

The crystal structure and growth direction of Cu₂S nanowire arrays fabricated on a copper surface

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Received 8th May 2001, Accepted 15th June 2001

First published as an Advance Article on the web 18th July 2001

We examine the crystal structure and growth direction of Cu₂S nanowire arrays grown from copper surfaces at room temperature. By using X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction (ED) techniques, the monoclinic Cu₂S nanowires are shown to grow preferentially along the *c*-axis, characterized by a layered structure. This result may shed light on the unusual growth mechanism of the Cu₂S nanowires.

I. Introduction

There is a keen interest in the synthesis of one-dimensional (1D) nanomaterials.¹ Strategies have been developed to synthesize 1D materials under ambient or mild conditions.^{2–10} On this line, we have recently discovered that by exposing a surfactant-treated copper surface to H₂S in air at room temperature, straight and long Cu₂S nanowire arrays are grown directly from the copper surface with a good crystallinity and a large aspect ratio.^{11,12} This has opened opportunities to study the effect of dimensionality on the electronic properties of the semiconducting Cu₂S, which is an important photovoltaic material.¹³ Further experiments showed that under appropriate conditions, the Cu₂S nanowires could be grown even without the surfactant treatment.¹⁴ The traditional vapor–liquid–solid mechanism does not appear to be applicable in the Cu₂S nanowire growth under such a mild condition. Therefore, the question as to how the Cu₂S nanowires grow on the copper surface remains to be answered.

In order to unravel the growth mechanism of the Cu₂S nanowires, it is important to study the crystal structure and the growth direction of the nanowires. This presents a formidable challenge because the room temperature phase of Cu₂S is monoclinic. Fortunately, the Cu₂S nanowires could be grown in arrays approximately perpendicular to the copper surface, and this facilitates the XRD analysis. In the work presented below, we investigate the structural aspect of the Cu₂S nanowires using XRD, TEM and ED techniques.

II. Experimental

The procedure for Cu₂S nanowire synthesis on copper surface has been described elsewhere.^{11,12,14} Copper foils (99.8%, Aldrich) with a majority of the (200) and (220) crystal planes parallel to the surface were found to be effective in producing the Cu₂S nanowires. Before use, copper foils with a thickness of 0.25 mm were carefully cleaned for ~5 min in ultrasonic baths of diluted hydrogen chloride solution and absolute ethanol, respectively, followed by drying in a vacuum or an inert gas atmosphere. The copper foils (0.5 cm × 0.5 cm) were placed in a reactor.¹⁴ A gas flow consisting of a mixture of

oxygen (99.8%) and hydrogen sulfide (99.8%, Aldrich) at a molar ratio of O₂ to H₂S between 2 : 1 and 3 : 1 was directed to the reactor. The total pressure in the reactor was kept at ~1.05–1.08 atm. The reaction lasted for 8–10 h at room temperature. During reaction, the reactor was kept in the dark. Powder samples were obtained by carefully peeling off the Cu₂S nanowires from copper surface. Powder X-ray diffraction measurements were carried out with a Philips PW 1830 instrument with a 1.54 Å Cu rotating anode point source. Two samples were measured using XRD: the Cu₂S nanowire arrays on a copper surface and the Cu₂S nanowire powder with relatively random orientations on a glass substrate. TEM imaging and electron diffraction experiments were performed on JEOL 4000EX and Hitachi HF-2000FE transmission electron microscopes, under operating voltages of 400 and 200 kV, respectively. For TEM observations, the Cu₂S powders were transferred to copper grids coated with holey carbon films. Large area images were taken with a scanning electron microscope (JOEL 6300 SEM operated at 15 kV).

III. Results and discussion

When exposed to a mixture of H₂S and O₂, the copper surface turned dark red immediately, and then shining cyan and gray in a short time span. After 10 h reaction, the copper surface became black and fluffy, indicating the formation of dense Cu₂S nanowire arrays. Fig. 1 shows a typical SEM image (side view) of the as-prepared Cu₂S nanowire arrays on the copper surface. The nanowires are ~5 μm long and ~50 nm thick with a reasonable uniformity, as confirmed by TEM observations. They are straight, evidently well-aligned, and approximately perpendicular to the copper surface.

XRD patterns of the Cu₂S nanowire array sample on a copper surface and the Cu₂S nanowire powder sample are shown, respectively, as traces a and b in Fig. 2. All the apparent peaks in the XRD pattern for the powder Cu₂S nanowires can be indexed according to the monoclinic Cu₂S^{15,16} as indicated in Fig. 2b. There is a small shoulder, however, at about 39° in the XRD pattern of the Cu₂S nanowire powder (Fig. 2b). This diffraction peak cannot be assigned to any crystal plane of the monoclinic Cu₂S, but can be indexed as the (200) diffraction of monoclinic copper oxide (CuO).¹⁵

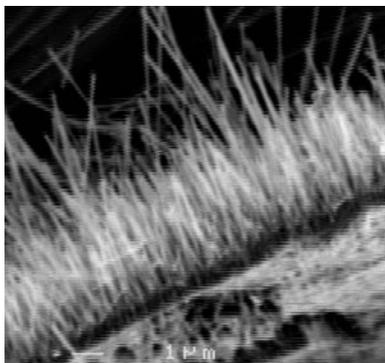


Fig. 1 A side-view SEM image of the Cu_2S nanowire arrays on a copper foil substrate. Note that the Cu_2S nanowires are roughly aligned perpendicular to the copper surface.

When the XRD pattern was recorded directly on the as-prepared Cu_2S nanowires on the copper surface, the diffraction peaks became sharper and cleaner, and many diffraction peaks which appeared in Fig. 2b became smaller or disappeared (Fig. 2a). This is clearly a consequence of the alignment of the straight Cu_2S nanowires perpendicular to the copper surface as already revealed in the SEM image in Fig. 1. By comparing the intensities of the diffraction peaks of traces a and b in Fig. 2, it is found that the intensity of the (204) diffraction peak has undergone the largest increase from the powder sample to the nanowire array sample. This indicates that the (204) crystal plane of the Cu_2S nanowires are parallel to the surface of the copper substrate. In conjunction with the SEM image of the as-prepared Cu_2S nanowires (Fig. 1), the nanowires are likely to grow in a direction closely perpendicular to the (204) crystal plane, *i.e.* the c axis of the monoclinic Cu_2S because the angle between the (204) plane and the c axis is 90° .

Although the average alignment direction of the Cu_2S nanowires is perpendicular to the copper surface, some nanowires are tilted from the copper surface normal, as can be seen in the SEM image (Fig. 1). As a result, diffraction peaks from the crystal planes which are not parallel to the (204) plane, can still be observed but with a dramatically reduced intensity. We calculated the relative intensity $(I(hkl)/I(204))/(I^s(hkl)/I^s(204))$ of each diffraction peak based on the data in Fig. 2a, and plotted it as a function of the angle between the diffraction plane and the (204) plane as shown in Fig. 3. Clearly, the relative diffraction intensity decreases exponentially as the diffraction plane deviates from the (204) plane. This evidence

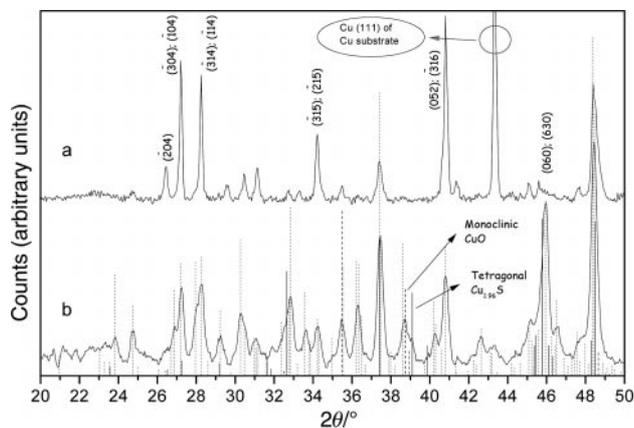


Fig. 2 XRD patterns of Cu_2S nanowires (a) from the as-prepared Cu_2S nanowires on a copper foil substrate, and (b) from a powder sample. The vertical dotted and dashed lines indicate the diffraction peak positions and intensities of powder monoclinic Cu_2S and CuO , respectively.

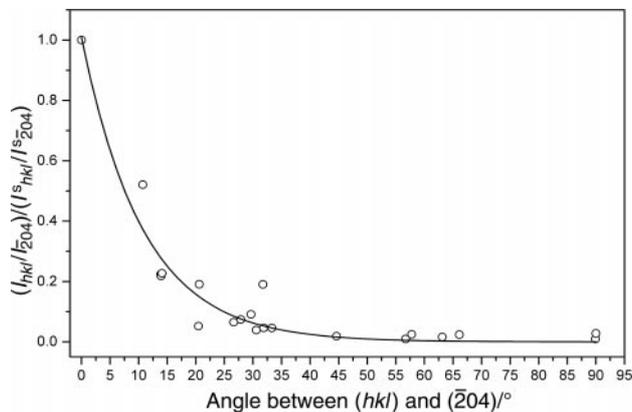


Fig. 3 The dependence of the relative diffraction peak intensities of crystal planes (hkl) on the angle between (hkl) and (204) . The solid line is obtained from fitting to an exponential function.

supports the conclusion that the growth direction of the Cu_2S nanowires is perpendicular to the (204) crystal plane.

Fig. 4a displays part of a single Cu_2S nanowire, which is straight with a uniform thickness of ~ 45 nm. A high resolution TEM image of this nanowire is shown in Fig. 4b. Clear-cut fringes are revealed in the core region of the nanowire, especially the fringes in a perpendicular direction which extend through the whole nanowire length with a fringe spacing of ~ 3.3 Å. The nanowire appears to be well-crystallized although the outer portion consists of some nanoparticles. Selected area electron diffraction (SAED) was conducted on this nanowire, and the pattern is shown in Fig.

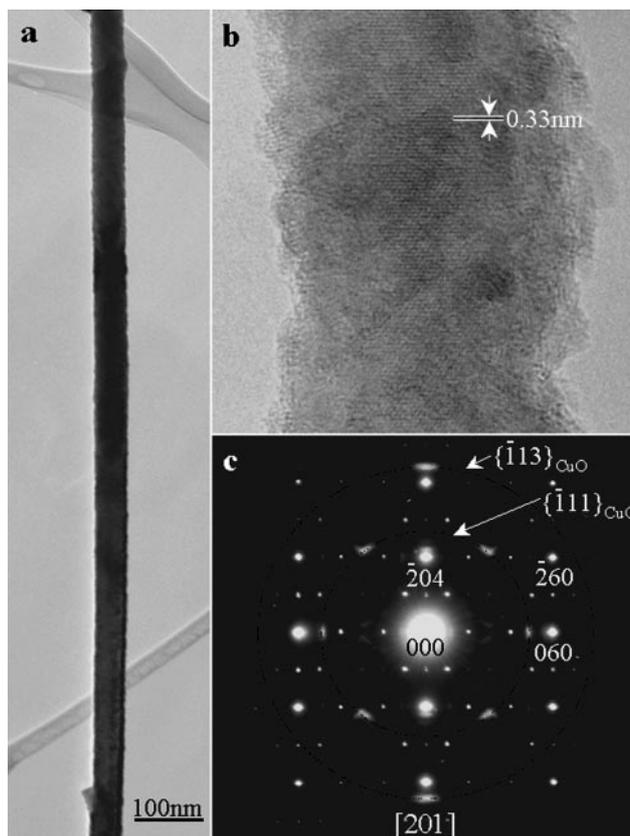


Fig. 4 TEM images and selected area electron diffraction pattern of a single Cu_2S nanowire. (a) A low magnification TEM image; (b) high resolution TEM image and (c) selected area electron diffraction pattern along the zone axis $[201]$ of Cu_2S .

4c. The well-defined diffraction pattern supports the good crystallinity of the nanowire. The periodically distributed diffraction reflections appearing in the pattern can be indexed as the [201] zone of the monoclinic Cu_2S . Combining the electron diffraction pattern (Fig. 4c) with the corresponding images shown in Fig. 4a and Fig. 4b, the growth direction of the Cu_2S nanowire is determined to be perpendicular to the (204) crystal plane of the monoclinic Cu_2S , which is consistent with that concluded by the XRD analysis. Besides the reflections of the [201] zone, there are eight diffuse and ill-shaped diffraction spots remaining in the diffraction pattern. Of those diffraction spots, four are located on the same ring (see Fig. 4c) with an inter-plane distance (d -spacing) of ~ 2.5 Å. This d -spacing is consistent with those of (002) and ($\bar{1}11$) of the monoclinic CuO .¹⁵ The other two diffraction spots are on a ring with ~ 1.5 Å d -spacing, which matches that of ($\bar{1}13$) of the monoclinic CuO . Therefore, in conjunction with the XRD analysis, it is suggested that the nanowires consist of a monoclinic Cu_2S core with the growth direction parallel to the c -axis and a shell of epitaxially grown copper oxide (CuO) nanoparticles.

Fig. 5a shows the atomic arrangement viewed along the c axis of the monoclinic Cu_2S . It can be seen clearly that in the sulfur-containing atomic layers, the sulfur atoms are arranged in a triangular lattice, and one third of the copper atoms are coordinated in the interstices. Each sulfur atom is coordinated

with 6 Cu atoms from the sulfur layer and from the neighboring copper layers. The layered structure can be better appreciated from Fig. 5b, where the atomic arrangement is viewed along the [201] zone axis. The sulfur layers and copper layers alternate along the c -axis. The inter-layer distance is 3.375 Å, which is consistent with the inter-plane distance of (204).^{15,16} This layer structure can reproduce the ED pattern in Fig. 4c and HRTEM image in Fig. 4b. Such a layer structure seems to be unique, which may explain why the c -axis is the preferred growth direction of the Cu_2S nanowires.¹⁷

IV. Summary and conclusions

Using SEM, TEM and XRD, we have examined the crystal structure of the Cu_2S nanowires directly grown from a copper surface. We have shown that the nanowires grow along a direction closely parallel to the c -axis of the monoclinic Cu_2S . This is likely to throw light on the growth mechanism of the nanowires. For example, the nanowires may follow a layer-by-layer growth mechanism by inlaying sulfur atoms into the copper crystalline domains. Certainly, one has to consider the thermodynamics such as the energy requirements and the kinetics such as the mass transfer of the growth process to attain a whole and coherent picture of the growth mechanism of the Cu_2S nanowires on copper surface.

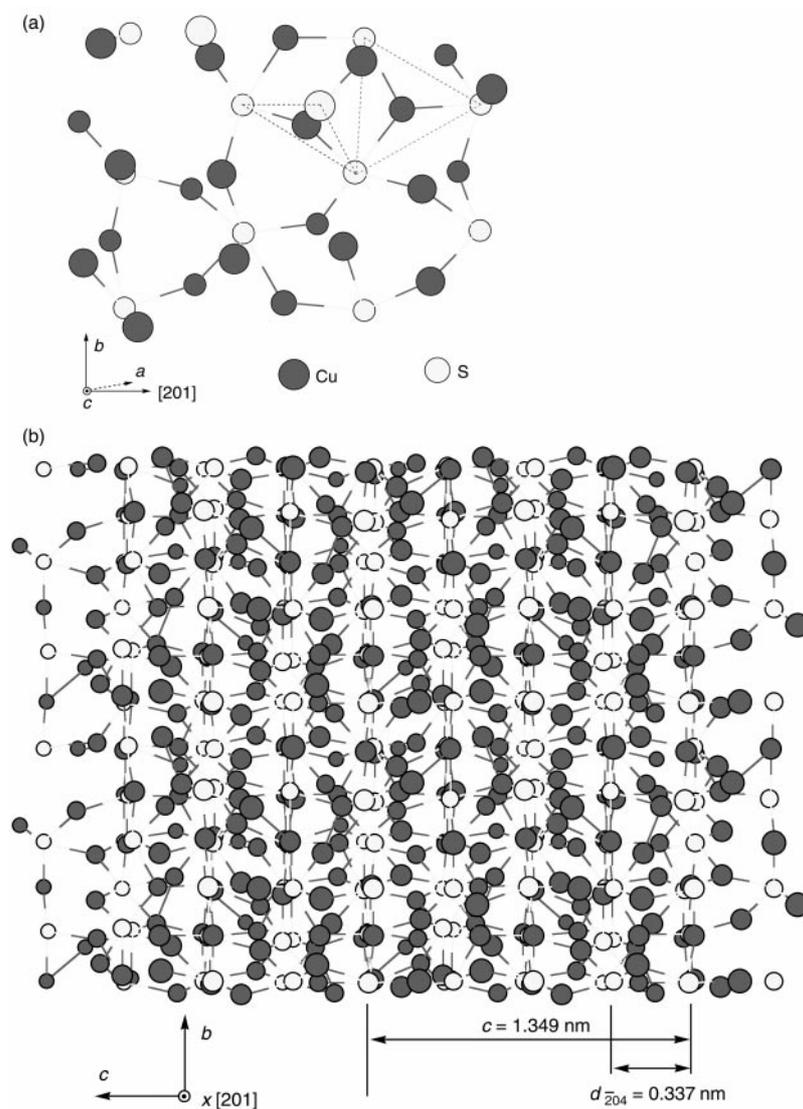


Fig. 5 Atomic arrangement of a monoclinic Cu_2S nanowire. (a) Viewed along the c axis; and (b) viewed along the [201] zone axis.

Acknowledgement

This work was supported by a RGC grant administered by the UGC of Hong Kong. We thank MCPF of HKUST for assistance in sample characterization.

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