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Application of Spectroscopic Ellipsometry to Study the Effect of Annealing on Cadmium Sulphide Thin Films

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Abstract

Multiple angle spectroscopic ellipsometery (SE) has been used to study the variation in the layer structure due to annealing of CdS thin films prepared by spray pyrolysis technique. The samples were studied using visible light having wavelength in the range 535 nm - 650 nm. The results obtained from the ellipsometric measurements were analysed assuming different multilayer models for the film structure. In the present work films of $\sim$ 200 nm thickness were analysed and found that annealing at 300^0 C results in a two layer structure in the film with a thin defective layer on the top (of thickness 35 nm) and a thick bottom layer of better crystalline quality. Annealing at lower temperature resulted in a thick top defective layer. Studies using lower wavelengths revealed that the thick top layer itself is divided into several sublayers.

Keywords: spectroscopy, thinfilms, optical materials

Introduction

Studies of CdS thin films (Pandya & Chopra 1981) are of high importance due to the relatively high efficiency and the low production cost of CdS based thin film solar cells. In the present paper the effect of temperature on the thickness of defective CdS layer is studied. Optical characterisation of CdS thin films was carried out using multiple angle SE (Nolly, Abdullah & Vijayakumar 1987). Thin films were grown by spray pyrolysis. The thickness of the film was $\sim$ 200 nm. In the analysis of the ellipsometric data obtained different models have been used and it is found that in certain cases a one layer model is suitable while in some other cases, two layer structure is necessary.

Theory

In an ellipsometric measurement plane polarised light is incident on the sample, and the ellipsometer detects the change in the state of polarisation of light reflected from the sample.

Let r^p be the complex amplitude reflection coefficient for P (amplitude parallel to plane of incidence) wave and r^s be the coefficient for S (normal) wave such that (Azzam & Bashara 1977)

$$\rho = r^p/r^s \tag{1}$$

The complex ratio ρ is calculated using the parameters Ψ and Δ that are obtained from an ellipsometric measurement hence

$$\rho = tan\Psi e^{i\Delta} \tag{2}$$

Here one can denote Ψ_e and Δ_e as the values of these angles obtained experimentally from the ellipsometric measurements. For a given reflection angle θ, wavelength λ and known material parameters N, it is possible to compute Δ and Ψ theoretically (Azzam & Bashara 1977). For an air/film/substrate sytem (Azzam & Bashara 1977),

$$tan\Psi e^{i\Delta} = \frac{(r_{01}^p + r_{12}^p e^{i2D}) * (1 + r_{01}^s r_{12}^s e^{i2D})}{(1 + r_{01}^p + r_{12}^p e^{i2D}) * (r_{01}^s + r_{12}^s e^{i2D})} \tag{3}$$

The subscripts stand for the particular interface in the system (eg. 01 for air/film etc.) and the factor D is defined as

$$D = (\frac{d}{\lambda})2\pi/N_f^2 - N_a^2 sin^2\theta \tag{4}$$

where d is the thickness of the film N_f and N_a are the refractive index of film and air respectively. In the present work, different models having one layer and two layers were used to compute values of Ψ and $\Delta(\Psi_c$ and $\Delta_c)$ using eqn.(3). Now the unknown material parameters were determined by minimising the function

$$Q = \sum_i [\Psi_e(\theta_i) - \Psi_c(\theta_i)]^2 + [\Delta_e(\theta_i)\Delta_c(\theta_i)]^2 \tag{5}$$

where the subscripts e and c stand for experimental and calculated values as defined earlier, and θ_i's are angle of incidence used in the measurements.

Experiment

The CdS film of thickness $\sim$ 200 nm was prepared by spray pyrolysis technique (Chamberlin & Sakarman 1966). The films were prepared at a temperature 280^0 C on a glass substrate. The spray rate was kept at $10ml/min$. The cooling rate of all the films prepared was $\sim 1.5^0 c/min$.

Table 1: Comparison of error factor of different models of the film annealed at 250^0C for the wavelength 646 nm

Model	Thick 1 nm	Thick 2 nm	Error Factor Q (arb.unit)
model 1	156	-	.0118
model 2	130	-	.007
model 3	32	15	.045

The ellipsometer using the Polariser/System/Analyser (PSA) arrangement was used (Azzam & Bashara 1977). The schematic view of optical parts of the ellipsometer is shown in Fig.1. The measurements were taken in the wavelength range 500-650 nm. The angle of incidence was in the range 71-75^0. CdS films were annealed in the temperature range 100-300^0C in air by keeping the heating/cooling rate at $2^0C/min.$ and ellipsometric readings were made in room air and room temperature.

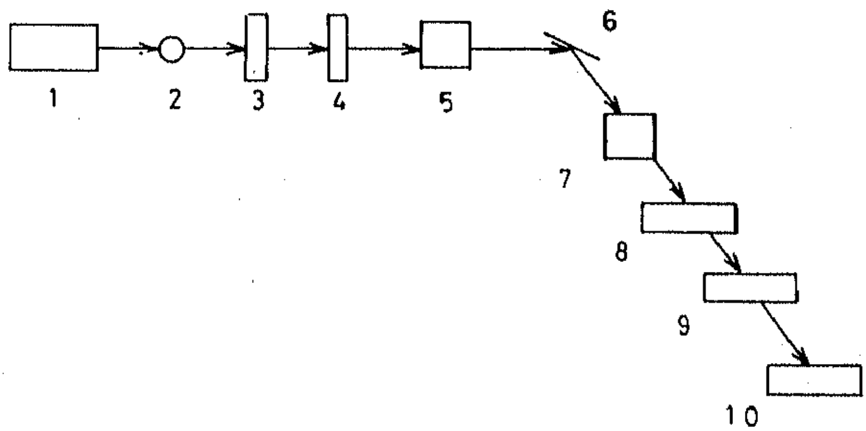

Figure 1. Experimental set up for ellipsometry. 1. Source, 2.lens system, 3.filter, 4.chopper, 5.polarizer, 6.sample, 7.analyser,8.detector, 9.tuned amplifier, 10.digital multimeter.

Results and Discussion

The first model used for the analysis was a single layer one consisting of air/CdS/glass. This study was performed for two different wavelengths viz, 535 nm and 646 nm. From this analysis it was found that at 150^0 and 250^0C this model give comparatively good accuracy as indicated in Fig.2(a). Even though the accuracy of this analysis was not quite good (here entire CdS layer was taken to be pure) this gave a clear hint towards the annealing temperature values at which a CdS layer of comparatively defective free material was formed.

Considering the above facts the single layer model was changed to have a different structure (viz, air/defective CdS/pure CdS) in which it was assumed that the defective layer

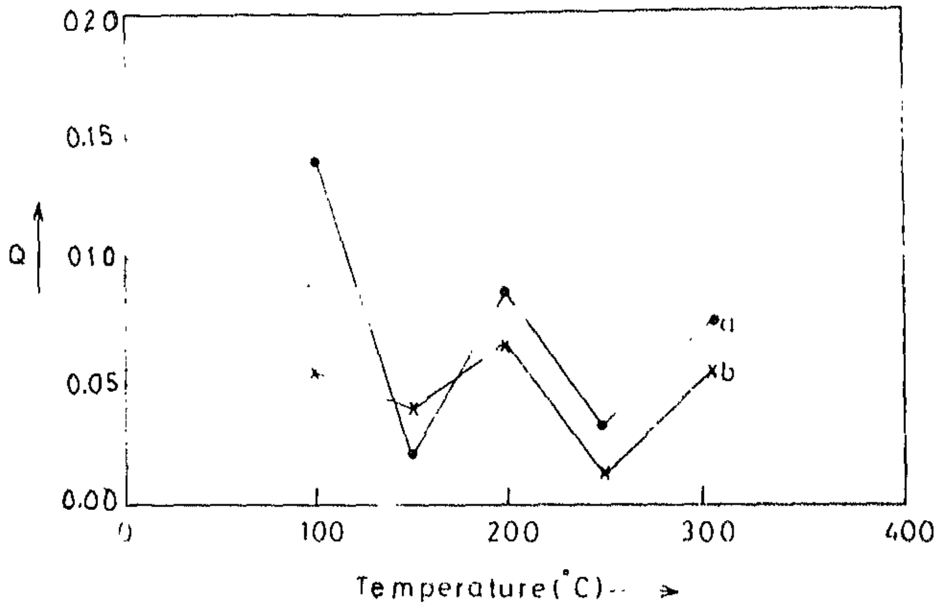

Fig.2(a)

Figure 2(a). Error factor (Q) of ellipsometric data of film annealed at different temperature. Model 1: Air/pure CdS/Glass; a-Q of 535nm; b-Q of 646nm.

was either thick or severely damaged so that light could not reach up to the glass surface. Again this analysis was done using 646 nm. The Fig.2(b) indicates that this model is best suited for film annealed at 250^{0}C. From the Table (1), one can see that the values of the error factor have been reduced by one order on using this model for the film annealed at 250^0. It also shows that on the top surface of the CdS film, a layer of ~ 130nm thickness is defective and below this layer one has a pure CdS layer.

As the second model is not suited for the film annealed at other temperatures, another complicated model having a double layer structure (air/defective CdS/pure CdS/glass) was used for the study of the film. Here also the wavelength selected for the study was 646 nm. From the Fig.2(c) one can also understand that this model is best suited for film annealed at 250^{0}C. Table 2 indicates the variation in the error factor Q from 6 x 10^{-2} to 7 x 10^{-3}, as one changes from the first model to the third model. In this Table results obtained from the analysis using wavelength 600 nm is also included to show that it very well corroborates the results obtained using 646 nm. Fig.2(c) also shows that this model is suitable for film annealed at 150^{0}C and 300^{0}C. In this, the film annealed at 300^{0}C has ~ 35nm thickness for the defective layer.

Table 2 Comparison of error factor of film annealed at different temperature

Model	Temp. 0^0C	Thick 1 nm	Thick 2 nm	Error Factor Q (arb.unit)
model 1				
646 nm	200	180	-	.066
600 nm	200	162	-	.118
model 2				
646 nm	200	145	-	.031
600 nm	200	194	-	.111
535 nm	150	17	-	.009
600 nm	150	190	-	.05
646 nm	150	100	-	.07
model 3				
646 nm	150	77	155	.016
	200	72	140	.007
	300	35	150	.016
600 nm	200	45	140	.008

In the present work light having wavelength 535 nm was also used for the analysis. The model selected for this wavelength was a three layer one (the second model). Due to the high

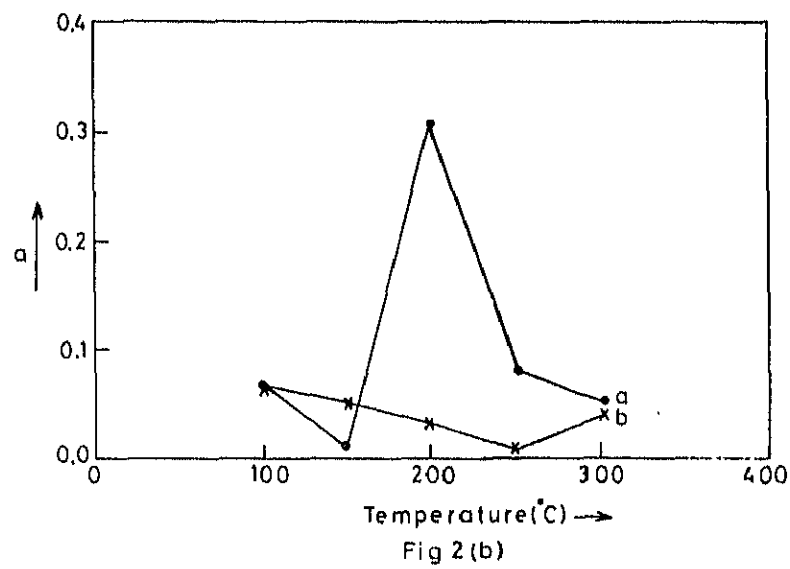

Figure 2(b) Error factor (Q) of ellipsometric data of film annealed at different temperature. Model 2: Air/defective CdS/Pure CdS; a - Q of 535nm; b-Q of 646nm.

absorption in this wavelength region multiple reflections are ineffective (Khawaja & Tomlin 1975). In this region presence of the glass at the bottom of CdS film was not considered due to its slow penetration depth. When this model was applied to all the samples annealed at different temperatures, it was found that this model was suitable for film annealed at 150^0C, as indicated in the Fig.2(b). This analysis revealed that for a film annealed at 150^0C, there is a thin surface layer of defective character having a thickness $\sim$ 17 nm. Comparing this thickness to that obtained for other wavelengths it is found that at lower wave lengths the actual structure of the CdS film is like air/defective CdS/pure CdS/defective CdS/pure CdS/glass. From the variation of error factor Q in Fig.2(b) one can also see that this model is more or less suitable for film annealed at 300^0C. This is in agreement with the results obtained for this film using wavelength 646 nm where it was found that the top defective layer was thin and has a thickness of $\sim$ 35 nm only.

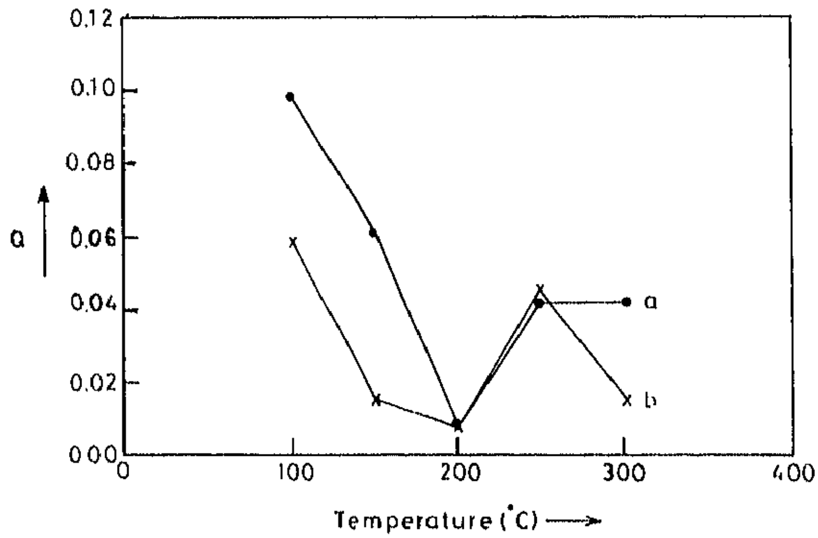

Figure 2(c). Error factor (Q) of ellipsometric data of film annealed at different temperature. Model 3: Air/defective CdS/Pure CdS/Glass; a-Q of 600nm; b-Q for 646nm.

Conclusions

For very thin p-n hetrojunction solar cells this study is important because one of the main draw back of thin film solar cell is it's degradation caused by grain boundaries. Comparing these results it is found that annealing below $\sim 250^0$C leads to comparatively thick defective top layer. On the other hand annealing at 300^0C gives a very thin ($\sim$ 30 nm) defective top layer. Hence films annealed at 300^0C can form p and n layers of better quality leading to better efficiency and low degradation. Another interesting point is that the studies using shorter wavelengths can be used for the 'fine structure' analysis of the top layer as revealed in the case of film annealed at 150^0C.

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