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Optical constants of CdS thin films prepared by spray pyrolysis

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Abstract. CdS thin films were prepared by spray pyrolysis techniques. Variable angle spectroscopic ellipsometry was used for optical constant calculations. Multiple angle measurements were taken in the most sensitive angle of incidence region. The sensitive regions of angle of incidence were obtained theoretically using 3-dimensional graph of $\delta\psi$ and $\delta\Delta$. Real part n and imaginary part k of the complex refractive index of the samples were calculated in the wavelength range 470–650 nm, taking into account surface roughness. Bruggeman's effective medium approximation is used for analysis of the surface rough layer of the thin films.

Keywords. Optical constants; ellipsometry; spray pyrolysis; CdS thin films.

1. Introduction

Polycrystalline thin-film semiconductors are suitable materials for low-cost photovoltaic devices. Among these, CdS thin films find extensive use. This material has a wide band gap ($E_g = 2{\cdot}4$ eV) and has been used as a window material in heterojunction solar cells together with several narrow band gap semiconductors like Cu_2S (Norian and Edington 1981), InP (Fraas and Ma 1977), $CuInSe_2$ (Basol *et al* 1991), CdTe (Arita *et al* 1991) etc. and also to form homojunctions with p-type CdS (Kashiwaba 1990) achieving efficiency of over 10%. Recently Basol *et al* (1991) reported that chemically prepared CdS thin films of very low thickness are more ideal window material in thin-film solar cells with $CuInSe_2$ as absorber. They have used ellipsometry for the optical characterization of chemical bath deposited CdS film. Hence a reliable determination of the extinction coefficient k and refractive index n of very thin chemically deposited CdS films is necessary to predict the optical absorption properties and hence photoelectric behaviour of the devices.

CdS films are prepared by different techniques like vacuum evaporation (Romeo *et al* 1978), chemical bath deposition (Kaur *et al* 1980), spray pyrolysis (Chamberlin and Sakarman 1966), etc. Spray pyrolysis technique is widely used for large-scale production due to its low production cost and simplicity of operation. The optical properties of CdS thin films are determined to a large extent by the microstructure of the film (Chopra and Das 1983). The vacuum-evaporated films are smooth and specularly reflecting and the optical constants of these films have been reported (Khawaja and Tomlin 1975). Little work has been done in the case of chemically prepared CdS thin films. The major difficulty faced in optical measurements on chemically prepared thin-film samples is the surface roughness and this may even affect the measured values of optical constants. In the present work we have calculated n and k of CdS thin films prepared by spray technique, as we use these films for solar cell fabrication, taking into account the surface roughness present on the sample such that it does not affect the measured values of n and k.

Many methods have been developed to determine the optical properties of semiconductor thin films (Denton *et al* 1972; Manifacier *et al* 1976; Klein *et al* 1990). Ellipsometry is most widely used for the optical analysis of thin films (Nolly *et al* 1987; Oikkonen 1987; Vijayakumar 1991a). This is nondestructive and extremely sensitive to the sample surface and subsurface conditions. The layer thickness and complex refractive index can be determined for layers within the absorption length of the sample. A major limitation of this is caused by correlation between the model parameters in the data fitting procedure (Snyder *et al* 1986). In general the parameter correlation tends to become more severe as the number of parameters increases and hence parameter sensitivity decreases. Thus in studying multilayer systems using this technique it is of crucial importance to maximize the sensitivity of ellipsometric measurements to the model parameters of interest.

2. Ellipsometry theory

Ellipsometry is an optical characterization technique in which change in polarization state of light due to non-normal reflection from the sample is measured and interpreted to determine the physical properties of the sample. Sample properties can be calculated from the optical model that relates the ellipsometric parameter ρ to the physical properties of the sample by a set of mathematical relations. For a multilayer system (Azzam and Bashara 1977),

$$\tan\psi\, e^{i\Delta} = \rho = \rho\{\varepsilon_a \cdots, \varepsilon_j \cdots, \varepsilon_s \cdots, d_j \cdots, \phi, \lambda\}, \tag{1}$$

where ε_a and ε_s are the dielectric constants of air and substrate and ε_j is that of the jth layer, d_j is the thickness of the jth layer, ϕ the angle of incidence, and λ the wavelength. The theoretical ψ_c and Δ_c are calculated using complex amplitude of reflection coefficients r_p and r_s for p and s polarized waves respectively. The experimental ψ_e and Δ_e are calculated from the light intensities of the reflected light at different azimuths of the analyser of the photometric ellipsometer. The required parameters of the film substrate system are determined by least squares regression analysis (LRA) by minimizing the factor Q using the relation (Oikkonen 1987),

$$Q = \sum_i ((\tan\psi_{c(\lambda i)} - \tan\psi_{e(\lambda i)})^2 + (\cos\Delta_{c(\lambda i)} - \cos\Delta_{e(\lambda i)})^2). \tag{2}$$

The best-fit optical model is calculated from the unbiased estimator values obtained from the ellipsometric calculation (Vedam *et al* 1985). A detailed theory of the ellipsometry is given elsewhere (Vijayakumar 1991a).

In the present study the CdS films are treated as nonhomogeneous along the thickness, due to the surface roughness of the film. The top surface layer can be considered as a mixture of two layers, i.e. air and CdS thin film. If ε_a and ε_b are the dielectric constants of the two components of the mixture layer and ε_c is that of the mixed layer, the Bruggeman's effective medium approximation is given as (Bruggeman 1935)

$$f\frac{\varepsilon_a - \varepsilon_c}{\varepsilon_a - 2\varepsilon_c} + (1-f)\frac{\varepsilon_b - \varepsilon_c}{\varepsilon_b - 2\varepsilon_c} = 0, \tag{3}$$

where f is the volume fraction of the component a.

3. Sensitivity analysis

For analysis of a complex material system such as a thin-film system with unknown refractive index and with rough top layer, which has a different effective refractive index, more angles of incidence must be used to minimize experimental errors and to get reliable values. The best analysis is done by making more ψ and Δ measurements than the number of parameters being solved through the regression analysis. It is more important that the ranges of angle of incidence and wavelength be carefully selected to maximize sensitivity and to avoid mathematically correlated variables (He and Woollam 1990).

The ellipsometric parameters ψ and Δ are functions of two experimental values, angle of incidence ϕ and wavelength λ, in addition to the physical constants of the samples such as complex refractive index N, thickness t, etc. In order to do sensitivity analysis 3-dimensional plots need to be drawn for both $\delta\psi$ and $\delta\Delta$ vs λ and ϕ based on an assumed optical model of the film system (He and Woollam 1990).

The $\delta\psi$ and $\delta\Delta$ are the changes in ψ and Δ of the system due to small perturbation of the values of a parameter of the thin-film system whose value is to be determined with good accuracy. For this, first the theoretical ψ and Δ are calculated for a certain range of wavelength and angle of incidence values. Next a second set of ψ and Δ values (say ψ' and Δ') are calculated by giving a small perturbation in one particular model parameter (e.g. a few angstroms change in layer thickness) (He and Woollam 1990). The difference between each theoretical ψ and Δ pair is calculated using a FORTRAN program to create a 3D sensitivity graph in which z-axis is either $\delta\psi$ or $\delta\Delta$, i.e.

$$\delta\psi = \psi - \psi' \text{ and } \delta\Delta = \Delta - \Delta'. \tag{4}$$

Thus from this graph one can find ranges of values of angle of incidence and wavelength in which $\delta\psi$ and $\delta\Delta$ are maximum. In this study we have plotted 3D graphs for the CdS thin-film system to find the most sensitive angle of incidence region for calculating the refractive index of spray-coated CdS thin film using a multilayer model. Sensitivity graph for the CdS system is plotted using the refractive index values of vacuum-coated CdS film (Khawaja and Tomlin 1975). The variation of ψ and Δ corresponding to the variation of two parameters, viz. thickness (t_2) and volume fraction (f), are calculated, as these are the two main parameters used in the modelling of film structure for refractive index calculation. Since the film is taken to be of two layers, variation of the thickness of the lower layer is considered for calculating $\delta\psi$ and $\delta\Delta$. Measurements at a few angles of incidence in the sensitive region are sufficient to get a reliable analysis.

Table 1 shows the sensitive angle ϕ and wavelength λ values of ψ and Δ parameters corresponding to different perturbations. The $\delta\psi$ and $\delta\Delta$ as a function of angle of incidence ϕ and wavelength λ are shown in figures 1 and 2. From these graphs it is clear that Δ is more sensitive than ψ. Figure 1 shows the sensitive region of ψ and Δ due to a perturbation of lower layer thickness (t_2) by an amount of 10%. The sensitive region of $t_2 + t_2 10\%$ for ψ is 57–68° and 56–64° and that of Δ is 63–71° and 56–60°. Another important parameter in the present system is the volume fraction f of air in the rough surface layer, which is considered as a mixture of air and CdS. Figure 2 shows the sensitive region of ψ and Δ due to a small perturbation (0·04) of

Table 1. Sensitive region of angle of incidence ϕ and wavelength λ corresponding to ψ and Δ for various perturbations.

	Perturbations	
	$t_2 + 10\%\, t_2$	$f + 0{\cdot}04$
Sensitive ϕ range for ψ	57-68°& 56-64°	61-67°& 59-66°
Sensitive λ range for ψ	525-580 nm & 710-740 nm	490-540 nm & 720-740 nm
Sensitive ϕ range for Δ	63-71°& 56-60°	61-68°& 57-67°
Sensitive λ range for Δ	500-580 nm & 690-730 nm	480-530 nm & 680-730 nm

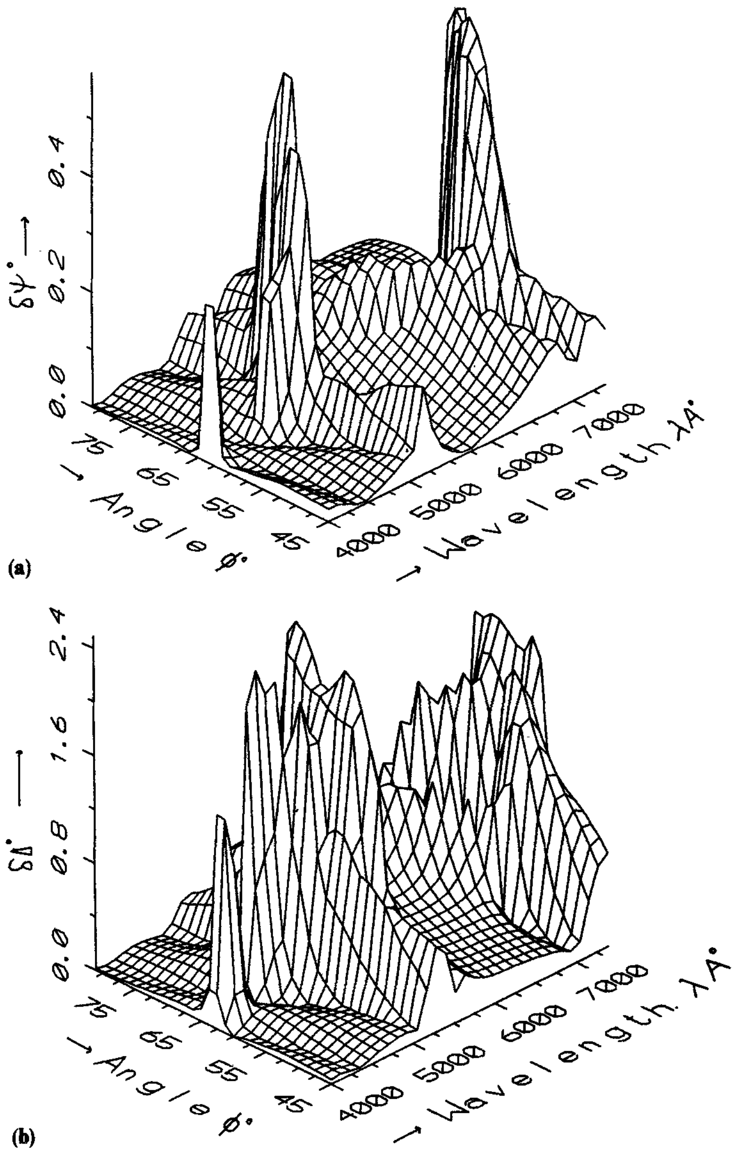

Figure 1. Sensitivity of (a) ψ and (b) Δ to change in bottom layer thickness t_2 by 10%.

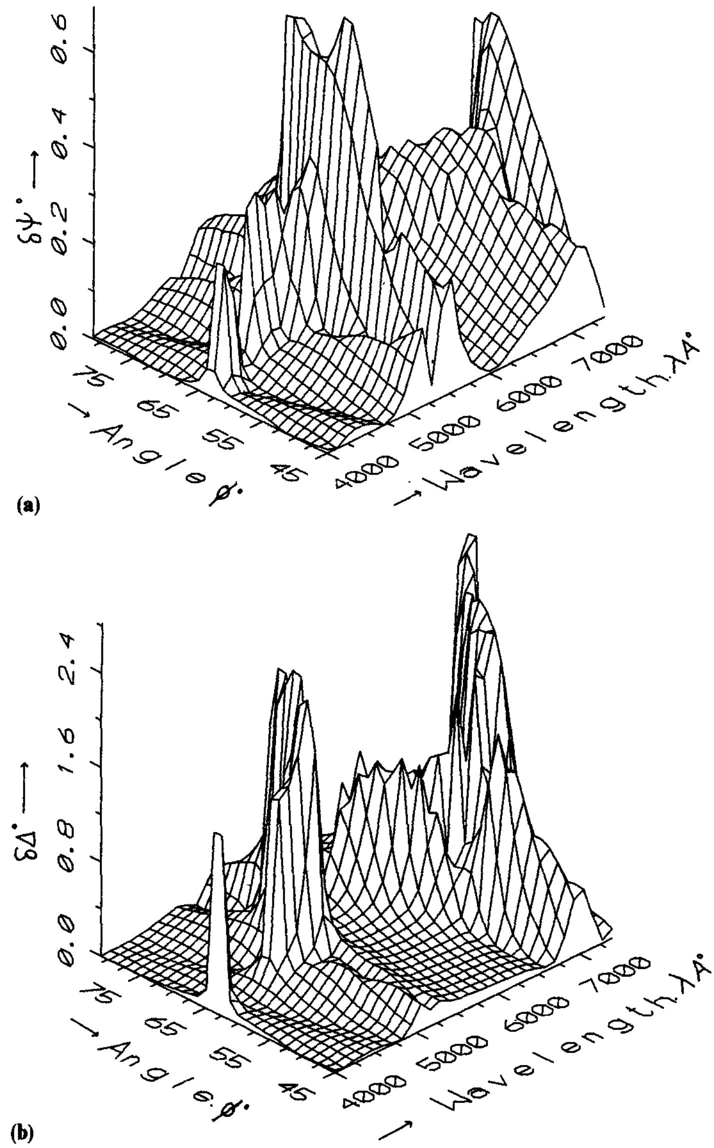

Figure 2. Sensitivity of (a) ψ and (b) Δ to change in volume fraction of top layer by 0·04.

the composition of top layer. The sensitive region of $f + 0{\cdot}04$ for ψ is 61–67° and 59–66° and that of Δ is 61–68° and 57–67°.

4. Measurements

The CdS thin films were prepared by spraying an aqueous solution of $CdCl_2$ and thiourea (0·01 M) on a substrate kept at 573 K. The substrates were glass slides with one side made rough to avoid back reflection during ellipsometric measurements. The atomization of the chemical solution into fine droplets was effected by a spray nozzle, with compressed air as carrier gas. Details of the preparation are given elsewhere (Vijayakumar 1991b). In the present work variable angle spectroscopic ellipsometry (VASE) was used for the analysis of as-prepared thin film. All measurements were made at room temperature and in air. The ellipsometer used for the analysis was photometric and polarizer–system–analyser type. Detailed description of the setup and measurements are given elsewhere (Vijayakumar 1991a). Multiple angle measurements were performed in the wavelength region 470–650 nm for all angles of incidence in the range 60–75°, at angle intervals of 2·5°, which is found to be the most sensitive region for the present thin-film system. Absorption spectra of thin films were recorded using a Hitachi spectrophotometer 3410 in the visible and NIR regions.

5. Results and discussion

In figure 3 the real part *n* of the complex refractive index of CdS film in the wavelength range 470–650 nm is shown and figure 4 shows the *k* value plotted against the same wavelength region. Figure 5 shows the absorption spectrum of CdS thin film. The refractive index calculation was done on as-prepared samples. For the ellipsometric analysis different optical models were selected (model a, air/CdS/glass; model b, air/surface layer/CdS; model c, air/surface layer/CdS/glass). The unbiased estimator values for different optical models, in table 2, show that model b is in good agreement with the physical system. In this model the CdS film is divided into two layers, one surface layer which is a mixture of air and CdS film and the bottom CdS layer. The optical properties of this top layer are described by Bruggeman's effective medium theory.

The refractive index of the lower CdS layer obtained from this analysis is shown in figures 3 and 4. The *n* value of the CdS prepared by spray coating is slightly less than that of CdS film prepared by vacuum evaporation as reported by Khawaja and Tomlin (1975). This is due to the non-perfect structure of the CdS thin film prepared

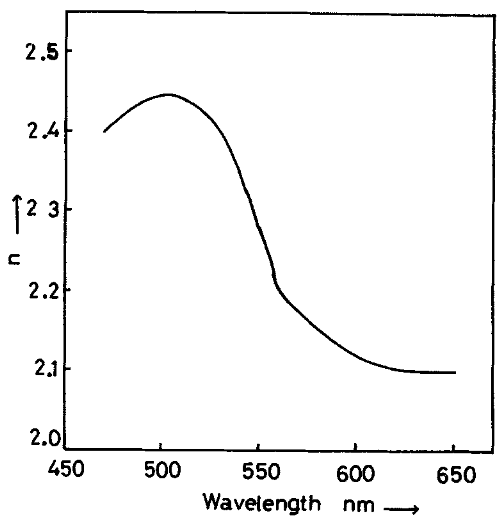

Figure 3. Real part *n* of the refractive index of CdS film prepared by spray pyrolysis.

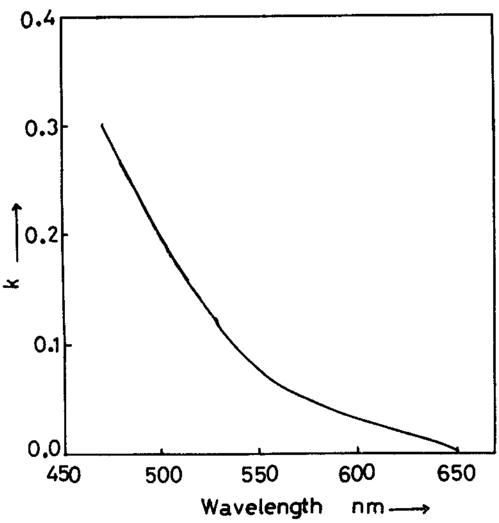

Figure 4. Imaginary part k of the refractive index of CdS film prepared by spray pyrolysis.

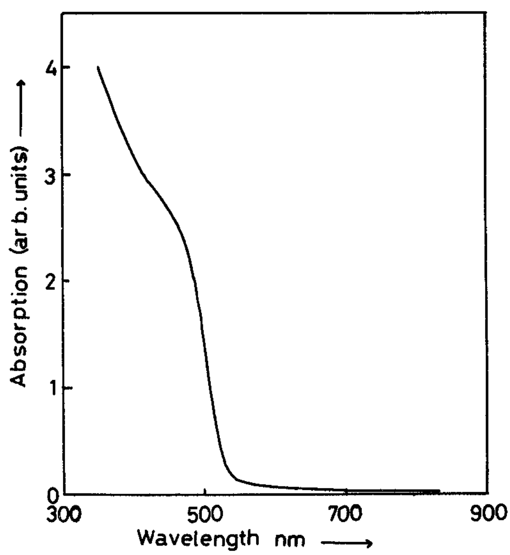

Figure 5. Absorption spectrum of CdS film prepared at 573 K.

Table 2. Unbiased estimator value of different optical models of CdS film. Model a is air/CdS/glass, model b is air/surface layer/CdS and model c is air/surface layer/CdS/glass.

Optical models	Estimator value δ
Model a	1·970
Model b	0·026
Model c	0·195

at 573 K. The film is considered as polycrystalline with small grain size. Due to this small grain size the n value of the film is smaller. The role of surface roughness is also very important in the optical analysis of the film. In the present study the effect due to the surface roughness is eliminated by taking the film as nonhomogeneous along the thickness and considering the film as a double-layer system with top rough layer and bottom layer with comparatively perfect structure.

In the case of the k value, spray-coated CdS film has slightly higher value than the vacuum-coated film. The imaginary part k of the complex refractive index N ($N = n - ik$) is the extinction coefficient of the material. In bulk material extinction can be considered as a result of the absorption of light by the atoms. In the case of a thin film the absorption may be modified by other factors such as rough surface, rough boundaries between the grains, etc. All these factors increase the attenuation of light in thin film. The small grain size of spray-coated CdS thin film is the reason for the comparatively high k value compared to vacuum-coated film. Near the absorption edge the k value increases rapidly due to the high absorption of CdS film, as shown in figure 5.

6. Conclusion

The real part n and imaginary part k of complex refractive index values of CdS thin film prepared by spray pyrolysis technique differ slightly from those of vacuum-coated film. It is inferred that this is due to the small grain size of the CdS film prepared at 573 K. VASE studies also show that the spray-coated thin film has two-layer structure. The surface layer has optical properties distinct from those of bottom film.

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