

## Photoelectric properties of pure and aluminium doped CdS films

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**Abstract.** Photoelectric properties of pure and Al doped vacuum deposited CdS films have been studied to explore the possibility of their application in photoactivated liquid crystal light valves. The effect of heat treatment in oxygen atmosphere, rate of deposition and the extent of Al doping, etc. on the resistivity, photo-response spectral characteristics, rise and decay time of photo-current, etc. have been investigated. It has been found that in contrast to pure CdS films, the properties of Al-doped films significantly depend on both the rate of deposition and the extent of Al doping. The dark resistivity in all cases was found to increase with heat treatment in oxygen. Unlike pure CdS films, Al doped films show photo-conductivity which is enhanced by heat treatment. Al doped films deposited at higher rates show better photo response even at lower light levels. At various light levels the rise and decay time of Al-doped films were found to be fairly constant and lower than that for pure CdS films. All these properties have been explained in terms of the presence of trapping levels due to doping. These trapping levels are also indicated by TSC, optical absorption and EPR studies.

**Keywords.** Cadmium sulfide thin films; photoconductivity; E. P. R.; T. S. C.; Optical absorption; liquid crystal light valve.

### 1. Introduction

Polycrystalline thin films of cadmium sulphide have received considerable attention during recent years because of their proven and potential applications in a variety of semiconductor devices such as solar cells, transistors and recently in light activated valves for large screen liquid crystal displays (Bube 1960; Beard *et al* 1973). Photoelectric properties of thin films of CdS required for use in these devices differ considerably. For example in the case of solar cell application, the requirements of CdS films are (i) large grain size, (ii) high mobility of the charge carriers (iii) high absorption in the visible region, etc. In contrast, the requirements of CdS film for application as a light valve in liquid crystal display are very different. It is therefore necessary that (i) the dark resistance of the CdS layer matches with the resistance of the liquid crystal layer, (ii) the intrinsic resistance of the photoconducting CdS film is high enough to prevent blurring of the image, (iii) mobility of the carriers in the photoconducting layer is high, (iv) there is no appreciable diffusion of carriers due to scattering from defects in the film, (v) the film shows high spectral response of photo-current for the green region and low response for the red region of the spectrum, and (vi) the photoconducting CdS layer has a high sensitivity for low light levels and its dependence on high intensity should match the contrast voltage relation of the liquid crystal display.

It is thus clear that CdS films used in different applications should yield films of desirable photoelectric properties. A thin CdS film can be deposited in a variety of

ways (Böer *et al* 1966; Kitamura 1960; Tekeuchi *et al* 1976) among which vacuum evaporation method has been established as convenient and reproducible. However, this process gives nonstoichiometric films due to different vapour pressures of the components Cd and S in CdS. Stoichiometry in the evaporated film can be controlled to a large extent by depositing films at an elevated substrate temperature (between 175–200°C). Even then it may not be possible to get films with the desired photoelectric properties mentioned above. Consequently, they have to be subjected to post deposition treatment in order to make films to suit a typical device such as liquid crystal light valve, solar cell, etc. In order to develop suitable CdS photoconducting films for liquid crystal light valve, we have carried out various post deposition treatments like heating the film at various temperatures and duration in various ambients such as oxygen, chlorine, argon, sulphur and cadmium and also in vacuum. Films were also heat treated to incorporate impurities like Ag, In, Cu, etc. The photoelectric properties such as rise and decay time, sensitivity to lower light levels, spectral response, etc have been studied with the view to investigate their suitability for application in photo activated liquid crystal valves (the results of these studies will be reported separately as part II). In this effort, the behaviour of CdS films, doped with Al during the growth of the films, has been studied. It is found that the photoelectric properties of heat-treated Al doped CdS films are more suitable for application in light valve. This paper, which forms part I of the series of our extensive investigations on CdS films, deals with this particular aspect of Al doped CdS films.

## 2. Experimental

Thin films of CdS are deposited on thoroughly cleaned microscope glass slides by vacuum evaporation at a pressure of the order of  $10^{-5}$  torr. The charge for evaporation consisted of processed 5 mm pellets of highly pure CdS powder from Koch-Light Labs. The substrates were maintained at 200°C during evaporation. Aluminium doped films were deposited in a similar manner. CdS powder was thoroughly mixed with pure fine mesh Al powder before the pellets are made. Subsequent to the deposition, the film thickness is measured using multiple beam interferometric techniques. The films are generally deposited at an average rate of 50 Å/min unless stated otherwise.

The samples are heat treated in sealed glass ampules filled with dry air or oxygen at atmospheric pressures. Resistivity measurements are carried out in surface configuration with evaporated Al contacts. The variation of photocurrent with white light intensity is measured using a set of neutral density filters. The spectral response is observed using a set of Carl-Zeiss interference filters and the optical absorption spectra were recorded on a Carl-Zeiss spectrophotometer model Specord UV/VIS.

## 3. Results and discussion

### 3.1. Dark and light resistivity

The resistivity data for a large number of pure doped and treated specimens are collected. Some representative results from amongst the above are presented in

**Table 1.** Resistivities of pure and doped CdS films, before and after oxygen treatment

Specimen	Resistivity before treatment (ohm cm)		D/L Ratio	Specimen after treatment	Resistivity after treatment (ohm cm)		D/L Ratio
	Dark	Light			Dark	Light	
F0	4.5	1.8	2.5	F2	$9 \times 10^3$	90	$10^2$
H0	$9 \times 10^2$	45	20	H2	$2.2 \times 10^4$	$1.08 \times 10^3$	20
I0	18	3.15	6	I2	$4.5 \times 10^4$	11.7	$3.8 \times 10^3$
J0	$1.53 \times 10^3$	$1.8 \times 10^2$	8.5	J2	$4.5 \times 10^5$	$4 \times 10^3$	$1 \times 10^2$

table 1. The resistivity of untreated pure CdS film (F0) is as low as 4.5 ohms cm. The change in the average rate of deposition within moderate limits (10 to 50 Å/min) does not affect the dark resistivity significantly. However, when these films are subjected to heat treatment in oxygen at 450°C for about 2 hr, the resistivity rises to  $9 \times 10^3$  ohms cm (sample F2). As reported earlier heating CdS films below 250°C in oxygen does not increase their resistivity significantly. When the films are heated above 250°C the resistivity increases and attains a maximum value at about 450°C. Further rise in temperature to 550°C does not show any significant increase in resistivity.

The behaviour of Al-doped films is, however, different. Dark resistivity of Al-doped CdS films shows marked dependence on the rate of deposition. For a film doped with  $\sim 100$  ppm Al (sample I0) and deposited at 50 Å/min, the resistivity is about 18 ohm cm. This rises to  $1.5 \times 10^3$  ohms cm when the rate of deposition is decreased to 8 Å/min (sample J0). Dark resistivity is also found to depend upon the amount of Al-doping; the resistivity decreases with increase in Al concentration. For films deposited at a slow rate (10 Å/min) (high concentration, 2% by weight) the resistivity is about  $9 \times 10^2$  ohm cm [sample (H0)].

Al-doped CdS films, like pure CdS films, show an increase in dark resistivity on heat treatment. However, they show a marked dependence on heat treatment, Al doping, rate of evaporation, etc. The increase in resistivity of Al-doped CdS films deposited at a lower rate of deposition is only two orders of magnitude (J2) whereas films deposited at higher rate of deposition show increase in resistivity by nearly four orders of magnitude (I2). An increase in Al concentration for low rate of evaporation (H2) reduces this increase to only one order of magnitude.

Untreated pure CdS films show very small photoconductivity ( $D/L=2$ ) for light levels as high as  $10^3$  lux. Heat treatment of these films increases the  $D/L$  ratio to  $10^2$  for light intensity of  $10^3$  lux. Al-doped films on the other hand show higher photoconductivity even in the untreated form. The  $D/L$  ratio for samples (J0) and (I0) is 8.5 and 6.0 respectively. The sample with higher Al concentration and low rate of evaporation (H0) yields  $D/L \approx 20$ . It would seem that photosensitivity increases with Al concentration for low rate evaporated CdS films.

Films (H0) after heat treatment (H2) show increase in both dark and light resistivities, the  $D/L$  ratio remaining almost the same. Irrespective of the rate of deposition, the dark resistivity for both low concentration Al-doped CdS films increases yielding high  $D/L$  ratio of nearly  $10^3$ .

These results clearly bring out the fact that dark resistivity of Al-doped films can be controlled by controlling the extent of doping and the rate of evaporation as also

the subsequent heat treatment. Indeed, by manipulating these three parameters, it is possible to get films of the required dark resistivity to match the resistivity of the liquid crystal film. In a typical situation, the liquid crystal layer (MBBA of  $12\mu$  thickness) had a resistance of  $10^6$  ohm. It was possible to match this resistance by preparing an Al-doped CdS film of thickness  $1\mu$  with Al concentration of 100 ppm evaporated at a rate of  $50\text{\AA}/\text{min}$  and subjected to heat treatment for 2 hr at  $420^\circ\text{C}$  in oxygen atmosphere.

### 3.2. Intensity response of photo-current

Variation of photo-current with white light intensity for some of the films is shown in figure 1. Oxygen treated pure CdS films show almost a linear rise in photo-current up to a certain intensity below which the response is relatively flat. Untreated Al-doped films also exhibit a linear dependence (sample I0). The untreated high Al concentration doped CdS film (H0), however, shows sublinear behaviour for low intensity of light. In contrast to treated pure CdS films (F2), Al-doped treated films (I2) show better response for lower light intensities. A typical plot for sample I2 shows superlinearity at lower light levels ( $\leq 40$  lux). The change in photo-current with light intensity for this sample (I2) above 40 lux is similar to that of untreated sample (I0).

It is clear therefore that Al doping improves the low intensity response of the photo-current without significantly affecting the high intensity response enhancing its utility in light valve applications.

### 3.3. Spectral response

The spectral response of photo current for some of the films is shown in figure 2. Air treated pure CdS film (sample F2) has a peak sensitivity at  $5000\text{\AA}$ , corresponding to the band edge of CdS, with shoulders at  $5500\text{\AA}$  and  $6000\text{\AA}$ . Untreated Al-doped

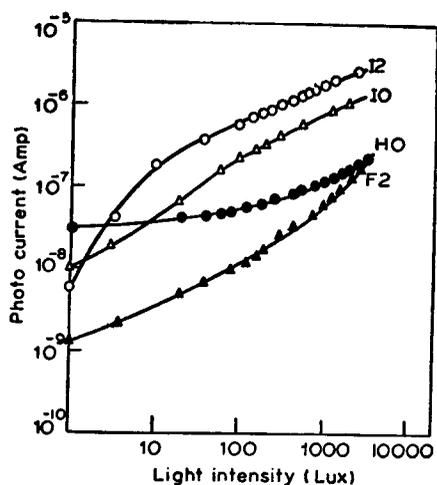


Figure 1. Photocurrent vs white light intensity for pure and Al-doped CdS films.

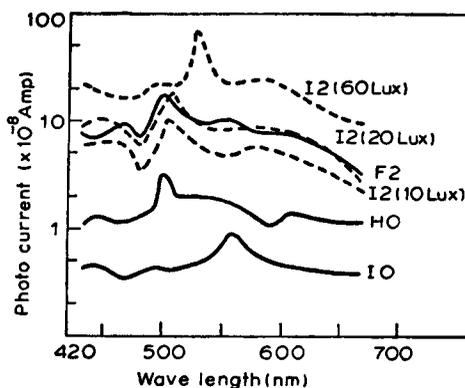


Figure 2. Spectral response of photocurrent for pure and Al-doped CdS films.

CdS films (I0) show a peak at 5500Å with a small shoulder at 5000Å. High concentration Al-doped untreated film (H0) shows a peak at 5000Å and a shoulder at 5500Å. Oxygen heat treatment changes the spectral response of low concentration Al doped sample (I0). In comparison to treated pure CdS film (F2), this treated Al doped film shows a peak at 5250Å with shoulders at 5000Å and 5500Å. The response above 6000Å varies in a manner similar to that for treated pure CdS film (F2). An interesting feature of this Al-doped treated film (I2) is the shift of the response peak with increase in intensity of excitation. For an intensity of 10 lux, the peak occurs at 5060Å. It shifts to 5150Å for 20 lux and occurs at 5250Å for 60 lux. The shoulder at 5800Å, however, shows no variation.

### 3.4. Rise and decay time

The dependence of rise time of the photo-current on the intensity of white light is shown in figure 3. The rise time in all cases decreases with increasing light intensity. The treated low rate evaporated Al-doped (sample H2 and J2) CdS films show a similar behaviour irrespective of the Al concentration. Treated pure CdS films (F2) also show a similar behaviour. Both, treated and untreated high rate evaporated Al-doped films (I0 and I2) show a behaviour different from other films. These films show comparatively flat response for all light intensities. The amount of Al doping and the rate of evaporation drastically affect the rise time at lower light levels.

The decay curves are shown in figure 4. Consistent with the rise time behaviour, decay time also decreases with increase in light intensity.

### 3.5. Optical absorption spectra

Optical absorption curves for various films are shown in figure 5. For pure untreated films (F0), the cut-off (where the transmission is minimum) wavelength lies at about

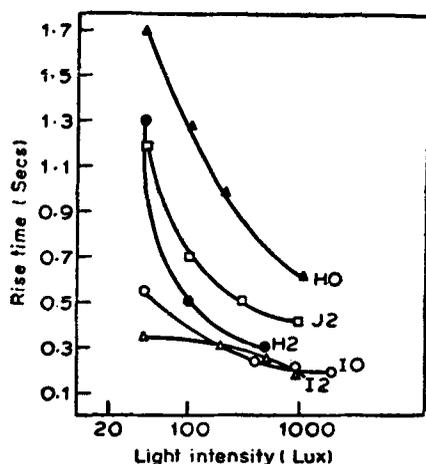


Figure 3. Rise time of photo-current vs light intensity for pure and Al-doped CdS films.

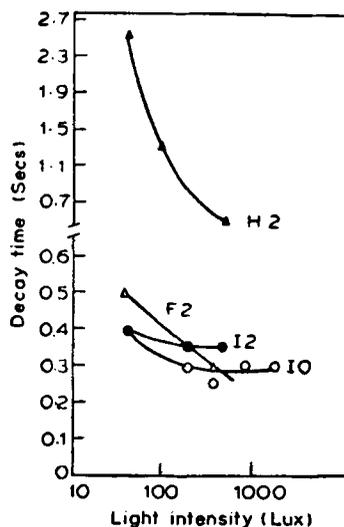


Figure 4. Decay time of photocurrent vs light intensity for pure and Al-doped CdS films.

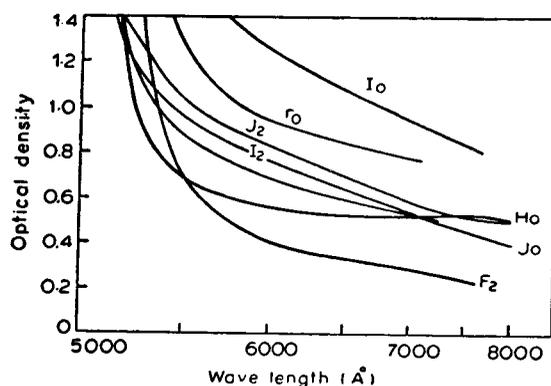


Figure 5. Optical absorption spectra for various pure and Al-doped CdS films.

5404Å. After oxygen treatment it shifts to 5263Å and the absorption falls rapidly for higher wavelengths. The cut-off value for untreated Al-doped films (J0) and (H0) lies between 5100–5200Å. Heat treatment does not change this value significantly but the fall for higher wavelengths becomes steeper. As has been reflected in many other properties, the rate of evaporation of Al-doped films causes considerable effect on the cut-off value. For example, the cut-off for untreated high rate evaporated Al-doped films (I0) occurs at 5714Å with a gradual fall for higher wavelengths. On the other hand, films deposited with the same amount of Al but deposited at a lower rate of evaporation (sample J0) show a cut-off much nearer to that for a pure CdS crystal. Heat treatment of this high rate evaporated film (I2) shows a remarkable shift in the cut-off now occurring at 5128Å with a steeper fall for higher wavelengths.

### 3.6. Thermally stimulated current

The TSC curves were analysed for the calculation of trap depth and trap density following the method employed by Kitamura (1961) and Bube (1955). The results are summarized in tables 2 and 3. The TSC glow curve for treated pure CdS film (figure 7) shows a broad distribution of traps. In the case of treated high rate evaporated Al-doped film (I2), however, only three peaks corresponding to shallow traps appear

Table 2. Major trap depths of pure and Al-doped CdS films obtained by analysis of the thermally stimulated current curves.

Preparation of specimen	Trap depths (eV)				
F2 (pure, heat treatment in air)	0.32	0.37	0.46	0.50	0.55
H0 (Al-doped, untreated)	0.30	0.46	0.50		
I2 (Al-doped, treated)	0.37	0.45	0.50		

Table 3. Density of the traps observed in pure and Al-doped CdS films

Specimen	Trap depths (eV)				
	0.30	0.37	0.46	0.50	0.55
F2	$1.2 \times 10^{14}$	$6.2 \times 10^{14}$	$1.7 \times 10^{16}$	$3.1 \times 10^{16}$	
H0	$2.7 \times 10^{16}$	—	—	$7.9 \times 10^{16}$	
I2	—	$4.4 \times 10^{16}$	$6.7 \times 10^{15}$	$2.4 \times 10^{14}$	

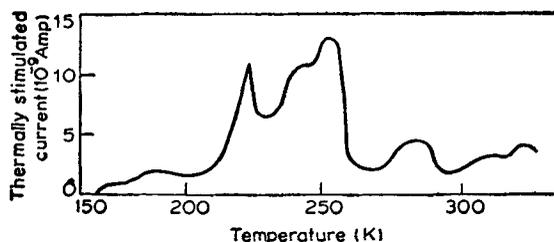


Figure 6. TSC glow curves for oxygen treated pure CdS films

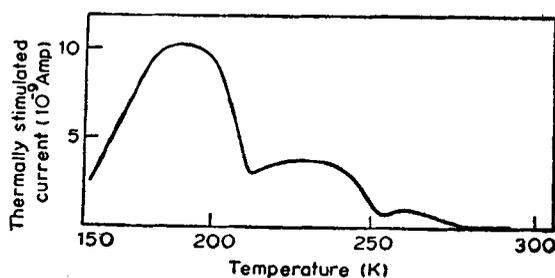


Figure 7. TSC glow curves for treated, high rate evaporated Al-doped CdS films

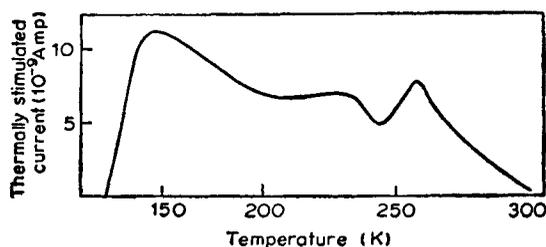


Figure 8. TSC glow curves for untreated high Al-concentration doped, low rate evaporated CdS films.

(figure 8). In contrast to the pure treated film peaks occurring at high temperature are not seen in these treated Al-doped (high rate evaporated) CdS films. It is also interesting to note that a peak corresponding to 192 K (0.37 eV) trap, seen in pure treated CdS film increases significantly in the treated Al-doped film evaporated at high rate (I2). For films with higher Al concentration (H0) the peak occurring at 260 K increases in intensity and a new peak occurs at 153 K. It appears that traps on the higher temperature side above 260 K vanish by doping the films with Al.

It is clear from table 3 that Al doping not only causes removal of deep traps present in the treated pure sample but also reduces the trap density of levels at 0.43 eV and 0.50 eV.

### 3.7. Electron paramagnetic resonance

In order to obtain information about the presence of defect centres in pure, doped and treated films EPR studies on these films have been carried out at room temperature. The  $g$  values for the resonance line observed in these films are presented in table 4. The  $g$  value suggests that the paramagnetic centre observed in the case of pure CdS film corresponds to  $F_3$  centres. The calculated  $g$  value agrees with the reported  $g$

**Table 4.**  $g$  values of resonance lines observed in pure and Al-doped films obtained from EPR spectrum

Sample	Calculated $g$ value	Attributed to centres	Reported $g$ value
F0	2.05	$F_3$	2.06
I0	2.0077	$F_2^+$	2.0034
J0	2.0077	$F_2^+$	2.0034
H0	2.05	$F_3$	2.06
I2	2.05	$F_3$	2.06
J2	2.05	$F_3$	2.06

value (Ekbote *et al* 1972) for such a centre. The  $g$  value for low concentration Al-doped films (I0 and J0) on the other hand is very close to that of free electron  $g$  value, suggesting the presence of  $F_2^+$  centres (Auzins *et al* 1962). As seen in table 4, the  $g$  value for films with 2% Al-doping (H0), corresponds to  $F_3$  centre similar to that in untreated pure CdS film. After oxygen treatment Al-doped films (I2 and J2) show a conversion of  $F_2^+$  centres to  $F_3$  centres. The reason for this clustering could not be ascertained.

The above results clearly bring out the fact that the various photoelectric properties of vacuum evaporated CdS films such as dark resistivity,  $D/L$  ratio, spectral response, rise and decay time, etc. are considerably affected by Al doping and that the extent of changes in these parameters is determined by (1) Al concentration in the film (2) rate of evaporation and (3) subsequent heat treatment. It may be pointed out that extensive investigations on the photoelectric properties of CdS crystals doped with various dopants have been reported in the literature (Bube 1955; Susa *et al* 1975). In these crystals, the photoelectric properties can be modified suitably by varying the dopant concentration and subjecting the samples to appropriate heat treatments. However, in thin films relatively scanty data are available. Our results bring out the fact that in addition to the dopant concentration and heat treatment which affect photoelectric properties of CdS crystals, the rate of evaporation and substrate temperature also affect the photoelectric properties of CdS thin films.

It is well known that vacuum evaporated pure CdS thin films are non-stoichiometric. These films are essentially Cd rich and sulphur deficient. The deficiency in sulphur arises because of the difference in both the vapour pressures and the sticking coefficients of Cd and S. To an extent, sulphur deficiency in such films can be controlled by evaporating CdS films on substrates at elevated temperature and/or evaporating these films in sulphur atmosphere (Pizzarille 1964).

The effect of Al doping on various physical properties of CdS films can be studied by following different approaches. Considerable literature is available on the effect of thermal diffusion of indium, copper, aluminium, etc. in the already prepared films of CdS (Dressner and Shallcross 1963). In this process since the diffusion has to take place at elevated temperatures, sulphur (from the CdS film) has a tendency to escape from the film resulting in further sulphur deficiency. In addition, since Al goes in the trivalent state and replaces divalent cadmium, there is a possibility of  $Cd^+$  ions and/or Cd vacancies being formed to compensate the charge. The existence of such  $Cd^+$  ions in the doped films has been corroborated by the presence of donor centres in such films (Kroger *et al* 1964), whereas the presence of cadmium

vacancies is indicated by the observation of acceptor centres. In effect, therefore, thermally diffused Al-doped CdS films would exhibit a larger deficiency of sulphur than that existing in undoped films, as also the presence of  $\text{Cd}^+$  and  $\text{Al}^{3+}$  ions in the lattice.

Some attempts have also been made to thermally diffuse Al, In, etc. in the CdS in the presence of sulphur vapour (Kroger *et al* 1954) so as to regulate sulphur deficiency. However, the films would still show  $\text{Cd}^+$ , Cd vacancies and  $\text{Al}^{3+}$  ions in the lattice. Since in the former case, sulphur deficiency increases on doping as compared to virgin CdS films, the resistivity of Al doped CdS films (doping in uncontrolled atmosphere) would be much lower as compared to virgin CdS films. However, when Al doping is carried out in sulphur atmosphere, sulphur deficiency can be controlled and the resistivities of such films may be comparable to that of the virgin CdS films.

In our experiments, we avoid both these by evaporating Al doped CdS powder. The concentration of Al, Cd and sulphur in the film thus processed will depend upon a variety of factors such as vapour pressures and sticking coefficients of Al, Cd and sulphur, rate of evaporation, concentration of Al in the charge, etc.

Since the sticking co-efficient of Al is higher than that of sulphur, addition of Al to the charge leads to films with higher sulphur deficiency than in the films produced in an identical way from a charge which is undoped CdS. Since evaporation of Cd and Al takes place simultaneously, cadmium vacancies are not formed. It is, therefore, to be expected that the Al-doped CdS films thus produced will have resistivities much lower compared to CdS films produced under identical conditions. Similarly, since there is no possibility of cadmium vacancies being formed, these films will not show acceptor centres as in the case of thermally diffused CdS films.

The amount of Al that will get into the film will naturally depend upon the Al content in the charge, rate of evaporation, substrate temperature, etc. In turn, the sulphur deficiency and the decrease in the resistivity will be determined by all these parameters. It is obvious that the decrease in resistivity will be larger; larger the Al concentration in the charge, higher the rate of evaporation, etc. It is significant to point out that our results are indeed in agreement with the above expectations. In fact it is possible to control the resistivity of the films fairly reliably by controlling the Al concentration, rate of evaporation, substrate temperature, etc.

Our EPR studies are also in good agreement with the above mechanism. In undoped CdS films prepared by vacuum evaporation, there is excess of Cd and deficiency of sulphur. This is reflected in the observation of  $F_3$  centres. In the thermally diffused Al-doped CdS films, EPR shows the presence of  $\text{Cd}^+$  donor and Cd vacancy acceptor centres. In the Al-doped CdS films prepared by vacuum evaporation, there will be considerable deficiency of sulphur with Al in the trivalent state and Cd in the divalent state. In such a situation, an extra electron in Al may get trapped in an anion vacancy to give  $F_2^+$  centre. It is indeed interesting to note that our EPR studies convincingly bring out the presence of  $F_2^+$  centres in such films. It has also been seen that oxygen treatment of Al doped CdS films prepared by vacuum evaporation leads to the formation of  $F_3$  centres. The reason for the clustering of vacancies to give  $F_3$  centres is not fully understood. It is interesting to observe that in high concentration Al doped films (H0), one observes  $F_3$  centres in addition to  $F_2^+$  centres. The presence of  $F_3$  centres in such films reflecting the clustering of anion vacancies is due to the fact that higher concentration of Al in the film leads to a large number of sulphur vacancies.

Spectral response of these films is also understood on the basis of the mechanism outlined above. Undoped virgin CdS films are cadmium rich and sulphur deficient. Excess of cadmium gives rise to donor levels in the band gap of CdS. A large concentration of Cd in the lattice makes these donor levels degenerate and merge into the conduction band of CdS. This is reflected in the higher red response and the higher cut off wavelength (5405Å) in these films as compared to stoichiometric CdS. In Al doped films prepared vacuum evaporation, sulphur deficiency is increased still further. In addition, one has Al donor levels, whose concentration depends upon the Al content in the charge, rate of evaporation, etc. It is likely that these Al donor levels also degenerate as the Al concentration increases. The higher deficiency of sulphur, and the higher density of donor levels of Al would cause the shift of the cut-off wavelength to lower energies or higher wavelengths as is indeed observed in the case of sample (I0) wherein the cut-off is at 5714Å. On similar reasoning it is easy to understand why this specimen shows higher photo response for higher wavelengths; response peak occurring at 5600Å (figure 2). The other two samples with Al-doping, evaporated at low rate and therefore more compensated show low cut-off wavelength at 5140Å. The spectral response curves of these films show prominent peak at 5100Å and a weak response peak at 5600Å. The sample which is evaporated at a higher rate (I0) on the other hand shows weak response near the band edge (5100Å).

The effect of heat treatment of films in oxygen atmosphere is also expected. When evaporated films of CdS are exposed to oxygen atmosphere, oxygen molecules get physically absorbed on the surface. Oxygen being highly electronegative and CdS being *n* type semiconductor, oxygen negative ions are formed by trapping electrons from the conduction band by the physically adsorbed oxygen. These chemisorbed oxygen ions are essentially localized near sulphur vacancies on the surface causing a depletion layer. At elevated temperatures, these oxygen ions diffuse inside the bulk of the film making them more stoichiometry (Bhide *et al* 1977, Woodbury 1967). The improvement in stoichiometry is reflected in increase in dark resistivity and shift in the cut-off wavelength to shorter wavelengths in absorption spectra.

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