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Elastic deformation of nanometer-sized metal crystals in graphitic shells

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The elastic deformation of nanometer-sized metal crystals is achieved by encapsulating them in carbon nanotubes or carbon onions. Electron irradiation of these core-shell particles leads to high pressure in their center due to a shrinkage of the graphitic shells. Pressures in the range of 10–30 GPa are found by measuring the decrease in lattice spacings in the encapsulated metal crystals. Hence, it is quantitatively shown how closed graphitic shells can be applied as compression cells on the nanoscale. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2403898]

The structure and properties of materials are considerably altered under the application of high pressure. Extreme pressure has been exerted onto macroscopic samples, for example, in diamond anvils where pressures up to 400 GPa can be achieved.[1–3] Now, in the age of nanotechnology, experiments on the behavior of individual nanosized systems under high pressure are of interest because most physical properties of nanosystems are a function of their size. Nevertheless, not much knowledge exists about high-pressure properties of nanoparticles due to the difficulty of designing appropriate compression cells on the nanoscale.[4,5]

In the last years it has been demonstrated that closed graphitic structures such as carbon nanotubes or carbon onions act as compression cells when subjected to irradiation with energetic electrons.[6–8] The contraction of closed graphitic structures has been observed in electron microscopy experiments and explained in terms of structural rearrangements in the layers after atom ejection.[9–11] Since carbon nanotubes or onions can encapsulate foreign materials (e.g., metal nanocrystallites), the self-compression of these cylindrical or spherical cages can exert pressure onto the materials in their cores. Due to the high elastic modulus and tensile strength of graphitic layers,[12,13] nanotubes or onions act as nanocontainers of exceptional strength. Several high-pressure effects in carbon nanocages have already been observed, e.g., the nucleation of diamond crystals in carbon onions,[6] the plastic deformation of encapsulated metal nanocrystallites inside carbon onions,[7] or the deformation and extrusion of metal crystals from collapsing nanotubes.[8,14]

Although several compression experiments have already been carried out, the magnitude of the pressure inside nanometer-sized graphitic compression cells is still unknown. However, this information can be gained by precisely measuring the lattice spacings of crystals which are surrounded by compressing graphitic shells. When the compression modulus of the crystals is known, the pressure can be calculated from the measured decrease in lattice spacings. This has already been tried tentatively in recent studies of metal-filled nanotubes under electron[8] or ion[15] irradiation, but careful measurements have so far not been undertaken. In the present work, lattice spacings in metal crystals inside compressing carbon onions and nanotubes are measured and related to the pressures.

Carbon onions encapsulating metal crystals were generated in an arc-discharge apparatus.[7] Nanotubes with metal fillings were synthesized by a modified chemical vapor deposition process.[16,17] The materials were sonicated in ethanol and deposited onto metal grids for use in electron microscopy. A transmission electron microscope operating at 300 keV (FEI Tecnai-F30) was used. The specimens were heated to 600 °C in a heating stage and held at this temperature during the whole irradiation and inspection period. High specimen temperature was chosen because *in situ* annealing of radiation defects in graphitic structures has been found to occur at temperatures higher than 300 °C.[6] The nanoencapsulates were irradiated with an electron beam of several tens of nanometers in diameter at beam current densities of 45–200 A/cm^2. During the compression of the particles (increase of pressure), which typically happens within a few minutes, lattice images were taken with a slow-scan charge coupled device camera. Fourier transformation of the lattice images leads to diffractograms showing spots whose distance from the center corresponds to the average reciprocal lattice spacings of the encapsulated crystals. In such a way, changes in lattice spacings were measured by overlapping diffractograms from before and after the compression.

However, a slight rotation of the carbon-metal nanoparticles often occurs during the irradiation period. This can lead to a change of the imaging conditions because the crystal (whose compression is to be monitored) undergoes a tilt relative to the optical axis. Therefore, image series were chosen where the rotation of the objects was small and the lattice orientation was maintained within a tolerable angle.

Figure 1 shows two lattice images of a gold crystal encapsulated in a spherical carbon onion. Figure 1(a) shows the particle after a short irradiation period and Fig. 1(b) after

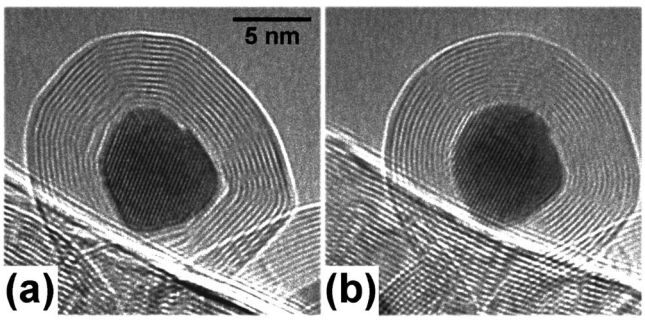

FIG. 1. Carbon onion encapsulating a gold crystal. (a) After a short period of electron irradiation; (b) After further 37 min of irradiation.

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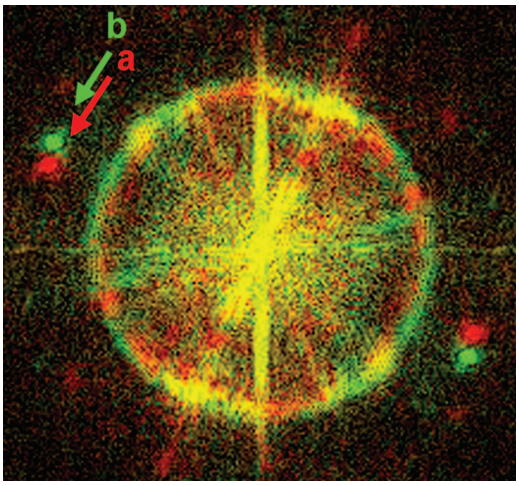

FIG. 2. (Color) Overlapping diffractograms obtained by Fourier transformation of the images in Fig. 1(a) (displayed in red) and Fig. 1(b) (displayed in green). The distance of the spots from the center reflects the reciprocal spacings of the (111)-lattice fringes before and after irradiation. The lattice compression in Fig. 1(b) is reflected by the larger spacing between the green spots. (The spikes are due to Fourier transformation effects of the limited image sizes and not of interest here).

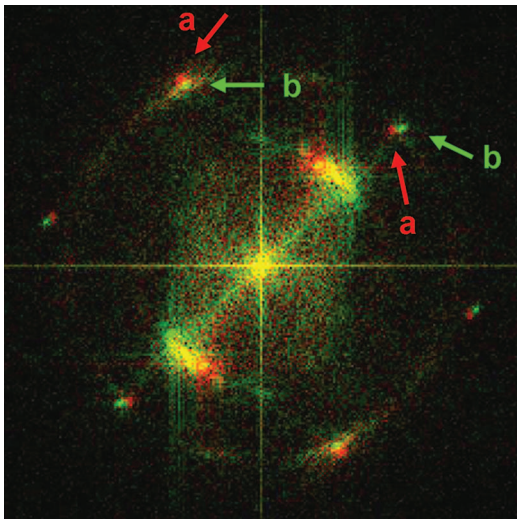

FIG. 4. (Color) Overlapping diffractograms from the images in Fig. 3(a) (red) and Fig. 3(b) (green), showing the relative changes of lattice spacings. In the radial direction of the tube, the Co crystal is under compression while an expansion appears in the axial direction (arrowed).

further 37 min of moderate electron irradiation (45 A/cm^2). The Fourier transforms of both images are overlapped in Fig. 2 in such a way that the Fourier transform of Fig. 1(a) is displayed in red, of (b) in green color. Perfect overlap of red and green appears in yellow. The shells of the onions give the prominent circle, whereas the straight (111)-lattice fringes of Au are seen as the red and the green spots (arrowed). It can be clearly seen that the red diffraction spots are closer to the center of the diffractogram than the green spots. (A slight rotation of the particle has led to a small rotation angle between the two diffractograms.) Therefore, in real space, the spacing between the (111) planes of the Au crystal before irradiation [Fig. 1(a)] was larger than after irradiation [Fig. 1(b)]. Measuring the different spacings gives a relative lattice compression of $\Delta a/a=0.025$.

Figure 3 shows an example of a multiwall nanotube filled with a Co crystal (fcc phase). Irradiation (150–200 A/cm^2) in the time interval between Figs. 3(a) and 3(b) has resulted in a deformation and bending of the tube so that the Co crystal was subjected to stress and slightly extruded. Applying the same technique as in Fig. 2 results in the diffractogram in Fig. 4 [red: before irradiation, Fig. 3(a); green: after irradiation, Fig. 3(b)]. Now, the red and the green spots are not always on the same side. While

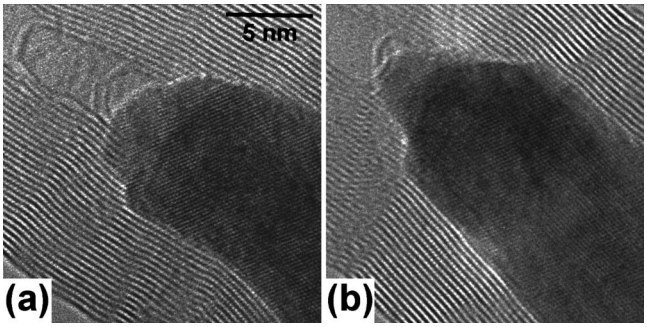

FIG. 3. Cobalt crystal inside a multiwall carbon nanotube under electron irradiation. The lattice projection is close to the (110) direction. (a) After a short period of irradiation, (b) After further 3 min of irradiation.

the lattice is compressed in the radial direction, we see a lattice expansion in the direction of the axis. The lattice compression is $\Delta a/a$ (radial)$=0.049$ and the expansion $\Delta a/a$ (axial)$=0.035$. Furthermore, shear strain in the lattice has led to a tilt of lattice fringes relative to each other.

Before analyzing the diffractograms, diffraction and imaging effects were considered which could lead to deceptive lattice spacings when the crystals are tilted relative to the optical axis during the course of the measurements.[18,19] To account for such possible errors, uncovered Au crystals with sizes comparable to the ones as used in the compression experiments were imaged and tilted deliberately so that the excitation error from the Bragg conditions of the imaged lattice planes was varied. The change of spacings due to tilt was found to be in accordance with the simple cosine law[18] and, within the whole tilt range of visibility of the respective lattice planes, clearly smaller than the compression effects.

With the measured $\Delta a/a=0.025$ of the Au crystal in Fig. 1 and the bulk compression modulus of polycrystalline Au ($K=170$ GPa), we obtain a pressure difference of $\Delta p = K\Delta V/V=12$ GPa prevailing inside the onion. However, we have assumed that the reference image [Fig. 1(a)] shows an uncompressed state which is most likely not the case. Therefore, the actual pressure in Fig. 1(b) might be higher (although on the same order of magnitude).

Estimating the pressure in the radial direction inside the nanotube in Fig. 3 (the radial strain is $\varepsilon_r=\Delta a_r/a_r=0.049$) by using the compression modulus of Co in the hcp phase ($K=200$ GPa), we obtain a radial pressure difference between Figs. 3(a) and 3(b) of 28 GPa. The maximum pressure that a multiwall nanotube can buildup under electron irradiation has been calculated and found to be approximately 40 GPa,[8] therefore the order of magnitude of the pressures as measured here appears reasonable. With the measured elongation in the axial direction ($\varepsilon_a=\Delta a_a/a_a=0.035$), we obtain a ratio of $\varepsilon_r/\varepsilon_a=1.4$. Elasticity theory relates biaxial strain (due to radial compression of a rod with rectangular cross-section) to Poisson's ratio ν by $\varepsilon_r/\varepsilon_a=(1-\nu)/2\nu$. With the value for

polycrystalline bulk Co (ν=0.31), we would expect $\varepsilon_r/\varepsilon_a$ =1.1, which is close to the measured value.

As pointed out above, the absolute values of the pressures as measured here are most likely underestimated because a comparison with the initial and perfectly uncompressed states was difficult. Furthermore, the compression modulus of nanometer-sized crystals could be slightly different from the bulk value but has not been measured to date. The present results confirm that pressures of at least 10–30 GPa can be built up in carbon nanotubes or onions under electron irradiation. Since the graphitic shells are transparent to electrons, all structural changes can be monitored *in situ* in the electron microscope. Several previously reported phenomena[6–8] become understandable if pressures of tens of gigapascals prevail inside carbon onions or nanotubes.

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