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The effects of sputtering power on optical and electrical properties of copper selenide thin films deposited by magnetron sputtering

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ABSTRACT

The p-type copper selenide thin films were deposited on glass substrate at room temperature by magnetron sputtering. The effects of sputtering power on crystallinity, surface morphology, optical and electrical properties of the copper selenide thin films were investigated. By adjusting the sputtering power, the thickness of as-deposited films varied between 225 nm and 375 nm. The crystallinity, the optical band-gap as well as the electrical conductivity of the as-deposited films were improved substantially. The copper selenide thin film deposited under optimal sputtering power possesses best crystallinity, widest optical band-gap of 2.40 eV and lowest electrical resistivity of $3.94 \times 10^{-4}\ \Omega\,\mathrm{cm}$.

1. Introduction

Copper selenide is a p-type semiconductor material which has suitable electrical and optical properties for many applications in various devices such as solar cells, super ionic conductors and photo-detectors [1–4]. It has many phases including stoichiometric Cu_2Se, Cu_3Se_2, CuSe, and $CuSe_2$, as well as non-stoichiometric $Cu_{2-x}Se$. Among these phases, it has been demonstrated that the non-stoichiometric $Cu_{2-x}Se$ thin films has been used to form a junction with n-type semiconductors either as absorber in heterojunction with CdS or as window material in heterojunction with *n*-Si. Chen et al. [1] developed a polycrystalline thin film solar cell back wall designed heterojunction structure based upon p-type $Cu_{2-x}Se$ and n-type CdS semiconductor materials showing device efficiency of 5.38%. However, the works about copper selenide are relatively rare and the motivation of copper selenide thin film studies mainly focus on application in absorber layer of solar cell. In fact, except for application in solar cells, the copper selenide thin film could have unique electrical and optical performance. It is evident that the average transmittance may be related to the absorption edge or optical band-gap. Previous work reported that $Cu_{2-x}Se$ films possessed a direct band-gap of 2.2 eV for $x = 0.2$ [5], but the average transmittance was not high. It could be an opportunity to improve optical transmittance of copper selenide films through shifting the absorption edge towards higher energy side (above 2.21 eV). In addition, human eyes are most sensitive to the light of wavelength 560 nm corresponding to the band-gap of 2.21 eV, which also shows the potential in application of transparent semiconductor material. On the other hand, the electrical property of copper selenide films was also studied. Okimura et al. [3] prepared p-type conductive $Cu_{2-x}Se$ thin films with low resistivity, which opens an important gate for obtaining high conductivity thin film. Thus, if the band-gap could be expanded to above 2.21 eV, it has great potential in applications such as electro-conductive electrode or TCMs (transparent conductive materials) for copper selenide thin films.

In the previous reports, a number of fabrication methods including various deposition techniques like vacuum evaporation [5], melting of Cu and Se [6], electro-deposition [7,8], solution growth [9] and chemical bath deposition [10] were reported. There were far few reports about deposition of copper selenide films or analogous chalcogenide compound films by magnetron sputtering so far. Only Kim and coworkers [11] prepared CZTSe films by magnetron sputtering. The non-adoption of the method may be due to its relatively high cost or non-control of stoichiometric in films. As was well known, the property of film largely depends on crystalline quality which is related to fabrication methods. In exception of obtaining high crystalline quality, the magnetron sputtering can offer other advantages such as large area fabrication and high deposition rate, which actually decrease the cost from another viewpoint. Thus, the magnetron sputtering is deserved for adoption and exploration.In our research, the p-type conductive copper selenide

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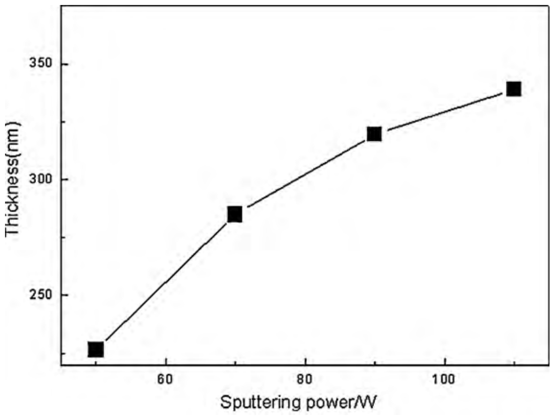

Fig. 1. Plot of thickness of as-deposited films with sputtering power.

thin films were deposited on glass substrates at room temperature by magnetron sputtering. The process parameters of magnetron sputtering including chamber pressure and sputtering power all take effects on properties of as-deposited films. Thus in order to prepare high performance and reproducible film material, it is necessary to study the effects of single parameter on the properties of as-deposited films. In this paper, we mainly study the effects of sputtering power on the optical and electrical properties of as-deposited films. Low electrical resistivity and modulation of optical band-gap were realized via adjusting the sputtering power. The paper deals with crystalline, compositional, optical and electrical properties of copper selenide thin films.

2. Experimental details

The target used powder was prepared by the solid reaction of Cu and Se powder in the ratio of 1:1 at a temperature of 500 °C under vacuum in a sealed quartz tube. And then the powder was pressed into pellet which was sintered at 900 °C under atmosphere of Ar for preparing the target. The copper selenide thin films were deposited on glass substrates at room temperature by magnetron sputtering. The vacuum was pumped to 3×10^{-4} Pa and the chamber Ar pressure was 0.8 Pa, sputtering time was 60 min. The as-deposited films were named after S1, S2, S3, S4, corresponding to the given sputtering power of 50 W, 70 W, 90 W and 110 W, respectively. In Fig. 1, the thickness of as-deposited films varied from about 225 nm to 375 nm with the increasing of sputtering power. The thickness was measured by mechanical profilometer (Dektak-150). Crystalline structures of the as-deposited films were analyzed using an X-ray diffractometer (Bruker, AXS, Cu Kα in thin film mode); morphology property was characterized by scanning electronic microscopy (JSM-6510); the optical transmission spectra were obtained by UV–visible spectrophotometer (Hitachi U-4100) in wavelength range of 200–800 nm. The electrical resistivities, Hall mobilities, and carrier concentrations were determined from Hall-effect measurement equipment using a Van der Pauw method. For compositional analysis, inductively coupled plasma-atomic emission spectrometry (ICP-OES, varain vista pro) analysis was carried out to study the chemical composition of copper selenide thin films.

3. Results and discussion

3.1. Crystalline and compositional properties

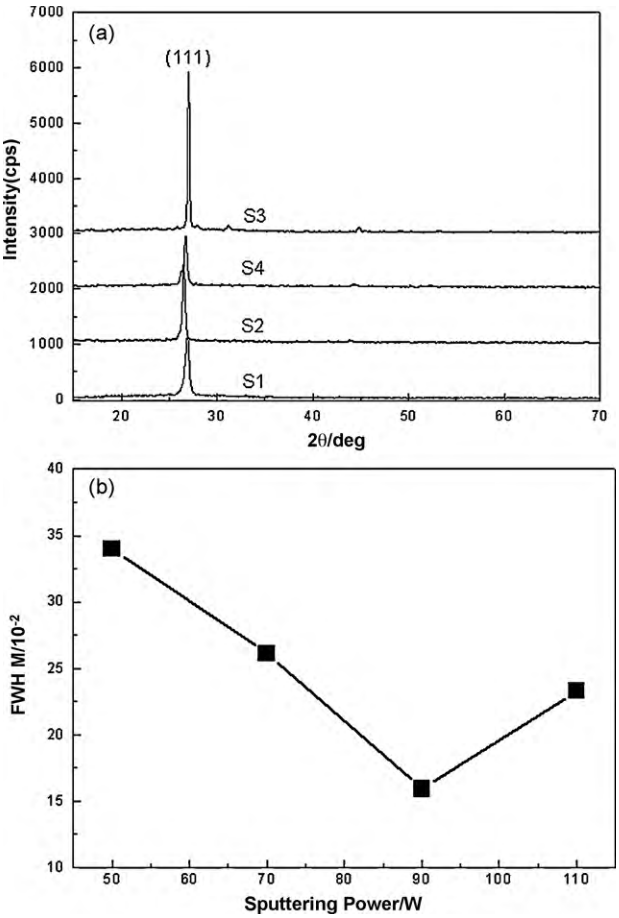

Fig. 2. (a) XRD pattern of as-deposited films. (b) Plot of FWHM of as-deposited films with sputtering power.

In Fig. 2(a), X-ray profiles of the as-deposited copper selenide thin films are plotted in 2θ range of 15–70°. It was observed that the films show a strong peak from (1 1 1) plane located at 2θ position of about 26.578–27.078°, indicating a typical cubic structure with (1 1 1) preferred orientation. A comparison of observed and the standard $(h\,k\,l)$ plane ensures that the as-deposited films are of $Cu_{2-x}Se$ (mineral berzelianite) with cubic structure. The impurity phase may increase with increasing the sputtering power as results of main phase/impurity phase ratio decreasing. When the power was 90 W, S3 films demonstrate most evident additional weak peaks in the XRD data, which may be due to separation of impurity phase from the main phase. But with further increasing power, the impurity phase may be prone to be dissolved into the main phase and the impurity phase decreases. In Fig. 2(b), the full width of half maximum (FWHM) varies with increasing sputtering power. The grain size estimated by using well known Sherrer relationship taking into account the instrument broadening were 17.9 nm, 28.3 nm, 41.6 nm and 33.2 nm for S1, S2, S3 and S4 films, respectively. In Fig. 3, microscopy of surface view observed for copper selenide films by using scanning electron microscopy are presented. Course columnar structure is evident for the S2, S3and S4 films. It can be seen that the as-deposited films were uniform, and the grains size observed were consistent with the results estimated from Sherrer relationship. Considering the minor variation of XRD peak positions, which indicates the minor compositional variation, the compositional analysis can be studied by the ICP. Table 1 shows the variations of atomic percentage of Cu/Se obtained by ICP-OES analysis. The atomic percentages of Cu/Se in the as-deposited films were 65.21:34.79, 64.67:35.33, 63.77:36.23 and 64.89:35:11 for S1, S2, S3 and S4, respectively. The atomic percentages of Cu/Se in the as-deposited films indirectly confirmed the existence of $Cu_{2-x}Se$ phase. The ratio of Cu/Se decreases in the sequence S1–S2–S3, and suddenly increases in sequence S3–S4. At meanwhile, the diffraction angle of main peak position decreases

Table 1
Atomic percents of as-deposited thin films.

Elements	S1	S2	S3	S4
Cu	65.21%	64.67%	63.77%	64.89%
Se	34.79%	35.33%	36.23%	35.11%

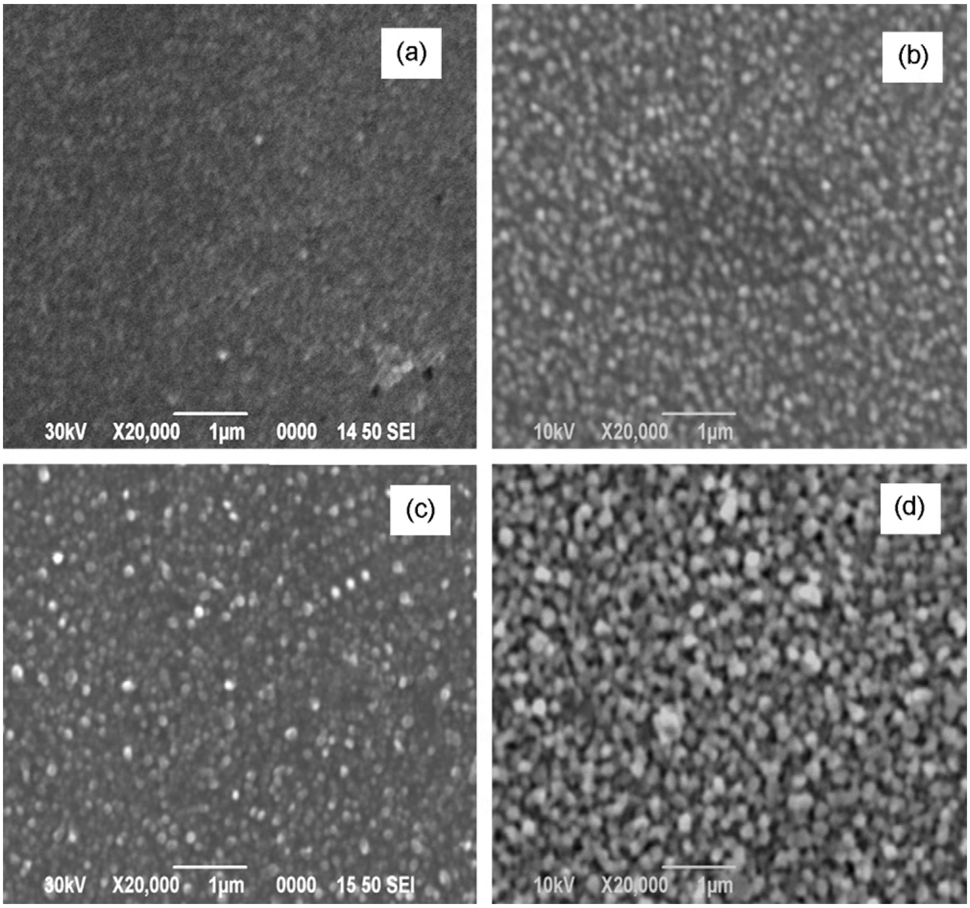

Fig. 3. SEM of as-deposited films: (a), (b), (c), and (d) represents S1, S2, S3 and S4 sample, respectively.

in sequence S1–S2 and increases in sequence S2–S4. The out of sequence of S3 sample could be due to the existence of Cu-poor impurity phase that can be observed in XRD pattern. It shows that the Cu/Se was related with the main peak position in XRD data, which indicates that sputtering power takes effects on chemical compositions.

3.2. Optical and electrical properties

The optical band-gap and the nature of optical transitions can be obtained in dependence of absorption coefficient on photon energy. The optical band-gaps of copper selenide films were estimated by plotting the variation of $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion near the onset of absorption edge to the energy axis, which are plotted in Fig. 4. Absorption edge of the as-deposited copper selenide films varied with increasing sputtering power. The absorption edge of S2, S3 and S4 films were located at higher energy side than that of S1 film. Direct allowed band-gap of copper selenide films were evaluated optically by using relation of $\alpha h\nu = A(h\nu - E_g)^{1/2}$ (for $h\nu > E_g$), where α is the absorption coefficient, E_g is the band-gap, $h\nu$ is the photon energy. The optical band-gap exhibited an increasing tendency with increasing sputtering power. For film deposited under low sputtering power of 50 W, the magnitude of optical band-gap was 2.21 eV that was reported [5]. By increasing the sputtering power, the optical band-gap was improved, and the estimated band-gaps of S2, S3 and S4 were 2.26 eV, 2.40 eV and 2.27 eV, respectively. Based on Figs. 4 and 5(a), the variation of optical band-gap with increasing carrier concentration was demonstrated, showing a typical Burstein–Moss shift. For films with low carrier concentration, the optical band-gap was lower than that with high carrier concentration. It was assumed that the carrier concentrations of as-deposited films were related to the copper content in as-deposited films. According to ICP data, it was clear that the Cu-rich S1 film has narrow band-gap, and the Cu-poor S3 has wide band-gap. It was reconfirmed that the holes carrier was mainly induced by the deficiency of copper ions. The same phenomenon has been found in $Cu_{2-x}S$ series, the electrical conductivities and the indirect band-gaps increase for the Cu-poor phases [12].

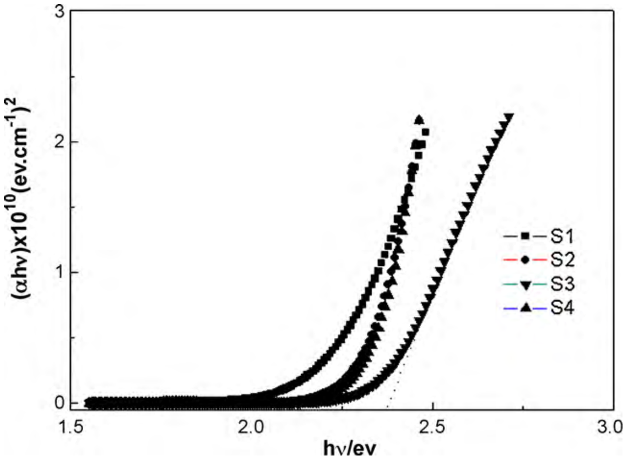

Fig. 4. Plot of $(\alpha h\nu)^2$ with $h\nu$ for as-deposited films (square symbol represents S1, round symbol represents S2, inverted triangle symbol represents S3 and triangle symbol represents S4).

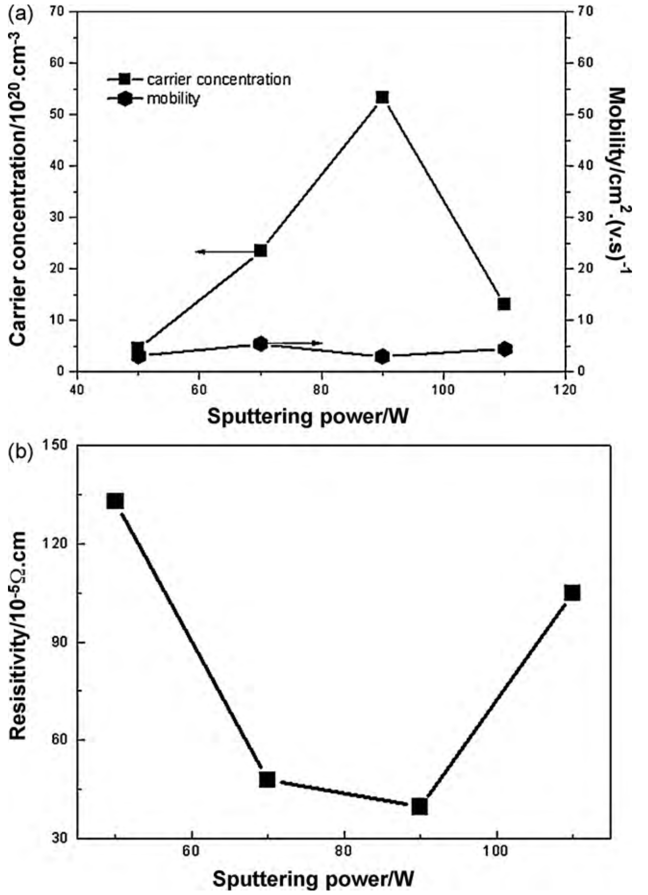

Fig. 5. (a) Plot of carrier concentration and mobility of as-deposited films with sputtering power (square symbol represents carrier concentration, hexagonal symbol represents mobility). (b) Plot of electrical resistivity of as-deposited films with sputtering power.

From the positive polarity of Hall coefficient, it was evident that the as-deposited films were p-type semiconductor. Fig. 5(a) shows the Hall mobilities and the carrier concentrations of the as-deposited copper selenide films plotted against the sputtering power. The Hall mobility varied between 2.5 $\mathrm{cm}^2\,(\mathrm{v\,s})^{-1}$ and 5.5 $\mathrm{cm}^2\,(\mathrm{v\,s})^{-1}$, and the carrier concentration varied between $4 \times 10^{20}\ \mathrm{cm}^{-3}$ and $5 \times 10^{21}\ \mathrm{cm}^{-3}$. The resistivity of the as-deposited films plotted against the sputtering power was shown in Fig. 5(b), which showed a typical valley like behavior with respect to sputtering power, having minimum resistivity at intermediate sputtering power of 90 W. For all as-deposited films, the electrical resistivities were $1.4 \times 10^{-3}\ \Omega\,\mathrm{cm}$, $4.75 \times 10^{-4}\ \Omega\,\mathrm{cm}$, $3.94 \times 10^{-4}\ \Omega\,\mathrm{cm}$ and $1.08 \times 10^{-3}\ \Omega\,\mathrm{cm}$ for S1, S2, S3 and S4 films, respectively. Based on the ICP data in Table 1 and Fig. 5(b), it was concluded that less copper content may lead to better electrical conductivity. It was found that the variation of mobility is minor compared to that of carrier concentration. As the electrical resistivity ρ is equal to $1/ne\mu$, it is evident that the electrical conductive mechanism of as-deposited films is dominated by the carrier concentration. It is also worth mentioning that the as-deposited films provided moderate Hall mobility values. It is well known that Hall mobility is related to S (scattering factor) which includes grain boundary related S_g, carrier concentration related S_c and lattice defect related S_d. The total $1/S$ is equal to $1/S_g + 1/S_c + 1/S_d$, which indicates that Hall mobility is determined by complex of many types of scattering factor. Further studies were carried out via temperature-dependent Hall measurement. Fig. 6 shows a plot of inverse absolute temperature versus $\log\rho$ for S1 film. The film showed a decreasing behavior of resistance with increasing temperature of up to about 400 K, which confirms the semiconducting behavior of the films. The room temperature electrical resistivity was found to be $1.4 \times 10^{-3}\ \Omega\,\mathrm{cm}$, which is lower than the reported value and approximately close to the resistivity seen from Fig. 5(b). The similar behavior has been reported by earlier workers [2,13] for copper selenide films. The conductivity is a thermally activated mechanism, which may be attributed to the thermal excitation of charge carrier from grain boundaries to the neutral region of the grains.

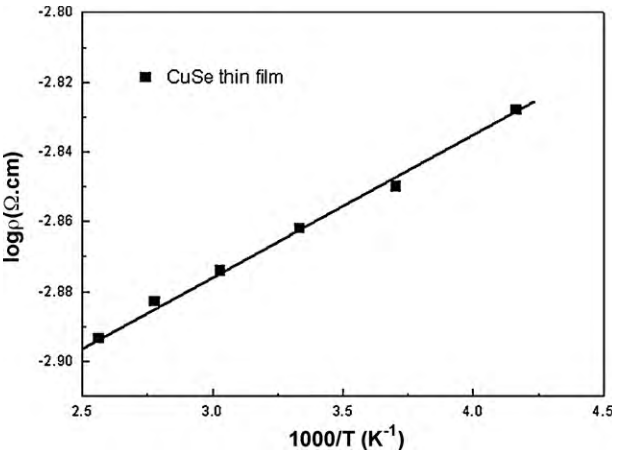

Fig. 6. Plot of log ρ vs. 1000/T for as-deposited film.

4. Conclusion

In summary, the p-type cubic structural copper selenide thin films with orientation along (1 1 1) plane were deposited on glass substrate at room temperature by magnetron sputtering. By adjusting sputtering power, the as-deposited films show high crystalline quality, uniform morphology with average grain size of about 16–42 nm. The optical band-gaps of the as-deposited films varied between 2.23 eV and 2.40 eV, while the electrical resistivity varied between $1.4 \times 10^{-3}\ \Omega\,\mathrm{cm}$ and $3.94 \times 10^{-4}\ \Omega\,\mathrm{cm}$. The copper selenide film deposited under optimal sputtering power possesses lowest electrical resistivity of $3.94 \times 10^{-4}\ \Omega\,\mathrm{cm}$ and widest optical band-gap. It can be analyzed that the variation of optical band-gaps were due to Burstein–Moss shift, and the electrical conductive mechanism was dominated by carrier concentration. Further work about the effects of other parameters on the properties of as-deposited film will be continued, and the copper selenide film reveals the potential application of p-type TCM film or electro-conductive electrode.

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