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Optical and structural properties of CdS/ZnSe bi-layer thin films prepared by e-beam technique

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Abstract: Single and bi-layer thin films of Cadmium Sulphide (CdS) and Zinc Selenide (ZnSe) were prepared on glass and ITO/Glass substrates by e-beam technique. Spectral transmittance of bi-layer thin film showed red shift with prolonged interference effect. The decrease in Urbach tail of bi-layer thin film signifies the decreased band gap with increased grain size. Single layer CdS film has prominent (002) hexagonal peak where as bi-layer thin film confirm with (002) hexagonal and (111) cubic peaks of CdS and ZnSe respectively. CdS grain size was found to be 14.5, 17.1, and 33.1 nm on glass, ITO/Glass and ZnSe/ITO/Glass substrates respectively.

Keywords: Bi-Layer, Cadmium Sulphide, E-Beam Technique, Thin Films, Zinc Selenide

1. Introduction

Among wide range of semiconductors, cadmium sulphide (CdS) is considered as one of the important material for applications in opto-electronic devices [1-2]. This material has also been proved to be an efficient window material in solar cells [3]. The focus of research in Cadmium Telluride (CdTe) based thin film solar cell to obtain higher efficiency is by reducing the thickness of the CdS window layer [4]. The reduction in thickness of CdS will admit large amount of photons to the junction and absorber layer. However, thinner CdS also leads to high minority carrier recombination losses. In order to fulfill the recombination losses, the buffer layer is used prior to CdS deposition which will form a hetero junction hence reducing the recombination losses [5-6]. Out of various buffer layer materials Zinc Selenide (ZnSe) is considered to be a potential contender in photovoltaic solar cells which can substitute the CdS window material [7]. Numerous researches have been done on ZnSe thin films related to structural and Opto-electronic properties. However, the studies on ZnSe as a buffer material for hetero-junction solar cell are sparse. Various deposition techniques [8-11] have been adopted by several researchers to prepare CdS and ZnSe thin films. Vacuum evaporation is considered to be the efficient way due to its simple, inexpensive and mainly stoichiometric effects. In this view, we have carried out the systematic investigation on optical and structural properties of CdS thin films deposited on glass, ITO/Glass and ZnSe/ITO/Glass films by vacuum deposition.

2. Experimental

2.1. Preparation of Thin Films

The thin films of CdS and ZnSe were prepared by e-beam mediated physical vapour deposition technique. The 99.99% pure CdS and ZnSe powders were procured from Sigma Aldrich, molybdenum crucible was used as sample holder. The separation between crucible and the substrate is 13.5 cm; the substrate holder is aided with continuous rotation for the formation of uniform films. The obtained thin films were about 300 nm under the standard rate of deposition (3-5 A°/Sec). The thickness and deposition rate were measured by using inbuilt quartz crystal thickness monitor (DTM-101). CdS thin films were deposited under 130 ºC substrate temperature condition where as ZnSe thin films were deposited at normal chamber temperature and subsequently annealed in air at 200 ºC for 3 hr.

2.2. Characterization

The optical properties of prepared thin films were determined by Ultraviolet - Visible - Near Infrared Spectrophotometer (Ocean Optics, USB4000-XR, USA). The illumination at normal incidence of light by spectrophotometer for optical analysis of bi-layer thin film is shown in Fig. 1.

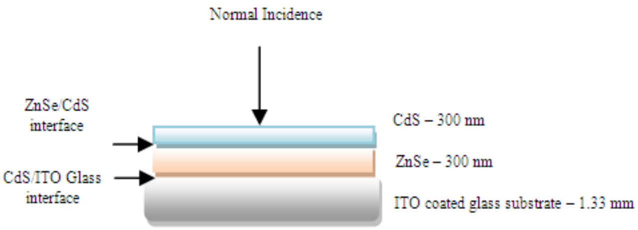

Figure 1. *Light illumination at normal incidence by spectrophotometer on bi-layer thin film.*

The refractive index was estimated by using transmittance spectra by envelope technique [12] and the optical band gap was obtained by using Tauc's equation [13]. The structural properties of thin films were determined by using a Philips X-ray diffractometer with monochromatic Cu-Kα radiation (λ= 1.54 A°). Surface morphology was determined using ULTRA - 55, Field emission Scanning Electron Microscopy (SEM).

3. Results and Discussion

3.1. Optical Analysis

The optical transmission spectrum in the range of 300 - 1100 nm of single and bi-layer thin films of CdS and ZnSe were shown in Fig. 2. All thin films have shown sharp fall in transmittance at the band edge. Interference effect between the film and substrate increased with increase in thin film layers. The single layer CdS film has 87% and 80% optical transparency on glass and ITO/Glass substrates respectively. The absorption edge shift in single layer CdS on ITO is mainly due to a wide band gap of ITO/Glass substrate [14]. Bi-layer thin film revealed maximum interference effect with three transparencies (75, 79 and 82%) two in visible and one in infrared regions, this may be due to the wide band transparency of ZnSe thin film from 450 nm to 2.5 µm [15].

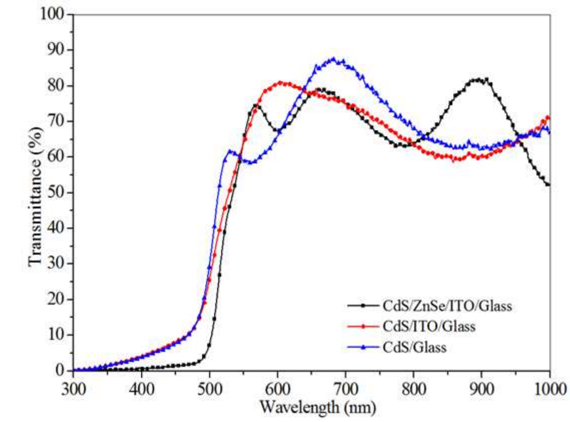

Figure 2. *Transmittance spectra of single and bi-layer thin films.*

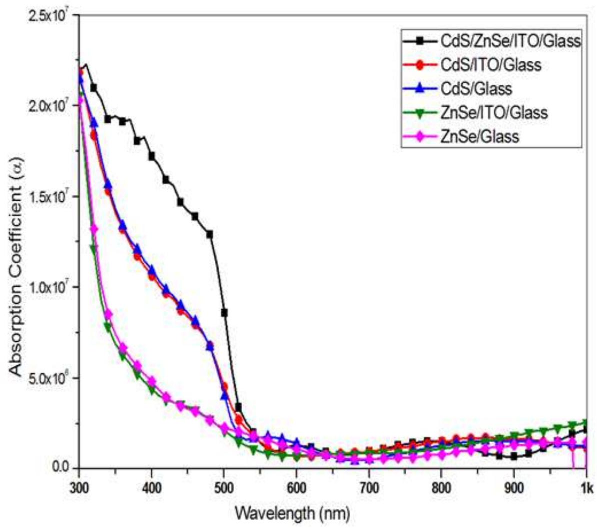

Figure 3. *Absorption coefficient as a function of wavelength*

The absorption coefficient versus wavelength of ZnSe, CdS and CdS/ZnSe were represented in Fig. 3. ZnSe and CdS thin film deposited on glass and ITO clearly reveals that ITO has not affected the absorbance of the thin films, whereas absorption edge of single layer ZnSe, CdS and bi-layer CdS/ZnSe shows a gradual shift from 490 to 520 nm. CdS thin film showed an intermediate absorption shift in absorption edge towards higher wavelength compared to ZnSe thin films. Significant increase in absorption band with incorporation of CdS layer over ZnSe thin film is also evident from transmission spectra. Similar trend of observation was reported for CdSe and CdTe single and bi-layer thin films [16].

Table 1. *Variation of Refractive Index at different wavelengths estimated by transmission spectra*

Thin film	Wavelength	Transmittance Maxima (T_{max})	R.I (n_f)
CdS/Glass	605	0.807	2.54
ZnSe/Glass	700	0.847	2.71
	568	0.745	2.35
CdS/ZnSe/ITO Glass	665	0.783	2.46
	895	0.819	2.59

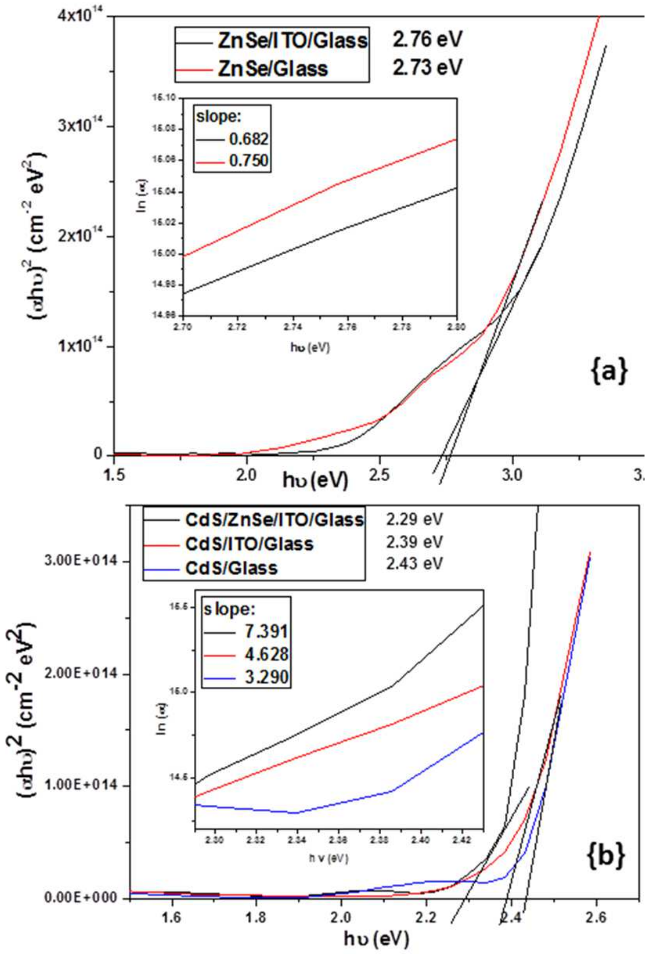

Figure 4. *Variation of Band gap with respect to photon energy (eV). Inset: ln (α) vs photon energy*

Fig. 4 illustrates the variation of $(\alpha h\upsilon)^2$ versus hυ of single and bi-layer ZnSe, CdS thin films. ZnSe film has the direct band gap of 2.73 eV and 2.76 eV which is nearly equal to the standard bulk band gap [17], also the film reveals slight blue shift of 0.10 eV for ZnSe deposited on ITO/Glass substrate (Fig. 4a). The optical band-gap value for CdS/Glass and CdS/ZnSe/ITO/Glass is found to be decreased from 2.43 eV to 2.29 eV (Fig. 4b). This thickness dependent optical band gap trend is because with increase in film thickness, bi-layer thin films do not induce free atoms in turn there is no possibility of creating overlapping energy levels. Also, the decrease in band-gap value may be attributed due to the increase in particle size, which is evident from XRD represented in Fig. 5. This phenomenon can be explained by Urbach tail [18], which signifies the characteristic phenomena of absorption curve with respect to photon energy. The minimum tail width of 3.29 eV showed by CdS/Glass thin film, whereas CdS/ZnSe/ITO/Glass has higher tail width of 7.39 eV (Inset of Fig. 4b).

The variations of refractive index of single and bi-layer thin films were shown in table 1. The refractive index was estimated through transmission spectra considering the transmittance maxima, given by the following equation,

$$n_f = \left[n_s \times \frac{1+\sqrt{T_{max}}}{1-\sqrt{T_{max}}} \right]^{1/2} \quad (1)$$

The 'n_s' and 'n_f' are the refractive index of the substrate and the thin film respectively. The refractive index of 2.54 for single layer CdS thin films has good agreement with the reported values [19]. The bi-layer thin films possess refractive index of 2.35 to 2.59 through the wavelength 568 to 895 nm. This maximum value of refractive index is due to the better stoichiometric values between Cd/S and Zn/Se thin films with increased packing density [20]. Also, the high refractive index value minimizes the scattering losses and enhances the light extraction efficiency [21].

3.2. Structural Analysis Using XRD

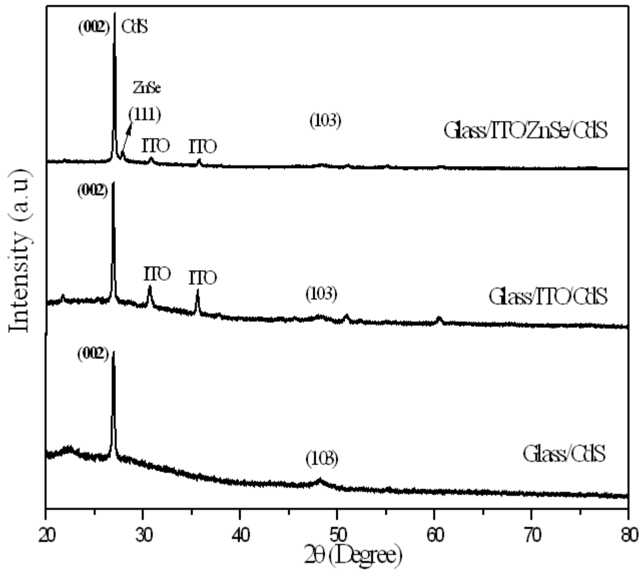

Figure 5. *XRD pattern of deposited thin films*

Structural properties of CdS thin film on different substrates were analyzed using XRD. The phase of crystallites and the average crystallite size were obtained by the X-ray analysis is shown in Fig. 5. The prominent peak of (002) plane exhibit by CdS films at 23.56° referred to JCPDS No: 77-2306. Another prominent (111) peak at 27.80º in case of bi-layer thin film corresponds to ZnSe thin film. This confirms the presence of CdS and ZnSe thin films with hexagonal and cubic structures respectively. The crystallite size of the thin film was calculated using well known scherrer's equation [22],

$$D = \left(0.94\lambda / \beta \cos\theta\right) \quad (2)$$

Where 'D' is the crystallite size, 'λ' wavelength of the incident ray, 'β' is the full width half maximum (FWHM), 'θ' is the bragg's angle. The estimation of crystallite size considered by this method was found to be 33.1 and 66.1 nm for (002) and (111) orientation of CdS/ZnSe/ITO/Glass thin film, whereas single layer CdS thin film has 14.5 and 17.08 nm crystallite size on glass and ITO/Glass substrate respectively. Increased crystallite size in case of bi-layer CdS/ZnSe/Glass thin film can reduce the additional treatment applied to increasing the crystallite size [23-24].

3.3. Morphological Analysis

Surface morphologies of ZnSe/Glass, CdS/Glass, CdS/ITO/Glass and CdS/ZnSe/ITO/Glass single and bi-layer thin film were confirmed using scanning electron microscope (SEM) shown in Fig. 6. All films showed smooth and uniform distributed surface morphology. It is seen that the cluster of particles has formed batches on the surface of samples. As the layer is increased for single CdS to bi-layer CdS/ZnSe, particle size has increased, which is evident for surface morphology which can be correlated with XRD patterns.

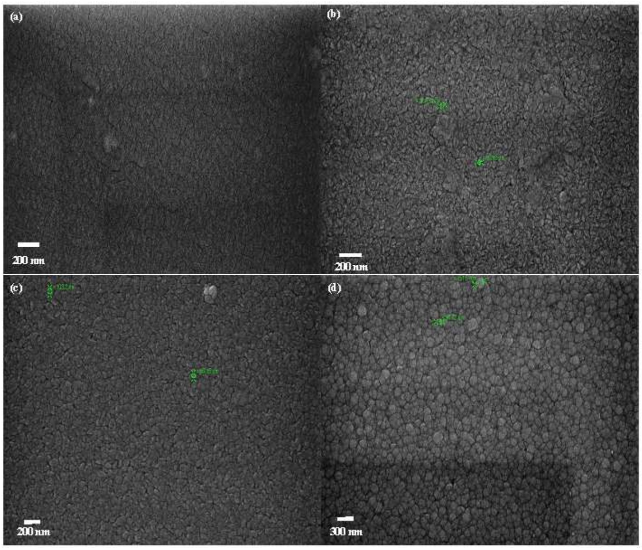

Figure 6. *SEM image of a) ZnSe/Glass, b) CdS/Glass, c) CdS/ITO/Glass and d) CdS/ZnSe/ITO/Glass.*

4. Conclusion

CdS and ZnSe single and bi-layer thin films on glass and ITO glass substrates were deposited using e-beam evaporation technique. The optical spectra clearly indicate that the bi-layer thin film has extended transmission up to near IR region compared to single layer thin film. The high refractive index value of bi-layer thin film is found to be diverging in the range of 2.35 to 2.59 along the optical wavelength. The higher tail width is evident for increased particle size of 33.1 nm for CdS/ZnSe thin film. Single layer CdS thin film revealed minimum grain size of 14.5 nm on glass substrate. The estimated refractive index was found to be nearly equal to bulk value for single layer thin films. Further, the result of bi-layer thin film gives precise impact on optical parameters towards photovoltaic application.

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