TAILORING THE ATOMIC STRUCTURE AND ELECTRONIC PROPERTIES OF CARBON AND BORON-NITRIDE NANOMATERIALS USING ELECTRON AND ION IRRADIATION

A. V. Krasheninnikov[a,b*], **J. Kotakoski**[a], **O. Lehtinen**[a], **H. Ålhgren**[a], **K. Nordlund**[a], **J. Keinonen**[a], **N. Berseneva**[b], **K. Saloriutta**[b], **A.-P. Jauho**[b], **U. Kaiser**[c], **J. C. Meyer**[c], **C. H. Jin**[d], **K. Suenaga**[d], **O. Cretu**[e], **J.A. Rodriguez-Manzo**[e], **F. Banhart**[e] and **R.M. Nieminen**[b]

[a]Department of Physics, University of Helsinki, Finland
[b]Department of Applied Physics, Aalto University, Finland
[c]Electron Microscopy of Materials Science, University of Ulm, Germany
[d]Nanotube Research Center, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan
[e]Institut de Physique et Chimie des Materiaux, Universite de Strasbourg, Strasbourg, France
[*]Corresponding author: *akrashen@acclab.helsinki.fi*

Recent experiments (see Refs. [1,2] for an overview) on ion and electron bombardment of nanostructures demonstrate that irradiation can have beneficial effects on such targets and that electron or ion beams can serve as tools to change the morphology and tailor mechanical, electronic and even magnetic properties of various nanostructured materials.

We systematically study irradiation effects in nanomaterilas, including two-dimensional (2D) systems like graphene and hexagonal boron-nitride (h-BN) sheets. By employing various atomistic models ranging from empirical potentials to time-dependent density functional theory we simulate collisions of energetic particles with 2D nanostructures and calculate the properties of the systems with the irradiation-induced defect [3,4]. In this talk, our latest theoretical results on the response of graphene and h-BN to irradiation will be presented, combined with the results obtained in collaboration with several experimental groups [5-7].

Specifically, we will first discuss the response of graphene to electron irradiation [4]. Using electron irradiation an sp^2-hybridized one-atom-thick flat carbon membrane with a random arrangement of polygons, including, surprisingly, four-membered carbon rings, was created, Fig. 1. We show how the transformation occurs step-by-step by nucleation and growth of low-energy multi-vacancy structures constructed of rotated hexagons and other polygons. Our observations, along with first-principles calculations, provide new insights to the bonding behavior of carbon and dynamics of defects in graphene. The created domains possess a band gap, which may open new possibilities for engineering graphene-based electronic devices. It should be pointed out that an amorphous 2-D material has not been reported before. The results of electronic transport calculations for graphene with extended defects formed by the electron beam will also be presented.

Reconstructed point defects in graphene created by electron irradiation and annealing can be used to bind metal atoms [4]. By applying electron microscopy and density functional

theory, we show [5] that the strain field around these defects reaches far into the unperturbed hexagonal network, Fig. 2, and that metal atoms have a high affinity to the defected and strained regions of graphene. Metal atoms are bonded with energies of about 2 eV, which makes it possible to use them for tailoring graphene properties.
Then we proceed to the response of graphene to ion irradiation [8]. Using atomistic computer simulations based on analytical potential and density-functional theory models, we simulated impacts of energetic ions onto graphene. We identify the types and concentrations of defects which appear in graphene under impacts of various ions with energies ranging from tens of eV to MeV. We demonstrate that the conventional approach based on binary-collision approximation and stochastic algorithms developed for bulk solids cannot be applied to graphene and other low-dimensional systems. We will further discuss how ion irradiation can be used to introduce impurities in graphene and BN sheets, and outline possible avenues for tailoring the electronic and magnetic structure of graphene by ion implantation [9].
The effects of electron irradiation on boron-nitride sheets [7] and nanotubes will also be touched upon. Finally, we will discuss how electron irradiation and electron beam-assisted deposition can be used for engineering hybrid BN-C nanosystems by substituting B and N atoms with carbon with high spatial resolution, and present our preliminary results of electronic transport in hybrid BN-C nanosystems.

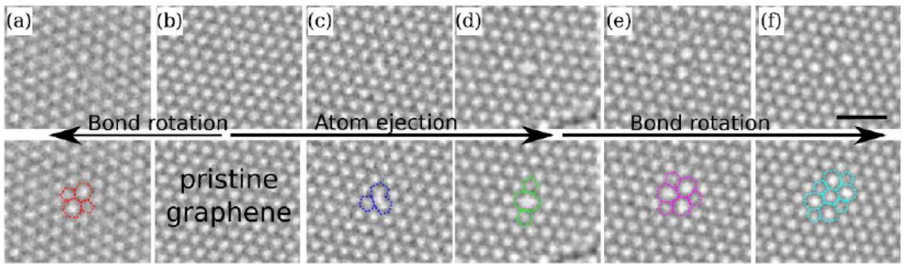

Figure 1: Elementary defects and frequently observed defect transformations under irradiation. Atomic bonds are superimposed on the defected areas in the bottom row. Creation of the defects can be explained by atom ejection and reorganization of bonds via bond rotation. (a) Stone-Wales defect, (b) defect-free graphene, (c) single vacancy, (d-f) divacancy and defects derived from the divacancy by bond rotations. Scale bar is 1 nm. From Ref. [4]

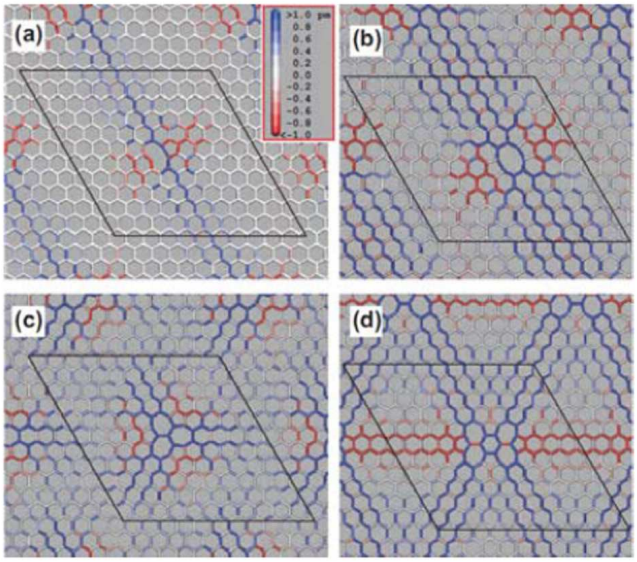

Figure 2: Atomic structures of a single vacancy (a), di-vacancy (b), and the reconstructed divacancy (c-d) from first principles simulations. The bonds are colored according to an increase (blue) or decrease (red) in the bond length (given in picometers). The bonds close to pentagons are contracted, but most C-C bonds are stretched. The red lines outline the simulation supercell (10x10 graphene units).

References

[1] A.V. Krasheninnikov and F. Banhart, Nature Materials, 6 (2007) 723.
[2] A.V. Krasheninnikov and K. Nordlund, Appl. Phys. Rev., 107 (2010) 071301.
[3] F. Banhart, J. Kotakoski and A.V. Krasheninnikov, ACS Nano, 5 (2011) 26.
[4] J. Kotakoski, A.V. Krasheninnikov, U. Kaiser, and J. Meyer, Phys. Rev. Lett., (2011) in press.
[5] A.V. Krasheninnikov, P.O. Lehtinen, A.S. Foster, P. Pyykko, and R.M. Nieminen, Phys. Rev. Lett., 102 (2009) 126807.
[6] O. Cretu, A.V. Krasheninnikov, J.A. Rodriguez-Manzo, L.Sun, R.M. Nieminen, and F. Banhart, Phys. Rev. Lett., 105 (2010) 196102.
[7] J. Kotakoski, C.H. Jin, O. Lehtinen, K. Suenaga, and A.V. Krasheninnikov, Phys. Rev. B, 82 (2010) 113404.
[8] O. Lehtinen, J. Kotakoski, A.V. Krasheninnikov, A. Tolvanen, K. Nordlund and J. Keinonen, Phys. Rev. B, 81 (2010) 125442.
[9] H. Ålhgren, J. Kotakoski, and A. V. Krasheninnikov, Phys. Rev. B (2011) in press.