Tailoring the properties of graphene, dichalcogenides and other 2D materials through electron irradiation: insight from DFT simulations and TEM experiments

Arkady V. Krasheninnikov,[1,2] Hannu-Pekka Komsa,[1] Natalia Berseneva,[2] Simon Kurasch,[3] Jani Kotakoski,[1,4] Ossi Lehtinen,[1] Ute Kaiser,[3] Jannik Meyer,[4] Risto Nieminen[2]

1 Department of Physics, University of Helsinki, P.O. Box 43, 00014 Helsinki, Finland
2 Department of Applied Physics, Aalto University, P.O. Box 1100, 00076 Aalto, Finland
3 Central Facility for Electron Microscopy, Group of Electron Microscopy of Materials Science, Ulm University, 89081 Ulm, Germany
4 Department of Physics, University of Vienna, Boltzmanngasse 5, 1090 Wien, Austria

akrashen@acclab.helsinki.fi

Recent experiments on electron and ion bombardment of 2D materials 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 low-dimensional materials. In this presentation, our latest theoretical results on the response of graphene [1-2], h-BN [3] and several dichalcogenides (MoS2, MoSe2, WS2, etc) [4] to irradiation will be presented, combined with the experimental data obtained in collaboration with several groups.

Transformation of graphene to an amorphous 2D sheet (Fig. 1) by the beam of energetic electrons will be discussed. It will be shown that bond rotations near vacancy-type defects (Fig.2) induced by energetic electrons are the main mechanism of the transformation. We will further study the stability of graphene ribbons under electron irradiation. It will be shown that the response of the ribbons to irradiation is not determined by the equilibrium energetics as assumed in previous experiments, but by kinetic effects associated with the dynamics of the edge atoms after impacts of energetic electrons, Fig.3. We will demonstrate an unexpectedly high stability of armchair edges, comparable to that of pristine graphene, and show that the electron energy should be below ~50 keV to minimize the knock-on damage at the edges. The electronic structure of graphene sheets with defects will be addressed as well, and possible avenues for tailoring the electronic structure of graphene by irradiation-induced defects [5] and impurities will be introduced.

We will also 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 C atoms, Fig. 4. Using density-functional theory static and dynamic calculations, we show that the substitution process is governed not only by the response of such systems to irradiation, but also by the energetics of the atomic configurations, especially when the system is electrically charged. We suggest using spatially localized electron irradiation for making carbon islands and ribbons embedded into BN sheets.We further study the magnetic and electronic properties of such hybrid nanostructures and show that triangular carbon islands embedded into BN sheets possess magnetic moments, which can be switched on and off by electrically charging the structure.

Finally, we present the results of firs-principles calculations [4] for displacement thresholds in various dichalcogenides. We will further touch upon the most frequent defect structures which appear in these materials under electron irradiation and compare the calculated defect configurations to those found in the transmission electron microscopy experiments [6]. Similar to h-BN, we explore how electron-beam-assisted deposition can be used to change the atomic structure of dichalcogenides and tailor their electronic properties through doping.

References

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Figures

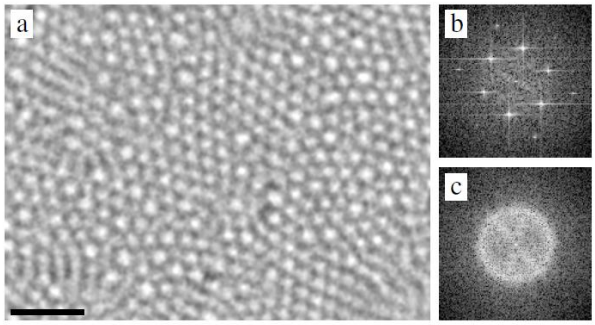

Fig.1. (a) Amorphous two-dimensional sp^2-bonded carbon membrane created by a high-dose exposure of graphene to 100 keV electron irradiation in an HRTEM. Scale bar is 1 nm. (b) Fourier transforms from HRTEM images of the initial graphene configuration and of the amorphous 2D carbon (c). Courtesy of J.C. Meyer and U. Kaiser.

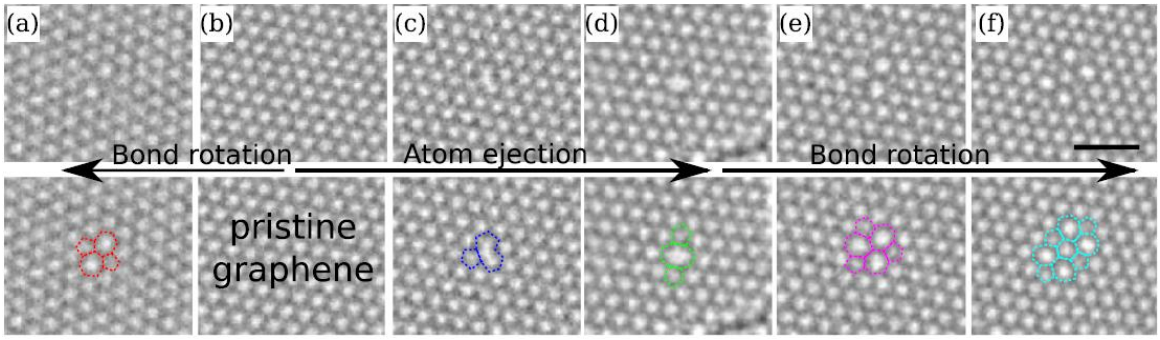

Fig. 2. Elementary defects and frequently observed defect transformations under irradiation. Atomic bonds are superimposed on the defected areas in the bottom row. Creation of the defects can be explained by atom ejection and reorganization of bonds via bond rotation. (a) Stone-Wales defect, (b) defect-free graphene, (c) single vacancy, (d) Divacancy, (e) 555-777 divacancy, (f) 5555-6-7777 divacancy. Scale bar 1 nm. Courtesy of J.C. Meyer and U. Kaiser.

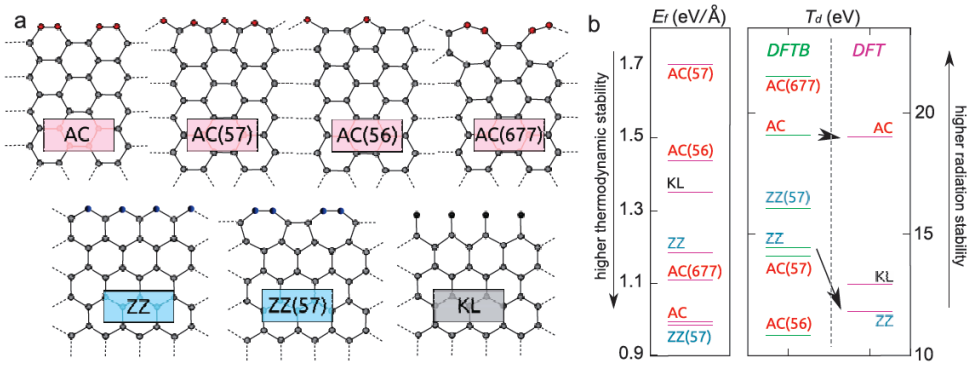

Fig.3 Different edge reconstructions as optimized with DFT (a) and their formation energies Ef and displacement thresholds Td (b). Displacement thresholds as calculated with both DFT and DFTB methods are presented.

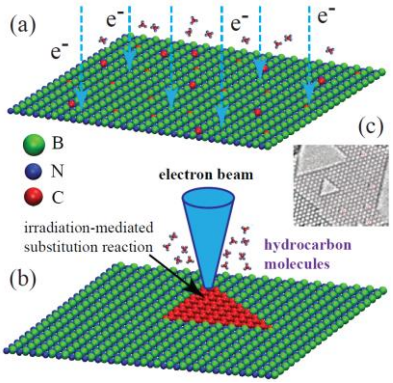

Fig. 4 Schematic representation of the electron-beam-mediated substitutional doping of boron nitride monolayer. Hydrocarbon molecules decomposed by the beam provide carbon atoms which preferentially take place of boron atoms displaced by the beam or due to beam-induced substitution reaction. (a) Irradiation of the whole sample as done experimentally [X. Wei et al., ACS Nano 5, 29162922 (2011).] (b) Possible engineering of carbon island in BN matrix due to focused electron beam. (c) Experimental TEM image of a triangular hole formed in single BN sheet due to the electron beam [J. C. Meyer et al., Nano Lett. 9, 2683 (2009)].