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The effect of grain boundary diffusion processes on the formation of Cu_2S layers on polycrystalline CdS films

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Abstract. A new model has been developed to account for the Cu_2S layer growth rate variations observed when polycrystalline films of CdS are immersed in CuCl solution. The model assumes diffusion-limited growth at both the grain boundary and mid-grain regions and excellent agreement with experimental data is obtained provided that the growth process at the grain boundaries is assumed to be delayed for a short interval after the start of the reaction at the main CdS surface. The cause of the delay and the experimental factors influencing the delay time are discussed.

1. Introduction

Much attention has been paid to the possibility of using $\text{Cu}_2\text{S}/\text{CdS}$ heterojunction devices in large-scale solar-energy collection schemes and energy conversion efficiencies of close to 10% have been achieved in such devices in thin film form [1]. The standard fabrication method involves evaporation of a CdS layer ($\sim 30 \mu\text{m}$ thick) onto a metal substrate and subsequent formation of a thin Cu_2S layer by a chemiplating process according to the exchange reaction:



This process is usually accomplished by immersing the CdS film in a CuCl solution at about 95°C for a few seconds but the composition of the solution, the temperature and the immersion time all have an influence on the resultant stoichiometry and thickness of the copper sulphide layer produced.

When this chemiplating process is performed on single crystals of CdS, the Cu_2S thickness d is found to grow in proportion to the square root of the immersion time t and, therefore, the Cu_2S layer formation is assumed to be a diffusion-limited process. However, when the plating process is performed using evaporated films of CdS, the resultant Cu_2S layer has a distinctly non-uniform thickness due to more rapid formation in the grain boundary regions.

Evaporated CdS films are polycrystalline and usually have a columnar structure as a result of preferential growth in the c -axis direction so that the c -axis of individual crystallites (typically a few μm wide) tend to lie perpendicular to the substrate plane. For good photovoltaic performance, the thickness of the Cu_2S layer over the top of the grains should be approximately 0.1 – $0.2 \mu\text{m}$ but due to the preferential growth at the grain boundaries, the Cu_2S protrusions between the grains can reach significantly

greater depths. The presence of these grain boundary protrusions clearly increases the effective junction area and, accordingly, has a strong influence on the cell characteristics. Thus, it is of critical importance to understand how the interface topography develops during the Cu_2S formation process in order to achieve the optimum operational characteristics for the cell. In this paper we present a theoretical model for the Cu_2S layer formation process and show that this can account satisfactorily for the observed time dependence for the process under different experimental conditions.

2. Experimental details

The Cu_2S layers were formed on polycrystalline CdS films which had been produced by thermal evaporation of high purity CdS from a quartz crucible onto zinc-coated copper substrates at approximately 220 °C. The CdS films were approximately 30 μm thick and scanning electron microscope studies revealed a columnar structure with the grains being typically 2–4 μm wide as in previous studies [2]. For Cu_2S layer formation, the CdS films were immersed in an aqueous solution of CuCl with a predetermined strength, acidity and temperature. The average thickness of the resultant Cu_2S layers was measured by means of electrochemical analysis [3] using a 0.1 M sodium acetate solution.

3. Results and discussion

3.1. Observed variation of Cu_2S layer thickness with time

Figure 1 shows a typical set of results for six CdS samples immersed in CuCl solution for times between 2 and 12 s. The non-linear structure of this plot of average Cu_2S layer thickness as a function of time is typical of such data but, as shown by previous work in this laboratory [2] and elsewhere [4], the exact form of the curve is critically dependent on the concentration, acidity and temperature of the CuCl solution.

In general terms, the form of the Cu_2S layer growth curve in figure 1 is assumed to be associated with the clearly demonstrated different rates of growth at the CdS surface and in the grain boundaries. However, previous attempts to model the Cu_2S growth process in terms of these two elements of the Cu_2S layer development have not been entirely satisfactory, as indicated in the next section.

3.2. Theory of the Cu_2S layer growth kinetics

As mentioned in section 1, the growth of Cu_2S on a single crystal CdS surface has been found to follow a parabolic law [5, 6] as would be expected for a diffusion-limited growth process. A similar process is expected to apply at the upper surface regions of the individual crystallites in a polycrystalline CdS film. However, in addition to this, a faster, more nearly linear, growth process occurs in the grain boundary regions to give rise to the characteristic, deep protrusions of Cu_2S observed in the CdS films. Thus, the growth of the Cu_2S layer can be described in terms of two thickness parameters: d_1 the thickness over the upper surfaces of the columnar grains and d_2 the depth of penetration along the grain boundaries, as shown in figure 2 which assumes a simple cylindrical grain structure for the CdS layer on which the Cu_2S is formed.

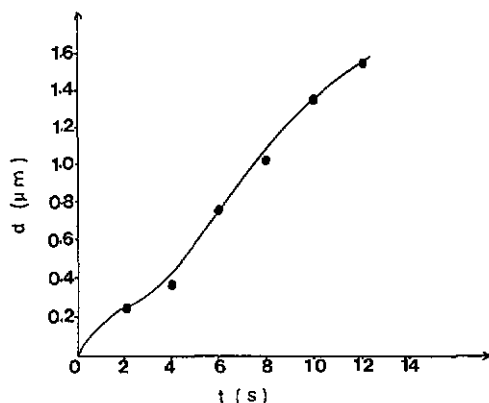


Figure 1. Average Cu_2S layer thickness as a function of dipping time in CuCl solution (3 g l^{-1}) at 95°C .

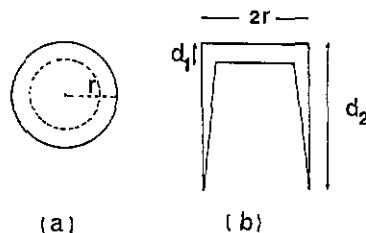


Figure 2. Plan view (a) and cross-section (b) through a single grain of CdS after formation of a Cu_2S layer.

A similar simple flat top cylindrical grain was adopted by Rothwarf [7] for his analysis of the Cu_2S growth kinetics while Salkalachen and co-workers [4] chose a hexagonal grain structure with a pyramidal top. However, while both models have been developed to simulate the Cu_2S growth process by considering how the contributing thicknesses d_1 and d_2 increase with time, there is a clear disagreement in the choice of a suitable function to express the time dependence of d_2 . In the former case [7], the growth process at the grain surface and in the boundaries are both assumed to be diffusion-limited and, accordingly, are expressed in similar terms. Thus the thickness at the upper surface, d_1 , as a function of time t is given by $d_1 = c_1 t^{1/2}$ while the depth of penetration at the grain boundaries d_2 is given by $d_2 = c_2 t^{1/2}$ where c_1 and c_2 are constants, with the assumption that $c_2 \gg c_1$. This appears to be an over-simplification of the growth mechanism in the boundary region where the growth process will involve transfer of atoms between the grain boundary and the crystal interior in a direction parallel to the film surface as well as along the grain boundary itself. In the second treatment [4], d_1 is again assumed to have the form $d_1 = c_1 t^{1/2}$ while the faster growing d_2 component is given by the empirically based expression $d_2 = c_2 t$.

In the treatment of this problem outlined later, use has been made of the grain boundary diffusion theory developed by Whipple [8] and Le Claire [9] who considered an idealized grain boundary structure in the form of an isotropic slab of material of width δ normal to the top surface of an otherwise homogeneous section of semiconductor. Diffusion processes within the grain boundary and within the bulk semiconductor were assumed to be characterized by diffusion coefficients D_{gb} and D_g respectively, with the expectation that $D_{gb} \gg D_g$ to give the deep grain boundary penetration normally observed.

Using this model, Le Claire [9] has shown that, assuming a constant surface concentration for the diffusing species, the average concentration C of the diffusant as a function of depth y (as would be measured by a standard depth-profiling technique) is

given by $\ln C \propto y^{\delta/5}$. In fact, such a relationship has been observed experimentally [10] for Cu in CdS layers which had been immersed in CuCl solution. Accordingly, this result supports the proposition that the reaction between CuCl solution and CdS is a diffusion-limited process governed by effective diffusion coefficients D_g for the grains and D_{gb} for the grain boundaries. However, for the experiment described in section 3.1. it was not the depth profile which was measured but the effective planar thickness d of the Cu_2S layer. This, again, can be approached using this analysis which was developed in terms of the dimensionless parameters.

$$\eta = \frac{y}{(D_g t)^{1/2}} \quad \text{and} \quad \beta = \frac{D_{gb} \delta / 2}{D_g (D_g t)^{1/2}} \quad (2)$$

As might be expected, for large values of β , the predicted constant concentration profiles are found to exhibit very deep protrusions in the vicinity of a grain boundary, in comparison with the penetration in the mid-grain regions. Thus, a large value of β can be assumed for the CdS- Cu_2S cell formation process which leads to Cu_2S layers with the characteristic structure represented in figure 2.

In order to examine how the Cu penetration along the grain boundaries varies with time, use can be made of Le Claire's observation [9] that for $\beta > 10$, the concentration of diffusant in a grain boundary is a function only of $(\eta\beta^{-1/2})$. Thus the progression of any fixed concentration contour (such as that corresponding to the concentration at the tip of a Cu_2S protrusion) is such that $\eta\beta^{-1/2}$ remains constant provided that β is sufficiently large. Thus

$$\eta\beta^{-1/2} = \frac{y}{(D_g t)^{1/2}} \left[\frac{D_g (D_g t)^{1/2}}{D_{gb} \frac{1}{2} \delta} \right]^{1/2} = \text{constant} \quad (3)$$

and it follows that $y \propto t^{1/4}$ or, in terms of the notation for the model in figure 2, $d_2 \propto t^{1/4}$. It is easy to see that, for this grain model, the value of the average planar thickness is given by

$$d = \frac{\text{total volume of } \text{Cu}_2\text{S}}{\text{planar surface area}} = d_1 + \frac{d_1 d_2}{r} \quad \text{for} \quad d_2 \gg d_1. \quad (4)$$

Assuming that d_1 is proportional to $t^{1/2}$ and d_2 is proportional to $t^{1/4}$ as discussed earlier, it follows that

$$d = at^{1/2} + bt^{3/4} \quad (5)$$

where a, b are constants.

A plot of d as a function of t , according to equation (5) is presented in figure 3 (curve (i)) and it is clear that this function, with its steadily decreasing slope cannot be made to fit the experimental data of figure 1 which is also included in figure 3. However, an excellent fit to the experimental data is seen to be achieved by curve (ii) which is also based on equation (5) but in this case it was assumed that the start of the Cu_2S growth process in the grain boundaries was deferred for 4 s. Thus the value of d , (and, therefore, the second term in equation (5)) was assumed to remain at zero

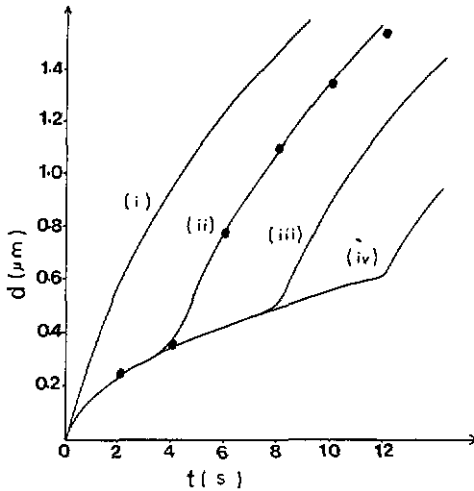


Figure 3. Curve (i), theoretical time dependence of average Cu_2S layer thickness according to equation (5) (see text) with constants $a = 1.7$ and $b = 2.05$. Curves (ii), (iii) and (iv), as for curve (i) but with delays of 4, 8 and 12 s respectively before growth in grain boundaries begins. Full dots are the experimental data from figure 1.

until $t = 4$ s. Figure 3 includes the theoretical variation for d assuming delay times of 8 and 12 s (curves (iii) and (iv) respectively).

As grain boundaries are known to act as sinks for impurities, it is possible that the (ultimately faster) formation of Cu_2S in the grain boundaries is initially hindered by either bulk- or surface-derived impurities which have accumulated at the grain boundary terminations. If so, it might be expected that the delay time prior to Cu_2S growth in the grain boundaries would depend on the preparation of the CdS surface before immersion in the CuCl solution as well as on the composition and temperature of the solution. Accordingly, this offers an explanation for the results of previously published studies [2, 4] in which sets of experimental $d-t$ curves, similar in structure to the theoretical set in figure 3, have been generated by changing the CdS surface preparation or varying the acidity or temperature of the CuCl solution.

4. Summary and conclusions

A theoretical model has been developed to account for the experimentally observed time dependence of average Cu_2S layer thickness d formed on polycrystalline CdS when immersed in CuCl solution. The model assumes diffusion limited growth of Cu_2S both at the CdS surface and in the grain boundaries. Making use of results obtained from a detailed analysis of grain boundary diffusion, previously developed by Whipple [8] and Le Claire [9], the model leads to a theoretical $d-t$ relationship in excellent agreement with experimental data provided that a short delay time is assumed between the start of Cu_2S growth at the CdS surface and that in the grain boundaries. It is postulated that this delay time is associated with the presence of impurities at the grain boundaries and the expected dependence of the delay time on factors such as the initial preparation of the CdS surface and the composition of the CuCl bath is consistent with previously published data for Cu_2S layer growth obtained under a variety of experimental conditions.

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