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Citation: *J. Appl. Phys.* **65**, 237 (1989); doi: 10.1063/1.342578

View online: <http://dx.doi.org/10.1063/1.342578>

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Instability in resistance and variation of activation energy with thickness and deposition temperature of CdSe_{0.6}Te_{0.4} thin films deposited at high substrate temperatures

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(Received 25 May 1988; accepted for publication 12 September 1988)

CdSe_{0.6}Te_{0.4} thin films deposited at high substrate temperatures showed a rapid increase in resistance when exposed to oxygen and atmosphere. This behavior is explained by an oxygen adsorption model. A decrease in activation energy with an increase in thickness and deposition temperature is explained by the fact that the depth of the impurity levels is reduced with an increase in thickness and deposition temperatures. The low activation energy obtained in oxygen or atmosphere heated films is accounted for by the fact that oxygen acceptor levels are very shallow from the conduction band.

INTRODUCTION

The study of polycrystalline II-VI compound semiconductors is important due to their application in semiconductor device technology. CdSe_xTe_{1-x} (0 < x < 1) are very promising ternary systems in this category. Thin films of CdSe_xTe_{1-x} are used in the fabrication of transistors,¹ solar cells,² photoconductors,³ etc. Other applications include variable gap structures, vidicons, and photodetectors. There are very few published works on the electrical transport mechanism of CdSe_xTe_{1-x} thin films deposited on glass substrates. Uthanna and Reddy⁴ have reported the dependence of electrical resistivity and Hall mobility on the percentage of selenium present in the compound. Their results showed that the resistivity decreased exponentially with x and Hall mobility increased with x. Also films deposited at high substrate temperatures showed a reduction in resistivity. Belyaev, Kalinkin, and Sanitarov¹¹ have conducted studies on resistivity and Hall-mobility dependence on temperature of the films deposited at 430 °C on mica by the heat screen method. They have taken the measurements in the 100–300 K range. No work has so far been reported on the instability in resistance of CdSe_xTe_{1-x} thin films when exposed to different gas atmospheres.

The aim of this investigation is to study the stability of CdSe_{0.6}Te_{0.4} thin films when exposed to different environments and the dependence of conduction activation energy on thickness of the film, as well as the deposition temperatures. All the measurements were taken in the temperature range 300–403 K. The temperature response of resistance measurements was carried out on all the films in different environments, first keeping the deposition temperature at 373 K and changing the thickness of the films. For a particular thickness, films deposited at different substrate temperatures were studied to understand the activation energy dependence on deposition temperature. Films deposited at room temperature and at different high substrate temperatures were exposed to different gas atmospheres to study the stability of the films in these environments. The temperature response of resistance measurements were carried out in all the above environments with an aim of understanding the modification of conduction activation energy.

EXPERIMENTAL DETAILS

The bulk sample of CdSe_{0.6}Te_{0.4} was prepared by sealing research grade CdSe and CdTe in appropriate quantities into evacuated quartz tubes, and heating in a furnace at 950 °C for about 24 h before cooling to room temperature. Films were deposited on thin glass substrates. An ultrasonic cleaner was used for cleaning the glass substrates. The well-cleaned glass substrates were kept on holders at a distance of 20 cm from the source.

A resistive heating technique was used for deposition of the films. Precoated indium contacts were used for resistance measurement. The contact was found to be ohmic. Very thin copper wires were used as leads for resistance measurements. The resistance of the film was measured using a Keithley 610C electrometer. To ensure that the film was heated uniformly, a radiant heater was used. The thickness of the film and the deposition rates were monitored using a quartz-crystal monitor. The pressure inside the vacuum chamber was maintained at less than 10⁻⁵ Torr during deposition and measurements. The temperature of the film was measured using a copper-constantan thermocouple connected to a millivoltmeter. Different gases were admitted into the chamber using a control valve. The structure of the film was studied using an x-ray diffractometer. Grain sizes were calculated from x-ray diffractogram data. The composition of the bulk as well as the films was confirmed by electron probe microanalysis (EPMA).

RESULTS AND DISCUSSIONS

The structural analysis by the x-ray diffractogram method showed that all the films deposited at temperatures from room temperature to 430 K were of cubic type (zinc blende). This result agrees well with those of previous researchers.⁴ The crystallites of the polycrystalline film were found to be oriented in the (111) direction as shown in the diffractogram of Fig. 1. Grain size calculations were done using the Scherrer formula,⁵

$$I = \lambda / D \cos \theta,$$

where I is the grain size, λ is the wavelength of radiation used, D is the full width at half maximum, and θ is the dif-

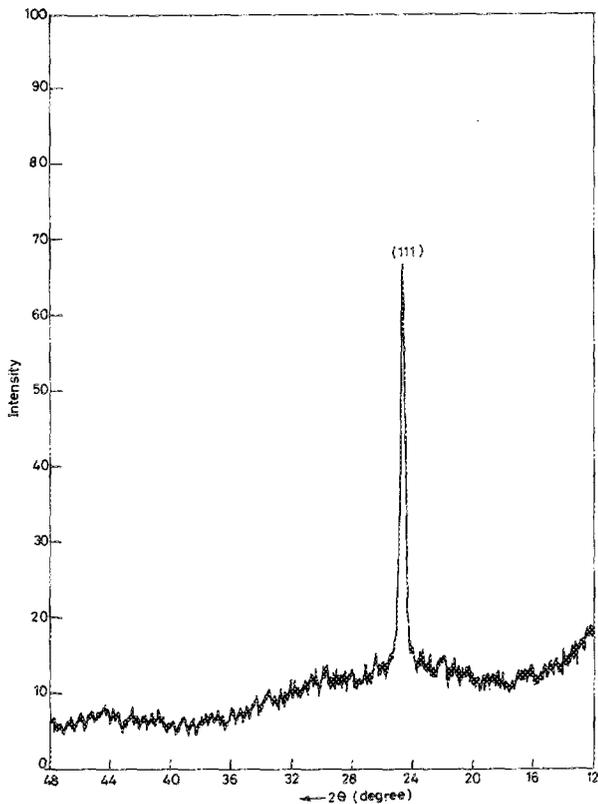


FIG. 1. Typical x-ray diffractogram of $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films.

fracting angle. Grain size was found to increase with thickness of the film as well as deposition temperature.

$\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films of various thicknesses were deposited on glass at a substrate temperature of 373 K. As-deposited films were cooled down to room temperature and exposed to different gas atmospheres. Film resistance remained steady in the presence of nitrogen gas, showing that nitrogen has no role to play in the aging of $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films. Films exposed to oxygen or atmosphere showed a rapid increase in resistance. Figure 2 shows the variation of normalized resistance (R/R_0) with time t for films of thicknesses 3200 and 4400 Å exposed to oxygen or atmosphere, R is the resistance of the film in $M\Omega$, and t is the time in minutes. Both oxygen and atmosphere exposed films showed the same type of variation.

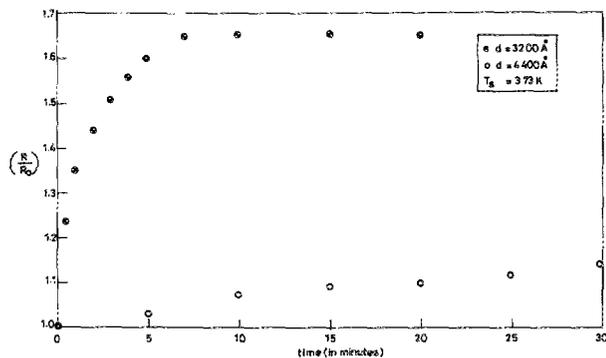


FIG. 2. Variation of normalized resistance (R/R_0) with time t in oxygen or atmosphere for films deposited at 373 K.

Earlier workers have reported on the interaction of II-VI compound film surface and oxygen atoms. Somorjai⁶ has reported the interaction of oxygen atoms with CdSe film surface. The chemisorbed oxygen atoms act as acceptor impurities at the film surface. They capture the conduction electrons, thereby reducing the film conductivity considerably. The same adsorption phenomenon has been observed by Wagner and Breitweiser⁷ in CdSe films. Several workers have suggested that both physisorption and chemisorption are responsible for the resistance increase in II-VI compounds. Chan and Hill⁸ have reported chemisorption as the reason for aging in CdSe films when exposed to oxygen or atmosphere. But Bhide, Jatar, and Rastogi⁹ have reported that physisorption followed by chemisorption is the cause of aging in CdSe thin films when the film is exposed to oxygen.

Figure 3 gives the variation of normalized resistance R/R_0 with time for films of thickness 3200 Å deposited at different substrate temperatures. From Figs. 2 and 3 we see that thinner films and those deposited at low substrate temperature show more aging when exposed to oxygen or atmosphere. This is because of the large surface-to-volume ratio in the case of thinner films and a greater number of surface defects for films deposited at low substrate temperatures.

This suggests an oxygen adsorption mechanism on the film surface to account for the resistance increase in $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films when exposed to oxygen or atmosphere. Oxygen atoms adsorbed at the film surface capture free electrons from the conduction band and get chemically adsorbed as acceptor impurities with a finite activation ener-

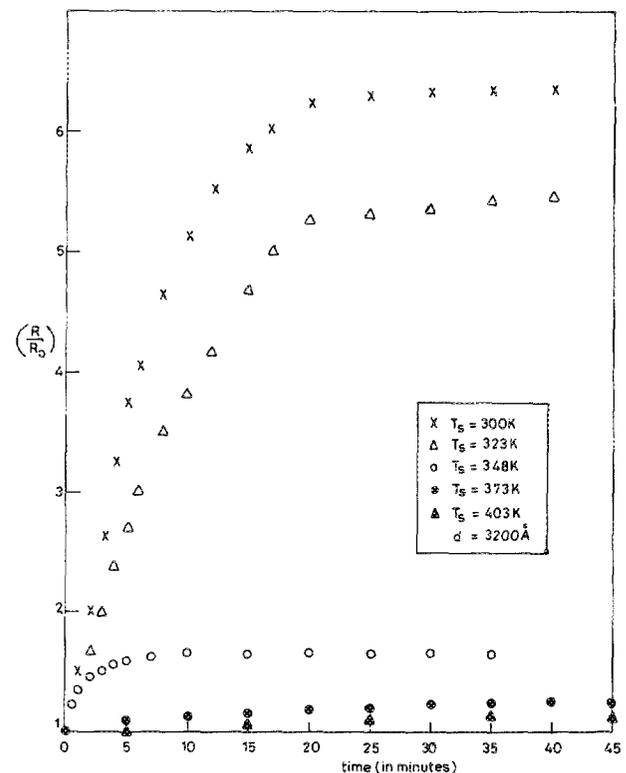


FIG. 3. Variation of normalized resistance (R/R_0) with time t in oxygen or atmosphere for films of thickness 3200 Å deposited at different substrate temperatures.

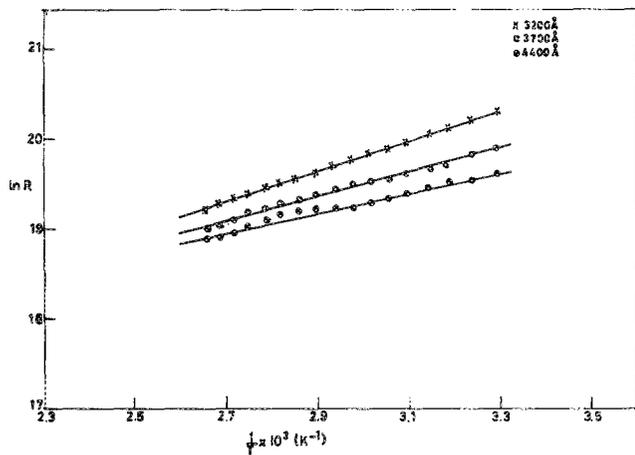


FIG. 4. $\ln(R)$ vs $1/T$ plot in vacuum for films deposited at 373 K.

gy of adsorption. This was further confirmed by the thermoelectric power measurement studies, showing that $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films are n -type semiconductors. This capturing of free electrons from the conduction band will reduce the number of free electrons available for electrical conduction. Hence the resistance of the film increases. A depletion region is formed between the oxygen ions and the donor atoms. The surface of the film becomes negatively charged with a positive region below it separated by the depletion region.¹⁰ The formation of this depletion region stops further capturing of free electrons by adsorbed oxygen atoms. Thus the resistance of the film gets stabilized. From Figs. 2 and 3 we see a linear dependence of resistance on $\ln(t)$, where t is the time in minutes. This functional dependence follows the relation

$$R = a + b \ln(t). \quad (1)$$

The rate equation for the decrease of conduction electrons can be written as⁹

$$\frac{dn}{dt} = -nNpv \exp\left(\frac{-E}{kT}\right), \quad (2)$$

where n is the number of conduction electrons, N is the number of physisorbed oxygen atoms, p is the capture cross section of physisorbed oxygen atoms for conduction electrons, v is the thermal velocity, E is the activation energy for adsorption. For thicker films and those deposited at high substrate temperatures, the number of grain boundaries and other surface defects is very much reduced. This is quite evident from the grain size calculations. This fact explains why thinner films and those deposited at lower substrate temperatures age rapidly in oxygen.

TABLE I. The variation of conduction activation energy with thickness, in vacuum as well as in oxygen or atmosphere, of films deposited at 373 K.

d (Å)	E_a (eV)	E'_a (eV)
3025	0.15	0.025
3200	0.14	0.025
3700	0.12	0.025
4400	0.10	0.025

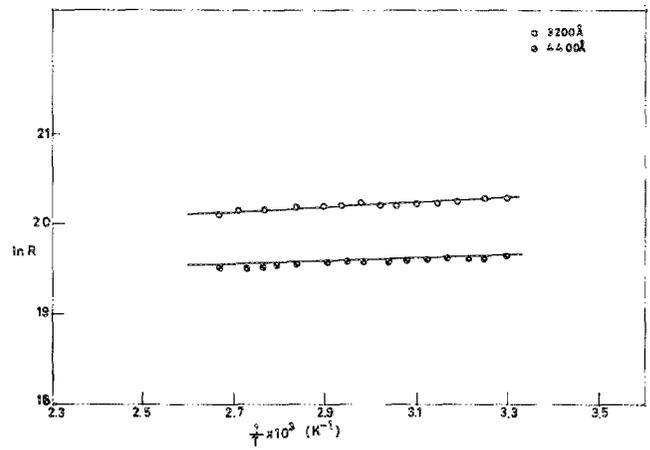


FIG. 5. $\ln(R)$ vs $1/T$ plot in oxygen or atmosphere of films deposited at 373 K.

Figure 4 gives the plot of $\ln(R)$ vs $1/T$ in vacuum for films of different thicknesses deposited at 373 K, where T is the film temperature in degrees Kelvin. Table I gives the corresponding variation of conduction activation energy with thickness of the film. From Table I we see that activation energy decreases with increase in thickness of the film deposited at 373 K in vacuum. The second column (E'_a) gives the conduction activation energy for those films deposited at 373 K and heated in oxygen or atmosphere. From the value of E'_a we can say that there is only one value of activation energy = 0.025 eV, which is very low compared to those values obtained in vacuum. Hence, we are able to say that this activation energy results from the excitation of electrons from the impurity oxygen levels, which are very shallow and at a depth of 0.025 eV from the conduction band. Figure 5 gives the $\ln(R)$ vs $(1/T)$ plot for films deposited at 373 K and heated in oxygen or atmosphere. The thickness dependence of activation energy for those films heated in vacuum can be explained by the following argument. Belyaev, Kalinkin, and Sanitarov¹¹ have reported that at temperatures above 280 K, the process of conduction in $\text{CdSe}_x\text{Te}_{1-x}$ solid solution films is due to the activation of charge carriers from deep levels to the conduction band. When the thickness of the film increases, the grain size in-

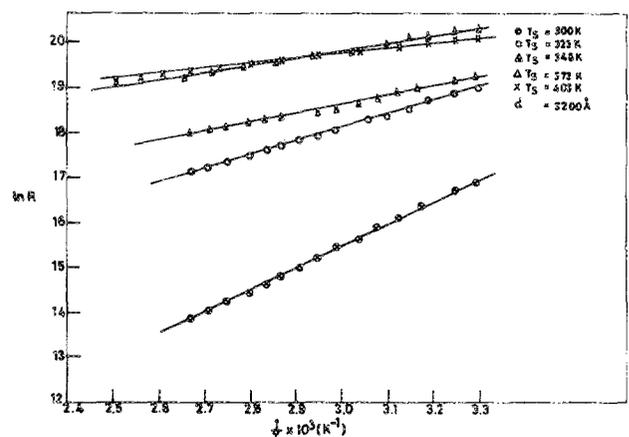


FIG. 6. $\ln(R)$ vs $1/T$ plot in vacuum for films of thickness 3200 Å and deposited at different substrate temperatures.

TABLE II. The variation of conduction activation energy with deposition temperature, in vacuum as well as in oxygen or atmosphere, of films of thickness 3200 Å.

T_s (K)	E_a (eV)	E'_a (eV)
300	0.4	0.20
323	0.29	0.09
348	0.17	0.04
373	0.14	0.025
403	0.10	...

creases and the grain boundary width decreases. Also, the impurity levels become less deep. Hence, the energy needed for activation of charge carriers to the conduction band is reduced. This explains the decrease in activation energy with an increase in film thickness.

Figure 6 gives $\ln(R)$ vs $1/T$ plot for films of the same thickness (3200 Å) deposited at different substrate temperatures. Table II gives the variation of activation energy with deposition temperature T_s for films heated in vacuum as well as in oxygen or atmosphere. The variation is plotted in Fig. 7 taking activation energy versus T_s . For films heated in vacuum we see that activation energy decreases with increase in T_s . This decrease is more rapid in the case of oxygen or atmosphere heated films and is explained by the fact that films deposited at high substrate temperatures have good crystallinity, reduced grain-boundary width, and fewer surface defects. This will reduce the depth of impurity levels, and hence reduce the conduction activation energy. For oxygen or atmosphere heated films, one can see from Table II that oxygen impurity levels become more and more shallow as the deposition temperature increases.

CONCLUSION

The instability in resistance of $\text{CdSe}_{0.6}\text{Te}_{0.4}$ thin films when exposed to oxygen or atmosphere can be explained by an oxygen adsorption model. Thinner films and those deposited at low substrate temperatures showed more instability in oxygen and atmosphere. The dependence of conduction

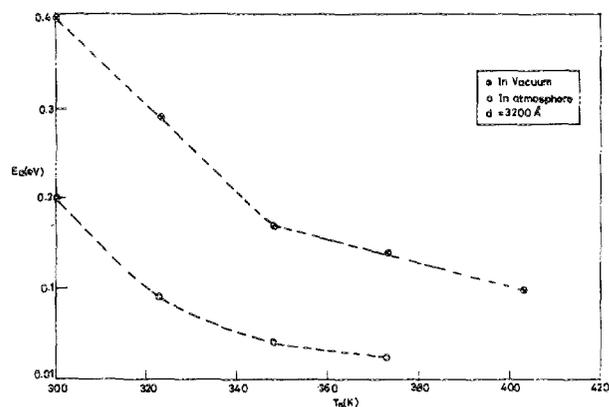


FIG. 7. Variation of activation energy with deposition temperature in vacuum and oxygen or atmosphere for films of thickness 3200 Å and deposited at different substrate temperatures.

activation energy on thickness of the film and the deposition temperature can be explained on the basis of the variation of the depth of impurity levels from the conduction band. The reduced value of conduction activation energy for films heated in oxygen or atmosphere showed that oxygen impurity level are very shallow from the conduction band.

ACKNOWLEDGMENTS

The authors thank Dr. M. S. Murali Sastry and Dr. M. Pattabi for their assistance and useful suggestions.

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