Journal of Ovonic Research Vol. 10, No. 5, September - October 2014, p. 185 - 190

OPTO-ELECTRICAL PROPERTIES OF In DOPED CdS THIN FILMS BY CO-SPUTTERING TECHNIQUE

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Indium (In) doped CdS thin films has been prepared by co-sputtering of CdS and In target on glass substrates at 300 °C for a window layer of solar cells. UV-Vis, and Hall Effect measurements were performed to characterize the growth and doping impact of In in the CdS thin films. The experimental results show that the carrier concentration and Hall mobility increased with increasing In concentration at certain limits and then decreased with a further increase of In concentration, while the resistivity changed reversely. The optical band gap increased with increasing of In as well as electron concentration due to the increase of the Fermi level in the conduction band. The band gap was also decreased after a certain limit of In concentration. The highest carrier concentration and optical band gap was observed for the film of In RF power 0.5 watt/cm^2.

(Received August 28, 2014; Accepted October 20, 2014)

Keywords: CdS:In thin film; Electrical properties; Band gap; Co-sputtering

1. Introduction

For the fabrication of high efficiency photovoltaic devices and gas sensors, doped CdS thin films is one of the important factor [1-3]. Undoped CdS thin films generally show high electrical resistivity, even window material with high optical transmittance and low resistivity is highly desirable for high efficiency solar cells [4]. To reduce the resistivity of the CdS thin films, one can either vary the ratio of Cd to S or add dopants such as Cu, Al, Zn and In. However, Cu is a fast diffuser into the CdS crystal lattice and will give a p-type semiconductor [5], for which it is not applicable for fabrication of highly stable thin film solar cells. Moreover, Al doped CdS films exhibited lower crystallinity than undoped CdS [6], which represents a disadvantage for high efficiency solar cells fabrication. Again, Zn doping to the CdS thin films increase the resistivity and decrease the optical transmittance as well [7], which adversely affect the carrier generation and transportation in the solar cells. Indium is found as effective and suitable dopants to obtain n-doped CdS with larger grain size without introducing much distortion in the crystal structure [8]. In this doping process, the extra electrons are coming from the In^{3+} ion is placed substitutionally in Cd^{2+} sites, and increase carrier concentration and reduce the resistivity of the films.

In this study, In dopent is added to the CdS thin films by co-sputtering technique. The dopant amount is varied by varying the In deposition power. The effects of In on the optical, and electrical properties of CdS films have been carried out extensively.

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2. Experimental details

The CdS and CdS:In thin films of thickness around 200 nm are deposited by co-sputtering of CdS and In target on the ultrasonically cleaned soda lime glass substrates. The CdS and In targets were put in two different gun for co-sputtering, where the CdS deposition rate was fixed by RF power of 2.0 watt/cm^2. The In concentration in CdS thin films was varied by changed the RF power ranging from 0.25 watt/cm^2 to 1.5 watt/cm^2. The working ambient pressure of argon was 1.81 Pa and the substrate temperature was 300 ^oC. The rate of deposition was varied from 1.19-1.90 Å/sec depends on the RF power of In observed from the thickness profiler embedded with the sputtering system. The rate of deposition corresponding to the RF power of CdS and In are putted in Table 1.

The optical properties such as transmittance, absorbance and optical bandgap were carried out using 'Lambda 900 UV/Vis/NIR' spectrometer. The films crystallite size was also calculated from the optical bandgap using Brus's equation. The carrier concentration, mobility, resistivity and hall coefficients are measured by Hall Effect measurement tool 'ECOPIA 3000'.

3. Results and Discussion

Fig. 1 shows the optical transmittance spectra with wavelengths from 300 to 900 nm for the CdS and In doped CdS thin films. When the In dopants were added, the average transmittances in the visible region are increased. The main reason is that when a certain amount of In dopants were added into the CdS film, the growth of CdS crystallization was suppressed to form a fine structure, resulting in a reduction in surface roughness. Merely, the smoother surface morphology enhanced the optical transmittance by reducing the optical scattering [9, 10]. However, the average transmittances of doped films with In (≥1.0 watt/cm^2) is lower than its prior doped films (≤1.0 watt/cm^2). The cause of this reduction may be due to the formation of $CdIn_2S_4$ compound by the excess In atoms, which is discussed at bellow.

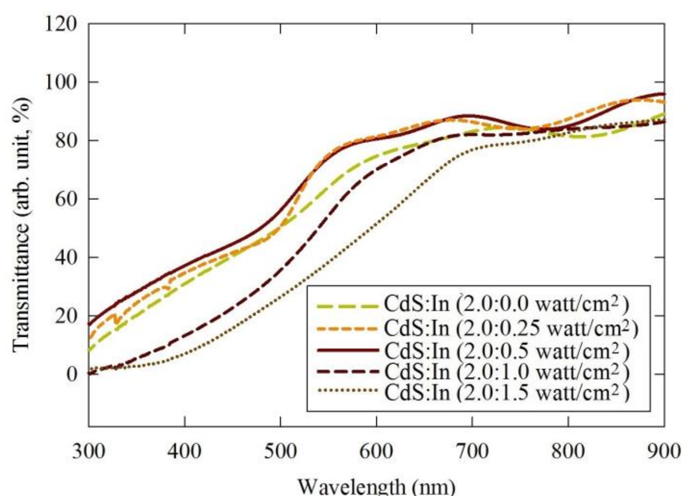

Fig.1 UV-Visible transmittance spectra of In doped CdS thin films

From the figure of transmittance spectra, all samples are shown sharp absorption edges in the UV region, and this absorption edges slightly shifted to shorter wavelengths (blueshift) for the In doped CdS thin films for In deposition power 0.25 watt/cm^2 and 0.5 watt/cm^2. This optical blue shift is indicating the poor crystallinity of In doped CdS thin films. The absorption coefficient (α) is calculated by using the following equation [11]:

$$\alpha = \ln(1/T)/d \quad (1)$$

Where, T is the transmittance index and d is the film thickness. In the direct transition semiconductor, the optical band-gap dependence on the absorption coefficient and derived from the following equation [12, 13]:

$$\alpha = [A(h\gamma\text{-}Eg)^n]/h\nu \quad (2)$$

Where, A is constant, α is the absorption coefficients, hγ is photon energy and Eg is the bandgap. For the direct bandgap semiconductors, the above equation fitted well with the measured absorption data, when n = ½, [14]. By considering, n = ½, the graphs of $(\alpha h\nu)^2$ vs hγ are plotted in Fig. 2 enabling the energy bandgaps of the films to be determined. The values of the optical bandgap energies (Eg) were obtained by extrapolating the lines to the hγ-axis at (αhγ) = 0. The band gaps were found to be in the range 2.17 eV-2.60 eV. The optical band gap for CdS was found 2.45 eV, which increases to 2.6 eV with increasing In concentration up to deposition RF power 0.5 watt/cm^2, and then decreases to 2.17 eV with further increases in RF power. Such widening of the optical band gap with indium doping can be described by Burstein–Moss effect [15-18]. The Burstein–Moss effect is occurred by reason of the carrier contribution from the In^{3+} ions on substitutional sites of Cd^{2+} ions. Consequently, In interstitial atoms increases the carrier concentration, and the band gap of the doped material is increased due to the Fermi level moving into the conduction band.

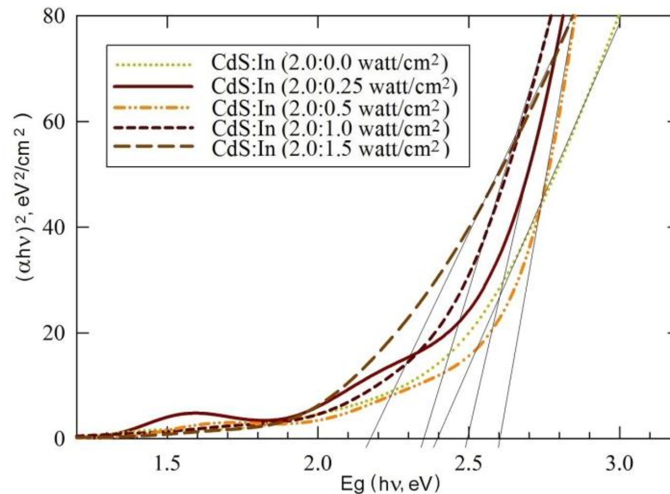

Fig. 2 Graph of $(\alpha h\gamma)^2$ versus photon energy, hγ for In doped CdS thin films

However, a decrease in the band gap is observed for CdS:In films deposited with In deposition power 1.0 watt/cm^2 and 1.5 watt/cm^2, respectively. Mohanty et al [19] has been explained this unusual red-shift for Al doped ZnO films in terms of stress relaxation mechanism. However, the over doped In atoms may introduce defect states just below the conduction band. This defect state arises due to hybridization between states of the CdS matrix and of the In dopant [20]. May be such formation of donor levels compensates the Burstein–Moss effect and narrowing the effective band gap of the In doped CdS thin films. However, at longer wavelength region, the average transmittance was about 85%, regardless of In concentration. The higher optical band gap and maintaining high optical transmittance are advantageous features of In-doped CdS thin films for a window layer in solar cells.

If it is considered that the crystallites of the CdS:In films are spherical in shape, then, the average crystallite size as a function of RF power can be determined using the simplified Brus equation [21, 22],

$$E_{gn} - E_{gb} = [\hbar^2\pi^2/2R^2][\,1/m_e^* + 1/m_h^*\,] \quad (3)$$

Where, h is plank's constant, $m_e^* = 0.16\ m_e$ is the effective mass of electron, m_h^* (= 0.8 m_e) is the effective mass of hole, R is the radius of the crystallites, E_{gn} is the bandgap of the samples

and E_{gb} is the bandgap of the bulk CdS (2.42 eV) [23]. The particle size gives an important indication about the change of optical properties with structural variation of the films. Generally, particle size reduces with the increase of bandgap, but some other internal parameters of thin films such as surface roughness, morphology and extinction co-efficient affect the relation. However, this method is more effectively used for the films with amorphous form. The highest bandgap 2.6 eV was found for the crystallite radius, 3.67 nm in this study.

Table 1 Bandgap and crystalline size analysis from the EMA of CdS:In thin films

Sample ID	RF power ratio (CdS:In), watt/cm^2	Deposition rate ratio (CdS:In), Å	Deposition rate (co-sputtering), Å	Bandgap, eV	Crystallite's radius, nm
A1J1	2.0:0.0	1.19:0.0	1.19	2.42	-
A1J2	2.0:0.25	1.19:0.20	1.39	2.49	5.91
A1J3	2.0:0.50	1.19:0.39	1.58	2.60	3.67
A1J4	2.0:1.0	1.19:0.55	1.71	2.35	6.99
A1J5	2.0:1.5	1.19:0.71	1.90	2.17	3.13

The electrical properties of the CdS and CdS:In thin films were investigated at room temperature by resistivity and Hall Effect measurements with an integrated resistivity/Hall measurement system (ECOPIA 3000). In this study, the used magnitude of the magnetic field and the current source was 0.55 T at the maximum and 50 nA, respectively. The carrier concentration, mobility, resistivity and hall coefficients were deduced from this study. The measured mobility, resistivity, hall coefficients and carrier concentration are presented in Fig. 3, and Table 2, respectively.

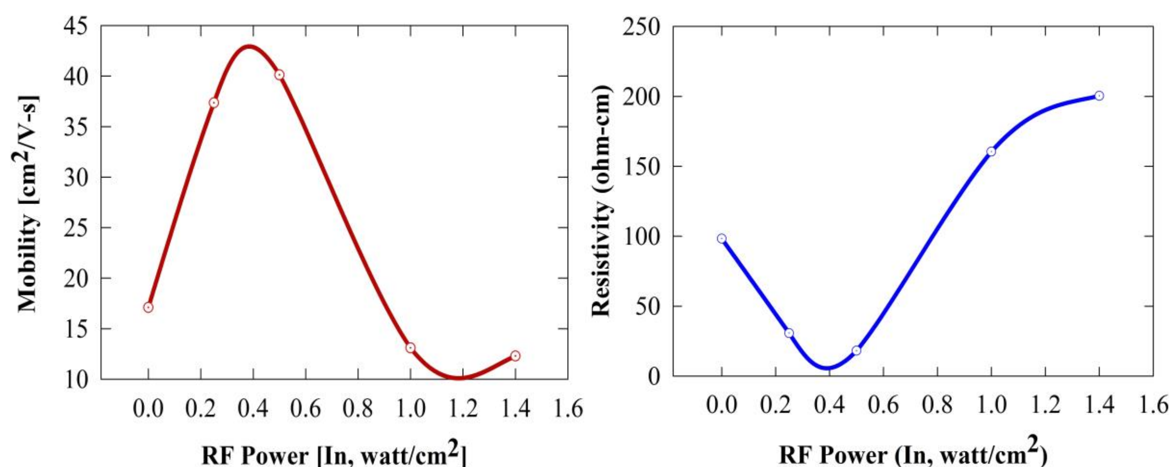

Fig. 3 Variation of mobility and resistivity of CdS:In films with the In deposition power

Table 2 Electrical properties of In dope CdS thin films

Sample ID	RF power ratio (CdS:In), watt/cm^2	Deposition rate ratio (CdS:In), Å	Carrier concentration [x10 ^{16}] (cm^{-3})	Hall co-efficient [10^2] (cm^3/C)
A1J1	2.0:0.0	1.19:0.0	0.25	10.74
A1J2	2.0:0.25	1.19:0.20	18.9	0.33
A1J3	2.0:0.50	1.19:0.39	51.7	0.19
A1J4	2.0:1.0	1.19:0.55	36.81	0.22
A1J5	2.0:1.5	1.19:0.71	7.88	0.98

The mobility of the films is observed to increase, and resistivity is decreased with the increase of In concentration up to In RF power 0.5 watt/cm^2, while they changed oppositely with the further increase of In RF power. On the other hand, the carrier concentration of the CdS:In films increased with increasing In concentration up to In RF power 1.0 watt/cm^2, and then decreases with the further increase of RF power. These variations of the electrical properties with the increase of In concentration can be explained by the doping effect of In in CdS. The carrier concentration is increased by coming extra electrons from the In^{3+} ion which is placed substitutionally in Cd^{2+} sites and reduces the grain boundary potential barrier. As a result, the carrier mobility of the films also increases [24]. The carrier concentration and mobility of heavily doped films are decreased may be due to form a secondary phase in CdS:In thin films. Dhere et al. [25] reported that heavily In-doped CdS films prepared by a hot wall technique formed the $CdIn_2S_4$ compound at the grain boundary. Kim et al. [26] considered that the solubility limit of In in CdS is 3 x 10^{20} cm^{-3} and the excess In could form the secondary phase, which is possibly segregated at grain boundaries. This segregation adversely affects the Hall mobility of the films as seen in Fig. 3. The increase of the secondary phase with the increase of In concentration may result for decrease of carrier concentration and Hall mobility. Consequently, the resistivity is decreased with increasing In concentration, reached a minimum, and then increased with further increases of In concentration.

4. Conclusion

The opto-electrical properties of In doping on CdS thin films were studied because of their importance as an appropriate n-type window layer in several types of heterojunction solar cells. The band gap of the CdS film increases up to a certain level of In doping due to the increase of carrier density. Beyond this limit, narrowing of the bandgap is observed for higher In deposition rate probably indicating merging of an impurity band into the conduction band. The electrical resistance was also observed to decrease initially due to replacement of Cd^{2+} ion by In^{3+} ions. Beyond a certain level of In doping, the electrical resistance increases due to drastic fall in mobility arising out of segregation of excess In dopants at grain boundaries and form a secondary phase. The highest band gap 2.60 eV observed for the film of In RF power 0.5 watt/cm^2 with carrier concentration 5.17 x 10^{17} cm^{-3}. The experimental results indicating expected opto-electrical properties for doping with the low indium amount, and a degradation of the properties for high impurity densities.

Acknowledgement

This study is supported by the Fundamental Research Grant Scheme (FRGS) of the Ministry of Higher Education of Malaysia (MOHE) with the grant code of FRGS/1/2013/TK07/UKM/01/3. Authors would also like to extend their gratitude to the National University of Malaysia (UKM) for the logistic support throughout the research work.

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