Structural, optical and electrical properties of CuInSe2 solar cell films on Al, Cu, Poly-Si, SFO and Steel substrates

XIN JI[*], ZHI YAN[a], YIMING MI, CHAO MIN ZHANG
College of Fundamental Studies, Shanghai University of Engineering Science, Shanghai 201620, China
[a]College of Material Engineering, Shanghai University of Engineering Science, Shanghai 201620, China

Solar cell absorption layer based on $CuInSe_2$ films were successfully deposited on Al, Cu, Poly-Si (111), SFO and Steel substrates by magnetron RF-sputtering. The effect of the substrate materials on the film structures, morphologies, and properties was investigated in detail. The results indicated that substrate material was the key deposition parameter influencing the CIS film phase composition, which directly affected its photoelectric activity. The structure shapes and grain sizes were slightly different in the films on different substrates. Moreover, the CIS film on Cu substrate shows better electrical behavior than other films. Finally, the optical measurements suggest that the optical properties were affected by lattice defects and secondary phases on the various substrates.

Over the last few years, a great attention has been focused on the $CuInSe_2$ films due to its chalcopyrite structure, which is a promising material for thin film solar cells because of its extraordinary radiation stability [1]. Besides, $CuInSe_2$ films possess certain exceptional material characteristics including band-gap, absorption coefficient and minority carrier diffusion length which are particularly suitable for photovoltaic applications. $CuInSe_2$ thin films have been prepared by several methods such as r.f.sputtering [2], spray pyrolysis [3], co-evaporation [4], chemical bath deposition [5] and electrodeposition [6].

There are two different crystalline phases of $CuInSe_2$ namely chalcopyrite and tetragonal. Among them, the chalcopyrite structure is referred to be the most photoelectric structure [7]. However, the deposition of crystalline photoactive $CuInSe_2$ films without the substrate heating or a post-deposition thermal annealing has not been fully mastered yet. Among numerous deposition methods[8, 9], the magnetron sputtering is a promising one for the deposition of crystalline chalcopyrite $CuInSe_2$ films at the sputtering temperature (lower than 200 °C).

It is well known that properties of $CuInSe_2$ films are strongly dependent on the preparation methods and deposition parameters [10,11] due to obtained stoichiometry and microstructure. For this reason, it is essential to characterize their properties according to the deposition parameters.

In this work, it is presented the influence of the sputtering growth parameters such as substrate materials on the structures and on the optical properties of $CuInSe_2$ films. The acquired results and related discussions would be feasible for their potential applications.

1. Experiment

1.1 Synthesis of CuInSe2 thin films

The solar cell was prepared by a reverse-order method (Transparent electrode/ $CuInSe_2$/CdS/Black electrode). The absorbed layers ($CuInSe_2$ films) were deposited by RF-sputtering in argon gas atmosphere on the various substrates (Al, Cu, Poly-Si (111), SFO (SnO_2: F) and Steel). Substrates were ultrasonically and chemically cleaned in organic solvents. A cylindrical $CuInSe_2$ (Cu: In: Se = 1:1:2) ceramic target of 8.0 cm diameter was used. No changes in target composition where observed with time and usage. Deposition was performed at a sputtering temperature of 200 °C for 120 min. Finally, all the samples were deposited at a working gas pressure (argon) of 0.5 Pa and a RF power of 100W. The process parameters of CIS films used in RF magnetron sputtering are shown in Table 1.

Table 1. Sputtering parameters of $CuInSe_2$ films.

Sample	Substrate	Sputtering power / (W)	Sputtering temperature / (°C)
a	Al	100	200
b	Si (111)	100	200
c	Cu	100	200
d	SFO	100	200
e	Steel	100	200

1.2 Characterizations of CuInSe2 films

Optical properties were determined from measurements of optical transmittance at room temperature with unpolarized light at normal incidence in the photon energy range of 1.1-6.6 eV. The resistivity calculated from the sheet resistance measured by a four-point probe. To investigate crystallographic properties of the films, coupled θ-2θ X-ray diffraction (XRD) scans in the film mode were performed in the range of 2θ=20°-80° by use of the Cu Kα1 line of the X-ray source (Rigaku D/max2550). The surface morphologies of films were examined by scanning electron microscopy (SEM-3400-N).

2. Results and discussion

2.1 Structural studies of CuInSe$_2$ films

Fig. 1 shows the XRD patterns of CIS films deposited on different substrates at 200℃ by magnetron RF- sputtering. It is observed in Fig. 1 that two structures phase occurred in SFO-sub film. The chalcopyrite structure is mainly confirmed by the (1 1 2), (2 2 0) and（2 1 1）diffraction peaks at 2 theta = 26.7°, 34.2° and 38.6°, which followed by a tetragonal structure confirmed by (301) and (310) peaks at 2 theta = 48.6°, 51.8°[12]. As this peak is high and sharp, we believe that the film is composed of random large crystal grains because of the high energy for surface atoms to diffuse at the temperature (200°C).

When the materials (Steel, Al, Cu) are used to deposit the films, only three characteristic peaks (1 0 5), (3 1 0) and （3 0 1）are displayed in these samples, indicating that single phase (tetragonal structure) appeared in these films. But when the Si is chosen as a substrate, the crystalline quality of the films is degraded. No peaks but Si (111) peak can be found in this films on this substrate which means that amorphous structure appears. It can be interpreted by that the lattice constant of obtained films are different from the films on other substrates.
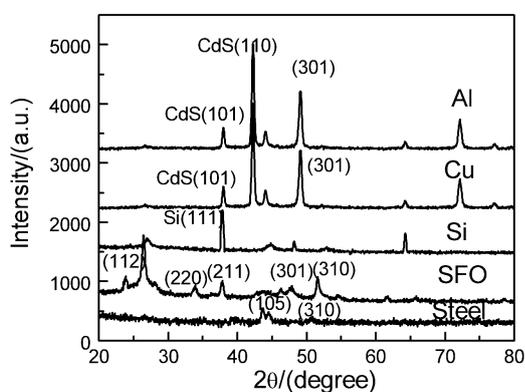
2.2 Morphological studies of CuInSe$_2$ films

Fig. 2 (a-e) shows the SEM images of the CIS films deposited on different substrates. The images were measured with a scanning area of 1 μm. It can be found that the CIS films deposited on the Al substrates have better crystalline grains with a clear grain boundary, and the fluctuation of the film surface is big. Also, the CIS film surface has many crystalline grains with a hexagon structure, and its surface roughness is larger than that of the film deposited on the other substrates. It is due to the indium incorporation in the CIS decreases at thedesposited temperature (200℃), thereby increasing the lattice mismatch between the CIS epitaxial layer and the Al substrate [13].

As a substrate material of the CIS film, Si has a large thermal conductivity. The mobility of the atoms on the Si substrate surface is larger than that of the adatoms on the SFO and Cu substrates. Thus, the size of the crystalline grains deposited on the Si substrate is larger than that on the other substrates. Also, the grains show an oval structure and the film is rough. Although the Si substrate has a high surface energy in the early stage of the formation of the thin film, the incident atoms have enough kinetic energy to form the atomic groups at a low surface energy position of the substrate.

SFO and Cu are metals with a low surface energy, while CIS has a high surface energy. The film exhibits a well crystallized, uniform and dense microstructure. It can be explained that CIS atoms are only absorbed onto the heated substrate at the low deposited temperature, when the incident atoms arrive at the surface of the substrates (SFO and Cu), they can diffuse and migrate on the substrate surface and thus produced a uniform adherent layer [14].

Steel is an unstable metal. During the process of the CIS growth on the Steel substrate, Steel atoms are able to diffuse into the film, which causes some holes at the interface between the film and the substrate. For the crystallization on Steel substrate, the smaller grain size of the CIS could be attributed to an abundance of nucleating sites based on the large number of defects such as dislocations, vacancies, and stacking faults within the films [15].

Fig. 1. XRD patterns of CuInSe$_2$ films prepared on various substrates.
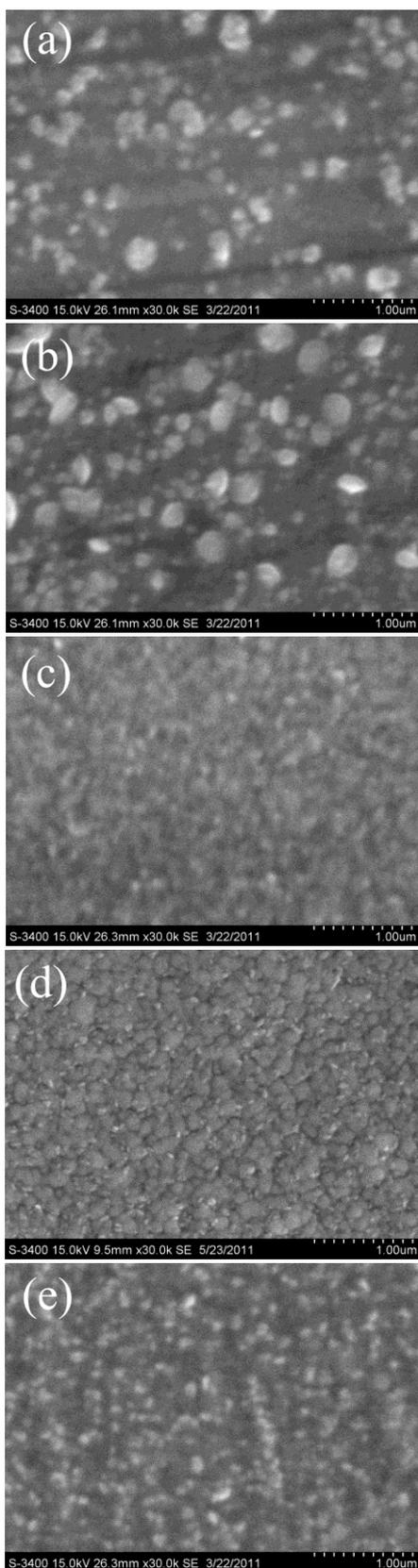
Fig. 2. SEM images of cross sections in CuInSe₂ films deposited on various substrates: (a) Al; (b) Si; (c) Cu; (d) SFO; (e) Steel

2.3 Electrical properties of CuInSe₂ films

Fig. 3 illustrates the resistivity calculated from the sheet resistance measured by a four-point probe for CIS films on different substrates. It was found that CIS films prepared at Cu and Al substrates exhibited the lower resistivity at a value of 4.68 and 12.49 kΩ.cm, therefore suggested that the conductivity of these films are higher. However, the value of current was found to decrease in SFO-sub and Si-sub films. One of the reasons for such a behavior may be due to the presence of well crystallized grains in such films. On the other side, defects apparently tended to segregate out of the CIS more rapidly [16].

Moreover, the highest resistivity 171.69 kΩ.cm in Si-sub films as shown in Fig. 3. The reduction of the electrical properties of the films was associated with number of cavities and large-angle grain boundaries, which will increase charge carrier scattering and results in decrease of carrier mobility [17].
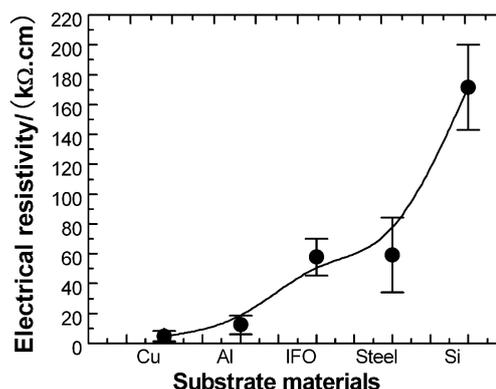
Fig. 3. The resistivity curves of CuInSe₂ films deposited on various substrates

2.4 Optical properties of CuInSe₂ films

Fig.4 shows the spectra curves of CIS films on different substrates in the wavelength range 200-1100 nm. It can be found in Fig.4 that the optical transmittance spectra of the SFO-sub films exhibited good transmission in the visible region and a sharp fall in the region, perhaps the improved transmittance is associated with the enhanced crystallinity of the CIS films compared with Al and Steel-sub films.

Moreover, it also can be found that the optical transmittances of the CIS films on the other substrates (Al, Cu, Si and Steel) were slightly degraded in the 400-550 nm range. This is attributed to the increase in free-carrier-like absorption due to lattice defects and secondary phases, which can produce the observed increase of the sub-band gap absorption in the visible light wave [18].
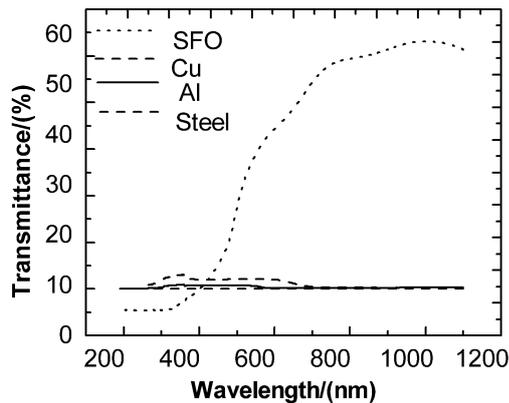
Fig. 4. Transmittance spectra curves of CuInSe$_2$ films deposited on various substrates.

3. Conclusions

1) The XRD patterns show that the CIS films on SFO substrates were found to exhibit chalcopyrite and tetragonal structures while that of (Steel, Al, Cu) substrates appear single phase (tetragonal structure). Also, the lattice constant of obtained films on Si are different from the films on other substrates.

2) The result of SEM morphologies indicated that the structure was changed from hexagon shape to oval shape due to the difference of surface energy and lattice mismatch between Al and Si substrates. However, the films on SFO and Cu exhibit a well crystallized, uniform and dense microstructure.

3) The resistivity curves observe that the electric conduction of CIS films on Cu and Al substrates show better electrical behavior than other films. The value of current was found to decrease in SFO-sub and Si-sub films, which may be due to the presence of well crystallized grains and defects in such films.

4) The optical transmittance spectra suggest that the SFO-sub films exhibited better optical properties than the other substrates. It is concluded that not only the lattice defects but also secondary phases affected the optical properties of CIS films.

Acknowledgements

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*Corresponding author: jixinyouxiang1@yahoo.com.cn