Oxygen interaction with CdS based gas sensors by varying different preparation parameters

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The interaction of oxygen gas atmosphere on CdS films prepared by spray pyrolysis is studied. Spray time and deposition temperature are taken as variable parameters. The prepared film structure is diagnosed by XRD to elucidate the film crystallinity, nature and size. Both thickness and crystallite size of the CdS films decrease as the deposition temperature increase from 340 to 490°C at constant deposition time. The opposite trend is observed when the films are deposited at different deposition time and constant deposition temperature. The resistance of films were measured by exposing them to different concentrations of oxygen to test its use as oxygen sensor. The thinner CdS films show higher sensitivity and shorter response time than the thicker films.

1 Introduction

The field of chemical sensors is a topic of interest because in many industries, gases are used as important raw materials. For this reason, it has become very important to develop highly sensitive gas detectors to prevent accidents due to gas leakage, thus saving lives and equipment. With this view, the influence of chemisorption on the electrical conductivity of thin film semiconductor and compound metal-oxide semiconductor with a wide band gap (>2eV), has been the subject of numerous experimental studies. The major advantages of solid-state sensors are their high sensitivity, small size and low cost. The major disadvantages of most solid-state chemical sensors are their lack of stability, non-reproducibility, and lack of selectivity. The research underway is devoted to avoid them. However, in many applications the disadvantages are not prohibitive, hence solid state sensors are commercially viable.

In this context, this paper reports the results of an attempt to prepare an oxygen gas sensor with an acceptable stability, sensitivity and reproducibility. The reduction in cost is the main objective by using the spray pyrolysis as a simple and low cost technique.

2 Experimental Procedure

Pure CdS thin films were prepared by spray pyrolysis technique. The starting solution was prepared from 0.1M solution of CdCl₂ and thiourea. The ratio of cadmium chloride solution to thiourea solution is 1:1. The spray process was repeated to ensure the film reproducibility. The details on the used spray system and preparation method are given elsewhere.

Phillips diffractometer model PW/1710 with Ni filter and CuKα radiation of wavelength 1.5418 Å at 40 kV and 30 mA was used to determine the structure of the film. The approximate crystallite sizes of the films were calculated from the peak profile of (112) plane using Scherrer's formula \( D = \frac{0.94\lambda}{\Delta(2\theta) \cos \theta} \) where, \( 2\theta \) is the full width at half maximum (FWHM) intensity, \( \lambda \) the wavelength of the incident X-rays and \( \theta \) the angle of incidence of X-ray beam.

The hot probe method was used to define the conduction type of film under consideration. Two indium electrodes were evaporated at vacuum of 10⁻⁵ torr to form ohmic contacts which is confirmed by the linearity of the I-V measurements.

A measuring cell was fabricated to test the effect of oxygen gas on the deposited CdS films. It consists of 2L volume cylindrical glass tube, the sample was placed inside it on a temperature controlled hot plate, with an accuracy ±1°C using the ULTRA-THERM temperature controller. Argon gas was used to flush the tube before inserting the oxygen gas, until it attains a constant resistance value. The examined oxygen gas was injected through a flow meter into the measuring cell with a flow rate ranging from 50 to 350 ml/min. The change in
sample resistance was measured at different operating temperatures, operating time and different oxygen flow rates. The sensitivity of the sample to oxygen gas is given by, \( S = \frac{(R_g - R_o)}{R_o} \times 100\% \), where \( R_g \) is the sample resistance in the presence of oxygen and \( R_o \) is the sample resistance in the presence of Ar.

3 Results and Discussion

The microstructure of the prepared samples was detected using XRD patterns, to determine the composition, crystallinity nature, orientation and crystallite size. A representative X-ray diffraction pattern is shown in Fig. 1(a) for samples deposited at two different deposition times 5 and 35 min at constant deposition temperature 440°C. XRD diffraction patterns for CdS samples prepared at different deposition time or temperature show the principal peaks (100), (200), (101) and (112), which dictate that the films are polycrystalline in nature regardless of the deposition time and temperature. No other peak except that for CdS indicates the absence of CdO. This confirms the formation of CdS only without any detectable CdO. Both the intensity and sharpness of the appeared peaks increase as the film thickness increased as shown in Figs 1(a) and (b). This reflects the induced amelioration in film crystallinity. The crystallinity improvement allows a probable increase in crystallite size as shown in Table 1. Thereby, an increase in free carrier density and their mobilities are expected to occur due to the reduction in grain boundary scattering.

Fig. 1a — XRD patterns of as-deposited 0.1 M CdS thin film prepared at deposition temperature 440°C and different deposition times 5 and 35 min.
CdS films with different deposition temperature (or time) are maintained at constant operating temperature and then exposed to oxygen gas for a definite time through a flow meter. The change in the CdS film resistance as a function of time at the moment of gas turn-on and turn-off is monitored. A representative data for CdS film prepared at 440 °C, 10 min and heated to 300 °C as an operating temperature, is shown in Fig. 2. The most interesting point in this figure is the sharp increase and decrease in CdS resistance at the moment of gas turn-on and turn-off. Nearly an order of magnitude increase in resistance was observed after the oxygen gas turn-on and when the oxygen turn-off the resistance is sharply decreased. The span time for CdS film to attain the higher resistance value after the gas turn-on moment is very short < 5 s. Also, at the gas turn-off the film resistance decreases sharply as shown in the inset of Fig. 2. This means that the CdS films have a promising response or sensitivity to the oxygen gas. It is seen that exposure of the surface of the prepared samples to oxygen result in nearly an order of magnitude increase in resistance, and when oxygen flow was cut-off, the resistance decreases to nearly its initial value. The increase in the resistance may be due to the initial adsorption of oxygen on the surfaces of CdS material after oxygen exposure leading to high resistance, since the adsorbed oxygen acts as an acceptor and CdS as n-type semiconductor. Subsequently the removal of oxygen lowers the resistance. The response is entirely reversible.

The results for the other CdS films with different preparation parameter condition are analyzed and the relevant parameters such as response time and sensitivity are correlated with operating temperature, deposition time and different concentration of oxygen flow rate.

Results in Figs 3 and 4 represent the operating temperature versus response time and sensitivity respectively, for CdS films prepared at constant deposition time of 35 min and two different substrate temperatures 340 and 465 °C. These figures demonstrate that there is a trade-off between the response time and sensitivity. At low operating temperatures < 150 °C both the response time and sensitivity are unfavourable, while in the range 200-350 °C of operating temperature the response time is very short and the sensitivity is high, which is a useful range for practical application of the devices. The CdS films prepared at 465 °C show a shorter response time and a higher sensitivity than that prepared at 340 °C. This may be due to the fact that CdS film prepared at higher deposition temperature are thinner than that prepared at low deposition temperature. The oxygen is adsorbed on the CdS surface as ionic molecules O$_2$ possibly diffuse in thicker films, as atomic ions O$^-$ along grain boundaries inside the film. The diffusing oxygen ions may act as acceptor in the grain boundary-O$^-$ along grain boundaries inside the film. The diffusing oxygen ions may act as acceptor in the grain boundary-O$^-$ along grain boundaries inside the film. The different activation energy related to molecular oxygen ion O$_2$ is 0.9 eV while that for atomic O$^-$ equal to 1.3 eV (Ref. 5,8). This means that the diffusion of negative atomic oxygen ion O$^-$ takes place at relatively high operating temperature. Therefore, the sensi-

<table>
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<th>Deposition times [min]</th>
<th>Crystallite size [nm]</th>
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<tr>
<td>5</td>
<td>390</td>
</tr>
<tr>
<td>10</td>
<td>403</td>
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<td>15</td>
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<td>454</td>
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Fig. 1b — The typical peak profile of the diffraction of the (112) plane of as-deposited 0.1 M CdS thin film prepared at deposition temperature 440 °C and two different deposition times 5 and 35 min.
tivity of CdS to oxygen is increased as the operating temperature increase as shown in Fig. 4.

Crystallite size and grain boundaries play an important role in the adsorption of oxygen gas. From XRD and Table 1 it is clear that the increase in the thickness due to the increase in the deposition time from 5 to 45 min induces an increase of crystallite size. This may lead to an increase in the electrical conductivity by decreasing both the grain boundary and the residual strain. Nevertheless, the thicker CdS films have an improved crystallinity and low grain boundaries, they have low sensitivity and large response time to oxygen gas at constant operating temperature. This means that the thinner films are more sensitive to oxygen absorption and desorption process on and from the film than the thicker films are shown Fig. 5a. This observation is in accordance with that obtained by others in ITO. This could be explained by the decrease in both the film thickness and in crystallite size (Table 2) as a result of the increase in deposition temperature from 340 to 490 °C. The decrease in the crystallite size allows an increase in surface area exposed to oxygen.

The effect of deposition temperature of CdS films on the oxygen sensing is shown in Fig. 5b. It is observed that the sensitivity increases by increasing the deposition temperature. Also it is known that there is a considerable amount of sulphur re-evaporation from the CdS films at higher temperature (> 300°C). Therefore, the

![Graph](image)

**Fig. 2** — Resistivity changes for CdS thin films prepared at 440°C and 10 min, for oxygen gas at operating temperature 300°C and at flow rate of oxygen 50 ml/min.
Cd:S ratio may be changed to get a non-stoichiometric CdS film enriched with cadmium. Golovanov et al.\textsuperscript{13} suggested that the enrichment of the films with cadmium atoms increased the amount of chemisorbed oxygen. This fact indicates that cadmium atoms at the surface are the basic centers for the chemisorption of oxygen on the surface of the investigated films. From the above results it was found that the sensitivity has an opposite trend relative to the crystallite size and the film thickness. This means that the sensitivity increases as the film thickness and the crystallite size decreases. In thicker films the oxygen is adsorbed on the film surface followed by diffusion in the film towards the grain boundaries. This increases relatively the response time of adsorption and desorption process, which gives gradual increase and decrease in film resistance. In other words no sharp

Table 2 — The effect of deposition temperatures on the crystallite size at constant deposition time 35 min

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<th>Deposition temperatures (°C)</th>
<th>Crystallite size [nm]</th>
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<tr>
<td>340</td>
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<tr>
<td>390</td>
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<td>490</td>
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Fig. 3 — Temperature dependence on the response time for 0.1 M CdS thin film prepared at 35 min for both deposition temperatures 340°C and 465°C at oxygen flow rate 50 ml/min

Fig. 4 — Dependence of oxygen sensitivity on the operating temperatures of 0.1 M CdS thin film prepared at 35 min with oxygen flow rate 50 ml/min and different operating temperatures from 50 to 350°C
Fig. 5a — Dependence of oxygen sensitivity on the deposition time of 0.1 M CdS thin film prepared at different deposition times with constant operating temperature 300°C.

Fig. 5b — Dependence of oxygen sensitivity on the deposition temperatures of 0.1 M CdS thin film prepared at deposition time and different deposition temperatures ranging from 340 to 490°C.
response for the oxygen gas turn-on and turn-off was obtained, which is considered as a disadvantage for gas sensing devices.

The flow rate of oxygen versus film sensitivity is shown in Fig. 6. The increase in flow rate here means the increase of oxygen concentration. It is clear that the increase in sensitivity for both films is reasonable at low flow rate, which tends to vanish at higher flow rates. At the same oxygen flow rate of 50 ml/min, the film deposited at higher deposition temperatures were thinner, which showed higher sensitivity in order of magnitude than that deposited at lower temperature.

The sensitivity is independent of the oxygen flow rate beyond 150 ml/min for CdS films deposited at 465°C, while it shows a slight dependence for films deposited at a lower temperature of 340°C. This may be due to the surface of the thinner film which is saturated only with the adsorbed oxygen atoms that gets diffused in the thicker films.

4 Conclusion

CdS thin films were deposited by spray pyrolysis technique using CdCl₂ and thiourea as main precursor. XRD patterns show that the samples were polycrystalline regardless of the deposition time and temperature. The CdS films show relatively high sensitivity to oxygen gas and very quick response and recovery behaviours towards low flow rate of oxygen. Therefore this technology for CdS fabrication could be applied for the development of the oxygen detecting microsensor system. The effect of oxygen absorption on the surface of CdS film causes an increase in the film resistance. The influence of deposition time and deposition temperature of CdS films on oxygen adsorption and desorption process show opposite trends. The optimum film deposition and operating temperatures are found to be 465 and 250°C respectively.

References