Comparative studies of the properties of CdS films deposited on different substrates by R.F. sputtering

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Abstract

CdS films have been prepared on polycarbonate, polyethylene terephthalate, and Corning 7059 substrates by R.F. magnetron sputtering technique at room temperature. A comparison of the properties of the films deposited on polymer and glass substrates was performed. In addition, the influence of the sputter power on the structural and optical properties of these films was evaluated. The XRD measurements revealed that CdS films were polycrystalline and retained the mixed structure of hexagonal wurtzite and cubic phase, regardless of substrate types. As the sputter power was increased from 75 to 150 W, the structure of CdS films was converted from the mixed of hexagonal and cubic phase to hexagonal phase. The morphology of CdS films is found to be continuous and dense. Also, the grain of CdS films is larger with increasing the sputter power. The average transmittance exceeded 80% in the visible spectrum for all films and decreases slightly with the sputter power.
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1. Introduction

Cadmium sulfide (CdS) has been the most widely used and most successful window layer for thin film solar cell application. Both CdTe and $Cu(In,Ga)Se_2$ thin film solar cells have utilized CdS films prepared by the chemical bath deposition (CBD) to demonstrate efficiencies in excess of 16.4% and 19.2%, respectively [1,2]. The CBD process is simple and very attractive for small area research devices. However, it must be considered that CBD is not fast and gives a liquid waste that needs to be recycled. Other deposition technologies such as closed space sublimation (CSS), sputtering, and MOCVD have also been utilized for CdTe thin films solar cells. The use of a plasma-based method such as magnetron sputtering can have significant advantages including the use of low energy particle bombardment to achieve lower growth temperatures and the use of excited state species to improve the doping control during growth [3].

CdS films deposited on polymer substrates, such as polycarbonate (PC) and polyethylene terephthalate (PET), have many merits compared with those deposited on glass substrates; they are light weight, of small volume and can make the obtained devices foldable, easy to carry. Development of thin film solar cells onto polymer substrates is interesting for many applications that require flexible and light weight sources of power [4]. Recently, efficient polycrystalline solar cells based on $Cu(In, Ga)Se_2$ and CdTe have been developed onto polyimide substrate [5–9].

In this work, we give a comparative study on the structural and optical properties for CdS films deposited on glass and polymer substrate, such as PC and PET substrate, by magnetron sputtering at room temperature. In addition, the effect of sputter power on the structural and optical properties of CdS films was investigated.

2. Experimental

The substrates used in this work were 7059 glass, PC, and PET film (100 μm). Before depositing the CdS thin films, the substrates were ultrasonically cleaned in a detergent bath, and dried in nitrogen. The CdS thin films were deposited by R.F. magnetron sputtering system from a commercially available, sintered ceramic CdS target with 99.999% purity of 3 in. in diameter. The separation between target and substrate was

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about 4.5 cm. The sputtering gas Ar was controlled by a mass flow controller and the sputter pressure was fixed to 1.0 Pa. After the chamber was evacuated to a base pressure below 6.6×10^{-4} Pa, presputtering of 10 min was carried out at an argon gas pressure of 1.0 Pa in order to clean the target surface. The R.F. sputter power was varied from 50 to 150 W. All the films were deposited at room temperature and the thickness is about 600 nm.

The film thickness was measured with the surface profile. X-ray diffraction (XRD) was used to study the crystallinity and crystal orientation of the films. The composition analysis of CdS films were carried out by X-ray photoemission spectroscopy (XPS). The surface morphologies of the films were observed by field-emission scanning electron microscope (FE-SEM). The optical transmittance of the films was measured by the UV–Visible spectrophotometer.

3. Results and discussion

The prepared films at optimum conditions on PC or PET substrates were physically stable and had good adhesion to the substrates. No cracking or peel-off of the films was observed after deposition. The color of the CdS film was transparently yellowish.

Fig. 1 shows the dependence of the growth rate of CdS films on the sputter power. It is observed a clear increase on growth rate as the sputter power increases. This increase indicates that the number of atoms sputtered from the target is proportional to the R.F. power. For higher sputtering power, the sputtered species get a higher energy that contributes to the film growth. These high energy particles have high surface mobility and therefore a higher growing process at the surface takes place.

Fig. 2 shows the XRD pattern of the CdS thin films deposited at a sputter power of 50–150 W. Polycrystalline hexagonal and cubic CdS of random orientation are known to show many strong X-ray diffraction peaks. The diffraction spectra were obtained by scanning 2θ in the range of 20–80°. It can be seen that the film deposited at 50 W has a mixed cubic and hexagonal structure of CdS. The very small difference between the position of the peak (1 1 1), (1 1 0) of the cubic structure and the peak (0 0 2), (2 2 0) of the more stable
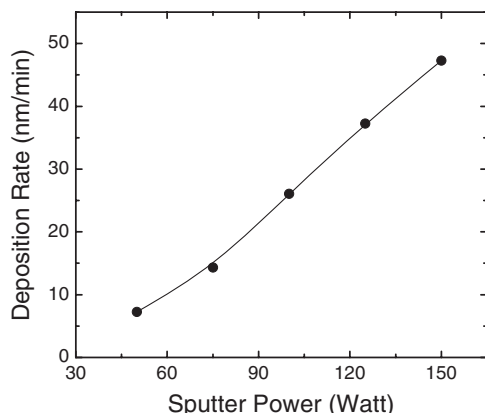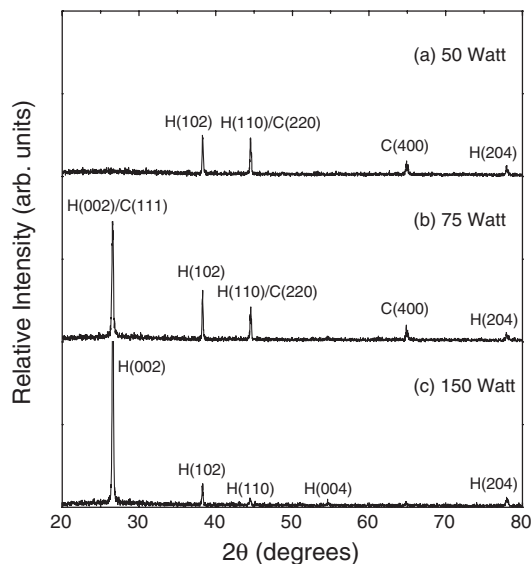

Fig. 2. XRD patterns of CdS films deposited at different sputter powers. The substrate type is the glass and the film thickness is about 600 nm.

hexagonal structure makes difficult to elucidate the crystalline structure of the sample [10–12]. The film exhibits two strong peaks at $2\theta = 38.28°$ and 44.56°, which are associated with the hexagonal (1 0 2) plane and the mixture of hexagonal (1 1 0) and cubic (2 2 0) planes, and two weak peat at $2\theta = 64.9°$ and 77.9°, which are associated with the cubic (4 0 0) and the hexagonal (2 0 4) planes. When the sputter power increases to 75 W, the peak at $2\theta = 26.58°$, which is associated with the mixture of hexagonal (0 0 2) and cubic (1 1 1) planes, appeared. The H(0 0 2)/C(1 1 1) reflection is the most intense for the films deposited at 75 W, while the H(1 0 2) and H(1 1 0)/C(2 2 0) planes were grown preferentially for the one deposited at 50 W. This means that the change in preferential plane growth of the wurtzite and/or cubic phase happened in films deposited from 50 to 75 W. As the sputter power increases

Fig. 1. Dependence of the growth rate on the sputtering power for CdS films deposited on glass substrate.
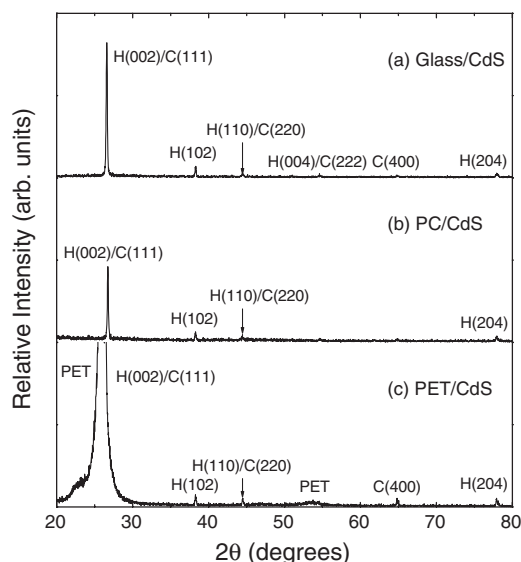

Fig. 3. XRD patterns of CdS films deposited on various substrate types. The sputter power is 150 W.

further, the locations of the measured diffraction peaks do not change significantly and the intensity of the H(0 0 2)/C(1 1 1) peak becomes more intense and sharper. This is due to the polycrystalline of the resulting films being improved and grain size becoming larger with increasing the sputter power. At the same time, a new peak appears at around $2\theta = 54.58°$, which is associated with the hexagonal (0 0 4) and/or cubic (2 2 2) plane, and the cubic (4 0 0) peak disappears. This indicated that the structure of CdS film changes from the mixed of hexagonal and cubic phase to hexagonal phase.

Fig. 3 shows the XRD pattern of CdS films deposited on various substrates. Compared with the films deposited on glasses, the intensity of the H(0 0 2) peak of the films deposited on PC is somewhat weak. This indicates that, under the same deposition condition, the H(0 0 2) preferential orientation of the films deposited on PC substrate is smaller than in the films deposited on glass. For PET substrate, the XRD spectra are very similar to those of other substrate types. However, the C(4 0 0) peak which disappeared for the glass and PC substrate is

shown. This means that the film deposited on PET substrate has a mixed structure of hexagonal and cubic phase, as seen at low sputter power.

Fig. 4 shows the SEM micrographs for the films deposited on different substrates. The sputter powers are 75 and 150 W, respectively. The morphology of CdS films is found to be continuous and dense. It can be seen that with increasing the sputter power, the crystallinity of the films is improved and the crystallite sizes become larger. However, the grain size of the CdS film is not much dependent on the substrate types.

The room temperature Raman spectra of the CdS films are shown in Fig. 5. The sputter power is changed from 50 to 150 W, and the substrate type is the glass. For PC and PET substrate, it is impossible to measure the Raman spectra because of the polymer substrate. A Lorentzian line shape is fitted to the Raman spectra from which the peak position and full width at half maximum (FWHM). The Raman spectra of the CdS films on glass present a well-resolved line at approximately 300 cm^{-1}, corresponding to the first order
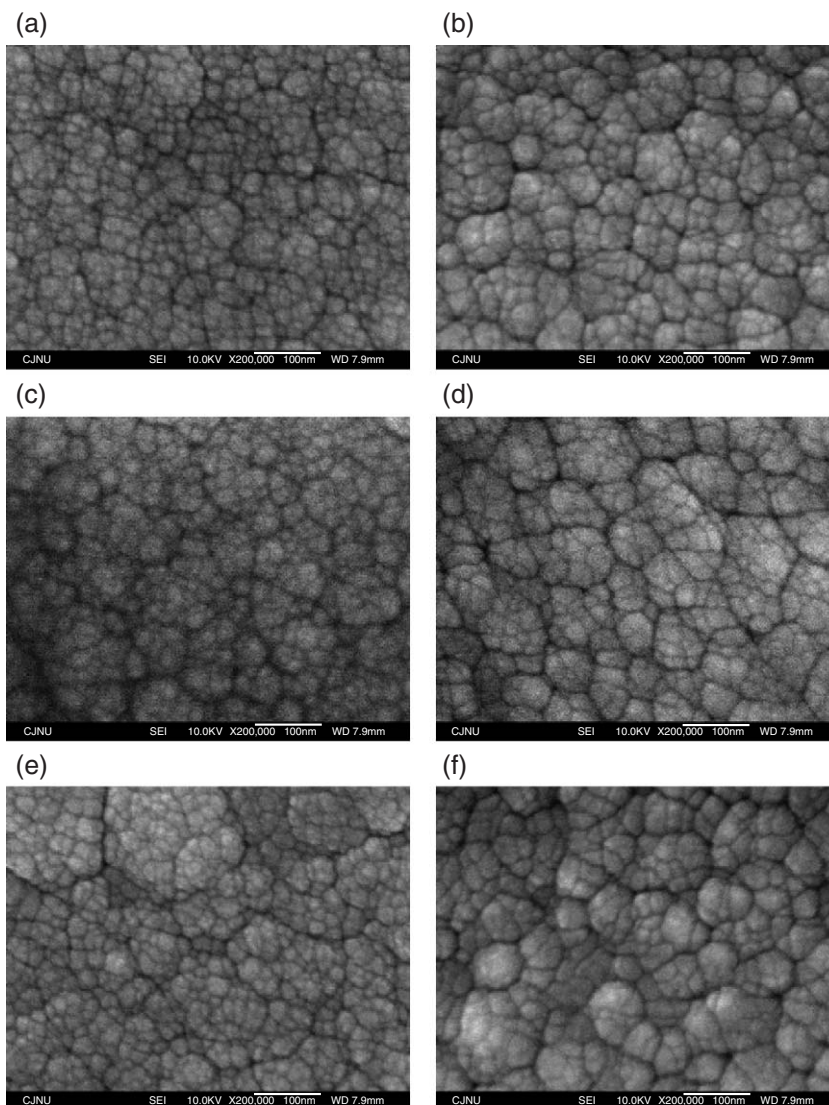

Fig. 4. SEM micrographs of CdS films deposited on different substrate types: (a) glass substrate, 75 W; (b) glass substrate, 150 W; (c) PC substrate, 75 W; (d) PC substrate, 150 W; (e) PET substrate, 75 W; (f) PET substrate, 150 W.
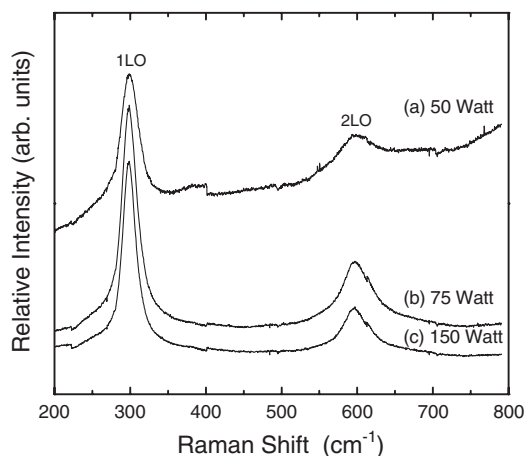
Fig. 5. Raman spectra of the CdS films deposited at different sputter powers. The substrate type is the glass and the spectra are measured at room temperature.

Fig. 7. Average transmittance in the range of 550~850 nm for CdS films deposited at different sputter powers.

scattering of the longitudinal optical (LO) phonon mode. CdS can take both hexagonal wurtzite and cubic zinc blende structures, and it was reported that for both the structures, the zone-center longitudinal-optical A_1(LO) phonon frequency is about 305 cm^{-1} [13,14]. The FWHMs of the 1 LO peak are 27.8, 23.7, and 20.6 cm^{-1}, for 50, 75, and 150 W, respectively. These values are much larger than that (6.5 cm^{-1}) for melt-grown single-crystal CdS. Usually, very large width indicates poor crystallinity (lack of long-range order) in the films, but the well-defined peak indicates the crystalline nature of the films. Hence, the large FWHM in the present case can be attributed to a polycrystalline effect in the as-deposited film [15]. This is corroborated by the appearance of various peaks in the XRD pattern of the as-deposited film. The broad second-order scattering of LO phonons is also visible at approximately 600 cm^{-1}, regardless sputter power. The main characteristic of the Raman spectra of our films is the broadening of the LO peak in the samples deposited at lower power, which is due to the increasing compositional and structural disorder. The peak position did not change much and remained almost constant

with increasing sputter power. The apparent small increase in the peak position is insignificant.

Fig. 6 shows the transmittance spectra as a function of wavelength in the visible spectrum for the samples deposited at different sputter powers. The spectra show the usual interference pattern of a high refractive index film in the range of low absorption with a sharp fall of transmittance at the band edge, which is an identification of the good crystallinity of the film. As the sputter power decreases, the transmittance improves, especially at around 540 nm, and the absorption edge shifts towards the shorter wavelength. From the transmittance data it is possible to infer the optical gaps of the films by plotting $(\alpha h\nu)^2$ vs. $h\nu$ (where α is the absorption coefficient, and $h\nu$ the photon energy) and by extrapolating the straight line portion of this plot to the energy axis. These plots yield optical gaps of 2.47, 2.43, and 2.40 eV for the films deposited at 50, 75, and 150 W, respectively. The optical band gap decreases with the
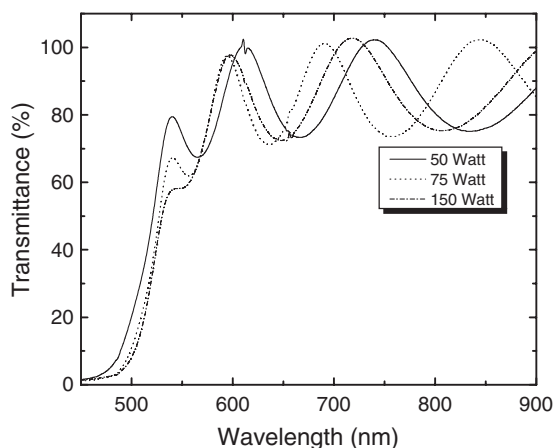

Fig. 6. Optical transmittance spectra of CdS films as a function of wavelength for the samples deposited at different sputter powers. The substrate type is the glass.
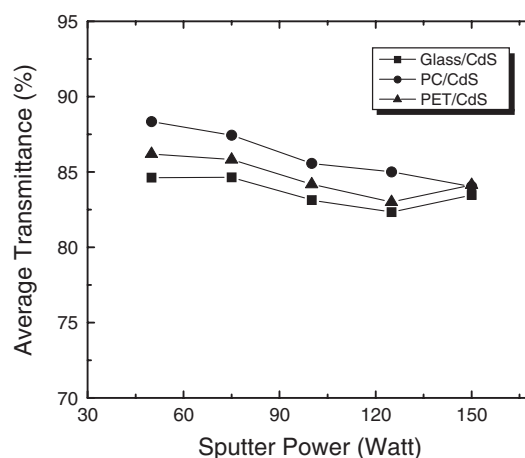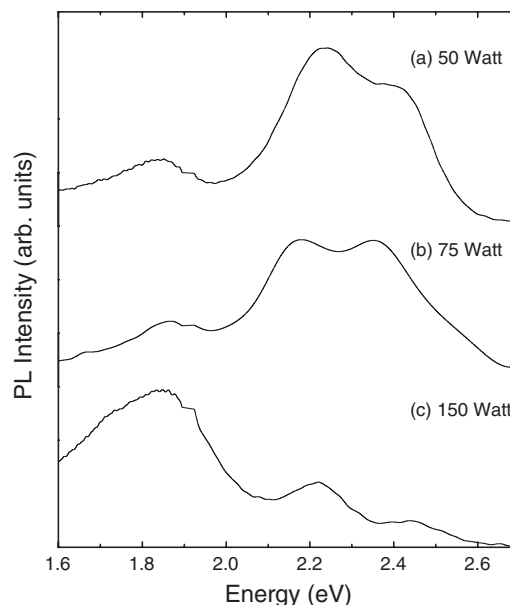

Fig. 8. Photoluminescence spectra of CdS films deposited at different sputter power. The substrate type is the glass, and the PL spectra were measured at 4 K.

sputter power and approaches the values of single crystalline CdS (2.43 eV) [16], regardless of substrate types. The obtained values for PC and PET are not consistent with the optical gap of CdS films deposited on glass substrates. This means that these values are due to the optical properties of the polymer substrate, which is partly absorbing in the high energy range of the visible spectrum.

Fig. 7 shows the average transmittance in the range of 550~850 nm as a function of the sputter power for CdS films deposited on various substrate types. The average transmittance is over 80% for all films. A slight improvement of the transmittance is observed for lower sputter power. It is seen that the average transmittance of these samples on PC substrate shows the highest value.

The PL spectra of the CdS films deposited at different sputter powers are shown in Fig. 8. Three peaks can be observed at around 1.77, 2.25, and 2.45 eV, regardless of sputter power. Agata et al. [17] reported that one red band, one yellow band, and two green bands can be observed in their CdS photoluminescence spectra. In their study, the red band was ascribed to the transition of bound electrons from surface states to the valence band. The yellow band was attributed to the transition of Cd interstitial donors to the valence band. The green bands originated from the transition of S-vacancy donors to the valence band and the recombination of donor–acceptor pairs, respectively. In our case, one weak red band, two strong yellow and green bands were observed at 50 and 75 W. This means that these samples were cadmium rich. This is consistent with the previous reports for CdS films produced by the sputtering process [18]. As the sputter power increases from 50 to 75 W, the peak positions of yellow and green bands shifted toward lower energies. The yellow band shifted from 2.23 to 2.17 eV, while the green band peak shifted from 2.43 to 2.35 eV. In addition, the intensity of yellow band decreased slightly with increasing the sputter power. As the sputter power increases further to 150 W, the red band appeared clearly, however, the yellow and green band was very vague.

4. Conclusion

CdS films were deposited on polymer and glass substrate by R.F. magnetron sputtering at low substrate temperature. The growth rate of CdS film increases with increasing R.F. power. All the CdS films show obvious (0 0 2) preferred orientation except for the low sputter power. The crystallinity of the resulting films is improved when the R.F. power is higher. Although the quality of the films deposited on polymer is somewhat worse than that on glass substrate, PC and PET can be used as substrate in preparing CdS films by R.F. magnetron sputtering, and these films deposited on PC and PET may eventually be useful in some applications.

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