Review Report on PhD Thesis

Faculty: **Central European Institute of Technology**
Brno University of Technology in Brno

Academic year: **2022/2023**

Student: **Anton Olegovich Makoveev**

Doctoral study program: **Advanced Materials and Nanosciences**

Field of study: **Advanced nanotechnologies and microtechnologies**

Supervisor: **Assoc. Prof. Jan Cechal, Ph.D.**

Reviewer**:** **apl. Prof. Dr. Benedetta Casu**

PhD thesis title: Molecular self-assembly on surfaces: the role of coverage, surface orientation and kinetics

Topicality of doctoral thesis:

Anton Olegovich Makoveev's work belongs to the field of investigations on the growth of organic materials. This topic is important because understanding growth is beneficial not only from the academic point of view but also for introducing new materials to applications.

In particular, this work is focused on the self-assembly of 4,4'-biphenyldicarboxylic acid (BDA) on silver substrates. The systems are taken as a model to identify and clarify the parameters that play a role, by using a combination of experimental approaches that are described in detail. The supporting theoretical concepts are also discussed.

Meeting the goals set:

The goals of the work, related to self-assembly, are clearly set in the introduction of the thesis: understanding the self-assembly in diffusion-limited conditions; understanding the role of the surface-plane orientation of the substrate; understanding the influence of non-thermal activation by low-energy electrons on the kinetics of the self-assembly. The work answers all questions, chapter by chapter. This is also supported by the publication of the included papers. Together with the combination of several experimental techniques, it is also noticeable the use of low energy electron microscopy which is rarely used to investigate organic growth on inorganic substrates. This technique is fundamental in studying growth phenomena in real-time, in situ, under very controlled conditions, thus, avoiding artefacts that might stem from small differences in the environment during measurements, especially if these are not performed in situ and in real-time.

Problem solving and dissertation results:

To answer the posed questions, XPS, STM, and LEEM are the techniques of choice. The sample preparation is done under controlled conditions. The UHV cluster allows growing the systems and performing their investigation without breaking the vacuum because each experiment is connected to the same transfer line. This allows reproducibility of the results and avoids artefacts.

Makoveev studied the self-assembly under diffusion-limited conditions, in high coverage on Ag(001) single crystals, identifying the occurrence of a deprotonation reaction, giving rise to a BDA phase, which is very similar to the as-deposited fully protonated alpha phase, however, with various fractions of deprotonated carboxyl groups. This phase is strongly modulated by the Ag(001) surface and shows some additional periodicity, evidenced by the additional spots in the diffraction pattern. This is a non-equilibrium phase that transforms into the alpha phase if there is enough available space on the surface.

To understand the role played by the geometry of the substrate, Makoveev compared the assembly of BDA on Ag(001) and Ag(111) single crystals. The structural motifs for intact and fully deprotonated BDA are similar on both surfaces. The investigation evidences the occurrence of a series of intermediate phases comprising partially deprotonated BDA that differ in structure and chemical composition.

The study also found a so-called burst transformation, a combination of burst nucleation, stabilization of a deprotonation state within the condensed phase, and rapid deprotonation on a free substrate.

Importance for practice or development of the discipline:

The work elucidates specific phenomena of the growth of organic molecules on inorganic substrates. This is of fundamental importance not only for the basic understanding of the physics and chemistry of these systems but also for introducing new materials for applications and optimising the growth processes in this view.

A very interesting part of the work is the comparison of two different geometries of the silver substrate. This is an aspect that is rarely deeply investigated. Conversely, the Author demonstrates the impact of choosing different substrate geometries.

Formal adjustment of the thesis and language level:

The study is good, robust, well-organised, and written.

(The study is duly completed by a state doctoral examination and the defense of a dissertation, which proves the ability and readiness for independent activity in research or development or for independent theoretical and creative artistic activity. The dissertation must include original and published results or results accepted for publication.)

Questions and comments:

1) I would be very happy to have more details on the XPS fits: for example, how was determined the Lorentzian width for the various core levels?

2) How is it possible to translate the present results to other surfaces?

3) BDA behaves on silver very similarly to PTCDA. What happens/it is expected in the case of gold surfaces (less reactive) and copper (more reactive) than silver?

Conclusion:

In my opinion, the reviewed thesis **fulfills** all requirements posed on theses aimed at obtaining the PhD degree. This thesis **is** ready to be defended orally, in front of the respective committee.

In Tübingen, 01.04.2023

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apl. Prof. Dr. Benedetta Casu