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Study on the Gas-Sensitive Effect of $CdIn_2O_4$ Thin Films

By

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Transparent and conductive $CdIn_2O_4$ (CIO) thin films are prepared by rf reactive sputtering from a Cd–In alloy target in Ar + O_2 mixtures. The sensitivity of $CdIn_2O_4$ thin film sensors to the LP, CO, H_2, and C_2H_5OH gas together with their mechanism were studied. The effects of the film deposition conditions to the gas-sensitive effect are also discussed.

1. Introduction

The study of transparent and highly conductive semiconductor films have attracted the interest of many research workers because of their wide application in both industry and research [1]. The electrical and optical properties of cadmium indate ($CdIn_2O_4$) thin films and its preparation by various methods have been reported by many authors [2 to 6]. $CdIn_2O_4$ thin films are n-type defect semiconductors in which oxygen vacancies provide the donor states and the free carrier concentration is up to the order of 10^{26} m^{-3} [7]. The results of study on the structure, electrical, and optical properties of $CdIn_2O_4$ thin films indicated that they may be used as transparent electrodes and heat mirrors in optoelectronics and solar energy conversion technology. However, the gas-sensitive effect of the films has not been reported by the previous investigations.

In this work we want to show the sensitivity of $CdIn_2O_4$ thin films prepared by rf reactive sputtering from a Cd–In alloy target to different gases. The effect of the deposition condition on the gas-sensitive effect is also discussed.

2. Experiment

2.1 Film preparation and characterization

$CdIn_2O_4$ thin films were obtained by rf reactive sputtering from a Cd–In alloy target in an Ar–O_2 mixture atmosphere and deposited onto cleaned glass substrates. A Cd–In alloy target with an atomic ratio of 1:2, 100 mm in diameter, made of metallic Cd and In of purity 99.99% was used. The preparation of the films was carried out under the following conditions: target-to-substrate spacing 30 mm, sputtering power 400 W, total pressure in the chamber 1.33 Pa. The substrate was heated by a tungsten lamp and the temperature was measured with a Pt–Rh thermoelectric couple. The deposition time was 30 min for all samples. The film thickness determined by multiple beam interferometry was about 300 nm. X-ray diffraction analysis revealed that the films were polycrystalline with a cubic spinel $CdIn_2O_4$ phase and a In_2O_3 phase (Fig. 1). The ingredient analysis of the sample was carried out by an EDAX-9100 energy spectrometer. The measurement result showed that the atomic

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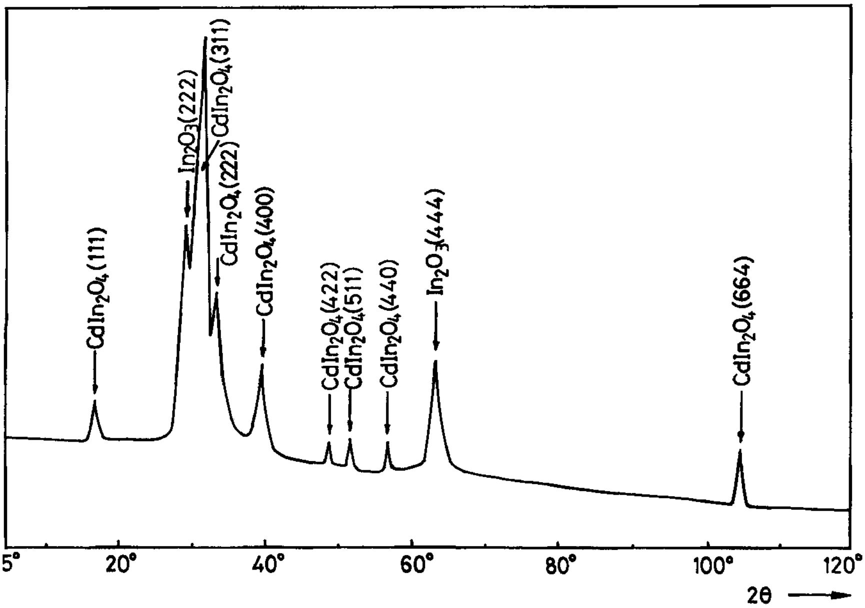

Fig. 1. X-ray diffraction pattern for a $CdIn_2O_4$ film deposited at 300 °C in an Ar–20% O_2 atmosphere

ratio of cadmium to indium is 1 : 2.28 and slightly higher than that of the stoichiometric $CdIn_2O_4$ film. This indicates that the $CdIn_2O_4$ phase in the films is predominant, but the amount of the In_2O_3 phase is very small. The carrier concentration dependence on the oxygen concentration in an Ar + O_2 mixture is plotted in Fig. 2. It is convenient to distinguish between two ranges of oxygen concentration: the first one (30 to 100% O_2) in which the carrier concentration increased with increasing oxygen concentration and the second one (8 to 30% O_2) in which the carrier concentration increased with decreasing oxygen concentration.

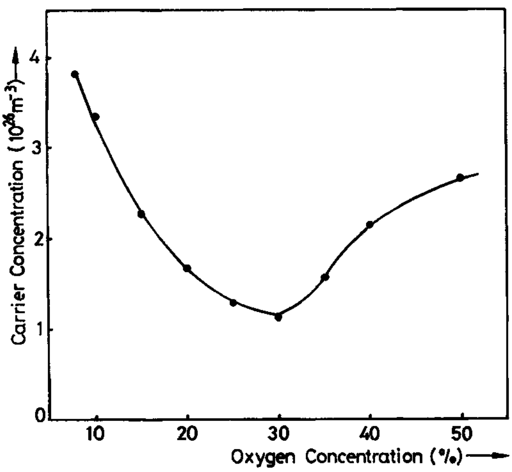

Fig. 2. Carrier concentration of $CdIn_2O_4$ films deposited at 300 °C as a function of oxygen concentration in an Ar + O_2 mixture

2.2 Tests of temperature-rising curve and the gas-sensitive effects

The substrates on which the $CdIn_2O_4$ films were deposited were cut into 6×10 mm^2 chips, and then gas sensors can be made through Pt electrodes being stuck on the film surface with a silver paste. The film was heated from outside. The temperature ranged from room temperature to 400 °C and was measured with a Pt–Rh thermoelectric couple. Static gas distribution was adopted in this experiment and the density of the gases was expressed as the volume ratio to air.

In order to observe apparently the gas-sensitive effect of the $CdIn_2O_4$ gas sensor, we had attached a first-order linear voltage amplification circuit to the film electrodes.

3. Experimental Results

3.1 The changing laws of conductance of the sensors with temperature

The conductance (expressed as voltage) of the sensors has a close relation with the working temperature. When the temperature rose from room temperature at a certain rate, the resistance of the sensors decreased. At about 320 °C, conductance peaks appear. At this time the resistance had a minimum and then increased with further rising temperature (Fig. 3). The position of the conductance peak in the temperature-rising curves is related to the temperature-rising rate β. The conductance peak moves towards high temperature with increasing β.

3.2 The gas-sensitive effect of the sensors

The sensitivity of the thin film sensors to the LP (liquified petroleum), CO, H_2, C_2H_5OH gas, and CH_4 is shown in Fig. 4. V_0 and V_j are the voltages measured at the gas concentration of 0 and C_j, respectively. The gas-sensitive effect is expressed as $(V_j - V_0)/V_0$. As shown in Fig. 4, the gas-sensitive effect increases with increasing gas concentration and the curves become steep at low concentration. But at higher gas concentration the curves become flat and the gas-sensitive effect tends towards saturation. This indicates that the sensors are

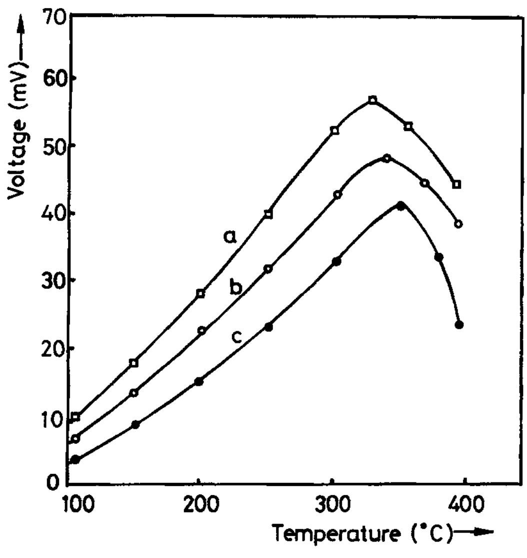

Fig. 3. The conductance of the sensors vs. working temperature and temperature-rising rate β. (a) $\beta = 0.35$, (b) 0.44, (c) 0.67 K/s

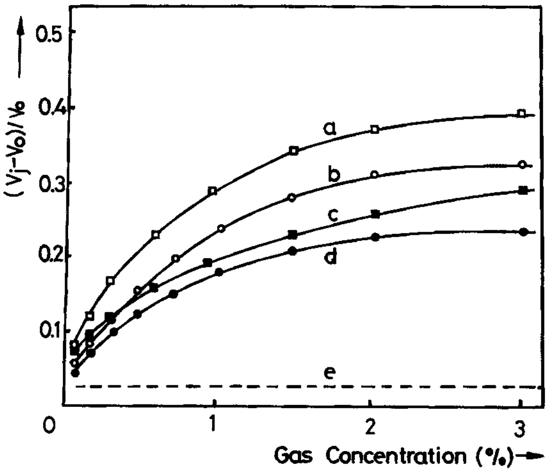

Fig. 4. The gas-sensitive effect vs. gas concentration at a working temperature of 316 °C. (a) LP, (b) CO, (c) C_2H_5OH gas, (d) H_2, and (e) CH_4

very sensitive to low concentration gases. Therefore, the $CdIn_2O_4$ thin film gas sensors are suitable for detecting gas of low concentration.

It can also be seen from Fig. 4 that this kind of sensors has no gas-sensitive effect to CH_4 when its concentration is lower than 3% at a working temperature of 316 °C. This means that the gas-sensitive effect of the sensors has selectivity to gases.

3.3 Effects of deposition conditions of $CdIn_2O_4$ films on the gas-sensitive effect of the sensors

Fig. 5 is the test result of the gas-sensitive effect of the thin films to the CO gas which were deposited at a substrate temperature of 300 °C for oxygen concentrations of 10%, 30%, and 50%, respectively. It is obvious that the gas-sensitive effect of the films is related with its deposition conditions. The sensitivity of $CdIn_2O_4$ thin films deposited in 10% and 50% oxygen concentrations to the CO gas is higher than that of the film deposited in 30% oxygen concentration. This may be accounted for by an analysis from Fig. 2. The carrier

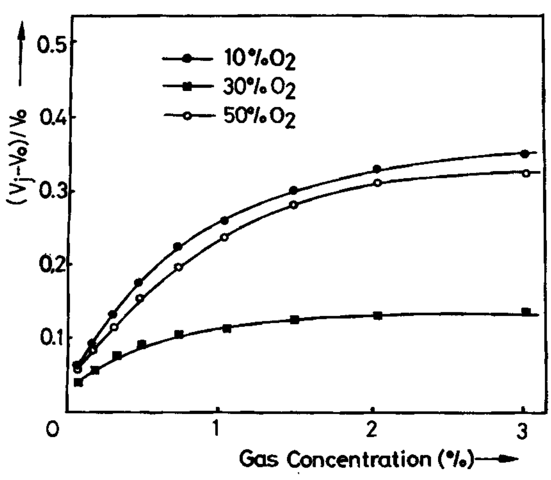

Fig. 5. The influence of the deposition condition of the films on the gas-sensitive effect

concentration of the film deposited in 30% oxygen concentration is the lowest and the quantity of oxygen vacancies is minimum, and then, the adsorption amount of the sensor to reducing gases is the lowest. Thus, the change of resistance is minimum and the gas-sensitive effect is not quite clear.

4. Discussion

4.1 Factors effecting the temperature-rising curve

The temperature-rising curves in Fig. 3 can be explained from the adsorption of oxygen on the $CdIn_2O_4$ thin film surface and semiconductor conduction theories. The adsorption of oxygen is very weak at low temperature and at this time the temperature effect on conductance is primary. With rising temperature the electron velocity and mobility in the films become larger, and in the meantime the conductivity also increases with rising temperature. When the temperature is at about 300 °C, the average energy of oxygen molecules in air is higher than the adsorption-activation energy of the film, so the quantity of the adsorption increases rapidly. However, the adsorption of oxygen makes the charge density of the film surface decrease. The conductivity decreases with further increasing temperature. When the adsorption of oxygen becomes maximum the conductance presents a minimum. Thus, the conductance peaks appear in the temperature-rising curves.

The above explanation is supported further by Fig. 6. When the temperature increases at a certain rate in air, there is a conductance peak in the temperature-rising curve. But at the same initial temperature and the same temperature-rising rate, till 400 °C the peak has not appeared yet in argon gas and the value of the conductance is higher than that in air at the same temperature. Argon hardly interacts with the $CdIn_2O_4$ thin film surfaces and hardly makes electrons to migrate towards the surface. The reason for this phenomenon can only be that, when the sensors are in argon gas, oxygen adsorbed on the films are desorbed. Because of no adsorption of oxygen, the conductance peak does not appear in the temperature-rising curve.

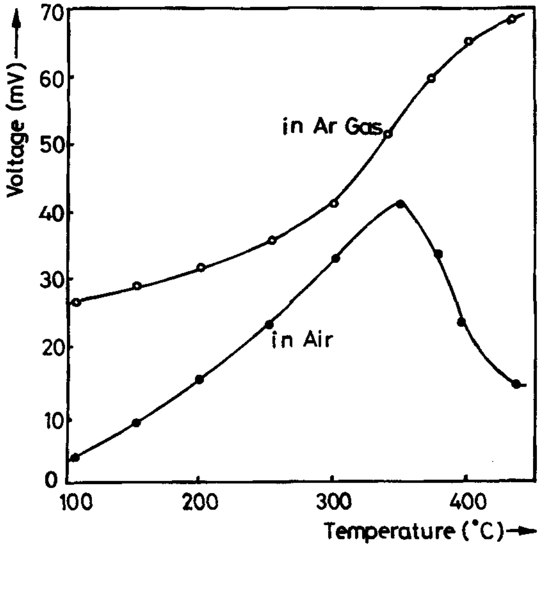

Fig. 6. The effect of environmental atmosphere on temperature-rising curve

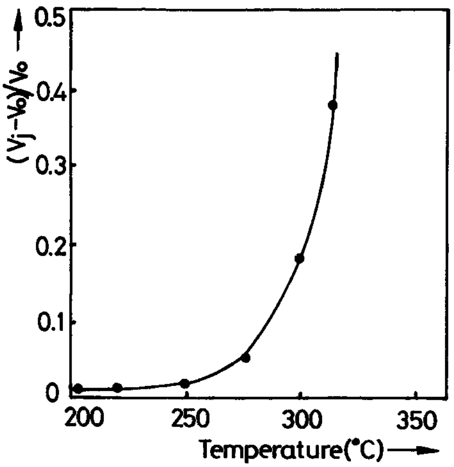

Fig. 7. The gas-sensitive effect of the sensor to CO gas of 2% concentration vs. working temperature

4.2 Determination of the lowest working temperature

Fig. 7 shows the relation between gas-sensitive effect and the working temperature. The sensitivity of the sensor to the CO gas increases with rising working temperature. The gas-sensitive effect increases very slowly below 300 °C, but it increases rapidly above 300 °C with increasing working temperature; 300 °C is just close to the temperature of the conductance peak. This means that the gas-sensitive effect of the sensors is weak below the temperature of the conductance peak. In fact, though the positions of conductance peaks are a little different for the different working circumstances, no matter what temperature the peak appears at, the gas-sensitive effect is weak below the peak temperature. As a result, $CdIn_2O_4$ thin film gas sensors must work above the peak temperature.

5. Conclusion

Transparent and conductive $CdIn_2O_4$ thin films can be easily prepared by rf reactive sputtering from a Cd–In alloy target in an Ar + O_2 gas mixture. All films prepared contained the cubic spinel phase of $CdIn_2O_4$ while a secondary phase of In_2O_3 was also present. The gas sensors made of $CdIn_2O_4$ thin films had a gas-sensitive effect to the LP, CO, H_2, and alcohol gas and were especially sensitive to gases of low concentration (0.1 to 1%). The gas-sensitive effect resulted from the adsorption of the reducing gases on the film sensors, and the proper working temperature of the sensors was about 300 °C. In addition, the gas-sensitive effect of the sensors is also related with the deposition conditions of $CdIn_2O_4$ thin films. The carrier concentration in the films can be changed in a large range by properly controlling the oxygen concentration of the Ar + O_2 mixture in the sputtering chamber and, therefore, this led to the different gas-sensitive effect of the sensors.

Acknowledgements

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