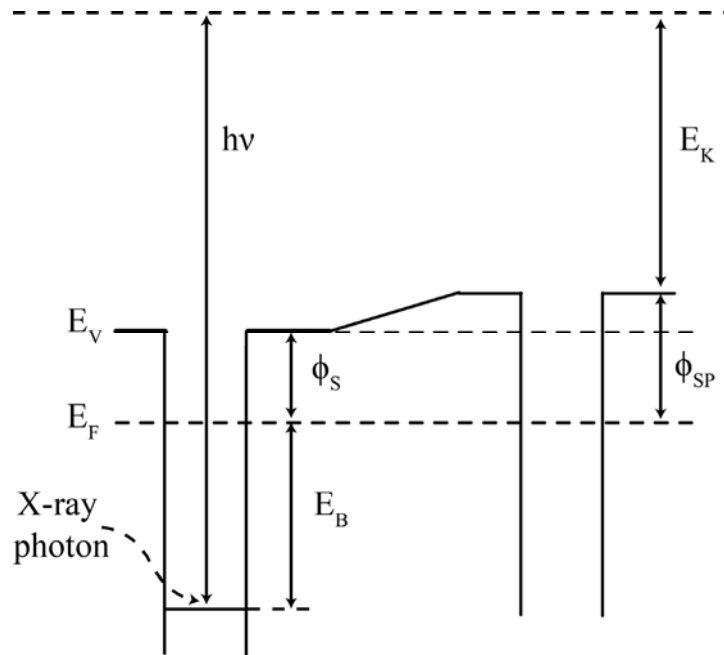


Figure 17: Scheme of a typical XPS experiment; E_B is the binding energy of the electron, ϕ_s the workfunction of the sample and ϕ_{sp} the workfunction of a spectrometer.

Following simple energy conservation rules, the binding energy of an electron in the sample can be related to the measured kinetic energy by the relation:

$$E_k = h\nu - E_B - \Phi_{sp}, \quad (14)$$

where $h\nu$ is the (known) energy of the X-ray photons, ϕ_{sp} the effective workfunction of a spectrometer, which includes the contribution from the analyzer, E_B is the binding energy of the emitted electron (referenced to the Fermi level) and E_k is its measured kinetic energy. Since the workfunction can be compensated through spectrometer calibration to the binding energy of the known elements, the binding energy can be effectively described as:

$$E_B = h\nu - E_k, \quad (15)$$

and the measured distribution of kinetic energies of the photoelectrons emitted from the sample can be easily transformed into the distribution of their binding energy.

The distribution of the binding energies of emitted photoelectrons shows peaks at the elemental binding energies of the atoms forming investigated samples, creating a fingerprint of a given compound. Several different effects can modify or split the binding energy peaks, making it possible to extract much more information about the compound than simple information about its composition. The exact position of a given peak can change, depending on the chemical environment of a given element, which is known as a **chemical shift**. If there are atoms in several different chemical environments, their peaks will be shifted towards higher or lower binding energies, creating a set of neighboring peaks in the spectrum, with different energies specific for those environments. For peaks corresponding to the unpaired electrons in a degenerate orbitals (i.e. p, d, f), due to the interaction between orbital angular momentum and spin angular momentum, i.e. **spin-orbit splitting**, new energetic states will appear, corresponding to different values of the total electronic angular momentum, given by:

$$J = |L \pm S|, \quad (16)$$

where L is the orbital angular momentum ($L=0,1,2,\dots$), S is the spin angular momentum ($S=1/2$) and J is the total angular momentum ($J=1/2, 3/2, 5/2$). For a given value of L , XPS spectrum will show either a single peak for $J=1/2$ (in case of $L=0$, or the s shell), or a doublet, for example for $J=1/2$ and $J=3/2$ (in case of $L=1$, or the p shell), or $J=3/2$ and $J=5/2$ (in case of $L=2$, or the d shell). The degeneracies of these states is equal to $2J+1$ and the relative intensities of the peaks are given by the ratio of the degeneracies (for example, for the p shell, the area ratio of $J=1/2$ and $J=3/2$ peaks is equal to 1:2, while for the d shell, the area ratio of $J=3/2$ and $J=5/2$ peaks is equal to 2:3).

Different initial-state or final-state effects might lead to the detection of different **satellite peaks** around the main peak for a given state. **Shake-up** and **shake-off** peaks occur at higher binding energies, then the initial peak, due to the emission of a photoelectron from an excited state of

the atom – which often results from the previous ground-state photoemission from the same atom. Additionally, other effects often result in the detection of **plasmon loss**, **Auger electron**, or **ghost peaks** (coming from X-ray photons emitted by the impurities in the X-ray source, commonly Mg impurities in the Al source).

Despite these complications, XPS can be used for a reliable semi-quantitative analysis, based on the fact that the ionization probability (cross section) of a core level is practically independent from the valence state of the element [114]. This means that the peak intensity (integrated area under a given peak) is proportional to the number of atoms of the given element, in the particular chemical state. For a homogeneous sample, intensity of a peak can be expressed as:

$$I = KN\sigma\lambda AT, \quad (17)$$

where I is the intensity of a peak, K is a constant, N is the number (or density) of atoms in a given state, σ is the photoionization cross section, λ is the inelastic mean-free path of an electron, A is an area of the sample and T is the analyzer transmission function. If we define the sensitivity factor S for an element x as:

$$S_x = K\sigma\lambda AT, \quad (18)$$

then the relative concentration of different atomic species is proportional to peak intensities:

$$N_x = I_x/S_x. \quad (19)$$

The situation is further simplified, if we are comparing the relative concentrations of different chemical states of a given element, for example carbon in either graphene, where only C-C bonds are present, or in bulk SiC, when it is covalently bound to silicon, as the sensitivity factor, in principle, doesn't need to be known. Of course, this is only true for uniform thin films and many other effects, such as surface inhomogeneities and morphological factors complicate the analysis. This approach, however, works well as the approximation of the true relative concentration of a different chemical states of the element. For the comparison of different elements, there are many works describing their relative sensitivity factors, both empirically and theoretically [115, 116]. In case of heterogeneous samples, such as the ones studied in this work, the results have to be treated with caution, hence XPS is described only as a semi-quantitative method. However, experimental results confirm the relative accuracy of this kind of analysis, especially for the overlayer-type samples (such as graphene/buffer layer/bulk SiC system studied in this work), with regard to the determination of the coverage of thin overlayers.

2.1.2 Angle-resolved UV photoelectron spectroscopy

All of the considerations mentioned above, regarding energy conservation and conversion of the kinetic energy of the electrons to their binding energy, continue to apply to the angle-resolved UV photoelectron spectroscopy. In case of this technique, however, the excitation energy of UV photons is much lower, so the photoelectrons come from the valence band of the material. Additionally, besides measuring the energy distribution of the emitted photoelectrons, their angular distribution after emission is measured as well. The scheme of a typical ARPES experiment is shown in Fig. 18.

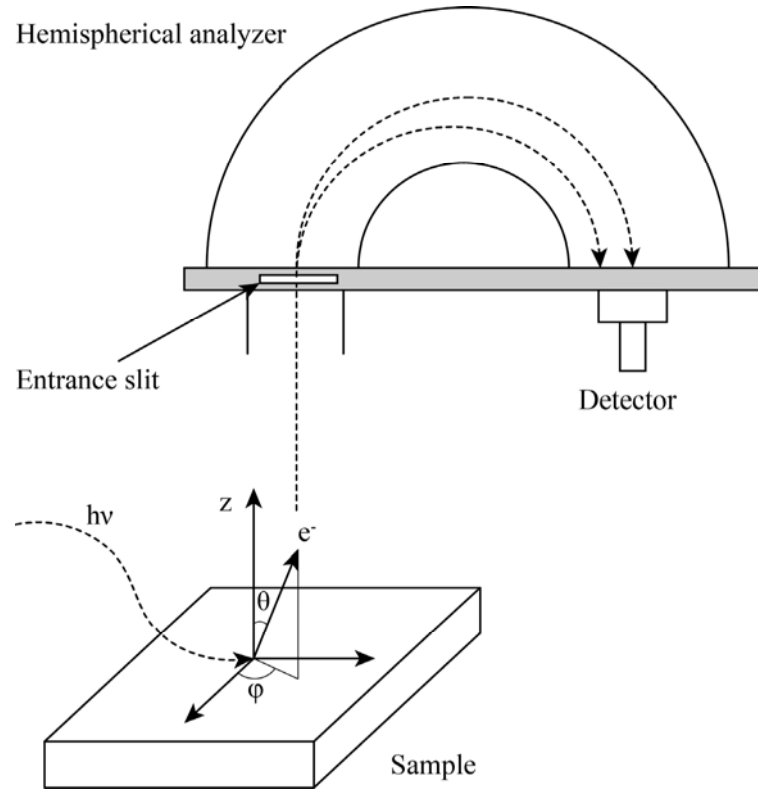


Figure 18: Scheme of a typical ARPES experiment.

For further considerations, it is useful to consider the electron behavior upon irradiation with UV photons in terms of a so-called three-step model, which is a phenomenological description developed by Berglund and Spicer in 1964 [117]. According to the model, three steps involved in a photoemission process are:

1. Optical excitation of the electrons in solid – direct (momentum-conserving) excitation of an electron to the final state. It is assumed that the whole volume of the solid within the penetration depth of UV photons has the same probability of participating in the process. Excited electron can be then described in a semi-classical fashion, because, on average, the

excited wave packet is well localized with respect to the distance from the surface [118]

2. Transport of the electron to the surface – taking into account the dominant scattering mechanism, which is electron-electron interaction, and assuming isotropic scattering frequency, the mean-free-path of an excited electron is equal to

$$\lambda = \tau v_g, \quad (20)$$

where τ is the lifetime and v_g is the group velocity of a wavepacket. The fraction of the photoelectrons reaching the surface, excited within the mean-free-path distance from the surface, in the classical treatment and in the limit of low mean-free-path, as is the case for an ARPES experiment, can be expressed as:

$$d = \alpha \lambda, \quad (21)$$

where α is the optical absorption coefficient of light [117].

3. Escape of the electron into vacuum – described using the “escape cone” argument, according to which only electrons, which have the component of the kinetic energy perpendicular to the surface sufficiently large to overcome the surface potential barrier, are transmitted into vacuum, while the others are totally reflected back into the crystal. In Fig 14, the scheme of a photoelectron emission into vacuum is shown.

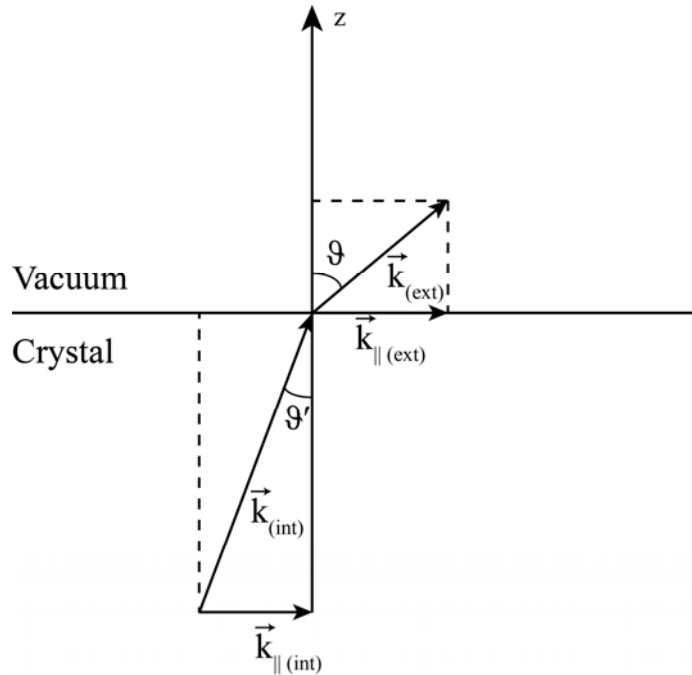


Figure 19: Scheme of a photoelectron emission into vacuum.

While the component of the electron momentum perpendicular to the surface is changed, the component parallel to it is conserved, while crossing crystal-vacuum boundary. In the free-electron final state model, the final state of the electron is characterized by the purely parabolic dispersion. The wave vector of the photoelectron in vacuum is given by the intersection of a free-electron parabola (with zero energy at the vacuum level) and the energy of the final state of the electron. It can be then shown that the parallel component of the electron momentum is given by:

$$\vec{k}_{||(\text{int})} = \vec{k}_{||(\text{ext})} = \sin(\vartheta) \left(\frac{2m}{\hbar} E_{\text{kin}} \right)^{1/2}. \quad (22)$$

Since the escape angle outside the crystal (ϑ) is larger than the “incidence” angle of an electron inside the crystal (ϑ'), for a given final state energy there is a maximum angle inside the crystal, at which the electrons can pass the crystal-vacuum boundary. This angular region defines a so-called “escape cone” of an electron.

The three-step model has some limitations. It doesn't allow for the determination of the momentum component perpendicular to the surface, due to the assumption of a step-function potential at the surface of the crystal; it also violates the uncertainty principle [119], in the assumption of a localized and isolated excitation of an electron, which is followed by the energy loss only after the excitation. These approximations are further extended, by neglecting the momentum of the incoming photon, applying sudden approximation, which leaves the electron states in the crystal unchanged after the excitation of a single electron and by ignoring multi-electron interactions. However, despite those simplifications, countless experiments have shown, that the model is a very useful and accurate representation of the photoemission process and that the introduced approximations can be reasonably applied.

Using Eq. 15, with the reference energy equal to the Fermi energy, and Eq. 22, with the electron emission angles measured by a hemispherical electron analyzer, a whole band structure of the solid (dispersion relation of the electrons in the valence band: $E_{||}(\mathbf{k})$) can be reconstructed and directly visualized. The situation is simplified in case of graphene, because for a two-dimensional material, only the component of the electron momentum parallel to the “surface” is present, so that the measured dispersion relation is equal to the electronic structure of the material. In case of three-dimensional materials, ARPES experiment is able to measure only the surface-projected band structure and the presence of various effects, such as surface states and surface resonances, might complicate the analysis. Measurement of the momentum

component parallel to the surface, is also possible, by measuring a series of spectra for $k_{\parallel}=0$ (at the normal emission), with varying photon energy.

2.2 Low energy electron diffraction

Low energy electron diffraction is a surface-sensitive diffraction technique, using the beam of low-energy (most often 25-600eV) electrons as the probe. The diffraction is possible due to the dual (wave-particle) nature of an electron, observed as early as 1927 by Davisson and Germer in the experiments concerning “the reflection of electrons by a crystal of nickel” [120]. The expression of a wavelength λ that can be attributed to the electron with a mass m and energy E has been predicted by de Broglie in 1924 [121] and has the form of:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}, \quad (23)$$

where p is the electron momentum and h is the Planck’s constant.

In the energy range typically used in LEED experiments, the electron wavelength is equal to around 0.25-2.5Å, making it suitable to study the atomic arrangement of a crystal’s surface. The typical setup of a LEED experiment is shown in Fig. 15

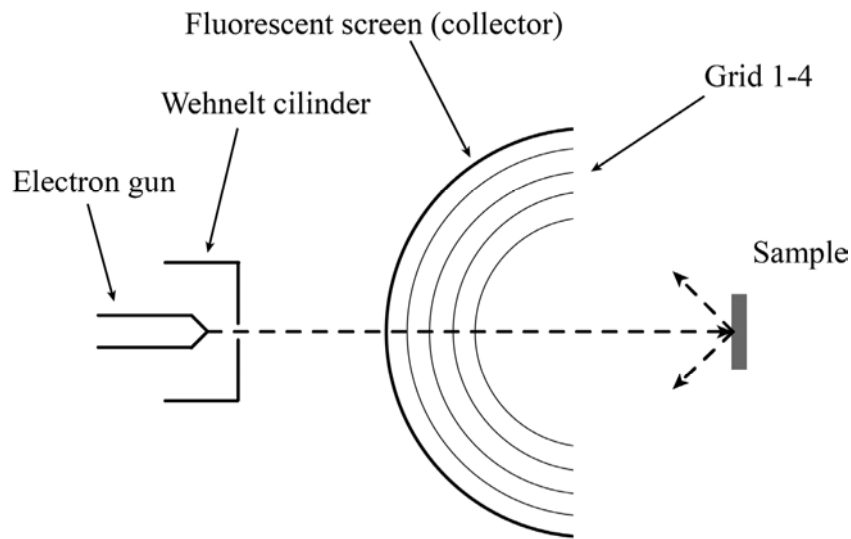


Figure 20: Typical setup of a low energy electron diffractometer

A collimated electron beam, emitted by the electron gun, is accelerated towards the sample, usually at normal incidence, where it becomes reflected and diffracted. The diffracted electrons are then passed through a number of grids, designed to filter only elastically scattered electrons, and then accelerated towards a detector, most often a fluorescent screen, where the diffraction pattern of a sample can be observed. Typically, the electron gun has a cathode filament with Wehnelt cylinder, acting as a control grid and a convergent electrostatic lens for the emitted

electron beam, followed by the set of other electrostatic lenses. The cathode is kept at a negative potential, while the last lens aperture, the sample and the first grid are grounded [122]. The second and third grids are designed to filter inelastically scattered electrons and are being held at a voltage similar to the cathode's voltage, but slightly changed by a tunable value of ΔV (thus allowing for the control of the filtering range), while the fourth grid is again grounded, to shield second and third grids from the fluorescent screen's accelerating voltage (typically 2-5kV).

Since the mean-free path of low-energy electrons diffracted by the sample is very short (on the order of a few atomic layers), most of the elastically scattered electrons will come from the surface of the sample, making this technique suitable to study the two-dimensional atomic arrangement of the crystal's surface (and topmost sub-surface layers). Laue's condition for the diffraction, in case of 2D surface, can be expressed as:

$$\Delta \vec{k} = \vec{G}_{hk}, \quad (21)$$

where $\Delta \mathbf{k}$ is the electron scattering vector (the change of the wave vector of the electron scattered by lattice) and $\mathbf{G}_{hk}$ is the surface reciprocal lattice vector. This applies only to the component parallel to the surface, since component normal to the surface (2D lattice) is not restricted directly by the scattering but only by the general energy conservation rule. Ewald's construction for LEED diffraction is shown in Fig. 21

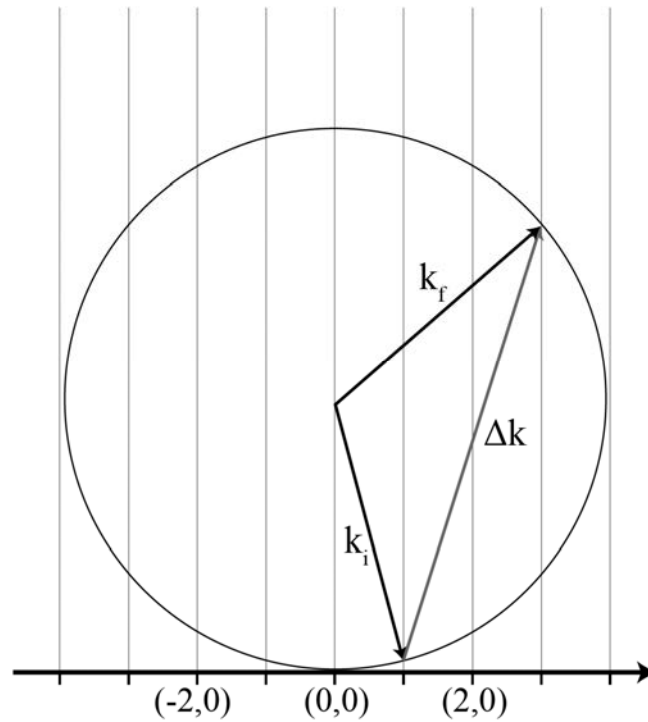


Figure 21: Ewald's construction for LEED diffraction.

Diffraction rods, present in the construction instead of the usual diffraction points (found in case of the 3D crystals), reflect the fact that, for scattering on a 2D lattice, the wavevector component normal to the lattice is not restricted in scattering and the circle provides energy conservation. The wavevector component for a diffraction spot from a 2D lattice is observed, when the scattering vector ($\Delta\mathbf{k}=\mathbf{k}_i-\mathbf{k}_f$) intersects with one of the diffraction rods (in other words, the momentum condition: $\Delta\mathbf{k}=\mathbf{k}_i-\mathbf{k}_f$ and energy conservation condition must be satisfied simultaneously).

LEED is a useful tool allowing for the determination of the crystal symmetry of the surface, however, much more information can be extracted from the analysis of a diffraction pattern. Any disorder on the surface will cause an increase in the background intensity, weakening and, in some cases, broadening of the diffraction spots (spot width is determined by the number of interfering beams, so it is influenced by the coherence length and is sensitive to the size of crystalline domains). Spot profile, i.e. the intensity distribution in a single diffraction spot, contains further information about any deviation from a perfect 2D periodicity of the surface (for example the domain size, since the spot width is inversely proportional to the number of scattering units). Even in case of a perfect 2D periodicity, intensity of the spots is modified by so called “structure formfactor”, containing information about the local atomic environment. This can lead to varying intensity or even disappearance of certain diffraction spots from the pattern. Since the penetration depth of the electrons isn’t limited to a single, two-dimensional layer, there is also a contribution from the 3D crystal ordering. Altogether this is the basis of dynamic LEED experiments (analysis of the relationship between spot intensity and the accelerating voltage, in the form of I-V curves), which probe, model and refine this intensity variation, which can be then used to solve the crystal structure of the surface. However, even simple LEED experiments are extremely useful in terms of the identification of surface symmetries and structures (since their diffractograms are unique and can be used as fingerprints), as well as the qualitative assessment of the ordering quality.

2.3 Scanning probe microscopy

Scanning probe microscopy (SPM) is a broad term describing a set of various microscopic techniques, which use a certain physical signal (a probe), which can be mechanical, electrical, or electromagnetic in nature, in order to scan the surface of the sample in a raster fashion. Most SPM techniques measure more than one signal simultaneously, providing information other than just the surface morphology. In most cases, scanning is performed with the use of a physical, sharp tip, which is controlled electronically with help of various feedback loops, in

order to stay either in a constant height above the surface, or in a constant interaction with the surface, during the raster scan. The microscopic images obtained using SPM are not diffraction-limited and can reach atomic resolution. The movement of the tip (or the sample) is precisely controlled using, in most cases, piezoelectric actuators. External vibration of the environment has to be adequately suppressed, with help of different passive and active components, in order to achieve desired stability, allowing for precise imaging of the surfaces.

2.3.1 Atomic force microscopy

Atomic force microscopy (AFM) is a SPM technique, using physical interaction of the tip with the surface, as the scanning probe. The interaction of the tip with the surface, in case of chemically passive contact and lack of other interactions between the tip and the surface of the sample, can be approximated using Lennard-Jones potential in the form of:

$$V(r) = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right), \quad (22)$$

where r is tip-surface separation, ε is the depth of the potential well and σ is the distance, at which the potential between the tip and the surface is equal to zero. Plot of the potential is shown in Fig. 22.

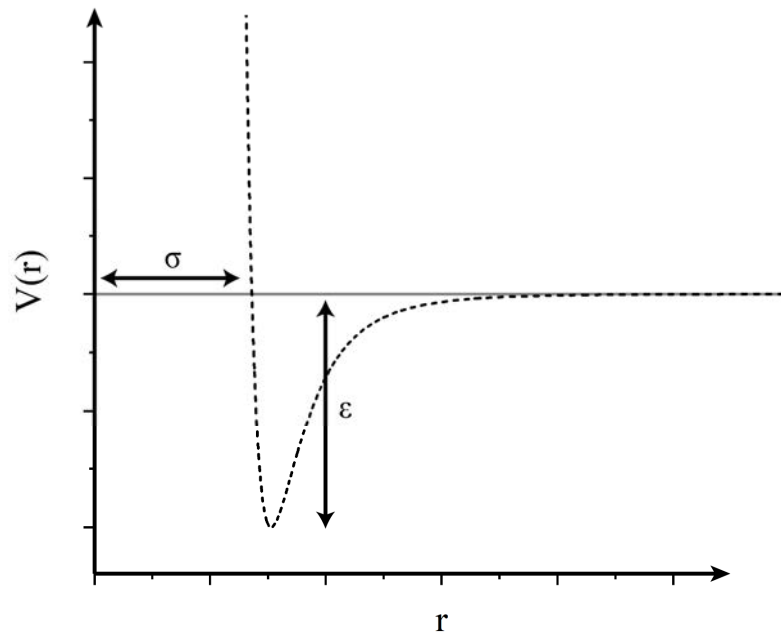


Figure 22: Plot of the Lennard-Jones potential

The potential consists of two main parts: repulsive short-range interaction (positive values of the potential for $r < \sigma$) and attractive, long-range interaction (negative values of the potential for $r > \sigma$) with the surface. AFM can operate in different modes and probe different interactions with the surface. If the tip is brought close to the surface, it is said to operate in a “contact mode”,

operating in the repulsive regime of the interaction and being in a direct mechanical contact with the sample. If it's far away, it's in a "non-contact" mode, operating in the attractive regime – in this case the tip is usually vibrated at a resonant frequency and the interaction is detected by the shift in the oscillation amplitude or frequency. The intermediary mode is so called "tapping", "dynamic force" or "intermittent contact" mode, in which the tip is vibrated at a resonant frequency, and operates between the repulsive and attractive regimes, periodically coming into the direct contact with the sample.

The scheme of a typical AFM experiment operating in the dynamic force mode is shown in Fig. 23.

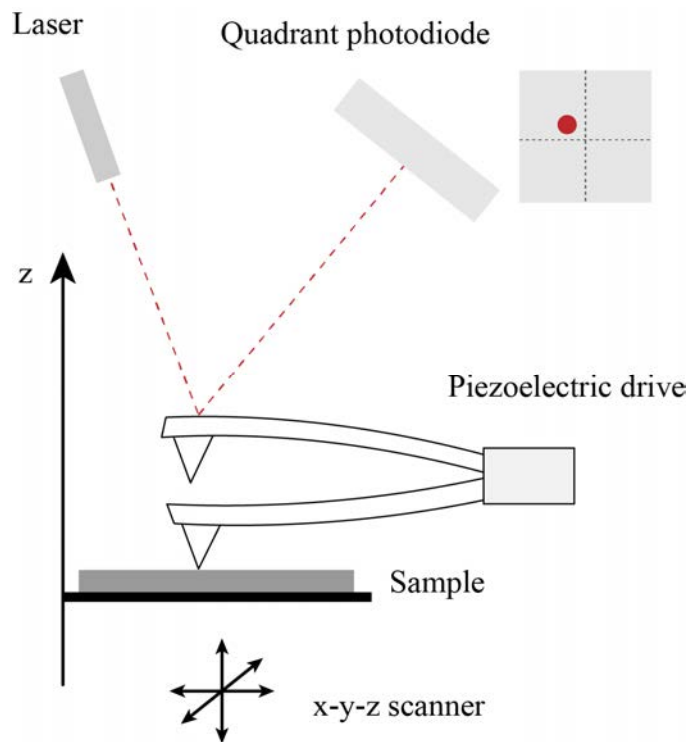


Figure 23: Scheme of a typical AFM experiment in a dynamic force mode.

The motion of the tip is measured using a laser beam, reflected from the tip of the cantilever and detected by the position-sensitive detector, such as a quadrant photodiode. The tip is oscillated at its resonant frequency and the phase and amplitude of the oscillation is measured. Due to the interaction with the surface, the resonant frequency changes, followed by the change of tip oscillation amplitude and phase, which can both be used as inputs for the feedback loops controlling the tip-surface separation. Usually, the constant-amplitude and frequency signal from the function generator, which is driving the piezoelectric element and, in turn, the cantilever with the tip, is also used as a reference signal for the lock-in amplifier and compared with the actual resulting amplitude or phase shift of the vibration. This allows for the

reconstruction of surface topography, while avoiding the lateral tip-sample forces, which can negatively affect the resolution of the images obtained using conventional contact mode AFM, where the tip and the sample are in direct contact. Dynamic force AFM is a useful technique for studying relatively large areas on the surface of the samples (on the order of $10 \times 10 \mu\text{m}$) and investigating surface morphology. While AFM measurements don't usually reach atomic resolution, with the exception of rather complex non-contact AFM experiments, performed in vacuum [123], often with the aid of tips functionalized with various molecules, such as CO [124], the resolution, especially in the vertical direction, offered by the tapping mode with high-quality tips is sufficient to study atomic terraces, step-bunching phenomena and growth mechanisms of graphene on SiC (0001).

2.3.2 Scanning tunneling microscopy

Scanning tunneling microscopy (STM) is a SPM technique, utilizing electrical current, tunneling between the conductive tip and the slightly separated from sample's surface, as the scanning probe. The physical basis of this technique is tunneling of an electron through a potential barrier. In a quantum mechanical description, the particle with an energy E has a non-zero probability of passing through a barrier having the height U_0 , higher than the particle's energy, which would be impossible in a classical description. In case of STM, depending on the electrical bias, electrons are either tunneling from the tip to the sample (probing the unoccupied electronic states), or from the sample to the tip (probing the occupied electronic states), with the thin layer of air or vacuum, separating the tip from the surface, acting as a potential barrier. Similarly to AFM, discussed in section 2.3.1, the tip is then raster-scanned across the surface of the sample and the semi-topographic image, which will be discussed in more detail below, can be reconstructed from the spatial variation of the tunneling current (if the tip-surface separation is held constant), or the variation of tip-surface separation, adjusted by the feedback loop (if the tunneling current is held constant and used as the input to the feedback loop). The tunneling current decreases exponentially with the increasing barrier width (tip-surface separation), making this technique extremely sensitive to the local height variation in the sample. For example, in case of the work function of a material equal to 5eV and the height increase of $1\text{\AA}$, tunneling current decreases nearly an order of magnitude. Because of this sharp decay, it is assumed that a single atom on a tip, being the closest one to the surface of the sample, carries the majority of the tunneling current, making it possible to obtain atomic resolution of the images.

Even though the interpretation of the STM images seems straightforward, they are in fact not true topographic images, because they contain information about the electronic states of both imaged sample and the tip, at a given tip position. For the metallic sample and small bias U applied to the surface (satisfying the condition that the variability of the electronic structure over the energy change by eU at the Fermi level may be neglected), the tunneling current $I(d,U)$ can be approximated by:

$$I(d, U) \propto eU \rho_{\text{sample}}(z = d, E_F), \quad (23)$$

where U is the bias potential between the tip and the sample, d is the tip-sample separation and ρ_{sample} is the local density of states of the sample at the Fermi energy, at a distance d . In real measurements, especially of semi-conductors, the situation is even more complicated and different states can be probed by using varying tip-sample bias. Time-dependent perturbation theory calculations (so-called Bardeen approach [125]) led to the theoretical interpretation of tunneling spectroscopy measurements, during which the bias voltage between the tip and the sample is varied and the dynamic tunneling conductance dI/dV is measured. Assuming a free-electron tip the measured conductance can be approximated by

$$dI/dV \propto \rho_{\text{sample}}(E_F - U), \quad (24)$$

where ρ_{sample} is the local density of states of the sample at the energy equal to the difference between Fermi energy and the applied bias voltage.

Interpretation of the STM images is not straightforward and requires consideration of multiple effects, compensation for image artifacts, and quite often, simulations of the electronic structure of a given surface. However, the possibility of achieving atomic resolution and directly imaging the surface symmetries, presence of defects, and other phenomena, makes it very suitable for studying the detailed structure of graphene on SiC (0001), as well as the underlying buffer layer.

2.4 Experimental setup

The main experimental system used for graphene synthesis and characterization consists of 3 vacuum chambers: load lock, used for fast sample loading and unloading, preparation chamber, where graphene is prepared, and analytical chamber, where spectroscopic and diffraction measurements are performed. The base pressure in the preparation chamber is equal to around 4×10^{-10} mbar and in the analytical chamber to around 5×10^{-11} mbar. Samples are transferred between the chambers using a linear transfer system and a sample storage system is available. Ultrahigh vacuum is obtained and maintained with use of turbomolecular, ion and titanium

sublimation pumps. Vacuum properties and residual gas composition are regularly monitored using a quadrupole mass spectrometer (RGA).

Preparation chamber has several viewports and ports for evaporators. The main heating element used for graphene synthesis is an electron-beam type heater, in which a beam of energetic electrons directly hits the backside of the samples, accelerated by the voltages ranging from 200 to 1000V. Measured emission current of the heater is usually in the range of 0-150mA/cm² and sample temperatures can reach up to 2000°C. Because the thermal contact between the sample and the rest of the manipulator is poor, and the heating power is directly focused on the sample, heat losses are mostly radiative, leading to high heating efficiency and minimal contamination of the vacuum by degassing metal elements. Pressure during high-temperature annealing remains below 1x10⁻⁸ mbar, most often in the mid 10⁻⁹ mbar range. Electron beam heater uses accelerating voltage as a method of temperature control. Because the surroundings of the sample aren't heated, this allows for very fast-responding and precise control of heating and cooling rates of the samples, which can be easily varied from several to several hundred °C per minute. Temperature is measured using an infrared pyrometer, with an emissivity calibrated to the melting point of silicon. It has to be noted, however, that the absolute values of the surface temperature are difficult to be accurately measured. The emissivity of the surface is unsure (usually it's assumed that it's equal to $\epsilon=0.9$) and can change slightly following graphene growth. However, the temperature measurement for a given emissivity is repeatable.

Silicon sublimation source SUSI 40 produced by Dr. Eberl MBE Komponenten [126] is used to produce silicon flux at the annealed surfaces. High purity intrinsic Si filament, shielded by pure silicon parts and lack of ceramic parts in the hot zone of the source, results in a very high purity of the flux. Si filament, which is directly heated by the passing current, has the resistivity higher than 1 kΩ/cm, translating into >99.9999% purity. Si beam equivalent pressure of around 10⁻⁷ mbar is typically used in the experiments, which translates into an extremely low value of BEP of the impurities equal to around 10⁻¹³ mbar. Si flux at the sample is calibrated using quartz microbalance, positioned at the same distance from the silicon source as the sample, and re-calibrated on a regular basis. Measured growth rate of Si varies between 1Å/min and 30Å/min, which translates into Si flux densities of 0.06 to 2.5 ×10¹⁴ cm⁻² s⁻¹. It should be noted that the flux used in the experiments is atomic/molecular in nature and contains only silicon atoms, in contrast to the background vapor of silane or disilane, which many authors often refer to as “Si flux” [111]. While the difference might seem elusive, in case of gaseous silicon compounds, such as silanes, different reactions have to occur on the annealed surface, with regard to

molecule adsorption and Si-H bonds breaking, while in case of atomic/molecular Si flux, such additional steps are removed.

Photoelectron spectroscopy measurements are performed in an analytical chamber, with the use of a hemispherical Gammatdata-Scienta R4000/WAL/ARPES energy analyzer, equipped with MCP detector and a single electron imaging system. The analyzer is capable of imaging up to 600 angular channels covering between 7° and 30° and up to 1000 energy channels. The energy resolution of the analyzer is equal to around 10meV, while the angular resolution to around 0.1° . High brightness HeI/HeII RF-type UV photon source (Gammatdata-Scienta VUV5000) and a monochromator (Gammatdata-Scienta VUV5040) are used for ARPES, while the unmonochromatized PREVAC RS 40B1 X-ray source, with dual Mg/Al anode is used for XPS measurements. UV spot size on the sample has the lateral dimension of around 3mm^2 and the XPS source illuminates the whole surface area. Selection of a photoelectron-emitting area is then a result of the spectrometer entrance lens. Sample is mounted on a 5-axis manipulator/goniometer with a flow-type cryostat, capable of cooling the samples down to 6K, however used mostly in nitrogen temperatures. The whole system is computer-controlled and allows for full 3D electronic structure mapping, with the reciprocal lattice coverage achieved by the physical rotation of the sample alongside two rotation axes. LEED measurements are based on a mesh OCI-BDL-800-MCP diffractometer with an electron multiplier, using the same manipulator as ARPES spectrometer. LEED system is well shielded from external electromagnetic fields and allows for the diffraction studies using incident electron energies as low as 1eV.

AFM measurements are performed in air, using NanoSurf EasyScan microscope operating in a dynamic force mode, with commercially available ACL-A tips. STM measurements are performed in a different UHV system (base pressure $< 2 \times 10^{-10}$ mbar) equipped with an Omicron RT-STM/AFM microscope, using etched tungsten tips as probes. Samples are transferred between UHV systems in the medium vacuum suitcase ($p < 1 \times 10^{-6}$ mbar), or in air, followed by the degassing in temperatures up to 400°C . Part of ARPES measurements are performed at the ARPES beamline of the National Synchrotron Radiation Centre SOLARIS, after transferring samples in air. Part of XPS measurements are performed at the Academic Centre for Materials and Nanotechnology at the Cracow University of Technology AGH, using PHI 5000 VersaProbe II spectrometer, after transferring samples in air.

2.5 Process design

Graphene growth process described in this work is designed to slow down silicon loss from the (0001) surface of SiC, by means of applying an external atomic/molecular Si flux to the annealed sample. This also allows to increase the graphitization temperature, without increasing the graphene coverage as described in section 1.7.

Epitaxy-ready, semi-insulating, research-grade SiC wafers obtained from MSE Supplies are used in the experiments. Diameter of the wafers is equal to around 4 inches (100 ± 0.5 mm) and an orientation of the surface used for experiments is on-axis (0001), with the possible deviation of up to $\pm 0.5^\circ$. Micropipe¹ density for the wafers is equal to around 15 cm^{-2} and the surface roughness is equal to 0.5 nm for the Si face, which is chemically-mechanically polished (CMP). The C-face is optically polished, with resulting surface roughness of 1 nm. LTV/TTV/Bow/Warp parameters [127] are equal to $4 \mu\text{m}/10 \mu\text{m}/25 \mu\text{m}/35 \mu\text{m}$, respectively.

Wafers are cut into $10 \text{ mm} \times 10 \text{ mm}$ chips and placed on a tantalum holder, with a circular aperture with a diameter of 10 mm positioned at the center. Samples are rinsed in isopropanol, blown dry with an inert gas (helium) and introduced into the load lock of the UHV system. After the transfer of the samples on a manipulator, the holder aperture is positioned directly above an circularly-symmetric electron beam (EB) heater, allowing for direct heating of the backside of the samples. They are then degassed in the temperature of up to 400°C , until the pressure of the system returns to values $< 1 \times 10^{-9}$ mbar.

Samples are then annealed in the temperature of around 900°C , in a Si flux with the density of $6 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, to clean the surface from the contaminants and form crystallographically well ordered (3x3) surface reconstruction. Since the wafer is epitaxy-ready and Si flux is known to have a cleaning effect on SiC, no further cleaning or etching steps are required at the beginning of the process.

Afterwards, graphene growth is conducted in the temperatures of $1400\text{-}1900^\circ\text{C}$, in the Si flux with the density varied between 6×10^{12} and $2.5 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$. Heating and cooling rates of the samples are controlled and in most experiments vary between “slow” rate of $0.35^\circ\text{C}/\text{min}$, unless stated otherwise, and “fast” rate of around $100^\circ\text{C}/\text{min}$, which is possible to achieve because the

¹ Micropipes are major defects in commercially-produced silicon carbide wafers, and are thought to originate from superscrew dislocations with a large Burgers vector, significantly larger than the unit cell dimension (F. C. Frank, "Capillary Equilibrium of Dislocated Crystals," *Acta Cryst.*, vol. 4, p. 497, 1950)

sample temperature responds rapidly to changes in the accelerating voltage of the electrons in the EB heater. The fast rate is useful for precisely determining the beginning and end of the graphitization process, while for the slow rates, the exact time when the silicon starts and stops sublimating from the surface is somewhat more difficult to determine. The constant Si flux is applied to the surface already at the temperature of $\sim 900^\circ\text{C}$ (i.e. the temperature of the formation of the 3×3 reconstructed surface), well below graphitization temperatures, and it isn't switched off until the sample cools down to the same temperature. In case of slow heating, the complete process takes between 20 and 40 minutes. The scheme of the process in either fast or slow heating regime is shown in Fig. 24.

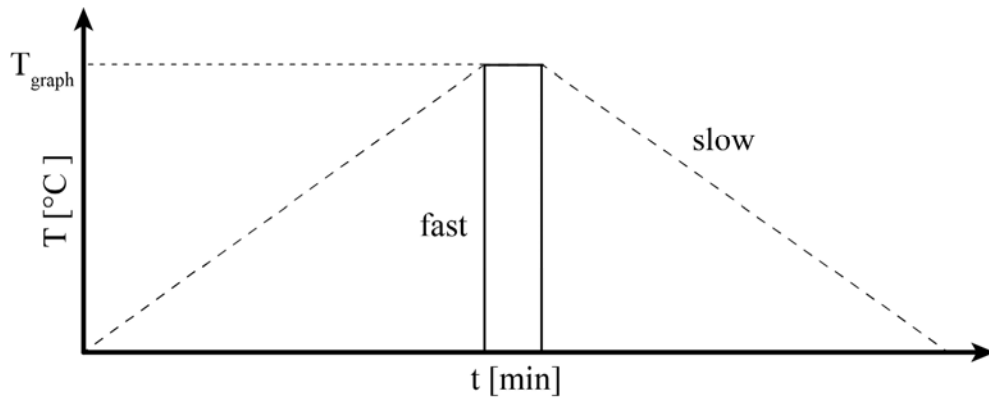


Figure 24: Scheme of the two variants of graphitization used in the experiments, utilizing either: fast (solid line) or slow (dashed line) heating/cooling rate and annealing at the graphitization temperature T_{graph} (time is not to scale); arrows represent times when the flux of Si atoms was switched on and off (black for the slow and grey for fast heating/cooling (reproduced from own work: [129])).

Chapter 3

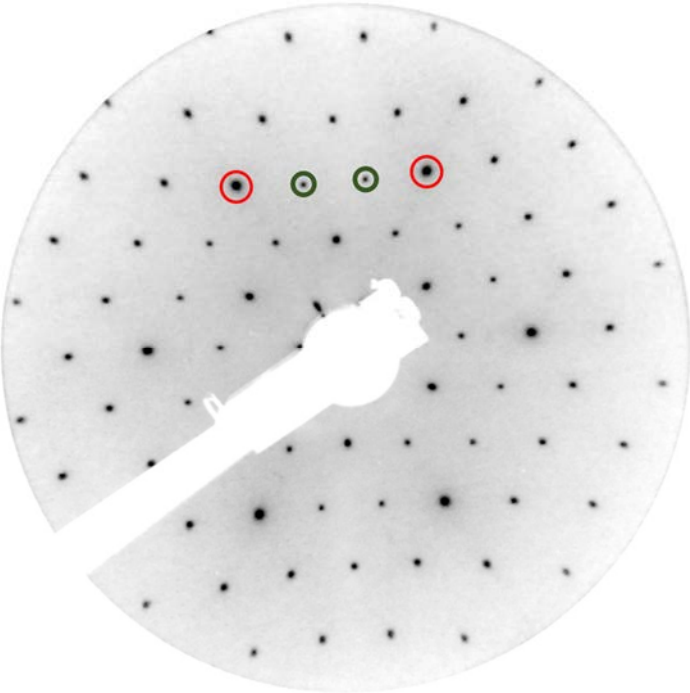
Si beam-assisted graphitization of SiC (0001)

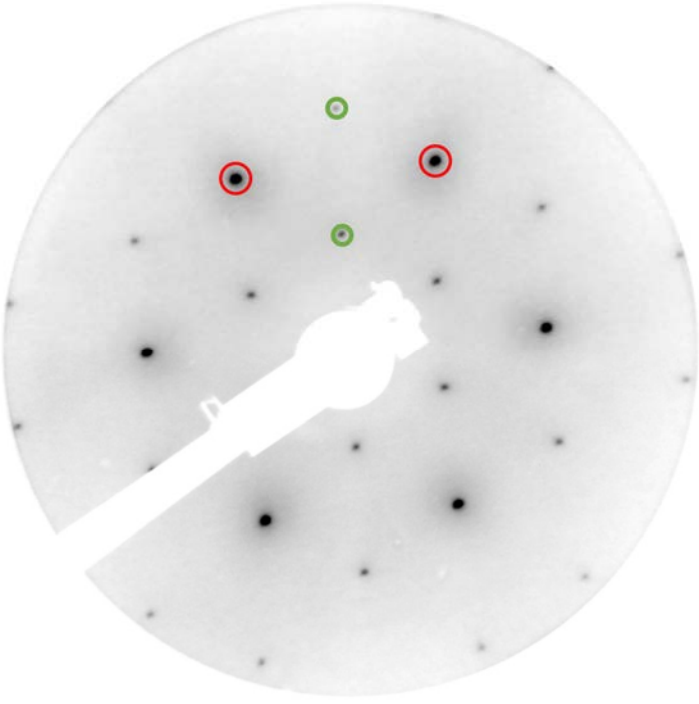
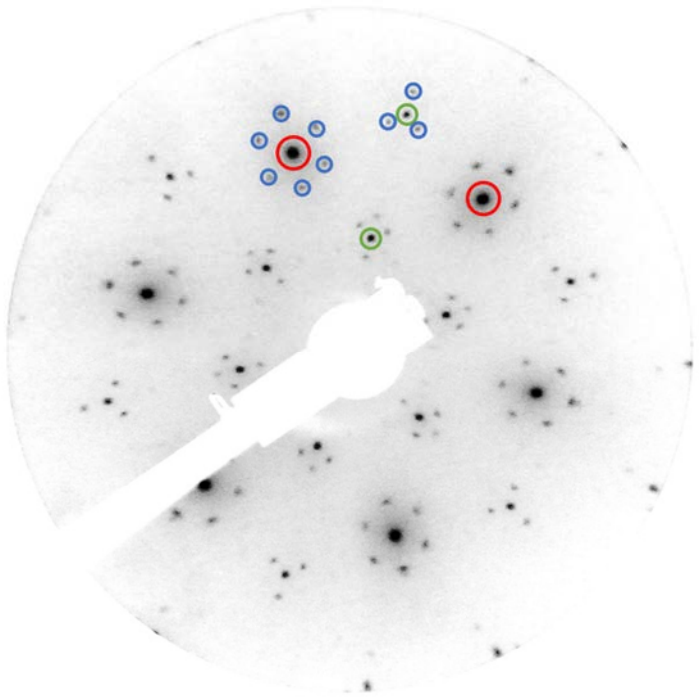
This chapter will focus on the properties of the (0001) surface of silicon carbide annealed in the external silicon flux. Firstly, major reconstructions of the surface will be discussed, as they serve as a template for graphitization in higher temperatures. The process of graphene formation in ultrahigh vacuum conditions and in the Si flux will be then analyzed, alongside with the discussion of the process dynamics. Properties of the material formed using two approaches will be compared and contrasted, followed by the investigation of phenomena occurring at semi-equilibrium growth conditions in Chapter 4.

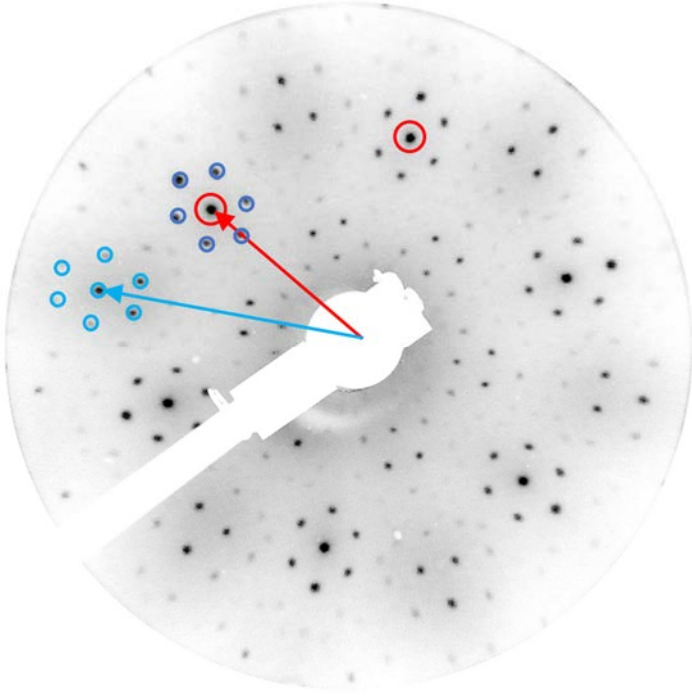
3.1 Surface reconstructions of SiC (0001)

Before graphene synthesis, the initial SiC (0001) surface is prepared by annealing it in varying temperature in the Si flux of $\Phi=5\times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$. Table 1 summarizes the diffraction patterns of the major surface reconstructions obtained in a given annealing temperature.

Table 2: Diffraction patterns of the major SiC (0001) surface reconstructions.

No.	Diffraction pattern ($E_{\text{inc}}=156\text{eV}$)	Surface reconstruction
1		(3×3) $T_{\text{anneal}}=950^{\circ}\text{C}$

2		$(\sqrt{3} \times \sqrt{3}) R30^\circ$ $T_{\text{anneal}} = 1000^\circ\text{C}$
3		$(\sqrt{3} \times \sqrt{3}) R30^\circ /$ $(6\sqrt{3} \times 6\sqrt{3}) R30^\circ$ $T_{\text{anneal}} = 1050^\circ\text{C}$

4		$(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ $T_{\text{anneal}}=1200^\circ\text{C}$
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Diffraction spots related to (1×1) symmetry are marked with red circles, (3×3) symmetry with dark-green circles (observed for the sample annealed at $T_{\text{anneal}}=950^\circ\text{C}$), $(\sqrt{3}\times\sqrt{3})R30^\circ$ symmetry with light-green circles (observed for the samples annealed at $T_{\text{anneal}}=1000^\circ\text{C}$ and $T_{\text{anneal}}=1050^\circ\text{C}$) and $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ symmetry with dark and light blue circles (observed for the samples annealed at $T_{\text{anneal}}=1050^\circ\text{C}$ and $T_{\text{anneal}}=1100^\circ\text{C}$).

While the interpretation of the diffraction patterns for the (3×3) and $(\sqrt{3}\times\sqrt{3})R30^\circ$ phases is rather straightforward, the pattern of the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction is very complex. This reconstruction is characteristic for the presence of the buffer layer – and possible graphene overlayers – on the substrate (see section 1.6 and Fig. 12). Due to the structure formfactors, not all of the diffraction spots are visible and they form characteristic flower-like hexagons patterns around the central spots. In Fig. 25, reciprocal lattice of the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction is shown and the spots visible in LEED diffractograms are marked.

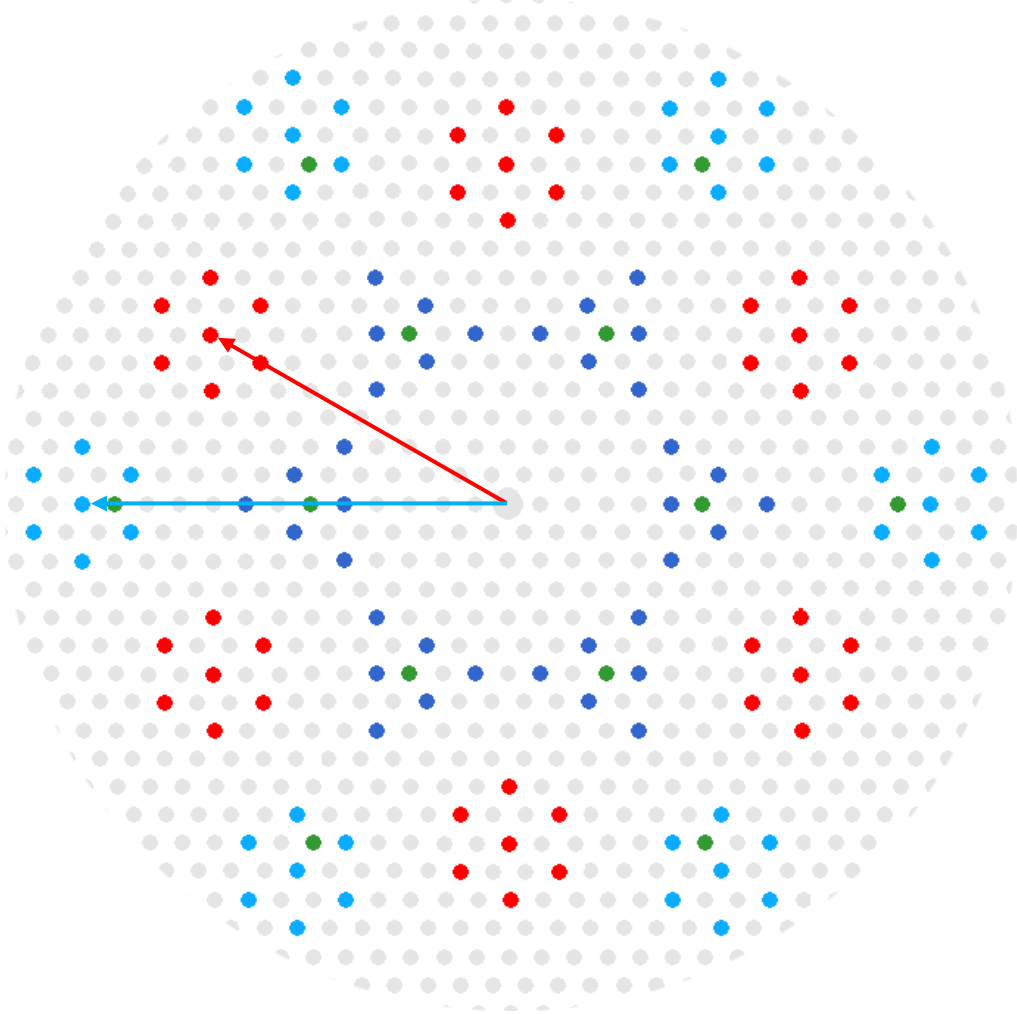


Figure 25: Reciprocal lattice of the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction (light grey) with selected spots visible in LEED patterns marked in color; basis vectors of the surface projected bulk SiC and graphene lattices are shown respectively as red and blue arrows.

Spots on the $(\sqrt{3}\times\sqrt{3})R30^\circ$ lattice, which coincide with the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ lattice are marked in green (they are visible for the samples annealed at $T_{\text{anneal}}=1000^\circ\text{C}$ and $T_{\text{anneal}}=1050^\circ\text{C}$), while the rest of the marked spots is visible only on the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ lattice. Spots marked with red are the spots visible near the (1×1) spots of SiC, associated with bulk substrate symmetry, while spots marked with light-blue are the spots visible near the spots associated with the symmetry of the graphene lattice. Lattice vectors associated with the two symmetries are also marked at the picture and the corresponding diffraction pattern in Table 2.

Experiments using Si background pressure in the vacuum chamber have shown that the exact formation temperature of different reconstructions might vary with changing partial pressure of Si [111]. These experiments, however, used disilane (Si_2H_6) background gas as a silicon source, which makes them different from this work, where molecular/atomic Si beam was used, eliminating any adsorption and dissociation reactions, as well as presence of hydrogen near the

surface. The study also used an infrared pyrometer for temperature measurement, likely facing the same challenges as the one faced in this work, and reported a rather large sample-to-sample variation in the formation temperature of different reconstructions (30K). Nonetheless, a phase diagram obtained in this study is shown in Fig. 26.

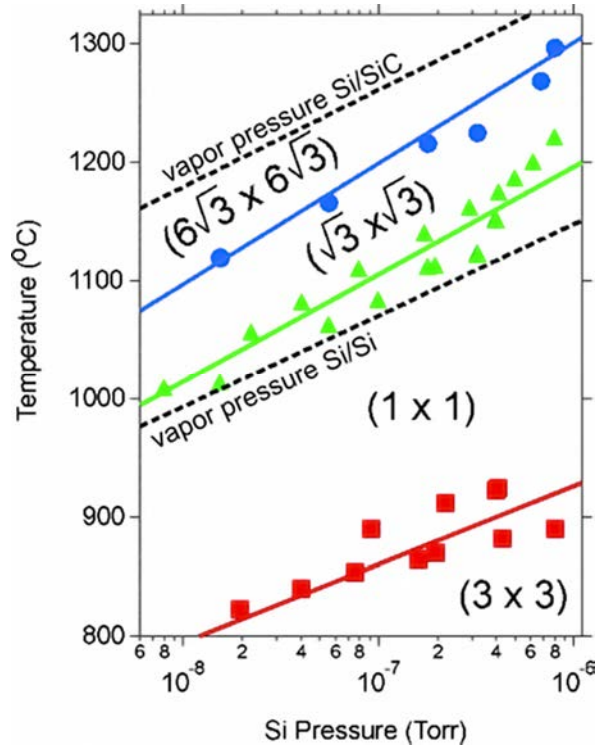
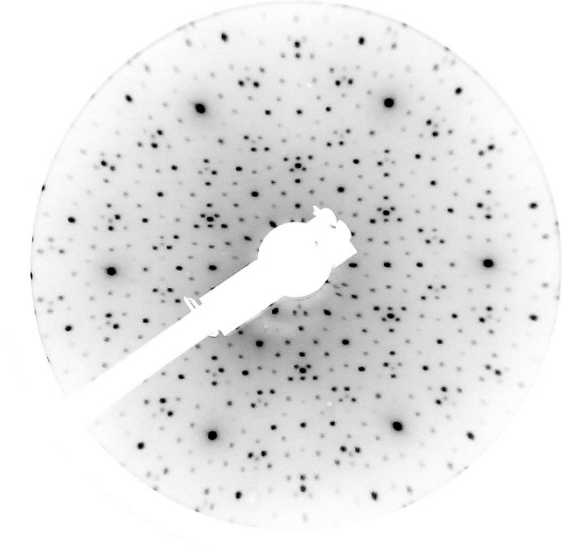
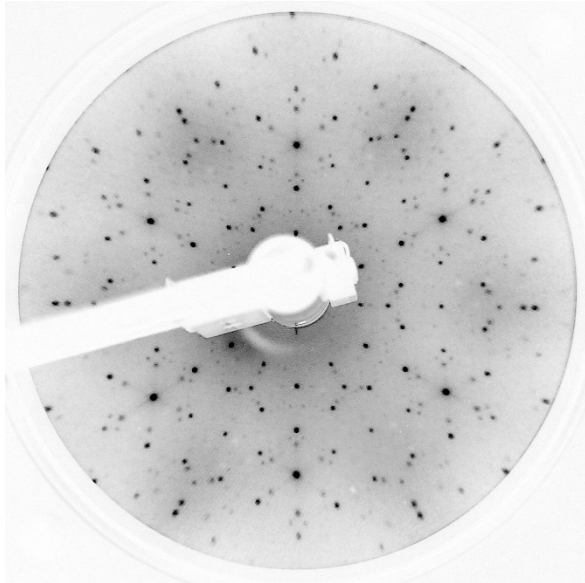
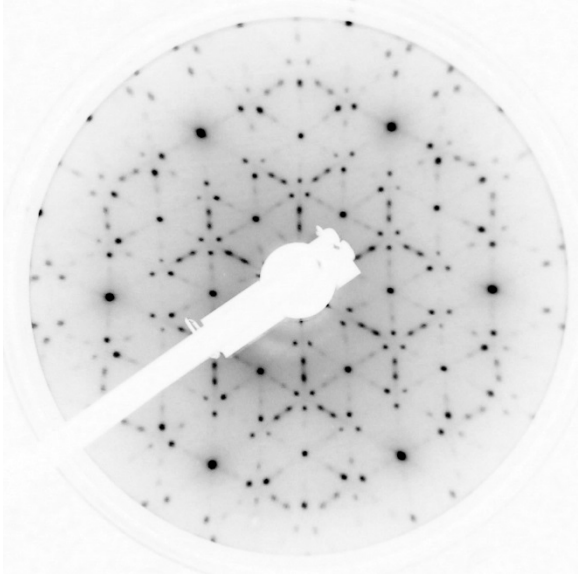
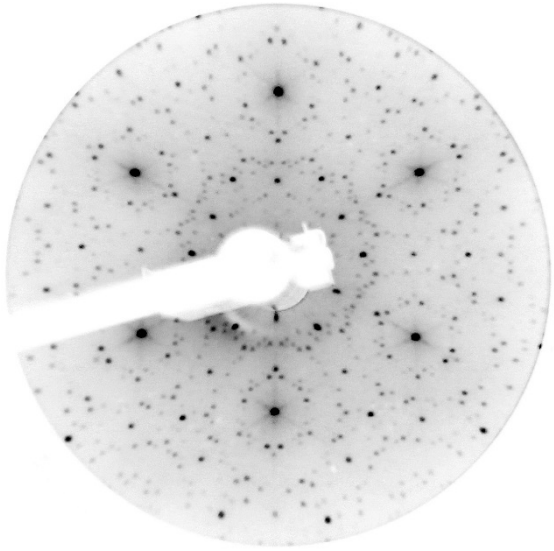
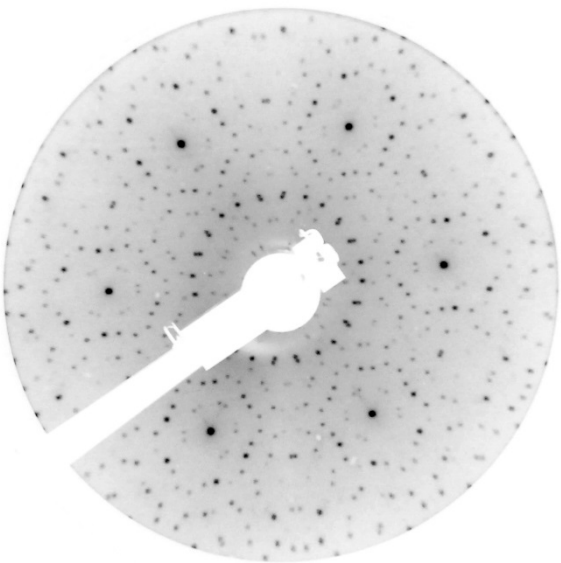


Figure 26: Phase diagram of the different SiC (0001) surface reconstructions obtained by annealing the surface in the background pressure of disilane gas (reproduced with permission from: [111]).

While the general sequence of surface reconstructions observed with increasing annealing temperatures is the same as the one obtained in this study, we didn't observe formation of (1x1) structure, when any Si flux was present at the surface, which is supported by the observations of other authors [114]. In contrast to the simple phase diagram presented above, we found that depending on the details of sample preparation, many more surface structures can be formed at SiC (0001). These structures usually form in a Si-rich environment, between the temperature of the formation of $(\sqrt{3} \times \sqrt{3})R30^\circ$ and $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstructions, in a given Si flux. Most of the structures observed in this work haven't been described in literature yet. However, since determining their exact symmetry and structure isn't the main goal of this work, the topic will be only briefly introduced. Table 2 summarizes diffraction patterns of various Si-rich superstructures obtained by annealing SiC (0001) samples in the Si flux.

Table 3: LEED diffractograms of the Si-rich superstructures obtained through SiC (0001) annealing in Si flux or in UHV conditions, after Si deposition.

No.	Diffraction pattern ($E_{inc}=156\text{eV}$)	Preparation details
1		$T \approx 1065^\circ\text{C}$ $\Phi_{Si} = 6 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$
2		$T \approx 1495^\circ\text{C}$ $\Phi_{Si} = 2.5 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ slow annealing and cooling down of the sample ($v \approx 20^\circ\text{C}/\text{min}$)

3		$T \approx 1075^\circ\text{C}$ $\Phi_{\text{Si}} = 6 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$
4		$T \approx 1065^\circ\text{C}$ $\Phi_{\text{Si}} = 0$ (no Si flux) annealing after the room temperature deposition of $\sim 1\text{nm}$ of Si
5		$T \approx 1075^\circ\text{C}$ $\Phi_{\text{Si}} = 5 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$

The structure of those structures is unknown and they seem to be formed via many different paths. Patterns of the structures 1-3 resemble the expected diffraction patterns for the known lattices, with some variation in the structure factors, enabling the observation of different diffraction spots than in the usual case, combined with some degree of disorder in the main crystallographic directions (see elongated rods in structure 3). Patterns of the structures 4-5 appear to preserve the local rotational symmetry around the (1x1) spots, with some degree of disorder (indicated by the blurring of the (1x1) spots, with six-fold rotational symmetry in the structure 4). While it might be tempting to explain some of the obtained superstructures by the presence of the macroscopic domains on the surfaces, with crystal lattices rotated with respect to each other, a closer examination reveals that it is unlikely. If there are several regions on the surface of the sample, large enough to diffract an incoming electron beam, covered with the same structure, but with the lattices rotated by a specific angle, a diffraction pattern observed for the sample would be an incoherent sum of the individual diffraction patterns of the regions. Fig 27 shows the superposition of two $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ lattices, rotated with respect to each other by 7° , with the positions of (1x1) spots of bulk SiC marked in dark grey. It is clear that the rotation results in the loss of local rotational symmetry around the 1x1 spots, which was not the case for any of the observed Si-rich superstructures. Since this loss is true for every rotation angle, the observed, complex diffraction patterns are unlikely to be a result of a presence of macroscopically rotated domains on the surface.

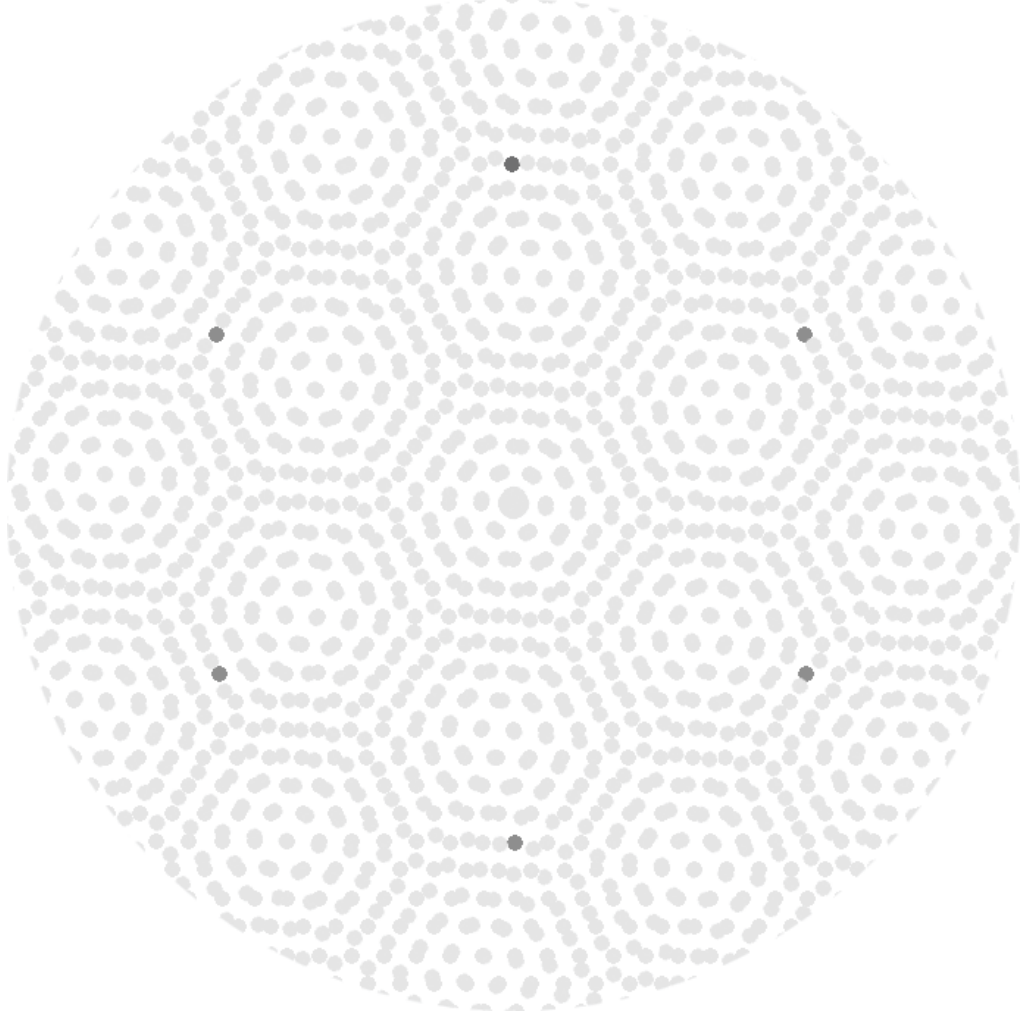


Figure 27: Simulated pattern of the incoherent sum of the two $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ lattices rotated by 7° , with (1×1) spots marked in dark grey.

However, some observed patterns (for example 4 and 5), which have the $p6m$ symmetry, could be interpreted as a superposition of a few different hexagonal lattices. In general case, the hexagonal, reconstruction, which we may describe using Wood's notation as:

$$(\sqrt{n^2 + m^2 + nm} \times \sqrt{n^2 + m^2 + nm})R\left(\text{ArcCos} \frac{2n+m}{2\sqrt{n^2+m^2+nm}}\right), \quad (25)$$

n, m being any integer numbers ≥ 0 , destroys surface lattice mirror symmetries. However, two equivalent reconstructed domains (corresponding to interchanging n and m), rotated in the opposite directions, are possible, which eventually results in the mirror symmetries observed in the diffraction patterns 4 and 5. Additionally, due to the inherent presence of left and right rotated domains, each basic (1×1) spot becomes surrounded with the ring of twelve closest diffraction spots, having the radius equal to reciprocal reconstructed lattice constant (only for the special case of 30° rotation, left and right domains are redundant and in this case the “usual” hexagonal pattern is observed). Within the ring, the spots are mirror-symmetrically arranged,

with reference to the symmetry axes of the basic lattice, at angles corresponding to the reconstruction angle. Thus by examination of the neighborhood of a given (1x1) spot, both the reconstruction rotation angle, and the reconstruction factor can be relatively easily identified [128]. As mentioned before, the study of the Si-rich superstructures is not the main goal of this work and their structural details will not be discussed here. It is, however, important to note, that the SiC (0001) surface annealed in Si flux forms a very complex system and the details of its structure, thermodynamics and kinetics are far from understood.

Diffraction studies are very useful for the identification of the type of reconstruction of the initial surface of SiC (0001), which will be graphitized in the next steps. However, for graphene-covered samples, this work focuses on other characterization methods. Although it is possible to estimate the number of layers of graphene with LEED, as well as assess the average degree of crystallographic ordering, other spectroscopic and microscopic methods, which will be discussed in the following sections, provide much more accurate information about graphene structure and its broadly defined quality.

3.2 Dynamics of SiC (0001) graphitization in Si flux

The main tool used to study the dynamics of the process of SiC (0001) graphitization is quantitative X-ray photoelectron spectroscopy. Fig. 28 shows XPS spectra, in the C1s binding energy region used for the quantification of graphene coverage, of the three SiC (0001) samples prepared in the same temperature, but in the Si flux gradually increasing from 0 (UHV conditions) to $1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$.

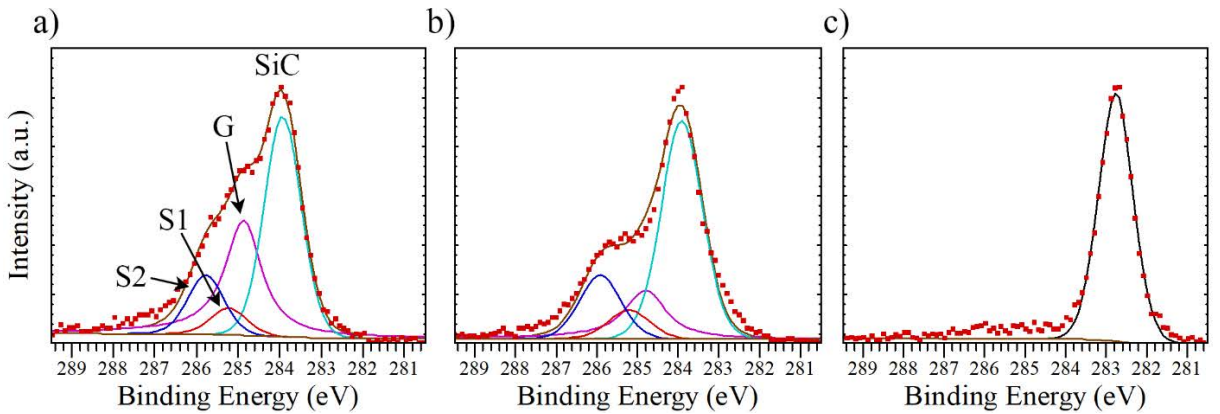


Figure 28: XPS spectra of SiC (0001) samples annealed for $t=5\text{min}$, at $T=1350^\circ\text{C}$ in: a) UHV conditions; b) Si flux of $\Phi=1.0 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$; c) Si flux of $\Phi=1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$.

C1s XPS peak of the samples is characterized by the presence of four main components: SiC, related to carbon in bulk SiC (shown in cyan), G, related to carbon in graphene layer (magenta), S1 (red) and S2 (blue), related to carbon in the buffer layer. Graphene peak, because of its

metallic behavior, is fitted using Doniach–Sunjic profile [129] (numerically convolved with a Gaussian function), while the rest of the peaks is fitted using Gaussian-Lorentzian profile. Binding energy of the bulk SiC component is equal to around $E_B \approx 283.9$ eV, of the graphene component to $E_B \approx 284.8$ eV and of the S1 and S2 components to $E_B \approx 285.2$ eV and $E_B \approx 285.8$ eV, respectively. In case of a clean SiC surface, prepared in Si flux, a significant shift of SiC component towards lower binding energies, by around 1.1 eV, is observed, likely due to the band bending effects.

Graphene coverage of a surface is proportional to the area of the G component. The only parameter that is different between the three samples from Fig. 24, is the Si flux applied to the annealed surface. It is evident from the XPS data, that it has significant impact on the amount of created graphene. As expected, increasing Si flux decreases graphene coverage of the surface for a given temperature. For the temperature of 1350°C, Si flux of $\Phi = 1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ is sufficiently high to fully inhibit graphitization of the surface.

In order to study the process dynamics, three SiC (0001) samples were annealed at 1350°C for a prolonged period of time (50 min) in varying Si flux. The relative area of the G component of the samples was monitored and the results are shown in Fig. 29.

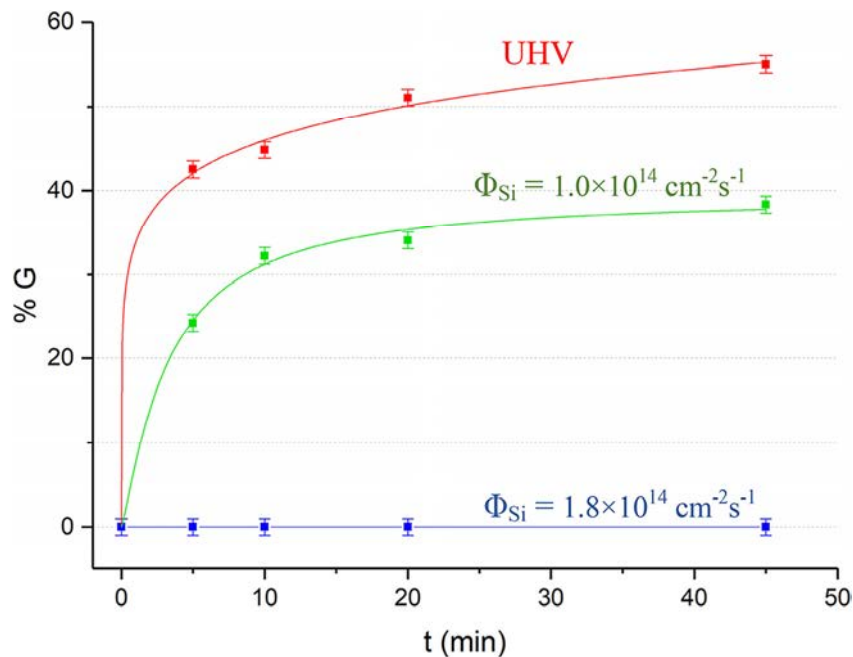


Figure 29: Time evolution of the relative area of the G component in the C1s XPS spectra of the samples annealed at $T=1350^\circ\text{C}$ in UHV conditions (red), b) Si flux of $\Phi=1.0 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ (green); c) Si flux of $\Phi=1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ (blue; reprinted from own work under CC BY 4.0 license: [109]).

Data was fitted using a logistic-type function, in the form of

$$y = \frac{A_1 - A_2}{1 + (x/x_0)^p} + A_2. \quad (26)$$

This function no immediate physical meaning, but captures the essential behavior of the change in graphene coverage with time. Three main conclusions can be made from the study.

Firstly, even after prolonged annealing, no graphene formation is observed for the Si flux of $\Phi = 1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. This proves, that this Si flux is in fact sufficiently high to reduce the effective Si sublimation rate in this temperature very close to zero. This is approximately consistent with results obtained by Fissel et. al. [130], who was studying Si partial pressure over annealed SiC (0001) surface. For the temperature of 1340°C, measured Si partial pressure was equal to $2.5 \times 10^{-6} \text{ mbar}$, which corresponds to the flux of around $\Phi = 3.1 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. Even though this is around 70% higher than the Si flux value identified in this work, as high enough to counteract the outgoing Si flux, the exact values can be burdened with significant uncertainty. Other effects related to Si adsorption and desorption also play a role in the process, so the agreement can be judged satisfactory. Secondly, graphene growth in time shows mixed behavior and seems to be happening in two phases. At first, growth rate is inversely proportional to the graphene coverage. This is because nucleation happens at different spots on the surface and the amount of the clean SiC surface, available for the nucleation, is inversely proportional to the amount of created graphene. Growth kinetics in this first phase resembles first-order, self-limiting chemical reaction, with the graphene coverage C in time t proportional to:

$$C(t) \propto \frac{1}{1 + \exp(-t)}. \quad (27)$$

In the second phase, growth is mainly limited by the ability of the desorbing Si atoms to diffuse through the defects in the first graphene layer, leading to approximately linear change of graphene coverage in time, resembling zero-order chemical reaction. This reaction kinetics is consistent with the current understanding of graphene growth mechanisms, which are described in section 2.6. The third observation is that applying external Si flux doesn't seem to change the overall behavior of graphene coverage in time and the reaction kinetics. External Si flux seems to reduce growth rate both in the first, nucleation phase, and in the second, diffusion-limited phase.

In order to gain a better understanding of the influence of temperature on the graphene coverage, a series of samples annealed for the same time of 5min is prepared, in the constant Si

flux of $\Phi=1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, but at increasing temperatures. In Fig 30, a relative concentration (area share) of the different C1s components is shown.

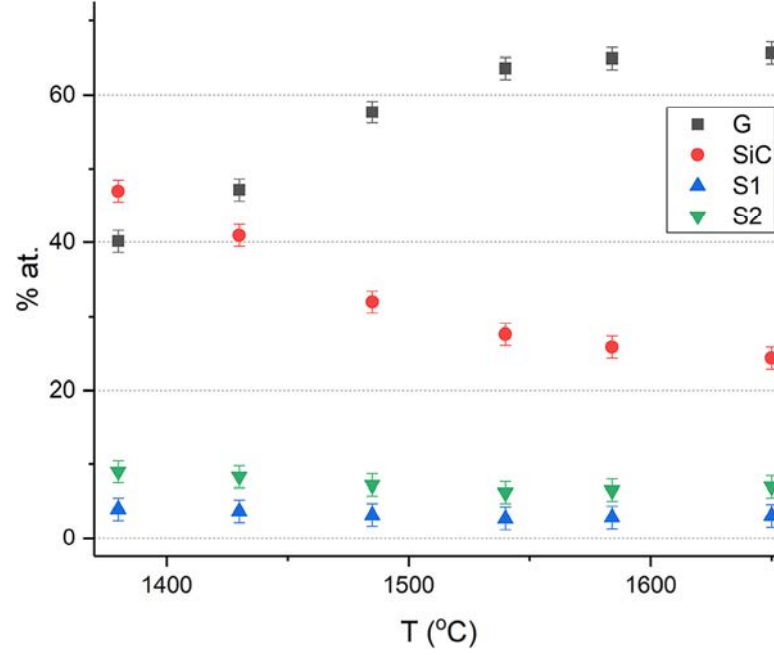


Figure 30: Relative concentration (area share) of the different C1s components for the samples annealed for 5min, in the constant Si flux of $\Phi=1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ (reprinted from own work under CC BY 4.0 license: [109]).

The share of the G component, associated with graphene, increases with increasing annealing temperature, and stabilizes at the nominal concentration of around 65%, for annealing temperatures above 1600°C. This is accompanied by the decrease in the intensity of the SiC component and slightly decreasing intensity of the buffer-layer components S1 and S2, as a result of signal attenuation by thicker graphene layers.

It is evident, that in certain growth conditions, applying Si flux to the surface of the annealed sample can fully inhibit its graphitization (here this was obtained for annealing temperature equal to $T=1350^\circ\text{C}$, see Figs. 28 and 29). In those conditions, we can very precisely control the growth rate of the material, by varying the density of Si flux emitted by an external source. The system is then in a quasi-equilibrium state, which might constitute a “true” reaction equilibrium, in a chemical sense, or be only an effect of the equivalent pressure of Si beam, counteracting Si desorption from the surface. Phenomena occurring in the quasi-equilibrium conditions will be discussed in detail in Chapter 4 and the interpretation of its nature will be provided, while the rest of this chapter will focus on conditions which are far from equilibrium.

In case of growth in those conditions, Si flux cannot fully inhibit graphitization of the annealed SiC, but can influence the evolution of surface structure and, to some extent, slow down

graphene growth. The reasons for operating in the far from equilibrium regime are mostly practical. From the point of view of the mobility of carbon atoms on the surface, which is linked to the quality of synthesized graphene, highest process temperatures are desired. However, the usual factor limiting the use of increased temperatures is the Si flux density, which is determined by the type of Si source and cannot be easily increased. For example, in case of Si flux of $1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, the maximum temperature at which graphene growth can be completely inhibited is equal to around 1350°C. Graphitization in higher temperatures, in the same Si flux, will inevitably happen far from equilibrium.

There are several other arguments for growing graphene in these conditions. Preparation of samples is in general much faster – in case of graphitization in 1350°C, time required to grow a full monolayer of graphene in Si flux of $1.0 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, in semi-equilibrium conditions is equal to 75min, which is 15 times higher than in case of UHV growth (5min). Increased annealing time can be linked to the occurrence of enhanced step-bunching on the surface. It also increases surface exposure to potential impurities, especially in systems using high vacuum (chamber pressure in 10^{-8} mbar range), rather than ultra-high vacuum (chamber pressure in 10^{-9} - 10^{-10} mbar range).

3.3 Valence band electronic structure of graphene on SiC (0001)

Angle-resolved photoelectron spectroscopy is a technique allowing for the direct observation of the valence band electronic structure of materials, as discussed in section 2.1.2. In case of this work, the main focus of the technique is the electronic structure of graphene, introduced in section 1.1. Since the substrate is a wide band-gap (semi-insulating) semiconductor, no influence of its valence-band structure is expected near Fermi energy, where the graphene band structure is visible. In Fig. 31, APRES spectra of the mono and bilayer graphene grown in Si flux are shown.

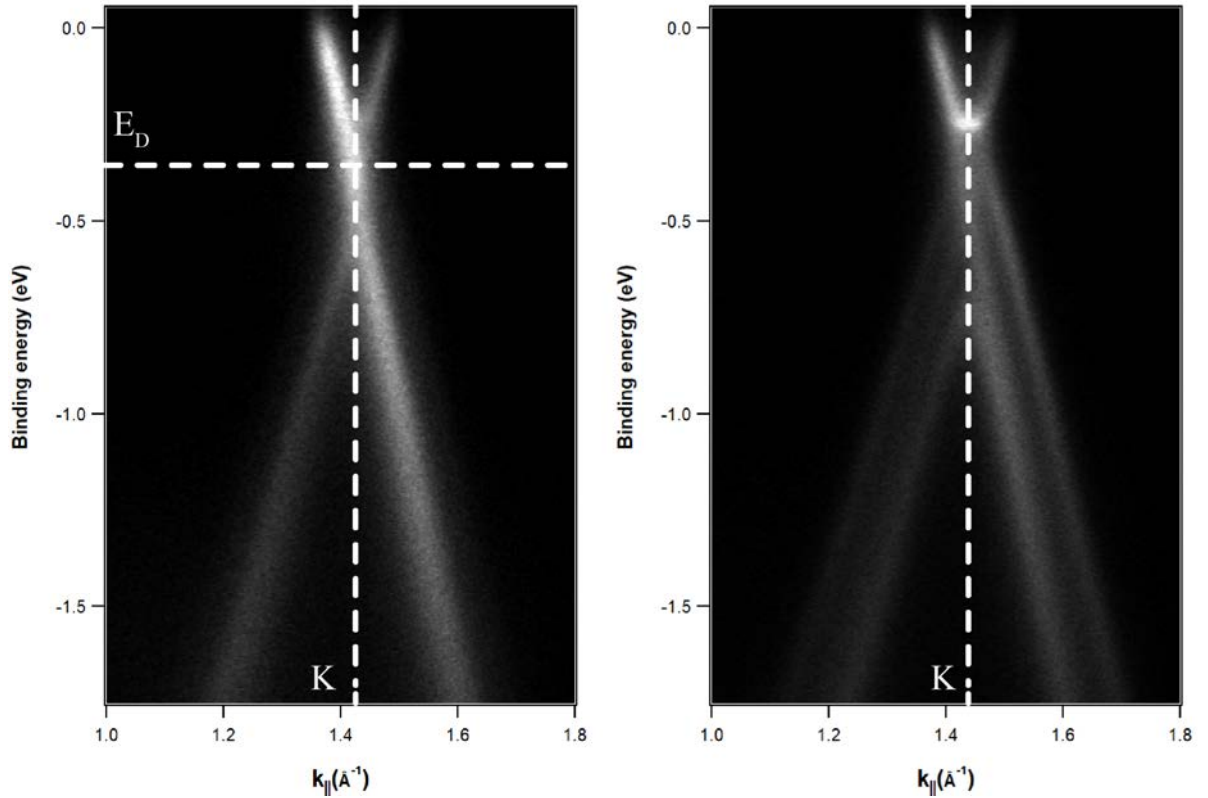


Figure 31: ARPES spectra taken around the K point in the reciprocal lattice of: a) monolayer graphene, grown at $T=1430^{\circ}\text{C}$, in the Si flux of $\Phi=1.8\times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ and b) bilayer graphene, grown at $T=1580^{\circ}\text{C}$, in the Si flux of $\Phi=1.8\times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$; position of the K point of the reciprocal lattice of graphene is marked with K and the Dirac point energy with E_D .

ARPES spectra show the presence of characteristic Dirac cones, with rotational symmetry around the K point of the reciprocal lattice of graphene and the linear electron energy dispersion near the Fermi energy. This confirms the presence of epitaxial graphene on the annealed surfaces and allows for the relatively easy determination of the number of graphene layers grown on the substrate, by counting the number of the visible bands in the spectra (in this case 1 or 2 layers). Obtained spectra also show that the graphene structure is shifted with respect to the Fermi energy by around 0.4eV towards lower binding energies, then would be expected for

pristine, isolated graphene. This is explained by the influence of the buffer layer $((6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction of SiC (0001)), which has been shown to electrostatically dope the overlying graphene layers.

Constant-energy maps, showing the cuts through the Dirac cone of the monolayer graphene, obtained at the SOLARIS National Centre for Synchrotron Radiation are shown in Fig. 32.

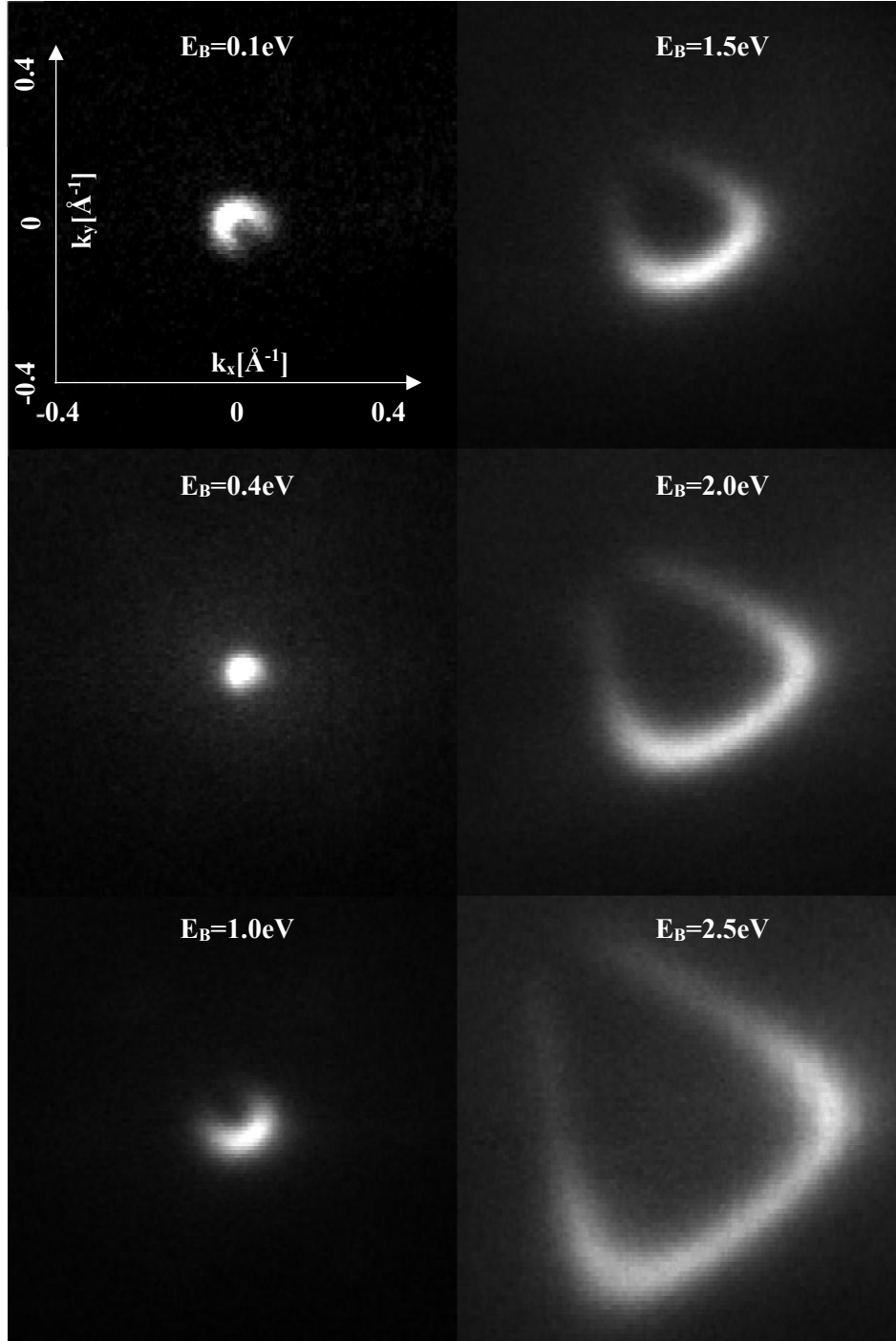


Figure 32: Constant-energy ARPES scans of the monolayer graphene.

These maps illustrate the 3D nature of the Dirac cone observed for monolayer graphene. While ARPES spectra shown in Fig. 27 represent a cut through the cone for the fixed value of electron

momentum in one direction ($\mathbf{k}_x$), synchrotron measurements allow for the observation of the energy dispersion with respect to the electron momentum in both directions ($\mathbf{k}_x, \mathbf{k}_y$) and for the direct visualization of the 3D electronic structure of the material. This is achieved by taking a large number of “cuts” through the 3D electron momentum space, with a fixed value of electron momentum in one direction ($\mathbf{k}_x$) and software-assisted reconstruction of the dispersion in the perpendicular direction ($\mathbf{k}_y$). Constant-energy maps confirm the expected rotational symmetry of the cones around the K point of the reciprocal lattice (which is the center of the spectra), especially near the Dirac point of the structure, located around $E_B=0.4\text{eV}$. However, rotational symmetry is distorted for larger binding energies, which reflects so called trigonal warping of the structure, explained as the influence of Rashba spin-orbit coupling [131]. One half of the cone has also much higher intensity observed in the ARPES spectra, which is the effect of the matrix elements, affecting transition probabilities.

3D visualization of the ARPES spectrum of monolayer graphene, with two cuts through the momentum axes, for $\mathbf{k}_y = \mathbf{k}_x = 0\text{\AA}^{-1}$ (relative to the position of the K point in the reciprocal lattice of graphene) and one constant-energy cut for $E_B=2\text{eV}$ is shown in. Fig 33.

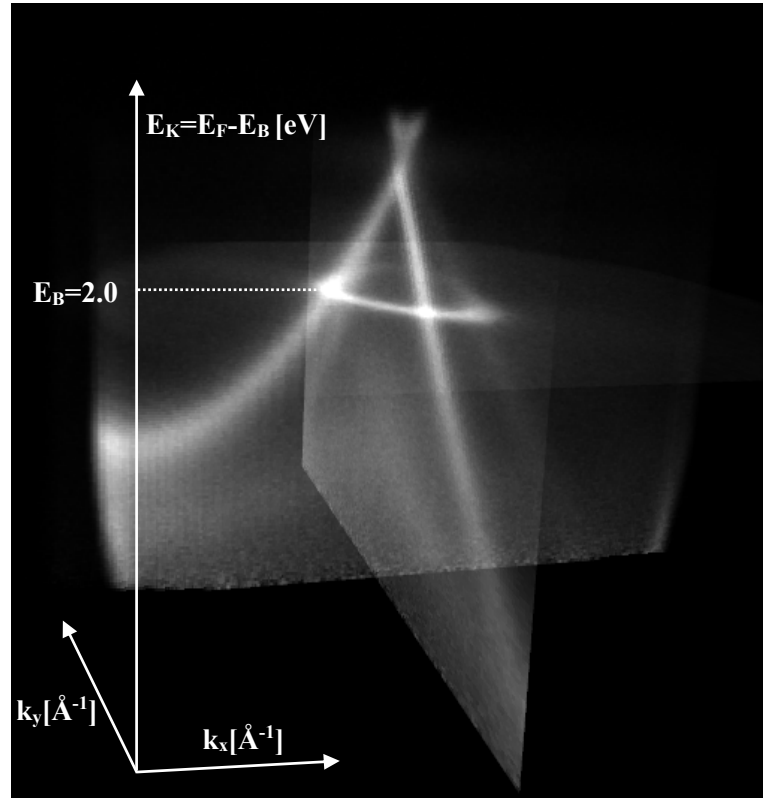


Figure 33: 3D visualization of the ARPES spectrum of monolayer graphene.

More detailed discussion of the electronic structure of the few-layers graphene will be presented in Chapter 5, based on the samples obtained using the optimized growth process.

3.4 Surface structure and morphology

In order to study the influence of Si flux on the structure of the synthesized graphene, I have prepared a series of samples, annealed either in UHV conditions or in varying Si flux. The samples discussed in this section have been prepared in far from equilibrium conditions, as mentioned in section 3.2. Their surface structure and morphology was investigated in small-area scans (up to $400\text{nm} \times 400\text{nm}$) by STM and in large-area scans (up to $10\mu\text{m} \times 10\mu\text{m}$) by AFM.

In Fig. 34, STM scans of the samples annealed at $T=1400^\circ\text{C}$ for 5 min either in UHV conditions (a, b) or in Si flux of $\Phi=0.4 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$.

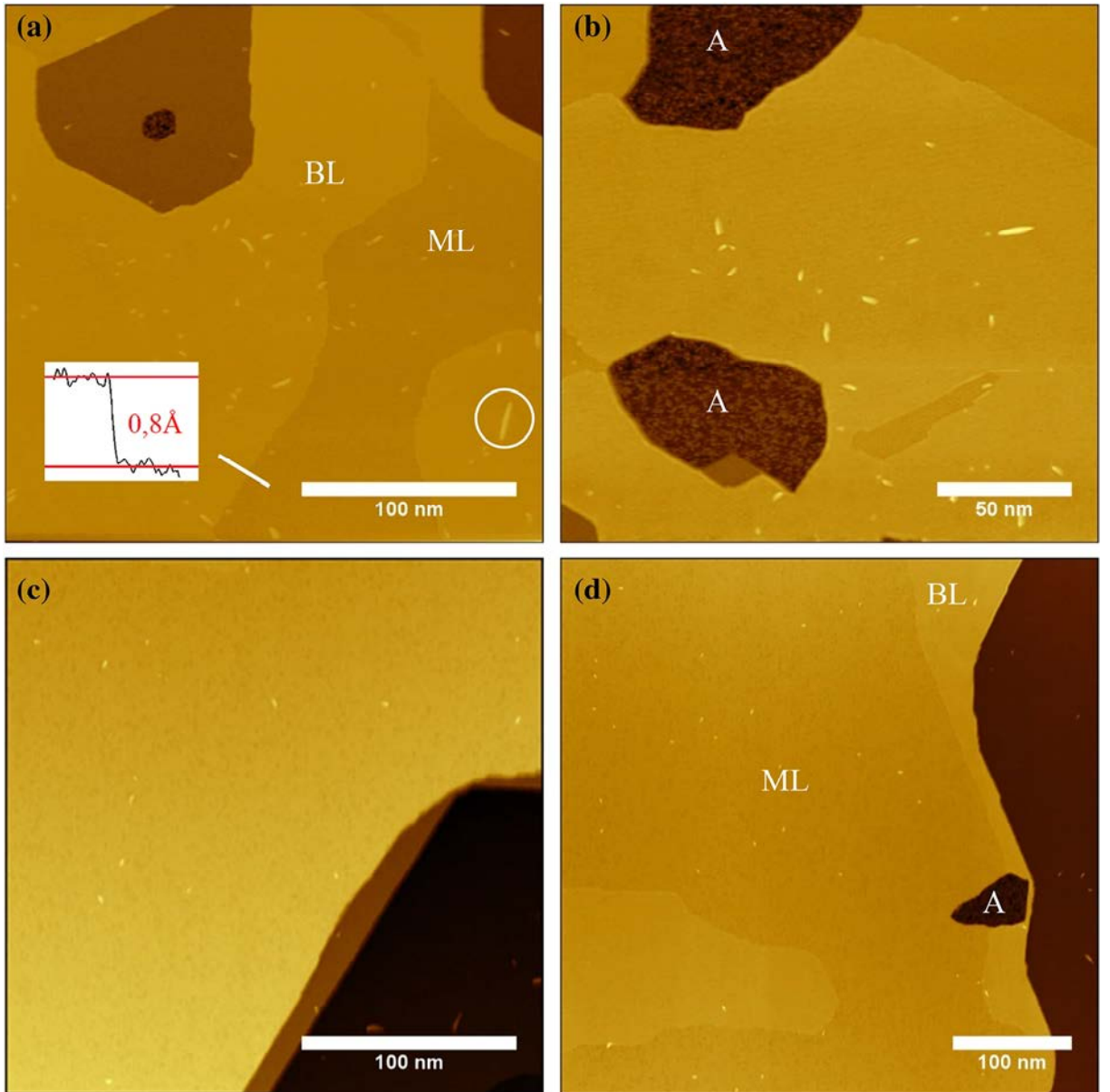


Figure 34: STM images of SiC samples annealed in $T=1400^\circ\text{C}$ for 5 min: a, b without Si flux, c, d in Si flux of $0.4 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. Imaging parameters are: a $I = 12 \text{ pA}$, $U = 400 \text{ mV}$; b $I = 15 \text{ pA}$, $U = 400 \text{ mV}$; c, d $I = 20 \text{ pA}$, $U = 400 \text{ mV}$; inset in Fig. 34a shows the height profile along the white line marked in the figure (reprinted from own work under CC BY 4.0 license: [109]).

There are several features visible for both samples. While the majority of the observed surfaces is covered with monolayer graphene (marked in the figure as ML), as determined by ARPES measurements, on both samples patches of bilayer graphene (marked as BL) can be additionally observed. They are identified by the measurement of the apparent step height between the two areas equal to around $0.8\text{\AA}$, which is consistent with the bottom-up growth model of graphene described in section 1.6 (see Fig. 16 for detailed explanation) and with numerous reports in literature. An example of a height profile along the ML-BL boundary is shown in Fig. 28a. Both surfaces are partly covered with amorphous pits (marked as A), with the usual depth of around $7.8\text{\AA}$ (close to the height of 3 SiC bilayers: $7.5\text{\AA}$), in case of the sample annealed in UHV, and with the depth of around $5\text{-}6\text{\AA}$ (close to the height of 2 SiC bilayers: $5\text{\AA}$), in case of the sample annealed in the Si flux. Presence of numerous point- or line-type defects (an example is marked by a circle in Fig. 28a) is also observed, especially for UHV-grown samples. These defects have been observed by other authors and are attributed either to carbon nanotubes, which are sometimes unintentionally grown during graphene growth, or off-plane defects in graphene.

Even though all the aforementioned features are observed for both samples, it seems that the Si flux is effective in reducing the number of all three types of structural imperfections: bilayer graphene patches, amorphous pits and point- or line-type defects. In order to gain a better understanding of the phenomena happening at the atomic level and the influence of Si flux on the properties of the graphene, STM measurements of the atomic structure of the surfaces grown in varying conditions have also been performed. In Fig. 35, $10\text{nm} \times 10\text{nm}$ STM images of the graphene grown either in: (a,b) Si flux or (c, d) UHV conditions are shown.

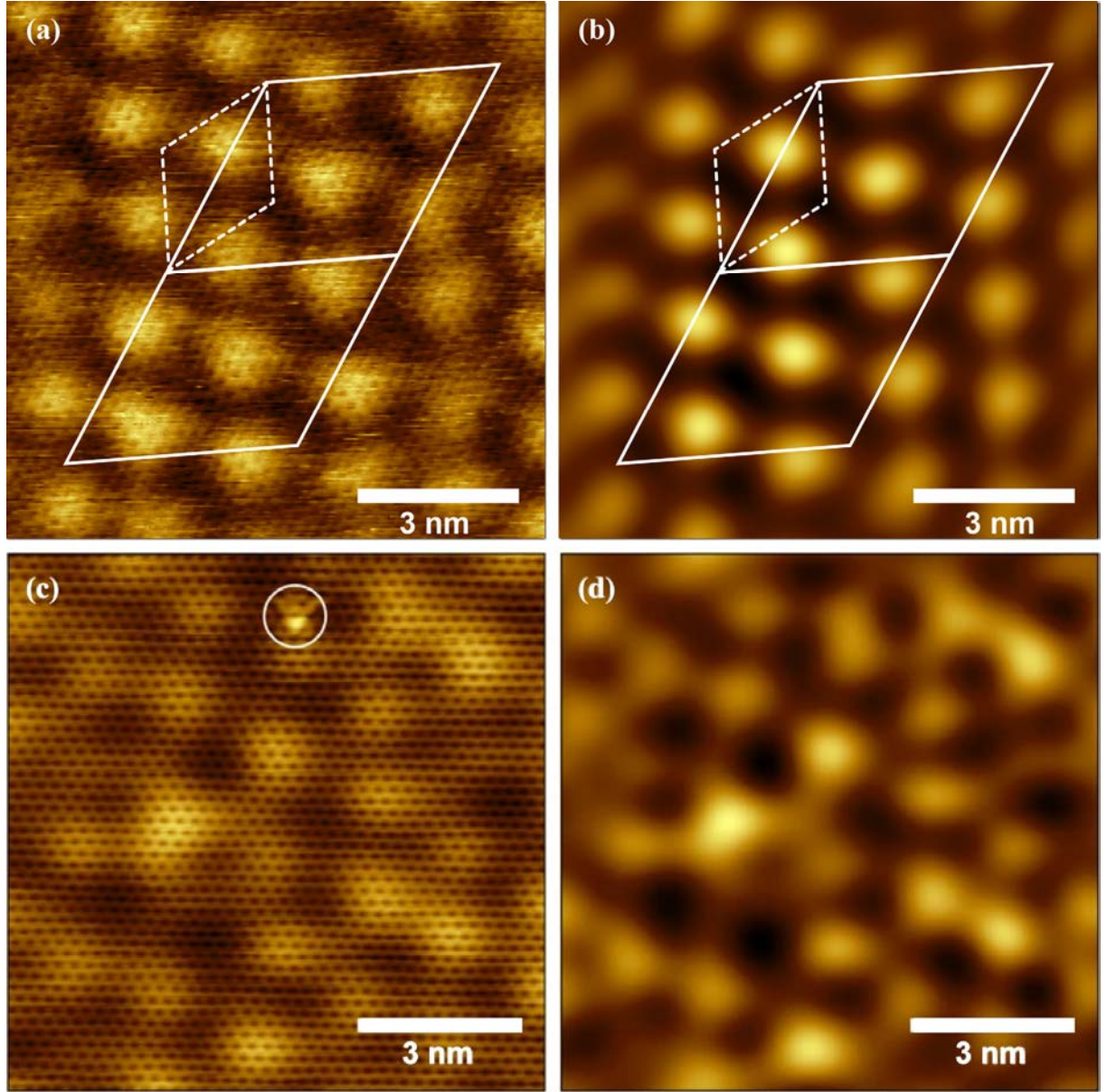


Figure 35: Atomically resolved STM images of graphitized SiC(0001) samples annealed at $T = 1400^{\circ}\text{C}$ for $t = 5$ min: a, b in the Si flux of $0.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ and c, d in UHV. Maps b, d are obtained from the maps a, c correspondingly, using 2D FFT filtering. Imaging parameters: a, b: $I = 25 \text{ pA}$, $U = 20 \text{ mV}$; c, d: $I = 102 \text{ pA}$, $U = 20 \text{ mV}$ (partly adapted from own work under CC BY 4.0 license: [109])

Structure of the graphene layer is visible in Fig. 29 a and c as the fine grid with a lattice constant of around 0.25 nm , overlaid at the lattice with much larger constant of around 3.1 nm , consistently with earlier studies [132]. Note, that in Fig 29a, graphene lattice appears distorted, due to the effects concerning relatively “noisy” STM tip and thermal drift. Graphene layer can be imaged directly only using low tunneling bias (in this case, 20 mV) and it appears transparent for the bias voltage far from the Fermi energy ($\geq 0.5 \text{ V}$), for which the tunneling current flows primarily to the underlying buffer layer [133]. Two unit cells of a larger lattice – $(6\sqrt{3} \times 6\sqrt{3})R30^{\circ}$, or $6R3$ reconstruction – are marked in Fig. 29a and Fig. 29b by solid white

diamonds. The unit cell of the 6R3 reconstruction corresponds directly to the model presented in Fig. 8. and observed periodicities are in line with previous observations [134]. The origin of the large-scale features observed in the center of the unit cell, which form an additional, triangular lattice, has been debated and is often described as the effect of a Moiré effect of the graphene layers overlaid on the buffer layer [135]. Some argued, however, that it can be associated with the physical Si adatom features on the reconstructed SiC (0001) interface beneath the graphene. These Si adatoms would have the form of tetramers, similarly to the tetramers present in the (3x3) surface reconstruction of SiC (0001). Potential presence of other Si adatoms at the interface, on the positions resembling the $(\sqrt{3}\times\sqrt{3})R30^\circ$ lattice has been observed at higher bias voltages. Observed features associated with those atoms form hexagons with two slightly different sizes, which are especially visible for higher bias voltages (for example, see Fig. 2a in Ref. 134, obtained with the bias voltage of +1.7V), observed as the apparent quasi-(6x6) periodicity (a single unit cell of a quasi-(6x6) symmetric structure is marked by a dashed white diamond in Fig. 35). The possible arrangement of the Si adatoms in the form of the tetramers, observed in Ref. 133 (red, green, blue and light-gold circles) and hexagons, observed at higher bias voltages (red circles) is shown schematically in Fig. 36.

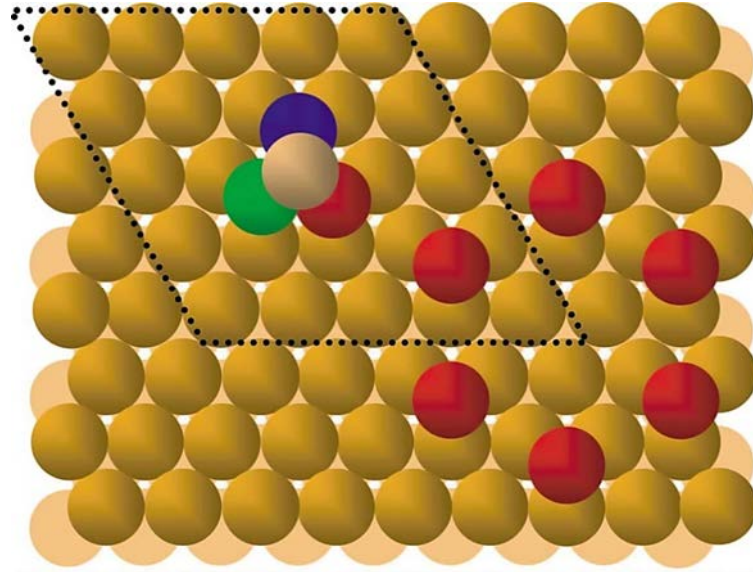


Figure 36: Positions of the three different possible Si adatoms at the SiC interface, marked in red, green and blue (adapted with permission from: [133]).

For the bias voltages used in this work, these structures are not visible. However, the periodicity of the underlying lattice carries information about long-range order in the buffer layer and the graphene-SiC interface.

In terms of surface quality and degree of ordering, the observed graphene layers appear almost defectless within the imaged area, regardless to whether they were prepared in UHV conditions

or in the Si flux. The observed area seems to be much smaller than the graphene grain size. However, a pronounced point defect, marked by the white circle in Fig. 6c, is observed for the sample grown without Si flux. Its presence does not strongly perturb the image of the graphene lattice around it, making it most likely a defect described in literature as the type A defect, located in the buffer layer beneath graphene [136]. I found no defects of this type for the samples grown in Si flux (6 of the samples grown in Si flux were observed by STM with sufficient resolution, and multiple areas were probed on their surfaces).

The most apparent difference between the atomically-resolved structure of the samples annealed in UHV and in Si flux concerns the regularity of the $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ sub-surface lattice. In order to expose the patterns clearly, 2D fast Fourier transform was performed, filtering out the graphene lattice (see Fig. 35 b, d). In case of UHV-grown sample, the pattern is barely visible and characterized by a very large degree of disorder, while for the Si beam-assisted growth, the regularity of the lattice is near perfect. While the regions with the disordered sub-surface lattice pattern are prevalent in UHV-grown samples we found no such regions for samples annealed in Si flux (several regions were probed with sufficient resolution, on the surface of two samples grown in UHV and six samples grown in Si flux). A similar type of disorder was observed in other studies, in which the method of flash annealing in UHV conditions was used to produce bilayer graphene on 6H-SiC (0001) (for example, see Fig. 1b. in Ref. [137]). To a lesser extent, the disorder in the buffer layer is also visible for the samples prepared by atmospheric-pressure graphitization (for example, see Fig. 2a, b in Ref. [134]).

It appears that the most striking effect due to resupplying Si atoms to SiC surface during graphitization in non-equilibrium conditions is the elimination of a disorder in the interfacial buffer layer and an apparent decrease in various surface defects and imperfections (based on the STM observations of 8 different samples grown in the Si flux). This could have significant influence on the electron transport in graphene on SiC, since any irregularity in the periodic, electric potential perpendicular to the surface will contribute strongly to the scattering processes of the conduction electrons in the material. Even in case of perfectly periodic structures, a spatially dependent electrostatic potential is likely to be problematic and is considered as one of the main reasons of reduced electron mobilities of graphene on SiC (0001). However, despite this negative influence, it is the interface layer that makes it possible to achieve epitaxial growth of graphene on SiC, with few, identically oriented grains over macroscopic surfaces.

The degree of large-scale surface homogeneity is another important factor, affecting the macroscopic properties of graphene. Since the scans, possible to obtain with the STM device

available for this study, can reach the lateral size of up to several hundreds of nanometers, this technique is difficult to apply to study the overall surface morphology. In order to assess these properties at the micro scale, large-scale AFM imaging of the graphene grown on SiC (0001) in varying conditions was performed. For reference, Fig. 37 shows the AFM scan of a clean SiC (0001) surface, covered with (3×3) reconstruction prior to the graphitization .

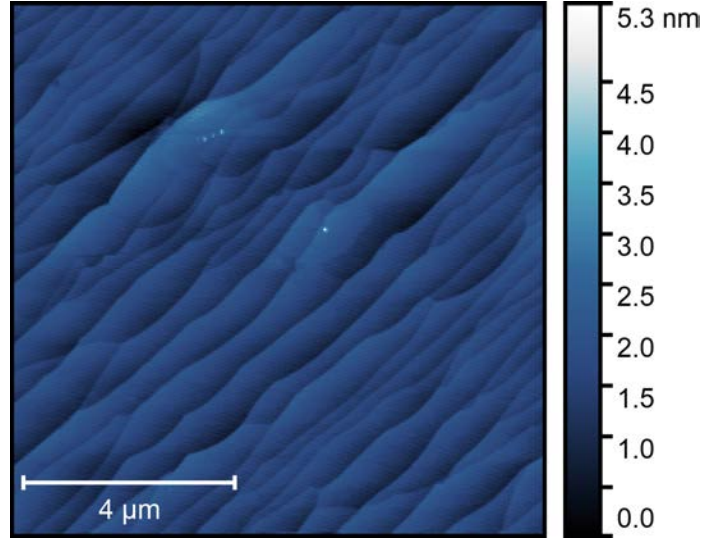
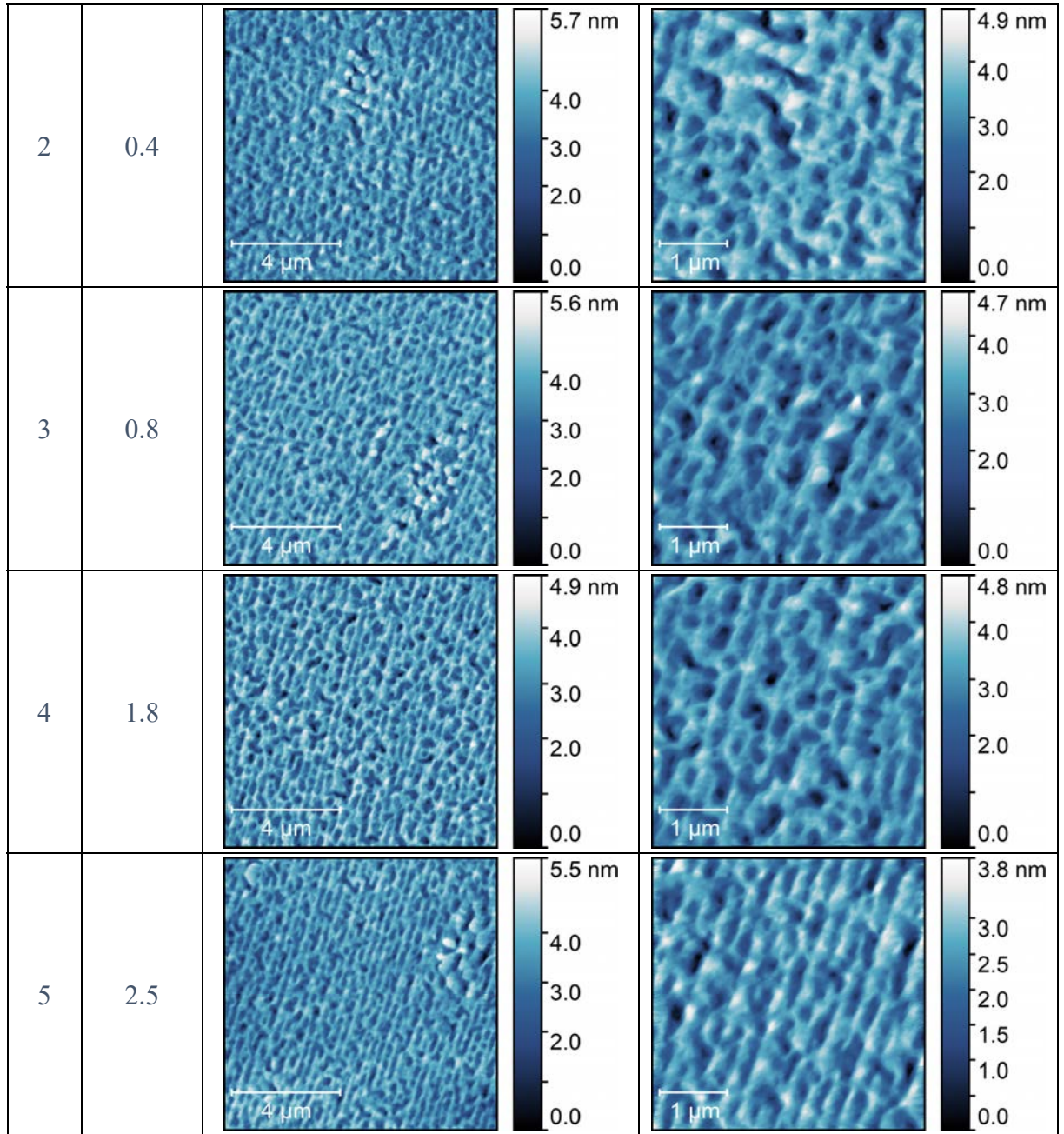


Figure 37: AFM image of a clean, (3×3)-reconstructed SiC (0001).

Consistently with earlier studies [138], the surface is covered with regular terrace structure. Terraces have the width of around 0.5-1μm and the step heights vary between 0.5 and 1.25nm, indicating some degree of step-bunching on the surface. Tables 4 summarizes 10μm×10μm and 4μm×4μm AFM scans, of the samples annealed for t=5min in T=1400°C (same conditions as the samples described above), in the Si flux varying from $\Phi=0$ (UHV) to $\Phi=2.5\times 10^{14}$ cm⁻²s⁻¹.

Table 4: 10μm ×10μm and 4μm × 4μm AFM scans of the samples annealed in T=1400°C in varying Si flux.

No.	Φ_{Si} ($\times 10^{14} \text{cm}^{-2} \text{s}^{-1}$)	10μm ×10μm	4μm ×4μm
1	0 (UHV)		



Several qualitative observations can be made from these large-area measurements. The surfaces of all samples undergo drastic morphological changes during annealing (which is expected for the processes involving partial surface erosion). Remains of an ordered terrace structure, similar to the structure present at the surfaces before graphitization (see Fig. 37), are to some extent visible for all the samples after graphene growth. However the terraces are distorted by the numerous elongated islands and pits. The surface of the sample 1, grown in UHV conditions, is the least homogenous, while increasing the Si flux density results in the gradual ordering of the step structure. This is especially visible for samples 4-5, for which the surface begins to take an ordered terrace-like morphology, albeit covered with the network of meandering pits, with

the depth of up to 6nm. Interestingly, pits present at the UHV-grown sample, are much shallower and have the depth of just 1-2nm. As a consequence, RMS roughness of UHV-grown sample 1, measured over the area of $10\mu\text{m}\times 10\mu\text{m}$ scan and equal to $\text{RMS}_1=0.26\text{nm}$, is much lower than the RMS of the samples grown in Si flux. Roughness of the samples 2-5 has the value of: $\text{RMS}_2=0.73\text{nm}$, $\text{RMS}_3=0.7\text{nm}$, $\text{RMS}_4=0.72\text{nm}$, $\text{RMS}_5=0.69\text{nm}$ and doesn't change significantly with increasing Si flux density. These observations are very interesting, because both annealing time and annealing temperature are the same for all the samples and the only varying factor is the Si flux.

Combined AFM and STM studies of the surface structure and morphology show that while applying Si flux significantly reduces the degree of disorder in the graphene and buffer layer at the nano-scale (point defects, structure of the buffer layer, multi-layer graphene patches), it is insufficient to achieve an optimal, ordered terrace structure at a micrometer-scale. Application of the atomic/molecular Si flux likely changes the mechanism and kinetics of graphene growth on the SiC (0001) surface, as evidenced by the changes in the surface morphology. While the exact growth mechanism is at the moment unknown and its identification requires further studies, one possible explanation could result from the preferential transient adsorption of the incoming Si atoms at the step edges, compared to the adsorption at the atomically flat areas of the terraces. This preferential adsorption is expected from the simple theory of the adsorption of atoms and molecules on the crystalline surface and could result in a decrease in the usual step erosion in the reverse step-flow mode, leading to an enhanced graphene nucleation in the terrace pits. This could explain the emergence of deep pits, observed for graphene grown under Si flux. While this is one possible hypothesis, explaining phenomena happening during graphene growth, it is clear that the described process requires additional improvement, if it is to be used to produce uniform, high-quality graphene.

Chapter 4

Quasi-equilibrium phenomena and process optimization

This chapter focuses on the study of phenomena occurring at quasi-equilibrium growth conditions and their applicability to the optimization of the process. In the beginning, a discovery of the reversibility of graphitization will be discussed, followed by the introduction of the concept of quasi-equilibrium graphene growth. Applications of this discovery in improving large-scale surface ordering of the graphene on SiC will then be discussed. Surface morphology and electronic structure of the obtained high-quality, few-layer graphene will be analyzed, followed by the summary and conclusions in Chapter 6.

4.1 Reversibility of graphene formation

The topic of quasi-equilibrium graphene growth conditions was briefly introduced in section 3.2. Quantitative XPS measurements showed, that in certain conditions, in this case for the annealing temperature of $T=1350^{\circ}\text{C}$, Si flux applied to the surface can fully inhibit its graphitization and the growth rate of the material can be adjusted freely. The question remains, whether these conditions are “true” equilibrium conditions, in a chemical sense, or just an effect of the equivalent beam pressure, counteracting Si desorption from the surface. If a system is in a “true”, chemical equilibrium, graphitization reaction, which can be represented as:



should, in fact, be reversible and represented as:



In order to study this, I have prepared a partly graphitized sample, by annealing it in the temperature of around 1352°C , in the Si flux of $\Phi=1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, for 5 minutes. This temperature, for the given Si flux, is slightly above the quasi-equilibrium temperature (see section 2.6). After the initial step, the sample was annealed for a prolonged period of time (total annealing time equal to 210min), in the same Si flux, but in the temperature lowered by around 5°C ($T=1347^{\circ}\text{C}$), shifted slightly below the quasi-equilibrium temperature. To investigate this process the annealing was stopped several times and quantitative XPS measurements were carried out. If the reaction is temperature-activated and reversible (i.e. if it is in a “true” chemical equilibrium), by lowering the temperature we should be able to shift the equilibrium towards the reactant side (which is the substrate, silicon carbide) and observe the recovery of a

clean surface, not covered by graphene. If, however, the reaction is irreversible, no such effects would be observed.

Fig 38 shows XPS spectra in the C1s region, of the sample annealed in the Si flux of at: a) $T=1352^{\circ}\text{C}$ for 5 min. (initial partial graphitization) followed by the annealing at $T=1347^{\circ}\text{C}$ in the same Si flux for: b) 60 min and c) 210 min.

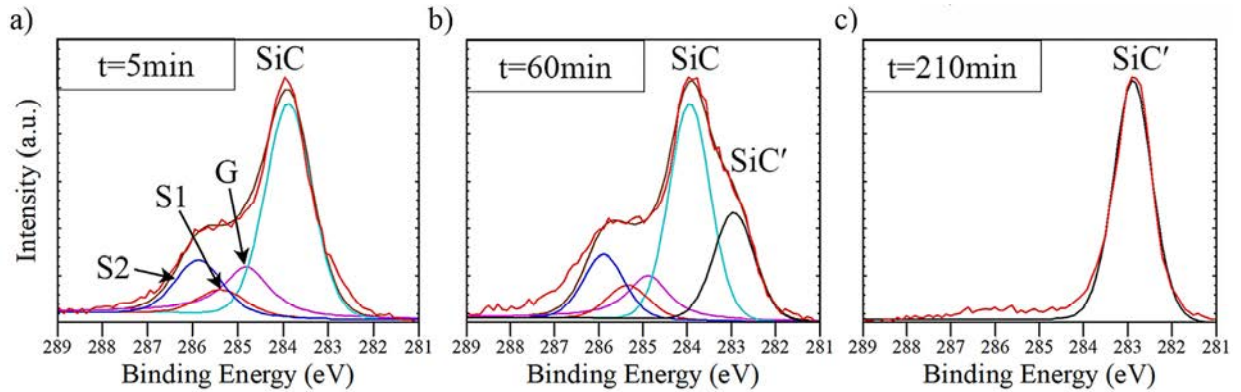


Figure 38: XPS spectra of the SiC sample annealed at: a) $T=1352^{\circ}\text{C}$ for 5 minutes, followed by the annealing of the same sample at 1347°C : b) for 60 min; c) for additional 150 min (total annealing time equal to 210min); components in the XPS spectra are assigned to: bulk SiC (SiC: cyan) beneath graphene (G: magenta) and buffer layer (S1: red, S2: blue), and ungraphitized SiC (SiC': black; adapted from own work [132]).

After the first annealing step, the sample is, as expected, partly graphitized, with a sub-monolayer coverage of graphene, determined by the share of the G component of the spectrum. S1 and S2 components, associated with the buffer layer are also visible. After annealing the sample for 60 min in the temperature slightly lower then the equilibrium temperature, all the aforementioned components remain visible. However, an additional SiC' component can be observed at $E_B=282.9\text{eV}$, which is shifted by around 1eV to lower binding energies, relative to the bulk SiC component. The relative intensity of SiC, G, S1 and S2 is also consequently decreased. After annealing the sample for 210 min, only the SiC' component can be clearly distinguished in the spectrum. Its binding energy is similar to the component observed for the sample annealed at $T=1350^{\circ}\text{C}$, in the Si flux of $1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, for which the surface graphitization was completely inhibited by the incoming Si flux (see Fig. 28c).

Fig. 39 shows core-level spectra of the Si 2p region for the sample annealed in $T=1347^{\circ}\text{C}$, in Si flux of $1.8 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ for 150min and 210min.

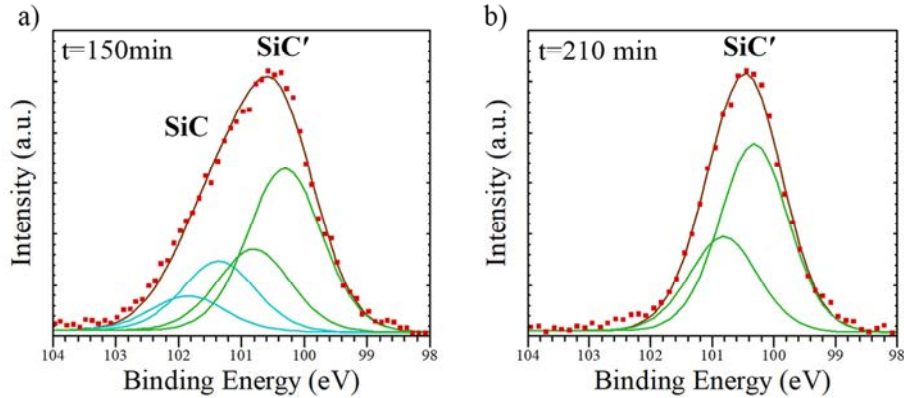


Figure 39: Time evolution of the Si2p region of the XPS spectrum of the sample annealed in sub-equilibrium conditions for: a) 150 min, b) 210 min (reprinted from own work: [132]).

Spectra in the Si 2p region can be fitted either with a pair of 2p doublets (corresponding to the $2p_{1/2}$ and $2p_{3/2}$ energy levels, with the area ratio of 1:2), in case of annealing time equal to 150min, or with a single doublet, in case of annealing time equal to 210min. The separation between the doublets is equal to around 1eV, which is the same as the observed shift between the SiC and SiC' components in the C1s region of the spectrum. XPS data also indicates that there are no measurable number of Si-Si bonds on the samples with SiC' phase. Based on those observations, the SiC' components can be assigned to the the restored, reconstructed surface of silicon carbide. The binding energy of those component is shifted with respect to the energy of a SiC component most likely due to band bending effects and such shift was observed before (see Fig. 28c and Ref. [109]).

Because of the shift, it is easy to differentiate the signal coming from SiC, located beneath graphene and the buffer layer (SiC component) and from SiC, located beneath the reconstructed surface, free from overlying graphene and the buffer layer (SiC' component). This suggests, that prolonged annealing in the temperature slightly below equilibrium temperature leads to the recreation of a clean, Si-rich surface of silicon carbide. Its growth mechanism cannot be explained solely by the presented XPS dataset, but the domains of re-created SiC have to be coherent and rather large, in order to induce changes, observed in the XPS spectra.

This interpretation is further strengthened by ARPES measurements. In Fig 40, ARPES spectra, measured around the K point in the reciprocal space of the graphene lattice for the samples annealed at $T=1347^{\circ}\text{C}$ for: a) 150 min and b) 210 min are shown.

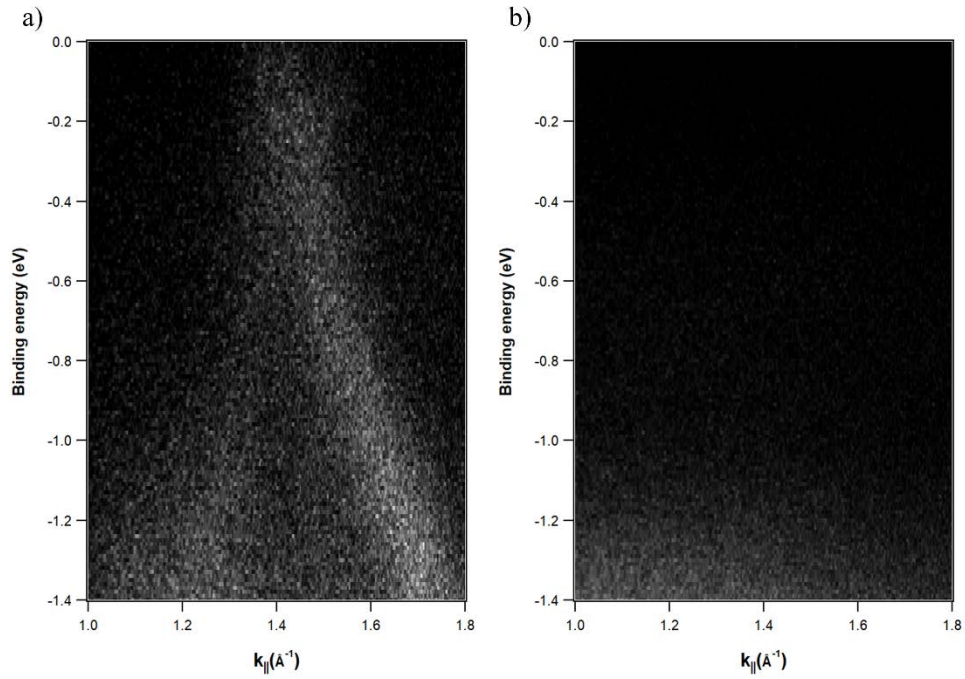


Figure 40: ARPES spectra of the sample annealed at $T=1347^{\circ}\text{C}$, in the Si flux of $\Phi=1.8\times 10^{14}\text{ cm}^{-2}\text{ s}^{-1}$ for: a) 150 min, b) 210 min.

Since the size of the spot of UV beam irradiating sample and causing photoemission from the valence band is macroscopic (it has the lateral size of around 1,5mm x 2 mm), it irradiates both graphitized and ungraphitized areas, where clean SiC was restored. Therefore, a presence of a very weak Dirac cone, characteristic for the monolayer graphene shows, that even after annealing the sample at temperature slightly below equilibrium temperature for 150min, there are still some areas on the surface covered with continuous graphene film. However, after 210min, all such areas disappear, confirming the assignment of the SiC' component in the XPS spectrum to the areas of restored, reconstructed surface of silicon carbide.

Evolution of the area share of different C1s spectrum components in time is shown in Fig. 41.

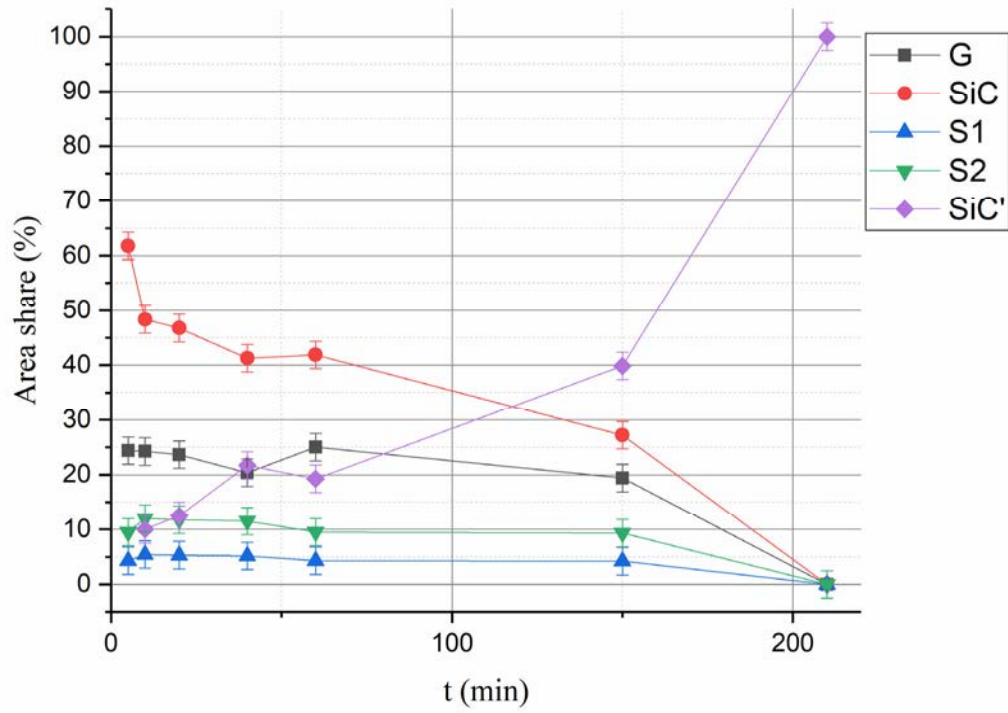


Figure 41: Time evolution of the area share of G, SiC, S1, S2 and SiC' components for the sample annealed in the quasi-equilibrium conditions.

In order to better visualize the reaction kinetics, the plot of the time-evolution of the reciprocal area share of all the components other than SiC' is shown in Fig. 42.

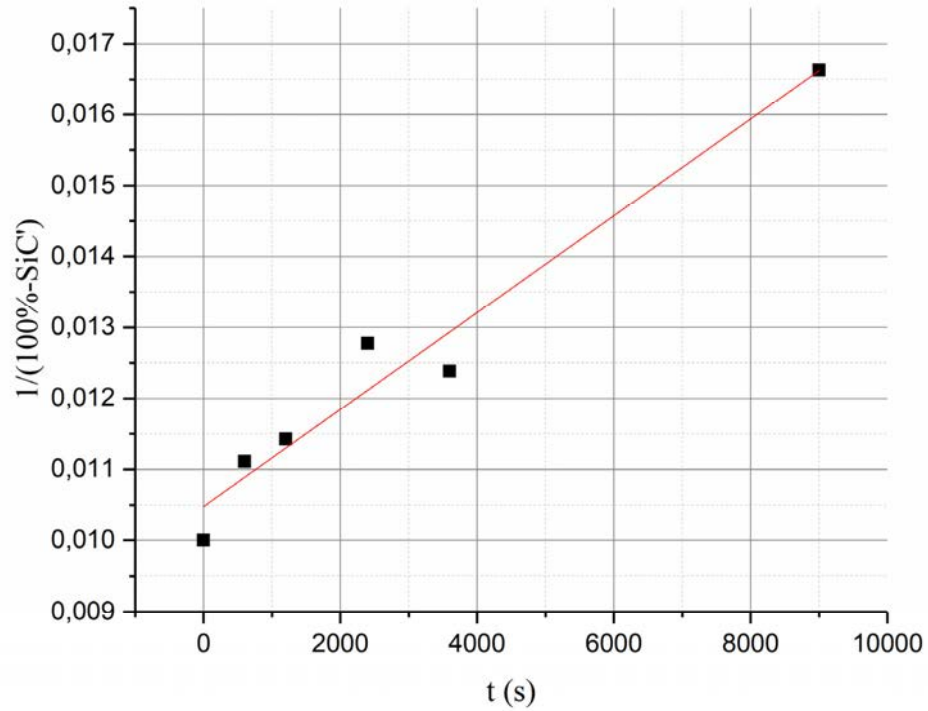


Figure 42: Time-evolution of the reciprocal area share of the C1s components different then SiC'.

Although these results are burdened with uncertainty, the linear plot of the time evolution of $(100\% - [\text{SiC}'])^{-1}$ resembles the behavior of the second-order chemical reaction, for which the linear relationship between the reciprocal of a reagent concentration and time is expected. The plot is fitted with a straight line, with a reasonable value of $R^2=0,95$. The slope of the line, which is theoretically equal to the reaction rate, has the value of around $k=6.8 \times 10^{-7} \text{ s}^{-1}$.

Although more research is required to accurately determine the reaction rate and its activation energy, it is evident from the results that the clean SiC can be restored from previously grown graphene overlayers. This shows, that the graphitization reaction is in fact reversible. Inhibition of graphene growth for SiC samples annealed under a Si beam, is therefore a result of the dynamic equilibrium ($\text{SiC} \rightleftharpoons \text{Si} + \text{G}$), resembling “true” chemical equilibrium. In our experiments, initial graphitization of the sample is performed in the temperature slightly above the equilibrium temperature, for the given Si flux density, which shifts the reaction towards the products side ($\text{Si} + \text{G}$). The following prolonged annealing is performed at the temperature slightly below the equilibrium temperature, for the applied Si flux, which shifts the reaction back towards the reactant side (SiC substrate). Although a formation of silicon carbide “islands” on a graphitized sample, annealed at temperatures of 1000-1100°C after Si deposition, has been previously observed by Xia et. al. [139], it hasn’t been thoroughly investigated so far.

The possibility of conducting graphene growth near the equilibrium conditions makes the synthesis process described in this work significantly different from the alternative methods based on silicon carbide. This is because the Si flux incoming on the annealed surface can be higher than the Si flux emitted from it, unlike for high-pressure/confinement graphitization processes.

AFM images, showing morphology of the surface annealed for 210min, containing only restored, clean SiC, are shown in Fig. 43.

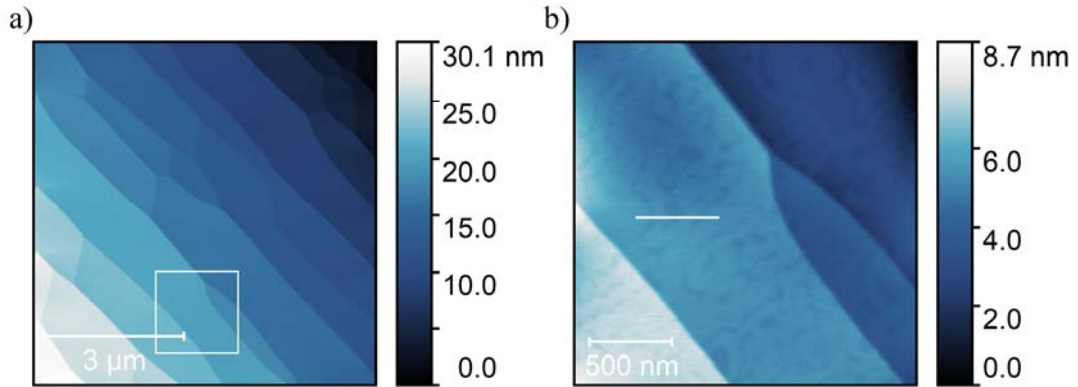


Figure 43: AFM images of the sample annealed at $T=1347^{\circ}\text{C}$, in the Si flux of $\Phi=1.8\times 10^{14}\text{ cm}^{-2}\text{s}^{-1}$ for 210 min. Fig. 43b is the enlarged scan of the area marked by the white square in Fig. 43a.

Surface morphology after prolonged annealing is completely different than the morphology of the samples of graphene on SiC (0001), grown in comparable temperatures (see Table 4). It is characterized by a very ordered and regular terrace structure. Terraces have the width of around $1\mu\text{m}$ and the height of around 3-4nm, showing the effects of step bunching: 4nm is the height of 16 SiC bilayers. The surface seems very smooth and uniform, however, upon closer inspection, the terraces appear to be covered in the elongated, meandering pits. Fig. 44 shows the height profile, measured around the line marked in Fig. 43b and averaged over 3 neighboring pixels.

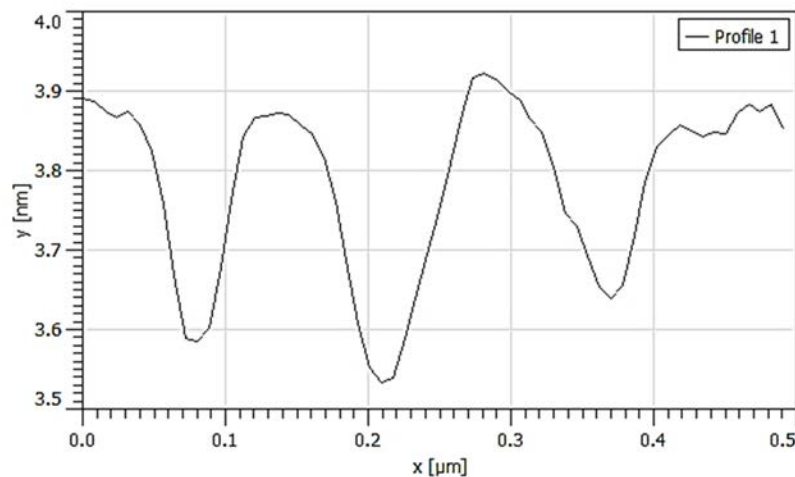


Figure 44: Height profile taken along the line marked in Fig. 33.

The pits seem to have the height of around 0.25-0.3nm, which is approximately equal to the height of a single SiC bilayer. The origin of the pits remains unknown; it's possible that even

longer annealing would lead to their disappearance. However, it is evident that the recovered SiC surface has a very ordered morphology, with relatively wide, step-bunched terraces.

In order to study surface ordering, LEED experiments were also performed. Fig 45 shows LEED patterns of the sample annealed for 210min, with fully reversed graphitization, for two different incident electron energies.

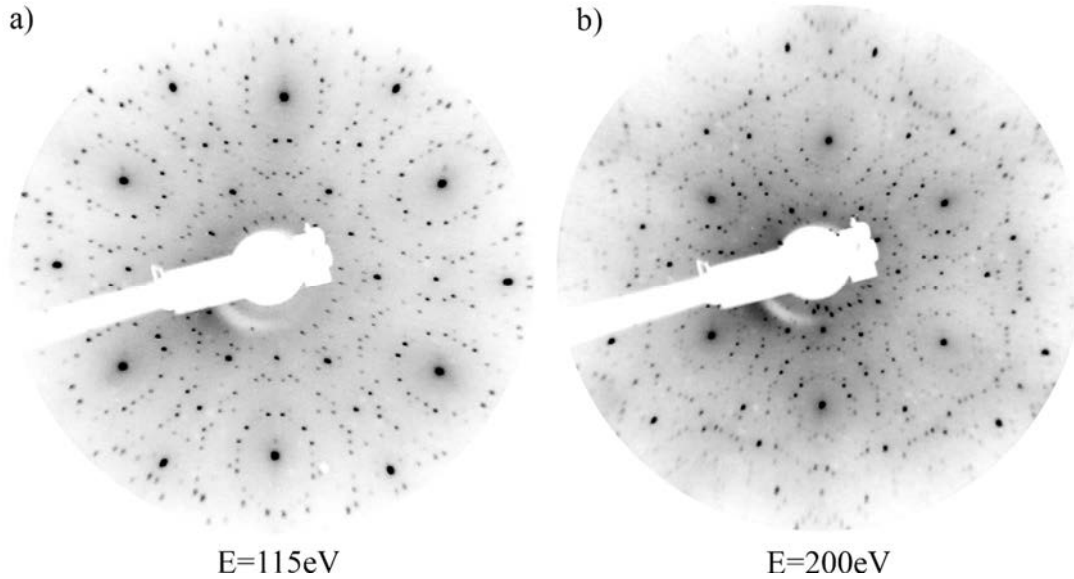


Figure 45: LEED pattern of the sample annealed for 210min, obtained for the incident electron energy equal to a) 115eV and b) 200eV.

The pattern is very complex and numerous diffraction spots can be observed. It is clear that while the surface contains only silicon carbide, its surface reconstruction has changed. Sharp diffraction spots and low background indicate that the surface is crystallographically well ordered, having large, coherent domains. The symmetry of the pattern is $p6m$, showing that it is a hexagonal reconstruction. More detailed analysis of the symmetry has been performed and the presence of $(3\sqrt{7} \times 3\sqrt{7})R \pm 19,1^\circ$ and $(\sqrt{19} \times \sqrt{19})R \pm 23,4^\circ$ reconstructed domains has been confirmed, with the additional possibility of the $(\sqrt{21} \times \sqrt{21})R \pm 10,89^\circ$ domains [132], through a procedure briefly described in section 3.1. Due to the distortions in the LEED imaging, caused by the projection and residual electrical fields, some errors are expected, but the estimates show that they shouldn't be higher than 0.25 for the factors and 1° for the angles. Observed structure is qualitatively very similar to the structure obtained through annealing the surface covered with 1nm-thick layer of Si in $T=1065^\circ\text{C}$ and contains has the same symmetry elements (see Table 3-4), including rotational symmetry around (1x1) spots, which supports the conclusions regarding graphitization reversibility. The observed surface phase bears similarity to the Si-rich phases on 6H-SiC(0001) surface reported by Starke et al. [89] and Heinz et al. [140], although some differences are also observed. Those phases have their Si content between that of 3 x 3

and ($\sqrt{3}\times\sqrt{3}$) SiC phases. I expect that the Si content in this case is likely similar to that of ($\sqrt{3}\times\sqrt{3}$) phase, because other Si-rich superstructures, discovered in this work, were formed in the temperatures close to the formation temperature of ($\sqrt{3}\times\sqrt{3}$) phase.

4.2 Improvement of the graphene growth process

Experimental results presented in Chapter 3 show, that applying Si flux during temperature-activated growth is beneficial for the quality of graphene synthesized on SiC (0001). The effect of the Si beam is especially visible on the nano-scale, in terms of the improved ordering of the buffer layer and the reduction of the concentration of various surface and sub-surface defects. However, the studies of the morphology of the obtained samples on the micro-scale show, that the surfaces remain rather inhomogeneous, and that the growth method needs to be improved to enable the growth of high-quality, uniform films of graphene (see section 3.4).

It is clear, that the process would benefit from highest attainable growth temperatures, as the mobility of carbon atoms on the surface is temperature-dependent and is a major factor determining the homogeneity of the final surface. However, the net Si flux emitted from the graphitized surface strongly increases with an annealing temperature, and needs to be effectively counteracted in order to avoid the formation of multi-layer graphene, or graphite. In case of this work, it is an external Si atomic/molecular beam hitting the annealed surface, that slows down Si sublimation. The limiting factor in increasing the process temperature, in this case, is the maximum available Si flux density, which is determined by the type of the source and the geometry of the system, especially a distance from the source to the sample. The maximum Si flux available in case of this work is equal to $\Phi=2.5\times10^{14} \text{ cm}^{-2}\text{s}^{-1}$, which corresponds to the nominal Si growth rate of $30\text{\AA}/\text{min}$. This flux is considerable, nonetheless, in case of SiC (0001) surface, it can fully inhibit its graphitization for the temperatures of up to around 1380°C , which, as evidenced by AFM measurements (see Table 4), is not enough to achieve satisfactory surface homogeneity. It is also much lower than the temperatures used in the buffer gas- or confinement- controlled graphitization, which are typically higher than 1700°C .

The reader can now realize the main challenge of optimizing this growth method, which can even seem paradoxical: how to increase the process temperature by a few hundred degrees, which will inevitably lead to the massively enlarged Si sublimation rate from the surface, when the maximum available Si flux density, slowing down this sublimation and controlling graphene coverage, remains low and cannot be easily increased. In short, the answer is to make use of the previously described reversibility of SiC graphitization. The process has to consist of at

least two steps, designed to: (1) grow thicker, multi-layer graphene in high temperatures, which ensure the high mobility of carbon atoms on the surface and its homogeneity and then to: (2) “thin down” multi-layer graphene to the desired thickness, by reversing the graphitization process through annealing the surface in the Si flux.

This should be possible to achieve by utilizing slow heating and cooling rates. When the temperature of SiC is slowly increased, the reaction equilibrium (Eq. 27) shifts slowly towards the products side, until the final process temperature is reached, which is accompanied by the formation of graphene overlayer. Its thickness is then reduced when the temperature is slowly decreased, shifting the reaction equilibrium back towards the substrate (SiC) side.

In order to test this hypothesis, I have prepared two samples in the highest Si flux possible to obtain in the system used in this work, equal to $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, at the temperature of 1410°C. The first sample was prepared utilizing the usual fast heating and cooling scheme. The second sample was prepared in an identical conditions, but with heating and cooling rate equal to around 20°C/min (see Fig. 24 in section 3.5). XPS spectra of the two samples in the C1s region are shown in Fig. 46.

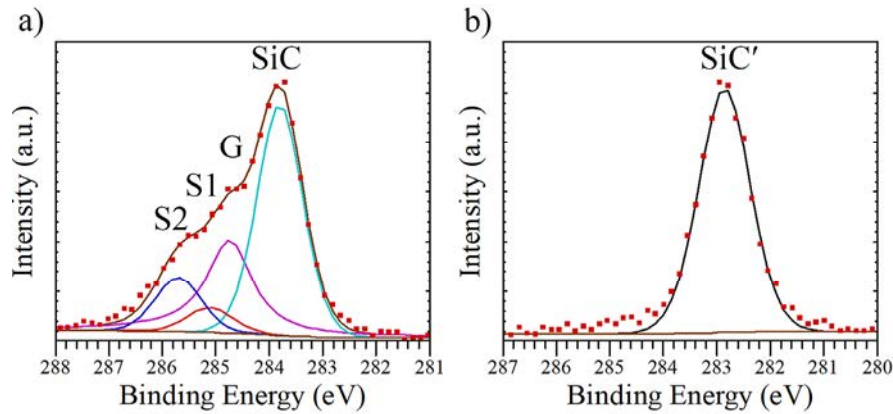


Figure 46: XPS spectra in the C1s region of SiC(0001) annealed in $T=1410^\circ\text{C}$, in the Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, using: a) fast, b) slow heating and cooling scheme.

XPS spectra show a striking difference between the samples, which were prepared in identical conditions, with the exception of the applied heating and cooling rate. The spectrum of the sample annealed within the fast heating/cooling scheme contains four components associated with graphene overlayers: SiC, G, S1 and S2 and the graphene coverage is equal to around a single monolayer. The spectrum of the sample annealed utilizing slow heating and cooling contains however only one component: SiC', characteristic for the ungraphitized surface. This is confirmed by the ARPES spectra, which show no graphene signal for the sample prepared

within the slow heating/cooling scheme, and a characteristic single-band dispersion relation for the sample prepared using fast heating and cooling, as shown in Fig 47.

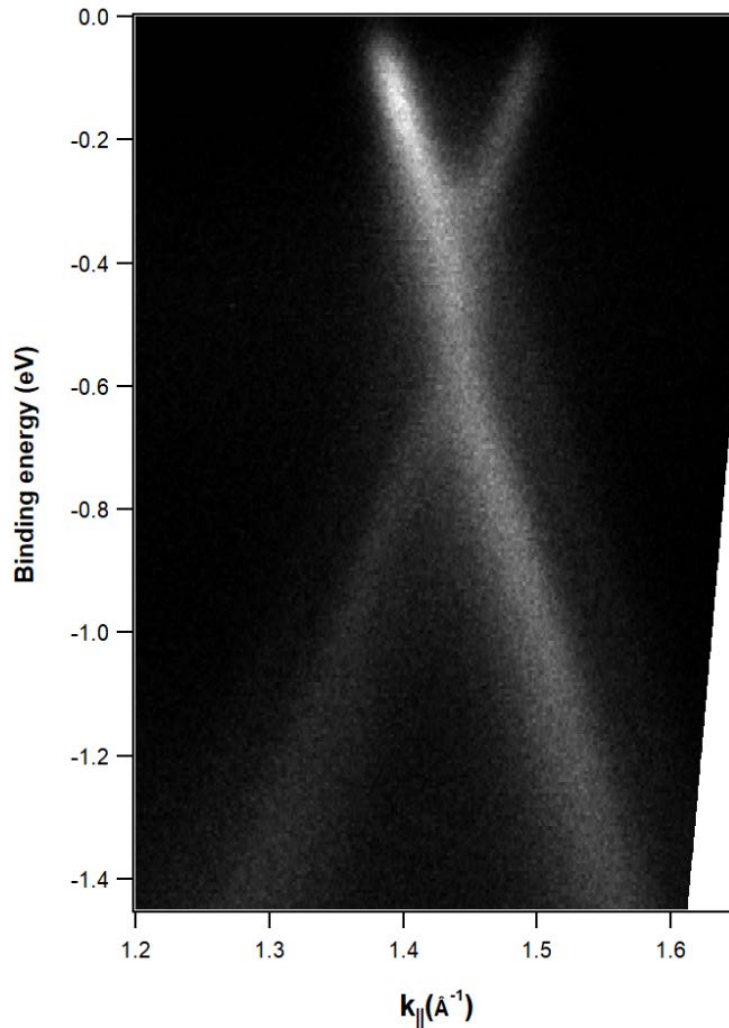


Figure 47: ARPES spectrum of the sample annealed using fast heating and cooling measured around the K point of the reciprocal lattice of graphene.

These results prove, that using the heating and cooling rate of around 20°C/min is low enough, to induce the etching of a single graphene layer with the Si flux during the reaction reversal phase (the cooldown of the sample). This means, that using this variation of the graphene growth method, one can effectively increase the maximum temperature of the process, increasing the mobility of the carbon atoms on the surface, which is crucial to obtaining high-quality material.

Using this new process design, in the Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, it is possible to completely avoid graphene formation for the temperatures of up to around 1495°C (which is understood as a maximum processing temperature, for which no graphene signal is detected in the ARPES spectra after the cooldown). This is almost 150°C higher than the highest temperature at which

it is possible to fully inhibit surface graphitization using fast heating and cooling scheme (1350°C). Starting from the maximum process temperature of around 1500°C, the cooldown rate of 20°C/min isn't slow enough to fully reverse the formation of the first graphene layer. XPS spectrum of the sample annealed in such conditions in the C1s region is shown in Fig. 48.

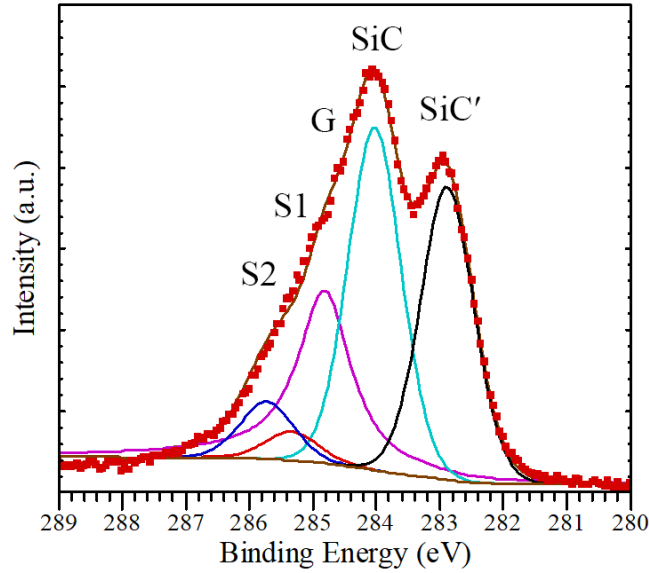


Figure 48: XPS spectrum in the C1s region, of the sample annealed at $T=1500^{\circ}\text{C}$ in the Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, using heating and cooling rate equal to 20°C/min.

Obtained spectrum consists of the 4 previously identified components: SiC, G, S1, S2 and SiC' component, characteristic for the surface with partly-reversed graphitization. The share of the SiC' component (around 30%) is similar to the case of the sample annealed for $t=150$ min at sub-equilibrium temperature of 1347°C (see Fig. 33), using fast heating and cooling scheme. It has to be noted, however, than in this case, maximum process temperature is much higher and equal to 1500°C. This indicates that the reversal of graphitization in higher temperatures happens in the similar mechanism to the samples annealed at near-equilibrium conditions. It also confirms the validity of the working hypothesis, which assumes that equilibrium phenomena happening at the surface can be utilized through the application of slow heating and cooling. XPS results suggest, that at least two separate regions coexist on the surface. The first region consists of graphene with the underlying buffer layer and bulk SiC (SiC, G, S1 and S2 peaks) and the second region is composed of clean, ungraphitized SiC, recreated during the slow cooldown of the samples (SiC' peak).

Fig. 49 shows the large-scale AFM map of the same sample.

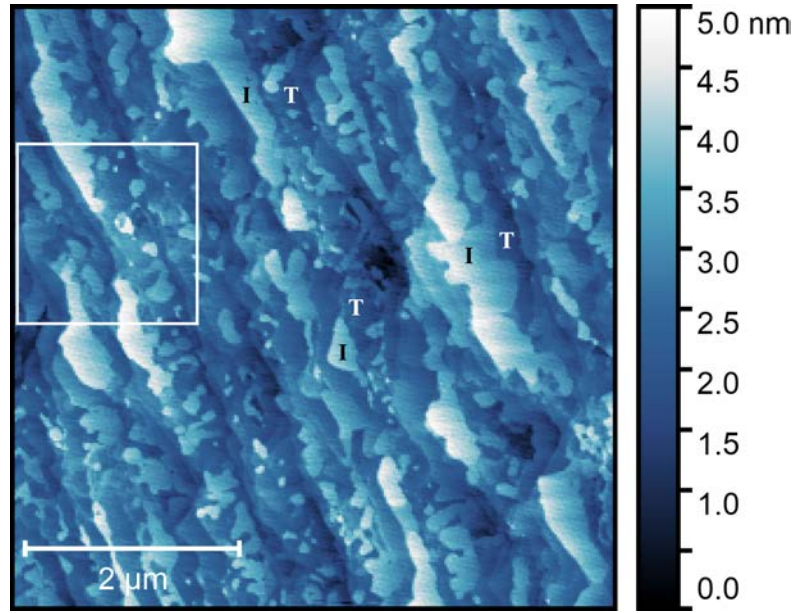


Figure 49: Large-scale AFM map of the sample annealed at $T=1500^{\circ}\text{C}$ in the Si flux of $\Phi=2.5\times 10^{14}\text{ cm}^{-2}\text{s}^{-1}$, using heating and cooling rate equal to $20^{\circ}\text{C}/\text{min}$.

As expected from the XPS measurements, the surface is inhomogeneous. It consists of at least two distinct regions: (1) terraces, arranged in a rather ordered step structure (three exemplary terraces are marked in the picture by T) and (2) islands of varying shape and size positioned both in the middle of the terraces and on their edges (three exemplary islands are marked in the picture by I). A few pits, with the depth of up to 2nm and lateral size of a few tens of nanometers, are also observed.

The identification of the islands and terraces can sometimes be difficult, especially in case of large islands growing on both lower and upper sides of terrace edges. It is however clear, that the morphology is changed by the presence of the islands, as compared to the regular, ordered terrace structure (compare with, for example, Fig. 37).

Fig. 50 shows an enlarged part of the AFM map, marked the white square in Fig. 49.

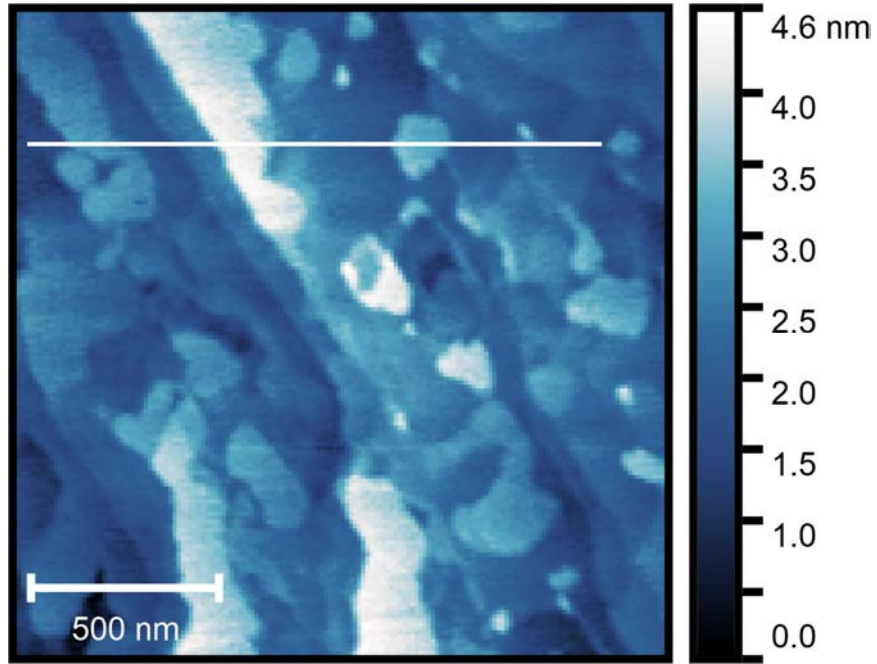


Figure 50: Small-scale AFM map of the sample annealed at $T=1500^{\circ}\text{C}$ in the Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, using heating and cooling rate equal to $20^{\circ}\text{C}/\text{min}$.

Fig. 51 shows the height profile taken along the white line in Fig. 42, with measured height differences between the islands and terraces.

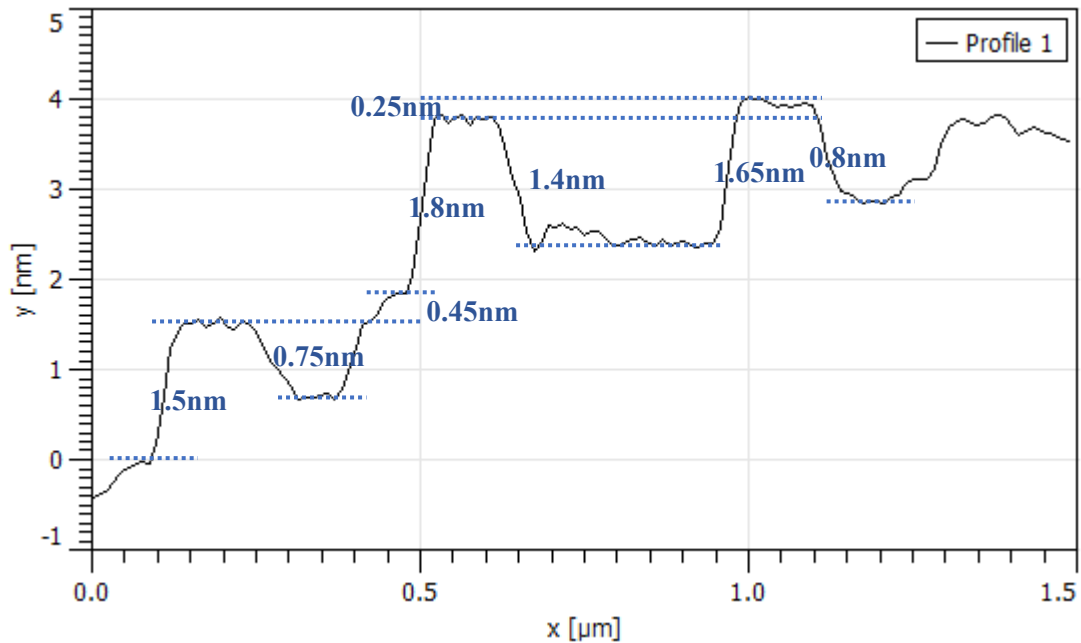


Figure 51: Height profile taken along the line marked in Fig. 33.

AFM data show that the islands are positioned both near the step edges and in the middle of the terraces. The former become often elongated along the step edges and reach the lengths of up to several micrometers, while the latter are usually smaller with the lateral size of several

hundreds of nanometers. Their height, with respect to the terraces, varies usually from around 0.75nm to 1.5nm, which is the height of 3-6 SiC bilayers.

It's worth noting, that 3 SiC bilayers have the same carbon content as a single graphene layer (or a buffer layer) and that the SiC' signal in the XPS spectra can be assigned only to the completely restored SiC, with no overlying buffer layer. This means, that the regions of the sample, which will be assigned to the SiC' signal, need to have the height of at least 1.5nm compared to the graphene layer (according to the XPS data, graphene is also present on the surface). That is because 1.5nm is the height of 6 SiC bilayers, which are created from a single graphene layer and a buffer layer during sample cooldown. Therefore the areas, positioned 1.5nm lower than the island tops and located within the same terrace, can be identified as graphene, which was not etched by Si during the reversal of graphitization. The islands themselves are likely the islands of re-grown silicon carbide and can be assigned to the SiC' signal in the XPS spectrum. When the height difference between the island and the underlying terrace is lower than 1.5nm, it is likely a result of a partial etch of the graphene layer initially present on the whole terrace. For example, the height difference equal to 0.75nm, means that three full SiC bilayers have already grown on the whole terrace (etching the graphene, but not the buffer layer), while 6 full bilayers have grown on the area of an island (etching both graphene and the buffer layer). The details of the growth mechanism of the SiC' phase will be discussed later, but based on the presented dataset, it is not possible to conclude, whether the growth happens from the top (at the surface of graphene, which would mean that the buffer layer remains intact, below the first 3 re-grown SiC bilayers), or from the bottom (at the SiC/buffer layer interface, after the diffusion of Si atoms through defects in the overlying graphene).

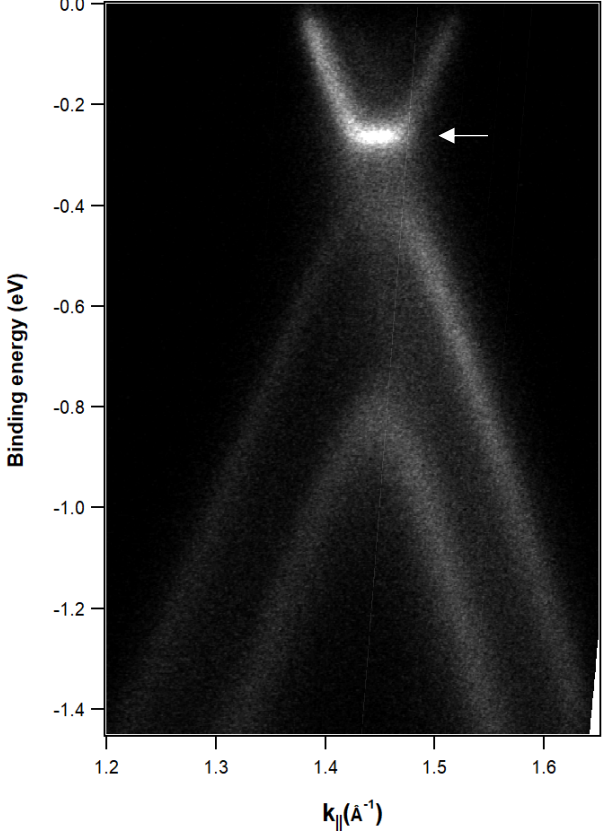
Further growth of SiC is possible only on the terraces partially covered with graphene and/or the buffer layer, since they are effectively a carbon source for the reaction. This is backed up by the observation that SiC surfaces don't accumulate excess silicon in temperatures higher than 900°C. As a consequence, the growth will continue, until a whole terrace is covered with restored SiC. This should result in the formation of a regular terrace structure, akin to the structure observed for the sample annealed for 210min. in the sub-equilibrium temperature (see Fig. 43a). The previously observed elongated ripples (see Fig. 43b) might be the remains of the coalescence boundaries between SiC islands growing in different parts of the terrace, where only 5 SiC bilayers are re-grown, as opposed to complete 6 bilayers re-grown at the islands covering the rest of the terrace (which would create a height difference of 0.25nm).

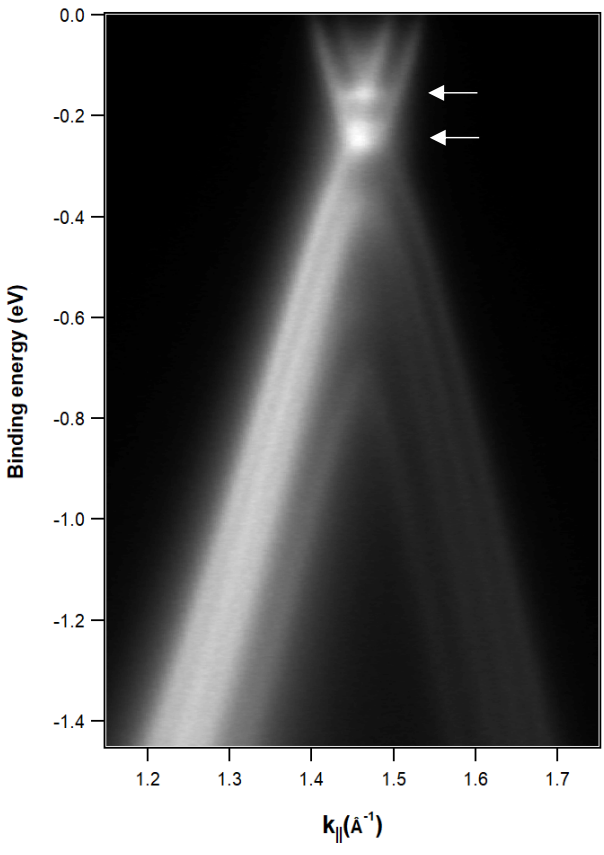
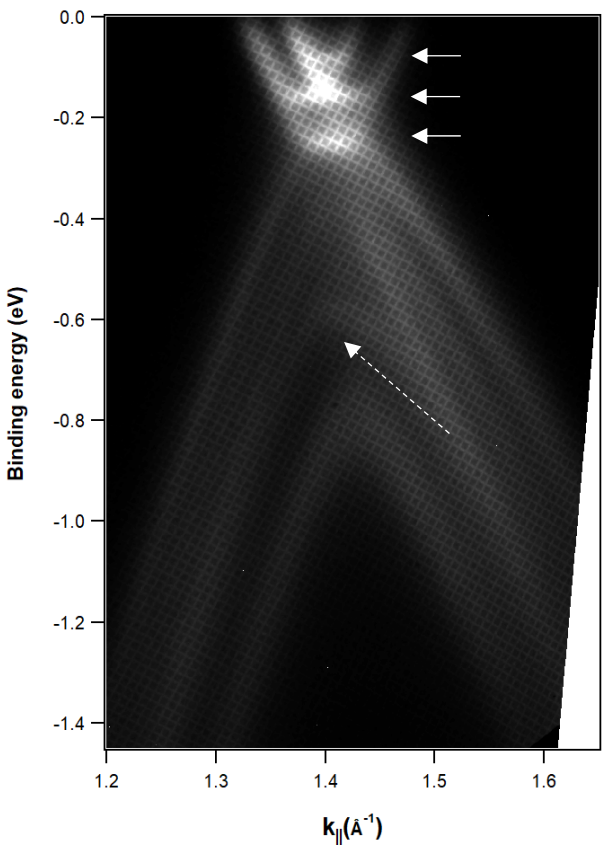
Results presented here confirm that clean SiC can be regrown on the previously graphitized surface, through etching the graphene overlayer(s) with Si atomic/molecular beam in high temperatures. This is a result of the reversal of the graphitization reaction, achieved by applying slow heating and cooling rates to the samples and can be used to increase process temperature, while avoiding a strong increase in the surface coverage with graphene.

4.3 High-temperature growth of few-layers graphene

Using the improved process flow, which utilizes slow heating and cooling of the samples under largest possible Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, a series of samples graphitized in temperatures higher than 1500°C is prepared. For those samples, amount of graphene grown in the first heating phase is expected to be higher, than the amount of graphene eroded during the cooldown phase and the reversal of graphitization process. This should result in the formation of graphene overlayers on the surface. ARPES spectra of the samples annealed at 1700°C , 1750°C and 1810°C , measured around the K point of the graphene lattice, are shown in Table 5.

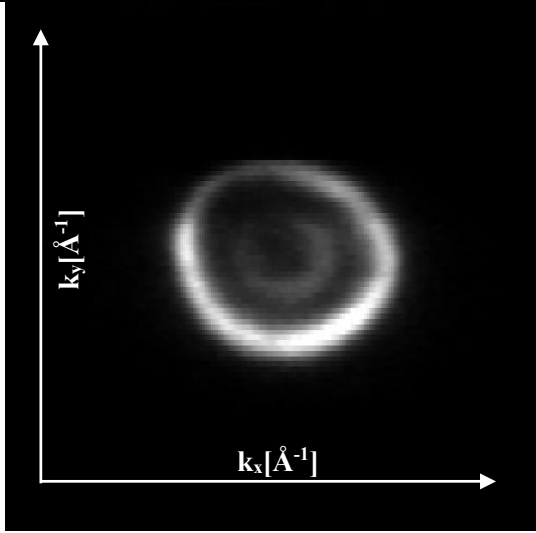
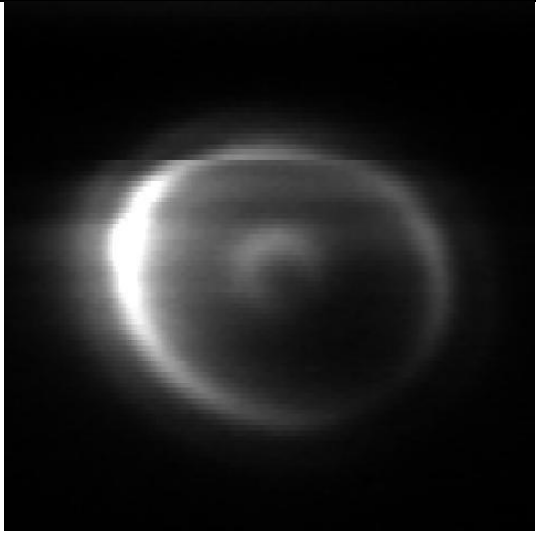
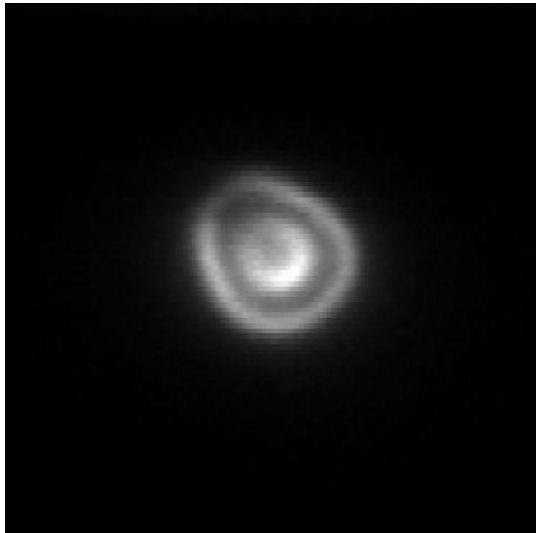
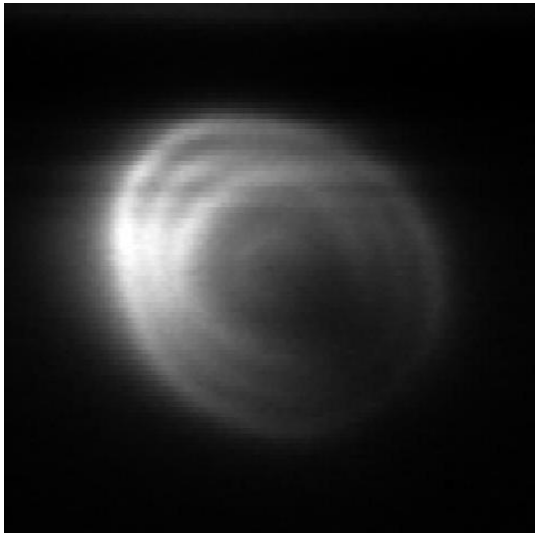
Table 5: ARPES spectra of the graphene grown via high-temperature annealing.

No.	T	No. of layers	ARPES spectrum
1	1700°C	2	

2	1750°C	4	
3	1810°C	5	

The number of graphene layers is determined by counting the number of bands visible in the ARPES spectra. In case of bi- and tetra-layer graphene, four branches can be easily recognized, while in case of 5-layer graphene, the fifth branch is somewhat less pronounced and is marked by a dashed arrow. The constant-energy ARPES spectra, obtained at the SOLARIS National Centre for Synchrotron Radiation, for bi- and tetra-layer graphene, are shown in Table 6.

Table 6: Constant-energy spectra of bi- and tetra-layer graphene.

	$E_B=0.05\text{eV}$	$E_B=0.8\text{eV}$
BL G		
4LG		

Constant energy maps confirm the presence of 2 or 4 layers of graphene on the annealed surfaces, as indicated by the presence of 2 or 4 bands. Created graphene is n-doped by the buffer layer, as expected for graphene grown on silicon carbide. In case of tetralayer graphene, the band structure is characteristic for the predicted structure of ABC-stacked graphene (see Table. 1 and Ref. [20]). This is consistent with observations of other researchers, who found

that ABC-stacked graphene forms preferentially on SiC (0001) [141], although growth of up to three layers of graphene has been demonstrated [142].

All obtained dispersion map contain characteristic flat parts of the electron band(s) located near the Fermi energy (marked by white, solid arrows in Table 6), which are often referred to as “Sombbrero” structures. This characteristic structure is especially visible in case of bilayer graphene and the presence of flat bands means that a high density of states exists in a narrow energy range. This has been studied before for bilayer graphene and identified as the 2D-extended van Hove singularity [143]. Due to the indications of enhanced electron-phonon coupling, it was theorized that this could help achieving superconductivity of graphene. Spectrum of tetra-layer graphene confirms the presence of two flat parts of the electron bands, while the electronic structure of 5-layer graphene contains an additional, third flat part, near the Fermi level, as shown in detail in Fig. 52.

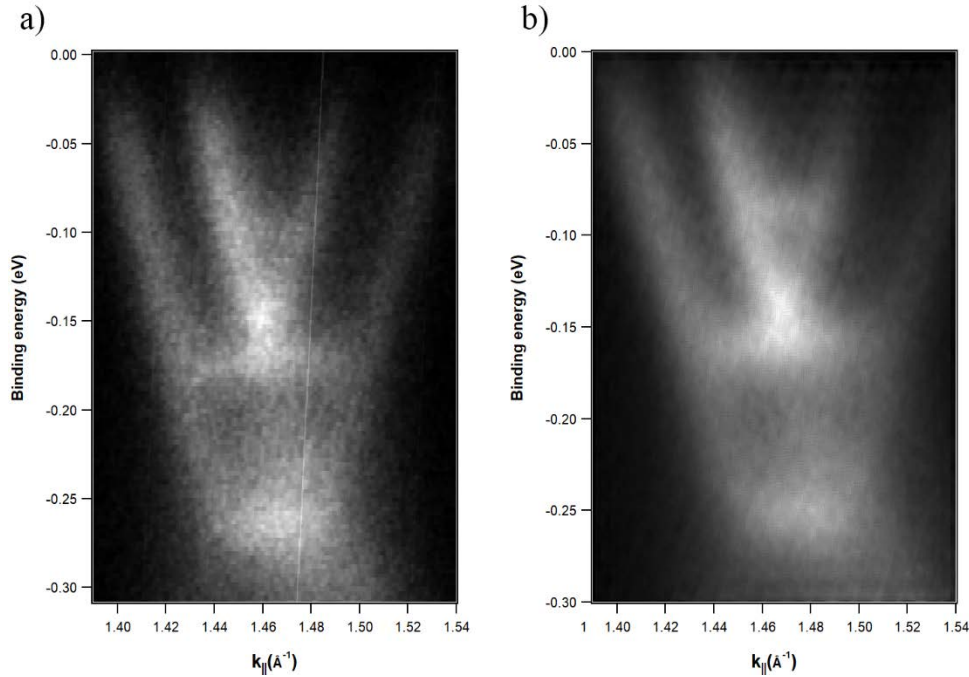
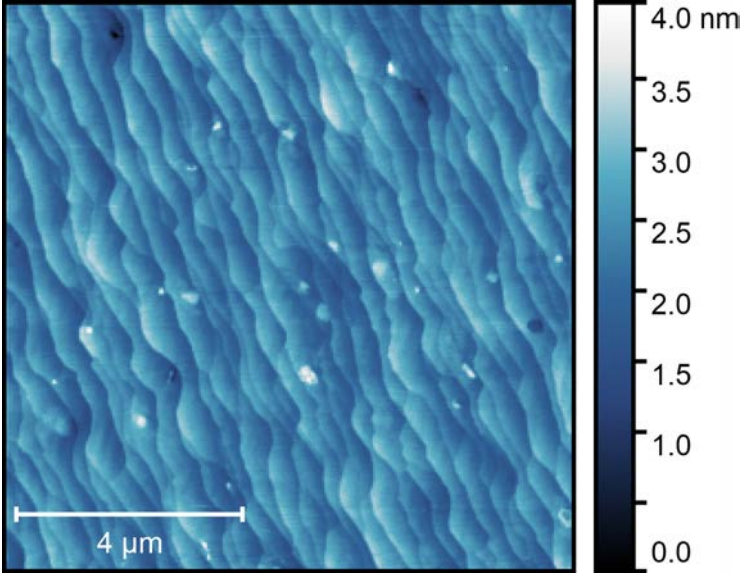
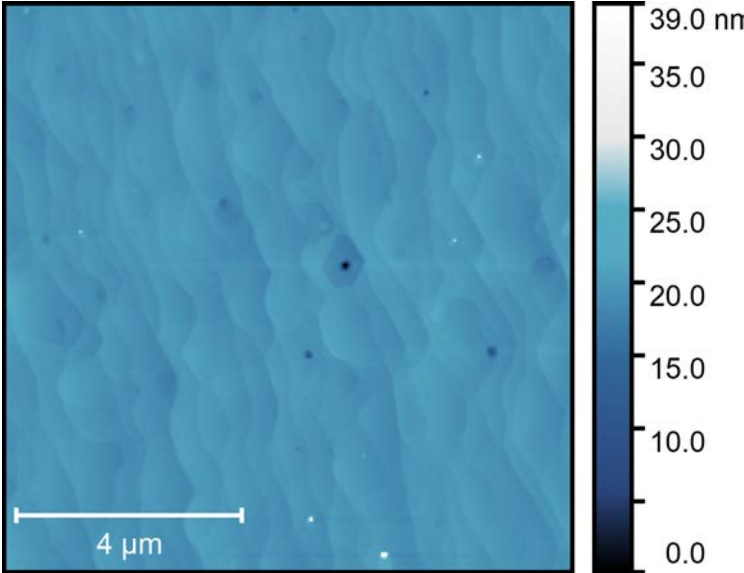


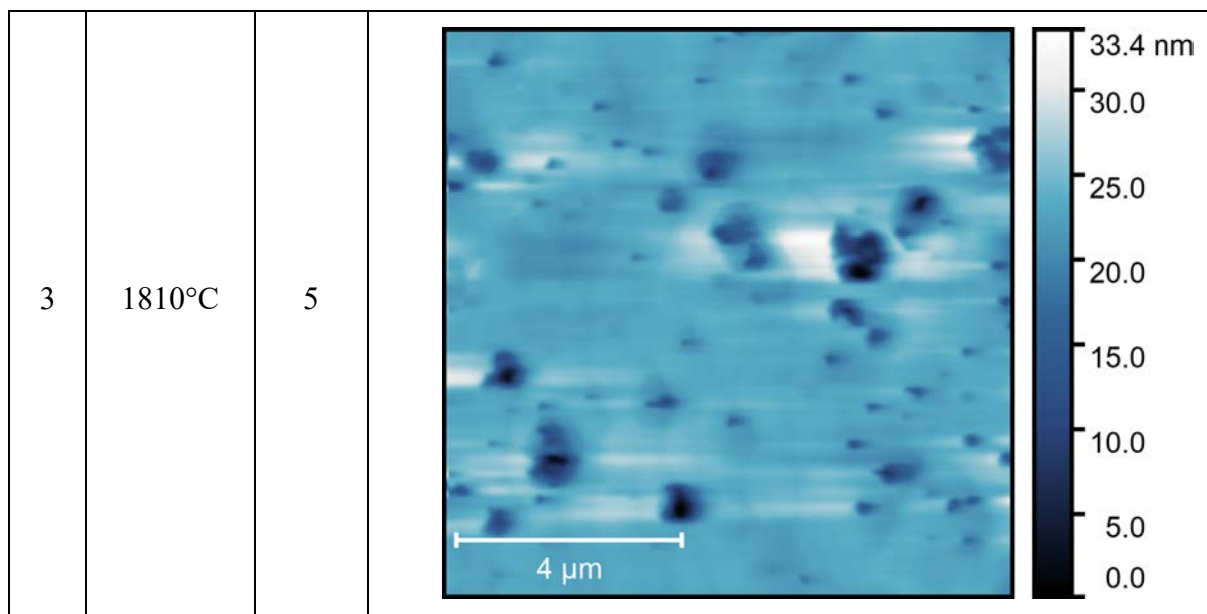
Figure 52 ARPES spectra around the K point of the reciprocal lattice of: a) tetra- b) 5-layer graphene.

Detailed spectra taken near Fermi energy, shown in Fig. 52, reveal that in case of tetra- and 5-layer graphene, the upper bands (located at $E_B \approx 0.15 \text{ eV}$) might show some dispersion near the K point of the reciprocal lattice, creating a small, but detectable “kink”. Additional flat band in 5-layer graphene is located at $E_B = 0.07 \text{ eV}$. To our knowledge, it is the first observation of a multiple flat bands in a multi-layer graphene grown on SiC (0001).

AFM measurements of the surface morphology of the samples grown in high temperatures were also performed and the results are summarized in Table 7.

Table 7: AFM maps of the samples grown in high temperature.

No.	T	No. of layers	AFM map
1	1700°C	2	
2	1750°C	4	



These images are representative for the studied samples and AFM measurements were repeated on the multiple spots on the surface of each sample. The surface of bilayer graphene seems to be most homogeneous of all the prepared samples. Even though some small islands, with the height of 3-4nm are observed, the terrace structure is otherwise very regular and well-developed. The terraces are very narrow, with the width of several hundreds of nanometers. The islands are likely agglomerates of silicon, formed due to the excess Si left by the beam during sample cooldown.

As the annealing temperature increases, deep pits begin to form on the surface. In case of tetra-layer graphene, only few, narrow pits are observed, with the height of up to 20nm and the width of around few tens of nanometers. Otherwise, the terrace structure remains well ordered, although the terraces, on average, tend to be wider, some having the width of over 1μm. (this is based on the observations of multiple areas on the surfaces of the samples covered with both bi- and tetra-layer graphene). However, in case of 5-layers graphene, numerous pits start to dominate the surface morphology, with the width of up to 1μm and depth of up to 30nm. The step structure of the surface is almost invisible due to AFM artifacts, caused by the pits.

Presence of pits of various sizes is visualized in 3D images, with the surface of the samples pointing downwards, shown in Fig. 53.

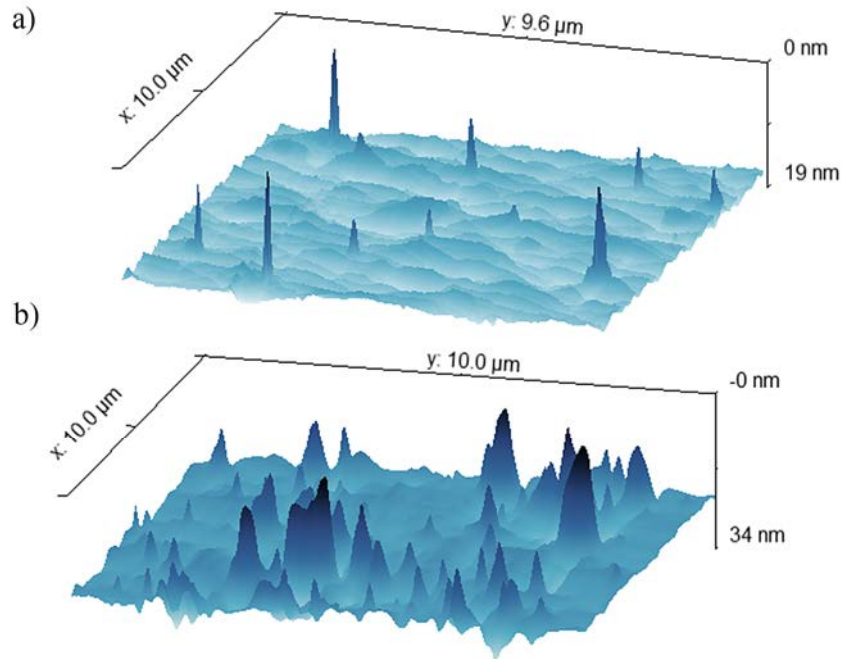


Figure 53: 3D visualization of the pits formed on the surface of: a) tetralayer and b) 5-layer graphene.

Obtained results show, that increasing an annealing temperature above 1700°C, for a Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, and a heating/cooling rate of 20°C/min, leads to an increased concentration of deep pits formed on the surface of SiC, with the depth of 10-15 SiC bilayers. Formation of deep pits during graphene formation has been reported, although their depth was usually smaller than in our case and equal to around 6nm [144].

It has been shown, that after the growth of the buffer layer, there are two main diffusion pathways of Si atoms desorbing from bulk SiC: either vertically, through the buffer layer and/or overlying graphene layers to the surface, or laterally, through the bulk to step edges [145]. While in UHV conditions, desorption through the step edges is energetically preferred, under Si flux both pathways can be activated. Lateral diffusion of the Si atoms to the step edges is known to facilitate the formation of deep pits during graphene growth. On the other hand, when Si desorption is limited (such as in case of this work, by the application of an external Si flux), its desorption via a vertical diffusion pathway facilitates pit-free graphene growth. Therefore it is likely, that using higher Si flux, which would further suppress the desorption of Si atoms from the step edges, could lead to a more controllable process and lead to the growth of pit-free graphene with the thickness of more than 4 layers. Due to the fact that the reaction is partly reversed during sample cooldown, it is also possible, that utilizing even slower cooling rate

could also lead to SiC re-growing in the pits. That is because graphene etching, leading to the growth of SiC in the reversal phase of the process, depends on the ability of Si atoms to diffuse inside the pits. Nonetheless, using the reversible graphitization method in the current form, up to 4 layers of graphene can be grown on an almost pit-free surface.

An important parameter characterizing graphene on silicon carbide, is the average step height. The topic was introduced in section 2.7. In short, graphene formation on SiC (0001) with other growth methods, such as confinement-controlled growth, or atmospheric-pressure graphitization, results in the formation of macro-steps on the surface, with the height of up to several tens of nanometers, via the step-bunching mechanism. Formation of such macro-steps is considered to be one of the main factors, hindering practical applications of graphene on silicon carbide, as they strongly scatter conduction electrons and introduce anisotropy of the electrical parameters of graphene.

Fig. 54 shows small scale AFM maps of bi- and tetra-layer graphene, prepared in $T=1700^{\circ}\text{C}$ and $T=1750^{\circ}\text{C}$, respectively.

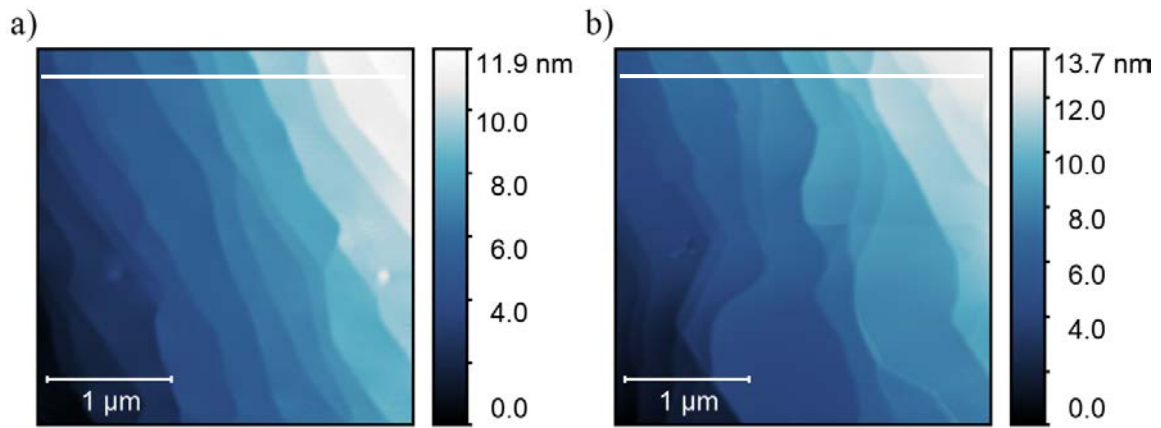


Figure 54: Small-scale AFM maps of: a) bilayer graphene, prepared in $T=1700^{\circ}\text{C}$, b) tetra-layer graphene prepared in $T=1750^{\circ}\text{C}$.

In the small, $3 \times 3 \mu\text{m}$ scans, observed terrace structure is well ordered and devoid of pits and large islands. For bilayer graphene, terraces are more parallel to each other, while in case of tetralayer graphene, neighboring terraces sometimes undergo coalescence via the step-bunching mechanism. Fig 55 shows height profiles measured along the lines marked in Fig. 54, with the measured step heights.

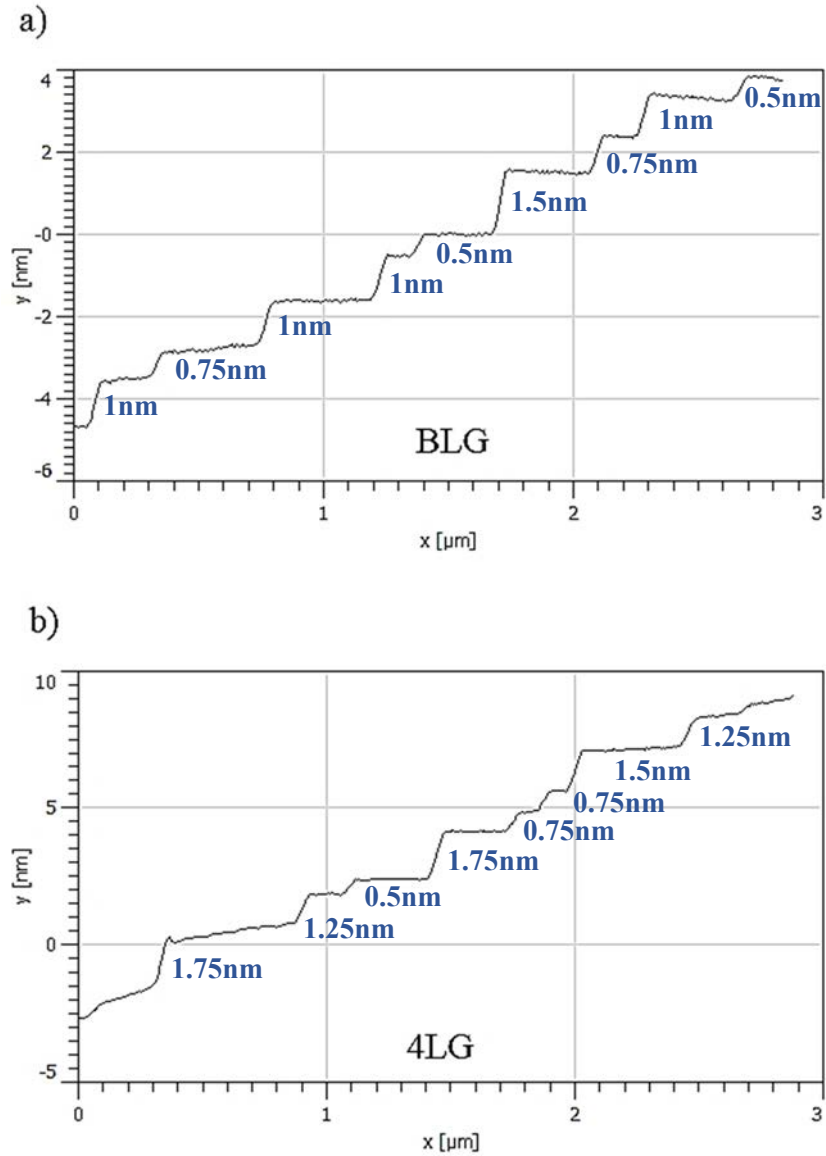


Figure 55: Height profiles measured along the lines in Fig. 46 for the: a) bilayer graphene, prepared in $T=1700^\circ\text{C}$, b) tetra-layer graphene prepared in $T=1750^\circ\text{C}$.

Observed step heights vary from 0.5nm (2 SiC bilayers) to 1.75nm (7 SiC bilayers). It is evident that, to a certain extent, step bunching occurs on the surfaces. After probing multiple areas on the surface, for bilayer graphene, steps with height between 0.25 and 2.5nm were observed, with the average step height close to 0.7nm (height of around 3 SiC bilayers), while for tetra-layer graphene, step heights between 0.25 and 2.75nm were observed, with the average step height close to 1.1nm (height of around 4 SiC bilayers). Similarly low values are found for all samples prepared using our slow scheme.

Substantial effort has been put in recent years into understanding step-bunching phenomena occurring during graphene growth and minimizing its effects. Bao J. et. al. has reported step heights of 0.75-1.5nm, using sequential control of step bunching [107], while Kruskopf M., et.

al. reported step heights between 0.25 and 2.5nm [108], utilizing polymer adsorbate for the enhanced buffer layer nucleation. It is clear that the method of partially reversible graphitization in Si flux, developed in this work, is comparable to the best literature examples, even though its optimization potential is far from being exhausted (note, that without controlling this process, step heights can reach values higher than 50nm and the phenomenon is often referred to as “giant step bunching” [146])

Amount of step-bunching on the G/SiC(0001) surface has been previously linked to the heating rate of the substrate, however, previous reports seem to be contradictory to our findings. While in our case, low heating and cooling rate resulted in the minimal step-bunching on the surface, Bao J., et. al., have found, during their experiments concerning graphene growth in atmospheric pressure buffer gas [107] that low heating rate increases step-bunching. They also found, that step bunching occurs to the highest extent at temperatures between 1200°C and 1600°C, below the temperature of graphene formation, while the graphene film on the surface actually inhibits the step bunching. Therefore long annealing below graphene formation temperature inevitably leads to the formation of macro-steps at the surface.

The key difference between the method studied here and the atmospheric-pressure buffer assisted graphitization, is that external Si atomic beam may shift the surface stoichiometry to the Si-rich while at the absence of such beam it tends to be Si deficient. This should not be understood as a formation of solid Si on surface. Fissel et al. [135] reported that SiC(0001) 3×3 surface does not accumulate excess Si even at temperatures as low as 900°C. Nevertheless, the Si atoms coming on the surface with the considerable rate of $2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$, (corresponding to growth rate of 30Å/min, if 100% condensation occurred) have certain residence time on the surface and at step edges. Results obtained here show that their transient presence is sufficient to inhibit graphitization up to the temperatures 1350°C and on the other hand it strongly reduces the surface step flow/bunching.

4.4 Further optimization of the method

Repeated experiments show, that the reversible graphitization growth method can be used to grow high-quality bi- to tetra- layer graphene, with minimal concentration of defects and homogeneous, minimally step-bunched surface, devoid of deep pits. Samples show large degree of ordering both at nano- and at micro-scales and the method has been validated multiple times. However, attempts to grow single-layer graphene in a similar fashion faced some challenges.

Fig. 56 shows the ARPES spectrum of the sample annealed using the slow scheme (heating/cooling rate of 20°C/min), in the maximum Si flux of $\Phi=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ at $T=1550^\circ\text{C}$.

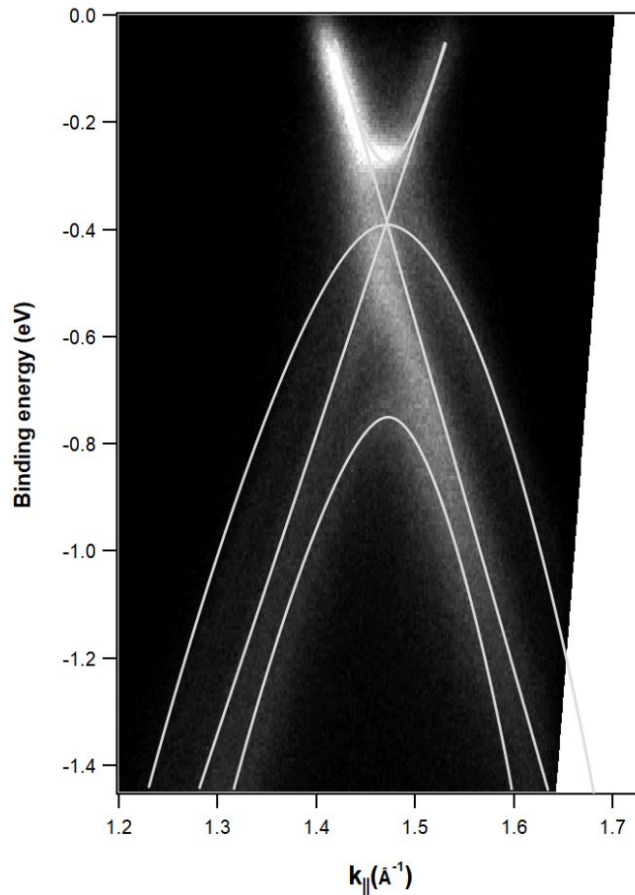


Figure 56: ARPES spectrum of graphene grown at $T=1555^\circ\text{C}$ with theoretical dispersion relation expected from the mixture of monolayer and bilayer graphene.

At first sight, it appears that three distinct branches of the Dirac cone can be detected in the spectrum, however, this isn't backed up by other observations. The process temperature is in this case lower than in case of previously synthesized bilayer graphene (1700°C) and the XPS spectrum shows lower area share of the G component. Average graphene coverage in this case is equal to around 1.5ML. It appears that the observed ARPES spectrum is, in fact, a sum of the spectra of mono and bilayer graphene; such spectra have been observed before [152]. This

means that the surface consists of coherent domains of two different thicknesses of graphene. This is backed by the AFM measurements of the surface, shown in Fig. 57.

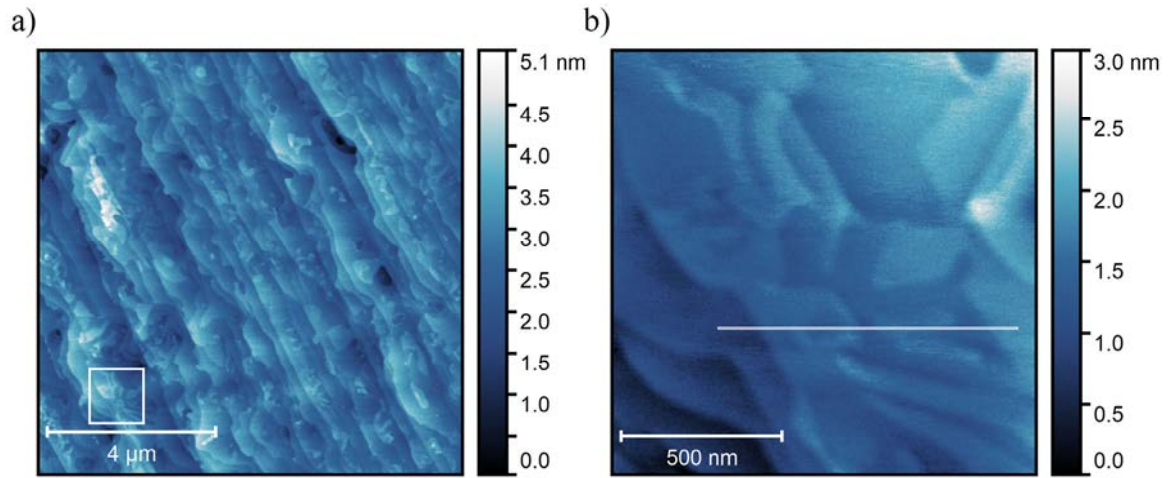


Figure 57: AFM maps of the SiC (0001) sample prepared in $T=1555^{\circ}\text{C}$, covered, on average, with 1.5L of graphene.

While the step structure of the surface is regular and well ordered, similarly to the samples prepared in higher temperatures, terraces are covered with islands of varying height and shape. Fig. 57b shows the enlarged, small-scale scan of the area marked in Fig. 57a. Height profile, measured along the line marked in Fig. 57b is shown in Fig. 58.

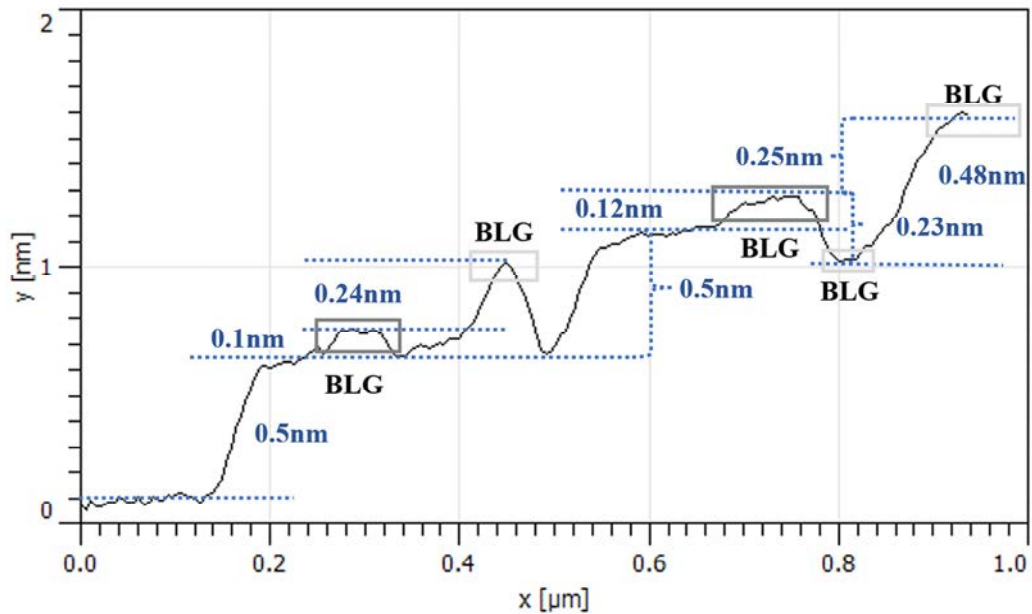


Figure 58: Height profile measured along the line marked in Fig. 50b, with measured step heights.

According to the bottom-up growth model, introduced in section 2.6 (see Fig. 11), bilayer graphene islands have an apparent step height of around 0.1nm. Based on that, two likely areas of bilayer graphene are marked in the height profile by dark-grey rectangles. It can be easily shown that any area, positioned $n \times 0.25\text{nm}$ ($n \times$ height of a single SiC bilayer) higher or lower from the bilayer graphene island will also contain bilayer graphene. This is because the change in graphene coverage from a one to two layers will have the observed height of $0.34\text{nm} \pm n \times 0.25\text{nm}$, i.e. the height of bilayer graphene spacing with additional difference in the number of underlying SiC bilayers. Such areas are marked by the light-gray rectangles.

It is clear, that for the process temperature of around $T=1550^\circ\text{C}$, the surface undergoes significant reorganization during the cooldown. However, further reduction of annealing temperature makes the process increasingly more difficult to control. Samples prepared in lower temperatures are characterized by a sub-monolayer coverage of graphene, because of the high degree of the reduction of graphene thickness occurring during the cooldown. In this work, I didn't find the exact combination of parameters that would result in the growth of an exactly monolayer graphene. This suggests that the buffer layer and the first graphene layer are characterized by the different kinetics of the (reversible) graphitization reaction then the overlying graphene. This difference in reaction kinetics has actually been observed in this work and is described in section 3.2 (see Fig. 30). Quantitative measurements show, that the graphene coverage in time changes in two phases. The kinetics of the first phase resembles self-limiting, first-order chemical reaction, inversely proportional to the amount of ungraphitized silicon carbide left at the surface. In contrast, the kinetics of the second phase, resembles zero-order chemical reaction, as the graphene growth is limited by the ability of Si atoms to diffuse through overlying carbon-rich layers.

It is worth noting, that carbon atoms in the buffer layer are already partially covalently bound to the silicon atoms in the substrate and, consequently, some C-C bonds in the buffer layer are less stable then C-C bonds in graphene, despite their identical spatial arrangement. Therefore, one can expect that re-creation of Si-C bonds between carbon atoms in the buffer layer and silicon atoms adsorbed on the surface (from an external beam) will be much easier than similar process in the extremely chemically inactive, complete graphene layer. This suggests that if there are a few graphene layers on the surface, new SiC is likely to be formed through the reaction with carbon atoms in the original buffer layer, after the diffusion of Si atoms through the defects in the overlying graphene. After such process, Si-C bonds are formed again between

the newly created SiC and the first overlaying graphene layer, transforming it into the new buffer layer.

In order to test this hypothesis and to gain an understanding of the mechanism of SiC re-growth we have performed a soft-XPS (SXPS) measurements at the UARPES beamline of the National Synchrotron Radiation Centre SOLARIS on a sample, for which graphene coverage was reduced from around 1.5ML to around 0.7ML through the graphitization reversal. The SXPS spectra have been measured, for the photoelectron emission angles 0° and 65° , with respect to the surface normal, and for the photon energies (PhE) in the range of 350 – 600 eV. It is important to note, that for these photon energies, the inelastic mean free path of the photoelectrons is around its minimum and corresponds to 1-2 atomic layers at 400 eV PhE and 2-3 atomic layers at 600 PhE [147]. It makes this method very surface sensitive, depending also on the tilt applied to the sample.

Fig. 59 shows spectra obtained for all incoming photon energies and two photoelectron emission angles used in the experiment.

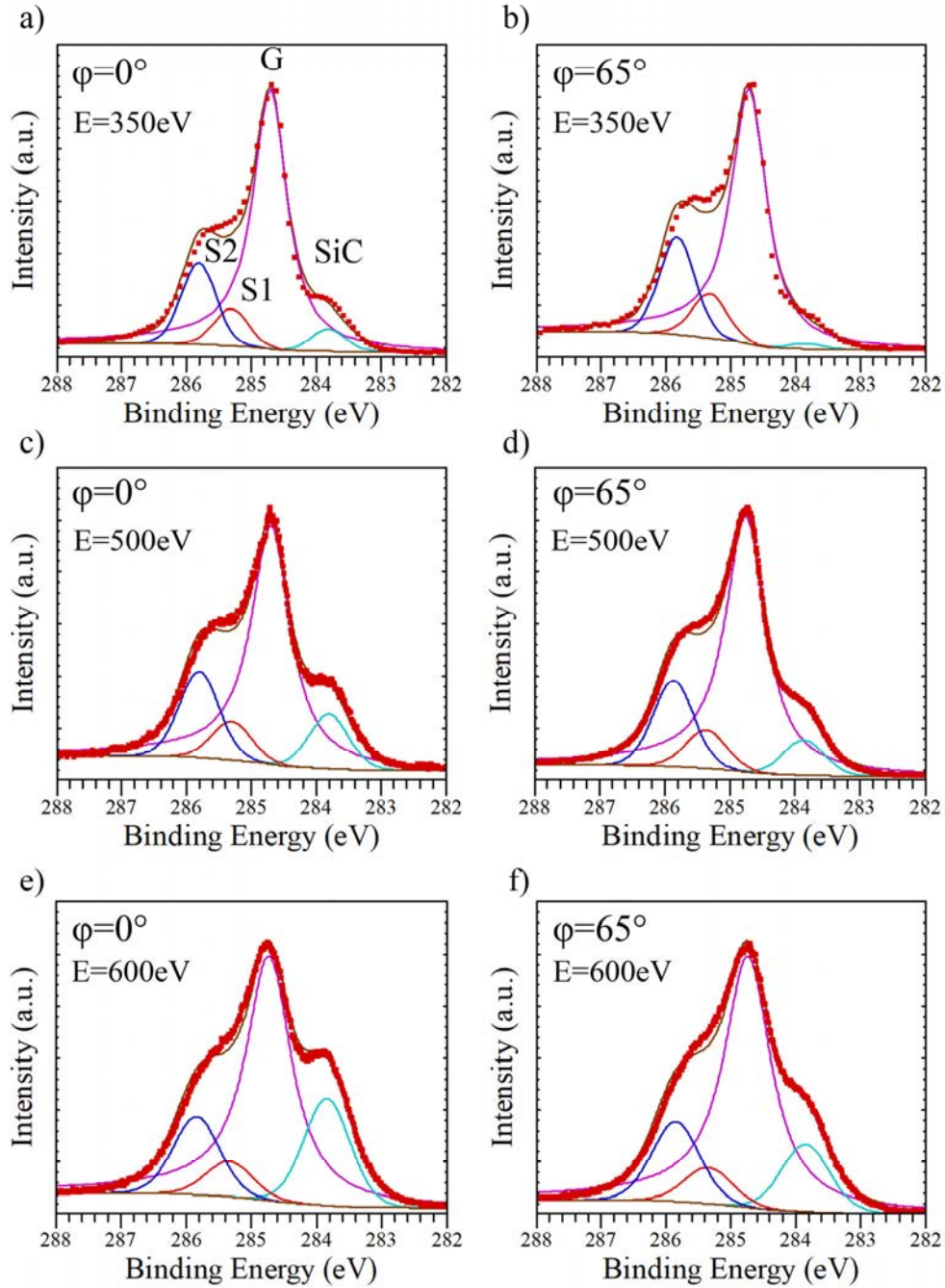


Figure 59: XPS spectra in the C1s region, of the partly graphitized sample, prepared using the reversible graphitization growth method, measured for the photoelectron emission angle, with respect to the normal to the surface, equal to: a, c, e) 0° and b, d, f) 65° , for the excitation energy equal to: a, b) 350eV, c, d) 500eV, e, f) 600eV.

Relative intensities of the G, S1 and S2 components are greatly enhanced for all incoming photon energies, compared to using the standard $\text{MgK}\alpha$ radiation (excitation energy equal to 1253.6eV; see for example Fig. 29) and dominate the spectra, which is expected for SXPS measurements. This effect becomes even more pronounced after increasing the photoelectron

emission angle. (S1+S2)/G ratio changes weakly upon sample tilt indicating that prevailing sources of these components are located in the top atomic layer. In contrast, the SiC component changes considerably which means that its sources are located below the top layer. At minimum probing depth, (350 eV, 65° emission angle) corresponding roughly to 1 ML of carbon, this component is hardly observable. The dataset is fully compatible with the abovementioned conclusions ensuring that we have properly interpreted this results as the emitter depth-induced effect and have not mistaken it with a photoelectron diffraction or other phenomena.

SXPS spectra don't show the presence of a SiC' component. This component would be observed if either: (1) the growth of SiC' phase happened in the topmost atomic layer of the samples, or: (2) the process happened below the topmost atomic layer, but progressed further, leading to the growth the islands of the SiC surface completely free from graphene and the buffer layer, resulting in the shift of the binding energies of the components due to band bending effects. These results show that the SiC regrowth happens beneath the surface, at the interface between graphene/buffer-layer and bulk SiC.

The process is, in principle, very similar to the intercalation of graphene on SiC (0001) with Si atoms, described in literature [147]. In those cases, silicon doesn't form chemical bonds with the original buffer layer, but rather diffuses beneath it, separating it from the underlying substrate. Intercalation, however, occurs at much lower temperatures; reported values range from 750 to 800°C. Full de-intercalation and desorption of Si atoms from the buffer layer – SiC interface occurs for temperatures higher than 1000°C [147], making it likely the reason why no chemical bonds between C and Si atoms are formed. In our case, desorption of Si atoms from the buffer layer through the structural defects in graphene is fully inhibited by the large flux of incoming Si atoms for temperatures much higher than 1000°C, which provides enough thermal energy to overcome the energetic barrier, associated with the formation of Si-C bonds and reversal of surface graphitization.

This also explains, why the process is more difficult to control as we get closer to the desired coverage of the surface with a single graphene layer. When no bilayer graphene is present at the surface, incoming Si atoms have a very low diffusion barrier before reaching the buffer layer, where Si-C bond formation and SiC nucleation will start. This effect is expected to be especially pronounced for the minimally step-bunched surfaces, such as the surfaces obtained in this work, because step edges form natural defects, where Si diffusion is likely to be the easiest (note, that bilayer patches for graphene on SiC are most often observed near the step edges). Therefore, the reaction rate will significantly increase as we get closer to the single

graphene coverage, resulting in the formation of either partly-graphitized samples, or samples with significant areas of bilayer graphene remaining after the cooldown. This effect is not a strong, fundamental barrier to achieving the growth of an exactly single layer of graphene using the method of partially-reversible graphitization, but it poses a significant optimization challenge.

It is very likely that this challenge will be solved in the future. One of the possible solutions is to strongly increase the cooling rate of the samples, immediately after the loss of protective bilayer graphene patches, which secure step edges from an enhanced erosion. This could be realized using a programmable electron beam heater, such as the one used in this work, with the immediate shut-down of an electron beam heating the backside of the sample at a requested time. This would require, however, either a knowledge of an exact temperature, at which such a loss occurs, or in-situ monitoring of graphene coverage.

Chapter 5

Summary

The aim of this thesis is to provide the Reader with the summary of the current knowledge about epitaxial graphene grown on SiC (0001) and to introduce the new growth method, which can be used by the scientific community to advance the field of two-dimensional materials.

Graphene is a first discovered 2D material, consisting of carbon atoms arranged in a honeycomb lattice. Thanks to its structure, it is characterized by a set of unique mechanical, thermal, chemical and electronic properties, which led many to speculate about its numerous applications and the potential to revolutionize different industries. However, these expectations haven't been yet realized, partly due to the lack of the established, repeatable, large-scale production methods of the material.

Epitaxial growth of graphene on the surfaces of silicon carbide, especially the Si-terminated (0001) surface, is one of the most promising synthesis methods, having the potential to introduce truly wafer-scale growth and processing methods into the field. It is based on the high-temperature surface decomposition of the compound and sublimation of the more volatile Si atoms into the environment. The main factor limiting the quality of synthesized graphene is the process temperature. Increasing the temperature increases the mobility of carbon atoms on the surface, leading to the formation of thermodynamically-preferred structures, but, at the same time it strongly increases Si sublimation rate from the surface. That's why several methods aiming at effectively decreasing Si sublimation rate have been developed. Two important examples are atmospheric pressure and confinement-controlled graphitization, in which Si sublimation is slowed down by either relatively high pressure of inert, buffer gases, or by an enclosure of annealed SiC in a small container, with Si leakage rate to the vacuum controlled by an aperture.

These methods are, however, facing several problems hindering their large-scale adoption. While they are successful in growing homogeneous layers of graphene, when applying those processes, underlying SiC surface often undergoes serious reorganization, including the formation of macro-steps, with the height ranging up to several tens of nanometers, in the step-bunching mechanism. These steps strongly scatter conduction electrons in the direction perpendicular to the terrace edges, worsening the macroscopic electrical parameters of the material and making its properties anisotropic. Additionally, annealed surfaces are exposed to a large number of unknown impurities, which can affect the properties of the final surface.

The new method, developed in this work, relies on annealing SiC (0001) in an ultra-clean, UHV environment, with an external Si beam applied to the surface, in order to slow down Si sublimation and achieve controllable graphene growth. I have shown, that in certain conditions, namely in the certain range of process temperatures, such Si beam can fully inhibit surface graphitization. As a consequence, for the given value of Si flux density and annealing temperature, the growth rate of the material can be freely controlled. STM measurements have shown, that the surfaces annealed in the Si flux in the temperature range of around 1350-1400°C have much higher quality on a nano-scale, then the samples grown in vacuum. This is a consequence of a smaller concentration of various surface and sub-surface defects and better ordering of the buffer layer, separating graphene from the bulk SiC. However, larger-scale AFM measurements on a micro-scale have revealed, that the homogeneity of the obtained surfaces remains far from satisfactory, even after the application of Si flux, because of the presence of deep pits and distorted, irregular terrace structure.

The main factor limiting the process temperature is, in this case, the maximum Si flux density of the Si beam, which is responsible for slowing down Si sublimation from the surface. This value is given by the type of source in the growth chamber and its geometry and, in our case, can't be higher than $\Phi_{\text{max}}=2.5 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$. This isn't enough to increase process temperature to more than around 1400°C, without losing the ability to control graphene growth, which means that simply increasing annealing temperature wouldn't be enough to solve the problem of an inhomogeneity of the obtained surfaces at a micro-scale. In other words, some creativity is required to overcome this issue.

One of the most important discoveries of this work is the fact, that the surface graphitization of SiC (0001) is actually a reversible reaction, in contrast to the commonly accepted view. By annealing the graphitized surface in the silicon flux, exceeding silicon flux emitted from it at a given annealing temperature, I was able to recreate clean SiC (0001) surface after prolonged annealing for over 3 hours. Based on this result, I designed and optimized a new process flow, based on very slow heating and cooling of the samples to the desired process temperature under highest attainable Si flux. It leads to the slow shift in the equilibrium of the graphitization reaction: $\text{SiC} \rightleftharpoons \text{Si} + \text{G}$, towards the product side, when the temperature is increased, and towards the substrate (SiC) side, when the temperature is slowly decreased. This means, that during the heating phase, a relatively thick graphene is formed, which is then thinned down to a desired coverage, via the reversal of the graphitization reaction during the cooldown phase.

This process flow enabled me to increase the temperature, at which graphitization is fully inhibited, for a given, maximum Si flux, by almost 150°C. It also allowed to prepare samples in a controllable way at temperatures exceeding 1700°C, which led to the formation of high-quality, ABC-stacked, 2- to 5-layers graphene. For graphene thicknesses of up to 4 layers, homogeneity of the samples obtained using the improved process is very high, with a very regular and ordered terrace structure, almost devoid of deep pits and other surface defects, which solves the main problem of the samples prepared in lower temperatures. The terraces are also remarkably low, with the average height of 0.75-1nm (3-4 SiC bilayers). This reduction of step bunching happening at the surfaces is a significant improvement over other commonly used growth methods.

ARPES measurements revealed, that the electron dispersion relations of the synthesised few-layers graphene contain 1-3 flat bands near the Fermi energy, a fact, that has been associated by others to the presence of extended 2D Van Hove's singularities. It was also theorized that such bands can be used to achieve the superconductivity of graphene. My results show, for the first time, that multiple flat bands can exist in the electron dispersion relation for tetra- and 5-layer graphene grown on SiC (0001). The developed method faces difficulties in creating a surface with an exact coverage of a single graphene layer, which I attribute to the enhanced reactivity of the surface with coverage lower than 2 graphene layers to the external Si flux. However, this is in principle an optimization problem, not a fundamental barrier preventing the application of the method.

The process of the partly-reversible graphitization of SiC (0001) is far from reaching its optimization potential. However, even before this point is reached, it already constitutes a very promising method of growing high-quality, ABC-stacked, few-layers graphene, on a defect-free, minimally step-bunched surface. The author of this work hopes, that it will become a useful tool, contributing to the research and development of graphene and graphene-based devices and eventual applications of this revolutionary, two-dimensional material in various fields.

The Reader will, of course, find out, whether these promises have actually been met.

Chapter 6

Bibliography

- [1] The University of Manchester, Graphene, Discovery of graphene, accessed: 13.05.2020, <https://www.graphene.manchester.ac.uk/learn/discovery-of-graphene/>
- [2] Nobel Media AB 2020, Press release, NobelPrize.org (05.10.2010), accessed: 13.05.2020, <https://www.nobelprize.org/prizes/physics/2010/press-release/>
- [3] X. Duan, C. Wang, A. Pan, R. Yu, X. Duan, Two-dimensional transition metal dichalcogenides as atomically thin semiconductors : opportunities and challenges, Chem. Soc. Rev. 44 (2015) 8859–8876. doi:10.1039/c5cs00507h.
- [4] Badami, D. V., Graphitization of α -Silicon Carbide, Nature 193 (1962), 569 doi:10.1038/193569a0.
- [5] P.R. Wallace, The Band Theory of Graphite, Phys. Rev. 71 (1947) 622–634. doi:10.1103/PhysRev.71.622.
- [6] S. Reich, J. Maultzsch, C. Thomsen, P. Ordejo, Tight-binding description of graphene, Phys. Rev. B. 66 (2002) 035412. doi:10.1103/PhysRevB.66.035412.
- [7] R.S. Deacon, K. Chuang, R.J. Nicholas, K.S. Novoselov, A.K. Geim, Cyclotron resonance study of the electron and hole velocity in graphene monolayers, Phys. Rev. B. 76 (2007) 081406. doi:10.1103/PhysRevB.76.081406.
- [8] A.H. Castro Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, The electronic properties of graphene, Rev. Mod. Phys. 81 (2009) 109–162. doi:10.1103/RevModPhys.81.109.
- [9] C. Bena, S.A. Kivelson, Quasiparticle scattering and local density of states in graphite, Phys. Rev. B. 72 (2005) 125432. doi:10.1103/PhysRevB.72.125432.
- [10] G.W. Semenoff, Condensed-Matter Simulation of a Three-Dimensional Anomaly, 53 (1984) 2449–2452. doi:10.1103/PhysRevLett.53.2449.
- [11] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, M.I. Katsnelson, I. V Grigorieva, S. V Dubonos, Two-dimensional gas of massless Dirac fermions in graphene, Nature. 438 (2005) 197–200. doi:10.1038/nature04233.

- [12] Y. Zhang, Y. Tan, H.L. Stormer, P. Kim, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature*. 438 (2005) 201–204. doi:10.1038/nature04235.
- [13] N. Stander, B. Huard, Evidence for Klein Tunneling in Graphene p - n Junctions, *Phys. Rev. Lett.* 102 (2009) 026807. doi:10.1103/PhysRevLett.102.026807.
- [14] H. Marsh, F. Rodríguez-Reinoso, CHAPTER 9 - Production and Reference Material, in: H. Marsh, F. Rodríguez-Reinoso (Ed.), *Activated Carbon*, Elsevier Science Ltd, Oxford, 2006: pp. 454–508. doi:10.1016/B978-008044463-5/50023-6.
- [15] Nanotechnologies — Vocabulary — Part 13: Graphene and related two-dimensional (2D) materials, ISO/TS 80004-13:2017, 2017
- [16] Y. Hatsugai, T. Morimoto, T. Kawarabayashi, M. Orlita, M. Potemski, Stacking-dependent optical absorption in multilayer graphene, *New J. Phys.* 15 (2013) 015010. doi:10.1088/1367-2630/15/1/015010.
- [17] E. McCann, V.I. Fal'ko, Landau-Level Degeneracy and Quantum Hall Effect in a Graphite Bilayer, *Phys. Rev. Lett.* 96 (2006) 86805. doi:10.1103/PhysRevLett.96.086805.
- [18] W. Zhang, C.-T. Lin, K.-K. Liu, T. Tite, C.-Y. Su, C.-H. Chang, Y.-H. Lee, C.-W. Chu, K.-H. Wei, J.-L. Kuo, L.-J. Li, Opening an Electrical Band Gap of Bilayer Graphene with Molecular Doping, *ACS Nano*. 5 (2011) 7517–7524. doi:10.1021/nn202463g.
- [19] A.J. Samuels, J.D. Carey, Molecular Doping and Band-Gap Opening of Bilayer Graphene, *ACS Nano*. 7 (2013) 2790–2799. doi:10.1021/nn400340q.
- [20] H. Min, Electronic Properties of Multilayer Graphene, in: H. Raza (Ed.), *Graphene Nanoelectronics: Metrology, Synthesis, Properties and Applications*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2012: pp. 325–356. doi:10.1007/978-3-642-22984-8_11.
- [21] Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, P. Jarillo-Herrero, Unconventional superconductivity in magic-angle graphene superlattices, *Nature*. 556 (2018) 43–50. doi:10.1038/nature26160.
- [22] Futurism, Graphene – Material of the Future? (04.04.2014), accessed: 13.05.2020, <https://futurism.com/graphene-material-future>

- [23] European Parliament, Graphene: the wonder material of the 21st century (04.06.2015), accessed: 13.05.2020, <https://www.europarl.europa.eu/news/en/headlines/economy/20150603STO62104/graphene-the-wonder-material-of-the-21st-century>
- [24] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, Mechanical properties of graphene and graphene-based nanocomposites, *Prog. Mater. Sci.* 90 (2017) 75–127. doi:<https://doi.org/10.1016/j.pmatsci.2017.07.004>.
- [25] C. Lee, X. Wei, J.W. Kysar, J. Hone, Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene, *Science* 321 (2008) 385–388. doi:10.1126/science.1157996.
- [26] C.S. Ruiz-Vargas, H.L. Zhuang, P.Y. Huang, A.M. van der Zande, S. Garg, P.L. McEuen, D.A. Muller, R.G. Hennig, J. Park, Softened Elastic Response and Unzipping in Chemical Vapor Deposition Graphene Membranes, *Nano Lett.* 11 (2011) 2259–2263. doi:10.1021/nl200429f.
- [27] A.A. Balandin, Thermal properties of graphene and nanostructured carbon materials, *Nat. Mater.* 10 (2011) 569–581. doi:10.1038/nmat3064.
- [28] L.A. Jauregui, Y. Yue, A.N. Sidorov, J. Hu, Q. Yu, G. Lopez, R. Jalilian, D.K. Benjamin, D.A. Delkd, W. Wu, Z. Liu, X. Wang, Z. Jiang, X. Ruan, J. Bao, S.S. Pei, Y.P. Chen, Thermal Transport in Graphene Nanostructures: Experiments and Simulations, *ECS Transactions* 28 (2010), 73-83. doi:10.1149/1.3367938.
- [29] K.M.F. Shahil, A.A. Balandin, Thermal properties of graphene and multilayer graphene: Applications in thermal interface materials, *Solid State Commun.* 152 (2012) 1331–1340. doi:10.1016/j.ssc.2012.04.034.
- [30] A.S. Mayorov, R. V Gorbachev, S. V Morozov, L. Britnell, R. Jalil, L.A. Ponomarenko, P. Blake, K.S. Novoselov, K. Watanabe, T. Taniguchi, A.K. Geim, Micrometer-Scale Ballistic Transport in Encapsulated Graphene at Room Temperature, *Nano Lett.* 11 (2011) 2396–2399. doi:10.1021/nl200758b.
- [31] J. Baringhaus, M. Ruan, F. Edler, A. Tejeda, M. Sicot, A. Taleb-Ibrahimi, A.-P. Li, Z. Jiang, E.H. Conrad, C. Berger, C. Tegenkamp, W.A. de Heer, Exceptional ballistic transport in epitaxial graphene nanoribbons, *Nature*. 506 (2014) 349–354. doi:10.1038/nature12952.

- [32] F. Schedin, A.K. Geim, S. V Morozov, E.W. Hill, P. Blake, M.I. Katsnelson, K.S. Novoselov, Detection of individual gas molecules adsorbed on graphene, *Nat. Mater.* 6 (2007) 652–655. doi:10.1038/nmat1967.
- [33] A.K. Geim, K.S. Novoselov, The rise of graphene, *Nat. Mater.* 6 (2007) 183–191. doi:10.1038/nmat1849.
- [34] K.S. Novoselov, Z. Jiang, Y. Zhang, S. V Morozov, H.L. Stormer, U. Zeitler, J.C. Maan, G.S. Boebinger, P. Kim, A.K. Geim, Room-Temperature Quantum Hall Effect in Graphene, *Science* (80-.). 315 (2007) 1379 LP – 1379. doi:10.1126/science.1137201.
- [35] K.I. Bolotin, K.J. Sikes, J. Hone, H.L. Stormer, P. Kim, Temperature-Dependent Transport in Suspended Graphene, *Phys. Rev. Lett.* 101 (2008) 96802. doi:10.1103/PhysRevLett.101.096802.
- [36] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, J. Hone, Boron nitride substrates for high-quality graphene electronics, *Nat. Nanotechnol.* 5 (2010) 722–726. doi:10.1038/nnano.2010.172.
- [37] P.J. Zomer, S.P. Dash, N. Tombros, B.J. van Wees, A transfer technique for high mobility graphene devices on commercially available hexagonal boron nitride, *Appl. Phys. Lett.* 99 (2011) 232104. doi:10.1063/1.3665405.
- [38] N. Tombros, C. Jozsa, M. Popinciuc, H.T. Jonkman, B.J. van Wees, Electronic spin transport and spin precession in single graphene layers at room temperature, *Nature.* 448 (2007) 571–574. doi:10.1038/nature06037.
- [39] S. Cho, Y.-F. Chen, M.S. Fuhrer, Gate-tunable graphene spin valve, *Appl. Phys. Lett.* 91 (2007) 123105. doi:10.1063/1.2784934.
- [40] K.F. Mak, M.Y. Sfeir, Y. Wu, C.H. Lui, J.A. Misewich, T.F. Heinz, Measurement of the Optical Conductivity of Graphene, *Phys. Rev. Lett.* 101 (2008) 196405. doi:10.1103/PhysRevLett.101.196405.
- [41] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine Structure Constant Defines Visual Transparency of Graphene, *Science* (80-.). 320 (2008) 1308 LP – 1308. doi:10.1126/science.1156965.

- [42] Z. Liu, X. Zhang, X. Yan, Y. Chen, J. Tian, Nonlinear optical properties of graphene-based materials, *Chinese Sci. Bull.* 57 (2012) 2971–2982. doi:10.1007/s11434-012-5270-4.
- [43] J.-L. Xu, X.-L. Li, Y.-Z. Wu, X.-P. Hao, J.-L. He, K.-J. Yang, Graphene saturable absorber mirror for ultra-fast-pulse solid-state laser, *Opt. Lett.* 36 (2011) 1948–1950. doi:10.1364/OL.36.001948.
- [44] H. Zhang, S. Virally, Q. Bao, L. Kian Ping, S. Massar, N. Godbout, P. Kockaert, Z-scan measurement of the nonlinear refractive index of graphene, *Opt. Lett.* 37 (2012) 1856–1858. doi:10.1364/OL.37.001856.
- [45] S.A. Mikhailov, Non-linear electromagnetic response of graphene, *Europhys. Lett.* 79 (2007) 27002. doi:10.1209/0295-5075/79/27002.
- [46] J.B. Khurgin, Graphene—A rather ordinary nonlinear optical material, *Appl. Phys. Lett.* 104 (2014) 161116. doi:10.1063/1.4873704.
- [47] S.A. Mikhailov, Comment on “Graphene—A rather ordinary nonlinear optical material” [*Appl. Phys. Lett.* 104, 161116 (2014)], *Appl. Phys. Lett.* 111 (2017) 106101. doi:10.1063/1.4997849.
- [48] A.K. Geim, Graphene: Status and Prospects, *Science* 324 (2009) 1530 – 1534. doi:10.1126/science.1158877.
- [49] P. Blake, E.W. Hill, A.H. Castro Neto, K.S. Novoselov, D. Jiang, R. Yang, T.J. Booth, A.K. Geim, Making graphene visible, *Appl. Phys. Lett.* 91 (2007) 63124. doi:10.1063/1.2768624.
- [50] T. Ando, Screening Effect and Impurity Scattering in Monolayer Graphene, *J. Phys. Soc. Japan.* 75 (2006) 74716. doi:10.1143/JPSJ.75.074716.
- [51] E.H. Hwang, S. Adam, S. Das Sarma, Carrier Transport in Two-Dimensional Graphene Layers, *Phys. Rev. Lett.* 98 (2007) 186806. doi:10.1103/PhysRevLett.98.186806.
- [52] S. Fratini, F. Guinea, Substrate-limited electron dynamics in graphene, *Phys. Rev. B.* 77 (2008) 195415. doi:10.1103/PhysRevB.77.195415.
- [53] J. H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, Intrinsic and extrinsic performance limits of graphene devices on SiO₂, *Nat. Nanotechnol.* 3 (2008) 206–209. doi:10.1038/nnano.2008.58.

- [54] M. Ishigami, J.H. Chen, W.G. Cullen, M.S. Fuhrer, E.D. Williams, Atomic Structure of Graphene on SiO₂, *Nano Lett.* 7 (2007) 1643–1648. doi:10.1021/nl070613a.
- [55] Y. Hernandez, V. Nicolosi, M. Lotya, F.M. Blighe, Z. Sun, S. De, I.T. McGovern, B. Holland, M. Byrne, Y.K. Gun'Ko, J.J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A.C. Ferrari, J.N. Coleman, High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat. Nanotechnol.* 3 (2008) 563–568. doi:10.1038/nnano.2008.215.
- [56] A.A. Green, M.C. Hersam, Solution Phase Production of Graphene with Controlled Thickness via Density Differentiation, *Nano Lett.* 9 (2009) 4031–4036. doi:10.1021/nl902200b.
- [57] G. Shao, Y. Lu, F. Wu, C. Yang, F. Zeng, Q. Wu, Graphene oxide: the mechanisms of oxidation and exfoliation, *J. Mater. Sci.* 47 (2012) 4400–4409. doi:10.1007/s10853-012-6294-5.
- [58] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S.T. Nguyen, R.S. Ruoff, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon N. Y.* 45 (2007) 1558–1565. doi:https://doi.org/10.1016/j.carbon.2007.02.034.
- [59] D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H.B. Dommett, G. Evmenenko, S.T. Nguyen, R.S. Ruoff, Preparation and characterization of graphene oxide paper, *Nature.* 448 (2007) 457–460. doi:10.1038/nature06016.
- [60] H. Ago, CVD Growth of High-Quality Single-Layer Graphene, in: K. Matsumoto (Ed.), *Frontiers of Graphene and Carbon Nanotubes: Devices and Applications*, Springer Japan, Tokyo, 2015: pp. 3–20. doi:10.1007/978-4-431-55372-4_1.
- [61] H. Ago, Y. Ito, N. Mizuta, K. Yoshida, B. Hu, C.M. Orofeo, M. Tsuji, K. Ikeda, S. Mizuno, Epitaxial Chemical Vapor Deposition Growth of Single-Layer Graphene over Cobalt Film Crystallized on Sapphire, *ACS Nano.* 4 (2010) 7407–7414. doi:10.1021/nn102519b.
- [62] B. Hu, H. Ago, Y. Ito, K. Kawahara, M. Tsuji, E. Magome, K. Sumitani, N. Mizuta, K. Ikeda, S. Mizuno, Epitaxial growth of large-area single-layer graphene over Cu(111)/sapphire

by atmospheric pressure CVD, Carbon N. Y. 50 (2012) 57–65. doi:<https://doi.org/10.1016/j.carbon.2011.08.002>.

[63] C.M. Orofeo, H. Hibino, K. Kawahara, Y. Ogawa, M. Tsuji, K. Ikeda, S. Mizuno, H. Ago, Influence of Cu metal on the domain structure and carrier mobility in single-layer graphene, Carbon 50 (2012) 2189–2196. doi:<https://doi.org/10.1016/j.carbon.2012.01.030>.

[64] V. Miseikis, D. Convertino, N. Mishra, M. Gemmi, T. Mashoff, S. Heun, N. Haghighian, F. Bisio, M. Canepa, V. Piazza, C. Coletti, Rapid CVD growth of millimetre-sized single crystal graphene using a cold-wall reactor, 2D Mater. 2 (2015) 14006. doi:[10.1088/2053-1583/2/1/014006](https://doi.org/10.1088/2053-1583/2/1/014006).

[65] X. Li, C.W. Magnuson, A. Venugopal, R.M. Tromp, J.B. Hannon, E.M. Vogel, L. Colombo, R.S. Ruoff, Large-Area Graphene Single Crystals Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper, J. Am. Chem. Soc. 133 (2011) 2816–2819. doi:[10.1021/ja109793s](https://doi.org/10.1021/ja109793s).

[66] J. Wu, Y. Li, D. Pan, C. Jiang, C. Jin, F. Song, G. Wang, J. Wan, Effect of grain boundaries on charge transport in CVD-grown bilayer graphene, Carbon N. Y. 147 (2019) 434–440. doi:<https://doi.org/10.1016/j.carbon.2019.03.029>.

[67] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, Science 324 (2009) 1312 – 1314. doi:[10.1126/science.1171245](https://doi.org/10.1126/science.1171245).

[68] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes, Nano Lett. 9 (2009) 4359–4363. doi:[10.1021/nl902623y](https://doi.org/10.1021/nl902623y).

[69] B. Alemán, W. Regan, S. Aloni, V. Altoe, N. Alem, C. Girit, B. Geng, L. Maserati, M. Crommie, F. Wang, A. Zettl, Transfer-Free Batch Fabrication of Large-Area Suspended Graphene Membranes, ACS Nano. 4 (2010) 4762–4768. doi:[10.1021/nn100459u](https://doi.org/10.1021/nn100459u).

[70] J.W. Suk, A. Kitt, C.W. Magnuson, Y. Hao, S. Ahmed, J. An, A.K. Swan, B.B. Goldberg, R.S. Ruoff, Transfer of CVD-Grown Monolayer Graphene onto Arbitrary Substrates, ACS Nano. 5 (2011) 6916–6924. doi:[10.1021/nn201207c](https://doi.org/10.1021/nn201207c).

- [71] T. Kobayashi, M. Bando, N. Kimura, K. Shimizu, K. Kadono, N. Umez, K. Miyahara, S. Hayazaki, S. Nagai, Y. Mizuguchi, Y. Murakami, D. Hobara, Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process, *Appl. Phys. Lett.* 102 (2013) 23112. doi:10.1063/1.4776707.
- [72] B.N. Chandrashekar, A.S. Smitha, Y. Wu, N. Cai, Y. Li, Z. Huang, W. Wang, R. Shi, J. Wang, S. Liu, S. Krishnaveni, F. Wang, C. Cheng, A Universal Stamping Method of Graphene Transfer for Conducting Flexible and Transparent Polymers, *Sci. Rep.* 9 (2019) 3999. doi:10.1038/s41598-019-40408-w.
- [73] L. Banszerus, M. Schmitz, S. Engels, J. Dauber, M. Oellers, F. Haupt, K. Watanabe, T. Taniguchi, B. Beschoten, C. Stampfer, Ultrahigh-mobility graphene devices from chemical vapor deposition on reusable copper, *Sci. Adv.* 1 (2015) e1500222. doi:10.1126/sciadv.1500222.
- [74] Y. Chen, X.-L. Gong, J.-G. Gai, Progress and Challenges in Transfer of Large-Area Graphene Films, *Adv. Sci.* (Weinheim, Baden-Wurttemberg, Ger. 3 (2016) 1500343. doi:10.1002/advs.201500343.
- [75] H. Morkoç, S. Strite, G.B. Gao, M.E. Lin, B. Sverdlov, M. Burns, Large-band-gap SiC, III-V nitride, and II-VI ZnSe-based semiconductor device technologies, *J. Appl. Phys.* 76 (1994) 1363–1398. doi:10.1063/1.358463.
- [76] G.R. Fisher, P. Barnes, Towards a unified view of polytypism in silicon carbide, *Philos. Mag. B.* 61 (1990) 217–236. doi:10.1080/13642819008205522.
- [77] M. Mehregany, C.A. Zorman, N. Rajan, C.H. Wu, Silicon carbide MEMS for harsh environments, *Proc. IEEE.* 86 (1998) 1594–1609. doi:10.1109/5.704265.
- [78] T. Kimoto, Bulk and epitaxial growth of silicon carbide, *Prog. Cryst. Growth Charact. Mater.* 62 (2016) 329–351. doi:10.1016/j.pcrysgrow.2016.04.018.
- [79] T. Kimoto, J.A. Cooper, Appendix C: Major Physical Properties of Common SiC Polytypes, in: *Fundam. Silicon Carbide Technol. Growth, Charact. Devices Appl.*, IEEE, 2014: pp. 521–524. doi:10.1002/9781118313534.app3.

- [80] M.J. Mehl, D. Hicks, C. Toher, O. Levy, R.M. Hanson, G. Hart, S. Curtarolo, The AFLOW Library of Crystallographic Prototypes: Part 1, *Comput. Mater. Sci.* 136 (2017) S1–S828. doi:<https://doi.org/10.1016/j.commatsci.2017.01.017>.
- [81] D. Hicks, M.J. Mehl, E. Gossett, C. Toher, O. Levy, R.M. Hanson, G. Hart, S. Curtarolo, The AFLOW Library of Crystallographic Prototypes: Part 2, *Comput. Mater. Sci.* 161 (2019) S1–S1011. doi:<https://doi.org/10.1016/j.commatsci.2018.10.043>.
- [82] U. Starke, J. Bernhardt, J. Schardt, K. Heinz, SiC surface reconstruction: relevancy of atomic structure for growth technology, *Surf. Rev. Lett.* 6 (1999) 1129–1141. doi:DOI: 10.1142/S0218625X99001256,.
- [83] D.A. Siegel, S.Y. Zhou, F. El Gabaly, A.K. Schmid, K.F. McCarty, A. Lanzara, Three-fold diffraction symmetry in epitaxial graphene and the SiC substrate, *Phys. Rev. B.* 80 (2009) 241407. doi:10.1103/PhysRevB.80.241407.
- [84] J.B. Hannon, R.M. Tromp, N. V Medhekar, V.B. Shenoy, Spontaneous Formation and Growth of a New Polytype on SiC(0001), *Phys. Rev. Lett.* 103 (2009) 256101. doi:10.1103/PhysRevLett.103.256101.
- [85] J. K. Cockcroft, Birkbeck College, University of London, A Hypertext Book of Crystallographic Space Group Diagrams and Tables (2009), accessed: 13.05.2020, <http://img.chem.ucl.ac.uk/sgp/large/186az1.htm>
- [86] J. K. Cockcroft, Birkbeck College, University of London, A Hypertext Book of Crystallographic Space Group Diagrams and Tables (2009), accessed: 13.05.2020, <http://img.chem.ucl.ac.uk/sgp/large/183az1.htm>
- [87] T. Seyller, Passivation of hexagonal SiC surfaces by hydrogen termination, *J. Phys. Condens. Matter.* 16 (2004) S1755–S1782. doi:10.1088/0953-8984/16/17/016.
- [88] J. Schardt, J. Bernhardt, U. Starke, K. Heinz, Crystallography of the (3×3) surface reconstruction of 3C–SiC(111), 4H–SiC(0001), and 6H–SiC(0001) surfaces retrieved by low-energy electron diffraction, *Phys. Rev. B.* 62 (2000) 10335–10344. doi:10.1103/PhysRevB.62.10335.

- [89] U. Starke, J. Schardt, J. Bernhardt, M. Franke, K. Heinz, Stacking Transformation from Hexagonal to Cubic SiC Induced by Surface Reconstruction: A Seed for Heterostructure Growth, *Phys. Rev. Lett.* 82 (1999) 2107–2110. doi:10.1103/PhysRevLett.82.2107.
- [90] I. Forbeaux, J.-M. Themlin, A. Charrier, F. Thibaudau, J.-M. Debever, Solid-state graphitization mechanisms of silicon carbide 6H-SiC polar faces, *Appl. Surf. Sci.* 162–163 (2000) 406–412. doi:https://doi.org/10.1016/S0169-4332(00)00224-5.
- [91] E.G. Acheson, *Manufacture of Graphite* (1896), United States Patent Office, no. 568,323
- [92] J. Hass, W.A. de Heer, E.H. Conrad, TOPICAL REVIEW: The growth and morphology of epitaxial multilayer graphene, *J. Phys. Condens. Matter.* 20 (2008) 323202. doi:10.1088/0953-8984/20/32/323202.
- [93] K. V Emtsev, F. Speck, T. Seyller, L. Ley, J.D. Riley, Interaction, growth, and ordering of epitaxial graphene on SiC{0001} surfaces: A comparative photoelectron spectroscopy study, *Phys. Rev. B.* 77 (2008) 155303. doi:10.1103/PhysRevB.77.155303.
- [94] T. Cavallucci, V. Tozzini, Intrinsic structural and electronic properties of the Buffer Layer on Silicon Carbide unraveled by Density Functional Theory, *Sci. Rep.* 8 (2018) 13097. doi:10.1038/s41598-018-31490-7.
- [95] T. Kimoto, A. Itoh, H. Matsunami, T. Okano, Step bunching mechanism in chemical vapor deposition of 6H- and 4H-SiC{0001}, *J. Appl. Phys.* 81 (1997) 3494–3500. doi:10.1063/1.365048.
- [96] M.L. Bolen, S.E. Harrison, L.B. Biedermann, M.A. Capano, Graphene formation mechanisms on 4H-SiC(0001), *Phys. Rev. B.* 80 (2009) 115433. doi:10.1103/PhysRevB.80.115433.
- [97] W. Norimatsu, M. Kusunoki, Formation process of graphene on SiC (0001), *Phys. E Low Dimensional Syst. Nanostructures.* 42 (2010) 691–694. doi:https://doi.org/10.1016/j.physe.2009.11.151.
- [98] H. Huang, W. Chen, S. Chen, A.T.S. Wee, Bottom-up Growth of Epitaxial Graphene on 6H-SiC(0001), *ACS Nano.* 2 (2008) 2513–2518. doi:10.1021/nn800711v.
- [99] S. Tanaka, K. Morita, H. Hibino, Anisotropic layer-by-layer growth of graphene on vicinal SiC(0001) surfaces, *Phys. Rev. B.* 81 (2010) 41406. doi:10.1103/PhysRevB.81.041406.

- [100] P. Avouris, C. Dimitrakopoulos, Graphene: synthesis and applications, *Mater. Today*. 15 (2012) 86–97. doi:[https://doi.org/10.1016/S1369-7021\(12\)70044-5](https://doi.org/10.1016/S1369-7021(12)70044-5).
- [101] K. V Emtsev, A. Bostwick, K. Horn, J. Jobst, G.L. Kellogg, L. Ley, J.L. McChesney, T. Ohta, S.A. Reshanov, J. Röhl, E. Rotenberg, A.K. Schmid, D. Waldmann, H.B. Weber, T. Seyller, Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide, *Nat. Mater.* 8 (2009) 203–207. doi:10.1038/nmat2382.
- [102] G.R. Yazdi, R. Vasilias, T. Iakimov, A. Zakharov, M. Syväjärvi, R. Yakimova, Growth of large area monolayer graphene on 3C-SiC and a comparison with other SiC polytypes, *Carbon N. Y.* 57 (2013) 477–484. doi:<https://doi.org/10.1016/j.carbon.2013.02.022>.
- [103] W.A. de Heer, C. Berger, M. Ruan, M. Sprinkle, X. Li, Y. Hu, B. Zhang, J. Hankinson, E. Conrad, Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide, *Proc. Natl. Acad. Sci.* 108 (2011) 16900 LP – 16905. doi:10.1073/pnas.1105113108.
- [104] C. Çelebi, C. Yanık, A.G. Demirkol, İ.İ. Kaya, The effect of a SiC cap on the growth of epitaxial graphene on SiC in ultra high vacuum, *Carbon* 50 (2012) 3026–3031. doi:<https://doi.org/10.1016/j.carbon.2012.02.088>.
- [105] H.B. Jin, Y. Jeon, S. Jung, V. Modepalli, H.S. Kang, B.C. Lee, J.-H. Ko, H.-J. Shin, J.-W. Yoo, S.Y. Kim, S.-Y. Kwon, D. Eom, K. Park, Enhanced Crystallinity of Epitaxial Graphene Grown on Hexagonal SiC Surface with Molybdenum Plate Capping, *Sci. Rep.* 5 (2015) 9615. doi:10.1038/srep09615.
- [106] M. Ridene, T. Wassmann, E. Pallecchi, G. Rodary, J.C. Girard, A. Ouerghi, Epitaxial graphene on step bunching of a 6H-SiC(0001) substrate: Aromatic ring pattern and Van Hove singularities, *Appl. Phys. Lett.* 102 (2013) 111610. doi:10.1063/1.4796170.
- [107] J. Bao, O. Yasui, W. Norimatsu, K. Matsuda, M. Kusunoki, Sequential control of step-bunching during graphene growth on SiC (0001), *Appl. Phys. Lett.* 109 (2016) 81602. doi:10.1063/1.4961630.
- [108] M. Kruskopf, D.M. Pakdehi, K. Pierz, S. Wundrack, R. Stosch, T. Dziomba, M. Götz, J. Baringhaus, J. Aprojanz, C. Tegenkamp, J. Lidzba, T. Seyller, F. Hohls, F.J. Ahlers, H.W.

- Schumacher, Comeback of epitaxial graphene for electronics: large-area growth of bilayer-free graphene on SiC, *2D Mater.* 3 (2016) 41002. doi:10.1088/2053-1583/3/4/041002.
- [109] P. Ciochoń, Ł. Bodek, M. Garb, Ł. Zając, J.J. Kołodziej, Si beam-assisted graphitization of SiC (0001), *Appl. Phys. A*. 124 (2018) 727. doi:10.1007/s00339-018-2145-9.
- [110] N. Srivastava, G. He, Luxmi, P.C. Mende, R.M. Feenstra, Y. Sun, Graphene formed on SiC under various environments: comparison of Si-face and C-face, *J. Phys. D. Appl. Phys.* 45 (2012) 154001. doi:10.1088/0022-3727/45/15/154001.
- [111] R.M. Tromp, J.B. Hannon, Thermodynamics and Kinetics of Graphene Growth on SiC(0001), *Phys. Rev. Lett.* 102 (2009) 106104. doi:10.1103/PhysRevLett.102.106104.
- [112] M.H. Kibel, X-Ray Photoelectron Spectroscopy, in: D.J. O'Connor, B.A. Sexton, R.S.C. Smart (Eds.) *Surface Analysis Methods in Materials Science*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003: pp. 175–201. doi:10.1007/978-3-662-05227-3_7.
- [113] A. Zangwill, *Physics at Surfaces*, Cambridge University Press, Cambridge, 1988. doi:DOI: 10.1017/CBO9780511622564.
- [114] C. Riedl, *Epitaxial Graphene on Silicon Carbide Surfaces: Growth, Characterization, Doping and Hydrogen Intercalation*, Friedrich-Alexander-Universität Erlangen-Nürnberg, 2010, <https://nbn-resolving.org/urn:nbn:de:bvb:29-opus-19920>.
- [115] C.D. Wagner, L.E. Davis, M. V Zeller, J.A. Taylor, R.H. Raymond, L.H. Gale, Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis, *Surf. Interface Anal.* 3 (1981) 211–225. doi:10.1002/sia.740030506.
- [116] M.P. Seah, I.S. Gilmore, S.J. Spencer, Quantitative XPS: I. Analysis of X-ray photoelectron intensities from elemental data in a digital photoelectron database, *J. Electron Spectros. Relat. Phenomena.* 120 (2001) 93–111. doi:[https://doi.org/10.1016/S0368-2048\(01\)00311-5](https://doi.org/10.1016/S0368-2048(01)00311-5).
- [117] C.N. Berglund, W.E. Spicer, Photoemission Studies of Copper and Silver: Theory, *Phys. Rev.* 136 (1964) A1030–A1044. doi:10.1103/PhysRev.136.A1030.
- [118] S. Hüfner, *Photoelectron Spectroscopy: Principles and Application*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003: pp. 1–60. doi:10.1007/978-3-662-09280-4.

- [119] C. Caroli, B. Roulet, D. Saint-James, Theory of Photoemission, in: L. Dobrzynski (ed.) Handbook of Surfaces and Interfaces, Vol. 1, Garland, New York 1978, doi:10.1002/bbpc.19790830323
- [120] C.J. Davisson, L.H. Germer, Reflection of Electrons by a Crystal of Nickel, Proc. Natl. Acad. Sci. 14 (1928) 317 LP – 322. doi:10.1073/pnas.14.4.317.
- [121] L. de Broglie, XXXV. A tentative theory of light quanta, London, Edinburgh, Dublin Philos. Mag. J. Sci. 47 (1924) 446–458. doi:10.1080/14786442408634378.
- [122] K. Oura, M. Katayama, A. V Zotov, V.G. Lifshits, A.A. Saranin, Surface Analysis I. Diffraction Methods, in: K. Oura, M. Katayama, A. V Zotov, V.G. Lifshits, A.A. Saranin (Eds.) Surface Science: An Introduction, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003: pp. 47–75. doi:10.1007/978-3-662-05179-5_4.
- [123] Y. Sugawara, H. Ueyama, T. Uchihashi, M. Ohta, S. Morita, M. Suzuki, S. Mishima, True atomic resolution imaging with noncontact atomic force microscopy, Appl. Surf. Sci. 113–114 (1997) 364–370. doi:https://doi.org/10.1016/S0169-4332(96)00877-X.
- [124] M. Kim, J.R. Chelikowsky, CO tip functionalization in subatomic resolution atomic force microscopy, Appl. Phys. Lett. 107 (2015) 163109. doi:10.1063/1.4934273.
- [125] C.J. Chen: Introduction to Scanning Tunneling Microscopy, Oxford University Press, Oxford, 2007, doi:10.1093/acprof:oso/9780199211500.001.0001.
- [126] MBE Komponenten, Dr. Eberl, SUSI Silicon Sublimation Source, accessed: 13.05.2020, <https://www.mbe-komponenten.de/products/mbe-components/effusion-cells/susi.php>
- [127] Wafer Technology Ltd., Wafer Flatness Specifications, accessed: 13.05.2020, http://www.wafertech.co.uk/_downloads/Wafer-Flatness.pdf
- [128] P. Ciochoń, M. Marzec, N. Olszowska, J.J. Kołodziej, Reversible graphitization of SiC: a route towards high-quality graphene on a minimally step bunched substrate, Applied Surface Science (2020), under review
- [129] S. Doniach, M. Sunjic, Many-electron singularity in X-ray photoemission and X-ray line spectra from metals, J. Phys. C Solid State Phys. 3 (1970) 285–291. doi:10.1088/0022-3719/3/2/010.pdf

- [130] A. Fissel, K. Pfennighaus, U. Kaiser, B. Schröter, W. Richter, Mechanisms of homo- and heteroepitaxial growth of SiC on α -SiC(0001) by solid-source molecular beam epitaxy, *J. Electron. Mater.* 28 (1999) 206–213. doi:10.1007/s11664-999-0015-0.
- [131] P. Rakytá, A. Kormányos, J. Cserti, Trigonal warping and anisotropic band splitting in monolayer graphene due to Rashba spin-orbit coupling, *Phys. Rev. B.* 82 (2010) 113405. doi:10.1103/PhysRevB.82.113405.
- [132] J.S. Custer, M.O. Thompson, D.C. Jacobson, J.M. Poate, S. Roorda, W.C. Sinke, F. Spaepen, Density of amorphous Si, *Appl. Phys. Lett.* 64 (1994) 437–439. doi:10.1063/1.111121.
- [133] G.M. Rutter, N.P. Guisinger, J.N. Crain, E.A.A. Jarvis, M.D. Stiles, T. Li, P.N. First, J.A. Stroscio, Imaging the interface of epitaxial graphene with silicon carbide via scanning tunneling microscopy, *Phys. Rev. B.* 76 (2007) 235416. doi:10.1103/PhysRevB.76.235416.
- [134] S. Goler, C. Coletti, V. Piazza, P. Pingue, F. Colangelo, V. Pellegrini, K. V Emtsev, S. Forti, U. Starke, F. Beltram, S. Heun, Revealing the atomic structure of the buffer layer between SiC(0001) and epitaxial graphene, *Carbon* 51 (2013) 249–254. doi:https://doi.org/10.1016/j.carbon.2012.08.050.
- [135] I. Forbeaux, J.-M. Themlin, J.-M. Debever, Heteroepitaxial graphite on 6H-SiC(0001): Interface formation through conduction-band electronic structure, *Phys. Rev. B.* 58 (1998) 16396–16406. doi:10.1103/PhysRevB.58.16396.
- [136] G.M. Rutter, J.N. Crain, N.P. Guisinger, T. Li, P.N. First, J.A. Stroscio, Scattering and Interference in Epitaxial Graphene, *Science* (80). 317 (2007) 219 LP – 222. doi:10.1126/science.1142882.
- [137] Q. Wang, W. Zhang, L. Wang, K. He, X. Ma, Q. Xue, Large-scale uniform bilayer graphene prepared by vacuum graphitization of 6H-SiC(0001) substrates, *J. Phys. Condens. Matter.* 25 (2013) 95002. doi:10.1088/0953-8984/25/9/095002.
- [138] K. Aït-Mansour, D. Dentel, L. Kubler, M. Diani, M. Derivaz, J.L. Bischoff, Original Ge-induced phenomena on various SiC(0 0 0 1) reconstructions, *J. Phys. D. Appl. Phys.* 40 (2007) 6225–6241. doi:10.1088/0022-3727/40/20/s08.

- [139] C. Xia, S. Watcharinyanon, A.A. Zakharov, R. Yakimova, L. Hultman, L.I. Johansson, C. Virojanadara, Si intercalation/deintercalation of graphene on 6H-SiC(0001), *Phys. Rev. B* (2012) 1–7. doi:10.1103/PhysRevB.85.045418.
- [140] K. Heinz, L. Hammer, J. Hass, W.A. De Heer, E.H. Conrad, Functional surface reconstructions of hexagonal SiC, *J. Phys. Condens. Matter.* 16 (2004) S1705–S1720. doi:10.1088/0953-8984/16/17/013
- [141] W. Norimatsu, M. Kusunoki, Selective formation of ABC-stacked graphene layers on SiC(0001), *Phys. Rev. B - Condens. Matter Mater. Phys.* 81 (2010) 1–4. doi:10.1103/PhysRevB.81.161410.
- [142] K. Sugawara, N. Yamamura, K. Matsuda, W. Norimatsu, M. Kusunoki, T. Sato, T. Takahashi, Selective fabrication of free-standing ABA and ABC trilayer graphene with/without Dirac-cone energy bands, *NPG Asia Mater.* 10 (2018) e466. doi:10.1038/am.2017.238.
- [143] D. Marchenko, D. V. Evtushinsky, E. Golias, A. Varykhalov, T. Seyller, O. Rader, Extremely flat band in bilayer graphene, *Sci. Adv.* 4 (2018) 1–8. doi:10.1126/sciadv.aau0059.
- [144] J.B. Hannon, R.M. Tromp, Pit formation during graphene synthesis on SiC(0001): In situ electron microscopy, *Phys. Rev. B* 77 (2008) 1–4. doi:10.1103/PhysRevB.77.241404.
- [145] G.F. Sun, Y. Liu, S.H. Rhim, J.F. Jia, Q.K. Xue, M. Weinert, L. Li, Si diffusion path for pit-free graphene growth on SiC(0001), *Phys. Rev. B.* 84 (2011) 195455. doi:10.1103/PhysRevB.84.195455.
- [146] Y. Ishida, T. Takahashi, H. Okumura, K. Arai, S. Yoshida, Origin of Giant Step Bunching on 4H-SiC (0001) Surfaces, *Mater. Sci. Forum.* 600–603 (2009) 473–476. doi:10.4028/www.scientific.net/MSF.600-603.473.
- [147] A. Jablonski, Practical expressions for the mean escape depth , the information depth, and the effective attenuation length in Auger-electron spectroscopy and x-ray photoelectron spectroscopy, *J. Vac. Sci. Technol. A* 27 (2009), 253. doi:10.1116/1.3071947.

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