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Structural, optical and electrical characterization of highly conducting Mo-doped In_2O_3 thin films

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Abstract

Highly conducting and transparent thin films of molybdenum-doped indium oxide were deposited on quartz by pulsed laser deposition. The effect of growth temperature and oxygen partial pressure on the structural, optical and electrical properties was studied. We find that the film transparency depends on the growth temperature. The average transmittance of the films grown at different temperatures is in range of 48–87%. The X-ray diffraction results show that the films grown at low temperature are amorphous while the films grown at higher temperature are crystalline. Electrical properties are found to be sensitive to both the growth temperature and oxygen pressure. Resistivity of the films decreases from 1.3×10^{-3} Ω cm to 8.9×10^{-5} Ω cm while mobility increases from 9 cm^2/V s to 138 cm^2/V s as the growth temperature increases from room temperature to 700 °C. However, with increase in oxygen pressure, resistivity increases but the mobility decreases after attaining a maximum. The temperature-dependent resistivity measurements show transition form semiconductor to metallic behavior. The film grown at 500 °C under an oxygen pressure of 1.0×10^{-3} mbar is found to exhibit high mobility (250 cm^2/V s), low resistivity (6.7×10^{-5} Ω cm), and relatively high transmittance (~90%).

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Keywords: Semiconductor; Electrical properties; Thin films; Indium oxide; Molybdenum; Optical materials and properties

1. Introduction

Transparent thin films having high carrier mobility and conductivity have attracted considerable attention of researchers not only for their wide application in optoelectronic industry but also for their high operational speed in electronic devices [1]. Hest et al. have recently shown that doping of indium oxide with molybdenum instead of tin produces transparent conducting films with higher carrier mobility (>65 cm^2/V s) [2]. Molybdenum-doped indium oxide (IMO) thin films having high carrier mobility (100 cm^2/V s) have been obtained using thermal reactive evaporation method [3]. Radio-frequency magnetic sputtering has been used to fabricate high mobility (83 cm^2/V s) IMO thin films with a carrier concentration of 3.0×10^{20} cm^{-3} [4]. Warmsingh et al. have studied the effect of molybdenum content on the electrical and optical properties of indium oxide thin films [5]. They report that IMO thin films having 2 wt% of molybdenum show best electrical properties. A mobility greater than 95 cm^2/V s has been observed for this film on yttria-stablized zirconia substrate.

The molybdenum-doped indium oxide films reported in the literature have been prepared mostly by sputtering and thermal reactive evaporation methods. In this communication we are reporting on the growth and characterization of molybdenum-doped indium oxide thin films by pulsed laser deposition (PLD). The PLD technique 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 [6]. In this communication we are reporting the effect of substrate temperature and oxygen pressure on the optical, electrical and structural properties of

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IMO thin films. The highest mobility which we have obtained in the films grown at 500 °C under an oxygen pressure of 1.0×10^{-3} mbar is 250 cm^2/V s.

2. Experimental details

The target for the pulsed laser deposition was prepared by the standard solid-state reaction method using high purity In_2O_3 (99.999%) and MoO_3 (99.999%). Required amounts of In_2O_3 and MoO_3 were taken by molecular weight and mixed thoroughly to get the In_2O_3 target with 2 at. wt% of molybdenum. The well-ground mixture was heated at 800 °C for 12 h. The powder mixture was cold pressed at 6×10^6 N/m^2 load and sintered at 850 °C for 12 h.

The IMO thin films were deposited on quartz substrate using KrF excimer laser (Lambda Physik COMPex, λ = 248 nm and pulsed duration of 20 ns) at different substrate temperatures and at different oxygen pressures in the PLD chamber. The laser was operated at a pulse rate of 10 Hz, with an energy of 300 mJ/pulse (1 mm × 1 mm spot). The laser beam was focused onto a rotating target at a 45° angle of incidence. Thin films were deposited at room temperature, 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C (under vacuum of base pressure 1.0×10^{-6} mbar) and under oxygen pressures of 2.5×10^{-4} mbar, 5.0×10^{-4} mbar, 7.5×10^{-4} mbar, 1.0×10^{-3} mbar, 5.0×10^{-3} mbar, 1.0×10^{-2} mbar, 5.0×10^{-2} mbar, 1.0×10^{-1} mbar and 5.0×10^{-1} mbar (at the substrate temperature of 500 °C). The deposition chamber was initially evacuated to 1.0×10^{-6} mbar and during deposition oxygen gas was introduced into the chamber to obtain the pressures mentioned above. The growth rate for the films was ∼3 nm/min.

The structural characterization was performed using X-ray diffraction (XRD) and Raman spectroscopy. The XRD spectra of all the films were recorded with Bruker AXS X-ray diffractometer using the 2θ–θ scan with Cu $K\alpha$ (λ = 1.5405 Å) radiation which operated at 40 kV and 40 mA. Micro-Raman scattering experiments were performed in perfect backscattering geometry using a fiber-optically coupled confocal micro-Raman system (TRIAX 320) which is equipped with a liquid N_2 cooled charge coupled detector. Atomic force microscopy (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–vis 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 thickness of the films was measured using AFM and is approximately 100 nm. The thickness of the films has been measured by height profile scanning. For this one has to scratch the film down to the substrate first and then scan the sample across the scratch to get a height profile. The film resistivities have been determined by taking the product of resistance and film thickness. The dimension of the substrate was 1 cm × 1 cm. The Hall effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [7]. Carrier concentration and carrier mobility were calculated at room temperature using Hall coefficient and resistivity data [8].

3. Results and discussion

3.1. Optical properties

The effect of substrate temperature and oxygen pressure on optical transmittance of the IMO films is shown in Fig. 1. It is

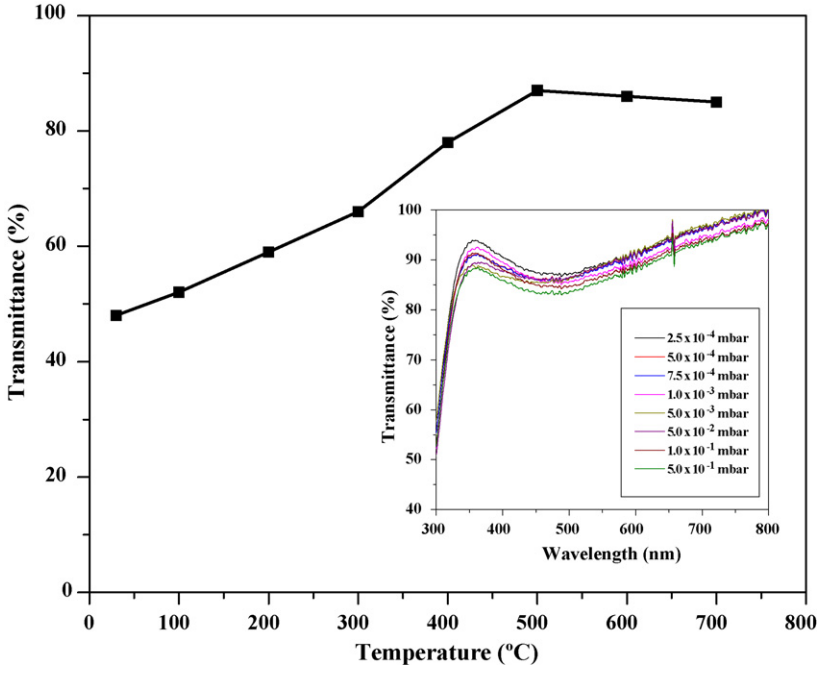

Fig. 1. Transmittance spectra of IMO films grown at different substrate temperatures and under different oxygen pressures (at 500 °C).

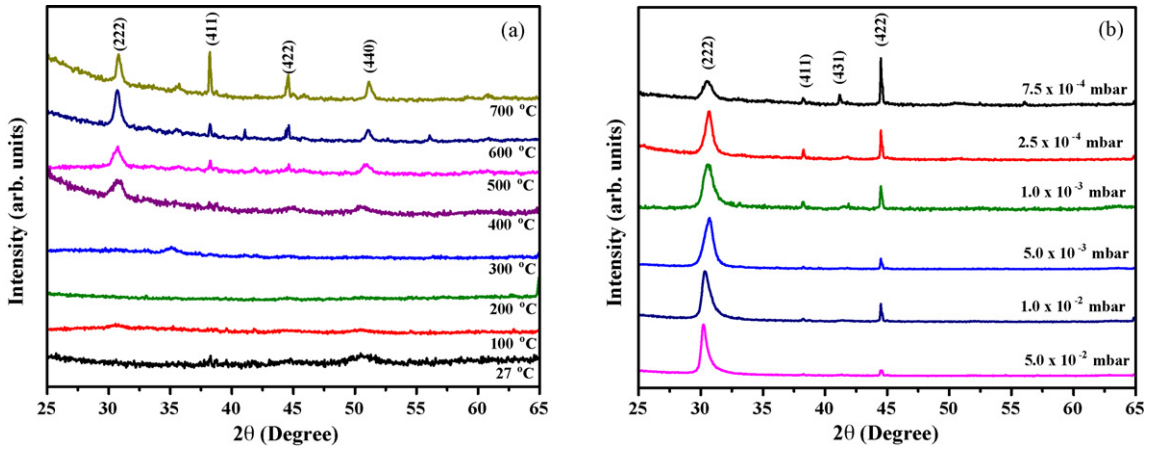

Fig. 2. XRD patterns of IMO film grown (a) at different temperatures, and (b) under different oxygen pressure on quartz substrate.

clear that the film transparency depends on the growth temperature and oxygen pressure. The films deposited at room temperature are brownish while the films deposited at higher growth temperatures are colorless. We find that transmittance of the films increases with an increase in substrate temperature up to 500 °C and after this temperature the transparency of the films is almost constant with temperature. The average percentage transmittance of the films grown at room temperature, 100 °C, 200 °C, 300 °C, 400 °C, 500 °C, 600 °C and 700 °C are 48%, 52%, 59%, 66%, 78%, 87%, 86% and 85%, respectively. The effect of oxygen pressure during growth on the optical transparency of the films is shown in the inset of Fig. 1. It is evident form the figure that these films are highly transparent. In general, films grown under oxygen atmosphere are more transparent compared with the films grown under vacuum at the same substrate temperature. However, excess oxygen during film growth decreases the film transparency. We find that in general a good transparent film is obtained for an oxygen pressure in the range 2.5×10^{-4} mbar to 5.0×10^{-3} mbar.

3.2. Structural properties

The X-ray diffraction patterns of IMO thin films grown at different temperatures under vacuum of base pressure 1.0×10^{-6} mbar are given in Fig. 2(a). The films grown at lower temperatures are found to be amorphous in nature (up to 300 °C), while films grown at higher temperatures show polycrystalline cubic bixbyite In_2O_3 phase. It is observed that the films are randomly oriented on the quartz substrate and all the peak positions are in good agreement with the JCPDS file card no. 06-0416 for In_2O_3 [9]. No extra peaks due to the addition of molybdenum in indium oxide films were observed which indicates the absence of an impurity phase in the films. That is, the diffractograms provide evidence of single phase crystalline indium oxide (body centered cubic lattice) [9,10]. 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 (2 2 2) diffraction line, and θ is the diffraction angle of the XRD spectra [11]. The average particle size in the films grown at 400 °C, 500 °C, 600 °C and 700 °C was calculated to be 7.4 nm, 10.1 nm, 15.6 nm, and 21.4 nm, respectively. The effect of oxygen pressure on the X-ray diffraction patterns of the IMO films grown at 500 °C is shown in Fig. 2(b). It is observed that the average particle size of the films is more or less the same and it is in the range 8–10 nm.

The Raman spectra of the IMO films grown at 500 °C under vacuum and under an oxygen pressure of 1.0×10^{-3} mbar are shown in Fig. 3. The indium oxide belongs to cubic C-type rare-earth oxide structure and for this type of structure the factor group analysis predicts $4A_g$ (Raman) + $4E_g$ (Raman) + $14T_g$ (Raman) + $5A_u$ (inactive) + $5E_u$ (inactive) + $16T_u$ (infra-red) modes [12]. Characteristic Raman peaks corresponding to indium oxide appeared at 496 cm^{-1} and 627 cm^{-1}. All the observed modes correspond well to the band positions reported in the literature for cubic indium oxide [13]. No additional peaks

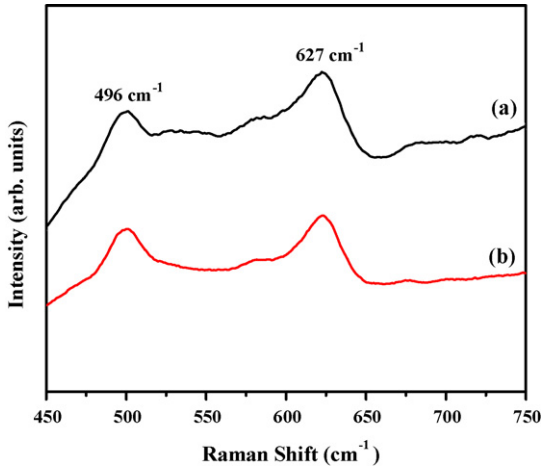

Fig. 3. Raman spectra of IMO thin films grown at 500 °C (a) under vacuum, and (b) at 1.0×10^{-3} mbar oxygen pressure.

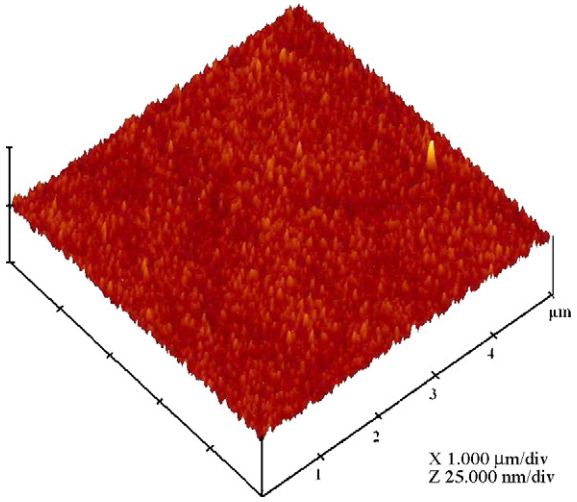

Fig. 4. AFM image of IMO film grown at 500 °C under an oxygen pressure of 1.0×10^{-3} mbar.

due to the addition of molybdenum are observed. This result indicates once again the absence of any impurity phase due to molybdenum doping in indium oxide.

Fig. 4 shows the AFM image of an IMO thin film which was grown at 500 °C under an oxygen pressure of 1.0×10^{-3} mbar. The surface of the film is seen to be very smooth which is believed to be due to the formation of a solid solution with a crystal structure. The root mean square (rms) roughness, the average roughness and the peak to valley roughness were found to be 1.18 nm, 0.93 nm and 15.31 nm, respectively. The peak to valley roughness is a very important parameter compared to the rms roughness for optoelectronic devices [14]. 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 [14]. The peak to valley roughness for our IMO thin films is comparable to it.

3.3. Electrical properties

The effect of substrate temperature and oxygen pressure on the electrical properties of IMO thin films which were grown under vacuum of base pressure 1.0×10^{-6} mbar and under oxygen pressure (at the substrate temperature of 500 °C) are discussed next. 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 the resistivity [8].

The effect of substrate temperature on electrical resistivity of IMO thin films is shown in Fig. 5(a). We find that the resistivity decreases continuously with increase in the substrate temperature, which is believed to be due to improvement in the film crystallinity at higher temperatures [15]. This is supported by X-ray diffraction analysis which indicates that the films grown at high temperature are more crystalline and the crystallinity increases with increase in growth temperature. An increase in grain size with an

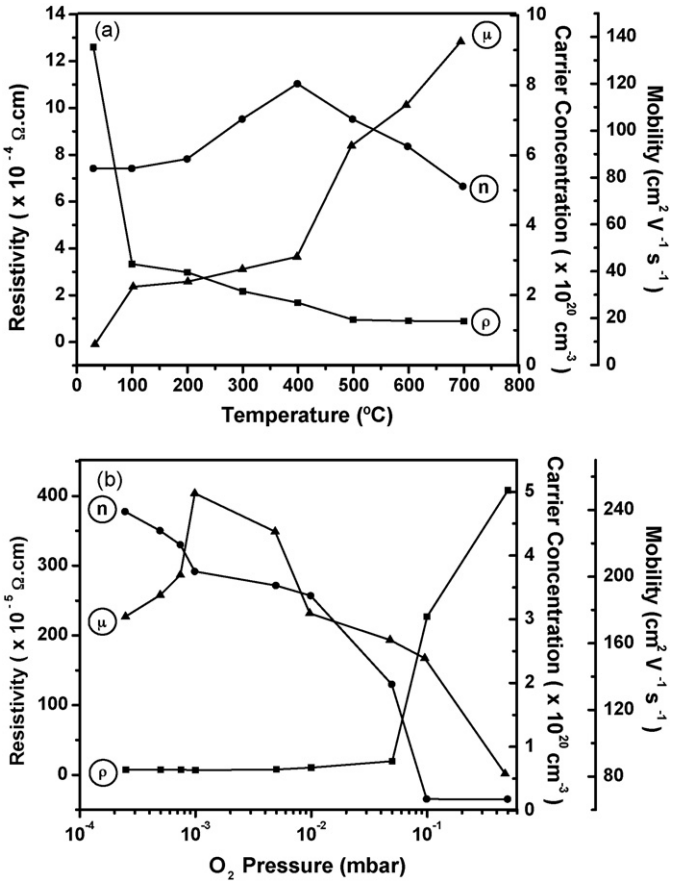

Fig. 5. (a) Effect of substrate temperature on resistivity (ρ), carrier concentration (n), and mobility (μ) of IMO films grown under vacuum. (b) Effect of oxygen pressure on resistivity (ρ), carrier concentration (n), and mobility (μ) of IMO films grown at 500 °C.

increase in the substrate temperature leads to reduced grain boundary scattering and thus a decrease in electrical resistivity [15]. We find that the carrier concentration increases with increase in substrate temperature up to 400 °C, after which the carrier concentration decreases with substrate temperature. The decrease in carrier concentration may be caused by the extinction of oxygen vacancies from the films at higher temperature [16]. However, Yoshida et al. have observed that the IMO thin films grown by radio frequency magnetic sputtering are relatively insensitive to deposition temperature [17]. The substrate temperature strongly affects the mobility of these films. The electron mobility continuously increases with increase in growth temperature. The mobility increases form 9 $cm^2/V\,s$ to 138 $cm^2/V\,s$ as the growth temperature increases from room temperature to 700 °C. The increase in mobility is believed to be due to better film crystallinity, which increases with an increase in substrate temperature.

Fig. 5(b) shows the dependence of oxygen pressure on the electrical properties of IMO films. It is observed that the resistivity, carrier concentration, and mobility are sensitive to oxygen pressure. The electrical resistivity of the films first decreases with oxygen pressure, attains a minimum at an oxygen pressure of 1×10^{-3} mbar, and then increases with an

increase in oxygen pressure. The carrier concentration, however, continuously decreases with oxygen pressure, decreasing from $4.69 \times 10^{20}\,cm^{-3}$ to $1.80 \times 10^{20}\,cm^{-3}$ as oxygen pressure increases from 2.5×10^{-4} mbar to 5.0×10^{-1} mbar. The mobility, on the other hand, initially increases with an increase in the oxygen pressure up to 1.0×10^{-3} mbar and then it decreases with an increase in oxygen pressure. Mobility as high as $250\,cm^2/V\,s$ has been obtained. 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 [18]. Films with minimum resistivity and maximum mobility thus correspond to an optimum energy window for the arriving oxygen and IMO atoms to create good films. Warmsingh et al. have observed mobility greater than $95\,cm^2/V\,s$ on yttria-stablized zirconia substrate for IMO thin films [5]. The high mobility obtained in our films may be due to good texture of the films [19]. Our films show very smooth surface with very low roughness. Also the resistivity of the films depends on the strain produced in the films due to substrate. We grow the film on quartz substrate and the resistivity of the films is quite low, although carrier concentration is approximately same as reported by Warmsingh et al. So the high mobility in our case may be due to good surface smoothness and low resistivity. It is observed that laser intensity can also affect the properties of films [20]. We have grown the films using 1 mm × 1 mm spot size, while Warmsingh et al. have used 1 mm × 3 mm spot size.

Temperature-dependent electrical resistivity of IMO thin films grown under vacuum at 500 °C is shown in Fig. 6. It is evident form the figure that transition form semiconductor to metallic behavior occurs around 109 K. The negative temperature coefficient of resistance (TCR) below the transition temperature and positive TCR above the transition temperature suggests that more than two competing mechanisms are operative. The negative TCR below the transition temperature indicates localization of electrons [21–22], and the positive TCR above the transition temperature shows delocalization. This delocalization of electrons leads to metallic conductivity, which is characteristic of a degenerate semiconductor [21].

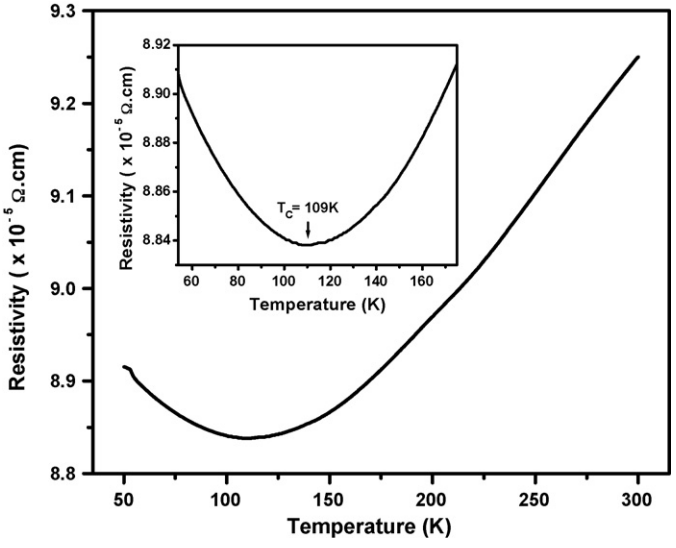

Fig. 6. Variation of electrical resistivity with temperature for IMO thin films grown at 500 °C under vacuum.

4. Conclusions

Highly transparent and conducting molybdenum-doped indium oxide films were grown on quartz substrate using the pulsed laser deposition technique. The structural, electrical and optical properties of the films depend both on growth temperature and oxygen pressure. The optical transparency increases with an increase of growth temperature but shows a small variation with oxygen pressure. The electrical properties, on the other hand, depend strongly on growth temperature as well as oxygen pressure. The resistivity of the films decreases, while mobility increases with growth temperature. However, with increases in oxygen pressure in the PLD chamber, resistivity increases and mobility decreases after attaining a maximum. The films grown at 500 °C under an oxygen pressure of 1.0×10^{-3} mbar show high mobility ($250\,cm^2/V\,s$), low resistivity ($6.7 \times 10^{-5}\,\Omega$ cm), and high transmittance (∼90%).

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