Electron Microscopic Characterization of Silver Nanowire Arrays

Hong et al. (1) reported that they had successfully produced arrays of single-crystal silver nanowires (of diameter 0.4 nm) formed in an ambient solution phase inside the pores of self-assembled calix[4]hydroquinone (CHQ) nanotubes. These nanowires, it was suggested, existed as coherently oriented three-dimensional arrays (1). The experimental identification and characterization of the suggested structure were based on high-resolution electron microscope (HREM) images and selected-area electron diffraction (ED) patterns.

Although the synthesis method proposed by Hong et al. is interesting, we disagree with their assessment and analysis of the actual experimental data. We suggest that the material that Hong et al. synthesized more likely constituted needlelike silver crystals—a common form of silver that has been observed before—and that those silver needles contained many defects, most of which were {111} stacking faults and twinning planes (2). In such a needlelike structure, the stacking faults and twinning planes are often parallel to the needle axis. The morphology of the needles is apparent in several of the electron micrographs presented by Hong et al. [figures 2A and 3J in (1)].

The sharp reflection peaks in the ED patterns shown in (1) indicate that the diffraction patterns were from samples containing fewer planar defects. We found that these patterns [figures 3D and 3G in (1)] are consistent with the (123)* and (110)* zone axis diffraction patterns, respectively, of the face-centered cubic (FCC) silver crystal with lattice constant \( a = 0.409 \) nm. The highly defected structure was demonstrated in several high-resolution electron micrographs presented by Hong et al. [figures 2C to E and 3E in (1)]. The observed Moiré fringes [figure 2D and figure 3E in (1)] were due to inclination of faulting planes with respect to the incident electron beam, a feature that has also been observed in silicon (Fig. 1).

The supplemental figures provided by Hong et al. on Science Online (3) offer more information to support our interpretation of the experimental data. Supplemental figure 1 shows more convincingly that the synthesized structure was needlelike and that the material contained a high density of planar defects. Supplemental figures 2 and 3 are consistent with the Moiré fringes due to the inclined planar defects, and supplemental figure 4 shows the (211)* diffraction pattern from the FCC silver.

In view of these data, we suggest that the material samples reported by Hong et al. actually represented not arrays of nanowires but highly defected needlelike silver crystals, with the needle axis along a \( \lambda \) direction and stacking faults and twinning on the \{111\} planes parallel to the needle axis. On the other hand, it would be very helpful to obtain electron micrographs, ED patterns, or both, from a single nanowire, if such a structure has been produced with the reported method.

Response: In our study of silver nanowires in pores of CHQ nanotubes (1), we indeed considered the problem of Moiré fringes, because, as noted by Iijima and Qin, such fringes have been observed in HREM images. Regarding that issue, however, solid crystals would be quite different from organic crystals with soft and rugged surfaces. The needlelike structure of organic nanotube templates (2), which often show asymmetrical facets on their edges, would govern the shape of the nascent nanowires.

The electron diffraction (ED) pattern of figure 3D in (1) is similar to the (123)* zone axis ED pattern of bulk silver. However, although the reciprocal distance between the linear spots is equal to the lattice spacing (0.76 nm) of the wire model along the [212] axis, it is very different from the lattice spacing (0.24 nm) in the (123)* pattern. The match of figure 3D with the Fourier-transformed image of figure 3E demonstrates that the pair of images originated from the same zone. Thus, it is inappropriate to conclude that one originated from the bulk ED pattern and the other from Moiré fringes. Also, the ED pattern does not show two sets of diffraction patterns due to the inclined twins. The observation of similar ED patterns for mercury in the CHQ tubes lends further credence to our results: Liquid mercury would not have twinning planes at room temperature. In the case of real Moiré fringes similar to the reported HREM images, we observed different ED patterns from the reported one. In figure 2E in (1), the width of a dark stripe is almost the same as that of a bright stripe; this does not agree with the criterion for

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Fig. 1. Comparison of observed EELS spectra of silver nanowires (black line) corresponding to the HREM image presented in figure 2 of (1) with predicted result for nanowires from density function theory (red line) and predicted result for bulk silver (blue line). The zero loss peak was excluded from the data.

Fig. 2. High-resolution electron micrographs of a silicon crystal containing an inclined twinning plane through the right half of the crystal. (A) Low-magnification image. (B) Image at atomic resolution.
translation Moiré fringes, which holds that the width of Moiré fringe should be smaller than the distance between Moiré fringes. Judging from the figure, which shows stronger excitation for [001] than for [110], Moiré fringes with periodicity of the [110] direction also seem unlikely. Incidentally, the distance between two adjacent stripes, at 1.2 nm, well represents the interspacing distance between stacked nanowires along the [110] direction. The electron energy loss spectroscopy (EELS) related to figure 2E of (1) supports the notion that the image represents formation of silver nanowires: The volume plasmon peak (7.4 eV) of bulk silver disappears, and the interband peaks of our nanowire model (~4 and ~6 eV) appear (Fig. 1).

Infrared spectra also support the notion of the wires’ formation inside the μm-size CHQ nanotube bundles (with ~10^3 × 10^3 pores). After the pure tube bundles are soaked into silver nitrate, the CHQ characteristic peak (1468 cm⁻¹) (2) disappears, and the calixquinone characteristic peak (1657 cm⁻¹) appears. This chemical change—associated with the formation of nanowires even in the absence of ultraviolet irradiation—would not be possible if Ag⁺ ions were not present in the core of the insulating CHQ bundles. The driving force for the Ag⁺ ion to go into the pores is considered to originate from the cation-π interaction and the free energy gain due to the chemical redox reaction (1).

Notwithstanding the evidence outlined above that affirms our earlier findings, we are carrying out further experimental investigations to examine the implications of the useful comments of Iijima and Qin. Regarding their suggestion that images of a single nanowire would be useful, we may indeed have observed the HREM image of such an isolated nanowire (Fig. 2), although the image is not clear, due to substantial radiation damage as well as background contrast from the carbon film.

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