

The Effect of Sintering Conditions on Screen-Printed CdS Films

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ABSTRACT

Microstructural studies of screen-printed CdS film reveal that the firing temperature and the amount of CdCl₂ added are the important factors in controlling the electrical properties of the films. The sintering atmosphere is also critical. Excess oxygen may result in impurities such as CdO, CdSO₄ and Cd crystals.

INTRODUCTION

CdS with a wide and direct bandgap of 2.43 eV is a good window layer material for the heterojunction CdS/CdTe solar cells. Screen-printing followed by sintering has been regarded as the most attractive production method because of its low cost, ease in scaling-up and mass production. Most of the CdS films are sintered in a controlled atmosphere with extremely low O₂ level. A few reports have elucidated the impurity phases and the chemisorption of oxygen of CdS films sintered in air (1,2). In this paper, we report the microstructure and electrical properties of CdS films prepared by sintering in an oxygen-free atmosphere and in air. Studies based on XRD, SEM, and ESCA on the air-sintered CdS:Cl films reveal that the impurity phases include CdO, CdSO₄ and Cd crystals.

EXPERIMENTAL PROCEDURE

Commercial CdS (5N), anhydrous CdCl₂ (4N) and 1,2-propanediol (GR grade) were used as starting materials. CdS was ground in ball mill and an average particle size less than 1 μ m was obtained. CdS pastes comprised of ground CdS, CdCl₂ and appropriate amount of 1,2-propanediol, all homogenized by a three-roll mill. CdS paste was applied onto a borosilicate glass substrate by a screen printer using a 325 mesh stainless screen, then dried in oven at 120 °C for 2 hours. The dried film thickness was about 25 μ m. The sintering was carried out in a box furnace with a retort under controlled atmosphere. The substrates were held in a 6 ×

6 (cm) alumina crucible with cover containing five 1 mm holes. The films were sintered in "oxygen-free" nitrogen gas (UHP N₂) and in air. The sintering temperature varied from 580 °C to 650 °C and the firing time was between 10-30 minutes. Electrical properties were measured by Hall measurement. The crystallinity of CdS films was identified by XRD. SEM/EDAX and ESCA techniques were used to analyze the microstructure and phases of the sintered films.

RESULTS AND DISCUSSION

Figure 1 shows the variation of the resistivity of CdS films sintered at different temperatures and for different CdCl₂ content. Film resistivity shows a minimum between 570°C and 650°C while reaches a minimum at CdCl₂ content equal or greater than 10%. It can be seen that there is an optimum in the sintering temperature and the amount of CdCl₂ determined by the residual amount of CdCl₂ and Cl diffusion (3).

SEM micrographs of Figure 2 confirm the role played by CdCl₂ and by firing temperature as discussed previously. In general higher amount of CdCl₂ flux results in favorable grain growth as is with higher temperature. It should be noted that there is a secondary phase at the grain boundaries as shown in Figure 3E at the intermediate firing temperature of 610 °C. Such phenomena were also observed by Im et al (4) where the secondary phase was reported to be CdCl₂. However data from SEM-back electron scattering and EDAX indicate that these phases are CdS. EDAX results in Figure 4 illustrate the mere detection of Cd and S elements on both the primary grains and the secondary phases. No Cl was detected. This may be caused by insufficient wetting during the sintering as often reported in studies involving liquid phase sintering (5).

The influence of oxygen on sintered CdS film properties was also studied. As shown by the XRD results in Figure 5, only hexagonal CdS was detected

when films were sintered in ultra-pure nitrogen (impurity less than 5 ppm) regardless the firing temperature and the flux content. However, when sintered in air or in ordinary nitrogen (O_2 greater than 50 ppm) atmosphere, a darker film surface is obtained and in addition to the CDS hexagonal phase, CdO and Cd were also present as illustrated in Figure 6. The role of oxygen can be further elucidated by the ESCA results. The binding energies (BE) of the S(2p) peaks are shown in Figure 7A. The peaks centered at 161.8 eV and 162.9 eV can be identified as a S^{2-} ion. Another peak centered at 170.4 eV can be identified as a SO_4^{2-} compound. Figure 7B shows the BE of the O(1s) peak centered at 532.2 eV which could be either associated with CdO or $CdSO_4$.

SEM micrograph illustrated in Figure 8 indicates clearly the presence of large crystals on the film. The accompanied EDAX studies on these crystals shown in Figure 9 reveal the presence of Cd only with barely detectable amount of S indicating that these are Cd crystals. These results show that an excess of oxygen will cause the formation of impurity phases such as CdO, $CdSO_4$ and crystalline Cd with high film resistivity, some nearly insulative. These results differ with those reported by Houngh et. al. and Amalnerkar et. al. (1,2). The detailed reaction mechanism will be reported later.

CONCLUSIONS

Sintering conditions and atmosphere are critical in controlling the electrical properties and microstructure of the CdS films. Studies show that an excess of oxygen will result in films of high resistivity and in impurity phases such as CdO, $CdSO_4$ and crystalline Cd, since among the reactions with O, Cl and S, oxide formation is preferential.

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4. H. G. Yang and H. B. Im, *J. Mat. Sci.* **21** (1986) 775-780

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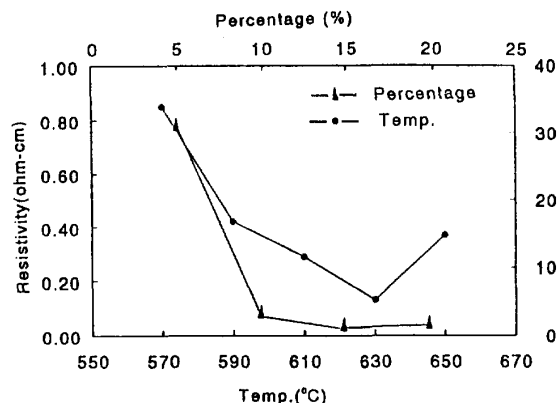
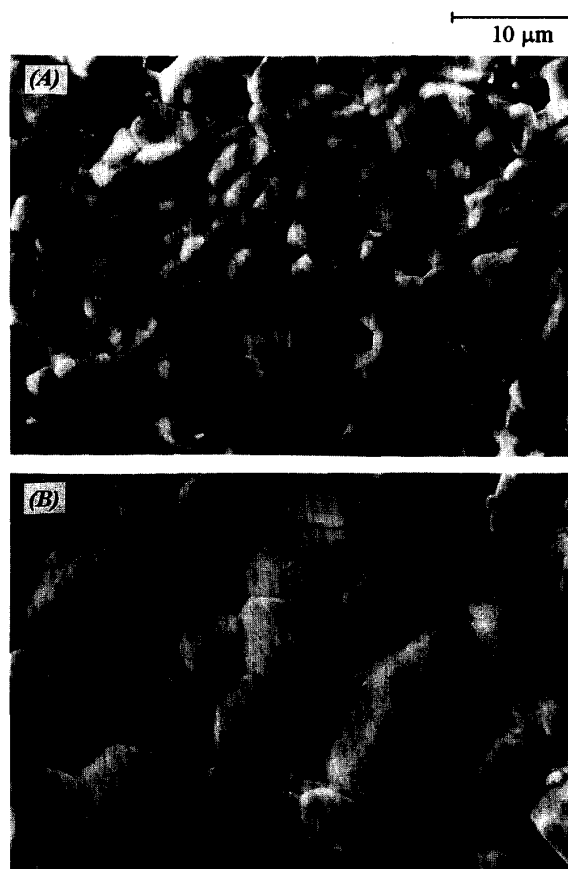


Figure 1 - Variation of resistivity of CdS films as a function of sintering temperature and percentage of $CdCl_2$ added.



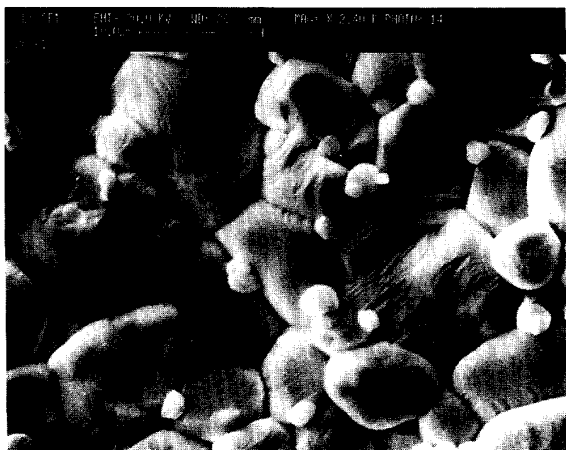


Figure 2 - SEM of CdS films sintered for 30 minutes at 650°C with 10% CdCl₂ (A), 650°C with 20% CdCl₂ (B) and at 610°C with 20% CdCl₂ (C).

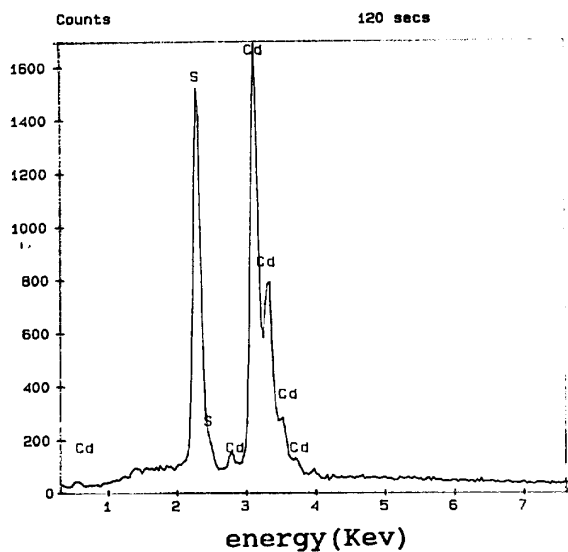


Figure 3 - EDAX analysis of the secondary phase of CdS film fired at 610°C with 20% CdCl₂ (Figure 2C).

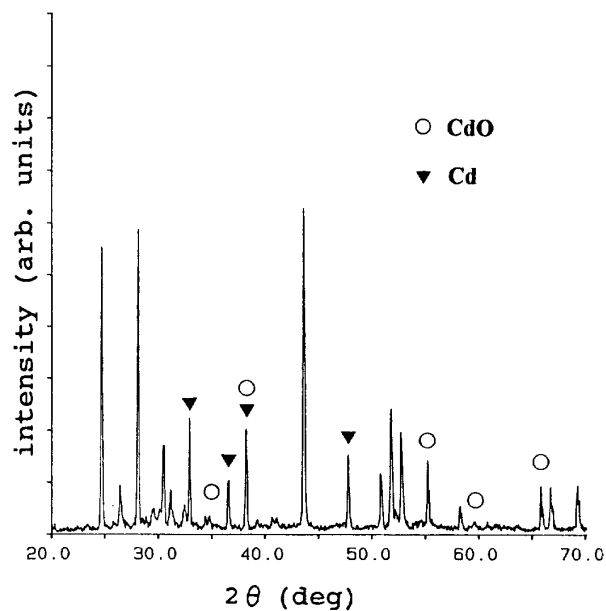
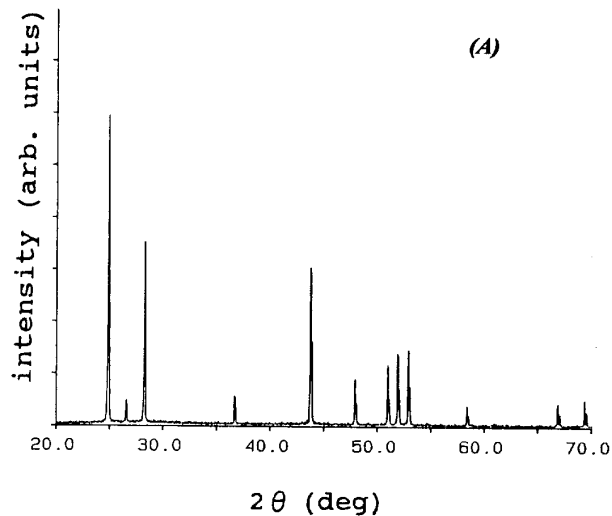


Figure 4 - XRD of CdS films sintered in UHP N₂ (A) and in Air (B).

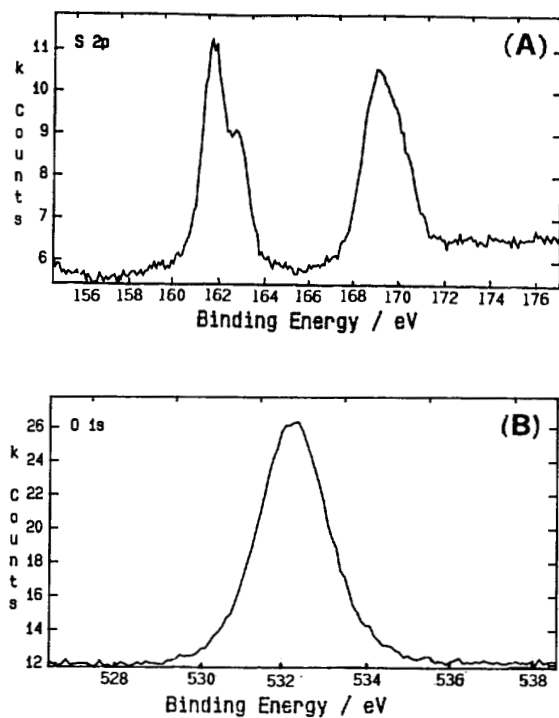


Figure 5 - ESCA spectra of S(2p) (A) and O(1s) (B) of CdS films sintered in air.

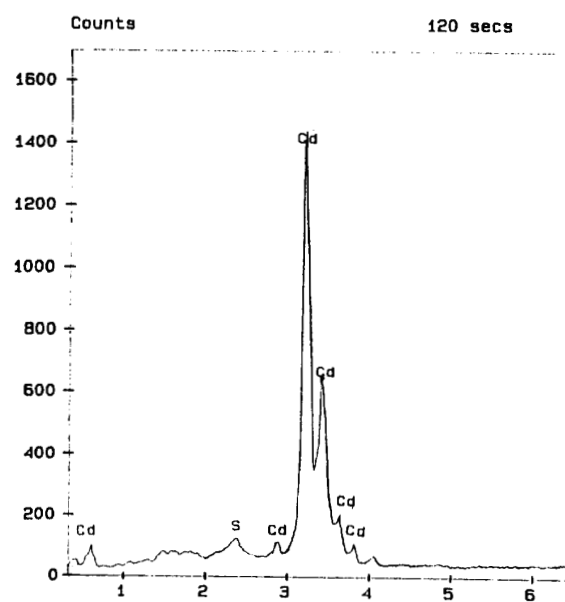


Figure 7 - EDAX of CdS film sintered in air.



Figure 6 - SEM of CdS film sintered in air.