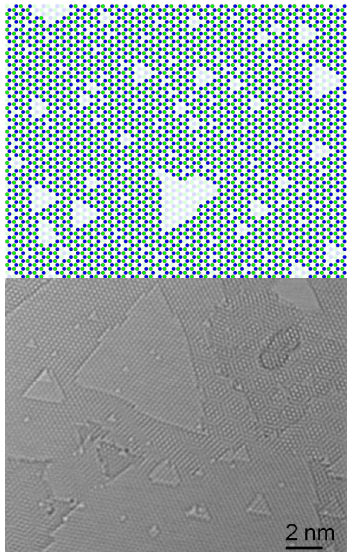
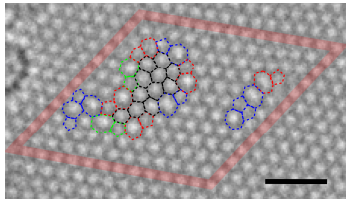
ATOM-SCALE MODIFICATIONS IN GRAPHENE AND WHITE GRAPHENE

The only known atomically thin two-dimensional materials are graphene and the hexagonal boron-nitride monolayer. They have a similar atomic structure, resembling a honeycomb or a chicken wire, but altogether different chemistry. Graphene is a single layer of the familiar layered carbon material graphite, kept together by the sp^2-hybridized covalent bonds between the carbon atoms, and exhibits semi-metallicity (or, in other words, is a zero-band gap semiconductor). Although many properties of graphene had been investigated theoretically as a prototype material for understanding the properties of graphite and carbon nanostructures, *e.g.*, fullerenes and carbon nanotubes, it was a surprise in 2004 when this material was experimentally shown to exist also in reality. Due to this breakthrough discovery, Konstantin Novoselov and Andre Geim received the 2010 Nobel Prize in physics. On the other hand, hexagonal boron nitride monolayer, the insulating counterpart of graphene sometimes called *white graphene*, is formed due to ionic bonding between the alternating boron and nitrogen atoms.



Triangular defects created into a hexagonal boron nitride monolayer by an electron beam with 80 kV acceleration voltage. Simulation result (top) and experimental result (bottom).



Example of a multi-vacancy defect structure in graphene created by an electron beam with 100 kV acceleration voltage. Scale bar is 1 nm.

Discovery of these materials was significantly aided by the recent advances in the high resolution transmission electron microscopy, especially via the introduction of aberration corrected devices, which allowed atomic resolution images at conditions which are not destructive to the targets. The initial experimental observations displayed, along with the materials themselves, a set of atomic defects which were either intrinsic or caused by the electron beam. Especially in the case of hexagonal boron nitride, the triangular vacancy structures caused much confusion in the field since they seemed to be unexplainable by the existing theories of damage production in this material. Through a collaboration of University of Helsinki and the National Institute of Advanced Industrial Science and Technology (AIST), Japan, we have been able to explain the formation of these defects by primary knock-on's between the electrons and the target atoms. The peculiar triangular shape of the defects is due to easier displacement of boron atoms in the system, which leads to vacancies terminated by

nitrogen atoms. For graphene, the observed defects have been much less controversial. However, as we show in our recent review (written in collaboration with University of Strasbourg, France), the flexibility of carbon chemistry allows for a breadth of different defect structures to be formed. As a result of collaboration of University of Helsinki and University of Ulm, Germany, we have recently found the lowest energy defect configurations in this material, which also introduce a band gap into this material. This may prove out to be an important step towards carbon-based electronics of the future. As the limiting case for the growing defect structures, we displayed the first-ever two-dimensional amorphous structure.

Kotakoski, J., Jin, C., Lehtinen, O., Krasheninnikov, A.V. and Suenaga, K., 2010. Electron knock-on damage in hexagonal boron nitride monolayers. Phys. Rev. B, 81, 113404.

Banhart, F., Kotakoski, J. and Krasheninnikov A.V., 2011. Structural defects in graphene. ACS Nano, 5, 26-41.

Kotakoski, J., Krasheninnikov, A.V., Kaiser, U. and Meyer, J.C., 2011. From point defects in graphene to two-dimensional amorphous carbon. Phys. Rev. Lett., *accepted for publication*.