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Sol–gel dip coated CdO:Al films

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ABSTRACT

Cadmium oxide (CdO) films were deposited by the sol–gel dip coating using acrylamide route. The films were doped with different concentrations of gallium in the range of 500–3500 ppm. X-ray diffraction studies indicated the films to possess cubic structure. The grain size, strain, lattice parameter, dislocation density, texture coefficient were estimated from the XRD pattern. The texture coefficient varies in the range of 0.16–0.61 for the different peaks. Optical transmission measurements indicated direct and indirect band gap values of 2.59 and 2.06 eV. Electrical conductivity of the undoped film was 0.5×10^3 mho cm^{-1}, after doping with aluminium, the conductivity increased to 1.5×10^3 mho cm^{-1}. Mobility decreased from 250 to 35 cm^2 V^{-1} s^{-1} with an increase of Al concentration. Solar cell studies made on the Si/CdO cells under an illumination of 90 mW cm^{-2} yielded an V_{oc} of 0.62 V, J_{sc} of 16 mA cm^{-2}, ff = 0.76 and η = 9.55%.

1. Introduction

In recent years, the metal oxide semiconductor materials have attracted much attention owing to their potential applications in electronic and photovoltaic devices. CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and possesses a direct band gap of 2.2 eV [1]. Its high electrical conductivity (even without doping) and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index make it useful for various applications such as solar cells, transparent electrodes, phototransistors, photodiodes, gas sensors, etc. [2,3]. Besides, the CdO will be attractive in the field of optoelectronic devices by making heterostructures with ZnO which has a band gap energy of 3.3 eV. A variety of techniques such as sol–gel [5], spray pyrolysis [6], sputtering method [3], chemical bath deposition (CBD) [1], Langmuir–Blodgett (LB) deposition [7], activated reactive evaporation [8] and metalorganic chemical vapor deposition (MOCVD) [9] have been employed to prepare CdO films. But almost all the reports were polycrystalline CdO with poor crystalline qualities which are not suitable for use in optoelectronic devices [3,5–9]. For undoped CdO films, the resistivity values of $2–20 \times 10^{-4}$ Ω cm are obtained for those deposited by sophisticated techniques such as reactive sputtering and metal organic chemical vapor deposition, whereas for simpler techniques such as chemical bath deposition and SG, resistivity values are obtained between 10^{-3} and 10^{-2} Ω cm. In this work, we present the results obtained on Sn-doped CdO thin films deposited by the sol–gel method starting from acrylamide precursor. The new precursor is based on cadmium chloride, acrylamide, N,N bis acrylamide and ammonium persulphate. The structural, optical and electrical properties of the films were studied.

2. Experimental methods

CdO films were deposited on clean glass substrates at a temperature of 70 °C. Prior to deposition, the glass substrates of size 2.5 cm × 7.5 cm were boiled in chromic acid for 1 h followed by rinsing in triple distilled water three times and finally cleaned in acetone by ultrasonic agitation. The precursor solution consisted of AR grade cadmium chloride. The pH of the solution was adjusted to 8 by adding AR grade ammonium hydroxide. To this AR grade acrylamide was added and the mixture was heated to 70 °C. N,N bis acrylamide was then added and the solution was stirred for about 10 min. For depositing aluminium-doped films, different concentrations of aluminium nitrate (99.99% pure) in the range of 0.5–2.5 g were added to the above mixture. A small amount of ammonium persulphate was added slowly to this mixture just before formation of the gel. The cleaned glass slides were dipped in the solution and withdrawn at a rate of 1 cm/s. One side of the glass substrate was masked with cellulose tape. The coated glass substrate was then dried in air for about 10 min after removing the tape from the uncoated side. The dried films were heat treated at different temperatures in the range of 200–450 °C for different durations. The duration of heat treatment was varied in the range of 1.0–5.0 h. The exact amount of aluminium incorporated into the CdO lattice was estimated by atomic absorption spectrometer (AAS). The films were dissolved in aqua regia and after dilution were used in AAS. The concentration of aluminium incorporated determined from AAS was in the range of 500–3500 ppm. The films were then characterized by X-ray diffraction by Philips X-ray diffraction unit with CuKα radiation. Optical transmission measurement was made using a Hitachi U3400 UV-Vis-NIR spectrophotometer. Surface morphology was studied by molecular imaging systems atomic force microscope. Electrical conductivity (σ) of the films was measured at room temperature by two-probe resistivity technique and by providing silver paste

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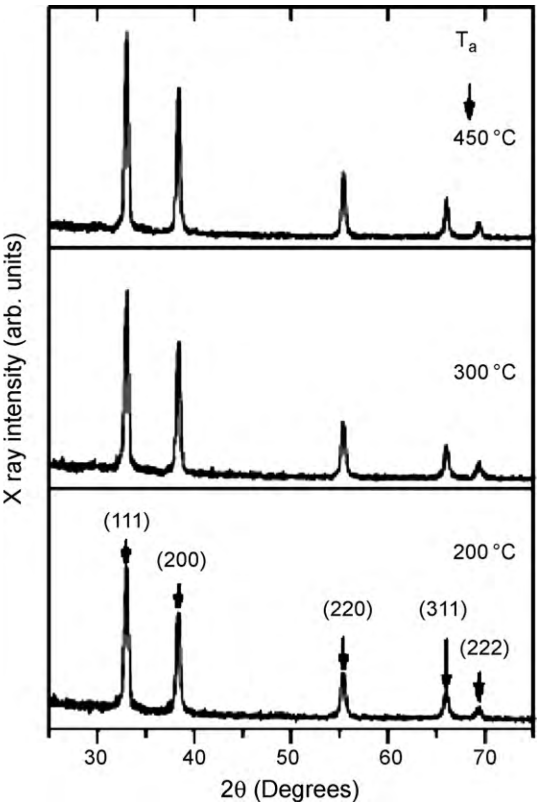

Fig. 1. X-ray diffraction pattern of CdO films post-annealed at different temperatures.

ohmic contacts at the edges of the films. Mirror-like single crystal p-Si (1 1 1) with a thickness of 250 mm and a resistivity of 1 Ω cm was used as a substrate in this study. These substrates were immersed in diluted HF solution and then washed with deionized water to remove the native oxide. On top of the Si substrate, CdO films were deposited by the above procedure. During deposition, one side of the silicon substrate was covered with cello tape, this tape was removed during the post-heat treatment. The uncoated side of the silicon wafer was etched again with HF to remove the oxide layer. Care was taken to see that the acid did not react with the CdO film formed on the other side. After this indium was vacuum evaporated on the sides of the top surface of CdO and Ga–In was deposited on the surface of the uncoated silicon side. Load characteristic of the solar cell was studied under an illumination of 90 mW cm^{-2} from a 250 W tungsten halogen lamp. A variable load resistance was connected to the cell and the open circuit voltage and short circuit current were noted for each load setting.

3. Results and discussion

X-ray diffraction studies indicated the CdO films to possess cubic structure with peaks corresponding to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) reflections (Fig. 1). The grain size, strain, lattice parameter, dislocation density and texture coefficient were estimated form the XRD pattern. It is observed that the grain size was estimated using Scherrer's equation [10]:

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

The grain size varied in the range of 7.0–12.0 nm. The lattice constant was calculated using software was 4.629 Å. The strain and dislocation density values were calculated using the standard relations [11]:

$$\text{strain}\,(\varepsilon) = \frac{\beta \cos\theta}{4}$$

$$\text{dislocation density}\,(\delta) = \frac{15\varepsilon}{a \times D}$$

Table 1
Values of lattice parameter, grain size, dislocation density, strain of the CdO films post-annealed at different temperatures.

Temperature (°C)	Grain size (nm)	Strain ($\times 10^3$)	Dislocation density ($\times 10^{15}$)
200	7.035	5.15	2.38
300	10.00	3.61	4.28
450	12.00	3.02	4.30

where '*a*' is the lattice parameter and '*D*' is the grain size. The strain values varied in the range of 3.0×10^{-4} to 5.01×10^{-4}. The dislocation density value was around $4 \times 10^{17}/\text{m}^2$. The texture coefficient value deviates far from unity, which implies the preferential orientation of the films. The values of lattice parameter, strain, grain size and dislocation density are indicated in Table 1. The texture coefficient defined by Barret and Massalski [12] has been used to describe the preferred orientation.

$$\text{TC} = \frac{I(h\,k\,l)/I_0(h\,k\,l)}{1/N \sum I(h\,k\,l)/I_0(h\,k\,l)}$$

where TC is the texture coefficients of the $(h\,k\,l)$ plane, I the measured intensity, I_0 the ASTM standard intensity of the corresponding powder, and N is the reflection number. From this definition it is clear that the deviation of the texture coefficient from unity implies the preferred orientation of the growth. The larger the texture coefficient deviates from unity, the higher will be the preferred orientation of a film. Table 2 shows the texture coefficient of the CdO films post-annealed at 450 °C. From the table it is observed that the texture coefficient varies in the range of 0.16–0.61 for the different peaks. A typical UV–vis spectrum of films with a thickness of 800 Å is shown in Fig. 2. It shows a transmission of 90% in the range of 700–1100 nm, which is similar to the earlier reports for CdO thin films [13–15]. The absorption coefficient α of the films was determined from the transmittance data obtained at normal incidence, using the following relation [16]:

$$\alpha = \frac{2.303 \log(1/T)}{d}$$

where T is the transmittance and d is the film thickness.

From Fig. 2, it can be observed that the increase in transmittance is not sharp, which indicates that the absorption band gap in the films is not due only to a direct gap. The values of a calculated from the relation presented above, were used to plot $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ (Fig. 3), from which a direct band gap and an indirect one were found, by extrapolating the linear portion of the curves to energy axis. The direct and indirect band gap values found were 2.59 and 2.06 eV respectively. Direct band gap values in the range 2.3–2.54 eV have been reported for CdO films deposited by sputtering [17], spray pyrolysis [13,17,18], chemical bath deposition [14,19], and sol–gel technique [15]. Only Gurumurugan et al. [21] have experimentally obtained an indirect band gap of 1.98 eV.

Electrical conductivity of the undoped film was 0.5×10^3 mho cm^{-1}, after doping with aluminium, the conductivity increased to 1.5×10^3 mho cm^{-1}. Hall effect measurement was made at room temperature in Al-doped CdO thin films. From the measured value of the Hall coefficients (R_H), the carrier concentra-

Table 2
Texture coefficient values of XRD peaks of CdO films post-annealed at 450 °C.

Intensity	I/I_0	$1/N\sum I/I_0$	TC
1760	100	236.94	0.422
1275	72.44	118.47	0.612
675	38.35	78.19	0.490
320	18.19	59.24	0.310
140	7.95	47.39	0.168

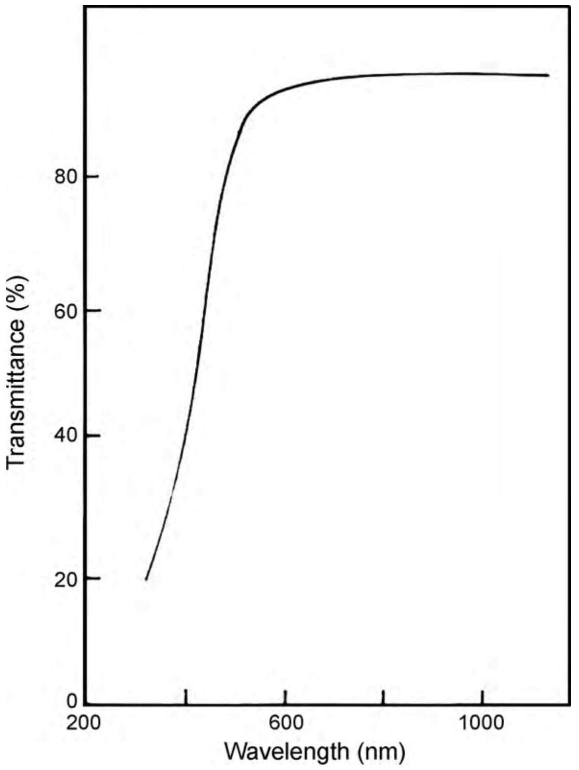

Fig. 2. Transmission spectra of CdO films post-annealed at 450 °C.

tion (n) was calculated for different percentages of Al-doped CdO films using the relation $R_H = 1/ne$, where e is the electronic charge. The mobility (μ) of the carriers was calculated from the relation $\mu = \sigma/ne$. The variation of carrier concentration and mobility, with the percentage of Al is indicated in Table 3. Mobility decreased from 250 to 35 $cm^2\,V^{-1}\,s^{-1}$ with the increase of Al concentration due to the increase in the ionized impurity scattering. The variation of carrier concentrations also follows inversely since the change of conductivity was small.

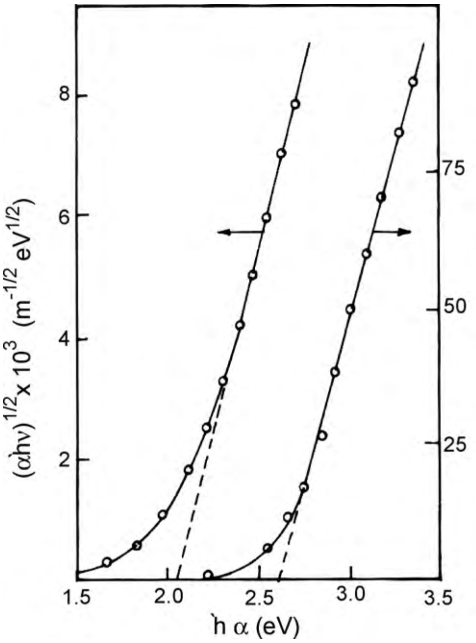

Fig. 3. Plots of $(\alpha h\nu)^2$ vs $h\nu$ and $(\alpha h\nu)^{1/2}$ vs $h\nu$ for CdO films post-annealed at 450 °C.

Table 3
Variation of mobility, conductivity and carrier concentration with aluminium doping.

Amount of Al added (ppm)	Conductivity (mho cm^{-1})	Mobility carrier ($cm^2\,V^{-1}\,s^{-1}$)	Concentration (cm^{-3})
0	0.5×10^3	25	1.25×10^{20}
500	0.8×10^3	250	2.00×10^{19}
1500	1.0×10^3	145	4.30×10^{19}
2500	1.2×10^3	70	1.07×10^{20}
3500	1.5×10^3	35	2.67×10^{20}

The values of mobility, carrier concentration and conductivity are quite comparable with earlier report [21]. To improve the conductivity, one can increase the carrier concentration. Increase of carrier concentration can be achieved by heavy doping. However, this will degrade the transparency due to the increasing free carrier absorption [22], while at the same time, it lowers the mobility due to more charge carrier scattering from the ionized impurities. The main scattering mechanisms for the charge carriers in thin films are lattice scattering, ionized impurity scattering and grain boundary scattering [23]. The lattice scattering mobility, μ_L, is proportional to the reciprocal of temperature [23]. Ionized impurity scattering mobility, μ_i, is independent of T, and decreases with the increase in the carrier concentration. There are different opinions about the role of grain boundary scattering.

According to earlier reports [24,25], the grain boundary scattering was important in limiting the mobility of their films, while others [22,26] concluded that it made a very small contribution to the mobility.

Solar cell studies were made on the Si/CdO cells under an illumination of 90 mW cm^{-2}. It was observed that the open circuit voltage was 0.62 V and the short circuit current was 16 mA cm^{-2}, ff = 0.76 and $\eta = 9.55\%$ for the cells made with CdO films post-annealed at 450 °C. The J–V characteristics under illumination for the cells are shown in Fig. 4. The values of the V_{oc}, fill factor (ff) and efficiency (η) are higher than the earlier report [27].

$$\text{Fill factor}\,(ff) = \frac{V_m I_m}{V_{oc} I_{sc}}$$

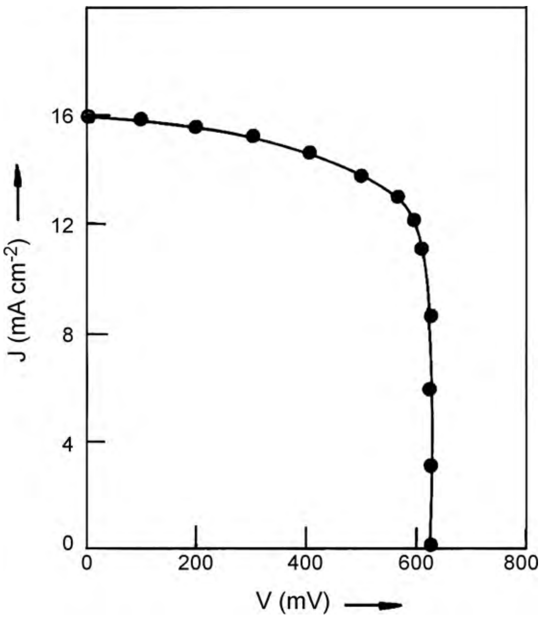

Fig. 4. J–V characteristics of p-Si/CdO solar cells illuminated at 90 mW cm^{-2}.

where V_m and I_m are the abscissa and ordinate of the maximum power point on the load characteristics.

$$\eta = \frac{V_m I_m}{P_{in} A}$$

where P_{in} is the incident optical power in $\mathrm{mW\,cm^{-2}}$ and A is the area of the exposed portion of the photoelectrode.

The J_{sc} value is lower than the earlier report [27], probably due to the high series resistance of 20 Ω. The cells were kept under ambient conditions and they were found to be stable for more than a year.

4. Conclusions

The results of this study clearly show that the CdO films post-annealed at 450 °C exhibit high conductivity in the range of 103 Ω cm. The films when deposited on p-Si for solar cell studies have yielded higher open circuit voltage, short circuit current and efficiency. This paves way for using these films for photovoltaic applications.

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