



Low temperature processed highly conducting, transparent, and wide bandgap Gd doped CdO thin films for transparent electronics

R.K. Gupta^{a,*}, K. Ghosh^a, R. Patel^b, P.K. Kahol^a

^a Department of Physics, Astronomy, and Materials Science, Missouri State University, Springfield, MO 65897, USA

^b Roy Blunt Jordan Valley Innovation Center, Missouri State University, Springfield, MO 65806, USA

ARTICLE INFO

Article history:

Received 6 July 2010

Accepted 4 January 2011

Available online 6 January 2011

Keywords:

Gadolinium

Cadmium oxide

Bandgap

Pulsed laser deposition

Thin film

ABSTRACT

Gadolinium (Gd) doped cadmium oxide (CdO) thin films are grown at low temperature (100 °C) using pulsed laser deposition technique. The effect of oxygen partial pressures on structural, optical, and electrical properties is studied. X-ray diffraction studies reveal that these films are polycrystalline in nature with preferred orientation along (1 1 1) direction. Atomic force microscopy studies show that these films are very smooth with maximum root mean square roughness of 0.77 nm. These films are highly transparent and transparency of the films increases with increase in oxygen partial pressure. We observe an increase in optical bandgap of CdO films by Gd doping. The maximum optical band gap of 3.4 eV is observed for films grown at 1×10^{-5} mbar. The electrical resistivity of the films first decreases and then increases with increase in oxygen partial pressure. The lowest electrical resistivity of $2.71 \times 10^{-5} \Omega \text{ cm}$ and highest mobility of $258 \text{ cm}^2/\text{Vs}$ is observed. These low temperature processed highly conducting, transparent, and wide bandgap semiconducting films could be used for flexible optoelectronic applications.

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1. Introduction

Cadmium oxide (CdO) is widely used as transparent conductors for its high electrical conductivity and optical transparency [1]. CdO is an n-type semiconductor having bandgap of 2.27 eV [2]. The high conductivity of undoped CdO is due to defects of oxygen vacancies and cadmium interstitials [1]. CdO was the very first reported transparent conducting film made by oxidation of sputtered metallic cadmium [3]. After that different techniques such as sol-gel [4], dc magnetron sputtering [5], radio-frequency sputtering [6], spray pyrolysis [7], chemical vapor deposition [2], chemical bath deposition [8], and pulsed laser deposition [9] is used for deposition of doped and undoped CdO films. Although CdO is highly conducting, but due to its relatively small bandgap, it is not extensively studied compared to other transparent conducting oxides such as zinc oxide, indium oxide, titanium oxide, etc.

There are few reports on improvement of optical bandgap of CdO by doping [10,11]. Saha et al. have reported an improvement in optical bandgap of CdO by titanium incorporation [12]. Yan et al. have observed that the optical band gap of tin doped CdO films first increases with increase in tin doping level and then decreases with further increase in tin doping [9]. The maximum bandgap of 2.87 eV is observed for 6.2 at% tin doping. The effect of growth temperature on optical bandgap of tin doped CdO film is studied [1].

Fluorine doped CdO films show an improvement in optical bandgap from 2.2 eV to 2.42 eV by 4 at% fluorine doping [13]. Recently, it is reported that the rare earth oxides are potential doping candidates to improve the optical and electrical properties of conducting metal oxides because of their high optical band gap [14,15].

The literature survey indicates that there is no report on optoelectrical properties of rare earth oxide doped CdO films using pulsed laser deposition technique. The aim of the present work is to study the effect of oxygen partial pressure on structural, optical, and electrical properties of Gd doped CdO (CdO:Gd) thin films prepared by pulsed laser deposition technique.

2. Experimental details

Standard solid-state reaction was used for preparation of Gd (2 at%) doped CdO target. High purity Gd_2O_3 (Alfa Aesar, USA) and CdO (Alfa Aesar, USA) were used. The well-ground mixture was heated at 900 °C for 10 h. The powder mixture was cold pressed at $6 \times 10^6 \text{ N/m}^2$ load and sintered at 950 °C for 12 h. The thin films were deposited on quartz substrate under different oxygen partial pressures at 100 °C. KrF excimer laser (Lambda Physik COMPex, $\lambda = 248 \text{ nm}$ and pulsed duration of 20 ns) was used for deposition. The laser was operated at a pulse rate of 10 Hz, with an energy of 300 mJ/pulse. The laser beam was focused onto a rotating target at a 45° angle of incidence.

The structural characterizations were performed using X-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD spectra of all the films were recorded with Bruker AXS X-ray diffractometer using the 2θ - θ scan with $\text{CuK}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation which operated at 40 kV and 40 mA. The AFM imaging was performed under ambient conditions using a Digital Instruments (Veeco) Dimension-3100 unit with Nanoscope III controller, operating in tapping mode. The optical transmittance measurements were made using UV-visible spectrophotometer (Ocean Optics HR4000).

* Corresponding author. Tel.: +1 417 836 6298; fax: +1 417 836 6226.
E-mail address: ramguptamsu@gmail.com (R.K. Gupta).

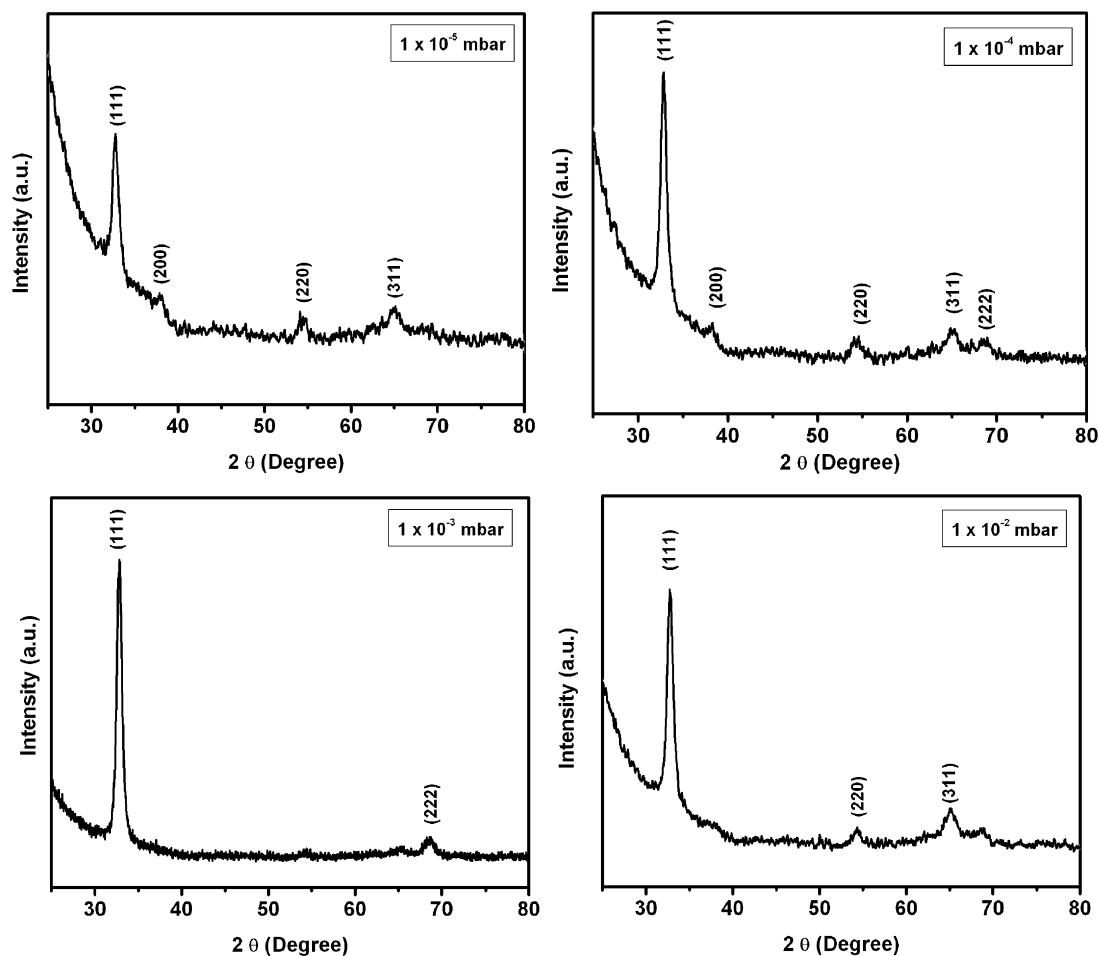


Fig. 1. XRD spectra of CdO:Gd films grown under different oxygen partial pressures.

The resistivity and Hall coefficient measurements were carried out by a standard four-probe technique. The thickness of the films was measured using AFM. The Hall effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [16]. Carrier concentration and carrier mobility were calculated at room temperature using Hall coefficient and resistivity data.

3. Results and discussions

3.1. Structural characterization

Fig. 1 shows the X-ray diffraction patterns of CdO:Gd films grown under different oxygen partial pressures. The observed diffraction patterns indicate the polycrystalline nature of the CdO with cubic structure on the basis of PDF Card No: 005-0640 [17]. No extra peaks due to the addition of gadolinium in CdO oxide films were observed and this indicates absence of an impurity phase in the films. It is seen that all the films have preferred orientation along (111) direction. 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 diffraction line, and θ is the diffraction angle of the XRD spectra [18]. The average particle size for the films grown under oxygen pressure of 1×10^{-5} mbar, 1×10^{-4} mbar, 1×10^{-3} mbar, and 1×10^{-2} mbar was calculated to be 11.1 nm, 10.1 nm, 12.3 nm, and 10.1 nm, respectively.

The surface smoothness is a very important parameter for any transparent electrode. The surface roughness of the films decides whether it could be used as an electrode or not for any optoelec-

tronic applications. The surface roughness of the films is studied using atomic force microscopy. The AFM images of CdO:Gd films grown under different oxygen pressures are shown in Fig. 2. The root mean square (rms) roughness of the films increases with an increase in oxygen partial pressure. The rms roughness of the films grown under oxygen pressure of 1×10^{-5} mbar, 1×10^{-4} mbar, 1×10^{-3} mbar, and 1×10^{-2} mbar was calculated to be 0.45 nm, 0.60 nm, 0.72 nm and 0.77 nm, respectively. The rms roughness of 4.7 nm is reported for CdO films grown using metal-organic chemical vapor deposition technique [19]. The peak to valley roughness, an important parameter to decide the suitability of these films for bottom electrodes, is calculated and is in the range of 3–6 nm. The peak to valley roughness of the devices based on tin doped indium oxide is 16.4 nm [20].

3.2. Optical characterization

Fig. 3 shows the effect of oxygen partial pressure on optical transparency of CdO:Gd films. The optical transparency and bandgap of the films are very important parameters for optoelectronic and photovoltaic applications. The optical transparency of the films increases with an increase in oxygen partial pressure. The average percentage transmittance of all the films is greater than 80%. The optical bandgap of the films is determined from transmittance vs. wavelength plot. The absorption coefficient (α) is given by

$$\alpha = \ln \left(\frac{1}{T} \right) / d \quad (1)$$

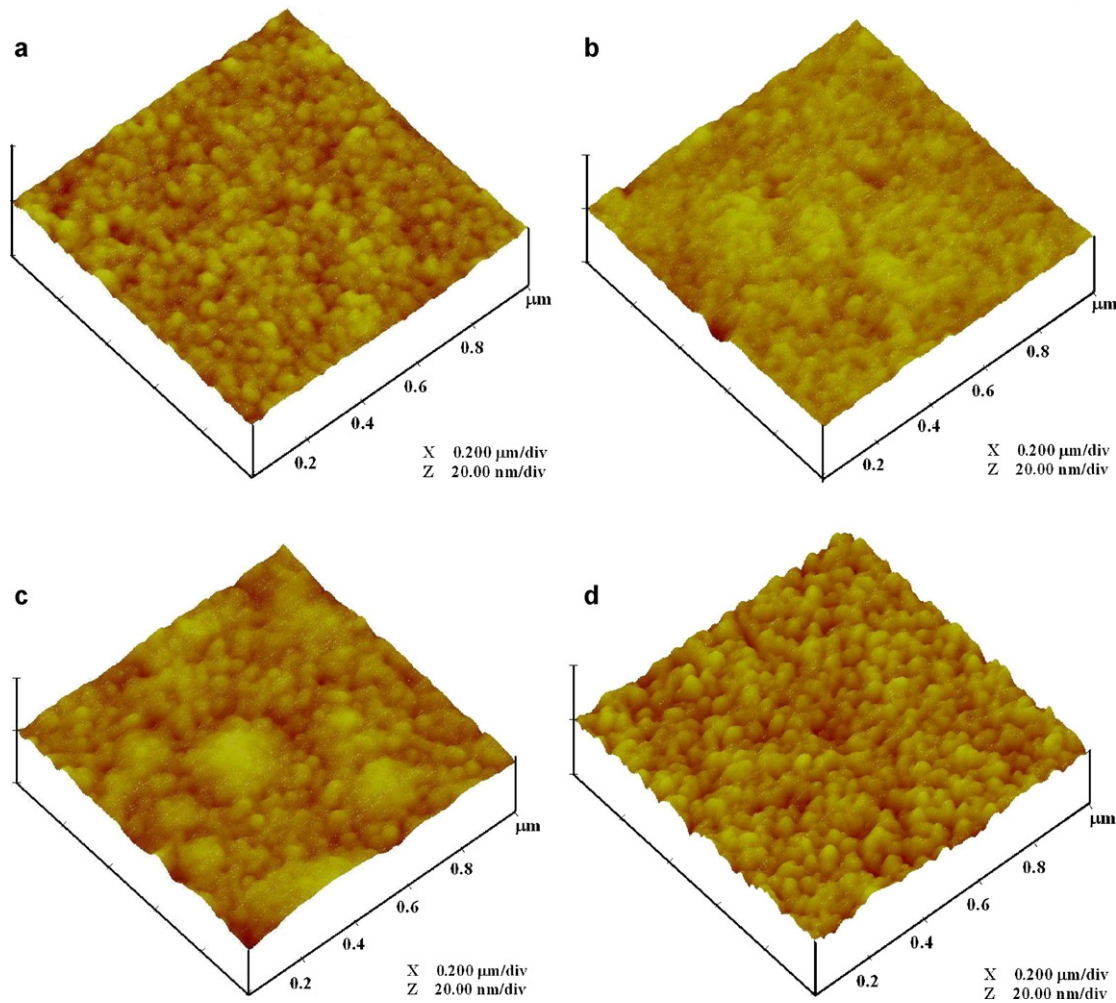


Fig. 2. AFM images of the films grown under different oxygen pressures.

where T is transmittance and d is film thickness. The relation between the absorption coefficient and the incident photon energy ($h\nu$) is given by the following equation [21]

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where A and E_g are constant and optical bandgap, respectively. The E_g can be determined by extrapolations of the linear regions of the plots to zero absorption. The inset of Fig. 3 shows the relationship

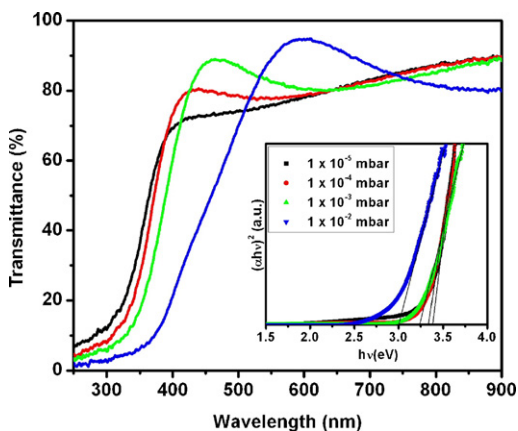


Fig. 3. UV-visible spectra of the films [inset figure $(\alpha h\nu)^2$ and $h\nu$ plots for CdO:Gd films].

between $(\alpha h\nu)^2$ and $h\nu$ for films grown at different oxygen partial pressures. The optical bandgap of the films decreases with increase in oxygen partial pressure and varies from 3.0 eV to 3.4 eV. Similar observations are reported by Subramanyam et al. for sputtered CdO films [22]. An increase in optical bandgap from 2.40 eV to 2.52 eV with an increase in oxygen partial pressure from 0.05 Pa to 0.5 Pa is observed. Our Gd doped CdO films show better improvement in optical bandgap compared to Ti, Sn, Al or F doped CdO films [9,12,13,23].

3.3. Electrical characterization

The dependence of electrical properties such as resistivity, carrier concentration, and mobility of CdO:Gd films on oxygen partial pressure is discussed next. The electrical parameters are calculated using standard equations [24]. The film resistivity is determined by taking the product of resistance and film thickness. The carrier concentration (n) is derived from the relation $n = 1/e \times R_H$, 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. It is observed that the carrier concentration of the films decreases with increase in oxygen partial pressure (Fig. 4). The carrier concentration decreases from $1.43 \times 10^{21} \text{ cm}^{-3}$ to $4.38 \times 10^{20} \text{ cm}^{-3}$ with increase in oxygen pressure from 1×10^{-5} mbar to 1×10^{-2} mbar, respectively. On the other hand, the resistivity of the films first decreases and then increases with increase in oxygen partial pressure. The low-

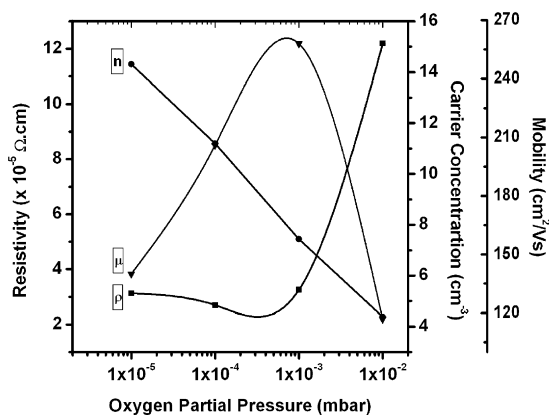


Fig. 4. Effect of oxygen partial pressure on electrical properties of CdO:Gd films.

est resistivity of $2.7 \times 10^{-5} \Omega \text{ cm}$ is observed for the films grown under 1×10^{-4} mbar oxygen pressure. The mobility of the films initially increases with an increase in the oxygen partial pressure up to 1.0×10^{-3} mbar and then decreases with an increase in oxygen pressure. 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. And the increase in resistivity and decrease in carrier concentration with oxygen pressure may be due to removal of oxygen vacancies from the films.

4. Conclusions

Pulsed laser deposition technique is used for growth of Gd-doped CdO films at low temperature. The effect of oxygen partial pressure on structural, optical, and electrical properties are studied. These (1 1 1) preferred oriented films are highly transparent. The optical bandgap of the films depends on oxygen partial pressure and varies from 3.0 eV to 3.4 eV. The lowest electrical resistivity and highest mobility of $2.71 \times 10^{-5} \Omega \text{ cm}$ and $258 \text{ cm}^2/\text{Vs}$, respectively,

are observed. These low temperature processed high mobility and wide bandgap semiconducting films could be used for flexible optoelectronic and photovoltaic applications.

Acknowledgement

This work is supported by National Science Foundation (Award Number DMR-0907037). Authors are thankful to Prof. R. Mayanovic, Missouri State University, for providing XRD facility.

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