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Effects of deposition pressure on Cu_2ZnSnS_4 films prepared by one-step sputtering with quaternary target

H.G. Yang [1,2,]*, J.D. Zhang [2], M.C. Li [1]*, R.T. Hao [3], G.L Song [2]

[1] *College of Renewable Energy, North China Electric Power University, Beijing 102206, China*
[2] *College of physics and materials scientific, Photovoltaic Materials Laboratory of Henan Province, Henan normal university, Xinxiang 453007, China*

[3] *Solar Energy Research Institute of Yunnan Normal University, Kunming 650092, China*

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Cu_2ZnSnS_4 (CZTS) films were deposited from single-phase Cu_2ZnSnS_4 quaternary compound target by RF sputtering without post sulfurization process. The as-prepared CZTS films were annealed with 400°C in Ar atmosphere to obtain the single-phase kesterite structure. The influence of sputtering pressure on surface morphology, crystal structure, optical absorption coefficient, band gap, and the influence of the chemical composition of CZTS films was investigated. The diffraction peaks of (112) are sharp and the characteristic peaks of the kesterite-type structure such as (220) and (312) are clearly observed in X-Ray Diffraction patterns. The composition and optical properties of the samples were determined with energy dispersive X-ray spectroscopy (EDS) and UV-VIS-NIR spectrophotometer. While at the sputtering pressure of 0.2 Pa, an attractive Cu-poor and Zn-rich, large grain size and single-phase CZTS film can be obtained. Research result show that the CZTS films exhibit a high absorption coefficient of the order of 10^4 cm^{-1}, and an optical band gap of 1.49 eV.

Keywords: Cu_2ZnSnS_4 (CZTS) thin film, Crystal structure, Band gap, Magnetron sputtering, Sputtering pressure.

INTRODUCTION

Copper zinc tin sulfide (Cu_2ZnSnS_4, CZTS) quaternary semiconductor is emerging as a potential candidate that has several promising attributes for efficient, inexpensive solar cells made from abundant and nontoxic elements. CZTS compound is derived by replacing indium (In) and gallium (Ga) elements with zinc (Zn) and tin (Sn) elements in the chalcopyrite-type lattice of $Cu(In,Ga)Se_2$ (CIGS). The band gap of CZTS has been reported to be about 1.5 eV, very close to the top absorbent layer band gap of the solar cell that results in a theoretical efficiency limit more than 32% [1-4]. The absorption coefficient of CZTS rises rapidly above the band gap energy and quickly reaches over 10^4 cm^{-1} so that a few microns thick film can absorb nearly all the solar radiation above the band gap. CZTS thin film solar cells have reached an efficiency of 8.6% and those based on a $Cu_2ZnSn(S,Se)_4$ absorber layer have reached an efficiency of 11.6% [5,6], demonstrating the promising prospect of the CZTS technology. However, there are no detailed reports on the study of CZTS cells in the past years due to the lack of complete understanding of the parameters governing the low-efficiency performance.

To simplify the preparation procedure, a straightforward one-step deposition of CZTS films by magnetron sputtering without post-annealing treatment has been explored. In this process, deposition parameters such as sputtering energy, substrate temperature and gas pressure could affect the film properties [7,8]. Sputtering pressure is one of the most important factors which affect the phase formation and morphology of the films by controlling the diffusion, aggregation and growth behaviors of deposited particles. In this work, polycrystalline CZTS films were deposited from single-phase Cu_2ZnSnS_4 quaternary compound target at different sputtering pressures by one-step radio frequency (RF) sputtering. The crystal structure, chemical composition, surface morphology and optical properties of CZTS films were examined.

EXPERIMENTAL DETAILS

Cu_2ZnSnS_4 thin films were directly deposited on glass substrates with a CZTS ceramic target by radio frequency magnetron sputtering process. The CZTS target used was composed of kesterite-structure Cu_2ZnSnS_4 powder through cold pressure method at 40MPa, the atomic ratios of the elements Cu, Zn, Sn, S was 2:1:1:4. Glass substrates were thoroughly cleaned with acetone and ethanol. Sputtering process was carried out in pure argon (99.99%) atmosphere with a substrate at room temperature. The distance between target and substrate was 15 cm and RF sputtering power was

* To whom all correspondence should be sent.
E-mail: : hgyang@htu.cn

70 W. Deposition pressure was maintained at 0.2 Pa, 0.3 Pa and 0.5 Pa, respectively. The total deposition time of the CZTS films was 60 min. The as-prepared CZTS films were annealed at 400°C in Ar atmosphere for 180 min.

The crystal structure of both target and thin films deposited on glass substrates were characterized by X-ray diffractometry (XRD, DX-2000). The surface morphology and composition of samples were determined by scanning electron microscopy (SEM, FEI Quanta FEG 250) and energy dispersive spectroscopy (EDS, FEI Quanta FEG 250). The optical reflectance and transmittance spectra were measured by UV-VIS-NIR spectrophotometry (Shimadzu UV-3600).

RESULTS AND DISCUSSION

Table 1 summarizes the chemical composition of CZTS thin films as a function of deposition pressure in the range from 0.2 to 0.5 Pa. The quaternary CZTS ceramic target used in this one-step sputtering process was a stable kesterite phase in which the sulfur element was well bonded to other elements. During the sputtering process, four elements were simultaneously sputtered by Ar ions and arrived on unheated substrates to directly form CZTS thin films. Energy dispersive spectroscopy (EDS) measurement results showed that all film compositions strongly depend on the sputtering pressure of the grown CZTS film. The spontaneously developed CZTS films on the unheated substrates by sputtering from a quaternary CZTS target provided a simple route to prepare CZTS absorbers with effective utilization of sulfur. It was found that the stoichiometry of quaternary CZTS films is easily controlled by the single-step sputtering deposition, and the composition of the as-grown films could be adjusted with changing the sputtering parameters [9-10]. The ratios of Cu/(Zn +Sn) and Zn/Sn of the thin film fabricated at different sputtering pressures were in the range of 0.54−0.78 and 0.69−0.80, respectively. On decreasing the sputtering pressure, the proportion of copper was gradually reduced, but Zn and Sn ratio was gradually increased, which indicates that the sputtering pressure drop will exacerbate the loss of Cu element. For the efficient absorption of the CZTS thin film solar cell, the ratio of [Cu]/([Zn]+[Sn]) was between 0.7~1.0, and [Zn]/[Sn] - between 1.0~1.4, this would dominate the conversion efficiency of CZTS thin film solar cell [9,11,12]. It is believed that the increase in the proportion of S and Zn in the target material may bring the chemical composition of the samples close to the expected value.

Fig. 1 shows the XRD patterns of the CZTS targets and the CZTS thin film samples. The diffraction peaks of CZTS targets are consistent with the diffraction peak of kesterite structure of CZTS. The four diffraction peaks at 2θ = 28.60°, 33.90° 47.58°, and 56.36° of the samples (a)-(c) can be attributed to the diffraction of (112), (200), (220), (312), respectively The peaks are specific to the kesterite structure of CZTS based upon JCPDS 26-0575 [13,14]. As the sputtering pressure decreases, the intensities of the (112), (220) and (312) preferred diffraction peaks become stronger. The peak intensity of the CZTS film increases due to the increase in the crystalline nature of the CZTS films. This is due to the decreased chance of sputtering target material particles to collide with gas molecules at low pressure, and higher energy reaches the substrate, which is propitious to produce large grains. Meanwhile it may be seen that diffraction peaks of the thin film samples (112), (220) and (312) become sharper as the sputtering pressure decreases, which shows that the lower sputtering pressure, the better will be thin film crystallinity. The optical characteristics of the CZTS films were evaluated in terms of the optical absorption coefficient and optical band gap. The optical transmittance and reflectance spectra of CZTS films were measured with UV-VIS-NIR spectrophotometer.

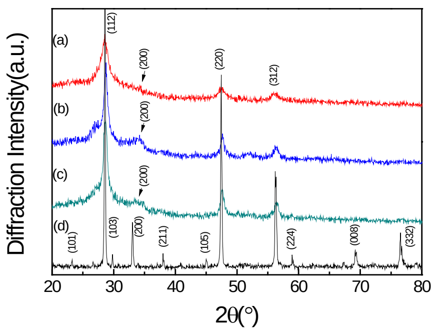

Fig. 1. XRD patterns of CZTS samples: (a), (b) and (c) correspond to their sputtering pressure, (a) 0.5Pa, (b) 0.3Pa and (c) 0.2Pa, (d) corresponds to target material.

Table 1. Chemical composition and compositional ratio of CZTS films

Deposition pressure	Cu (at%)	Zn (at%)	Sn (at%)	S (at%)	Cu/(Zn+Sn)	Zn/Sn
0.5 Pa	21.61	12.05	17.37	48.97	0.73	0.69
0.3 Pa	18.74	13.63	18.52	49.11	0.58	0.74
0.2 Pa	18.40	15.16	19.00	47.44	0.54	0.80

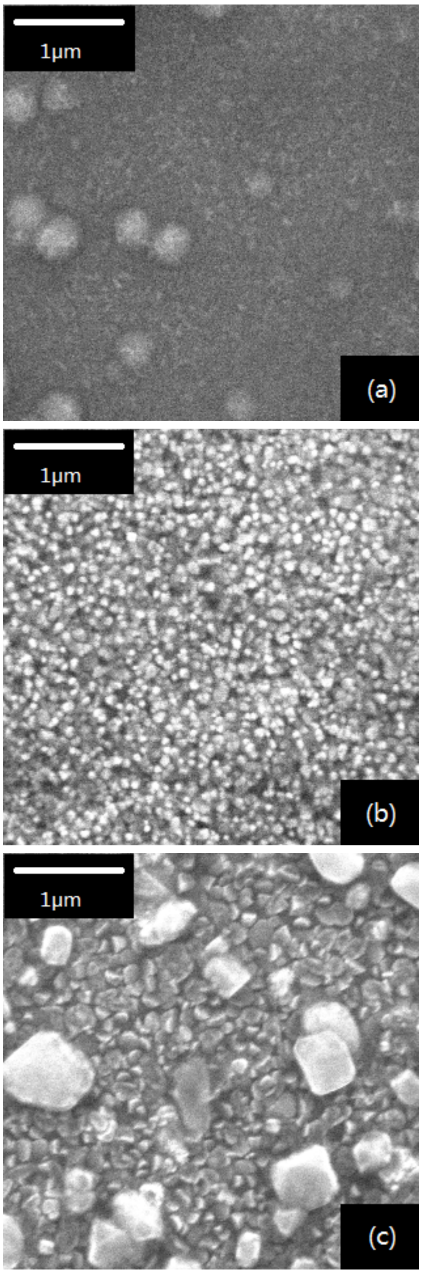

Fig. 2. SEM micrographs of the CZTS films at different sputtering pressures: (a) 0.5Pa, (b) 0.3Pa, (c) 0.2Pa.

Absorption coefficient α can be obtained by the transmittance and reflectance，α can be calculated by the following formula [10,17]:

$$\alpha = \frac{2\ln(1-R)-\ln T}{d},$$

where d is the thickness of the thin films, T is the transmittance, and R is the reflectance of the thin film samples.

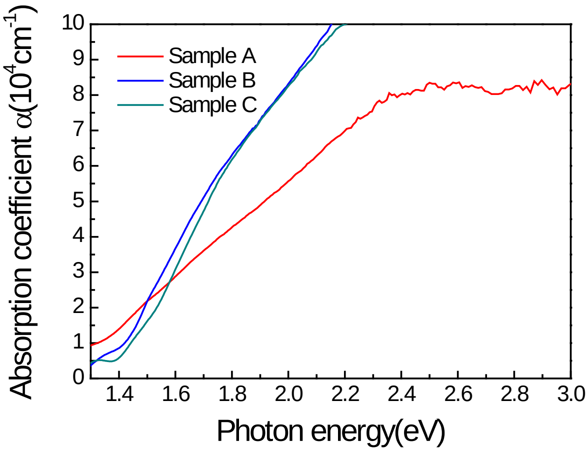

Fig. 3. Absorption coefficients of the CZTS films, the letters correspond to their sputtering pressure, A 0.5Pa, B 0.3Pa, C 0.2Pa.

Fig. 3 shows the plots of the absorption coefficient (α) *versus* photon energy (hv) for each CZTS film. A high absorption coefficient (>10^4 cm^{-1}) is observed for all films in the visible region, and it shows a distinct absorption edge at about 1.40 eV. CZTS is a direct band gap semiconductor, so the band gap E_g can use extrapolation through $(\alpha hv)^2$ with photon energy hv relationships obtained. Fig. 4, presents the band gap (Eg) estimated by extrapolating the linear region of the $(\alpha hv)^2$ plot. The single-phase CZTS film deposited at 0.5 Pa shows the smallest band gap (1.40eV), it is smaller than the reported experimental and theoretical values [18,19]. The Cu-rich and Zn-poor states of this film are probably responsible for the decrease of the band gap. The valence band maximum (VBM) of CZTS arises from antibonding of Cu 3d and S 3p orbitals. Therefore, excess Cu vacancies reduce the VBM so that the bandgap is blue shifted [19,20]. The larger Eg values of CZTS films deposited at 0.2 Pa may be attributed to the existence of Cu vacancies, which leads to a band gap of around 1.49eV [21].

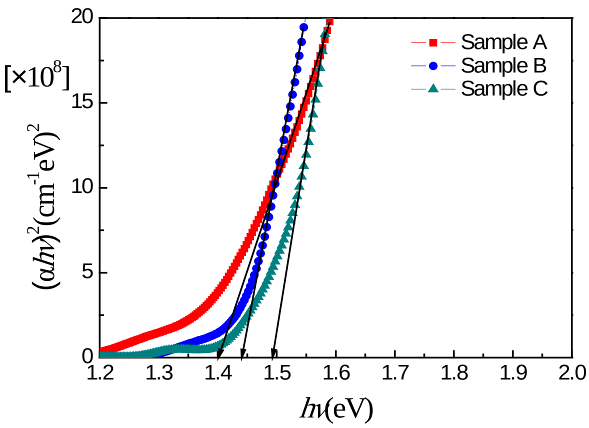

Fig. 4. Band gap energy of CZTS films: the letters correspond to their sputtering pressure, A 0.5Pa, B 0.3Pa, C 0.2Pa.

CONCLUSIONS

Cu_2ZnSnS_4 films with good crystallinity were successfully deposited using a single-phase kesterite-structure CZTS target material by RF magnetron sputtering method without sulfurization. The control of deposition pressure and film composition is considered to be crucial to obtain nearly stoichiometric single-phase films. The re-evaporation of volatile constituents during the sputtering process would lead to a deviation of film stoichiometry. CZTS films deposited at different deposition pressures show (112) preferred orientation and are poor in Cu and rich in Zn. A large fraction of Zn occurs in CZTS films deposited at pressure of 0.3 and 0.2 Pa, which is probably related to the enlargements of the band gaps ranging from 1.44 to 1.49 eV. The film deposited at 0.2 Pa has dominant single-phase structure, Cu-poor and Zn-rich state and large grain size. The CZTS thin films also exhibit high optical absorption ($>10^4$ cm^{-1}). These results suggest that quaternary CZTS would be a potential candidate for solar cell applications.

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ВЛИЯНИЕ НА НАЛЯГАНЕТО НА ОТЛАГАНЕ ВЪРХУ ФИЛМИ ОТ Cu_2ZnSnS_4, ПОЛУЧЕНИ ЧРЕЗ ЕДНОСТАДИЙНО РАЗПРАШАВАНЕ С ЧЕТВОРНА МИШЕНА

Х.Г. Ян [1,2,*], Дж.Д. Джан [2], М.Ц. Ли [1*], Р.Т. Хао [3], Г.Л. Сун [2]

[1] *Колеж по възобновяема енергия, Севернокитайски университет по електричеството, Пекин 102206, Китай*
[2] *Колеж по физика и материлознание, лаборатория по фотоволтаични материали на провинция Хенан, Университет на Хенан, Ксинксянг 453007, Китай*
[3] *Институт по изследване на слънчевата енергия, Университет на Юнан, Кунминг 650092, Китай*

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(Резюме)

Cu_2ZnSnS_4 (CZTS) филми са отложени от монофазова Cu_2ZnSnS_4 четворна мишена чрез RF разпрашаване без последваща сулфуризация. Получените CZTS филми са темперирани при 400°C в аргонова атмосфера за получаване на еднофазова кестеритна структура. Изследвано е влиянието на налягането на разпрашаване върху повърхностната морфология, кристалната структура, оптичния абсорбционен коефициент, разстоянието между ивиците, както и влиянието на химичния състав на CZTS филми. Дифракционните пикове на (112) са остри и характеристичните пикове на структури от кестеритов тип като (220) и (312) се наблюдават ясно в рентгеновите дифрактограми. Съставът и оптичните свойства на образците са определени с помощта на енергийно дисперсивна рентгенова спектроскопия (EDS) и UV-VIS-NIR спектрометрия. При налягане на разпрашаване от 0.2 Pa се получава перспективен беден на мед и богат на цинк монофазов CZTS филм с голям размер на зърната. Установено е, че CZTS филми проявяват висок абсорбционен коефициент от порядъка на 10^4 cm^{-1} и оптично разстояние между ивиците от 1.49 eV.