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Growth and characterization of In_2O_3 thin films prepared by pulsed laser deposition

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The effect of growth temperature and oxygen partial pressure on growth as well as electrical and optical properties of intrinsic indium oxide (In_2O_3) thin films was studied. High quality thin films were grown on quartz substrate by pulsed laser deposition (PLD) technique. Optical transmittances as well as electrical parameters such as electrical resistivity, carrier concentration, and mobility of these films depend on both oxygen pressure and growth temperature. A detailed study indicates that the films which are highly conducting and transparent correspond to an optimum growth temperature of 400 ˚C and an oxygen partial pressure of 1×10^{-6} bar. Higher transmittance (~90%), lower electrical resistivity (1.7×10^{-4} Ω.cm), and higher mobility (119 $cm^2V^{-1}s^{-1}$) of PLD grown intrinsic In_2O_3 films compared with tin doped indium oxide (ITO) suggest that PLD grown In_2O_3 could be an excellent material for optoelectronic applications.

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1. Introduction

Intrinsic and extrinsic transparent conducting oxides (TCO) have been widely used for opto-electronic devices such as light emitting diodes, photo-detectors, touch panels, flat panel displays, and solar cells [1-3]. Low resistivity, high mobility, and good transparency are the prime requirements for these devices [4-5]. There is an increasing interest in TCO with high mobility to decrease their electrical resistivity without a significant decrease in the optical transparency [6].

A number of doped TCO based on indium oxide (In_2O_3), such as indium tin oxide (ITO) [7], transition metal ion doped indium oxides [8], and silver doped indium oxide [9] have been studied extensively. High mobility transparent conducting films based on molybdenum doped indium oxide have also been fabricated by thermal reactive evaporation [10]. The fact that undoped transparent materials can be produced by controlling some of their deposition parameters [1], a number of techniques such as radio frequency plasma enhanced reactive thermal evaporation [1], sputtering [11], and spray pyrolysis [12], have been used for depositing thin films. In comparison with other techniques, pulsed laser deposition (PLD) has many advantages such as: (a) the ability to maintain target composition in the films; (b) smooth film surface; (c) high quality films can be deposited at room temperature due to high kinetic energy of atoms and ionized species in the laser produced plasma; and (d) the technique is clean and cost effective [13]. PLD is one of the promising techniques for preparing multi component nanostructured oxide films in the presence of oxidizing gases [14].

The present work deals with the fabrication and characterization of high mobility thin films of indium oxide using the PLD technique. In this paper we are reporting the effect of growth temperature and oxygen pressure on the structural, optical, and electrical properties of indium oxide thin films.

2. Experiment

Thin films of indium oxide were deposited using a sintered ceramic In_2O_3 target with a purity of 99.999%. For making the target, the indium oxide powder was cold pressed using a hydraulic press of 15 tons loads and sintered in air at 800 ˚C for 12 hours. Thin films were deposited on quartz substrate using KrF excimer laser (Lambda Physik COMPex) of frequency 248 nm at substrate temperature of room, 200 ˚C, 400 ˚C, and 600 ˚C (under vacuum of base pressure 1.2×10^{-9} bar) and under oxygen pressures of 5.0×10^{-7} bar, 1.0×10^{-6} bar, 2.5×10^{-6} bar, 6.0×10^{-6} bar, and 1.0×10^{-5} bar (at substrate temperature of 400 ˚C). The deposition chamber was initially evacuated to 1.2×10^{-9} bar and during deposition oxygen gas was introduced into the chamber to obtain the pressures mentioned above. The thickness of the films was approximately 100 nm. The laser was operated at a pulse rate of 10 Hz, with energy of 300 mJ/pulse. The laser beam was focused onto a rotating target at a 45˚ angle of incidence.

The optical transmittance measurements were done using UV-visible spectrophotometer (Ocean Optics HR4000). The resistivity and Hall coefficient of all films were measured by a standard four-probe technique. The magnetic field dependence of the Hall effect was measured with the field applied parallel to the *c* axis of the films (perpendicular to film surface) in the Van der Pauw configuration. 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 CuK_{α}. Micro-Raman scattering experiments were performed in perfect backscattering geometry using a fiber-optically coupled confocal micro-Raman system (TRIAX 320) equipped with a liquid N_2 cooled charge coupled detector. Film morphology was studied by atomic force microscopy (Veeco Dimension 3100).

3. Results and discussion

The optical transmittance spectra of In_2O_3 films deposited on quartz substrate at different growth temperature are shown in Fig. 1(a). It is observed that the growth temperature strongly affects the optical transmittance of these films. The films grown at room temperature have the least optical transparency. However, the optical transmittance increases with an increase in the growth temperature. The average percentage transmittance (in range of 500 nm-600nm) of the films grown under vacuum at room temperature, 200 ˚C, 400 ˚C, and 600 ˚C are 55 %, 72 %, 77 %, and 89 % respectively.

The effect of oxygen pressure on the optical transparency of the films is discussed next. We find that the films grown at fixed substrate temperature under partial oxygen pressure in the range 5.0×10^{-7} - 1.0×10^{-5} bar have virtually the same transmittance. However, there is improvement in the optical transparency for the films grown in oxygen atmosphere compared to the films grown under vacuum at same substrate temperature. The average percentage optical transparency for the films grown under oxygen atmosphere at room temperature, 200 ˚C, 400 ˚C, and 600 ˚C are found to be 66 %, 83 %, 89 % and 90 % respectively. Fig. 1(b) shows representative plots for the variation of oxygen pressure on the optical transparency of the films grown at 400 ˚C. We therefore report our electrical conductivity results first on films grown under vacuum and than on films grown under partial oxygen pressure in the range 5.0×10^{-7} - 1.0×10^{-5} bar.

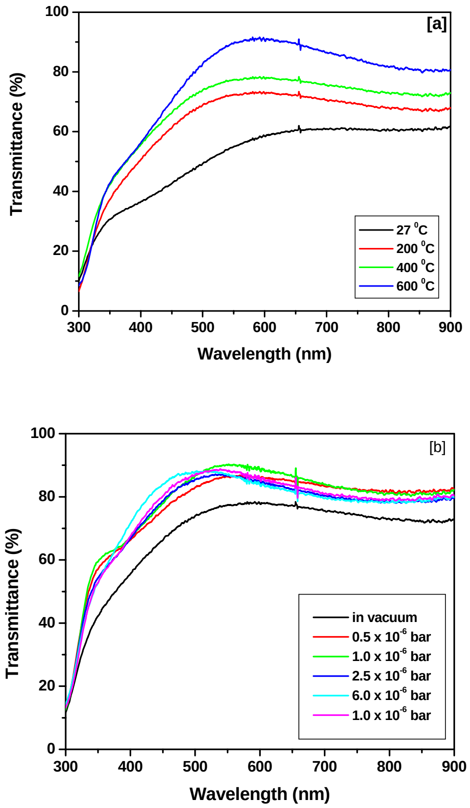


Fig. 1. Transmittance spectra of In_2O_3 films grown at (a) different temperatures in vacuum, and (b) different oxygen pressures at 400 ˚C.

The effect of the variation of substrate temperature on electrical properties of the indium oxide films grown under vacuum is shown in Fig. 2. The dependence of substrate temperature on the electrical resistivity of these films is shown in Fig. 2(a). The film grown at 200 ˚C has the least resistivity compared to the films grown at other temperatures. The carrier concentration (n) was obtained from Hall effect measurements in the magnetic field range -1.5 – +1.5 Tesla using the equation, $n = 1/eR_H$, where e is the electronic charge, and R_H is the Hall coefficient [15]. The film grown at 200 ˚C has the highest carrier concentration, but it decreases as the growth temperature increases (Fig. 2(b)). For example, the carrier concentration decreases from 6.1×10^{20} to 2.1×10^{20} cm^{-3} as the growth temperature increases from 200 ˚C to 600 ˚C. The carrier mobility (μ) of the films is calculated using the equation $\sigma = ne\mu$, where σ is the electrical conductivity [16]. The dependence of electron mobility on the growth temperature of In_2O_3 films in Fig. 2(c) shows that the mobility continuously increases with an increase of the growth temperature. For example, it increases from 32 to 98 $cm^2V^{-1}s^{-1}$ as the growth temperature increases from room temperature to 600 ˚C.

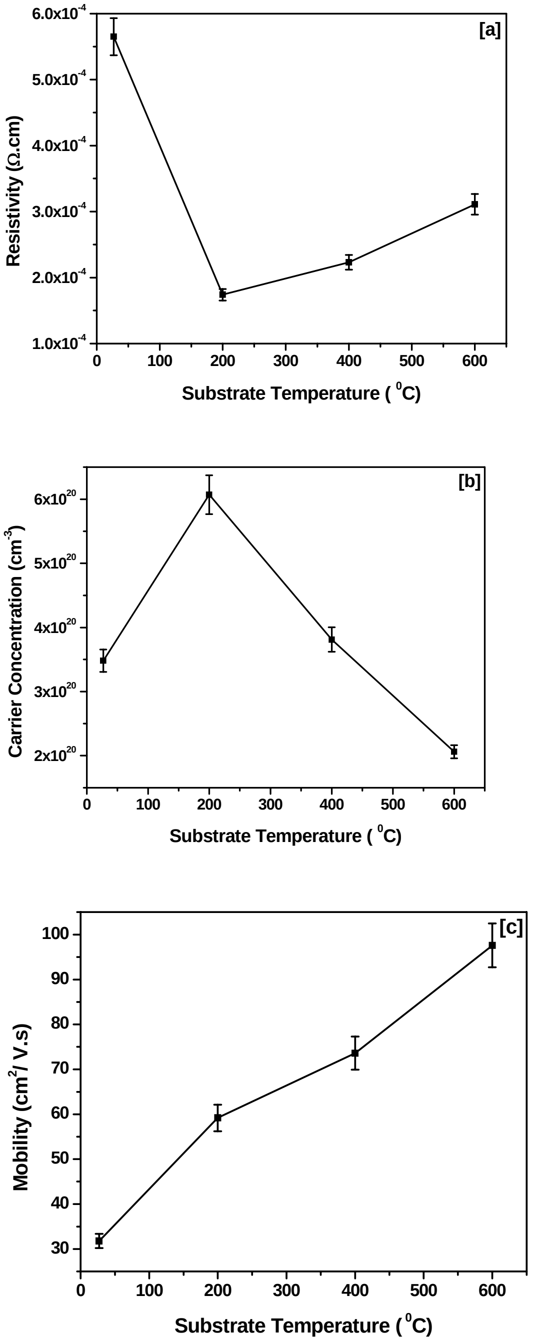


Fig. 2. Effect of substrate temperature on (a) resistivity, (b) carrier concentration, and (c) mobility of In_2O_3 films grown under vacuum (base pressure 1.2×10^{-9} bar).

A few observations based upon the optical and electrical properties are described next. First, the transmittance, both with and without oxygen pressure, of the room temperature grown films is low (< 66 %). The mobility of these films is 32 $cm^2V^{-1}s^{-1}$, which is also very small. Second, the transmittance for the films grown at 200 ˚C is 72 % under vacuum and 83 % under oxygen pressure in the range 5.0×10^{-7} - 1.0×10^{-5} bar. The mobility and conductivity of these films have increased compared to the room temperature grown films under vacuum. Third, the mobility of the films grown under vacuum at 400 ˚C and 600 ˚C are 74 $cm^2V^{-1}s^{-1}$ and 98 $cm^2V^{-1}s^{-1}$, which are among the highest reported in the literature [10]. Fourth, the transmittance of the films grown at 400 ˚C and 600 ˚C are 77 % and 89 % under vacuum and 89 % and 90 % under oxygen pressure. That is, the transmittance of the films grown under oxygen pressure at 400 ˚C and 600 ˚C are the highest for the samples investigated and approaches 90 %. Fifth, for device applications and particularly for transparent electrodes one prefers low temperature growth for avoiding inter diffusion between layers [7]. Thus, although films grown at 400 ˚C and 600 ˚C yield similar optical transmittance under oxygen pressure (≈ 90 %), similar electrical resistivity and good mobility under vacuum. We have, therefore, chosen the film grown at a fixed substrate temperature of 400 ˚C for studying the dependence of oxygen pressure on its electrical properties.

The dependence of oxygen pressure on the electrical properties of the indium oxide films grown at 400 ˚C is shown in Fig. 3. The resistivity of the films first decreases with oxygen pressure, attains a minimum at an oxygen pressure of 1×10^{-6} bar, and then increases with an increase in oxygen pressure (Fig. 3(a)). Fig. 3(b) shows that the carrier concentration first decreases with an increase in oxygen pressure up to 1.0×10^{-6} bar, and then it increases monotonically. The mobility of the films, on the other hand, first increases with an increase in the oxygen pressure up to 1.0×10^{-6} bar and then it decreases with an increase in oxygen pressure. Mobility as high as 119 $cm^2V^{-1}s^{-1}$ has been obtained. These results are shown in Fig. 3(c). From the above studies it is clear that a growth temperature of 400 ˚C and an oxygen pressure of 1.0×10^{-6} bar favor growth of highly conducting and transparent films which have better electrical and optical properties compared with ITO [17].

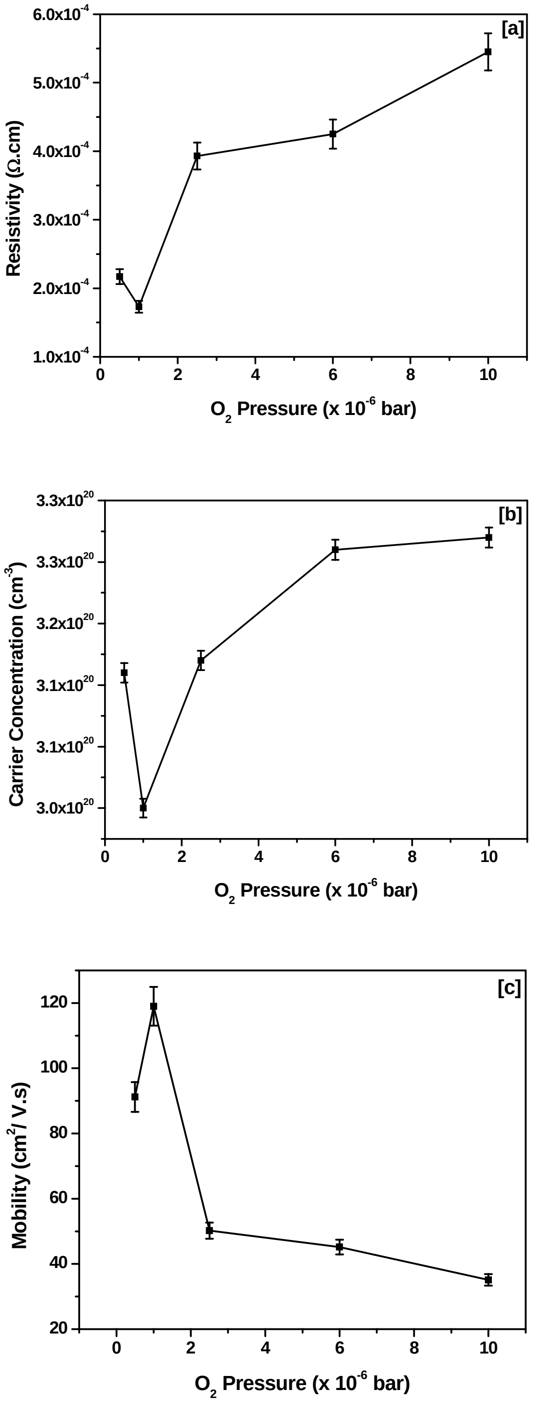


Fig. 3. Effect of oxygen pressure on (a) resistivity, (b) carrier concentration, and (c) mobility of In_2O_3 films grown at 400 ˚C.

In order to better understand the behavior of observed electrical properties, for films grown under vacuum (at various temperatures) and under oxygen pressure (at a fixed substrate temperature of 400 ˚C), we have also investigated structural properties. The structural characterization of In_2O_3 films has been performed using XRD, Raman spectroscopy, and AFM. The X-ray diffraction profiles of In_2O_3 films deposited on quartz at different growth temperatures under vacuum (Fig. 4(a)) show that the crystallinity in the deposited films depends on the growth temperature. Fig. 4(b) shows the effect of oxygen pressure on the crystallinity of the films grown at 400 ˚C. Low oxygen pressure in the PLD chamber during the film growth is observed to favor the formation of more crystalline films. The XRD patterns of Fig. 4 provide evidence for the presence of single phase crystalline indium oxide structure (body centered cubic lattice) [12]. 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 (222) diffraction line, and θ is the diffraction angle of the XRD spectra [18]. The effect of growth temperature and oxygen pressure on the particle size and the calculated percentage strain are shown in Fig. 5. As one would expect, the particle size increases with increase in growth temperature. Variation of oxygen pressure during growth of these films also affects the particle size, which decreases with an increase in the oxygen pressure in the PLD chamber.

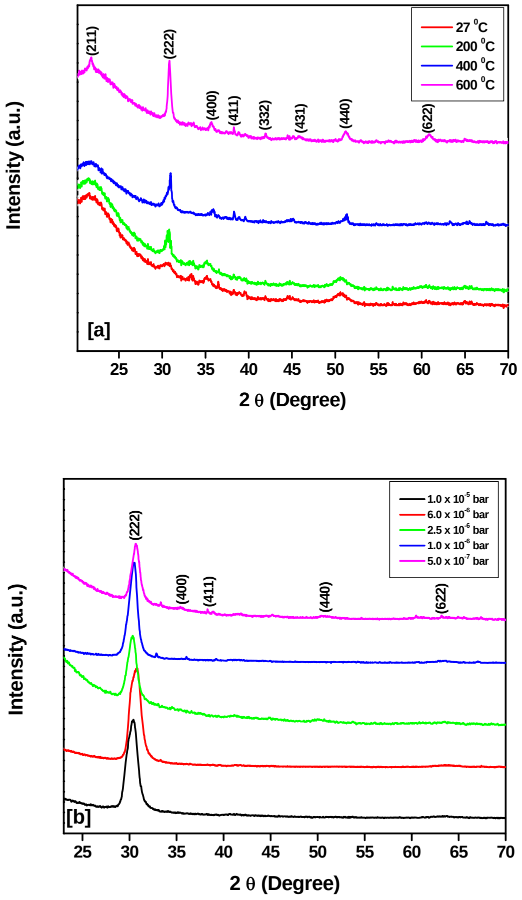


Fig. 4. XRD patterns of In_2O_3 films grown at (a) different temperatures in vacuum, and (b) different oxygen pressure (at 400 ˚C).

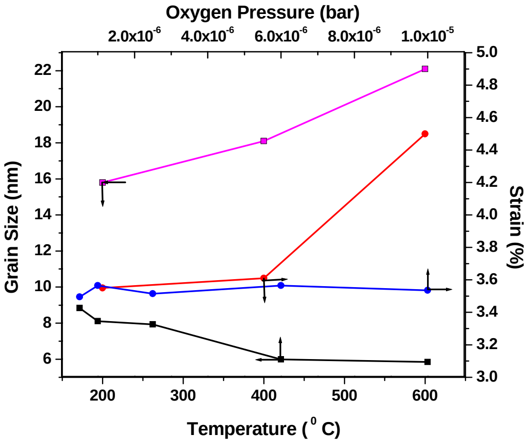


Fig. 5. Effect of growth temperature and oxygen pressure on grain size and percentage strain of In_2O_3 films.

Raman spectroscopic studies of all the In_2O_3 films have been performed at room temperature. Characteristic Raman peaks corresponding to indium oxide are observed at 496 and 627 cm^{-1} for all the films. The Raman spectra of a few selected indium oxide films grown under vacuum and under oxygen pressure are shown in Fig. 6. 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) + 16 T_u (i.r.) modes [19]. All the observed modes correspond to band positions reported in literature for cubic indium oxide [20]. Raman spectra and the x-ray diffraction analysis of the indium oxide films thus show the presence of a cubic phase.

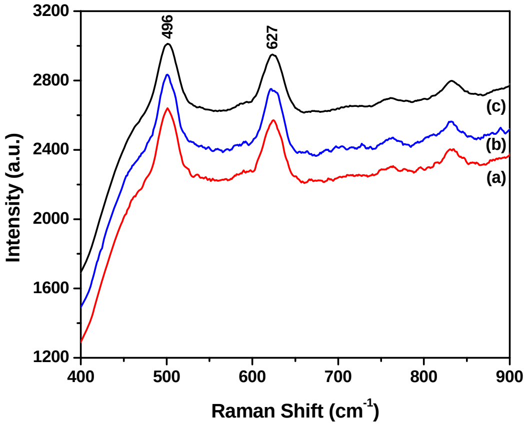
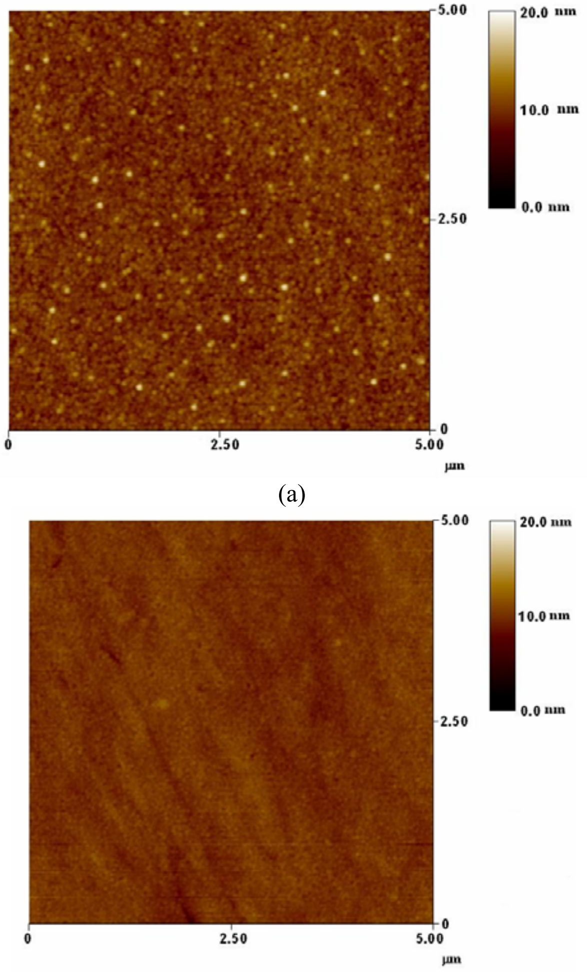


Fig. 6. Raman spectra of In_2O_3 thin films grown at 400 ˚C in vacuum (a), under oxygen pressure of 6 × 10^{-6} bar (b), and 1 × 10^{-6} bar (c).

Atomic force microscopy (AFM) results to examine surface morphology of the films are presented next in Fig. 7. The growth temperature is seen to play a significant role on film morphology. The film grown in vacuum at 200 ˚C is smoother and has less surface roughness compared to the film grown at 600 ˚C. The presence of oxygen during the film growth also plays a crucial role on the morphological properties of the indium oxide films. The most uniform films having least surface roughness were obtained for the films grown at 400 ˚C under an oxygen pressure of 1 × 10^{-6} bar (Fig. 7(b)), which is believed to be due to the formation of a solid solution with a crystal structure. The root mean square (rms) value of surface roughness of this film was found to be 1.1 nm over an area of 5 × 5 µm^2, indicating that the films have highly smooth surface.



(a)

(b)

Fig. 7. AFM images of In_2O_3 films grown at 400 ˚C under oxygen pressures of (a) 6 × 10^{-6} bar and (b) 1 × 10^{-6} bar.

The observed electrical properties of In_2O_3 films grown at different substrate temperatures can now be explained on the basis of crystallinity and number of oxygen vacancies. It has been observed that the grain size increases with increase in substrate temperature (Fig. 5) which lead to reduced grain boundary scattering and thus to decreased electrical resistivity [21]. However, creation of oxygen vacancies in films grown at different temperatures also determines free carrier generation, which can change the resistivity for the films. It is the combination of substrate temperature, oxygen vacancies, and the grain size which determine the film resistivity, the carrier concentration and the mobility. As the temperature increases, the grain size increasers but the oxygen vacancies decrease. Consequently, the carrier concentration decreases and the resistivity increases.

The highest mobility observed is 119 $cm^2V^{-1}s^{-1}$ and this occurs for films grown at 400 ˚C under an oxygen pressure of 1.0×10^{-6} bar. The mobility decreases with further increase of oxygen pressure. The low mobility of the films grown under high oxygen pressure is believed to be due to collisional energy loss of the indium oxide particles arriving at the substrate surface with the oxygen gas [22]. This energy loss considerably reduces surface mobility which gradually impairs the crystal quality. The minimum resistivity and maximum mobility films thus correspond to an optimum energy window for the arriving oxygen and indium oxide atoms to create good films. Thus the films grown at 400 ˚C under an oxygen pressure of 1.0×10^{-6} bar lead to highly conducting and highly transparent films, which have high mobility (up to 119 $cm^2V^{-1}s^{-1}$), low resistivity (1.7×10^{-4} Ω.cm), and relatively high transmittance of ~90 %.

4. Conclusions

The effect of growth temperature and oxygen partial pressure on growth as well as electrical and optical properties of PLD grown indium oxide thin films have been studied. The electrical and optical properties of these films depend on both substrate temperature and oxygen pressure in the deposition chamber. The optical transparency significantly increases with an increase of growth temperature but shows a small variation with oxygen pressure within the range 5.0×10^{-7} - 1.0×10^{-5} bar. The electrical properties, on the other hand, depend strongly on growth temperature as well as oxygen pressure. A growth temperature of 400 ˚C and an oxygen pressure of 1.0×10^{-6} bar favor the growth of highly conducting and transparent films which have better electrical and optical properties compared with ITO. Indium oxide thin films grown via pulsed laser deposition could be an excellent candidate for future optoelectronic devices.

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Reference

[1] C. N. Carvalho, G. Lavareda, A. Amaral, O. Conde, A. R. Ramos, J. Non -Cryst. Solids **352** , 2315 (2006).
[2] A. V. Singh, R. M. Mehra, J. Appl. Phys. **90**, 5661 (2001).
[3] J. H. Lee, S. Y. Lee, B. O. Park, Mat. Sci., Eng B **127**, 267 (2006).
[4] H. Kim, A. Pique, J. S. Horwitz, H. Murata, Z. H. Kafafi, C. M. Gilmore, D. B. Chrisey, Thin Solid Films **377**, 798 (2000).
[5] P. F. Newhouse, C. H. Park, D. A. Keszler, J. Tate, P. S. Nyholm, Appl. Phys. Lett. **87**, 112108 (2005).
[6] H. F. A. M. Hest, M. S. Dabney, J. D. Perkins, D. S. Ginley, Thin Solids Films **496** , 70 (2006).
[7] 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).
[8] In-Bo Shim, C. S. Kim, J. Magn. Magn. Mater. **272-276**, e1571 (2004).
[9] A. Subrahmanyam, U. K. Barik, J. Phys. Chem. Solids **67**, 1518 (2006).
[10] Y. Meng, X. Yang, H. Chen, J. Shen, Y. Jiang, Z. Zhang, Z. Hua, J. Vac. Sci. Technol. A **20**, 288 (2002).
[11] P. Malar, V. Vijayan, A. K. Tyagi, S. Kasiviswanathan, Nucl. Instrum. Meth. Phys Res. B **229** , 406 (2005).
[12] P. K. Manoj, K. G. Gopchandran, P. Koshy, V. K. Vaidyan, B. Joseph, Opt. Mater. **28**, 1405 (2006).
[13] B. D. Chrisey, G. K. Hubler, Pulsed laser deposition of thin films (Wiley, New York, 1994).
[14] A. Gupta, J. Appl. Phys. **73**, 7877 (1993).
[15] I. Yasuhiro, K. Hirokazu, Appl. Surf. Sci. **169**, 508 (2001).
[16] B. A. Cook, J. L. Harringa, J. Appl. Phys. **83**, 5858 (1998).
[17] S. H. Kim, N. M. Park, T. Y. Kim, G. Y. Sung, Thin Solid Films **475** , 262 (2005).
[18] X. D. Zhou, W. Huebner, Appl. Phys. Lett. **79**, 3512 (2001).
[19] W. B. White, V. G. Keramidas, Spectrochem. Acta Part A **28** , 501 (1972).
[20] M. Rojas-Lopez, J. Nieto-Navarro, E. Rosendo, H. Navarro-Contreras, M. A. Vidal, Thin Solid Films **379** , 94 (2000).
[21] H. Kim, J. S. Horwitz, G. P. Kushto, S. B. Qadri, Z. H. Kafafi, D. B. Chrisey, Appl. Phys. Lett. **78**, 1050 (2001).
[22] T. K. Yong, T. Y. Tou, B. S. Teo, Appl. Surf. Sci. **248** , 388 (2005).

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