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Fabrication and optical properties of CuS nanowires by sulfuring method

Yu Cheng Chen [a,*], Jen Bin Shi [b], Chien Wu [a], Chih Jung Chen [a], Ya Ting Lin [a], Po Feng Wu [b]

[a] The Graduate Institute of Electrical and Communications Engineering, Feng-Chia University, Taichung 40724, Taiwan
[b] Department of Electronic Engineering, Feng-Chia University, Taichung 40724, Taiwan

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Abstract

In this letter, we successfully synthesize Cu_xS nanowires by sulfuring the copper nanowires at varied temperatures. When the annealing temperatures reach 400, 450, and 500 °C, the x values are equal to 1.03, 1.26, and 1.43, respectively. The Cu_xS nanowire arrays are highly ordered and have high wire packing densities. At 400 °C sulfured temperature, the CuS nanowire phase with a strongly preferential peak [110] indicates that the nanowire arrays should point to the [110] direction. The UV–vis spectroscopy measurement shows only one broad absorption peak that appears at 802 nm in near-IR region. This proves that the sulfured nanowire has pure CuS phase.
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Keywords: Nanomaterials; CuS nanowires; Sulfuring; Optical materials and properties

1. Introduction

One-dimensional nanomaterials have become the focus of intense research, because they provide a good system for investigating the dependence of electrical, optical, and thermal transport or mechanical properties on dimensionality and size confinement [1,2]. A way for preparing nanostructural materials, entails fabricating the desired material within the pores of a template membrane [3–6]. The use of either direct current or alternate current for the nanowire deposition of a range of materials (such as CdSe, SnO_2, TiO_2, InO_2, Bi_2S_3 etc.) has already been shown to produce well ordered crystallized highly dense nanowire arrays.

Copper sulfide is an important basic material as absorber coating and is widely implicated in photovoltaic and photodetector applications due to its unique near solar control characteristics [7]. Recently, there are some methods to fabricate copper sulfide nanowires, such as microwave irradiation [8], soft colloidal templates [9], template-free synthesis [10], solid-state reaction route [11], biomolecule-assisted hydrothermal approach [12], that have been utilized to prepare one-dimensional CuS nanorods and nanowires, searching for a simple synthetic route is still an interesting subject worthy of further exploration. However, to the best of our knowledge, this is the first report to prepare the copper sulfide (CuS) nanowires by sulfuring Cu nanowires electrodeposited by an AC applied DC process in anodized aluminum oxide (AAO) templates with various temperatures.

2. Experimental details

High-purity (99.9995%) aluminum foil was used as the starting material. AAO was prepared by a two-step anodizing process [13]. The alumina template was formed by anodizing an Al plate in H_2SO_4 solution under constant voltage of 25 V. After anodization for several hours, the alumina membrane was immersed in an etching solution of H_3PO_4 to remove the alumina layer. Then, the aluminum foil was anodized again. After the anodization, the remaining aluminum was etched by $HgCl_2$. To widen the pore diameter, the alumina template was immersed in a solution of H_3PO_4. After this process, the diameter of the holes of the alumina membrane was adjusted to about 30 nm. Arrays of Cu nanowires were fabricated by electrochemical deposition into the nanometer-sized pores. To prepare Cu nanowires, a layer of Pt film was sputtered onto one side of the through-hole AAO template to serve as the working electrode in a two-electrode electrochemical cell. The electrodeposition was

* Corresponding author. Department of Electronic Engineering, Feng-Chia University 100, Wen-Hwa Rd, Seatwen, Taichung 40724, Taiwan. Tel.: +886 4 24517250x3997; fax: +886 4 24510405.
E-mail address: cbabylon2003@yahoo.com.tw (Y.C. Chen).

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carried out at appropriate voltage conditions, using an electrolyte containing $CuSO_4 \cdot 5H_2O$ and H_3BO_3. Then the samples together with the sulfur powder were annealed in vacuum sealed quartz tube for several hours at 400, 450, and 500 °C, respectively.

In order to achieve this objective, the form of CuS nanowires has been characterized by field-emission scanning electron microscope (FE-SEM), energy dispersive X-ray spectrometer (EDS) analysis and UV–visible absorption measurements in order to determine the morphology, composition and optical behavior of the products. UV–visible absorption spectroscopy is a useful technique to monitor the optical properties of the nanomaterials.

The morphologies of the as-prepared AAO template and the CuS nanowires were observed using a field-emission scanning electron microscope (FE-SEM; Hitachi, S-4800). While CuS nanowires were fabricated, we use NaOH to remove AAO membranes. We also observed the high-filling CuS nanowires without the AAO template by FE-SEM. The composite of CuS nanowires was observed by X-ray spectrometer (EDS). In order to observe the structure of the CuS nanowires, X-ray diffraction (XRD) analysis of the CuS nanowires with the AAO template removed by NaOH solution was performed using a diffractometer (SHIMADZU, XRD-6000). The UV–visible absorption measurement is used in order to determine the size, morphology, composition and optical behavior of the products.

3. Results and discussion

For alternate-current process, the alternation of the electric field will remove the undesired deposition which is deposited on the surface of the alumina membranes. For the direct-current process, the direction of the electric field results in a high density and high-quality deposition to form highly aligned ordered Cu nanowires. Therefore, we choose appropriate alternating current and direct current so that high-quality nanowires are produced.

In Fig. 1(a) and (b), the cross-section images of FE-SEM show that the CuS nanowires (sulfured at 400 °C) are about 30 nm in diameter and with 45 μm in length and the aspect ratio is above 1500. To observe the morphology of the CuS nanowires by FE-SEM, the AAO template was removed from the CuS/AAO assembly system by dissolving the AAO in NaOH solution and washing with distilled water. In Fig. 1(c), it is clearly seen that the CuS nanowires (sulfured at 400 °C) are parallel to each other, and have a very high aspect ratio. The CuS nanowires were highly ordered and had high wire packing densities. Fig. 1(d) shows the composition of the CuS nanowires and AAO template using an EDS. Quantitative analysis indicates an atomic composition of Cu, S, Al and O. Al and O elements found in Fig. 1(d) are from the AAO.

Fig. 2 shows that Cu nanowires that were sulfured at different temperatures have different Cu/S ratio. At 400 °C, the Cu/S ratio is an ideal stoichiometry of CuS (1.03 for the Cu/S ratio). At 450 °C and 500 °C, the Cu/S ratios are 1.26 and 1.43, respectively. Comparing our various sulfured temperatures of EDS, the Cu/S ratio is increasing when sulfured temperature is increasing.

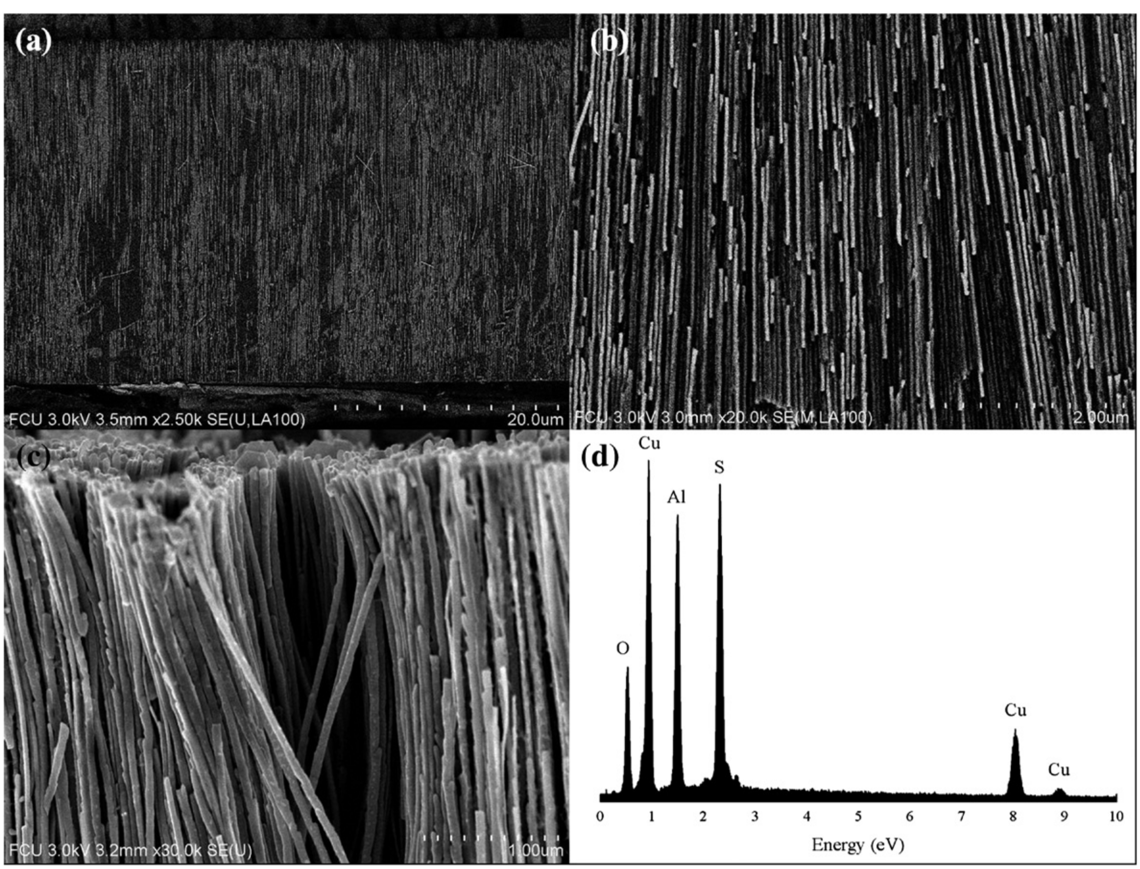

Fig. 1. (a) SEM image of the cross-section view of CuS nanowires (the sulfured temperature is at 400 °C) in the AAO with the pore diameter of 30 nm, (b) is the magnified SEM images of (a), (c) the SEM image of the cross-section view of CuS nanowires after absolutely dissolving the AAO template. (d) EDS spectrum of the CuS nanowires.

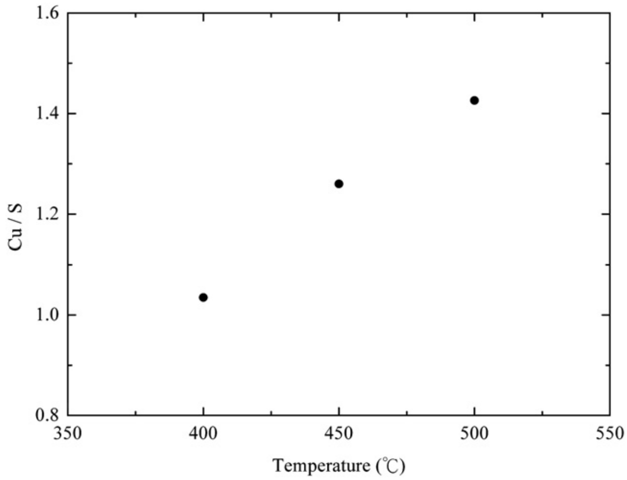

Fig. 2. The linear relation between the Cu/S ratio and the various temperatures is depicted.

XRD pattern of the phase structure of the CuS nanowires with the sulfured temperature at 400 °C is shown in Fig. 3. XRD spectrum is well matched with the standard values of CuS (JCPDS, 78-0879), the peaks are found at (100), (101), (102), (103), (106) and (110). The result indicates that the CuS nanowires have a preferred direction along the [110]. No characteristic peaks were observed for the other impurities, such as Cu_2S or S.

Fig. 4 shows absorption spectrum result of the nanowires in the range of 400–1300 nm (Cu nanowires are sulfured in sealed tube at 400 °C). In the Cu–S system, it has many known stable phases from chalcocite (Cu_2S) to sulfur-rich covellite (CuS). Each stable phase has its own characteristic optical property. In a previous study, CuS nanowires [14] have been reported by hydrothermal method. Optical absorption of it is reported, the product obtained at lower temperature (120–175 °C) with CuS nanowire shows a small absorption peak around 400 nm and has broad absorption in the near-IR. For some Cu–S system nanoparticles [15,16], they point out to have two phases (CuS and Cu_2S), the presence of a characteristic broad absorption band in UV region for Cu_2S and the other in near-IR region for covellite copper sulfide (CuS). Further study on the absorption spectrum of various phases of copper sulfides was reported by Haram et al. [16], a characteristic broad absorption band in the near-IR region which *increases* on increasing sulfur content (i.e., from covellite to digenite ($Cu_{1.8}S$) to djurleite ($Cu_{1.96}S$)) and is absent in the chalcocite phase (Cu_2S). Comparing the above mentioned reasons, our absorption spectra result of nanowire has a very strong absorption peak at 802 nm, and no other peak is observed. We infer that the absorption peak at 802 nm in near-IR is due to the phase of the copper sulfide covellite (CuS), and no absorption peak of Cu_2S is found in short wavelength. This result proves that our sulfured nanowires are pure CuS phase and is in accordance with our XRD and EDS results.

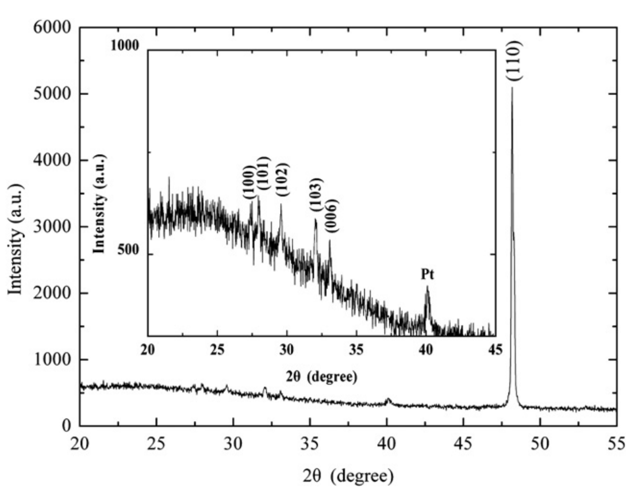

Fig. 3. XRD patterns of the CuS nanowires (the sulfured temperature is at 400 °C).

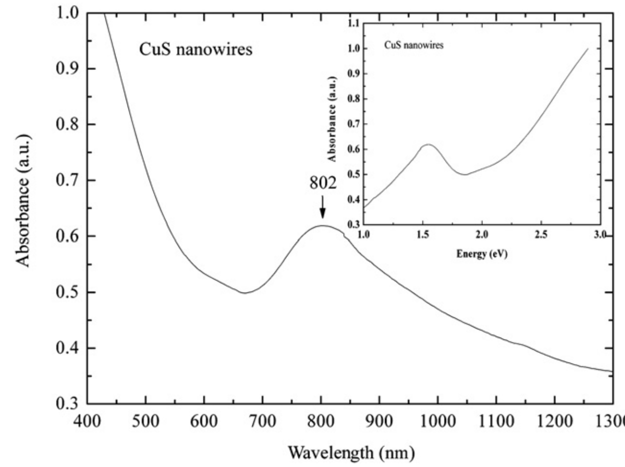

Fig. 4. UV–visible absorption spectrum of CuS nanowires (the sulfured temperature is at 400 °C).

4. Conclusion

In conclusion, Cu_xS nanowire arrays have been successfully fabricated within template by using the sulfurizing methods. The Cu/S ratio is linear from 1.03 to 1.43 when the sulfured temperatures increase from 400 to 500 °C. In XRD data, after sulfuring the Cu nanowire at 400 °C, the sulfured nanowires have CuS phase and a preferred direction along [110]. In optical analysis of nanowire only one absorption peak was observed at 802 nm. It indicated that the sulfured nanowire is pure CuS phase.

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