Reviewer report on doctoral thesis "Studying possibilities of graphene functionalization using AFM and STM techniques" by Mykola Telychko

Functionalization of graphene represents a prospective and vivid research area with potentially revolutionary applications in electronics, catalysis, or energy conversion and storage. The present thesis deals with design and investigations of novel experimental approaches towards functionalization of graphene by means of substitution doping. Presented are model experiments and ab-initio calculations on preparing nitrogen (N, n) and boron (B, p) doped graphene on SiC(0001).

The author describes a systematical buildup of experimental and knowledge base for preparing and understanding the properties of substitution-doped graphene. After a brief Introduction and an overview of the employed experimental techniques (Section 1) the author presents a microscopic study of morphology and nucleation dynamics of graphene on SiC(0001) (Section2), and describes experimental methods and results of experiments on N doped graphene (Section 3.2), B doped graphene (Section 3.3) and B,N co-doped graphene (Section 3.4). Results presented in the Thesis represent a significant advance of knowledge in the field of graphene properties and functionalization. Especially, the experimental techniques for preparing N and B doped graphene yield monodispersed, single-configuration N or B dopants representing very valuable model systems for substitution-doped graphene. The results of the present Thesis have been published in high-impact international scientific journals (ACS Nano) in publications where Mr. Telychko is appearing as the first author.

Mr. Telychko is presenting a carefully bulit-up study well documenting his capability of creative and productive scientific work in a multidisciplinary research team complementing experimental and theoretical approaches. Therefore I recommend that Mr. Mykola Telychko be awarded the title Ph.D.

I would like to ask the author several questions regarding the implications of the presented research.

1) In Section 3.2.3 you describe saturation of N doping of graphene at about 1.6% of N dopant concentration. Can you discuss the reason for the observed saturation? For B doped graphene, you propose in Section 3.3.3 that B concentration is limited by diffusion of B into the SiC bulk.

2) The main motivation for substitution-doping of graphene is the engineering of graphene electronic structure, particularly the Fermi-level position. In the Thesis, you are presenting indirect integral measurements of the electronic structure by scanning tunneling spectroscopy for N doped (Figure 3.10) and, partially, for B doped graphene (Fig.3.17). Are for your samples, eventually, measurements of electron structure by ARPES method available (cf. Fig. 3.1)? These measurements would be very valuable especially for B,N co-doped graphene where the information on the electron structure of your samples seems to be missing.

3) In Section 3.1 you are referring to a theoretical work predicting that B,N co-doping may be used for generating and engineering a band gap in the graphene electronic structure. Are the types and the concentrations of B and N defects you are obtaining in your experiments within the range required theoretically for the bandgap opening, and, may we expect achieving the bandgap opening on your model graphene samples?

Several minor questions are addressing the clarity of the presentation.

1) In the figure 2.16 you are comparing the morphology of graphene on SiC prepared by annealing in vacuum and by annealing in the Ar atmosphere. It is not clear which images belong to which sample, and, what actually is the difference in morphology between the two samples.

2) On page 54 you are referring to Figures 3.15 d, e for demonstrating a “dark halo” around the dopants in the empty states STM images of B doped graphene. Figure 3.15 e is however missing, and the dark halo is not apparent in Figures 3.15 a-d either. Can you give a more focused presentation of the dark halo?

3) In the Figures 3.22 and 3.23 it is difficult to distinguish among several types of B objects you are reporting on the surface – B clusters, B single dopants, and B double dopants. Can you give a more focused presentation of the different types of B objects?

Prague, July 27, 2016

Mgr. Josef Myslivеček, Ph.D.