Application of 80kV Cs-corrected TEM for nanocarbon materials

A. Chuvilin[1], U. Kaiser[1], D. Obergfell[2], A. Khlobystov[3], S. Roth[2]

1. University of Ulm, Central Facility of Electron Microscopy, Electron Microscopy Group of Materials Science, Albert Einstein Allee 11, 89069 Ulm, Germany.
2. Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart, Germany.
3. School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

andrey.chuvilin@uni-ulm.de
Keywords: TEM, Cs correction, carbon materials

Being one of the main methods for studying the atomic structure of carbon materials, high resolution TEM suffers from a serious flaw as the energy of electrons, necessary to obtain atomic resolution (200-300 keV), is far above the kick-off damage threshold for graphitic carbon (about 60 keV) [1], which means that carbon nanostructures are always observed with a structure more or less distorted by electron beam. Practical implementation of Cs correctors in the last decade [2] opened the possibility to decrease acceleration voltage of the microscopes significantly, yet preserving the resolution at reasonable level. Decreasing the energy of the electron beam, besides decreasing radiation damage, has the advantage of increasing the phase contrast [3]. Considering the possibility to visualize one single carbon atom, the increase of the contrast reduces quadratically the electron dose necessary for this.

Here we report our first experience in application of 80kV electron microscope with imaging Cs corrector (Titan 80-300, FEI, Holland) for studying carbon nanotubes, peapods and graphene. We show that nano-structures composed of graphitic carbon are stable under the conditions of observation for more than 30 minutes, that opens the possibility for monitoring of single atom dynamics, diffraction studies and EELS measurements without radiation damage induced by the electron beam. Visualization of one single carbon atom within a graphene network is electron-optically achievable, but is limited in a single shot by the dynamical range of the CCD camera. Thus a multiple frame acquisition-averaging method is proved to be adequate for accumulation the electron dose necessary for resolving single carbon atom. Direct visualization of defects within the graphene network is demonstrated (Figure 1); in particular the stability of a mono-vacancy is shown under the beam irradiation.

Though almost eliminating kick-off damage unavoidable at medium range electron energies, decreasing the energy to 80keV significantly increase ionization and heating of the sample. Ionization is not an issue for graphitic carbon materials due to high electrical conductivity, while special precautions should be taken against local overheat. From the other hand side the elevated temperature inside the beam spot opens possibilities for dynamical observation of heat activated chemical reactions and

S. Richter, A. Schwedt (Eds.): EMC 2008, Vol. 2: Materials Science, pp. 123–124,
DOI: 10.1007/978-3-540-85226-1_62,

structure transformations. On the example of a heat induced transformation of SWNT peapod into double wall nanotube it is shown that good heat sink is essential for observation of pristine atomic structure of sensible materials at low voltages. At the conditions, when an area under observation is thermally isolated, heat induced evolution of the structure of SWNT metallofullerene peapods is observed, namely: breakage of the walls and coalescence of fullerene balls, behavior and interaction of individual metal atoms, inner tube formation from fullerenes, coalescence and collective action of Dy atoms resulting in SWNT breakage, self curing of the tube. At similar conditions the dynamics of Ag atoms on the surface of graphene is monitored. A formation of unusual 2D surface crystals with 4-fold symmetry is shown.

Utilization of accelerating voltages below 100kV at Cs corrected TEM opens possibilities for a broad field of research of pristine atomic structure of materials including light elements like carbon and point defects like single vacancies.

1. R.F. Egerton, P. Li, M. Malac, Micron **35** (2004), p. 399.
2. M. Haider, H. Rose, S. Uhlemann, E. Schwan, B. Kabius, K. Urban, Ultramicroscopy **75** (1998), p. 53.
3. M.T. Hayashida, T. Kawasaki, Y. Kimura, Y. Takai, Nuclear Inst. and Methods in Physics Research **248** (2006), p. 273

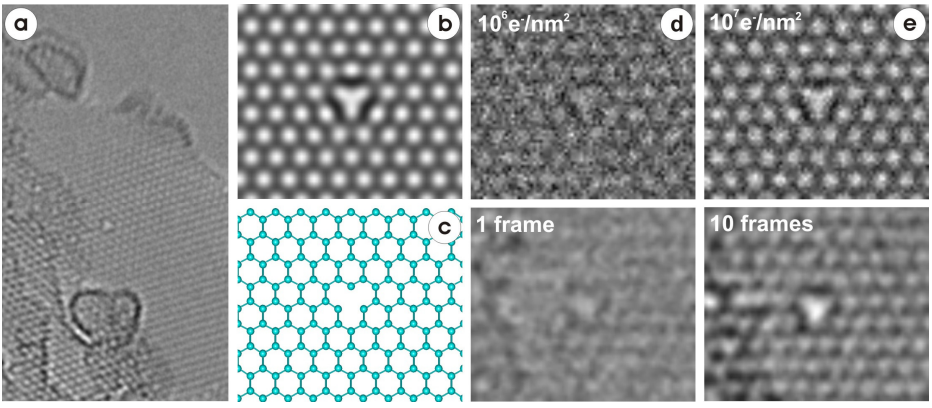

Figure 1 Monovacancy in a single graphene sheet. (a) Overview of graphene edge. The image is a drift corrected average of 10 frames. (b) Simulated image and (c) a model of monovacancy. Image is calculated for the conditions of the best visibility of the vacancy (Cs=-10μm, df=-8nm). (d) Simulated image considering electron dose of $10^6 e^-/nm^2$ (top) and experimental image obtained by single 1 sec exposition (bottom). (e) The same set as (d), but for the dose $10^7 e^-/nm^2$ and 10 frames average correspondingly.