In-situ electron microscopy of carbon nanomaterials with an aberration-corrected STEM

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Scanning transmission electron microscopes (STEM) a corrector for the spherical aberration allow the focusing of an intense electron beam onto a spot with a diameter on the scale of 1Å. Imaging and analysis with 1Å resolution can be carried out, but the highly focused electron beam also gives us the possibility of undertaking *in-situ* electron irradiation experiments at the atomic scale. Structural transformations can be induced in the specimen and "nano-engineering" becomes feasible if the electron energy exceeds the threshold for atom displacements. Experiments in graphitic nanomaterials, e.g., carbon nanotubes or graphene where the displacement threshold energy for the electrons is slightly below 100 keV, can be carried out with standard STEMs. The electron beam with a current density on the specimen of more than 10^5 A/cm^2 induces displacments of carbon atoms with rates of up to 50 s^{-1}.

An overview of the first *in-situ* experiments with an aberration-corrected STEM is given. Materials on the basis of graphitic carbon such as carbon nanotubes or graphene and composites of metal nanocrystals and carbon nanotubes are in the focus of interest. Single or multiple vacancies can be created with the focused electron beam in pre-selected positions of the graphenic lattice. This gives us the possibility of observing in real time the response of a material to the creation of point defects. It is shown that the reconstruction of the lattice after the creation of defects is decisively determined by the specimen temperature. By using a heating stage in the electron microscope, the temperature of the specimen can be varied in a wide range. The combination of high temperature and extremely intense and localized electron irradiation is a unique possibility of studying the formation and behaviour of point defects and of structuring materials at the atomic scale.

Figure 1 shows an example of the structural changes in a single-wall carbon nanotube after the beam-induced removal of atoms at a temperature of 420°C. Stable vacancies cannot be created; instead, an extended reconstruction of the graphenic lattice of the tube appears and the tube collapses. This is due to the high mobility of vacancies in nanotubes at high temperature. The situation is different in double-wall nanotubes where stable vacancies can be created by the focused beam at room temperature. This is shown in Figure 2. The low mobility of defects at room temperature and covalent links between the two shells of the tube stabilize the beam-induced vacancy and do not allow an extended reconstruction of the lattice [1].

Further *in-situ* experiments have been carried out on metal-carbon nanocomposites with electron irradiation on the scale of a few nanometres. Structures consisting of carbon nanotubes and metal nanocrystals show a variety of interesting effects when subjected to electron irradiation at high temperature. The formation of covalent junctions between carbon nanotubes and metal crystals can be carried out by electron irradiation of metal crystals on or inside nanotubes [2]. Further electron irradiation experiments on metal-carbon nanotube

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composites have been undertaken and are used to study the interaction between metals and graphitic structures. As an example, the growth of carbon nanotubes from catalytically active transition metal particles can be induced by electron irradiation and observed *in-situ* in the electron microscope [3].

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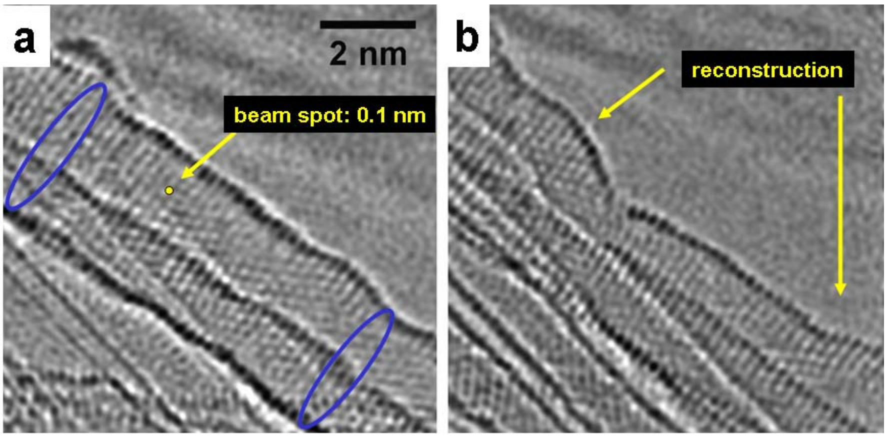

Figure 1. Bright field STEM images showing the effect of 10 sec irradiation of a single-wall carbon nanotube with an electron beam (200 keV) of 1Å in diameter. The temperature of the tube was 420°C. (a): before irradiation; (b): after irradiation. Although the irradiation was applied in an extremely localized region, the tube shrinks on a scale of several nanometers due to the migration of vacancies and the reconstruction of the graphitic network.

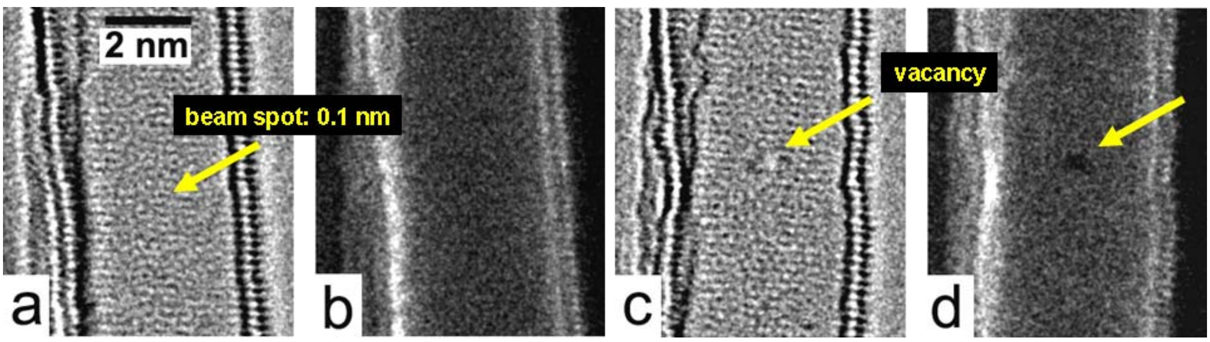

Figure 2. Bright field (a, c) and high-angle annular dark field (b, d) STEM images of a double-wall carbon nanotube before (a, b) and after (c, d) 5 sec of irradiation with an electron beam spot (200 keV) of 1Å in diameter. The tube was irradiated and imaged at room temperature. The formation of a vacancy consisting of 2-3 atoms in each layer is visible in both bright and dark field imaging.

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