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Effect of oxygen partial pressure on optoelectrical properties of tin - doped CdO thin films

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Tin–doped CdO thin films were deposited on quartz by pulsed laser deposition technique. The effect of oxygen partial pressure on structural, optical, and electrical properties was studied. It is observed that the (200) plane is highly preferred for the films grown under high oxygen pressure. Atomic force microscopy shows that the films are very smooth with root mean square roughness of 0.7 nm. The experimental results show that oxygen partial pressure influences the electrical properties. The electrical conductivity and carrier concentration decrease with increase in the oxygen pressure. The highest mobility of 238 $cm^2V^{-1}s^{-1}$) is observed. Low resistivity, high mobility, and high optical transmittance (~ 91%) make these films suitable for optoelectronic applications.

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1. Introduction

Thin films based on transparent conducting oxides (TCO) have received considerable attention because of their wide applications as transparent electrodes for optoelectronic applications such as flat panel displays, solar cells, and light emitting diodes [1-3]. Transparent electrodes based on doped zinc oxides, indium oxides, tin oxides, and cadmium oxides have attracted extensive attention because of their low resistivity and high optical transmittance [4-7]. Although these TCO are widely used for optoelectronic applications, research on improving the electrical and optical properties of these materials is continuing. Among these TCO, cadmium oxide (CdO) has received considerable attention for solar cell application due to its low electrical resistivity and high transparency in the visible range of solar spectrum [8].

Many techniques have been used to produce CdO thin films: sol-gel [9], dc magnetron sputtering [10], radio-frequency sputtering [11], spray pyrolysis [4], chemical vapor deposition [12], chemical bath deposition [13], and pulsed laser deposition [14]. Among these techniques, pulsed laser deposition has many advantages such as: (a) It has the ability to maintain target composition in the deposited thin films; (b) High quality films can be deposited at low temperature due to high kinetic energy of atoms and ionized species in the laser produced plasma, and (c) It is clean and relatively inexpensive [15]. It is reported that the low resistivity of CdO thin films is due to defects of oxygen vacancies and cadmium interstitials [16], it is important to study the effect of oxygen pressure on its optoelectrical properties. Literature survey reveals that there is no report on effect of oxygen pressure on optoelectrical properties of tin - doped CdO thin films by pulsed laser deposition technique.

In our previous paper we reported on preparation and characterization pulsed laser deposited In_2O_3 thin films [17].

In this paper, we are reporting the effect of oxygen partial pressure on structural, electrical, and optical properties of tin-doped CdO (CdO:Sn) thin films prepared by pulsed laser deposition..

2. Experimental details

Tin-doped CdO target for the pulsed laser deposition was prepared by a standard solid-state reaction method using high purity CdO (99.999 %) and SnO_2 (99.999 %). Required amounts of CdO and SnO_2 were taken by molecular weight and mixed thoroughly to get the target of CdO having two atomic weight percent of tin. The well-ground mixture was heated at 850 ˚C for 10 hours. The powder mixture was cold pressed at 6×10^6 N/m^2 load and sintered at 900 ˚C for 10 hours.

The CdO:Sn films were deposited on quartz substrate by pulsed laser deposition technique using KrF excimer laser (Lambda Physik COMPEX, $\lambda = 248$ nm and pulsed duration of 20 ns) under various oxygen pressures. The laser was operated at a pulse rate of 10 Hz and an energy of 300 mJ/pulse. The laser beam was focused onto a rotating target at a 45° angle of incidence. Thin films were deposited under oxygen pressures of 1.0×10^{-4} mbar, 5.0×10^{-4} mbar, 1.0×10^{-3} mbar, 1.0×10^{-2} mbar, 5.0×10^{-2} mbar and 1.0×10^{-1} mbar. All the films were grown at substrate temperature of 150 °C. The deposition chamber was initially evacuated to 1.2×10^{-6} mbar and oxygen gas was introduced into the chamber during deposition to obtain the above pressures. Prior to deposition, the substrates were cleaned ultrasonically and degreased in acetone.

The x-ray diffraction (XRD) spectra of all the films were recorded with Bruker AXS x-ray diffractometer using the 2θ-θ scan with CuK_α ($\lambda = 0.154$ nm). Atomic force microscopy (AFM) imaging was performed under ambient conditions using a Digital Instruments (Veeco) Dimension-3100 unit with Nanoscope® III controller, operated in tapping mode. The optical transmittance measurements were made using UV-visible spectrophotometer (Ocean Optics HR4000).

The resistivity and Hall coefficient measurements were carried out by a standard four-probe technique. Gold contacts were used for all electrical measurements. The film resistivities have been determined by taking the product of resistance and film thickness. The thickness of the films has been measured by height profile scanning using AFM [18]. The Hall effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [19]. The type of conducting carriers was confirmed to be *n* type for all samples from the observed negative slope in magnetic field versus Hall voltage plots. Carrier concentration and carrier mobility were calculated at room temperature using the Hall coefficient and the resistivity data [20].

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the x-ray diffraction patterns of CdO:Sn thin films grown under different oxygen pressures. It is seen that oxygen partial pressure influences the preferential growth of the films. It is observed that the films grown at low oxygen pressure have both (111) and (200) orientations, while the films grown under high oxygen pressure shows preferential (200) orientation. The films grown at high oxygen pressure are highly orientation along (200) plane. All the peak positions are in good agreement with the PDF card no. 005-0640 for CdO [21]. The average particle size (t) of the films was calculated using the Scherrer equation, $t = 0.9\lambda / \beta\cos\theta$, where λ is the x-ray wavelength, β is the full width at half maximum of the (200) diffraction line, and θ is the diffraction angle of the XRD spectra [22]. It is observed that crystallinity of the films increases with increase in oxygen pressure as particle size increases from 11 nm to 27 nm as the oxygen pressure increases from 1.0×10^{-4} to 1.0×10^{-1} mbar respectively.

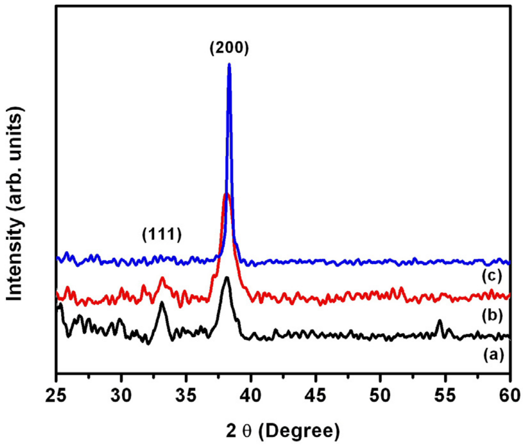

Fig.1. XRD patterns of CdO:Sn films grown at 150 °C under oxygen pressure of (a) 1×10^{-4} mbar, (b) 1×10^{-3} mbar, and (c) 1×10^{-1} mbar.

Fig. 2 shows the AFM topography of CdO:Sn film grown at oxygen pressure of 1.0×10^{-3} mbar. The scan was carried out in tapping mode. The spring constant of the cantilever was ~42 N/m. The cantilevered tip was oscillated close to the mechanical resonance frequency of the cantilever (typically, 200–300 kHz) with amplitudes ranging from ~10 to 30 nm. It can be seen that a rather smooth surface with root mean square (rms) values of surface roughness of 0.7 nm was obtained. The surface roughness of our film is superior to the commercially available indium tin oxide films (~ 4 nm) [23]. It is reported that the peak to valley roughness is also a very important parameter for optoelectronic devices [24]. The leakage current of the device increases with an increase in the peak to valley roughness. For devices based on tin doped indium oxide the peak to valley roughness is reported as 16.4 nm [24], while the peak to valley roughness for our film is 5.9 nm.

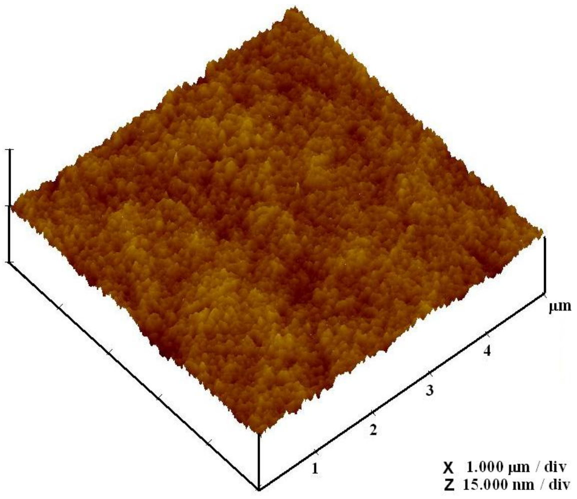

Fig. 2 AFM image of CdO:Sn films grown at 150 °C under oxygen pressure of 1×10^{-3} mbar.

3.2. Optical properties

Fig. 3 shows the optical transmittance spectra of CdO:Sn films ranging from 300 to 900 nm. It is observed that the optical transmittance of the films varies with oxygen pressure. It is evident form the figure that these films are highly transparent in the visible range. It can be observed that the average transmittance of the films is in the range of 73-92% in 400 - 900 nm range. It is observed in general that high oxygen pressure in PLD chamber degrade the optical transmittance of the films.

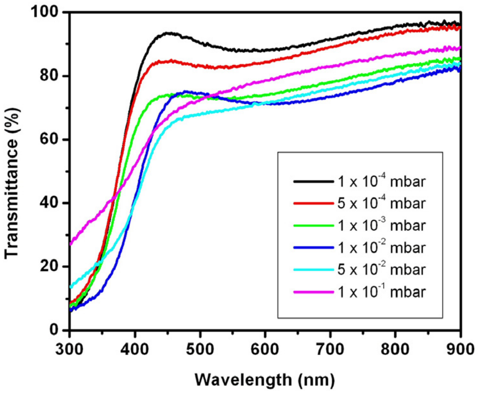

Fig. 3. Transmittance spectra of CdO:Sn films grown at 150 ˚C under different oxygen pressures.

3.3. Electrical properties

The effect of oxygen partial pressure on electrical properties of CdO:Sn thin films is shown in Figure 4(a).

The carrier concentration (n) is derived from the relation $n = 1/e.R_H$, where R_H is the Hall coefficient and e is the absolute value of the electron charge.

The carrier mobility (μ) is determined using the relation $\mu = 1/ne\rho$, where ρ is resistivity [20]. It is observed that the electrical resistivity of the films increases with oxygen pressure.

On the other hand, the carrier concentrations decrease with oxygen pressure. The electrical resistivity of the films increases from 1.51×10^{-5} to 9.89×10^{-4} Ω.cm as oxygen pressure increases from 1.0×10^{-4} mbar to 1×10^{-1} mbar respectively. Also the carrier concentration decreases from 1.78×10^{21} to 9.87×10^{19} cm^{-3} as oxygen pressure increases from 1.0×10^{-4} mbar to 1×10^{-1} mbar respectively.

On other hand, the mobility initially increases with an increase in the oxygen pressure up to 1.0×10^{-3} mbar and then decreases with an increase in oxygen pressure. These results indicate that the resistivity, carrier concentration and mobility of CdO:Sn films are sensitive to oxygen partial pressure.

Zhou *et. al* have studied the effect of oxygen pressure on properties of CdO films grown by dc reactive magnetron sputtering [25]. They observed that electrical conductivity, carrier concentration and mobility continuously decrease with oxygen pressure. The increase in resistivity and decrease in carrier concentration with oxygen pressure may be due to removal of oxygen vacancies form the films. The low mobility of the films grown under high oxygen pressure is believed to be due to collisional energy loss of the particles with oxygen during their arrival toward the substrate surface [26].

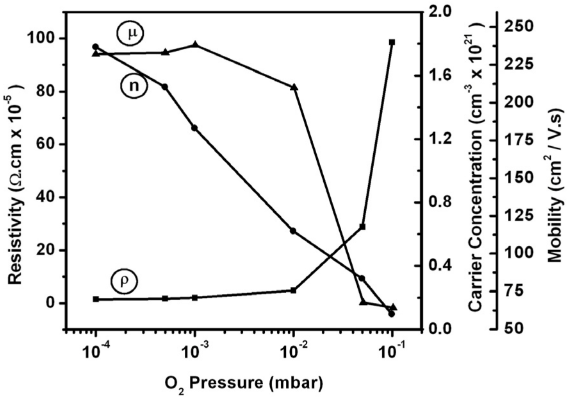

Fig. 4(a). Effect of oxygen pressure on resistivity (ρ), carrier concentration (n), and mobility (μ) of CdO:Sn films.

The effect of temperature on electrical resistivity of CdO:Sn films grown under different conditions have been measured in the range of 5-300 K.

It is observed that temperature dependence of electrical resistivity of the films depends on the oxygen pressure. It is seen that the films grown under low oxygen partial pressure show metallic behavior, i.e. resistivity increases as the temperature increases. On the other hand, the films grown under high oxygen pressure show semiconducting behavior, i.e. resistivity decreases as the temperature increases.

Figure 4(b) shows a representative plot for the film grown under oxygen pressure of 1.0×10^{-4} mbar.

The metallic behavior of doped semiconductors is also reported for tin – doped indium oxide films by Li *et. al.* [27] and Coutal *et. al.* [28]. They reported that this behavior is characteristics of a highly degenerate semiconductor. In these types of semiconductors, the Fermi level is localized in the conduction band and all donors are ionized [29].

It is observed by the close inspection of the resistivity versus temperature data in low temperature region that resistivity decreases with temperature up to 55K (inset of Figure 5). This may be due to weak-localization and electron- electron interaction effects [27].

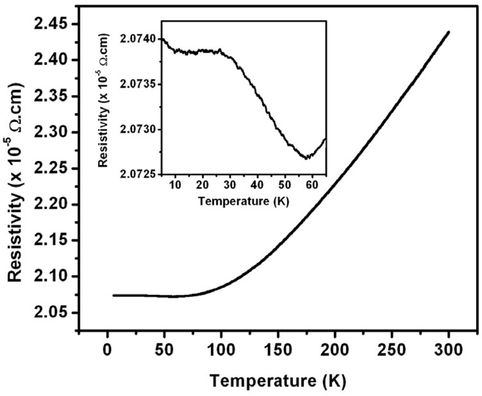

Fig. 4(b). Variation of electrical resistivity with temperature for CdO:Sn thin films grown at 150 ˚C under oxygen pressure of 1.0 × 10^{-4} mbar.

Fig. 5(c) shows the temperature dependence of electrical resistivity of CdO:Sn films grown under oxygen pressure of 1 × 10^{-1} mbar. The observed behavior is best fitted by the equation [30]

$$\sigma = \sigma_0 \exp\left(\frac{T_0}{T}\right)^{-1/4}$$

where σ_0 is temperature dependent ($\sigma_0 \sim T^{-1/2}$) and temperature T_0 is related to the density of states at the Femi level. The linear plot of $\ln(\sigma T^{1/2})$ vs. $T^{-1/4}$ confirms that the variable range hopping mechanism for the films grown under high oxygen pressure.

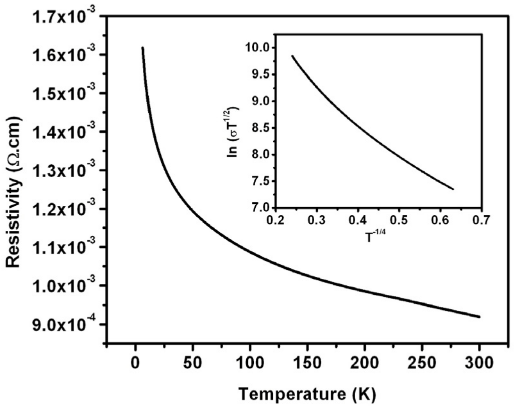

Fig. 4(c). Variation of electrical resistivity with temperature for CdO:Sn thin films grown at 150 ˚C under oxygen pressure of 1.0 × 10^{-1} mbar.

4. Conclusions

The effect of oxygen partial pressure on structural, optical and electrical properties of pulsed laser grown CdO:Sn films was studied. It is seen that film orientation depends on growth conditions. It is observed that the electrical properties of these films strongly depend on the oxygen pressure. The conductivity and carrier concentration of the films decreases with increase in the oxygen pressure. Low resistivity, high mobility and high transmittance suggest that these films have significant commercial relevance.

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References

[1] B. G. Lewis, D. C. Paine, MRS Bull. **25**, 22 (2000).
[2] H. Kim, C. M. Gilmore, A. Pique, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, D. B. Chrisey, J. Appl. Phys. **11**, 6451 (1999).
[3] J. A. A. Selvan, A. E. Delahoy, S. Guo, Y.-M. Li, Sol. Energy Mater. Sol. Cells **90**, 3371 (2006).
[4] L. Zhao, J. Lian, Y. Liu, Q. Jiang, Appl. Surf. Sci. **252**, 8451 (2006).
[5] F. O. Adurodija, L. Semple, R. Bruning, Thin Solid Films **492**, 153 (2005).
[6] I. Saadeddin, B. Pecquenard, J. P. Manaud, R. Decourt, C. Labruge`re, T. Buffeteau, G. Campet, Appl. Surf. Sci. **253**, 5240 (2007).
[7] C. H. Bhosale, A.V. Kambale, A.V. Kokate, K.Y. Rajpure, Mater. Sci. Engg. B **122**, 67 (2005).
[8] Y. Yang, L. Wang, H. Yan, S. Jin, T. J. Marksa, S. Li, Appl. Phys. Lett. **89**, 051116 (2006).
[9] R. Maity, K. K. Chattopadhyay, Sol. Energy Mater. Sol. Cells **90**, 597 (2006).
[10] T. K. Subramanyam, S. Uthanna, B. S. Naidu, Mater. Lett. **35**, 214 (1998).
[11] N. Ueda, H. Maeda, H. Hosono, H. Kawazoe, J. Appl. Phys. **84**, 6174 (1998).
[12] X. Liu, C. Li, S. Han, J. Han, C. Zhou, Appl. Phys. Lett. **82**, 1950 (2003).
[13] L. R. Gutierrez, J. J. C. Romero, J. M. P. Tapia, E. B. Calva, J. C. M. Flores, M. O. Lopez, Mater. Lett. **60**, 3866 (2006).
[14] M. Yan, M. Lane, C. R. Kannewurf, R. P. H. Changa, Appl. Phys. Lett. **78**, 2342 (2001).
[15] B. D. Chrisey, G. K. Hubler, Pulsed laser deposition of thin films, Wiley, New York, 1994.
[16] Z. Zhao, D. L. Morel, C. S. Ferekides, Thin Solid Films **413**, 203 (2002).

[17] R. K. Gupta, N. Mamidi, K. Ghosh, S. R. Mishra, P. K. Kahol, J. Optoelectron. Adv. Mater. **9**(7), 2211 (2007).
[18] R. K. Gupta, K. Ghosh, S. R. Mishra, P. K. Kahol, Appl. Surf. Sci. (In Press).
[19] L. J. Van der Pauw, Philips Res. Rep. **13**, 1 (1958).
[20] I. Yasuhiro, K. Hirokazu, Appl. Surf. Sci. **169/170**, 508 (2001).
[21] Powder Diffraction File, JCPDS-International Center for Diffraction Data, Pennsylvania, 1972.
[22] V. Khranovskyy, U. Grossner, O. Nilsen, V. Lazorenko, G. V. Lashkarev, B. G. Svensson, R. Yakimova, Thin Solid Films **515**, 472 (2006).
[23] W. E. Lee, Y. -K. Fang, J.-J. Ho, C. -Y. Chen, L. -H. Chiou, S. -J. Wang, F. Dai, T. Heieh, R. -Y. Tsai, D. Huang, F. C. Ho, Solid State Electron. **46**, 477 (2002).
[24] Y.-H. Tak, K.-B. Kim, H.-G. Park, K.-H. Lee, J.-R. Lee, Thin Solid Films **411**, 12 (2002).
[25] Q. Zhou, Z. Ji, B. Hu, C. Chen, L. Zhao, C. Wang, Mater. Lett. **61**, 531 (2007).
[26] T. K. Yong, T. Y. Tou, B. S. Teo, Appl. Surf. Sci. **248**, 388 (2005).
[27] Z. Q. Li, J. J. Lin, J. Appl. Phys. **96**, 5918 (2004).
[28] C. Coutal, A. Azema, J. C. Roustan, Thin Solid Films **288**, 248 (1996).
[29] I. Hemberg, C. G. Grandvist, J. Appl. Phys. **60**, R123 (1986).
[30] N. Brilis, D. Tsamakis, H. Ali, S. Krishnamoorthy, A. A. Iliadis, Thin Solid Films **516**, 4226 (2008).

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