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Facile fabrication of p-type Cu_xS transparent conducting thin films by metal sulfide precursor solution approach and their application in quantum dot thin films

Shenjie Li [a, b, *], Tianyong Zha [a], Qiang Wang [a], Chengyu Wang [a], Yujiao Ren [a], Yanyan Chen [a, b, **], Daocheng Pan [b, ***]

[a] School of Chemistry and Chemical Engineering, HeFei University of Technology, Hefei, AnHui, 230009, People's Republic of China
[b] State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

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ABSTRACT

We present a facile route for the fabrication of P-type Cu_xS transparent and conducting thin films (TCTFs) using copper (I) oxide and butyl-dithiocarbamic acid as precursors by pulling method on glass. The as-deposited highly conductive crystalline Cu_xS films showed high carrier concentration (~3.11 × 10^{22} cm^{-3}), low electrical resistivity (~1.02 × 10^{-4} Ω cm) and conclusive p-type conduction. X-ray diffraction studies showed high crystallinity, and the optical transmission spectra in UV–vis–NIR region of such films were recorded, indicating that the transparency was over 75% with a band gap of 1.52 eV. The room-temperature sheet resistance increased from 9.9 to 302.4 Ω sq^{-1} with increasing baking temperature. The Cu_xS/quantum dot bifacial thin films have been fabricated, and the experimental results indicated that luminescent, transparent, and conductive Cu_xS/Cu-doped $Zn_yCd_{1-y}S$ thin films have a very high potential application in thin film solar cells.

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1. Introduction

Transparent conducting thin films (TCTFs) have a wide variety of applications in thin-film solar cells, low-emissivity windows, liquid crystal display and light-emitting diodes. To date, the most commonly used TCTFs are indium-tin-oxide (ITO) [1,2] and fluorine-doped tin oxide (FTO) [3,4], which are also the most widely used materials in real-world applications. Both of them are n-type materials with free electron concentration values of the order of 10^{21} cm^{-3}, similar to those of typical metals. In recent years, carbon nanotube (CNTs) [5], graphene [6,7] and metallic nanowires (NWs) [8–11] films have been fabricated and shown the excellent conductivities and transmittances. By contrast, p-type TCTFs are comparatively less developed and less widely utilized. The delafossite-structured copper aluminum oxide ($CuAlO_2$) thin film was first reported by Kawazoe et al., in 1997 as an alternative material for a highly conductive p-type TCTFs [12]. Since then, there are a lot of research and applications about n-type TCTFs which cannot make a transparent photo-device nor a p-n junctions without the p-type ones [13]. However, to date, the fabrication of p-type thin films based on wide band gap compounds still required a high annealing temperature (~450 °C), which severely limit their applications in optoelectronic devices.

A series of p-type TCTFs based on narrow band gap materials (Eg < 3 eV) have also been reported [14,15]. Compared with other alternative materials, copper is cheaper and more abundant. Copper sulfide (Cu_xS, x = 1–2), as an important p-type semiconductor material which can exist in at least five phases which are stable at room temperature: CuS (covellite), $Cu_{1.12}S$ (yarrowite), $Cu_{1.75}S$ (anilite), $Cu_{1.8}S$ (digenite), $Cu_{1.95}S$ (djurleite) and Cu_2S (chalcocite) [16–18]. Cu_xS thin films has been widely used in many fields such as solar cells, transparent thin films, optical materials and electro-conductive coatings owing to their excellent optical, electrical, chemical and physical properties [19–28]. Cu_xS thin films have

* Corresponding author. School of Chemistry and Chemical Engineering, HeFei University of Technology, Hefei, AnHui, 230009, People's Republic of China.
** Corresponding author. School of Chemistry and Chemical Engineering, HeFei University of Technology, Hefei, AnHui, 230009, People's Republic of China.
*** Corresponding author.
E-mail addresses: shenjieli@hfut.edu.cn (S. Li), yanyanchen@hfut.edu.cn (Y. Chen), pan@ciac.ac.cn (D. Pan).

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been prepared by various methods, including vacuum evaporation, electrodeposition, chemical bath deposition and spray pyrolysis [29–37] which are not favorable to the large-scale deposition of transparent conducting thin films. Thus, it is necessary to develop a large-scale fabrication approach for high-quality Cu_xS thin films.

In this paper, we demonstrated a metal sulfide precursor solution approach for depositing Cu_xS TCTFs through pulling method. Compared with other methods, pulling method is very facile and cost-effective for preparing high quality semiconductors thin films, especially suitable for large-scale fabrication of TCTFs. After post-annealing treatment under moderate temperature for a period of time, the as-deposited Cu_xS TCTFs exhibit high carrier concentration (~3.11×10^{22} cm^{-3}), low electrical resistivity (~1.02×10^{-4} Ω cm) and conclusive p-type conduction.

2. Experimental section

2.1. Chemicals

Copper (I) oxide (Cu_2O, 99%), zinc oxide (ZnO, 99.99%), cadmium hydroxide ($Cd(OH)_2$, AR), carbon disulfide (CS_2, 99.9%), n-butylamine ($CH_3(CH_2)_3NH_2$, 99%), ethanol (CH_3CH_2OH, AR), 3-mercaptopropionic acid (MPA, $HSCH_2CH_2COOH$, 98%) were purchased from Aladdin. All chemicals were used as received without any further purification.

2.2. Preparation of metal sulphides precursor solution

Cu precursor solution (0.8 M) was prepared by dissolving 0.5720 g (4.0 mmol) of Cu_2O in 27.2 mL of ethanol, 4.8 mL of CS_2 (80 mmol), and 8.0 mL of 1-butylamine (80 mmol) under magnetic stirring on a hot plate at 60 °C until all the solid dissolved.

2.3. Preparation of transparent and conductive Cu_xS thin films

In a typical fabrication process of the Cu_xS transparent and conductive thin film, 20 mL of Cu stock solution was added to a 50 mL of beaker, and a rectangular glass substrate (25.4 × 75.6 × 1.2 mm) fixed on the syringe pump was immersed in the beaker. The glass substrates were pulling up at a constant speed at 5 cm min^{-1}. When the substrate passed through the liquid surface, the copper precursor solution will be attached on the glass substrate, due to the effect of gravity, and extra precursor solution will fall down vertically along the substrate. Finally, uniform thin film was prepared. By a sintering process on a hot plate at 180 °C for 15 s in open air, the Cu_xS transparent and conductive thin film was obtained by pulling method.

2.4. Preparation of transparent and luminescent Cu-doped $Zn_yCd_{1-y}S$ quantum dot thin films

The luminescent Cu-doped $Zn_yCd_{1-y}S$ quantum dot thin films were fabricated by following the literature method [43]. In a typical fabrication process of Cu-doped $Zn_{0.5}Cd_{0.5}S$ quantum dot thin film with a doping concentration of 1 at %, 1 mmol of ZnO, 1 mmol of $Cd(OH)_2$, 0.01 mmol of Cu_2O, 1.2 mL of CS_2, 2.0 mL of 1-butylamine and 7 mL of ethanol were added in a 25 mL conical flask under magnetic stirring on a hot plate at 60 °C until all the solid dissolved. Luminescent Cu-doped $Zn_{0.5}Cd_{0.5}S$ quantum dot thin film was spun on a coverslip (20 × 20 × 0.5 mm) at 3000 rpm for 30 s, followed by a sintering process on a hot plate at 210 °C for 15 s in the open air.

2.5. Preparation of transparent, luminescent and conductive Cu_xS & Cu-doped $Zn_yCd_{1-y}S$ quantum dot thin films

Cu_xS thin film was spun on the opposite side of Cu-doped $Zn_yCd_{1-y}S$ quantum dot thin film at 2000 rpm for 10 s, followed by a sintering process on a hot plate at 180 °C for 15 s in the open air, the transparent and luminescent Cu_xS & Cu-doped $Zn_yCd_{1-y}S$ quantum dot thin films were obtained.

2.6. Characterizations

For structural study, an X-ray diffractometer (Bruker Advance D8) was used. X-ray diffraction (XRD) patterns were measured in 2θ range of 20–70° using Cu-Kα radiation of wavelength λ = 0.154 nm. The SEM image of Cu_xS thin film was characterized on a Hitachi-4800 field-emission scanning electron microscope operating at an accelerating voltage of 20 kV. The CHN elemental analyses were carried out on a VarioEL analyzer. The samples were prepared by depositing the samples by pulling method on the substrates. Fourier transform infrared (FTIR) spectra were measured within a 4000-400 cm^{-1} region on an American BIO-RAD Company model FTS135 infrared spectrophotometer with the KBr pellet technique. The film thickness and surface roughness were measured by a step profilermeter (AMBIOS, XP-100). The UV–Vis–NIR spectrophotometer measurements were performed using a spectrophotometer and the spectra were recorded by taking a similar glass as reference and hence transmission due to the film only was obtained. Excitation and PL spectra were measured on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp as the excitation source, and the PL intensity was calculated by integration of PL curve. The electrical resistivity of Cu_xS films were measured by a Hall effect system (ET9000, East Changing Technologies, Inc.). The sheet resistance was measured using a 4-point probe method with a Keithley 2400 source meter (Sheet resistance = measured resistance × 4.532). The details of the characterization results are discussed below.

3. Results and discussion

In this article we present a facile route by preparing metal sulphide precursor solution. First, butyl-dithiocarbamic acid was in-situ synthesized in ethanol solution by the reaction of carbon disulfide and n-butylamine at room temperature. The ethanol solution of butyl-dithiocarbamic acid can react with many types of metal oxides and hydroxides as an organic acid, such as Cu_2O, ZnO, indium hydroxide ($In(OH)_3$), forming a series of metal-organic precursor solutions. Here, we fabricated Cu_xS transparent conducting thin films using copper (I) oxide and butyl-dithiocarbamic acid as precursors by pulling method.

Fig. 1 (a) shows a scanning electron microscope (SEM) image of Cu_xS film prepared by pulling method at 220 °C. The Cu_xS film revealed a compact and dense morphology. In addition, no pinholes or cracks were observed in the field of vision. Fig. 1 (b) shows the copper precursor solution by dissolving Cu_2O in the ethanol solution of butyl-dithiocarbamic acid. The color of the precursor solution was changed from dark black turbid to a yellowish transparent.

Fig. 2 shows the XRD pattern of Cu_xS thin film prepared by pulling method at 220 °C. All of the XRD peaks can be indexed to a hexagonal-phase Cu_xS (JCPDS No. 01-1281). No other peaks of impurities are found in XRD pattern. The standard XRD pattern of Cu_xS agrees with the experimental pattern in intensity and position, including (102), (103), (006), (110), (114) and (116) planes. By controlling the baking temperature, the sizes of nanocrystals and the conductivity of the films can be engineered. These results suggest that the method reported here is effective to synthesize

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