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Report on the thesis entitled *"Crystalline and electronic structure of functionalized layers of graphene, h-BN and their heterostructures"* submitted by Kirill A. Bokai to receive the academic degree of candidate of physical and mathematical sciences

The dissertation of Kirill Bokai is devoted to the application of different surface science methods, like photoelectron spectroscopy and diffraction (PES and PED), near-edge x-ray absorption fine structure (NEXAFS) spectroscopy and scanning tunneling microscopy and spectroscopy (STM and STS) for the investigation of the crystallographic structure and electronic properties of different epitaxial two-dimensional systems on the basis of graphene and h-BN. Two-dimensional systems, like graphene (pristine and doped), h-BN, and as well as lateral graphene/h-BN heterostructures were synthesised on metallic substrate of different geometry allowing to precisely tune the properties of 2D materials and study these changes using different spectroscopic methods accompanied by density functional theory (DFT) calculations. All experimental works were performed on different large-scale synchrotron facilities (HZB BESSY, SLS, MAX IV) and also using laboratory equipment at St. Petersburg State University. Theoretical modelling was performed using resources of computer centre of St. Petersburg State University.

The thesis is traditionally built and includes Introduction and 6 main chapters (Literature review, Description of experimental and theoretical methods, Description of experimental equipment, Investigation of features of atomic and electronic structure of 2D materials on Ni(111) and Co(0001), Study of the microstructure of graphene on Co(0001) using oxygen exposure, h-BN – graphene lateral heterostructures on Co(0001), Properties of N-graphene on stepped Ni surfaces), Conclusions, and the Bibliography (243 references).

After the introductory part explaining the aim of his research and including also the description of scientific novelty, practical significance, as well as the used methodology, the author turned to the overview of the available literature on the topic of dissertation. This first chapter is logically constructed, although in my view, it lacks many relevant references which are devoted to the studies of the electronic structure of graphene and h-BN epitaxial layers on metallic substrates. The second chapter is devoted to the discussion of the experimental and theoretical as well as technical details

and can be seen as an indicator of the author's very good background in experimental physics.

The third chapter is devoted to the studies of the atomic and electronic structure of 2D materials, B-doped graphene and h-BN on Ni(111) and Co(0001). Very elegant method of photoelectron diffraction and holography is applied accompanied by very intensive modelling and analysis. For the first time, the precise analysis of the crystallographic structure of the h-BN/Ni(111) and h-BN/Co(0001) interfaces is presented. The main conclusion are supported by the respective STM results and DFT calculations. Also, an asymmetric distribution of boron impurities over the two carbon sub lattices is observed in the single-crystal B-doped graphene layer grown on the Ni(111) surface, but it is less pronounced than in the analogous system on Co(0001). As a conclusion, the obtained results for the studied systems demonstrated the high efficiency of structural analysis of 2D materials using photoelectron diffraction and photoelectron holography methods at low kinetic energy of photoelectrons, which confirms the feasibility of further use of these methods for studies of low-dimensional systems.

The fourth chapter considers the intercalation of oxygen under the polycrystalline and single-crystalline graphene on the Co(0001) surface. The intercalation of oxygen under the polycrystalline graphene leads to the formation of cracks in the graphene, which appear along the boundaries of misoriented graphene domains. It was found that the efficient oxidation of the Co substrate occurs only in the areas not covered by graphene. The formation of cobalt oxide under the graphene occurs mainly due to the lateral expansion of the oxide regions along the atomic planes of cobalt. These studies were performed using XPS and NEXAFS methods and morphology of the systems was investigated using photoelectron microscopy. Unfortunately, no electronic structure studies using ARPES or theoretical analysis of the obtained experimental data is presented. However, the obtained results can be considered for further, more deep studies and analysis, of the graphene/oxygen/Co(0001) systems.

The fifth chapter is devoted to the investigation of very interesting lateral heterostructures on the basis of graphene and h-BN grown on the Co(0001) surface. A method has been developed for the formation of single-layer lateral h-BN – graphene heterostructures on the Co(0001) surface, in which the boundaries between the domains of h-BN and graphene are formed mainly by B-C bonds in the B-zigzag/C-zigzag and BC-zigzag configurations, the first of which is more preferred. In the course of CVD synthesis of lateral h-BN – graphene heterostructures on the Co(0001) surface, the formation of h-BN domains with the (1×1) structure promotes the strict orientation of graphene domains in a wide range of synthesis temperatures $(430 - 700^{\circ}\,\mathrm{C})$. The C-zigzag edges of graphene can be observed with STM due to the edge states localized on them. Here, the methods of photoelectron diffraction and holography were used accompanied by the intensive DFT modelling. These experiments can be considered as first steps on the implementation of the lateral 2D hybrid structures in electronics and spintronics and can be interesting for very broad community working in these areas.

The sixth chapter is devoted to the synthesis of N-doped graphene on a crystalline Ni surface with nonplanar morphology and studies its electronic properties. The combination of the photoelectron spectroscopy, including diffraction and holography method, and DFT modelling is used. The surface of the Ni/cW(441) substrate is used and consists of vicinal planes with Ni(111) terraces that are separated by steps with smoothly varying density. This allowed to study the influence of the step edges on the concentration and chemical environment of the impurity N atoms in graphene lattice. According to the analysis of the C 1*s* XPS spectra obtained at different points on the surface of the N-doped-graphene/Ni/cW(441) system, the weakening of the coupling between N-graphene and the Ni substrate is observed in the vicinity of the step edges. The significantly large area of graphene weakly bound to the Ni substrate is explained by kinks in the atomic structure of the step edges and

by local rearrangement of the steps, during which the single-atomic kinks are transformed into the zigzag edges consisting of the close-packed segments. The zigzag-like step edges observed in the N-doped-graphene/Ni/cW(441) system are more extended than the straight edges inherent to the cNi(111) substrate. It is also found that the pyridinic configuration of the N-centers is dominant in the regions where the graphene is strongly bound to the Ni substrate, whereas the graphitic configuration of the N-centers prevails where the interaction between the graphene and the substrate is weakened, namely near the edges of the atomic steps.

In conclusion, the work itself is written using correct scientific terminology. The presentation of the material is characterized by a clear logic sequence, which indicates the scientific maturity of the author. Apparently, the remarks made in the report are of a character of wishes and do not detract from the essence of the work. Evaluating the work as a whole, I believe that in terms of relevance, novelty, experimental and practical value of the results, the thesis fully meets the requirements for the dissertation submitted for the degree of candidate of physical and mathematical sciences and I therefore recommend its acceptance by the Dissertation Committee and rate it as very good.

Yours sincerely

(Yuriy Dedkov)