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Review report on PhD Thesis of Amir Abdulrahman Ahmad Zebari entitled "Engineering Nanostructures on Semiconducting Surfaces"

The reviewed PhD thesis of Amir A. Ahmad Zebari was prepared under supervision of prof. Marek Szymoński at the Department of Physics of Nanostructures and Nanotechnology of the Marian Smoluchowski Institute of Physics, Jagiellonian University in Kraków. The general aim of this work concerns experimental and theoretical comprehensive studies of selected surface phenomena which allow control fabrication of nanostructures on different semiconducting surfaces. Three systems and surface phenomena have been investigated and described in the thesis, namely: formation of nanoripples on TiO_2(110) surface by means of low energy ion beam sputtering, on-surface polymerization of DBBA organic molecules on reconstructed TiO_2(011) surface, and control fabrication and tip-assisted modification of 3D nanocrystals of organic semiconductor PTCDA on hydrogen passivated Ge(001) substrate. The undertaken topics are actual and important from the point of view of fundamental research in surface science, especially in areas dealing with formation of nanostructures, physicochemical properties of semiconducting surfaces and their interactions with organic adspieces. Moreover, it is evident that subject of the thesis is also important for practical applications in nanotechnology. The first system under investigation, concerning formation of nanoripples by ion irradiation, can be considered as effective method of "top-down" fabrication of nanostructures on solid surfaces. In contrast, the reminding two topics deal with selforganization of organic adspieces and are good examples of new promising "bottom-up" approach in nanotechnology. According to this strategy the fabrication of new materials with dimensions on the nanoscale is possible on the basis of spontaneous organization of small elements (atoms or molecules) into useful conformations. Thus, the elucidation of fundamental surface processes leading to this organization is still open and actually active area of research and constitutes further progress of these applications. The presented thesis of Amir A. Ahmad Zebari fits well to these necessities. On the basis of presented facts I would like to emphasize topicality and

significance of the thesis in terms of undertaken aims as well as investigated surface phenomena.

The dissertation contains 91 pages. It is divided into 8 chapters concerning introduction part (Introduction and Experimental), a set of three publications describing undertaken studies of three above mentioned surface phenomena, general conclusions, appendices, and bibliography. The list of references at the end of the thesis is directly related to introduction part and includes 95 correctly selected publications. The additional references are associated to each publication and support detailed discussion of presented results.

The first chapter (Introduction) gives review of fundamental terms in nanotechnology including comparison of two conventional 'top-down" and "bottom-up" techniques and provides general information about on-surface formation of molecular nanostructures in UHV conditions. Then Author presented more detailed literature review of investigated surface phenomena. This main part of the chapter is a solid background to the experimental results and discussion presented in the enclosed publications. It also shows high level of general knowledge of the Author in the field of undertaken investigations. The chapter ends with description of main goals of the thesis, statements of the Author concerning his participation in the undertaken studies and short glossary of the enclosed publications.

In chapter 2 (Experimental) detailed information about used experimental systems and procedures of sample preparation is provided. It is evident that control of nanostructures formation and their manipulation can be achieved using methods which are able to afford not only an averaged information on the large area but also the detailed structure of the surface in 'real' space. Author applied scanning tunneling microscopy in UHV conditions as a main tool for undertaken experimental studies. Three different STM/UHV systems were used enabling to perform microscopic investigations in nanometric scale at variable and low temperatures. At this point it is worth to emphasize that presented microscopic characterization of obtained nanostructures and their manipulations are characterized by highest level and in my opinion can be summarized as "the state of the art" of experimental work in this field of investigations. The quality of experimental results is a strong point of the thesis.

The next three Chapters (3-5) concern experimental results and their discussion. This main part of the dissertation is presented in a form of three enclosed publications which concern

separately three investigated topics. All papers are an effect of collaboration of several authors. Amir Zebari is a second co-author in two presented papers and a first co-author in one paper. His contribution in the undertaken studies is described in his statement presented in the first Chapter of the thesis. Moreover, all co-authors supported his dissertation by their own declarations. According to these documents we can state that in the case of two papers Amir Zebari has performed significant part of preparation and microscopic investigations of nanostructures, and in the case of one paper he was a main executor of experiments. It is important to emphasize that all papers were published recently (in 2013) in high-level scientific journals of international range, like: Physical Review B (American Physical Society, impact factor 3.8), Angewandte Chemie Int. Ed. (German Chemical Society, impact factor 13.7) and Beilstein Journal of Nanotechnology (Beilstein Institut, impact factor 2.4). The papers were therefore a subject of evaluations by several reviewers, worldly-known specialists, receiving positive final decisions about publications. After reading this part of the dissertation I fully agree with these decisions. The publications represent a high level of science. The undertaken topics are well investigated and obtained results are properly discussed. The most important scientific achievements of each part of undertaken investigations can be summarized as follows:

The first publication (Chapter 3) deals with control formation of nanoripples on TiO_2(110) surface by low energy ion irradiation. The STM observations exhibit intriguing feature of this surface phenomenon – strong dependence of orientation of generated nanoripples on the substrate temperature. The crucial part of this work concerns combined experimental (STM, EPR, LEED) and theoretical (DFT modelling) investigations and interesting discussion which finally enabled to determine reason of this dependence. Authors clearly demonstrated that observed feature is a consequence of anisotropic mass transfer of dispersed material realized by concerted titanium diffusion in assistance of oxygen adspieces. My question to this part of investigations concerns the expected changes of surface composition caused by ion irradiation. Could Author discuss in more details these changes and their influence on observed surface phenomenon?

The second publication (Chapter 4) concerns studies of on-surface polymerization of dibromobianthryl monomers on TiO_2(011)-(2x1) surface. The microscopic observations evidently confirmed course of the reaction in these conditions and indicated different mechanism then reported for metal substrates. It is worth to emphasize that on-surface polymerization of organic molecules is actually a very attractive area of investigations. To

the best of my knowledge all already published results in this field concern investigations of the reaction on metal substrates. The discussed work is therefore a first confirmation of polymerization reaction on semiconducting surface. The importance of this result was appreciated by publication in prestigious journal (Angewandte Chemie Int. Ed.).

In the third publication (Chapter 5) the STM tip-assisted manipulation of self-assembled 3D molecular crystals of PTCDA is described. The studied adsorbate molecules deposited on hydrogen passivated Ge(001) surface accumulate and form 3D nanocrystals according to Volmer-Weber growth mode. Amir Zebari and coauthors demonstrated that tip-induced generation of artificial defect (hole) on the top of the nanocrystal leads to spontaneous crystal modification by formation of ordered top-most molecular layer. This phenomenon is explained by energetically preferable movement of molecules attached to the edges of lower lying layers to newly generated edges on top layer offering convenient adsorption sites with higher binding energies. I agree with Authors that the studied phenomenon can be considered as a useful technique for precise tuning of the form of molecular nanostructures. I have question to the Author about the potential influence of temperature and bias voltage on this spontaneous nanocrystal modification?

In summary, I am fully convinced that the thesis of Amir A. Ahmad Zebari consists original scientific works. The obtained results are scientifically sound. They provide new and important information about formation and modification of nanostructures on semiconducting surfaces. I state that the demands of Polish legal acts about academic degrees (no. 13 from March 14, 2003 with later amendments) are fulfilled and recommend the thesis for public defense.

Warszawa, July 13th, 2014

Robert Nowakowski