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Variations of interlayer structure in Cu_xS/CdS bilayer thin film with annealing of CdS: an ellipsometric study

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Abstract. Irregularities at the interface in Cu_xS/CdS thin films can be controlled by annealing CdS film prior to chemiplating. The interlayer formed on CdS films annealed at 200°C is comparatively smooth. In CdS films annealed at higher temperatures, the interlayer is rather thick and the CdS intrusions into this layer are thin. An ellipsometric technique is used for this study and the effective medium theory which is utilized to interpret the results is based on the difference in reaction rate in the grains as well as grain boundaries during chemiplating.

Keywords. Cu_xS/CdS; interlayer ellipsometry; effective medium theory; chemiplating.

1. Introduction

The CdS/Cu_xS heterojunction is important for the fabrication of low-cost photovoltaic devices for terrestrial use as the materials required are rather inexpensive and available in plenty. The preparation technique is simple and suitable for large scale production (Hall and Meakin 1979; Bryant *et al* 1983). Even though an efficiency of the order of 10% had been achieved (Hall *et al* 1981; Barnett *et al* 1978), there are certain drawbacks. Several groups (Igalson *et al* 1988; Santamaria *et al* 1988; Iborra *et al* 1988; Partin 1988) have been working on different aspects affecting the lifetime of this device so as to make it more stable. Among the various problems causing instability of this heterojunction, the irregular shape of the interface is considered more important as it causes a shorting effect between the upper and lower electrodes resulting in local heating in the cell thus forming a large number of Cu vacancies in Cu_xS layer (Norian and Edington 1981). This effect in grains is caused by the difference between the reaction rates and the grain boundaries (Chopra and Das 1983a) during the chemiplating process which is the technique used for preparation of Cu_xS top layer over CdS films. Recently Cumberbatch *et al* (1988) reported that a comparatively smooth interface can be obtained by using organic solvents like benzo nitrile instead of water. This controls the reaction rate.

The present work aims at determining the effect of annealing of the CdS films (prior to chemiplating) on the junction structure. The variation in Cu_xS layer thickness grown over CdS film annealed at different temperatures is also studied to explain the changes in the interlayer.

The technique of multiple angle ellipsometry was used as it is a sensitive and non-destructive technique used for layer structure analysis of films (Vedam *et al* 1985), composition of different layers (Vedam *et al* 1985; Aspnes *et al* 1986), surface roughness (Petrovskii *et al* 1986; Logothetidis 1989) and even non-destructive depth profiling (Vedam *et al* 1987).

In §2 a brief theory of ellipsometric analysis is given followed by the experimental set-up for film preparation, annealing and ellipsometric measurement. Our results are presented in the last section.

2. Theory

In photometric ellipsometer (Azzam and Bashara 1977b,d) the sample is irradiated with plane-polarized and monochromatic light beam and the ellipsometric parameters ψ and Δ are calculated from the intensity of reflected beam at different analyser azimuths using the following equations (Azzam and Bashara 1977b)

$$\psi = [1/2]\,[\cos^{-1}\{(I_1-2I_2+I_3)/(I_1+I_3)\}], \tag{1}$$

$$\Delta = \cos^{-1}[\{(1/2)\sin 2\psi\}\{(I_3-I_1)/(I_1+I_3)\}], \tag{2}$$

where I_1, I_2 and I_3 are the intensities of reflected light from the film surface at three different azimuths of the analyser while the polarizer is kept at a fixed azimuth of $+45°$. But these two parameters ψ and Δ can also be computed theoretically using Fresnel coefficients for the parallel (p-component) and perpendicular (s-component) components according to the following equations (Azzam and Bashara 1977a).

$$\tan\psi\,\exp(i\Delta) = \frac{[\gamma^p_{01} + \gamma^p_{12}\exp(-i2D)][1 + \gamma^s_{01}\gamma^s_{12}\exp(-i2D)]}{[1 + \gamma^p_{01}\gamma^p_{12}\exp(-12D)][\gamma^s_{01} + \gamma^s_{12}\exp(-i2D)]} \tag{3}$$

The quantities r^p and r^s are the Fresnel reflection coefficients for p and s components. The subscripts stand for the particular interface in the system (e.g. 01 for air/film etc) and the factor D is defined as

$$D = (d/\lambda)\{2\pi(N_f^2 - N_a^2\sin^2\theta)^{1/2}\} \tag{4}$$

where λ is the wavelength of light used, d the thickness of the film, θ the angle of incidence and N_f and N_a the refractive indices of the film and air respectively. The unknown material parameters were determined by minimizing the function,

$$F = \sum_i [\psi_e(\theta_i) - \psi_e(\theta_i)]^2 + [\Delta_e(\theta_i) - \Delta_e(\theta_i)]^2 \tag{5}$$

where the subscripts e and c stand for experimental and calculated values of these parameters and θ_i's are angles of incidence at which the parameters ψ and Δ were measured.

We assume that the irregular interface between Cu_xS and CdS layers is sandwiched between two smooth plain surfaces as indicated in figure 1a with the distance between the two plain surfaces equal to the maximum height of the irregularities. Thus the thin film sample can be considered as having a three-layer structure consisting of Cu_xS/sandwiched interlayer/CdS. In this model, irregularities at the interface can be considered as intrusion of CdS into the interlayer. Hence the value of the volume factor of CdS intrusion into the interlayer indicates the size of irregularities present at the interface. This can be done using the Maxwell-Garnett

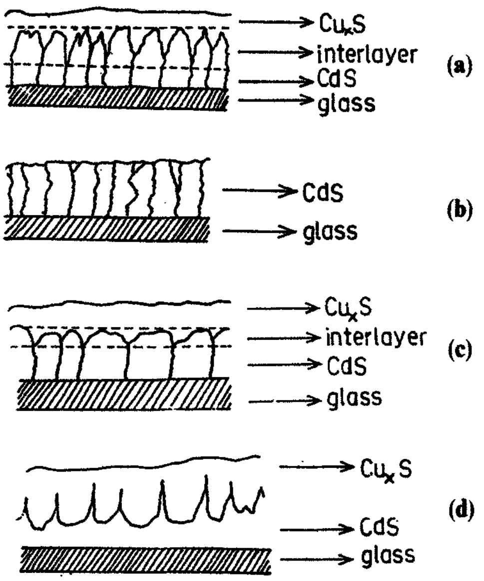

Figure 1. **a.** Irregular interface between Cu_xS and CdS layers. **b.** CdS film structure with its grains almost perpendicular to the substrate surface. **c.** Cu_xS/CdS bilayer film with a rather thin and smooth sandwich layer. **d.** Structure of Cu_xS/CdS bilayer film with a thick sandwich layer.

theory (Garnett 1904; Azzam and Bashara 1977c) in which the effective refractive index of a thin layer is related to the refractive index of the material protruding into the layer (N_f) refractive index of the material of the layer (N_a) and volume fraction (Q) of the irregularities of the intrusion by the equation

$$(N_e^2 - N_a^2)/(N_e^2 + 2N_a^2) = Q(N_b^2 - N_a^2)/(N_b^2 + 2N_a^2). \tag{6}$$

It is assumed that N_f becomes the refractive index of CdS while N_a is that of Cu_xS which forms the remaining part of the layer and N_e the effective refractive index of the sandwiched interlayer. The value of N_e can be computed from ellipsometric readings. Refractive indices of Cu_xS and CdS are taken from earlier studies (Rastogi and Salkalachen 1982; Chopra and Das 1983b). Hence the value of Q calculated from (6) gives an idea about the size of irregularities present in the interface.

Along with the effective refractive index (N_e) the thickness of the interlayer is also obtained from ellipsometry using (4). To evaluate these two unknown parameters, one should take ellipsometric readings at least for two angles of incidences. In the present work, measurements at three different angles of incidence were taken.

3. Experimental

The CdS thin films (thickness ~4500 A) were prepared by using spray pyrolysis (Nolly *et al* 1987) on glass substrates kept at 250°C. These films were then chemiplated to form a layer of Cu_xS over the CdS film. The reaction time was 40 s and the solution for chemiplating was kept at room temperature during the process. The samples were then rinsed in distilled water to remove any trace of $CdCl_2$ present on the Cu_xS surface.

Samples were also prepared with the CdS film annealed in air at different temperatures in the range 100–300°C. The heating/cooling rate in all cases of annealing was 2°C/min. These two types of samples were analysed using an ellipsometric set-up at room temperature.

The ellipsometric set-up consists of a photometric ellipsometer (Azzam and Bashara 1977b) with a rotating analyser and has a polarizer-film-analyser arrangement (Azzam and Bashara 1977d). The light source was a He-Ne laser (2 mW power; wavelength 6328 A). In the present work nine azimuths of the analyser were selected for measuring intensity values (as I_1 to I_9), and thus 84 values of ψ and Δ were obtained for each angle of incidence. The average of these values was taken as ψ_e and Δ_e so as to keep the error in the ellipsometric parameters to the minimum.

4. Results and discussion

In figure 4 the variation of thickness of the interlayer due to annealing is shown while figure 3 gives the changes in the volume fraction Q of CdS in this layer with annealing temperature. Figure 2 indicates the variations in thickness of Cu_xS layer grown over CdS films annealed at different temperatures.

Annealing of CdS films prior to chemiplating process is found to considerably affect the thickness of the interlayer. The thickness decreases in the case of CdS film annealed at a temperature equal to or lower than 200°C. If annealing temperature is increased above 200°C, figure 4 indicates a sharp increase in the interlayer thickness. This indicates a corresponding increase in the average height of the irregularities formed at the interface. The picture will be clearer if one considers the corresponding variations of the Q-factor or the volume fraction.

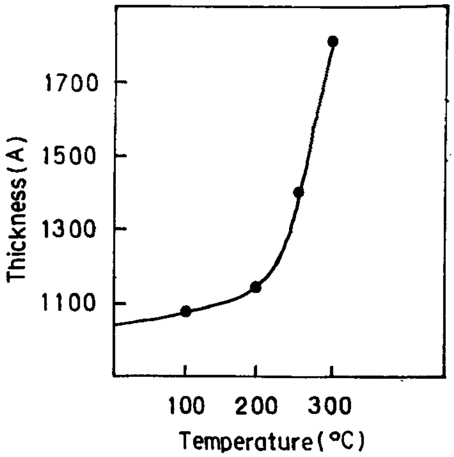

Figure 2. Variation of thickness of Cu_xS layer with annealing temperature of CdS prior to chemiplating process.

From figure 3 it can be understood that the volume fraction of CdS in the interlayer decreases from about 80% to 50% due to annealing up to 200°C and thereafter it was constant. But figure 4 shows that the thickness of the layer (which is the measure of the average height of the irregularities) increases steadily when annealing temperature increases beyond 200°C. This can be explained only by considering the difference in reaction rate in the grains and along the grain boundaries.

Several groups working on chemically prepared CdS films (using scanning electron microscopy) have pointed out that these films have grains along the direction perpendicular to the surface of the substrate (Norian and Edington 1981; Eser and Hall 1981) and the structure is represented in figure 1b. On dipping this film into $CuCl_2$ solution, reaction takes place forming a top layer of (*p*-type) Cu_xS over (*n*-type) CdS film. The reaction rate in grains is however different from that in grain boundaries (Chopra and Das 1983a) which results in the formation of an irregular junction as shown in figure 1a. One can thus say that if the interlayer thickness decreases then the height of the irregularities also decreases. This means that the reaction rate in grains is almost the same as that in grain boundaries and this situation is illustrated in figure 1c. On the other hand, if the volume factor Q becomes smaller, it indicates that the intrusions of CdS into the sandwich layer have become either smaller in number or thinner in size. The first case can occur due to growth of the grain size as a result of annealing. The second can take place when the reaction rate in the grains becomes larger than that along the grain boundaries. This condition represented in figure 1d shows that major portions in the CdS grains are converted into Cu_xS and CdS intrusions into the interlayer have really become thinner. In order to verify whether the reaction rate in grains has increased due to the annealing of CdS films, a separate experiment was performed where the thickness of Cu_xS layer formed on CdS films annealed at different temperatures (in the range 100–300°C) was measured using ellipsometry. These results are shown in figure 2. Here the dipping time of CdS films of $CuCl_2$ solution was always kept constant as mentioned earlier (i.e. at 40 s) so that any variation in the thickness of Cu_xS layer can be linked with the reaction rate. Figure 2 shows

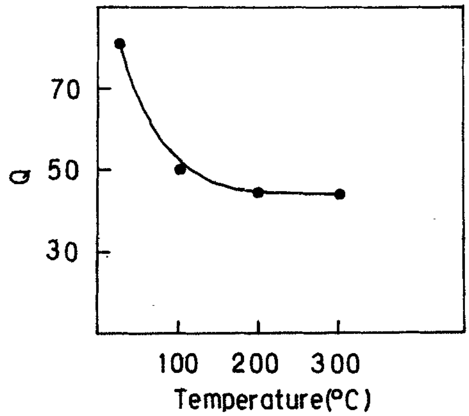

Figure 3. Changes in volume fraction Q of CdS in the sandwich layer with annealing temperature.

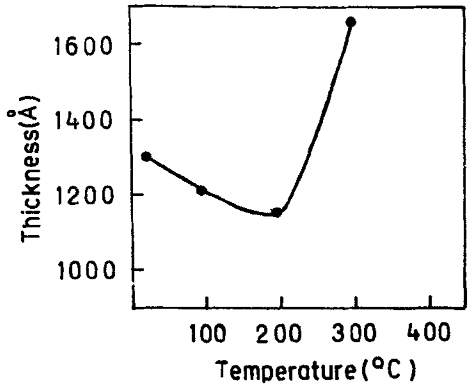

Figure 4. Variation of thickness of the interlayer with annealing temperature.

that thickness increases sharply when annealing temperature is increased above 200°C. As the thickness of Cu_xS is directly related to the reaction in the grains, one can say that the reaction rate in grains has increased considerably for the CdS films annealed above 200°C. This agrees with the earlier observation regarding irregularities at the interface.

5. Conclusion

The present study reveals that irregularities at the interface of a Cu_xS/CdS junction have a direct link with the annealing temperature of the CdS film. The junction formed on CdS films annealed at 200°C prior to chemiplating is rather smooth. But as the annealing temperature is increased above 200°C, the junction again becomes rough. This is explained on the basis of a difference between the reaction rates inside the grains and in the grain boundaries. These two reaction rates are equal in the case of CdS films which are annealed at 200°C. But for annealing temperature above 200°C, the reaction rate in grains is higher than that in grain boundaries.

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