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Cu_2CdSnS_4 THIN FILM PREPARED BY A SIMPLE SOLUTION METHOD

HAO GUAN[a,b,*], JINGCHUAN ZHAO[a], XU WANG[1], FANGLI YU[a]
[a]*School of Materials Engineering, Yancheng Institute of Technology, 9 Yinbing Street, Yancheng 224051, PR China*
[b]*College of Materials Science and Technology, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, PR China*

Cu_2CdSnS_4 thin film was prepared by sulfurizing (Cu, Sn)S/CdS structured precursors prepared by a combination of the successive ionic layer absorption and reaction method and the chemical bath deposition method. X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and UV-vis-NIR absorbance spectroscopy measurements show that the Cu_2CdSnS_4 thin film exhibits large agglomeration of grains, idea band gap (E_g=1.45eV) and high optical absorption coefficient ($>10^4cm^{-1}$).

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Keywords: Cu_2CdSnS_4; Thin film; Solution method; Sulfurization

1. Introduction

In recent years, there has been a great deal of interests in research of chalcopyrite semiconductors due to their suitable band gaps and high optical absorption coefficient for potential application in thin film solar cells [1-2]. Recently, the high power conversion efficiencies of solar cells based on Cu_2ZnSnS_4 and $Cu_2ZnSn(S, Se)_4$ as high as 8.4% and 10.1% have been reported [3-4]. Because Cu_2CdSnS_4 for structure analogues to Cu_2ZnSnS_4 has a band gap of 1.37eV and a large absorption coefficient over 10^4cm^{-1}, Cu_2CdSnS_4 is also considered as possible photovoltaic material.

A few works on Cu_2CdSnS_4 compounds have been reported. Cui *et al* [5] used a solvothermal process to synthesize Cu_2CdSnS_4 semiconductor nanorods with a wurtzite structure. Liu *et al* [6] characterized Cu_2CdSnS_4 colloidal nanocrystals with a tetrahedral coordinated structure by a facile solution chemistry method. The structure and optical properties of Cu_2CdSnS_4 nanoparticles were studied by Cao *et al* [7]. K. Ito *et al* [8] reported the preparation of Cu_2CdSnS_4 thin films by deposited using atom beam sputtering. However, all these reported methods involve some limitations, such as a long reaction time, complicated operations or high vacuum and so on. In this paper, we report a simple solution method to prepare Cu_2CdSnS_4 thin films deposited on glass, and investigate their structure, morphology, valence and optical properties. Based on the studies above, it is concluded that this approach may be more favorable for the preparation of Cu_2CdSnS_4 thin films as a new photovoltaic material.

*Corresponding author: guanhao@ycit.cn

2. Experimental details

Before the deposition of the precursor film, the glass substrate was firstly ultrasonically cleaned by acetone and then ultrasonically cleaned by de-ionized water. A mixed solution of $SnCl_2$ and $CuCl_2$ was used as the cationic precursor, and Na_2S solution was used as the anionic precursor. The concentration of $SnCl_2$, $CuCl_2$ and Na_2S in the solution was 0.03M, 0.06M and 0.05M, respectively. For the deposition process, a glass substrate was immersed in the cationic precursor solution where Sn^{2+} ions and Cu^{2+} ions were adsorbed on the substrate. After that the substrate was rinsed with de-ionized water to remove unabsorbed Sn^{2+} ions and Cu^{2+} ions from the substrate. Then the substrate was immersed in anionic precursor where S^{2-} ions diffuse from the solution in the diffusion layer and react with Sn^{2+} ions and Cu^{2+} ions. Further, rinsing again in de-ionized water to remove loose material from the substrate was followed. After 60 cycles of SILAR processes, the composite layer of (Cu, Sn) S was obtained.

Then $CdCl_2$ (0.1M), NH_4Cl (1M) and $CS(NH_2)_2$ (0.5M) were added in de-ionized water. Clear solution was formed after being stirred at room temperature for ten minutes, and proper ammonia were added to adjust the pH value of the deposition solution. After this, A glass substrate with the layer of (Cu, Sn) S was inserted into the solution, and the deposition takes place at 85 °C for 1 h.

After the deposition, the films were rinsed by de-ionized water and collected. Then they were annealed at 500 °C for 1h. During the annealing, the precursor was kept in an atmosphere of nitrogen and sulfur vapor.

The structure studies were carried out using a PANalytical X'Pert PRO diffractometer with Cu K_α radiation having wavelength λ=0.15406 nm and JY-T64000 Raman spectrometers. The microstructure was recorded using LEO-1530VP scanning electron microscope. X-ray photoelectron spectroscopy spectra were measured by Thermo Scientific Escalab 250. The optical characteristics were measured using Varian Cary 5000 spectrophotometer to calculate band gap energy.

3. Results and discussion

Fig.1 shows the typical XRD pattern of the annealed film. It can be seen that the XRD pattern matches well with the standard pattern of Cu_2CdSnS_4 (JCPDS NO.29-0537). The diffraction peaks at 2θ=22.5°, 27.9°, 32.2°, 36.2°, 40.5°, 46.5°, 54.7° and 56° can be attributed to the (110), (112), (200), (202), (114), (220), (312) and (116) plans of Cu_2CdSnS_4, respectively. From the XRD pattern of the Cu_2CdSnS_4 film, lattice parameters are calculated. The values of *a* and *c* are 5.428Å and 10.838Å, respectively. Comparing with standard bulk Cu_2CdSnS_4 powder data from JCPDS 29-0537, *a*=5.487Å and *c*=10.845Å, relative shifts of 1.07% and 0.06% are obtained. It is shown that the internal strain has no influence on the quality of the thin film due to low values, although it exists in the sample. The possible formation mechanism of Cu_2CdSnS_4 film can be explained by Equations. (1) - (3). At first, Cu^+ and Sn^{4+} can be obtained by SILAR method. Then Cu_2S reacted with SnS_2 to form Cu_2SnS_3. Finally Cu_2SnS_3 reacted with CdS, which can be obtained via chemical bath deposition, to form Cu_2CdSnS_4.

$$Cu^{2+} + Sn^{2+} \rightarrow Cu^{+} + Sn^{4+} \quad (1)$$

$$Cu_2S + SnS_2 \rightarrow Cu_2SnS_3 \quad (2)$$

$$Cu_2SnS_3 + CdS \rightarrow Cu_2CdSnS_4 \quad (3)$$

Through these reacting processes, the main impure phases in Cu_2CdSnS_4 are Cu_2SnS_3 and CdS. The structure of the annealed film was further investigated by Raman spectrum at room temperature. The inset in Fig.1 shows the Raman spectrum of the annealed film. From the Raman spectrum we can observe a very strong peak at about 333cm^{-1}, similar observation have not been reported previously, corresponding to Cu_2CdSnS_4. In addition, two weak peaks at about 286cm^{-1} and 304cm^{-1} are also observed corresponding to CdS and Cu_2SnS_3 phases, respectively, which cannot be confirmed by XRD due to low content.

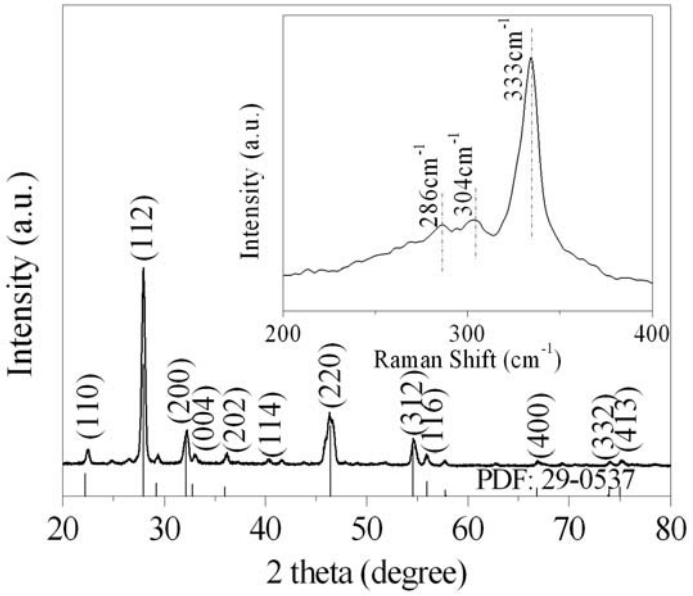

Fig.1 XRD pattern and Raman spectrum of the Cu_2CdSnS_4 film.

Fig.2 (c) and (d) shows the SEM images of the Cu_2CdSnS_4 film. For comparison, the SEM image of the precursor film (the (Cu, Sn) S/CdS film) is also shown. From Fig.2 (a) and (b), it can be seen that a large amount of microaggregate exist on the glass, which follows the hydroxide cluster mechanism. After the annealing, although the surface morphology is still coarse, large agglomeration of grains and few voids in the film are observed, which is beneficial in photovoltaic application. In addition, we also see that the grains are covered with cluster. The corresponding mechanics should be further analyzed.

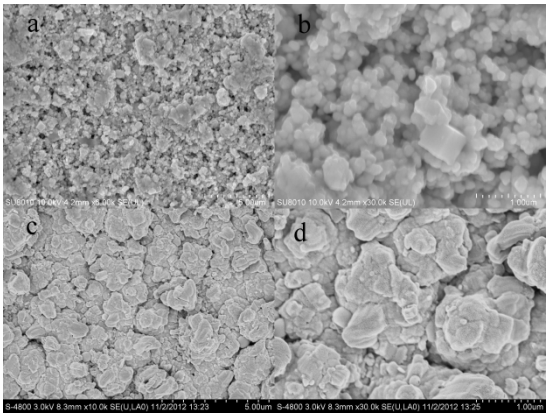

Fig.2 Low and high magnification SEM images of the (Cu, Sn)S/CdS film (a, b) and the Cu_2CdSnS_4 film(c, d).

Fig.3 shows the XPS analysis of the four constituent elements of the Cu_2CdSnS_4 film. The copper 2p peaks located at 931.6eV and 951.5eV indicative of Cu (□) with a peak separation of 19.9eV in agreement with the standard separation of 19.8eV [9]. The cadmium 3d peaks located at 405.3eV and 412eV show a peak splitting of 6.7eV, in agreement with the standard splitting of 6.76eV, indicating Cd (Ⅱ) [10]. The tin 3d peaks located at 485.8eV and 494.2eV confirm Sn (Ⅳ) with a peak separation of 8.4eV [11]. The sulfur 2p peaks located at 161.2eV and 162.4eV in the spectrum consist with the 160-164eV range for S in sulfides [12].

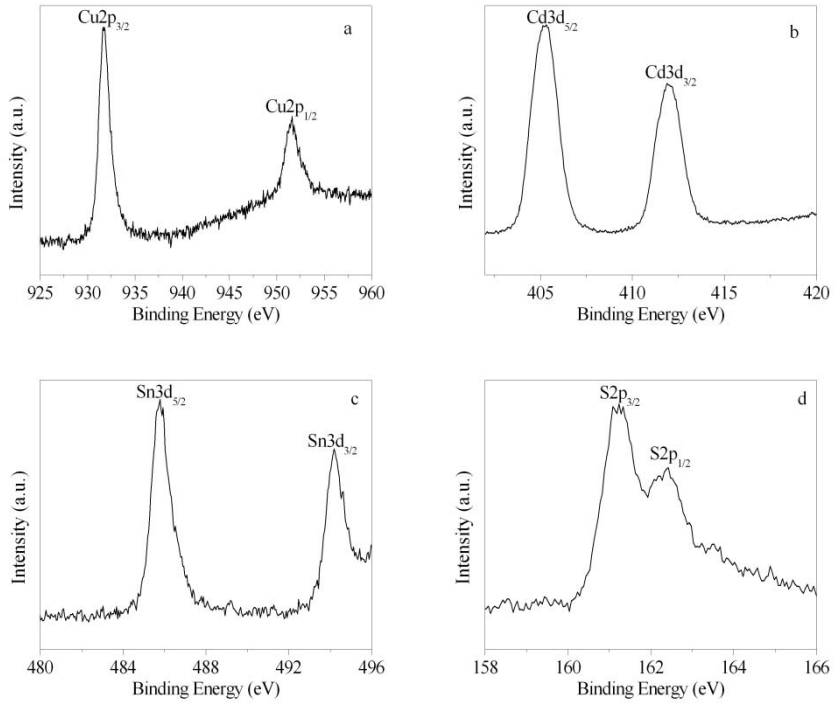

Fig.3 The XPS spectra of the Cu_2CdSnS_4 film: (a) Cu2p; (b) Cd3d; (3) Sn3d; (4) S2p.

The optical absorption coefficient versus the photo energy of the Cu_2CdSnS_4 film is shown

in Fig. 4(a). It can be seen that the annealed film has a large optical absorption coefficient, which is larger than $10^4 cm^{-1}$ in the visible wavelength region indicating the value is suitable for solar cell applications of thin films. The optical band gap energy of the Cu_2CdSnS_4 film can be estimated from the $(\alpha hv)^2$ versus hv graph by extrapolating the linear absorption edge part of the curve. The result shows that the optical bandgap of the Cu_2CdSnS_4 film is around 1.45eV as shown in Fig. 4(b).

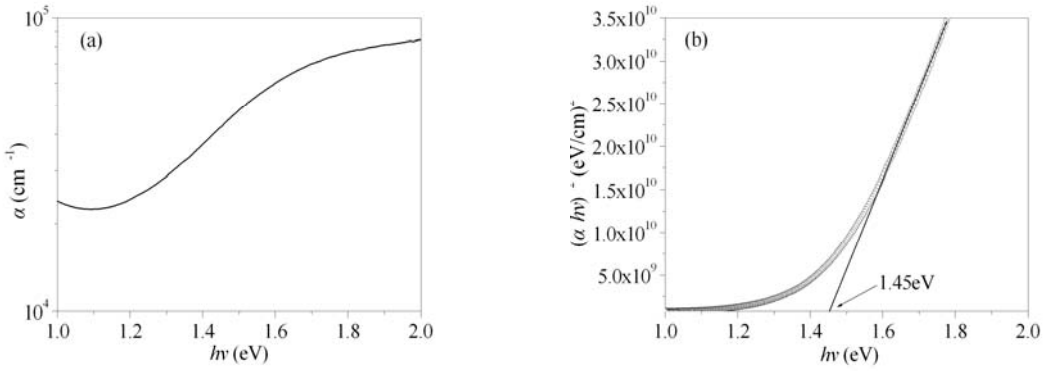

Fig.4 (a) Optical absorption coefficient curve (b) Optical bandgap estimation of the Cu_2CdSnS_4 film.

4. Conclusions

Cu_2CdSnS_4 film was prepared by a simple solution method. The precursor with the (Cu, Sn)S/CdS structure were prepared by a combination of the successive ionic layer absorption and reaction method and the chemical deposition method. After the sulfurization, Cu_2CdSnS_4 film was obtained. The optical band-gap of Cu_2CdSnS_4 film is around 1.45eV indicating the suitable optical properties for solar cell applications.

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