

## Effect of annealing time on dark and photo-currents of CdS : Na thin films

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(Received 23 June 1977)

Chemically deposited CdS thin films have been prepared with and without sodium dopant. The films have been annealed in air at 150°C for various periods up to 40 hours. Effect of annealing time on dark and photo-currents of the films has been investigated. The role of adsorption of oxygen and the formation of sulfur vacancies are discussed. The effect of light intensity on photocurrent has also been reported.

### 1 INTRODUCTION

As a part of continuing program (Pawar *et al* 1977, Shikalgar *et al* 1977) the effect of sodium dopant as well as annealing time on photocurrent and dark current in chemically deposited CdS thin films is being investigated. Until now very little work has been done on the photoconducting properties of sodium doped CdS. A few workers (Henry *et al* 1970, Yoshizawa 1976 and Tell 1971) have recently reported that the sodium and lithium are the good shallow acceptors responsible for photoconductance and photoluminescence. However, their main interest was to obtain *p* type material, but so far that was unsuccessful. These studies were made on single crystals and the doping of sodium in chemically deposited CdS thin films is few to date as far as the authors are aware of.

In the present investigation sodium doped CdS thin films have been prepared by chemical bath deposition technique. The effect of sodium dopant and annealing period on the dark and photo-currents of these films has been investigated. The variation in photocurrent with light intensity has also been studied.

### 2 EXPERIMENTAL

CdS : Na thin films have been prepared by chemical bath deposition technique following closely the method reported earlier (Pawar *et al* 1977). Briefly, for each deposition 20 c.c. of 1 mol. CdSO<sub>4</sub> solution and 100 c.c. of 2 mol. ammonia solution were mixed in a beaker to form a complex compound. To this complex 20 c.c. of 1 mol. thiourea and 0.01 wt percent of Na were added. The reaction vessel was heated to 90°C for 30 minutes. Four glass slides were mounted as the substrates on a sample holder which was kept rotating in the reaction mixture.

at a constant speed of 125 revolutions per minute. This served the purpose of stirring the chemical mixture, as well as exposing the substrates to fresh reactants which is important for uniform deposition of the films. The films were washed several times with distilled water, dried and preserved in a dark desiccator.

The films were annealed at 150°C in air for various periods with an interval of four hours and upto forty hours. For photoconductivity studies, a special holder was designed for giving the pressure contacts to the films which was mounted in a light tight box. The photocurrent was measured with Aplan TFM 13 JET nanoammeter. A 500 watt tungsten filament lamp operated at 2800°K was used as the source of light. A water filter was used in between film and lamp to avoid the heating of the film.

### 3. RESULTS AND DISCUSSION

Figure 1 gives the nature of variation of dark current  $I_d$  with the annealing time both for doped and undoped films. The increase in  $I_d$  with annealing time is attributed to the better crystallinity as well as to the formation of sulphur vacancies giving rise to the additional donor levels (Pavaskar 1976).

The other feature noted from figure 1 is that the  $I$  for doped films is smaller than that for undoped films. This is attributed to the following reasons:

- 1) In the present chemical bath deposition technique there is an excess of sulphur (Pavaskar & Menzes 1968) which maximizes the density of cadmium vacancies. As the sodium ions are rapidly diffusing and highly soluble these can enter easily at the substitutional sites giving rise to acceptor levels. This will decrease the density of electrons.
- 2) The doping of sodium may reduce the electron mobility either through introducing additional scattering centres or through altering the barrier heights at the intergrain barriers. (Wu & Bube 1974)
- 3) The sulphur atmosphere minimizes the density of simple intrinsic donor defects (sulphur vacancies or cadmium interstitials) which could compensate the sodium.
- 4) As observed from X-ray studies, the films are found to be less crystalline after sodium doping.

From the slopes of the plots in figure 1, it is seen that the rate of increase of  $I_d$  with annealing time for doped films is smaller than that for undoped films. This can be understood as follows: As described above (reason 1) there is a small number of cadmium vacancies in doped films than that of undoped films. At the annealing temperature of 150°C, there starts the process of formation of sulphur vacancies. Due to the comparatively less number of cadmium vacancies in doped films the rate of formation of sulphur vacancies is smaller than

that of undoped films. This reflects in the rate of increase of  $I_d$  with annealing time.

The variation of photocurrent  $\Delta I$ , with annealing time is shown in figure 2— for both doped and undoped films. The general behaviour of the plots is that  $\Delta I$  increases with annealing time, attains a maximum value at the annealing

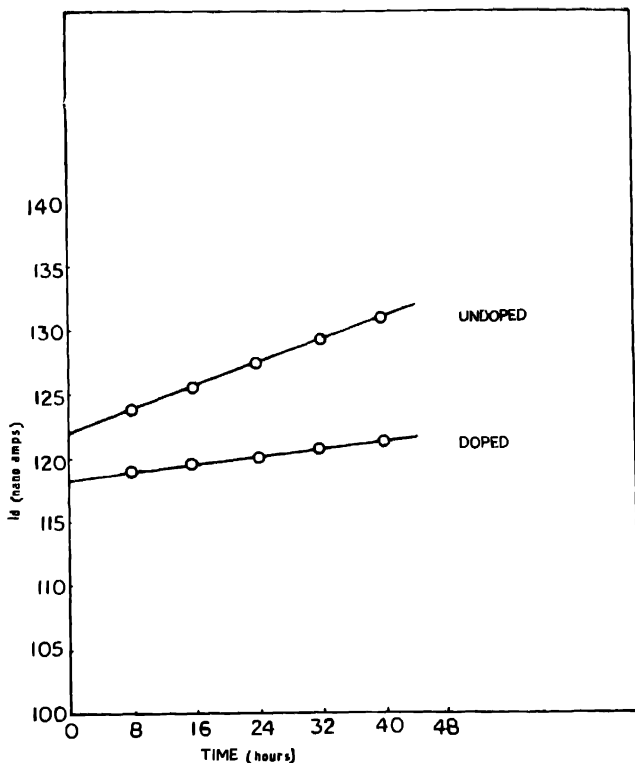


Fig 1. Dark current  $I_d$  at room temperature with the annealing time in hours for doped and undoped films.

period of 28 hours and then decreases. The increase of  $\Delta I$  is attributed to the crystallization of the film during the first few hours of annealing and to the formation of sulphur vacancies. The crystallization helps in increasing the mobility while the sulphur vacancies help in increasing the recombination centres.

The decrease in photocurrent after the 28 hours of annealing, can be understood as follows

For the longer annealed films, an oxygen plays an important role in decreasing the photocurrent. Oxygen molecules are known to be first physically adsorbed

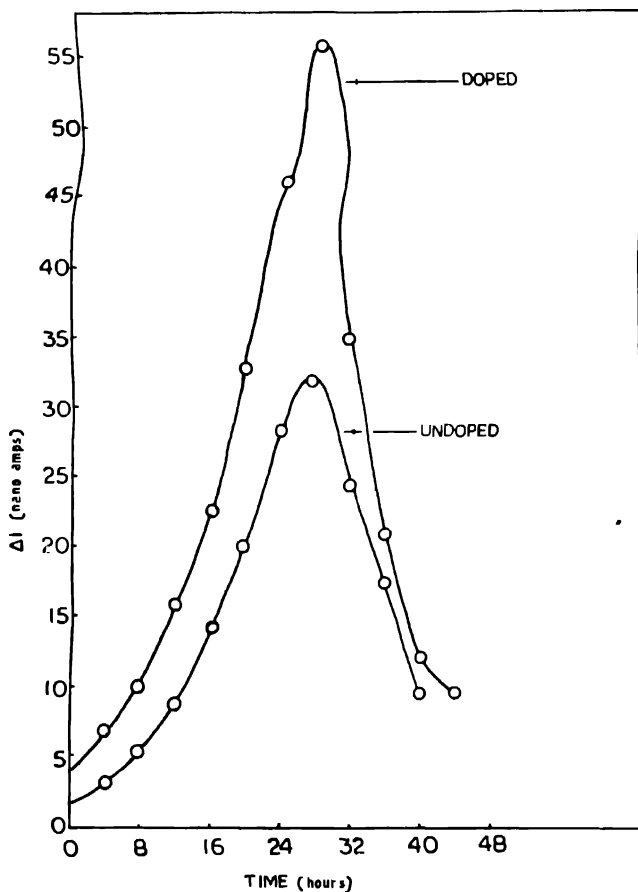


Fig. 2 Variation of photocurrent  $\Delta I$  at room temperature with the annealing time in hours for doped and undoped films.

on the CdS surface, and a transition from physical to chemical absorption then takes place by capture of conduction band electrons. At longer annealing period,

this process expands inside the film and oxygen molecules are adsorbed at the grain boundaries, which alters the barrier height and barrier width. Under photo-excitation the adsorbed oxygen at the film surface and at the grain boundaries act as additional recombination centres and reduces the photoexcited electron life time (Wu & Bube 1974). The adsorbed oxygen also decreases the tunneling probability for electron transport through the intergrain barriers. This gives rise to decrease in photocurrent of CdS films annealed for more than 28 hours.

From figure 2, it is seen that sodium doped films are more photosensitive. It is likely that sodium ions act as acceptors entering at the substitutional sites. This is similar to that of copper doping in CdS.

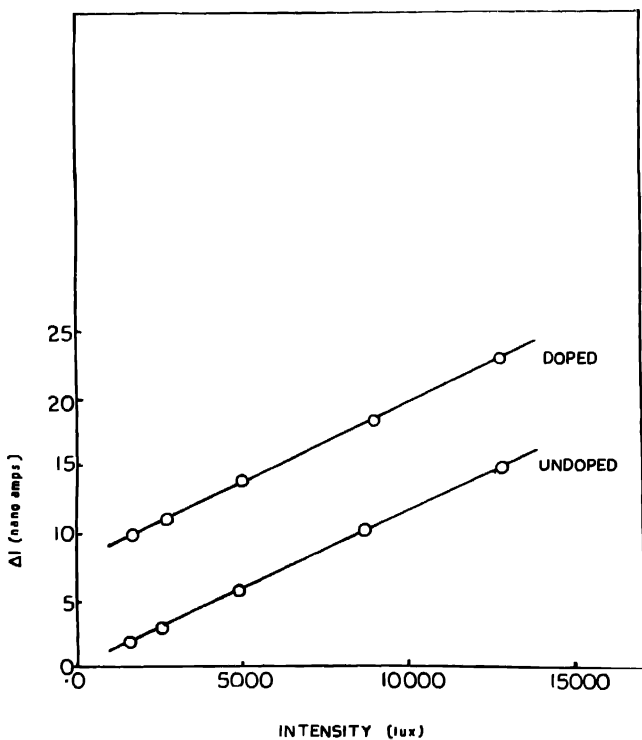


Fig. 3 Plot of photocurrent  $\Delta I$  versus incident light intensity in lux for doped and undoped films at room temperature.

The effect of light intensity on undoped and sodium doped CdS thin films annealed for 28 hours has been studied. The variation of  $\Delta I$  with light intensity is shown in figure 3. The linear nature of the plots indicates that the density of conduction electrons is directly proportional to the intensity of illumination and in turn reveals that the concentration of available recombination centres is higher than the concentration of free electrons.

#### ACKNOWLEDGMENT

The authors wish to thank Dr. R. N. Patil, for his constant encouragement and comments. One of the authors, A. G. S. expresses his deep sense of gratitude to C. S. I. R., Delhi for Junior Research Fellowship. This work was supported by grants for support of research in Universities from U. G. C., Delhi.

#### REFERENCES

- Henry C. H., Nassau K. & Shoover J. W. 1970 *Physical Review Letters* **24**, 820.  
 Puvastkar N. 1976 *Ph. D. Thesis* Poona University.  
 Puvastkar N. & Monozos C. A. 1968 *Jap. J. Appl. Phys.* **7**, 743.  
 Pawar S. H., Shikalgar A. G. & Bargale B. B. 1977 *Thin Solid Films* (submitted).  
 Shikalgar A. G., Bargale B. B. & Pawar S. H. 1977 *Ind. J. Pure and Appl. Phys.* (Submitted).  
 Toll B. 1971 *Journal of Applied Phys.* **42**, 2919.  
 Wu C. & Bube R. H. 1974 *J. Appl. Phys.* **45**, 648.  
 Yoshizawa Michio 1976 *Jap. J. Appl. Phys.* **15**, 2143.