Graphene – Twodimensional carbon at atomic resolution

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Graphene [1-4] is a single layer of carbon arranged in a twodimensional hexagonal honeycomb lattice that can be described as a single atomic layer extracted from graphite, an infinitely large singlewalled carbon nanotube, or as a giant polycyclic aromatic hydrocarbon [5, 6]. It is one of the most outstanding new materials in that it holds promises for a enormeously wide range of applications. The potential applications range from active elements in future microelectronics [79] via chemical sensors [10] and conductive transparent coatings [11] to novel composite materials [12], while research interests include new insights into quantum electrondynamics [13, 14]. Freestanding graphene, or graphene membranes, allow unprecedented electron microscopic studies: First, the structure, defects and edges of the graphene sheet itself are of great interest for all of its applications and are therefore an important target for microscopic studies [15-18]. Second, graphene membranes are a highly promising support film: With a thickness of only one atom, they constitute the thinnest conceivable membrane. The crystalline structure can be filtered out completely (if resolved by the microscope), and thus adsorbed objects can be imaged as if they were suspended in free space [18-20]. Third, graphene membranes constitute an ideal test object for microscopic developments due to the precisely defined in structure (including thickness) and high stability at electron beam energies below 100kV. In this respect, it is important to identify the presence of the single layer (e.g. by electron diffraction [21]).

As example, Fig. 1 shows imageside aberration corrected TEM images (FEI Titan 80-300) of a singlelayer graphene membrane observed at 100kV and 80kV. Imaging conditions are $C_s \approx 15\mu m$ and Scherzer defocus. Atoms apper black at these conditions. Graphene membranes prepared from highly crystalline graphite are nearly defectfree. We have tested different acceleration voltages (80, 100, and 120 kV) in order to estimate the thresholds and cross sections for knockon damage in graphene and to observe any effects that occur in result of beam damage. At 80 kV, clean and defectfree areas are highly stable. At 120 kV, damage proceeds rapidly and limits the image quality. However, 100 kV appears to be very close to the actual threshold; damage occurs at high electron doses but proceeds so slowly that changes in the atomic configuration can be easily followed atom by atom in direct images with each carbon atom clearly detected well above the noise. Fig. 1a shows the asprepared membrane, here observed at 100kV but prior to any significant radiation damage (the dose at the end of this exposure is ca. $6 \cdot 10^7 e/ nm^2$).

The 100kV irradiation slowly leads to vacancies and topological defects: Fig. 1b shows the same sample after 1.5 hours of continuous observation at atomic resolution; the total dose is ca. $1 \cdot 10^9 e/ nm^2$ at the end of the image sequence. Inset in Fig. 1b shows its Fourier transform. Here, the absence of dark rings or lines within the central disc confirms the full correction of aberrations up to the lattice spacing (first reflection) of 2.13 Angstrom. Together with the fact that this sample is thin enough to neglect multiple scattering, this means that the dark contrast in the image can be directly interpreted in terms of the atomic structure. Thus, the atomic configuration in the defect structures can be directly deduced for almost every carbon atom, except for the few that moved during exposure. Most remarkably,

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the vacancies in the graphene sheet do not remain isolated but merge into clusters, forming regions dominated by pentagons and heptagons in such a way that dangling bonds are avoided. The same experiment at 80kV, carried out to an at least 10x higher dose (using a higher dose rate) does not lead to any such changes (Fig. 1c). The single layer graphene sheet remains stable and defect free in the clean regions. However, holes can form in contaminated areas; this is not a knockon damage process but a beamdriven chemical modification. Here, beaminduced "etching" of the sample dominates the damage mechanism at energies below the knockon threshold and the contributions of adsorbates on the sample and of residual gases in the vacuum requires further studies.

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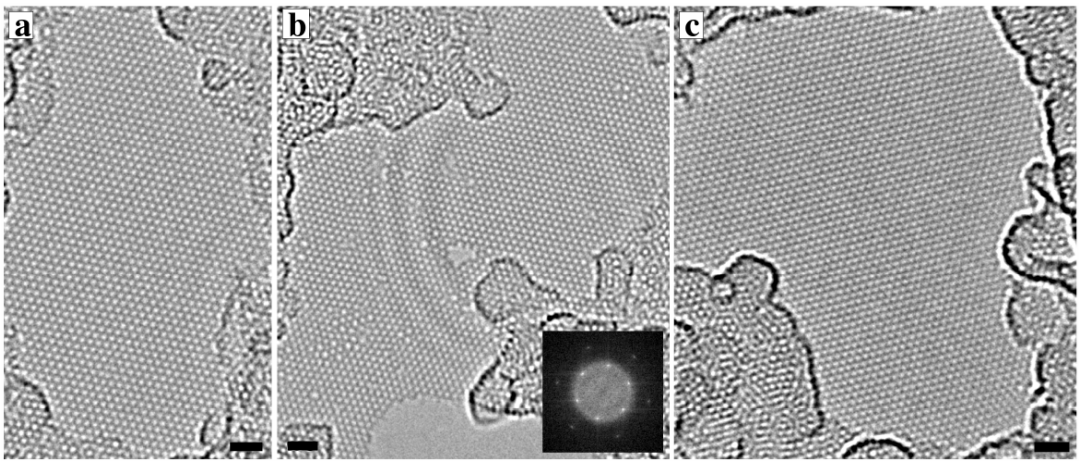

Figure 1. Atomically resolved TEM images of a graphene membrane and irradiationinduced defects (FEI Titan 80300 with imageside aberration corrector at 100kV (a+b) and 80kV (c)). (a) Asprepared graphene membrane. (b) Defects observed after a high dose (ca. 1·109e/ nm2) of 100kV electrons. Inset shows the Fourier transform of this image. (c) Graphene after an even higher dose (ca. 1·1010e/ nm2) of 80kV electrons, showing no defects within the clean region. All scale bars are 1 nm.

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