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Sintering behaviour and electrical properties of $Cd_{1-x}Zn_xS$ films containing $CdCl_2$

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Polycrystalline $Cd_{1-x}Zn_xS$ films were prepared by coating a slurry which consisted of CdS, $CdCl_2$, various amounts of ZnS and propylene glycol on to glass substrates and by sintering in a nitrogen atmosphere, and their sintering behaviours and electrical properties were investigated. As the amount of ZnS increases, the enhancing effects of $CdCl_2$ on sintering and doping decrease, due primarily to the formation of $ZnCl_2$ which evaporates rapidly during sintering, resulting in poor microstructure and a sharp increase in electrical resistivity. The sharp increase in the electrical resistivity is related to a sharp decrease in electron concentration which is caused by poor doping efficiency, and by an increase in the donor ionization energy of chlorine as the zinc content increases. The trap density of grain boundaries, on the other hand, decreases with increasing zinc content in sintered $Cd_{1-x}Zn_xS$ films.

1. Introduction

CdS with a direct band gap of 2.42 eV is a suitable window material for CdS/CdTe and CdS/Cu_2S heterojunction solar cells. ZnS with a band gap of 3.54 eV can be substituted into CdS to increase the band gap of the window material. The production of polycrystalline CdS films and $Cd_{1-x}Zn_xS$ films by various methods for the purpose of reducing the production costs of heterojunction solar cells have been reported. The electrical properties of polycrystalline $Cd_{1-x}Zn_xS$ films prepared by a vacuum evaporation method [1, 2] and by spray pyrolysis [3] have been reported, and $Cd_{1-x}Zn_xS/Cu_2S$ solar cells with an efficiency of 10.2% have been reported [4].

The method of coating and sintering is a convenient and economical method for the mass production of materials in the form of thin films on a substrate. Nakayama *et al.* [5] and Lee and Im [6] reported the production of sintered and stable all-polycrystalline CdS/CdTe solar cells with an efficiency of over 7%. Yang and Im [7, 8] reported the effects of $CdCl_2$ on the sintering behaviour of CdS films [7] and the electrical properties of such sintered films [8]. However, the sintering behaviour and the electrical properties of sintered $Cd_{1-x}Zn_xS$ have not been reported previously.

There is therefore ample interest to investigate the effects of sintering conditions and composition on the electrical and optical properties of sintered $Cd_{1-x}Zn_xS$ films. In this paper we report the results of an investigation of the sintering behaviour of $Cd_{1-x}Zn_xS$ films on amorphous glass substrates and the properties of such sintered films as a function of composition.

2. Experimental procedure

CdS and ZnS powders with 5 N purity were used in the present investigation. Anhydrous $CdCl_2$ was also used as a sintering aid as well as a chlorine dopant source. A number of slurries consisting of $Cd_{1-x}Zn_xS$ powders, 10 wt % of $CdCl_2$ and appropriate amounts of propylene glycol were prepared by mixing and dispersing with a mortar and pestle. The average particle size of the CdS and ZnS powders were approximately 1.5 and 0.5 μm, respectively, and the values of x were varied from zero to 0.2. Each slurry was coated on borosilicate glass substrates which had been cleaned in an ultrasonic bath with trichloroethylene and acetone, using a screen printer with a 120 mesh stainless steel screen, and dried at 120° C for 2 h in air to obtain dried films with a thickness of about 40 μm and with no cracks. A dried film was then placed in a quartz boat with a tight cover that had 5 holes with a diameter of 1 mm, and was sintered in a nitrogen atmosphere using a tube furnace with a quartz tube. The furnace was flushed with nitrogen before sintering and a nitrogen flow rate of $100\,cm^3\,min^{-1}$ was used to maintain the nitrogen atmosphere during sintering.

Ohmic contacts were provided by coating with an indium–silver paste which contained 20 wt % indium powder, and by annealing at 200° C for 10 min in nitrogen. Electrical resistivity was determined by the measurement of sheet resistance of the films using a four-probe method and by the measurement of film thickness, taking a photograph of a cross-section of the film using a scanning electron microscope (SEM). Carrier concentration and mobility were measured by the van der Pauw method. Energy-dispersive analysis of X-rays (EDAX) scans and X-ray diffraction patterns were taken to determine the composition, and SEM photographs of the surface of the films were taken to examine the microstructure of the sintered films.

3. Results and discussion

X-ray diffraction patterns for as-received powders showed that the crystal structures of the CdS and ZnS

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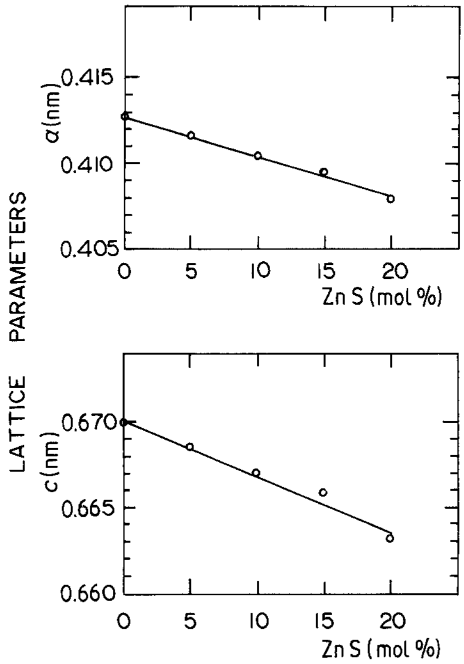

Figure 1 Variations of lattice parameters a and c of sintered $Cd_{1-x}Zn_xS$ films as a function of the amount of ZnS added. The films were sintered at 650° C for 1 h in nitrogen.

were hexagonal and cubic, respectively. An analysis of X-ray diffraction patterns for sintered films with initial compositions of $Cd_{1-x}Zn_xS$ up to $x = 0.2$ (before sintering) indicated that the structures of all sintered films were hexagonal. The variations in the lattice parameters of the films which were sintered at 650° C for 1 h in nitrogen as a function of the amount of ZnS added are shown in Fig. 1. It is seen that both the lattice parameters a and c of the sintered $Cd_{1-x}Zn_xS$ solid solution decrease with increasing amount of ZnS added. Comparing with those for single crystals of $Cd_{1-x}Zn_xS$ [9], the parameters decrease more slowly with increasing x. Since no significant amount of ZnS in the sintered films was observed from the X-ray diffraction patterns, it appears that evaporation of zinc occurred during the sintering. Fig. 2 shows the estimated compositions of the sintered films as a function of composition before sintering, using the reported single-crystal data on the lattice parameters of $Cd_{1-x}Zn_xS$ [9]. It shows that the mole percentage of zinc in the solid solution (y) is approximately 60% of the mole percentage of added ZnS (x), indicating that about 40% of the zinc had been evaporated during the sintering. Further evidence of zinc evaporation during sintering is indicated in Fig. 3, which shows the EDAX energy spectra of as-coated and sintered films which contained 20 mol % ZnS and 10 wt % $CdCl_2$ before sintering and were sintered at 650° C for 1 h in nitrogen. This is a surprising result since the vapour pressure of ZnS is lower than that of CdS [10].

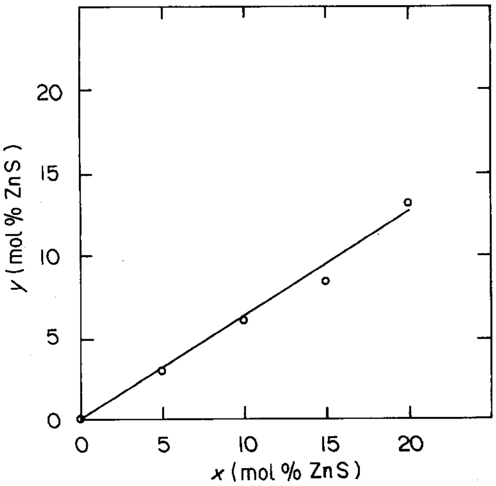

Figure 2 Estimated composition of sintered CdS–ZnS films (y) as a function of the amount of ZnS added (x).

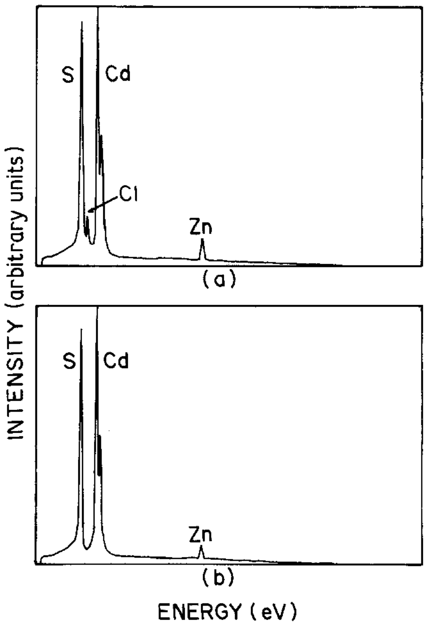

Figure 3 EDAX energy spectra of (a) as-coated film and (b) sintered film. The film contained 20 mol % ZnS and 10 wt % $CdCl_2$ before sintering and was sintered at 650° C for 1 h in nitrogen.

Fig. 4 shows the microstructures of $Cd_{1-x}Zn_xS$ films which contained 10 wt % $CdCl_2$ as a sintering aid and various amounts of ZnS before sintering,

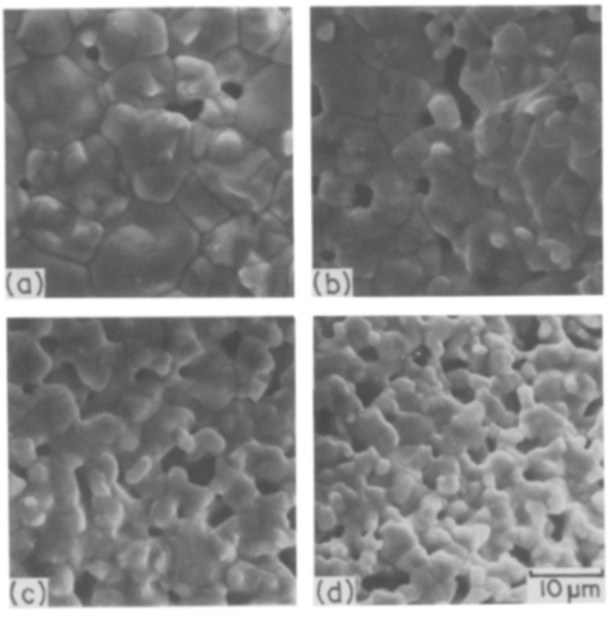

Figure 4 SEM photographs of the surface of $Cd_{1-x}Zn_xS$ films which contained 10 wt % $CdCl_2$ and various amounts of ZnS before sintering and were sintered at 625° C for 1 h in nitrogen. ZnS content (mol %): (a) 0, (b) 5, (c) 10, (d) 15.

sintered at 625° C for 1 h in nitrogen. As can be seen in the figure, the average grain size decreases and the porosity increases as the amount of ZnS increases. This result implies that the enhancing effect of $CdCl_2$ on the sintering of the $Cd_{1-x}Zn_xS$ films decreases as the ZnS content increases. It should be pointed out that the sintering aid $CdCl_2$, with a melting temperature of 568° C and a high vapour pressure, evaporates through the openings of the sintering ampoule during the sintering. It is reported that the $CdCl_2$ remaining in the films in the liquid state enhances the sintering of CdS films [7]. It is also reported, however, that the melting temperature of $ZnCl_2$ (365° C) is lower than that of $CdCl_2$ and that the vapour pressure of $ZnCl_2$ is much larger than that of $CdCl_2$ [10]. If a reaction of the type $ZnS + CdCl_2 \rightarrow CdS + ZnCl_2$ takes place to a certain degree during the sintering, the enhancing effect of $CdCl_2$ on sintering would decrease due to a decrease in the amount of $CdCl_2$ present in the films during sintering. This assumption is also consistent with the observed fact that the loss of zinc during sintering is surprisingly large (Fig. 3). Thus it appears that $ZnCl_2$ with its high vapour pressure evaporates too fast and behaves as a poor sintering aid under the sintering conditions used in the present investigation.

The variations of electrical resistivity of $Cd_{1-x}Zn_xS$ films which contained 10 wt % $CdCl_2$ and various amounts of ZnS, and were sintered for 1 h in nitrogen at various temperatures, are shown as a function of composition in Fig. 5. The electrical resistivity increases as the content of zinc increases, and decreases with increasing sintering temperature. Comparing the variation of electrical resistivity of the films sintered at 625° C with the corresponding microstructures shown in Fig. 4, it appears that the increase in the electrical resistivity with increasing zinc content is related to the microstructure. However, the consideration of grain size and contact area between grains alone appears to be inadequate to explain the variations in the electrical resistivity of two orders of magnitude for the films sintered at 625° C. It is reported that the presence of $CdCl_2$ in CdS films after sintering causes an increase in the electrical resistivity of the sintered CdS films [8]. We eliminate this possibility in the present case because the $CdCl_2$ in the $Cd_{1-x}Zn_xS$ films disappears faster than in CdS films during sintering, and EDAX scans on the sintered $Cd_{1-x}Zn_xS$ solid-solution films indicated little trace of chlorine. Strong dependence of the resistivity on composition in $Cd_{1-x}Zn_xS$ solid-solution films were also observed by Feigelson *et al.* [3] in samples prepared by the spray pyrolysis method. However, the resistivities of sintered $Cd_{1-x}Zn_xS$ are one or two orders of magnitude smaller than those reported by Feigelson *et al.*

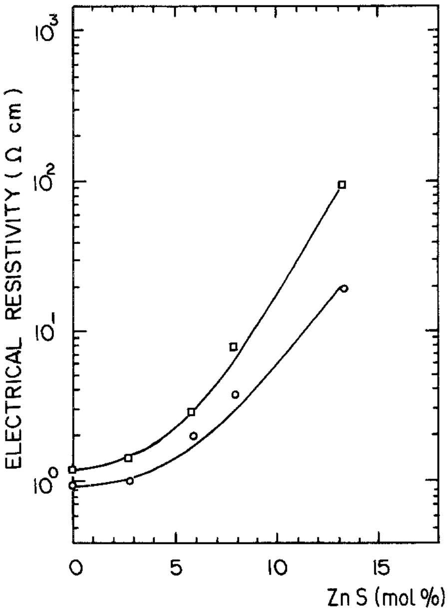

Figure 5 Dependence of electrical resistivity on the composition in $Cd_{1-x}Zn_xS$ films sintered for 1 h in nitrogen at (□) 625° C, (○) 650° C.

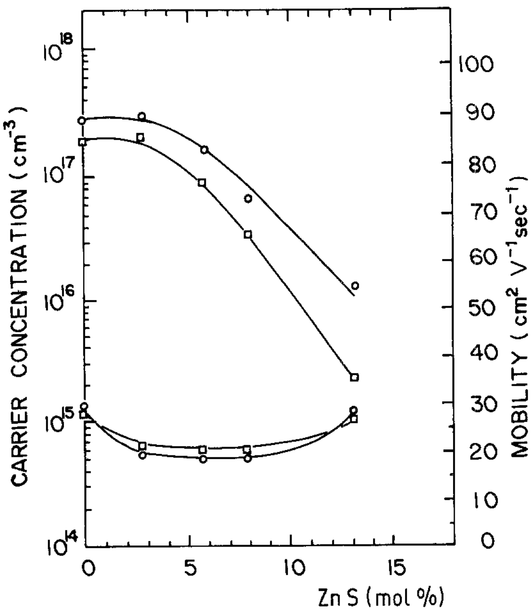

Figure 6 Electron concentration and mobility of $Cd_{1-x}Zn_xS$ solid-solution films, sintered for 1 h in nitrogen at (□) 625° C and (○) 650° C, as a function of composition.

To clarify the variations of electrical resistivity, Hall measurements were made. Fig. 6 shows the electron concentration and electron mobility of $Cd_{1-x}Zn_xS$ films sintered at various temperatures, as a function of composition. The electron concentration stays at about the same value as the zinc content increases up to 3 mol % and then decreases sharply with further increase in zinc content. The electron mobility, on the other hand, decreases with increasing zinc content up to 3 mol %, stays at about the same value for zinc content up to 8 mol % and then increases with further increase in zinc content. Thus the variations of the electrical resistivity of the sintered $Cd_{1-x}Zn_xS$ films are primarily related to the variations of carrier concentration.

According to the grain-boundary trapping model [11, 12], the activation energy of electrical resistivity E_A and the diffusion potential of the grain boundary ϕ_D of an n-type semiconductor can be expressed by

$$E_A = k\frac{\partial (\ln \varrho)}{\partial (1/T)} = \phi_B = \phi_D + E_C - E_f$$

$$\phi_D = \frac{q^2 N_t^2}{8\varepsilon n}$$

where ϱ is the electrical resistivity, ϕ_B the potential

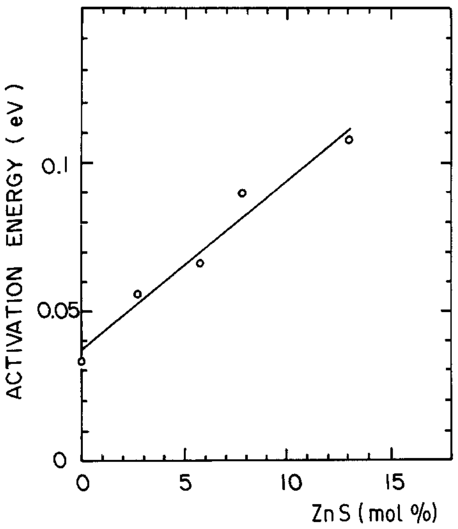

Figure 7 Activation energy of electrical resistivity against the composition of the sintered $Cd_{1-x}Zn_xS$ films, sintered at 625° C for 1 h in nitrogen.

barrier height, N_t the trap density of grain boundary, E_C the conduction band energy, E_f the Fermi energy, n the electron concentration and ε the permittivity of the semiconductor. For the specimens used in the present investigation, however, $E_A = \phi_D$ since the electron concentration n is independent of temperature in the temperature range used for the measurement of activation energy (exhaustion range) due to the small donor ionization energies of chlorine [13].

Fig. 7 shows the activation energy of electrical resistivity of the sintered $Cd_{1-x}Zn_xS$ films as a function of zinc content up to $x = 0.13$. From the measured values of the activation energy, the trap density of grain boundaries can be estimated, assuming ε to be independent of composition for small values of x. The trap density of grain boundaries decreases with increasing zinc content, and the estimated values were 5.57×10^{11}, 3.88×10^{11} and 1.41×10^{11} for compositions with $x = 0$, $x = 0.08$ and $x = 0.13$, respectively. The measured value of trap density of grain boundaries for CdS ($x = 0$) agree well with the value reported [8]. Thus the appearance of minima in the mobility against composition curve appears to be caused by the combined effect of grain size and the diffusion potential of the grain boundary. Using the reported values of chlorine donor ionization energy [13] and the measured values of electron concentration, the concentration of chlorine that was introduced during the sintering can also be estimated. The estimated values indicate that the effectiveness of chlorine doping, using $CdCl_2$ as a dopant source as well as a sintering aid, decreases with increasing zinc content under the sintering conditions used in the present investigation.

4. Conclusions

A number of slurries consisting of CdS powder, 10 wt % $CdCl_2$, various amounts of ZnS powder and appropriate amounts of propylene glycol have been prepared and were coated on to amorphous glass substrates. They were then sintered, in an ampoule with controlled openings, in a nitrogen atmosphere to investigate the sintering behaviour and the electrical properties of sintered $Cd_{1-x}Zn_xS$ films. $CdCl_2$, which was added as a sintering aid as well as a chlorine dopant source, enhances the sintering of $Cd_{1-x}Zn_xS$ films but the enhancing effect decreases with increasing zinc content due to the occurrence of the reaction $CdCl_2 + ZnS \rightarrow ZnCl_2 + CdS$ during sintering. The formation of $ZnCl_2$, which has a lower melting temperature and a much higher vapour pressure than $CdCl_2$, causes a decrease in the efficiency of chlorine doping into the $Cd_{1-x}Zn_xS$ films during sintering. Thus the average grain size decreases and the porosity increases in the sintered films as the zinc content increases. The electrical resistivity of the sintered films increases sharply as the zinc content increases, due to a sharp decrease in the concentration of chlorine introduced. The sharp increase in the electrical resistivity is also, in part, caused by an increase in donor ionization energy of chlorine in $Cd_{1-x}Zn_xS$ with increasing zinc content. The trap density of grain boundaries, on the other hand, decreases with increasing zinc content.

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