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Hall effect and surface characterization of Cu₂S and CuS films deposited by RF reactive sputtering

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Abstract

 Cu_xS is one of the most prevalent minor phases co-existing in $CuInS_2$ films. In order to understand its influence on $CuInS_2$, we first focus our study on the binary compound Cu_xS . Cu_2S , and CuS films were deposited on float glass substrates using a reactive RF sputter process with optimized sputter parameters, such as power, temperature of the substrate, and the gas flow of the H₂S. X-ray diffraction spectra showed that the Cu_2S films have (002) preferential orientation, and both compounds have a hexagonal structure. The surface morphology and the composition of the layers were analyzed by atomic force microscopy and Rutherford back-scattering spectroscopy, respectively. X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy were used to characterize the layer surfaces, as well as the surface composition. Hall-effect measurements were carried out to determine the electrical properties of the films. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

With a direct band gap of 1.55 eV and a high absorption coefficient of more than 10^4 cm^{-1} , CuInS₂ (CIS) has been regarded as a promising absorber for thin film solar cell applications [1]. So far, solar cells based on the CIS have achieved an energy total area conversion efficiency of 11.4% [2]. Cu_xS is one of the most prevalent minor phases co-existing in the CIS films independent from the production techniques and plays an important role both on the structural and electrical properties of the CIS. On the other hand, the Cu_xS (x = 1-2) thin films themselves are of interest due to numerous technological applications such as in applications of solar cells [3], in photothermal conversion of solar energy as solar

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absorber coatings [4], and as selective radiation filters in architectural windows [5], as well as in electroconductive coatings deposited on organic polymers [6]. So it is important and interesting to study Cu_xS films from both points of view.

Up to date, several methods have been used to produce CIS and Cu_xS films [1,7]. The sputtering technique has the potential for industrial applications due to its advantages of simple and flexible control of the film stoichiometry over a large scale at relatively low cost. The initial goal of this work is to deposit CIS films by radio frequency (RF) reactive sputtering in one step. Prior to this, Cu_xS films have been prepared by the same process for comparison.

2. Experimental

 $Cu_x S$ films were prepared on bare float glass substrates by a reactive sputtering process. High-purity

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(99.999%) argon was used to provide the plasma at a base pressure of 10^{-6} Torr, and H₂S (purity: 98.0%) was injected as reactive gas during the sputtering. A metallic 99.999% Cu circular plate with a diameter of 10.16 cm was used as the sputter target. The RF power was in the range between 50 and 300 W (0.62–3.70 W cm⁻²), while the H₂S flow was varied from 2.0 to 10 sccm. The substrate temperature was changed from room temperature to 500°C. Typically the film thickness was in the range between 50 and 600 nm mainly depending on the sputtering power and time.

The structure of the layers was studied by X-ray Diffraction (XRD) using a Siemens D5000 diffractometer with $\text{Cu} K_{\alpha} (\lambda = 1.5418 \text{ Å})$ radiation. The surface morphology of the layers was studied by atomic force microscopy (AFM). Photoemission (XPS, UPS) experiments were performed using a VG ESCA system at a photon energy of 1253.6 eV (Mg K_{\alpha} radiation). The sample surface was sputtered with 4 kV Ar ions. The electrical properties, such as the carrier concentration, Hall mobility, and specific resistivity of the films were characterized by Hall-effect measurements in the temperature range between 77 and 400 K.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD spetra of θ -2 θ mode of three samples, and the standard JCPDS patterns of Cu, Cu₂S and CuS for comparison. It is clearly seen that pure Cu co-exists in the film when the H₂S flow is too low (Fig. 1a). The pure Cu₂S films with hexagonal structure can be obtained when the H_2S flow is sufficient, i.e. in the range of 5.0-9.0 sccm. These films have highly (002)preferential orientation (Fig. 1b), since only reflections from the (002), (004), and (006) planes are detected by the XRD. The full-width at half-maximum (FWHM) of the (004) diffraction peak is about 0.24° , which means the crystallinity of the films is very good. In our experiments, the main parameter for controlling the Cu/S ratio of the films is the H₂S flow, as well as the sputter power. By increasing the H₂S flow and decreasing the sputter power at the same time, pure CuS films with hexagonal structure were deposited (see Fig. 1c). These films are randomly distributed polycrystalline films.

3.2. Atomic force microscopy and scanning electron microscopy

The Cu cones segregation on the surface of the samples sputtered with insufficient H_2S flow can be directly observed by scanning electron microscopy



Fig. 1. The XRD spectra of samples sputtered under different conditions. Sample (a) was sputtered at 500°C with a sputter power of 200 W and H_2S flow of 3.5 sccm; sample (b) was sputtered at room temperature with a sputter power of 200 W and H_2S flow of 8.0 sccm; and sample (c) was sputtered at 200°C with a sputter power of 50 W and H_2S flow of 10.05 sccm.

(SEM) as shown in Fig. 2a. This confirms the XRD measurement on the same sample (Fig. 1a). Both pure Cu_2S and CuS films have very good crystallinity, which is not only indicated by the XRD measurements, but also directly supported by the AFM images of the surface of the samples (see Fig. 2b–e). While the Cu₂S film has an average grain size of about 200 nm, the CuS films show relatively smaller grains of around 80 nm, which is mainly due to the relatively lower sputter power. Compared with the CuS films, the Cu₂S films show more uniform and well-grown columnar grains on the surface.

3.3. XPS and UPS characterization

For surface characterization, XPS and UPS studies of Cu_xS samples with varying *x* values were carried out. The spectra were obtained from films cleaned by a short Ar^+ ion etching prior to the measurement to remove the surface contaminants. Two different samples were chosen for comparison: a CuS film with a Cu/S ratio of 1:1 and another with a Cu/S ratio of 3:2. These stoichiometry values were calculated by quantitative analysis of the XPS-spectra (Fig. 3a and b).

The UPS spectra of these two films are shown in Fig. 3c. The most striking difference is a shift of curve A (stoichiometric CuS) towards lower binding energies.



Fig. 2. The SEM and AFM images of the surface of different samples. (a) The SEM image of Cu cones on the surface of sample (a) of Fig. 1; (b) two-dimensional and (c) three-dimensional AFM images of sample (b) of Fig. 1; (d) two-dimensional and (e) three-dimensional AFM images of sample (c) of Fig. 1.

The valence band maximum reaches the Fermi energy at 0 eV, indicating the metallic properties of the film. Curve B (Cu-rich sample) is clearly recognizable as semiconducting due to its gap of 0.5 eV between the valence band maximum and the Fermi energy. The XPS spectra (Fig. 3a and b) show the same shift switching from the metallic to the semiconducting state.

3.4. Hall-effect measurements

Hall-effect measurements were carried out to study the electrical properties of the Cu_2S and CuS films. The carrier (hole) concentrations, Hall mobilities, and specific resistivities of the Cu_2S films range from 1×10^{18} to 3×10^{19} cm⁻³, 10 to 4 cm² V⁻¹ s⁻¹, and 0.8 to 0.04 Ω cm, respectively, within the temperature interval from 90 to 400 K. At room temperature, the values are 1.0×10^{19} cm⁻³, $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and 0.1Ω cm, respectively, which is in agreement with the results of Ref. [8]. In principle, the hole concentration *p* is dependent on the temperature by

$$p \propto \exp\left[-\Delta E_{\rm A}/kT\right],\tag{1}$$

where ΔE_A is the activation energy of the acceptor, k is the Boltzmann constant, and T is the temperature. A semi-log plot of the hole concentration versus the reciprocal temperature for a typical Cu₂S film is



Fig. 3. The XPS spectra of Cu 2p (a) and S 2p (b) peaks, and the UPS spectra (c) of two films: A: CuS and B: Cu₃S₂.



Fig. 4. The temperature dependence of the hole concentration of the Cu_2S films.



Fig. 5. The temperature dependence of the specific resistivity of the CuS films and Cu_2S films.

presented in Fig. 4. Three activation energies can be estimated as 106 ± 5 , 38 ± 2 , and 4 meV, respectively. The first two are in line with the results given by Ref. [8], and may be related to intrinsic acceptors i.e. the Cu vacancies. The small activation energy observed at low temperatures indicates hopping transport.

Compared with Cu₂S, CuS has a much higher carrier concentration (hole) of around 10^{22} cm⁻³, which results in a remarkably lower resistivity of about $10^{-4} \Omega$ cm. The resistivity increases with temperature slightly and almost linearly (see Fig. 5), which is the typical characteristic of the metallic phase, in good agreement with the XPS and UPS results. The CuS film has a lower Hall mobility than the Cu₂S in the range of 1-4 cm²V⁻¹ s⁻¹ mainly due to the higher carrier concentration.

4. Conclusion

Cu₂S and CuS films with good crystallinity have been deposited on bare float glass substrates by RF reactive sputtering. Both films have hexagonal crystal structures at RT as studied by the XRD. Typically Cu₂S films are highly (002) oriented with the FWHM of the (004) peak of about 0.24°. There are Cu precipitate cones coexisting in the Cu₂S films when the H₂S flow during sputtering is not high enough. Two activation energies related to the intrinsic defects in the Cu₂S films have been found by Hall-effect measurements. The CuS is in the metallic phase at RT, and has a relatively high carrier concentration around 10^{22} cm⁻³, a much lower resistivity of about $10^{-4}\Omega$ cm, and a slightly lower Hall mobility of about $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared with the semiconducting phase Cu₂S.

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