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Characterization of RF reactively sputtered Cu–In–S thin films

Y.B. He*, A. Polity, R. Gregor, D. Pfisterer, I. Österreicher, D. Hasselkamp, B.K. Meyer

I. Physikalisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, D-35392 Giessen, Germany

Abstract

The ternary compound semiconductor $CuInS_2$ has attracted much attention owing to its potential applications in photovoltaic devices. We deposit $CuInS_2$ films on float glass substrates by a reactive radio frequency sputter process using a Cu–In inlay target and H_2S gas in one step. The morphology of the films was studied by Atomic Force Microscopy, X-ray Diffraction was used to check the crystal structure of the films. The composition of the layers was determined by Rutherford Back-scattering Spectroscopy and Energy-Dispersive X-ray Analysis. The electrical properties of the layers, i.e. the carrier concentration, Hall mobility, and specific resistivity and their dependencies on temperature were investigated by Hall effect measurements.

Keywords: $CuInS_2$; Thin films; Photovoltaic; Defects

1. Introduction

Recently the ternary compound semiconductor $CuInS_2$ (CIS) has attracted much attention due to its potential applications in photovoltaic devices. Solar cells based on CIS with a total area efficiency of 11.4% have been demonstrated using a rapid thermal process [1]. Usually, Cu-rich films are grown for efficient solar cells, which leads to the formation of a CuS secondary phase on the film surfaces. This phase is subsequently removed by chemical etching with potassium cyanide (KCN). From In-rich films, on the other hand, in which $CuIn_5S_8$ or In_2S_3 secondary phases co-exist, it was not possible to produce efficient solar cell devices [2,3].

We try to prepare CIS films by a radio frequency (RF) reactive sputter process, using a Cu–In inlay target with H_2S as reactive gas in one step. The crystallinity of the as-sputtered films is studied by X-ray diffraction (XRD) measurements, which indicate that the films are highly (1 1 2) oriented CIS films. The composition characterization of the films by both Rutherford back-scattering spectroscopy (RBS) and energy-dispersive X-ray analysis (EDX) reveals that the films are extremely Cu-rich, i.e. the Cu to In ratio strongly deviates from 1. To resolve the contradiction between XRD and composition results, only the Cu–S binary compound has been sputtered in the same equipment using a pure Cu target and H_2S gas. XRD shows that the sputtered Cu_xS films are also highly oriented, and their XRD peaks are very close to that of as-sputtered "CIS" films. This indicates that the main phases of our "CIS" films are CuS and Cu_2S, which clarifies the problem mentioned above.

2. Experimental

Cu–In–S films were prepared on bare float glass substrates by a reactive sputter process with a conventional RF (13.56 MHz) sputter setup. High purity (99.999%) argon was used to provide the plasma at a base pressure of 10^{-6} Torr, and H_2S (purity: 98.0%) was introduced as reactive gas during the sputtering. A Cu metal disk inlayed by In with the area ratio Cu/In about 1 and diameter of 10.16 cm was used as sputter target. The RF sputter power was in the range between 100 and 500 W (1.23–6.15 W cm^{-2}), while the H_2S flow was varied from 3 to 10 sccm. The substrate temperature

*Corresponding author. Tel.: +49-641-99-33137; fax: +49-641-99-33119.

E-mail address: yunbin.he@physik.uni-giessen.de (Y.B. He).

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was changed from room temperature to 400°C. Typically the as-sputtered film thickness was in the range from 175 to 1000 nm within a sputter time between 5 and 30 min.

The structures of the layers were studied by XRD using a Siemens D5000 diffractometer with Cu K_α ($\lambda = 1.5418$ Å) radiation. Atomic force microscopy (AFM) was used to observe the surface morphology of the layers. The composition of the layers was analyzed by EDX (SiLi-detector with an ultrathin window (UTW) installed in a Philips XL20 SEM equipment) and RBS, respectively. The electrical properties of the films in the range between 77 and 400 K were characterized by Hall effect measurements.

3. Results and discussion

Fig. 1 shows the AFM images on the surface of a typical film, which was sputtered for 15 min at 200°C with a sputter power of 300 W and a H_2S flow of 8.0 sccm. The surface is smooth with the root mean square (RMS) roughness of 4.05 nm, which is derived by AFM, consisting of uniformly sized and densely packed grains. The columnar-shaped and well-grown grains are distributed with an obviously preferential orientation as shown in Fig. 1a and b, which is also revealed by XRD measurements (see below).

A typical XRD spectrum of sputtered film is shown in Fig. 2a. There are only three diffraction peaks appearing at 2θ of 27.80°, 54.40°, and 57.40°, which seem to correspond to the (1 1 2), (1 1 6), and (2 2 4) peaks of CIS, respectively, as compared with the standard CIS pattern: Joint Committee on Powder Diffraction Standards (JCPDS) file 27-0159. It seems that the film is a nearly stoichiometric CIS film with a (1 1 2) preferential orientation in accordance with AFM measurements described above. However, the composition analysis as examined by RBS shows a surprising result—the film is extremely Cu-rich, and there is only very little In content in the film with Cu 49%, In 4%, S 47%, respectively (see Fig. 3a). To be sure, EDX measurements (Fig. 3b) have been carried out from the cross section of the same sample. A comparable result with RBS has been obtained: Cu 50%, In 8%, S 42%, respectively, which means that the In content is too low throughout the whole layer, not only in the surface region, but also in the bulk material. Usually, for Cu-rich CIS films deposited by other techniques, there is only In deficiency on the surface due to secondary phases such as CuS and Cu_2S segregations [2]. However, our sputtered films are completely non-stoichiometric CIS with a low In content through the whole layer in a way contradicting with the XRD measurements.

In order to clarify the problem, Cu–S binary compound films were sputtered with identical parameters for comparison. As can be seen in Fig. 2b the as-sputtered Cu_2S film is completely oriented with (0 0 2) plane parallel to the substrate, and its (0 0 2), (0 0 4) diffraction peaks overlap exactly with two peaks of "CIS" around 26.45° and 54.40°, which means the formerly identified "CIS" (1 1 6) peak actually originates mainly from Cu_2S (0 0 4). Similarly, comparing the XRD of the "CIS" film with that of CuS, one can clearly see that the formerly identified "CIS" (1 1 2) and (2 2 4) peaks are mainly from CuS (1 0 1) and (2 0 2) peaks, respectively. Now, our puzzle about the conflict between XRD and composition measurements has been clarified. The sputtered "CIS" films consist of three phases: CuS, Cu_2S, and $CuInS_2$, and the In to Cu ratio strongly deviates from 1. Although in Ref. [4] it is reported that

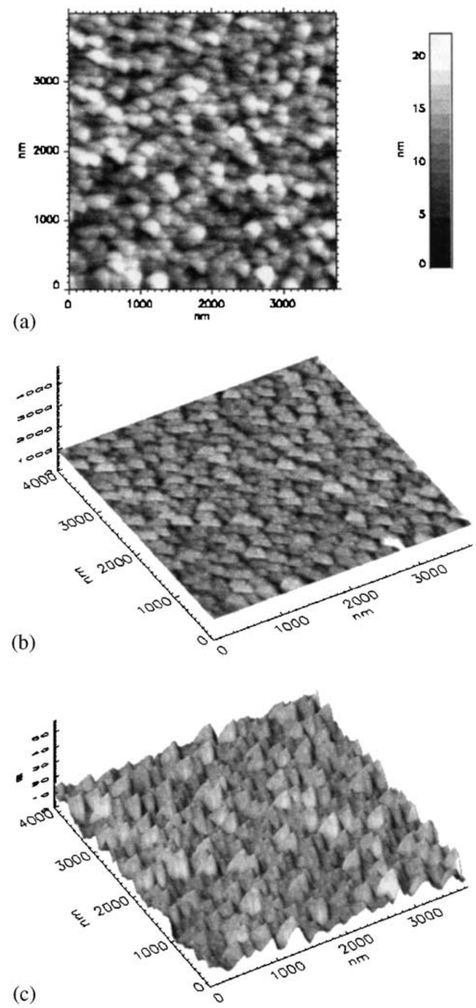

Fig. 1. AFM images on the surface of a typical as-sputtered film. (a) Top view (two-dimensional). (b) Three-dimensional image with the same Z scale as X, Y. (c) Three-dimensional image with the Z scale from 0 to 60 nm.

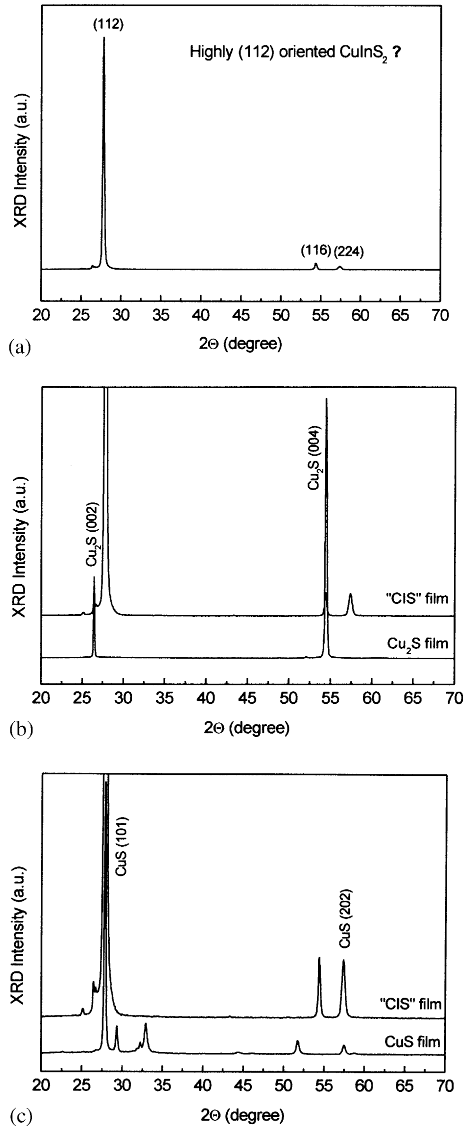

Fig. 2. (a) Typical XRD spectra of an as-sputtered "CIS" film; (b) Comparison of XRD spectra of sputtered a "CIS" film and a Cu_2S film; (c) Comparison of XRD spectra of sputtered a "CIS" film and a CuS film.

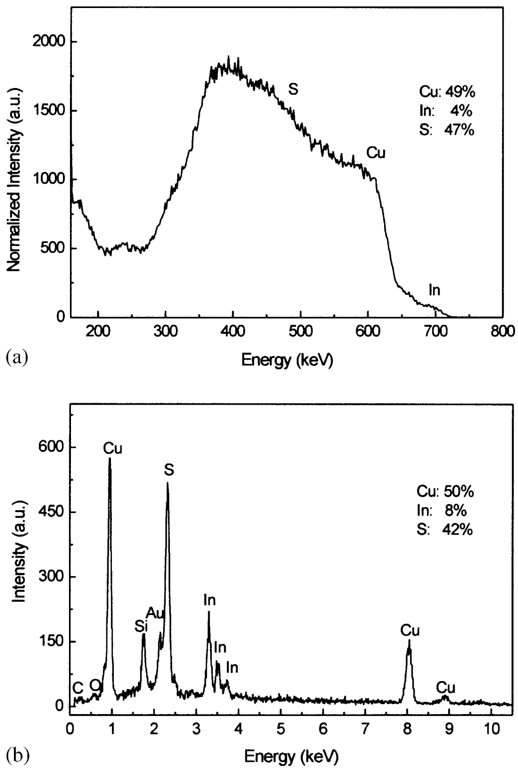

Fig. 3. Composition characterization of a typical film by (a) RBS and (b) EDX.

stoichiometric CIS films can be produced by a DC reactive sputtering process using a fan-shaped Cu and In metal target with CS_2 introduced as reactive gas, according to our experiments, it is hardly possible to deposit stoichiometric CIS films by a reactive sputtering process using a Cu–In inlay metallic target with a H_2S gas flow. We noticed that there is a black-colored top layer covering the surface of the In inlay after the target has been sputtered for several ten times. We speculate it is an In–S compound due to the reaction of the metallic In with the H_2S gas during sputtering. This top layer on the In inlay reduces the sputter rate of In, and results in a considerably lower In/Cu ratio in the sputtered films. So the In/Cu ratio in the sputtered films not only depends on its area ratio in the target, but is also influenced by the H_2S flow amount and period. Therefore, the content of Cu and In in the layers may strongly and in a delicate way deviate from its original ratio in the target. By using a Cu–In alloy target instead of the inlay target the problem described above has been overcome, and nearly stoichiometric CIS films have been deposited by the same sputtering process [5].

Characterization of the electrical properties of the films were done by Hall effect measurements. In general, the carrier concentration, Hall mobility and specific resistivity of the sputtered Cu-rich "CIS" films are in the range between 3.55×10^{17} to $1.58 \times 10^{19}\,cm^{-3}$, 4.15 to $1.15\,cm^2\,V^{-1}\,s^{-1}$, and 4.24 to $0.35\,\Omega\,cm$, respectively, for temperatures between 77 and 350 K. Compared with stoichiometric CIS single crystals and thin films, the Cu-rich "CIS" films have hole concentrations 2–3 orders of magnitude higher [6,7]. This is partly due to CuS and Cu_2S phases co-existing in the films. It is known that CuS is metallic at room temperature (RT) with a hole concentration of about $10^{22}\,cm^{-3}$. Cu_2S is a semiconductor but can have also relatively high hole

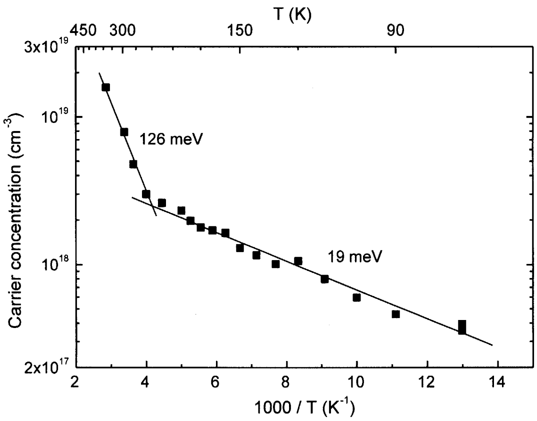

Fig. 4. The temperature dependence of carrier concentration of a sputtered Cu-rich "CIS" film.

concentrations around $10^{19}\,cm^{-3}$ at RT [8,9]. By a linear fit to the carrier concentration dependence on temperature (Fig. 4), two thermal activation energies of 126 ± 4 and $19 \pm 2\,meV$ can be deduced.

4. Summary and conclusions

Cu rich Cu–In–S films with good crystallinity were deposited on float glass substrates by a RF reactive sputter process using a Cu–In inlay target with H_2S as reactive gas in one step. The In/Cu ratio in the sputtered films is much less than 1 although its ratio is nearly 1 in the target. It not only depends on the different sputter yield of In and Cu, but is also influenced by an additional layer covered on the surface of the In inlay due to the reaction of H_2S and In inlay during sputtering. The sputtered film consists of CuS, Cu_2S, and $CuInS_2$ phases, which results in a strong deficiency of In in the layer. It is not always reliable to characterize the composition by XRD only. The combination with other kinds of methods for composition examination is necessary, especially when the film is highly oriented and only very few diffraction peaks show up in the XRD spectrum. The hole concentrations of the as-sputtered Cu-rich "CIS" films range between 3.55×10^{17} and $1.58 \times 10^{19}\,cm^{-3}$, for temperatures between 77 and 350 K. The carrier concentration can be tuned from 10^{19} to $10^{17}\,cm^{-3}$ by using a Cu–In alloy target as shown in Ref. [5]. From the sputtering process there is still enough freedom to produce CIS films appropriate for solar cells.

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