Bull. Mater. Sci., Vol. 17, No. 4, August 1994, pp. 421–427. © Printed in India.

Ellipsometric studies of microscopic surface roughness of CdS thin films

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MS received 2 November 1993; revised 14 June 1994

Abstract. Analysis of changes in surface roughness of CdS thin films with preparation temperature was carried out using variable angle spectroscopic ellipsometry (VASE). The films studied were prepared by spray pyrolysis technique, in the substrate temperature range 200–360°C. The VASE measurements were carried out in the visible region below the band gap ($E_g = 2.4$ eV) of CdS so as to reduce absorption by the film. The thickness of the films was in the range 500–600 nm. Bruggeman's effective medium theory was used for analysis of the surface roughness of the film. The roughness of the film had a high value (~ 65 nm) for films prepared at low temperature (200°C) and decreased with increase in substrate temperature. This reached minimum value (~ 27 nm) in the temperature range 280–300°C. Thereafter roughness increased slowly with temperature. The growth rate of the films was calculated for different temperature ranges. It was found that the deposition rate decreases with the increase in substrate temperature and have an optimum value at 300°C. Above this temperature deposition rate decreased sharply. The scanning electron micrograph (SEM) of the film also showed that the film prepared at 280–300°C had very smooth surface texture.

Keywords. Ellipsometry; surface roughness; CdS thin films; spray pyrolysis.

1. Introduction

At present CdS thin films are widely used as the window material in several CdS based thin-film solar cells $CdS/CuInSe_2$ (Basol *et al* 1991), CdS/CdTe (Arita *et al* 1991). Basol *et al* (1991) reported that the chemically prepared CdS film is a more ideal window material in thin-film solar cells. They have used ellipsometry for the calculation of optical constants of CdS films. The main objective of the study of polycrystalline CdS thin-films deposited by spray pyrolysis technique has been preparation of film with smooth surface, high transparency and high electrical conductivity in order to increase the efficiency of solar cells. CdS films are prepared by using different techniques such as vacuum evaporation (Kakayama *et al* 1976), MBE (Shay *et al* 1975), spray pyrolysis (Cameron *et al* 1979), CBD (Kaur *et al* 1981), etc. The optical properties of CdS thin films are determined to a large extent by the microstructure of the film (Chopra and Das 1983). Detailed studies were reported by various groups on electrical and structural properties of CdS film prepared by spray pyrolysis technique (Banerjee *et al* 1978; Gupta and Agnihotri 1978; Kwok 1980; Albin and Risbud 1987; Valyommana *et al* 1992), but fewer reports are available in the case of optical and surface properties of these films prepared by spray technique (Chow *et al* 1981; Escosura *et al* 1984; Nolly *et al* 1987).

In this work we have calculated the changes in surface roughness of CdS film prepared at different temperatures in the range 200–360°C. The variation in surface roughness was analysed using ellipsometry which is a highly sensitive and non-destructive optical technique for determining the optical and structural properties of thin films (Azzam and Bashara 1977). It is very sensitive to surface irregularities like

surface roughness, interdiffusion and interlayer formation in multilayer thin-film systems (Azzam and Bashara 1977). The CdS film analysis in the present work was carried out using variable angle spectroscopic ellipsometry (VASE) and we have calculated the changes in surface roughness as well as deposition rate with preparation temperature.

2. Theory

Ellipsometry is an optical characterization technique. In this the change in polarization state of light that occurs upon non-normal reflection from the surface of the sample is measured and interpreted to determine the physical properties of the sample. The sample properties can be obtained from the optical model which relates the ellipsometric parameter ρ to the physical properties of the sample through a set of mathematical relations. For example, for a multilayer system (Azzam and Bashara 1977),

$$\rho = \rho\{\varepsilon_a, \ldots, \varepsilon_j, \ldots, \varepsilon_s, \ldots, d_j, \ldots, \phi, \lambda\}, \tag{1}$$

where ε_a and ε_s are the dielectric constants of air and substrate and ε_j that of the jth layer, d_j the thickness of the jth layer, ϕ the angle of incidence, and λ the wavelength. The parameters are determined by least-square regression analysis. Theoretical values of the ellipsometric parameters ψ_c and Δ_c are calculated using Fresnel's reflection coefficients of the optical system. The experimental ψ_e and Δ_e are calculated from the intensity of light reflected from the thin-film system for different azimuths of analyser. The best-fit model is calculated from the unbiased estimator values obtained from the ellipsometric calculation (Vedam *et al* 1985). A detailed theory of ellipsometry is given elsewhere (Vijayakumar 1991a).

If the layer is not perfectly filled with a single material but has voids or inclusions of a different material, the optical properties of the mixed layer are no longer determined by the optical constants of one of the constituent materials alone. In the present study the top surface layer of the sample can be considered as a mixture of two components, 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 that of the mixed layer, the Bruggeman's effective medium approximation is given as (Bruggeman 1935)

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

where f is the volume fraction of the component a.

3. Experimental

The CdS thin films were prepared by spraying aqueous solution of $CdCl_2$ and thiourea (0·01 M) on glass substrates kept at different preparation temperatures. Atomization of the chemical solution into a spray of fine droplets is effected by a spray nozzle, with compressed air as carrier gas. The spray rate was kept at $12\,cm^3/min$. The details of the sample preparation are given elsewhere (Vijayakumar 1991b). The substrate was a clean glass slide without any additional polishing. The back side of each sample was roughened to eliminate the backside reflection. All measurements were done at

room temperature keeping the sample exposed to the ambient. The ellipsometer was of photometric type with polarizer-system-analyser (PSA) arrangement (Azzam and Bashara 1977). A detailed description of the ellipsometric system and calculation is given elsewhere (Vijayakumar 1991a). The analysis of double-layer thin-film system is done using a FORTRAN program incorporating Bruggeman's effective medium theory. Multiple-angle measurements were performed at all wavelengths with angle of incidence range 60–75° at an angle interval of 2·5°, which is found to be the most sensitive region of the present CdS thin-film system (Sunny and Vijayakumar 1984).

4. Results and discussion

The surface of CdS thin film prepared by spray pyrolysis technique is not smooth and has a microscopically rough top surface (Sunny and Vijayakumar 1994). In order to analyse the relation of this roughness with the substrate temperature at which the film is prepared, the film is assumed to have different layers as depicted in figure 1. Here the top layer contains the rough portion of the film as well as air and hence it has an effective refractive index as described in § 2. The thickness of the top layer is taken to be d_1, which is equal to the rms value of the height of the surface irregularities of the film. Hence the measure of this thickness gives direct information about the average height of roughness of the film.

Now using VASE the variation of d_1 for film prepared at different substrate temperatures is measured and shown in figure 2. From this figure it can be understood that the film prepared at low temperature has high surface roughness. This value decreases with increase in substrate temperature and reaches a minimum at ~ 280–300°C and thereafter the roughness value increases slowly with temperature. Figure 4 shows SEM photographs of surface roughness of CdS films prepared at different temperatures. From the SEM photographs it is clear that the CdS film prepared at 300°C has very smooth surface and below and above this temperature the roughness value increases as indicated by VASE measurements in figure 2. The variation in the surface roughness can be explained from the growth mechanism of the spray-coated CdS thin films.

Figure 3 shows the deposition rate r (Å/min) of CdS film at different substrate temperatures in the range 200–360°C. It can be seen that the deposition rate decreases with increase in substrate temperature. But the decrease is slow when the substrate temperature is in the range 200–300°C. The deposition rate decreases at a much

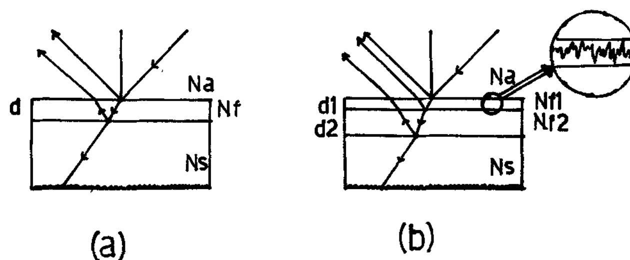

Figure 1. Model of the film used for the VASE analysis. This film is assumed to have two layers in which the top one contains the surface irregularities. (**a**) Air/film/substrate system, (**b**) air/rough layer/film/substrate system. d, d_1 and d_2 are the thickness of different layers. N_a, N_f, N_{f1}, N_{f2} and N_s are the complex refractive indices of different layers.

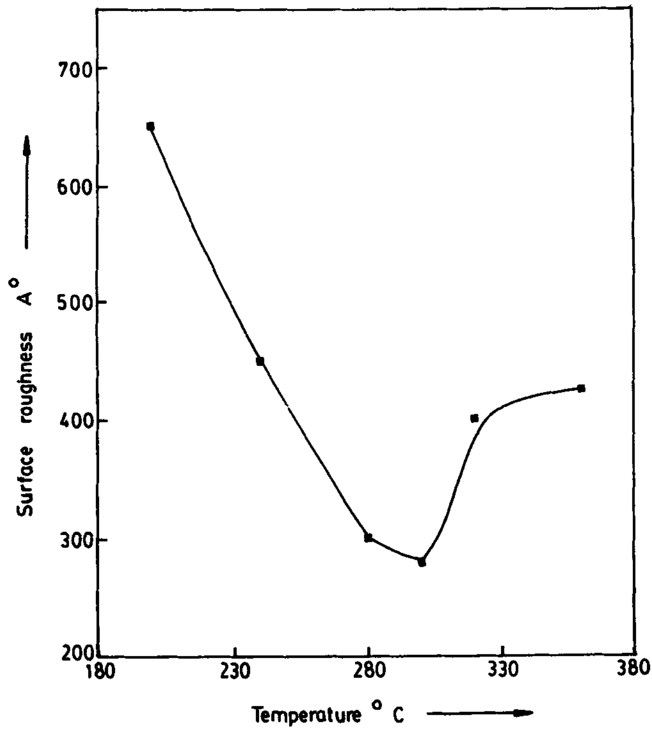

Figure 2. Variation of thickness of rough surface layer (i.e. average height of surface roughness) with temperature.

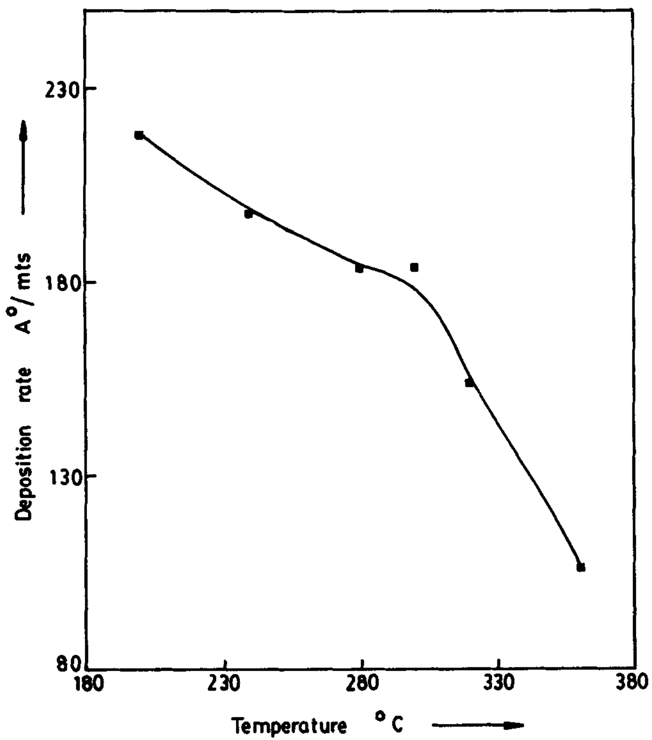

Figure 3. Variation of deposition rate of CdS film with substrate temperature.

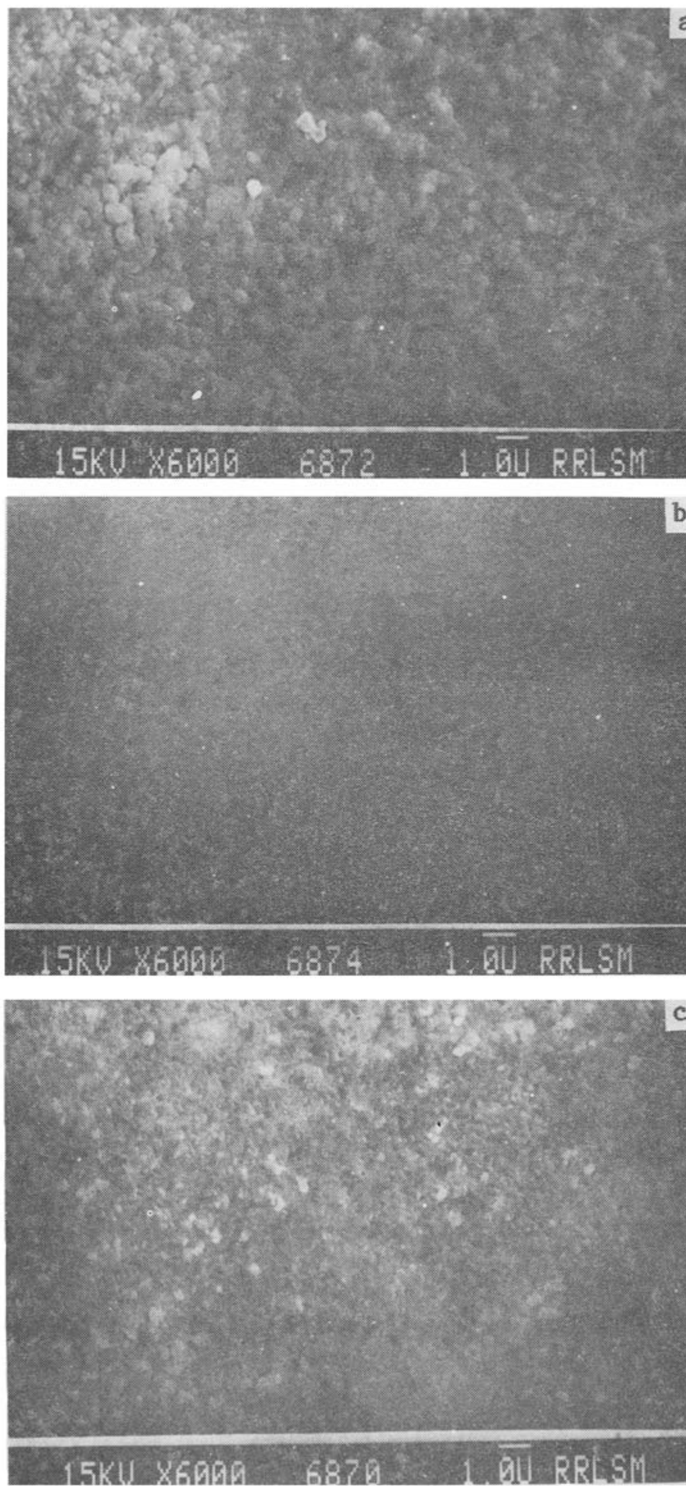

Figure 4. SEM photographs of CdS film prepared at different substrate temperature: (**a**) film prepared at 200°C, (**b**) at 300°C and (**c**) at 360°C.

higher rate as the substrate temperature goes above 300°C. At low temperature large droplets may not get sufficient heat energy to vaporize before reaching the substrate and hence comparatively large droplets reach the substrate. This results in a higher deposition rate and also makes the film surface rather rough. This is shown by the VASE measurements and the roughness has a high value of ~ 65 nm at 200°C. It is also clear from the SEM photograph (figure 4a).

At moderately high temperature (i.e. in the range 280–300°C) the droplets reaching the substrate may get reduced due to the vaporization and this may result in the reaction (leading to the formation of CdS) taking place completely over the substrate. This may be the reason for smoothness of the surface of film prepared in this temperature range, as revealed by the ellipsometric study as well as SEM (figures 2 and 3b). But at very high temperature considerable amount of the solvent is vaporized far away from the substrate. The chemical reaction leading to the formation of CdS will then occur in the vapour phase and this does not contribute to the growth of the film over the substrate surface resulting in a drastic reduction in film deposition rate. Moreover the fine particles of CdS thus formed may be adhering to the film surface making it rough again. This is also clear from the VASE studies as shown in figure 2. The SEM photograph shown in figure 4c also confirms the VASE measurements on surface roughness.

4. Conclusion

CdS films were prepared by spray pyrolysis technique over glass substrate at different substrate temperatures ranging from 200 to 360°C. VASE was used for the analysis of CdS thin films. Ellipsometric studies show that the films prepared at low and very high temperatures have rough surface layer, but films prepared at 280–300°C have very smooth texture with top rough layer having a thickness of ~ 27 nm. The growth rate is also affected by the substrate temperature. When the substrate temperature is increased from 200°C to 300°C the growth rate decreases rather slowly. But as the temperature goes above 300°C the decrease becomes faster. From this study it becomes clear that the films prepared at about 280–300°C have good optical and physical qualities than others and hence these films are best suited for solar cell applications.

Acknowledgement

One of the authors (SM) is thankful to CSIR, New Delhi, for financial support. Financial assistance from DAE (Government of India) is also gratefully acknowledged. We are thankful to Dr P S Mukherjee, Regional Research Lab, Trivandrum, for SEM analysis.

References

Albin D S and Risbud S H 1987 *Thin Solid Films* **147** 203

Arita T, Hanafusa H, Kitamura S and Takakura H 1991 *Conf. Records of 22nd Photovoltaic specialist conference*. Las Vegas, NV, USA, p. 946

Azzam R M A and Bashara N M 1977 *Ellipsometry and polarized light* (Amsterdam: North Holland) Chapter 4

Banerjee A, Nath P, Vankar V D and Chopra K L 1978 *Phys. Status Solidi (a)* **46** 723
Basol B M, Kapur V K and Halani A 1991 *Conf. Records of 22nd Photovoltaic specialist conference*. Las Vegas, NV, USA p. 893
Bruggeman D A G 1935 *Ann. Phys. Leipzig* **24** 636
Cameron D C, Duncan W and Tsang W M 1979 *Thin Solid Films* **58** 61
Chopra K L and Das S R 1983 *Thin film solar cells* (New York: Plenum Press) p. 297
Chow L W, Lee Y C and Lee Kwok H L 1981 *Thin Solid Films* **81** 307
Escosura L, Garcia-Camarero E, Arjona F and Rueda F 1984 *Solar Cells* **11** 211
Gupta B K and Agnihotri O P 1978 *Philos. Mag.* **B37** 631
Kakayama N, Matasumoto H, Yamaguchi K and Iegami I S 1976 *Jpn. J. Appl. Phys.* **15** 2281
Kaur I, Pandya D K and Chopra K L 1981 *J. Electrochem. Soc.* **127** 943
Kwok H L 1980 *J. Phys. D.* **13** 1911
Nolly J, Abdullah K K and Vijayakumar K P 1987 *Phys. Status Solidi (a)* **101** K35
Shay J L, Wagneer S, Bachman K, Buchler E and Kaspor H M 1975 *Proc. 11th Photovoltaic specialist conference*, Phoenix, New York, p. 503
Sunny M and Vijayakumar K P 1994 *Bull. Mater. Sci.* **17** 235
Valyommana A G, Vijayakumar K P and Purushothaman C 1992 *J. Mater. Sci. Lett.* **11** 616
Vedam K, Mc Marr P J and Narayan J 1985 *Appl. Phys. Lett.* **47** 339
Vijayakumar K P 1991a *J. Appl. Phys.* **69** 6771
Vijayakumar K P 1991b *Bull. Mater. Sci.* **14** 57