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Short communication

$CuInS_2$ nanowires prepared using a hydrothermal process through a polymer-type ion release source

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ABSTRACT

Chalcopyrite copper indium sulfide ($CuInS_2$, CIS) has a bandgap that is optimal for a solar energy conversion material. In this paper, we used a polymer-type ion release source to control the precursor concentration of the hydrothermal system to grow CIS nanowires. The analytical results indicate that the reaction process is based on the formation of CuS binary compound, which is then followed by indium intercalation, which induces the formation of the CIS chalcopyrite crystal structure. The products were characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The CIS nanowires were 100–300 nm in diameter and 2–5 μm in length.

1. Introduction

Semiconductor nanowire is an important material in photovoltaic devices [1,2]. Copper indium sulfide ($CuInS_2$) is a I-III-VI_2 semiconductor compound with a chalcopyrite crystal structure. With an energy band gap of 1.5 eV, the direct band gap matches the solar spectrum, and thus many studies have examined the synthesis of $CuInS_2$ nanowire using various methods.

CIS synthesis techniques include the evaporation method [3], molecular beam deposition [4], sputtering [5], spray pyrolysis [6], chemical vapor deposition (CVD) [7], hydrothermal systems [8] and chemical processes [9–11]. Some of these require special equipment, high temperatures or long periods of time to provide the energy necessary to overcome the activation energy needed for the chemical reaction. We thus chose a polymer-type ion release source (PIRS) in a hydrothermal system to synthesize CIS, which requires a lower temperature than other options. In other papers, PIRS are often used in the field of biotechnology, such as in antimicrobial substances [12,13]. The rate of release of ions in the solution is controlled by the polymer composite [12], and this rate can be controlled to achieve stability and sustainability. In our study, the PIRS is composed of Cu^{2+}, In^{3+} and S^{2-} ions dissolved in polyvinyl butyral (PVB) solution. We made this solution become composite fibers using an electrospinning method [14,15]. The PIRS fibers and a hydrothermal process were then used to prepare CIS nanowires. In this process the composite fibers are dissolved and the ions are gradually released.

As a result, the hydrothermal product is different in appearance from the electrospinning fibers. Therefore, we propose that the reaction occurs through a process of the fibers dissolving and recrystallizing. We call this process the release-recrystallize route (RRR) process, in which the PIRS releases metal ions slowly and stably in the solution. In traditional hydrothermal methods, when the concentration is high in the initial step of the reaction then the reaction rate is fast and the products easily grow into a large form. However, the direction selectivity of the products is low after the concentration falls near the final stage of the reaction, at which point the reaction rate is slow and the products readily grow fine fibers with high direction selectivity. Different to traditional hydrothermal methods, the use of PIRS can provide a stable concentration of an ion release source from start to finish. The use of the RRR process with PIRS in hydrothermal methods can thus allow the product to maintain a stable growth concentration and preferential direction.

2. Experimental procedure

2.1. Materials

Copper(II) chloride (AlfaAesar, 99.99%), indium(III) chloride (Acros, 99.99%), sodium hydroxide (Kanto, 95%) and thiourea (AlfaAesar, 99.9%) were used in this experiment. The PVB (average M_v~40 kDa) was obtained from Chang Chun Group Company (Kaohsiung, Taiwan). Ethanol (PA Panreac, 99%) and the deionized water (DI water) used in this work was obtained from EMD Millipore Corporation, and produced using the Direct-Q 3 system (Billerica, MA).

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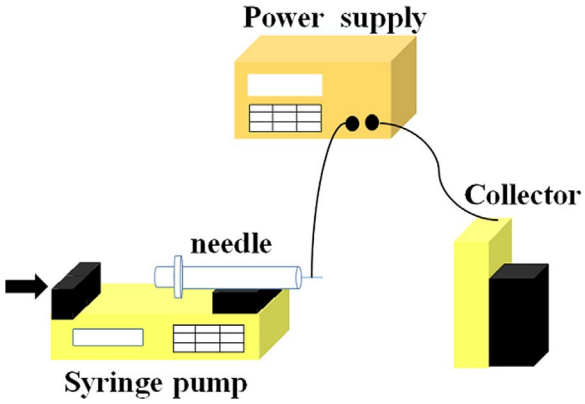

Fig. 1. Schematic diagram of the applied electrospinning system.

2.2. Synthesis of the $CuInS_2$ precursor

A mixture of $CuCl_2{\cdot}2H_2O$ (2 mmol), $InCl_3{\cdot}4H_2O$ (2 mmol), and thiourea (8 mmol) was first dissolved in 2 mL ethylene glycol (99.9%) and 3 mL ethanol absolute (99.9%) with magnetic stirring at room temperature for 3 h. This mixture was then added to a PVB solution, which was prepared by dissolving 0.75 g PVB powder in 5 mL ethanol absolute (99.9%) with magnetic stirring at room temperature for 3 h to obtain a homogenous precursor of Cu^{2+}, In^{3+}, S^{2-} ions in PVB solution.

2.3. Electrospinning process

The homogenous precursor was transferred to a syringe that was attached to a syringe pump with a flow rate of 0.5 mL/h, and a voltage of 6 kV was applied at an electrode distance of 15 cm, as shown in Fig. 1. The homogenous precursor is drawn into a filament-shaped composite nanofibers by an electric field between the tip and the collecting board.

2.4. Synthesis of the $CuInS_2$ nanowires

The Cu^{2+}, In^{3+}, and S^{2-} ions in the PVB composites nanofiber were loaded into a 40 mL Teflon-lined stainless steel autoclave along with 25 mL deionized water (DI water) and 0.2 mL (0.01 M) NaOH solution, and then heated at 120 and 180 °C for 12 h followed by slow cooling to room temperature. The product was washed with DI water and ethanol (95%) several times and finally dried at about 45 °C.

2.5. Characterization of $CuInS_2$ nanowires

The X-ray powder diffraction (XRD, operating at 8 kV) patterns of the as-prepared samples were recorded on a Shimadzu XRD-6000 X-ray diffractometer with Cu Ka radiation. The morphologies and micro-/nanostructures were investigated with a HITACHI 4200 A (Tokyo, Japan) scanning electron microscope (SEM) operating at 10 kV), a JEOL JEM-2100 F transmission electron microscope (TEM), and a high resolution TEM (HRTEM) operated at 200 kV. The energy dispersive spectrometer (EDS) measurements were performed using a Horiba EX220 (Kyoto, Japan), which was attached to the TEM for compositional analyses. UV–Vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer.

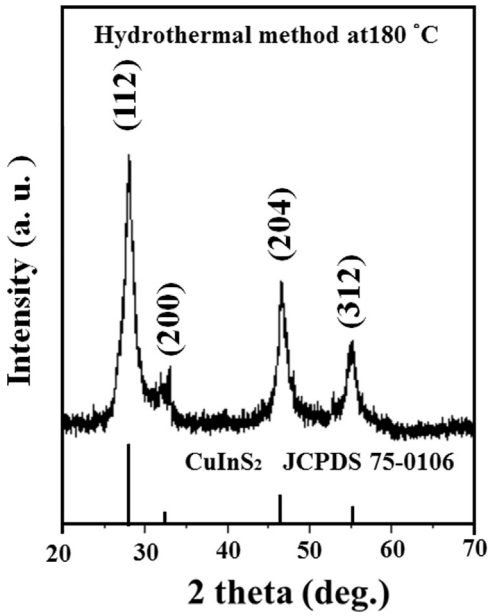

Fig. 3. CIS XRD patterns of the hydrothermal process at 180 °C.

3. Results and discussion

To achieve the best conditions to take advantage of the electrospinning-prepared Cu^{2+}, In^{3+}, and S^{2-} ions in PVB nanowire precursor, a 7.5% PVB concentration with a flow rate of 0.5 mL/h and a 15 cm working distance at a 6 kV voltage was used. The Cu^{2+}, In^{3+}, and S^{2-} ions in the PVB nanofiber precursor were placed into 25 mL DI water, loaded into a 40 mL Teflon-lined stainless steel autoclave, and then heated at 120 and 180 °C for 12 h, respectively.

The SEM images of the PIRS fibers in Fig. 2(a) show these have a width of about 200–400 nm and a length of several micrometers. The sample synthesized in the hydrothermal system at 120 °C for 12 h is shown in Fig. 2(b), the product is a mixture of particles that exhibit a short rod-like structure. These short rod-like structures have a width of about 300 nm and a length of about 2–5 μm. From the EDS/SEM analyses, the average chemical compositions of the synthesized samples were Cu: In: S=52.66: 0.71: 46.63. As a result, which was also checked by XRD, the product was CuS at 120 °C because the energy from the system was not enough to produce the pure phase $CuInS_2$.

Fig. 2(c) shows the SEM image of the CIS samples synthesized in the hydrothermal system at 180 °C for 12 h. The product is nanowire structures with diameters of about 50–300 nm and lengths of about 2–5 μm. From the EDS/SEM analyses, the average chemical compositions

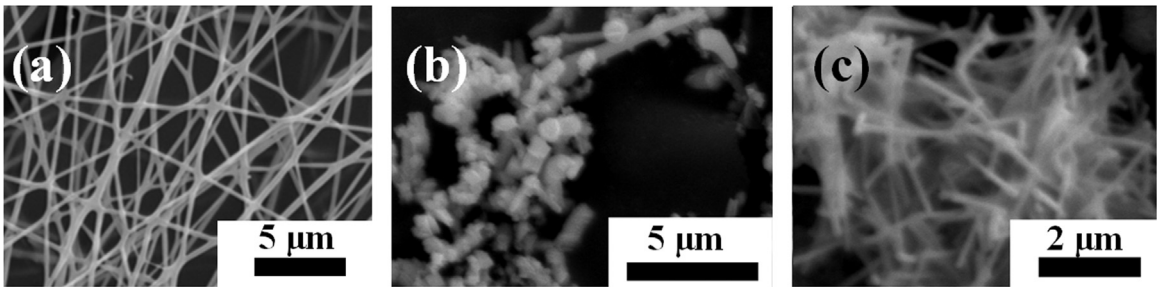

Fig. 2. SEM images of CIS (a) PIRS (b) hydrothermal process at 120 °C for 12 h, and (c) hydrothermal process at 180 °C for 12 h.