

Novel growth mechanism of single crystalline Cu nanorods by electron beam irradiation

Pei-I Wang, Y-P Zhao, G-C Wang and T-M Lu

Center for Integrated Electronics, and Department of Physics, Applied Physics, and Astronomy, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

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Abstract

Single-crystal Cu nanorods have been fabricated on carbon films by manipulating electron beam irradiation on a Cu powder charge in a transmission electron microscope (TEM). By adjusting the intensity of the electron beam, we observed lively nucleation and growth of the Cu nanorods with the TEM. Individual Cu nanorods are straight with diameters ranging from 40 to 50 nm. The length of the rods is controlled by e-beam irradiation duration, and can be extended to $\sim 1 \mu\text{m}$. Selective area electron diffraction showed that the sidewalls of the Cu nanorods were associated with the (110) planes, while facets on the tips were associated with the (111) planes. We believe that the growth process is mainly controlled by high surface mobility of Cu atoms on the C surface, and surface diffusion of the Cu atoms from high surface energy planes to low surface energy planes of the Cu nanorods.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Nanophase materials have received considerable attention during the past decade for their novel size-dependent chemical and physical phenomena compared to the bulk phase. Syntheses of the nanowires and nanotubes are particularly interesting because these one-dimensional (1D) nanostructures show great potential for nanoscale devices [1]. In recent years Cu nanorods have been fabricated by the reduction reaction in colloidal self-assemblies [2, 3]. Single-crystal Cu nanorod arrays produced by using electrodeposition in conjunction with template synthesis to fill the nanochannels have also been reported [4]. The fabrication of the metal nanorods has been achieved mostly through template synthesis. Other techniques to fabricate metal nanorods include step-edge decoration where a metal is selectively deposited at the step edges on a graphite surface and subsequently removed by chemical reactions [5], electrodeposition onto the cleaved edge of a distinct region on an assembly of semiconductor wafers [6], and the extrusion of metal nanorods from a precursor under the influence of an electron beam [7]. The development to synthesize 1D nanostructures has been well summarized in a recent review paper [1].

Here we report the discovery of a new method to fabricate single-crystal Cu nanowires by using electron beam heating of the Cu charge *in situ* in a transmission electron microscope (TEM). Interesting nucleation and growth of 1D nanostructures have been observed by manipulating the electron beam irradiating onto the Cu charge. This work demonstrates a new mechanism of crystal growth on the nanoscale as well as a novel approach to 1D Cu nanorod growth.

2. Experimental procedure

The TEM experiments were carried out using a Philips CM-12 microscope operating at 120 kV and 20 μA . The base pressure of the TEM chamber was in the 10^{-7} Torr range. A liquid-nitrogen-cooled anticontaminator was installed near the sample holder to reduce the carbon contamination of the sample during observation. The Cu nanopowder was obtained from a Cu film deposited on an Si substrate by the glancing angle deposition technique [8]. The technique allowed us to produce nanosize Cu clusters or powder. The Cu charge was then removed from the Si substrate by a razor blade. The charge was dispersed onto the lacy carbon film on a Cu grid (from Ernest F Fullam, Co) for TEM investigation. Figure 1(a)

shows the bright-field TEM image of the as-prepared Cu charge on the carbon substrate. The Cu powder aggregates together.

The electron beam of the TEM was used as the heating source to heat up the Cu charge and subsequently it induced the nucleation and growth processes of the Cu nanorods. *Heating of the sample was achieved by switching off the TEM condenser aperture in order to increase the intensity of the electron beam.* Selective area electron diffraction (SAED) was employed to characterize the crystal structure of individual Cu nanorods. An x-ray energy dispersive spectrometer (EDS) on a JEM-2010 electron microscope (JEOL Ltd) was used for element analysis.

3. Results and discussion

During the growth process the electron beam was gradually converged until the size of the central beam reached a spot size of about $3\ \mu\text{m}$ in diameter on the Cu charge (figure 1(b)). As the converged electron beam area approached this condition, the Cu charge was subjected to the electron dose at a range of 10^{-7} electrons nm^{-2} and we observed that the Cu charge slowly started to melt, and at a certain distance from the centre of the converged beam, small spots appeared on the TEM fluorescent screen. These small spots were the initial nucleation centres of Cu rods on the C film, as shown in figure 1(b). This figure was obtained after the converging e-beam irradiated the Cu charge for 5 s. Compared with figure 1(a), the amount of Cu charge was reduced due to the evaporation/migration of the Cu charge. Furthermore, in the surrounding area of the Cu charge (with a radial distance of $\sim 1.5\text{--}3\ \mu\text{m}$), many small nucleation centres (even nanocrystal rods) appeared. Continuous e-beam irradiation generated more nucleation centres in the surrounding area of the converged e-beam. As the e-beam irradiation further proceeded, some of the old nucleation centres disappeared, while some kept on growing towards the converged e-beam centre. The tips of these growing nanorods almost maintained the same size during growth. Their lengths were extended axially following the lead of the growing tips. Figures 2(a)–(d) show a sequence of enlarged TEM images of the Cu charge during the e-beam irradiation within the converged e-beam area. The real-time observation of the melting behaviour of the Cu charge clearly shows that the Cu charge was reduced with increasing e-beam irradiation time through supplying the charge to nanocrystal growth.

Figure 3 shows a selective area of the same sample after e-beam irradiation for 15 s. The amount of Cu charge was reduced further while many Cu nanorods were formed around the Cu charge. An enlarged image of a Cu nanorod is shown in figure 4. It clearly shows that the nucleation started from the C film, while the growth of the nanorod extended to the vacuum without further support. The diameter of the nanorods ranges between 40 and 50 nm. The side planes of the nanorods are perfectly single crystallographic planes, with pyramidal tips. All the SAED patterns of different nanorods (the insets in figures 3 and 4) indicate that the Cu nanorods were single crystals with a face-centred cubic (fcc) structure. Moreover, the diffraction patterns of the sidewalls of the Cu nanorods were associated with (110) planes. The length of the Cu nanorod can be extended to $1\ \mu\text{m}$ (see figure 5).

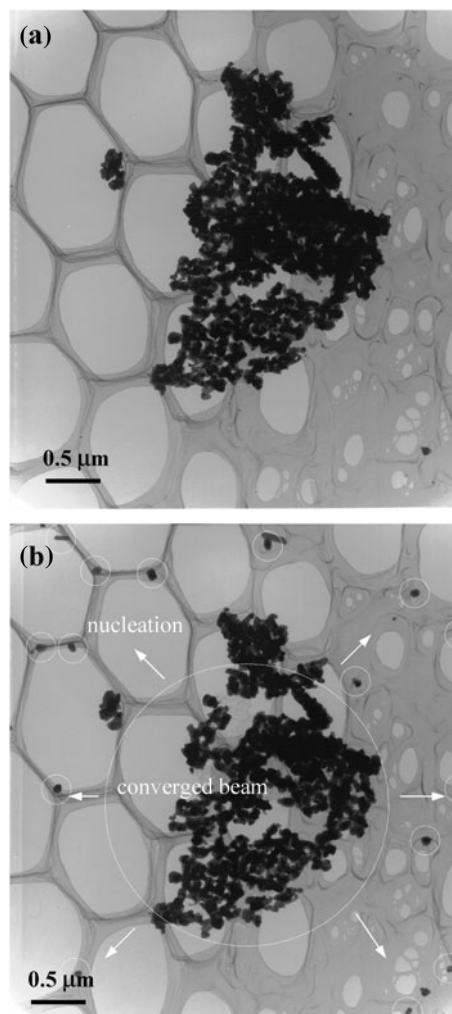


Figure 1. (a) A bright-field TEM image of as-prepared Cu charge on a carbon substrate. (b) Converged electron beam highlighted by a large dashed circle irradiating on the Cu charge for 5 s resulting in cluster nucleation. Note that the nucleation centres tend to be at the 'edges' of the lacy carbon substrate highlighted by the small dashed circles.

Figures 6(a) and (b) show the results of EDS analyses on an individual Cu nanorod and the location of the C substrate beside this Cu nanorod, respectively. A small Si peak observed in the spectrum of the Cu nanorod indicates that there is a traceable Si impurity in the Cu nanorod. Furthermore, an even larger Si peak (which was not observed in the as-received C substrate on the TEM grid) is seen in the spectrum of the C substrate near the C/Cu nanorod interface. Since a Cu peak also appears in this spectrum, it suggests that the Si was introduced through transporting the starting Cu charge during Cu nanorod growth. Figure 7 is the electron diffraction pattern of the Cu charge that clearly shows that the Cu charge is nanocrystals with fcc bulk structure. Also, a weak pattern associated with the Si is observed, suggesting that the Si contaminated the Cu charge during TEM sample preparation (see section 2). This Si contamination can significantly affect the Cu charge melting behaviour because a sufficient amount of Si can decrease the melting temperature of Cu to as low as $800\ ^\circ\text{C}$ [9]. A well study of the annealing of Cu nanocrystals has shown that their melting temperature changes with their structure, with defects

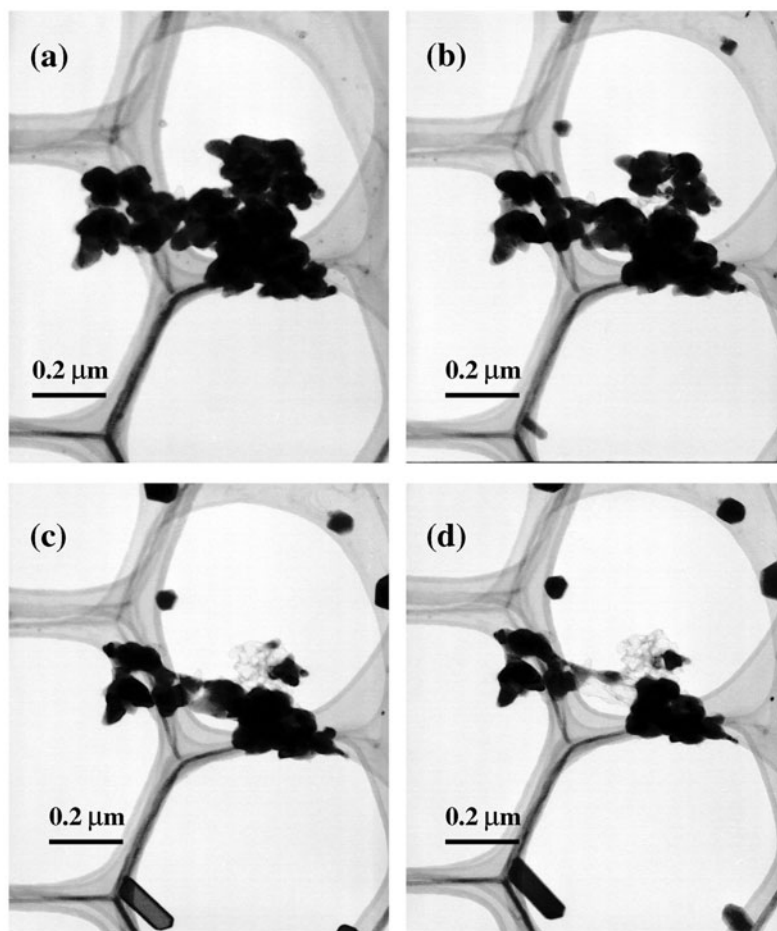


Figure 2. A sequence of enlarged TEM images of the Cu charge during the e-beam irradiation within the converged e-beam area. Note that the Cu charge melts and reduces while the nanocrystals are growing.

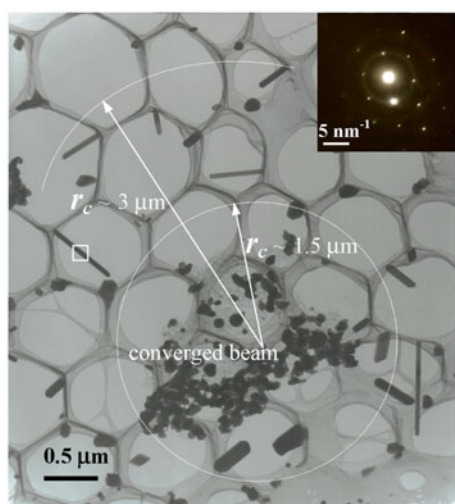


Figure 3. A bright-field image of Cu nanorods. The diffraction pattern of the sidewalls of the selective Cu nanorod marked by a square is associated with the (110) plane. Note that the Cu nanorods only form within certain distances ($\sim 1.5\text{--}3\ \mu\text{m}$) from the converged e-beam centre.

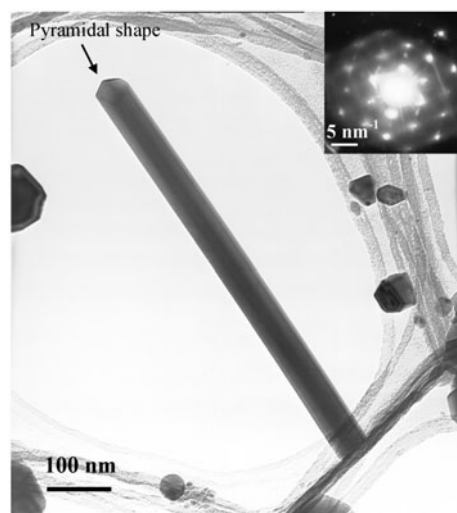


Figure 4. A bright-field TEM image of an individual Cu nanorod. The corresponding SAED pattern shown in the inset indicates that the sidewalls of the Cu nanorods are (110) planes. Note that the presence of the pyramidal shape facets is associated with the (111) planes at the tip of the Cu nanorod.

introduced during sample preparation, and most significantly with the size of the nanocrystals. These factors result in the

Cu nanocrystals starting to melt at a temperature lower than $400\ ^\circ\text{C}$ [2]. In our case, the Cu charge that is nanocrystals

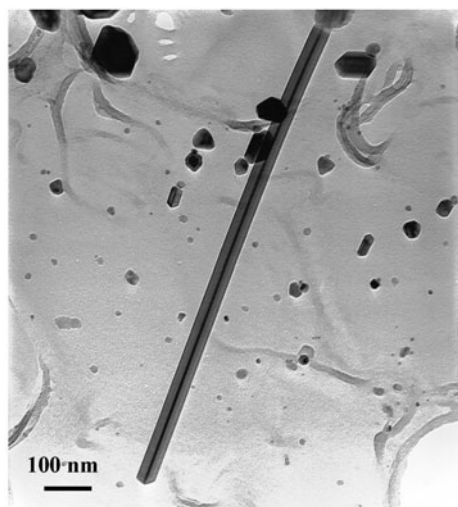


Figure 5. A bright-field TEM image of an individual Cu nanorod whose length is larger than $1 \mu\text{m}$.

has a comparable size with these experiments. Therefore, it is reasonable to conclude that the effects of size in conjunction with the presence of impurities are crucial to our success in melting the Cu charge by e-beam irradiation. Recently, Liu and Bando [10] reported the growth of Cu nanorods from Cu vapour by heating the Cu grid to $\sim 800^\circ\text{C}$ in the TEM chamber. The generation of copper vapour under this condition was essentially due to the vapour pressure of the Cu bulk [11]. Interestingly, there are great similarities between their results and those reported here regarding the characteristics of the Cu nanorods, despite the fact that different approaches were adopted in these two experiments. However, the growth mechanism of the former study was unclear and has not yet been elucidated [10].

In the following, we summarize some major characteristics of the Cu nanorod growth:

- (1) The Cu nanorods can grow on C films but not on Si oxide films. We have used Si oxide thin-film-based TEM grids, and performed similar experiments. No Cu nanorods were observed. This is probably due to the fact that the interaction between metal atoms such as Cu and the C substrate is weak so that the metal atoms are highly mobile on the carbon surface [12–14], whereas the interaction between metal atoms and Si oxide is stronger, and the metal atom mobility is lower (in fact, it may react with the Si oxide). Therefore, the high surface mobility of Cu atoms on the C substrate may play an important role in nanorod formation.
- (2) The Cu nanorods only appear within certain radial distances r_c ($\sim 1.5\text{--}3 \mu\text{m}$ for our experiments) from the converged e-beam centre. For distances larger than r_c , only small nucleation islands can be observed (figure 3). For distances smaller than r_c , larger single crystalline Cu grains are formed (figures 2 and 3). When the converged e-beam hits the Cu grid, it has two major effects. First, it melts the Cu charge on the grid, resulting in the evaporation of Cu and the formation of a high surface diffusion area. Second, it induces a temperature gradient on the substrate where the highest temperature is located

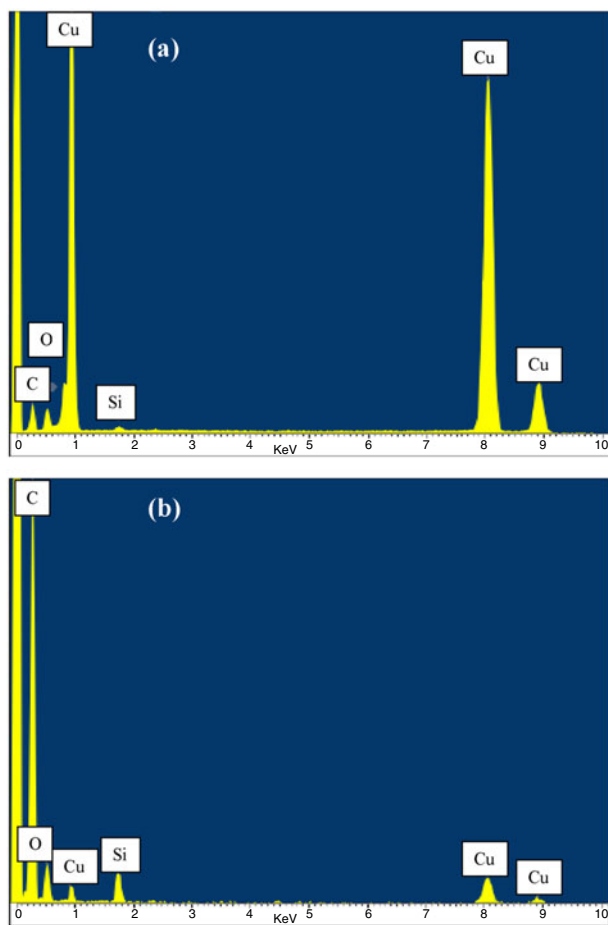


Figure 6. EDS spectra of (a) an individual Cu nanorod and (b) a C substrate beside the Cu nanorod.

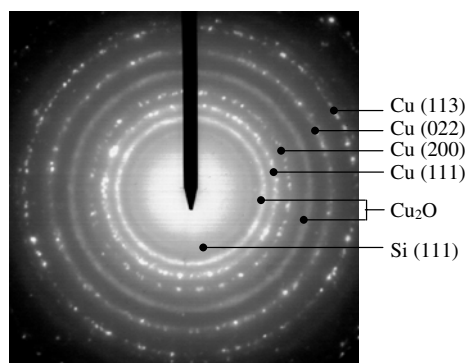


Figure 7. The SAED of the Cu charge shows that the charge contains Si that was introduced during TEM sample preparation.

at the centre of the converged e-beam, and the temperature decays outwards from the centre. This means the Cu atoms have a very high surface diffusion rate at locations close to the converged e-beam centre. This high diffusion rate appeared to induce the nanorod growth. The existence of r_c indicates that there is a critical temperature for nanorod formation.

- (3) The formation of the nanorods always starts from the nucleation sites of the Cu, and the rods are then grown into the vacuum without any further support. These nucleation sites may be related to the surface morphology of the

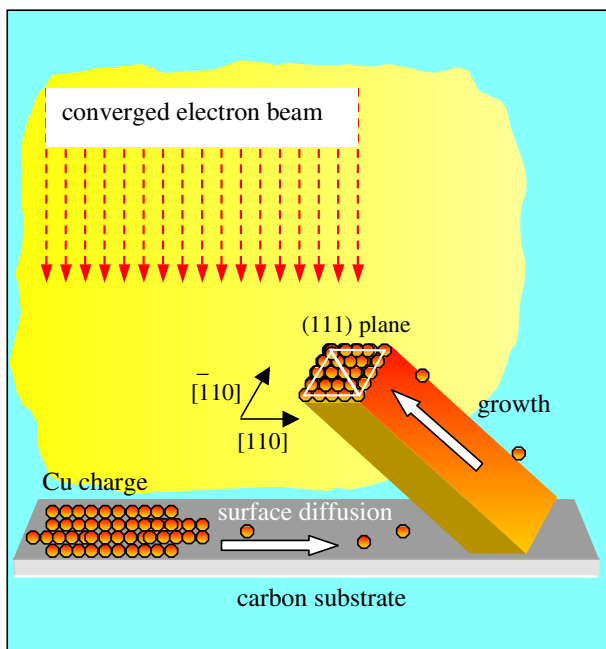


Figure 8. Schematic illustration of the mechanism of the growth of 1D Cu nanorods on a C substrate by e-beam irradiation.

C substrate [15] due to the fact that the nucleation sites tend to be located at the edges of the patterns and the wrinkles on the C substrate. The first arriving Cu atoms would go to these edges and form nucleation centres. The continuous e-beam irradiation on the Cu charge drives the Cu atoms along the substrate to supply the already grown rods with newly arriving Cu atoms (see figure 8). The initial crystalline orientation of the nucleation centre determines the further growth direction of the rods.

- (4) The length of the nanorods depends on the irradiation time. Some of the nanorods can be grown continuously, while others stop in the middle of the e-beam irradiation. For continuous growth, the tip of the nanorod has to be maintained at a critical temperature. In order intentionally to control the growth length of the nanorods, one could move the converged e-beam in the same direction as the individually growing nanorod. The constant distance between the tip of the nanorod and the converged e-beam centre would maintain a high temperature at the tip of the growing nanorod.

The above growth features indicate that the surface diffusion of Cu atoms on the C substrate plays an essential role in the formation of Cu nanorods. Apart from the surface diffusion, most of the growth features are similar to those of the well-known whisker growth [16, 17]: namely, a critical growth temperature and the formation of well-shaped single crystal fibres. In our case, since the source does not directly provide vapour to the tips of the nanorods, surface diffusion plays a critical role. As shown in figure 8, we propose the following growth mechanism. During e-beam irradiation, the Cu charge is melted, some atoms are evaporated and some of them migrate on the C substrate with a high mobility. Heterogeneous three-dimensional (3D) nucleation takes place when those Cu atoms

encounter irregular sites on the C film surface. Following the nucleation event, stable clusters and particles are formed. Clearly the particle size depends on the nucleation conditions such as the diffusion of Cu atom flux, substrate temperature and the interfacial properties between the depositing metal and the substrate. The particle shapes on the other hand are determined by the balance of the interfacial energy with respect to the interface between the nuclei and the substrate, and the surface energy with respect to the interface between the nuclei and the vacuum.

Cu atoms tend to migrate across the high surface energy planes of the Cu nanorods to the low surface energy planes due to the free energy minimization. It is known that the relation of the surface energy of bulk fcc metals, $\gamma_{111} < \gamma_{100} < \gamma_{110}$, generally holds. This anisotropy of the surface energy therefore drives the Cu atoms from the (110) sidewall planes upwards to the low-energy (111) planes at the tip of the rod.

4. Conclusions

We report a new crystal growth mechanism at the nanoscale to form 1D Cu nanorods. An electron beam irradiates the nuclei during the growth process in conjunction with the role of free energy minimization that drives the Cu atoms through high surface energy planes of the nuclei to the growth front to form a unique 1D structure. This approach has been utilized successfully to grow 40–50 nm diameter single crystal Cu nanorods with sharp facets on their tips. Individual Cu nanorods are straight and uniform with a length that is larger than 1 μm .

Acknowledgments

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