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Growth of Crystalline Cu_2S Nanowire Arrays on Copper Surface: Effect of Copper Surface Structure, Reagent Gas Composition, and Reaction Temperature

Suhua Wang and Shihe Yang*

Department of Chemistry, Institute of Nano Science and Technology, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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The effect of copper surface structure, reagent gas composition, and reaction temperature on the growth of Cu_2S nanowire arrays has been systematically investigated. Possible mechanisms for the Cu_2S nanowire growth on copper surface have been discussed on the basis of the results of the present and previous works. The common feature of the proposed mechanisms for the Cu_2S nanowire growth lies in the facile diffusion of the sulfur and copper species.

Introduction

Control over the diameter, length, and assembly of one-dimensional (1D) materials is an important goal of contemporary materials science.[1] To achieve this, a good understanding of the growth kinetics is imperative. On the other hand, inquiry into reaction conditions that affect the growth of 1D materials should throw light on the growth mechanism of the 1D materials. One of the most important and interesting mechanisms for the growth of crystalline semiconductor nanowires is the vapor−liquid−solid growth mechanism.[2] It generally requires high temperatures (e.g., by laser ablation) in the nucleation and growth stages.[3−7] By using nanotubes or nanochannels such as membranes, polymers, surfactant assemblies, and molecular sieves as templates, nonrods or nanowires of some materials have also been synthesized.[8−11] We recently reported a successful synthesis of crystalline Cu_2S nanowires by using a gas−solid reaction under ambient conditions.[11,12] The advantage of this synthetic route lies in its simplicity and mild reaction conditions, and the high quality of the grown nanowire arrays. This has opened a new avenue for convenient synthesis of 1D materials. In the work presented here, we undertook to investigate the effect of reaction conditions such as the copper substrate surface, the composition of the reagent gases, and the reaction temperature on the diameter, length, shape, and surface morphology of the Cu_2S nanowires.

Experiment Section

Before use, copper foils (99.98%, Aldrich) with a thickness of 0.25 mm were carefully cleaned for ~5 min in an ultrasonic bath of absolute ethanol. The gas−solid reaction was performed in a homemade reactor. The reactor is essentially a glass cylinder with two inlets on one end of the cylinder and one outlet on the other end. One of the inlets was used to control the flow of the O_2/H_2S gas mixture, and the other was connected to an inert gas (Ar or N_2). The outlet was used to control the reactor pressure. The glass cylinder has a volume of 255 mL, where gas−solid reactions and Cu_2S nanowire growth took place. The copper foils (0.5 × 0.5 cm) were placed in the reactor. A gas flow was directed to the reactor which consists of a mixture of oxygen (99.8%) and hydrogen sulfide (99.8%, Aldrich) at a given molar ratio. The total pressure in the reactor was kept at ~1.05−1.08 atm. Reaction temperatures above room temperature were obtained in a water bath (±0.2 °C), and the temperature at ~0 °C was obtained in an ice−water bath. The reaction time was set at 10 h on the basis of our previous experience with the synthesis of copper sulfide nanowires.[11,12] During reaction, the reactor was kept in the dark. When exposed to the mixture of H_2S and O_2, the copper surface became dark red immediately, and then shining cyan and gray in a short time. After 10 h reaction, the copper surface became black and fluffy, indicating the formation of dense Cu_2S nanowire arrays. Transmission electron microscopy (TEM) measurements were performed with a Joel 100CX II at an operating voltage of 100 kV. Samples for TEM observation were prepared by putting nanowire-covered copper foils over copper grids with carbon film, and then dragging the copper foils gently along the overlapping surface. Scanning electron microsopy (SEM) measurements were performed on a Joel 6300 Instrument at an accelerating voltage of 25 kV, and the copper foils were used directly with Cu_2S nanowires standing on their surface. Powder X-ray diffraction experiments were performed in a Philips PW 1830 instrument with a 1.54-Å Cu rotating anode point source.

Results and Discussion

A. Effect of the Copper Surface Structure. The crystal orientation of a substrate is crucial for epitaxial

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* Corresponding author. E-mail: chsyang@ust.hk.

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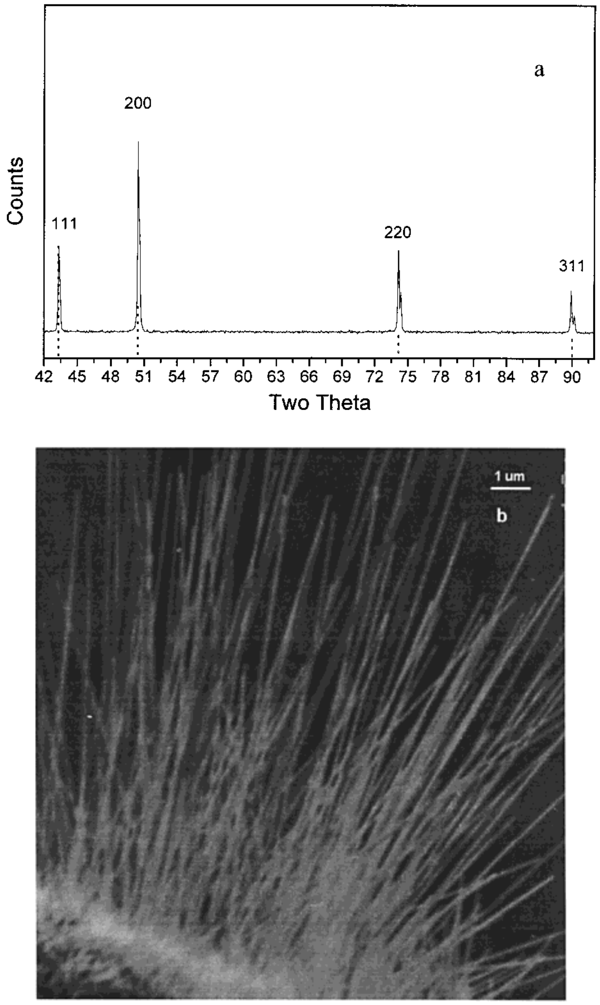

Figure 1. (a) Powder XRD patterns of the copper foil substrate before the formation of Cu$_2$S nanowires. The vertical dotted lines indicate peak positions and the intensities of random polycrystalline of face-center cubic Cu. (b) SEM image showing the facile formation of Cu$_2$S nanowires on the copper foil substrate. Reaction conditions: 22 °C, O$_2$:H$_2$S = 3:1, 9 h.

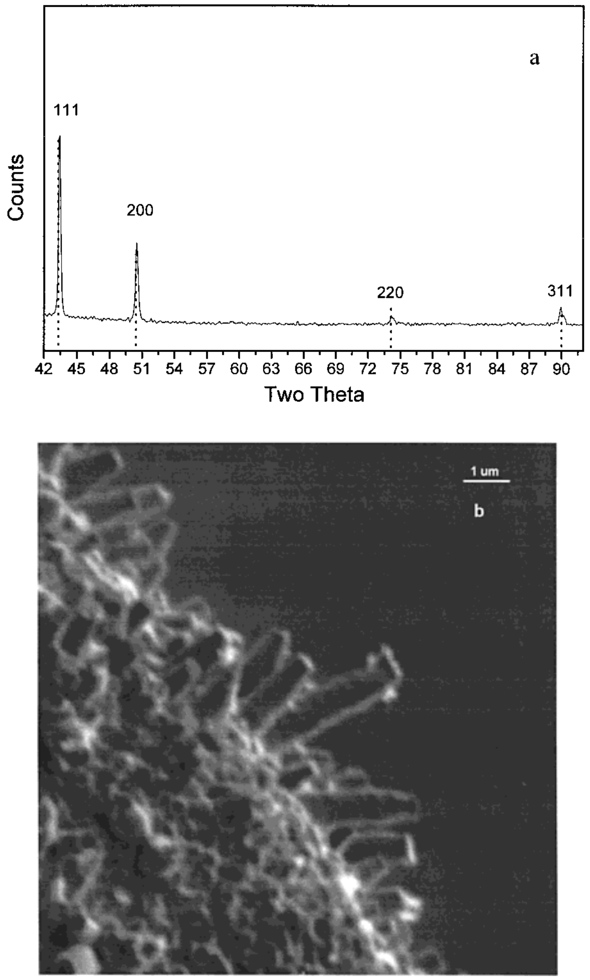

Figure 2. (a) Powder XRD patterns of the copper electrode substrate before the formation of Cu$_2$S nanowires. The vertical dotted lines indicate peak positions and the intensities of random polycrystalline of face-center cubic Cu. (b) SEM image showing little Cu$_2$S nanowire formation on the copper electrode substrate. Reaction conditions: 22 °C, O$_2$:H$_2$S = 3:1, 9 h.

growth.[13] Therefore, investigation of the effect of copper surface structure on the growth of Cu$_2$S nanowires should be important for understanding the growth mechanism. Figure 1a is the X-ray diffraction (XRD) pattern of a fresh copper foil before reaction. All the diffraction peaks can be indexed according to the face center cubic phase of copper, but the relative diffraction intensities are apparently different from those of the standard pattern. For example, the diffraction peaks of the (200) and (220) lattice planes are rather strong compared with that of the (111) lattice plane, indicating a preferred orientation of the (200) and (220) lattice planes parallel to the substrate surface. Note that the shoulders of the diffraction peaks (220) and (311) are because the X-ray source (Kα_1) contains another wavelength line (Kα_2) of half intensity. After exposure of H$_2$S/O$_2$ to the copper surface for 10 h, high-quality Cu$_2$S nanowires were formed as shown in Figure 1b. We also tested a different copper substrate (prepared from a copper rod, Aldrich), and the XRD pattern of this substrate showed that the lattice planes are approximately randomly oriented (Figure 2a). However, little Cu$_2$S nanowires were grown on this substrate after reaction under the same conditions as described above (Figure 2b). This shows that the Cu$_2$S nanowire growth depends critically on the crystalline orientation of the copper substrate.

The XRD pattern of the copper foil after reaction is shown in Figure 3 along with the XRD pattern before reaction. Clearly, the relative intensity of (200) to (111) decreased, whereas that of (220) to (111) increased after the gas−solid reaction. The relative intensity of all the diffraction peaks apparently decreased relative to that of the (220) diffraction peak. We suspect that the (220) surface of copper is the reactive surface on which the Cu$_2$S nanowires grew epitaxially. However, only the Cu$_2$S nanowires that are roughly perpendicular to the substrate surface [in this case, the (220) copper grain surface is roughly parallel to the copper substrate surface] could grow, whereas the growth of those nanowires along severely tilted directions could not continue. We have recently shown that the Cu$_2$S nanowires grow along the *c* axis of monoclinic Cu$_2$S.[15] The distances between neighboring Cu atoms in the face-centered cubic Cu are calculated to be 3.615 and 2.556

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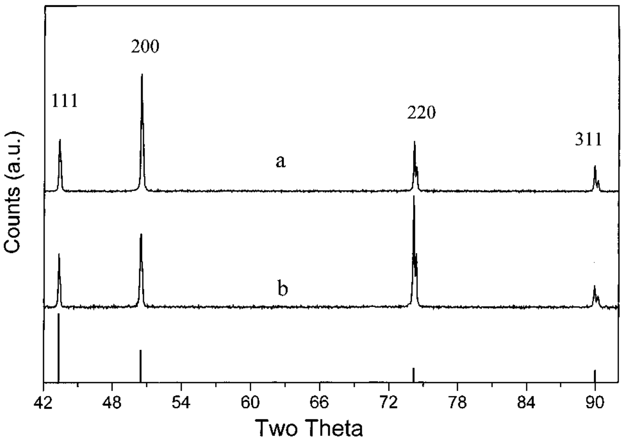

Figure 3. Powder XRD patterns of the copper foil substrate: (a) before the formation of Cu_2S nanowires; (b) after the formation Cu_2S nanowires. Reaction conditions: 22 °C, O_2:H_2S = 3:1, 9 h. The vertical solid lines indicate peak positions and the intensities of random polycrystalline of face-center cubic Cu.

Å in the crystal plane of (220), which are similar to the distances between Cu atoms of the copper layer of the monoclinic Cu_2S (3.62 ± 0.2 Å and 2.56 ± 0.26 Å). The average Cu−Cu distance in the Cu−S layer is ~4.1 Å. Apparently, in both the copper layer and the Cu−S layer of the monoclinic Cu_2S, the Cu−Cu distances are not far from those in Cu(220), although a certain extent of angular distortion of the Cu atoms has occurred because of the S-insertion. In addition, the interplane distance of (220) is 1.278 Å, which is also close to the spacing between the copper layer and copper/sulfur layer of monoclinic Cu_2S (1.123 Å) along the nanowire direction (the *c* axis).[15]

B. Effect of the Reagent Gas Composition. *Pure Hydrogen Sulfide Gas.* Little Cu_2S nanowires have grown on the copper foil surface after exposure to H_2S in the absence of oxygen. To remove any oxides on the surface, we treated the copper foil in a hydrogen chloride solution (2 M) for 5 min. Then the copper foil was washed five times in an ultrasonic bath of absolute ethanol and dried in an inert gas atmosphere. The copper foil was then loaded into the reaction chamber and subjected to a flow of pure hydrogen sulfide gas for 10 h. During the operation process above, care was taken to avoid oxygen in the reaction chamber. After reaction, the copper foil did not become black, although it was slightly darkened. SEM images exhibited little Cu_2S nanowires on the copper foil surface.

Mixture of Hydrogen Sulfide and Oxygen. In our previous work, we found that preoxidation of the copper foil surface is necessary for the growth of Cu_2S nanowires.[11,12] In the present work, we mixed oxygen with hydrogen sulfide to form the reagent gas flow at different molar ratios. By introducing oxygen into the flow of hydrogen sulfide in the reactor, Cu_2S nanowire arrays were formed on the copper foil surface after 10 h reaction. The result shows that the presence of oxygen in the reaction system is essential for growing Cu_2S nanowires on the copper foil surface. As an oxidant, O_2 serves to oxidize the copper surface, and this is followed by sulfidation with H_2S. By using the gas mixture to conduct the oxidation and sulfidation reactions at the same time ensures the smooth growth of the Cu_2S nanowires. These nanowires grown on the copper foil surface have a reasonably uniform diameter under a given growth condition.[12]

Although the length of the nanowires is primarily determined by the reaction time, their diameter, shape, and surface morphology depend sensitively on the molar ratio of O_2 to H_2S. Presented in Figure 4A−D are TEM images of Cu_2S nanowires grown at different molar ratios O_2:H_2S. In general, when the molar ratio O_2:H_2S increases, the mean diameter of the nanowires increases. For example, at 22 °C, the mean diameter of the nanowires increased to 66 nm from 36 nm when the molar ratio O_2:H_2S increased to 4.0 (Figure 4C) from 0.67 (Figure 4A). This tendency occurs at all temperatures we explored, and it is clearly depicted in Figure 5. To a certain extent, the size distribution of the nanowire diameters is also affected by the molar ratio O_2:H_2S. Specifically, as the molar ratio O_2:H_2S increases, the Cu_2S nanowire diameters become more nonuniform (see Figure 4C, D).

The molar ratio of O_2 to H_2S also influenced the shape and surface morphology of the Cu_2S nanowires as shown in the SEM images in Figure 6. At low molar ratios of O_2 to H_2S, long and straight Cu_2S nanowires with uniform diameters and smooth surfaces were produced (Figures 4A, B and 6A, B). At high molar ratios, however, the nanowire surfaces became rough, and short branches or small knops started to appear on the nanowire surfaces (Figures 4C, D and 6C, D). The shape of the nanowires also changed significantly as the molar ratio O_2:H_2S increased. Although the nanowire diameters are uniform from their roots all the way to the top ends (Figures 4A, B and 6A, B) at low molar ratios, the nanowires become nanocones or nanoneedles at high molar ratios (Figures 4C, D and 6C, D), with larger diameters at the roots but smaller diameters at the top ends.

C. Effect of the Reaction Temperature. The effect of temperature on the Cu_2S nanowire growth can be appreciated from Figure 5. One immediately notices that the diameters of the Cu_2S nanowires increase as the reaction temperature increases at a given molar ratio of O_2 to H_2S. At the same time, the size distribution of the nanowire diameters also becomes broader as the reaction temperature increases. At a given temperature, the nanowire diameters increase with the molar ratio O_2:H_2S, and this increase is more pronounced as temperature increases. Further, nanocones or nanoneedles are more readily formed at higher temperatures, and the turning point for their formation is ~30 °C. Therefore, to prepare Cu_2S nanowires with uniform diameters in tens of nanometer scale, the reaction temperature should be kept low, for example, at ~10 °C. However, at a low temperature and a low molar ratio of O_2 to H_2S, the yield of Cu_2S nanowires decreases significantly. For example, the Cu_2S nanowires produced at 0 °C decreased greatly (e.g., by a factor of ~10−20) when it was compared with that at 22 °C given that other reaction conditions are the same. We also found that the quantity of nanowires produced at lower molar

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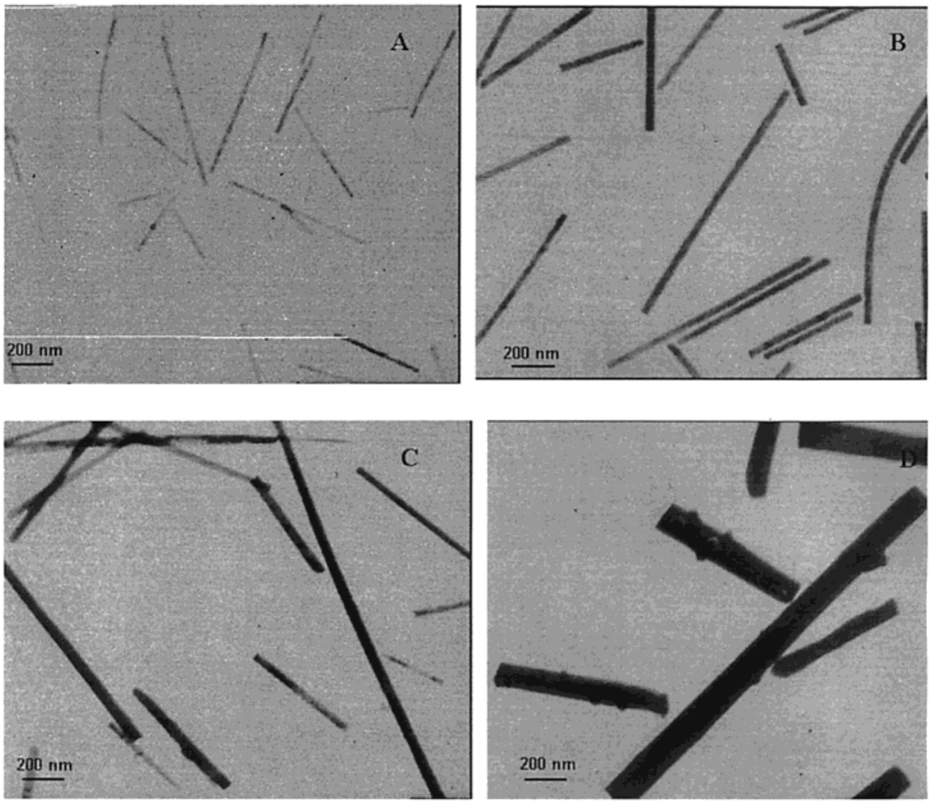

Figure 4. TEM images of the Cu_2S nanowires grown directly from the copper foil surface at different molar ratios of O_2 to H_2S at 22 °C. (A) O_2:H_2S = 2:3; (B) O_2:H_2S = 2:1; (C) O_2:H_2S = 4:1; (D) O_2:H_2S = 8:1.

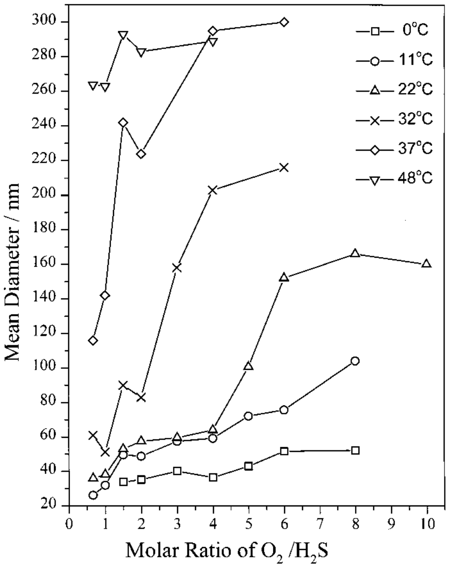

Figure 5. Dependence of the mean diameter of the Cu_2S nanowires on the molar ratio O_2:H_2S at different reaction temperatures.

ratios (e.g., 0.667) were far less than at higher molar ratios (e.g., 2.0) under the same reaction temperature.

D. Implications. Although the reaction $Cu(s) + H_2S(g) = Cu_2S(s) + H_2(g)$ is exergonic at room temperature ($\Delta G° = -52.8$ kJ/mol),[14] no Cu_2S nanowires were produced on the copper foil surface when exposed to pure H_2S. A possible explanation is that the reaction is perhaps too slow at room temperature. However, when O_2 was introduced, Cu_2S nanowires were formed with a remarkable crystallinity and aspect ratio. The nanowire formation is believed to start with an oxidation reaction $Cu(s) + 1/2O_2(g) = Cu_2O(s)$, followed by sulfidization $Cu_2O(s) + H_2S(g) = Cu_2S\ (s) + H_2O(g)$. The Cu_2S nanowires were likely grown on the (220) surface of copper in an epitaxial fashion, because this surface was found to be conducive to the nanowire formation. This is consistent with our finding that the nanowires grow along the *c* axis of the monoclinic Cu_2S.[15] But how do the nanowires actually grow? There are at least two possible mechanisms that differ in growth site. Whereas the first mechanism is characterized by the growth at the roots of the nanowires, the second mechanism insists that the growth has to be on the top of the nanowires. The biggest strength of the first mechanism is that the close-by copper surface provides the necessary feeding materials for the nanowire growth because the growth site is right between the Cu_2S nanowires and the copper surface. In this mechanism, however, the reaction site has to be delicately structured in such a way that the grown Cu_2S nanowires and the underlying copper substrate have a structural relationship. Most severely, the first mechanism cannot explain why the Cu_2S nanowires thicken as the reaction goes.

The second mechanism seems to explain all the facts observed so far. As shown in Figure 7 a, b, a key feature of the second mechanism is the fluid transport layer on the Cu_2S nanowire surfaces, which is remarkably efficient in the transport of the Cu and S species to the wire top to sustain the nanowire growth. Although this fluid transport layer is illusive, some evidence has already been obtained through high-resolution TEM. For example, one such TEM picture is shown in Figure 7c,[16] which shows a thin outer layer containing Cu, S, and O species. This on-top growth mechanism can naturally explain the epitaxial relationship between the

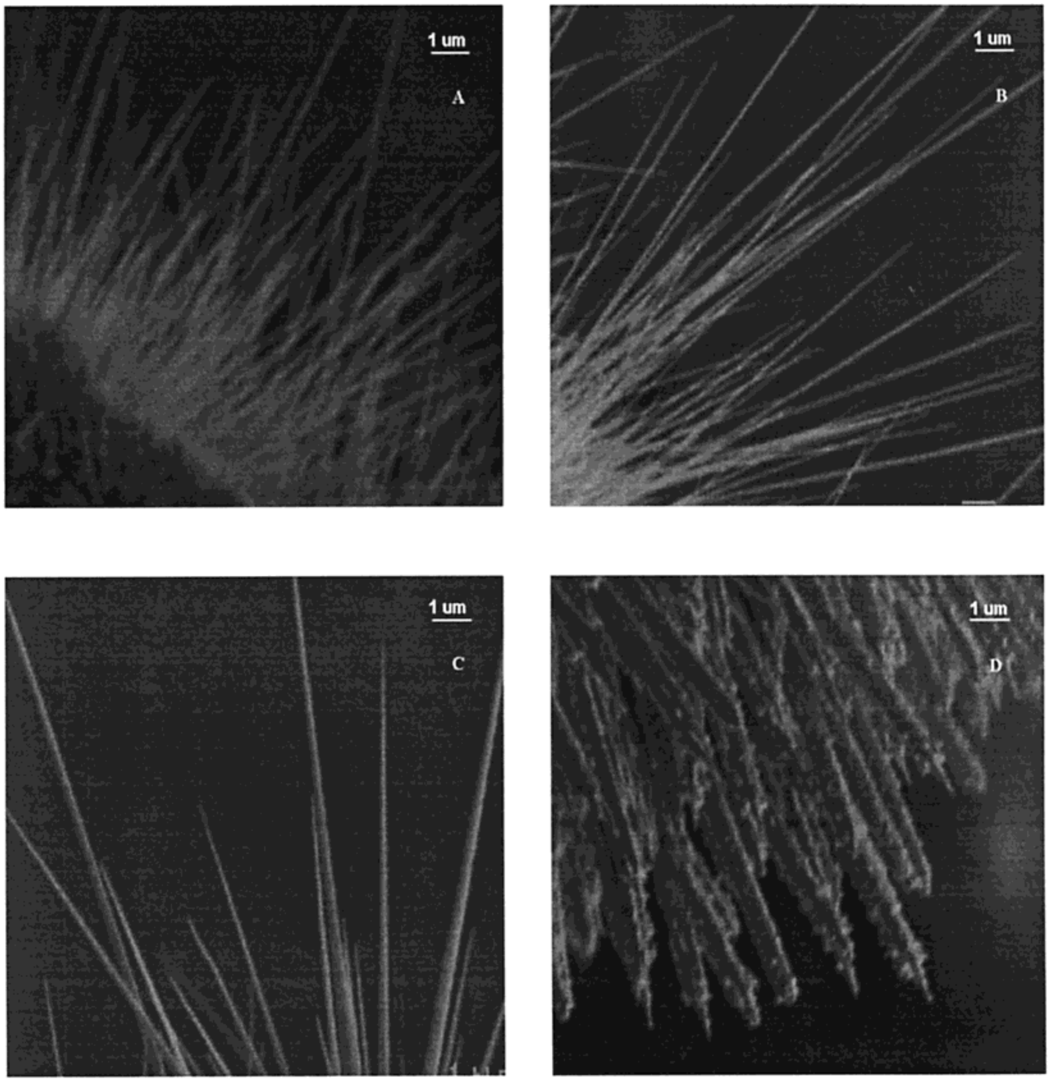

Figure 6. SEM images of Cu_2S nanowires grown directly from the copper foil surface at different molar ratios of O_2 to H_2S at 22 °C. (A) $O_2{:}H_2S = 2{:}3$; (B) $O_2{:}H_2S = 2{:}1$; (C) $O_2{:}H_2S = 4{:}1$; (D) $O_2{:}H_2S = 8{:}1$.

Cu_2S nanowires and the Cu(220) surface (Figure 7a, b). It also accounts for the nanowire thickening with reaction time, because the deposition of the Cu and S species on the nanowire surface from the fluid layer is facilitated under more reactive conditions, and sometimes nanoneedles and nanocones are formed in such cases.

As illustrated in Figure 7a, b, the initial nucleation reaction is on the Cu(220) surface, where oxidation and sulfidization occurs, forming Cu_2S nanoclusters epitaxially on the Cu(220) surface. The Cu_2S nanowires are then assembled on the top of the nanoclusters and grown outward continually. The copper grains of other orientations are then consumed and transported through the nanowire surface for the continuous growth of the Cu_2S nanowires. This growth scenario is demonstrated by the SEM images shown in Figure 8, which were taken, respectively, before the nanowire growth started (Figure 8a) and after the grown Cu_2S nanowires were washed away with an acidic solution (Figure 8b). Although the copper surface is smooth before the nanowire growth (Figure 8a), it is roughened after the gas−solid reaction (Figure 8b), and the Cu_2S nanowires apparently grow in patch patterns on the protruded areas, presumably the Cu(220) surface (Figure 8b, arrow A). The copper surfaces other than Cu(220) are evidently consumed for the Cu_2S nanowire growth (see the valleys in Figure 8b, e.g., arrow B).

The presence of sulfur may have drastically increased the mobility of copper atoms, which is important for the Cu_2S nanowire growth. It has recently been found that monolayer-high Cu islands on thick Cu(111) films ripen ∼3−4 orders of magnitude faster when S is adsorbed.[17] This has been explained by ab initio calculations.[18] The fact that low temperature is necessary for the synthesis of thin nanowires can be explained by noticing that (*i*) the atomic mobility on the nanowire surface increases with decreasing diameter of the nanowires and (*ii*) the deposition of Cu and S on the top of the nanowires is much more energetically favorable than on the periphery. At low temperatures, only those Cu_2S nanowires can grow that are so thin that the atomic mobility on the nanowire surface is sufficiently high. The Cu and S species are selectively deposited on the top of the nanowires. As temperature increases, the atomic mobil-

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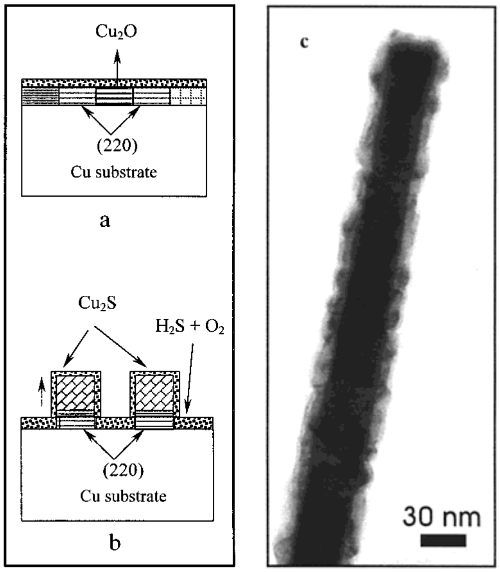

Figure 7. Illustration of a possible mechanism for the Cu_2S nanowire growth. (a) The nanowire growth starts on the Cu(220) surface in an epitaxial fashion; (b) the nanowire growth continues along the *c* axis of the monoclinic Cu_2S on the wire top, with the consumption of the neighboring Cu grains other than Cu(220) through a thin fluid transport layer on the Cu_2S nanowire surface; (c) TEM image of a single Cu_2S nanowire. It clearly shows a thin outer layer containing Cu, S, and O.

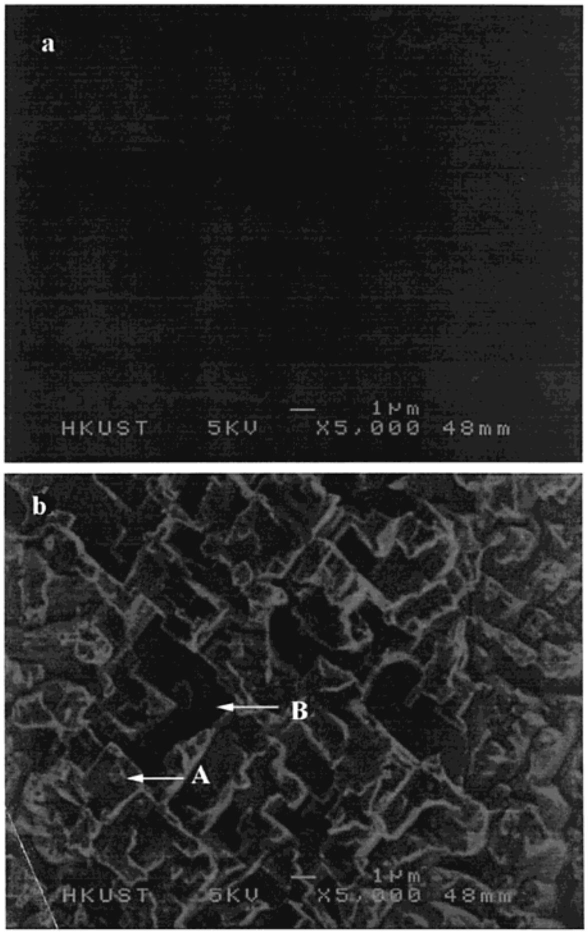

Figure 8. SEM images of the copper surfaces (a) before the Cu_2S nanowire growth and (b) after the grown Cu_2S nanowires were removed with an aqueous solution of hydrogen chloride. Arrow A, protruded area [Cu(220)] where Cu_2S nanowires grow; arrow B, valleys where copper atoms are consumed for the Cu_2S nanowire growth. Note that the SEM picture in a was taken after a fresh copper surface was treated with an acidic solution to remove the oxides.

ity increases, and thus the nanowire diameters and their distribution increase as observed. Furthermore, at higher temperatures, the gas−solid reaction becomes less selective, both the length and the diameter of the nanowires increase during reaction, and in some cases, Cu_2S nanocones or nanoneedles can be formed.

We next consider the effect of the molar ratio O_2:H_2S on the Cu_2S nanowire growth in the context of the mechanism proposed above. At low molar ratios of O_2 to H_2S at a given temperature, because the reaction is slow, only small-diameter nanowires grow. However, as the molar ratio O_2:H_2S increases, the reaction rate increases and, therefore, the reaction becomes less selective. Specifically, the growth of the Cu_2S nanowires is not only along the wire axis but also along the wire thickness. This naturally increases the nanowire diameters and broadens the size distributions. In a way similar to the high-temperature effect, the reaction becomes less selective at high molar ratios of O_2 to H_2S, leading to the formation of nanocones or nanoneedles. In general, the effect of the molar ratio O_2:H_2S on the Cu_2S nanowire growth is weaker than the temperature effect, because the thickness of the Cu_2S nanowires is primarily determined by temperature. At low temperatures, the effect of the molar ratio O_2:H_2S is not significant (Figure 5). It is only at high temperatures that the effect of the molar ratio O_2:H_2S becomes important because of the increase in the atomic mobility on the nanowire surface.

Conclusions

In this work, we have identified the important effects of copper surface structure, reagent gas composition, and reaction temperature on the growth of Cu_2S nanowires. The Cu_2S nanowires can only grow on a certain surface of copper, i.e., Cu(220). The nanowire diameters increase with increasing temperature, and to a lesser extent, with increasing molar ratio of O_2 to H_2S. At high temperatures and high molar ratios O_2:H_2S, the nanowires become thicker, less uniform in diameter, coated with nanoparticles, and even evolve into nanocones or nanoneedles. A plausible mechanism for the Cu_2S nanowire growth has been proposed which seems to accord with the experimental observations. This mechanism is characterized by a fluid transport layer on the Cu_2S nanowire surface, which is composed of Cu, S, and O. The monoclinic Cu_2S nanowires are assembled on the top of the nanowires and grow outward. This growth mechanism hinges on the high atomic mobility of the fluid transport layer, which supplies the necessary materials for the assembly of the Cu_2S nanowires on the top. Further experiments are needed to verify the mechanism under better-controlled conditions.

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