

Role of Sn doping in In_2O_3 thin films on polymer substrates by pulsed-laser deposition at room temperature

J. Matthijn Dekkers, Guus Rijnders,^{a)} and Dave H. A. Blank

MESA⁺ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, 7500AE Enschede, The Netherlands

(Received 10 September 2005; accepted 16 March 2006; published online 12 April 2006)

The influence of Sn doping in In_2O_3 thin films on conductance, transmission, and granular structure has been studied. By careful control of the pulsed-laser deposition parameters, films with high optical transmittance ($>85\%$) and low resistivity ($\rho=4.1 \times 10^{-4} \Omega \text{ cm}$) are grown at room temperature on polyethylene terephthalate substrates. The films ablated from Sn-doped targets are more resistive compared to samples of pure In_2O_3 . Due to increased scattering, the charge carrier mobility in Sn-doped films is lower compared to the undoped samples. A relation between the structural properties and the amount of Sn doping is observed. The electrical properties of films with different compositions are influenced by a different size and formation of grains during growth.

© 2006 American Institute of Physics. [DOI: 10.1063/1.2195096]

Indium tin oxide (ITO) films are widely used as transparent conductors in numerous applications, such as organic light-emitting diodes (OLED's), flat panel displays, and solar cells, because of the excellent optical and electrical properties. In many of these applications there is a strong need to replace the commonly used glass substrates for cheap, lightweighted, and flexible polymers. It is known that the properties of ITO films have been shown to depend mainly on the oxygen pressure and substrate temperature during growth.¹⁻³ Polymer substrates, however, cannot sustain the high temperatures (300–500 °C) normally used to grow ITO films with excellent properties, i.e., low resistivity and high optical transmittance. Donor generation in these ITO films is governed by two mechanisms: the creation of double charged oxygen vacancies, and the contribution of a single electron for each Sn^{4+} cation substituted on an In^{3+} site. Whereas the first is mainly dependent on the oxygen partial pressure during deposition, the second is dependent on SnO_2 doping concentration as well as deposition temperature, since it is a thermally activated mechanism. A precise control of the process parameters during growth is therefore required in order to obtain high quality films at low substrate temperatures. In the present study we use pulsed-laser deposition (PLD) to grow ITO films at room temperature on polymer substrates. In particular, the role of Sn doping on the grain growth during the PLD process will be investigated and related to the electrical properties of ITO.

ITO films, with thickness of 125 nm, were deposited on polyethylene terephthalate (PET) substrates. Material was ablated from pure and SnO_2 doped In_2O_3 targets (Umicore Specialty Materials) using a KrF excimer laser (Lambda Physik Compex 205). In contrast to the deposition pressure, the fluency on the target, laser frequency, and distance from target to substrate were fixed at 3 J/cm², 10 Hz, and 50 mm, respectively. The substrates were cut from commercially available 1 mm thick PET laminates (Kubra BV). Prior to deposition the PET substrates were ultrasonically cleaned in ethanol. Film thickness measurements were performed using a stylus profilometer (Alpha Step 250, Tencor Instruments).

Electrical resistivity and Hall mobility were measured at room temperature using a standard van der Pauw four-point probe technique. Optical data were collected with a Varian Cary 50 UV-Vis spectrophotometer. The bare PET substrates were used as a transmission reference. In order to check the structure and grain size, measurements were performed on a Philips CM30 transmission electron microscope (TEM). For this experiment films of 25 nm were deposited on Cu grid at similar conditions as the 125 nm films on PET. Atomic force microscopy data were obtained by means of a nanoscope III.

The existence of an optimum oxygen pressure for ITO growth at room temperature, where a high transmittance and low resistivity can be obtained, has been shown earlier by other authors.⁴⁻⁶ We examined this pressure regime for films with different compositions: pure, 2, 5, and 10 wt % SnO_2 doped In_2O_3 . For each composition a series of films is deposited on the polymer substrates at room temperature. Next to the composition, we varied the oxygen deposition pressure close to the optimum pressure in steps of 0.002 mbar. In this pressure regime ($P=0.003-0.033$ mbar) no noticeable thickness variations have been observed. Subsequently, the resistivity and the average optical transmittance in the visible spectrum (400–700 nm) are measured for different samples. The resulting curves of the electrical and optical data are plotted in Fig. 1.

In terms of resistivity, the data show an optimum around 0.015 mbar for all compositions. In this regime the resistivity is in the order of $5 \times 10^{-4} \Omega \text{ cm}$. However, in contrast to high temperature deposition,² lowest resistivity is observed for In_2O_3 films without additional SnO_2 doping. The In_2O_3 film grown at optimum conditions has a resistivity of $\rho=4.1 \times 10^{-4} \Omega \text{ cm}$. This value is comparable to that of films grown at high temperature. Only epitaxial films on yttria-stabilized zirconia (YSZ) show somewhat lower values⁷ ($\rho=7.7 \times 10^{-5} \Omega \text{ cm}$).

The optical transmittance is also at an optimum in this narrow pressure region around 0.015 mbar, and is as high as 85% [Fig. 1(b)]. At lower pressures the optical transmittance decreases rapidly. The increasing oxygen deficiency causes a darkening of these films. At higher pressures, the transmittance drops as a result of the narrowing band gap. These

^{a)}Electronic mail: a.j.h.m.rijnders@utwente.nl

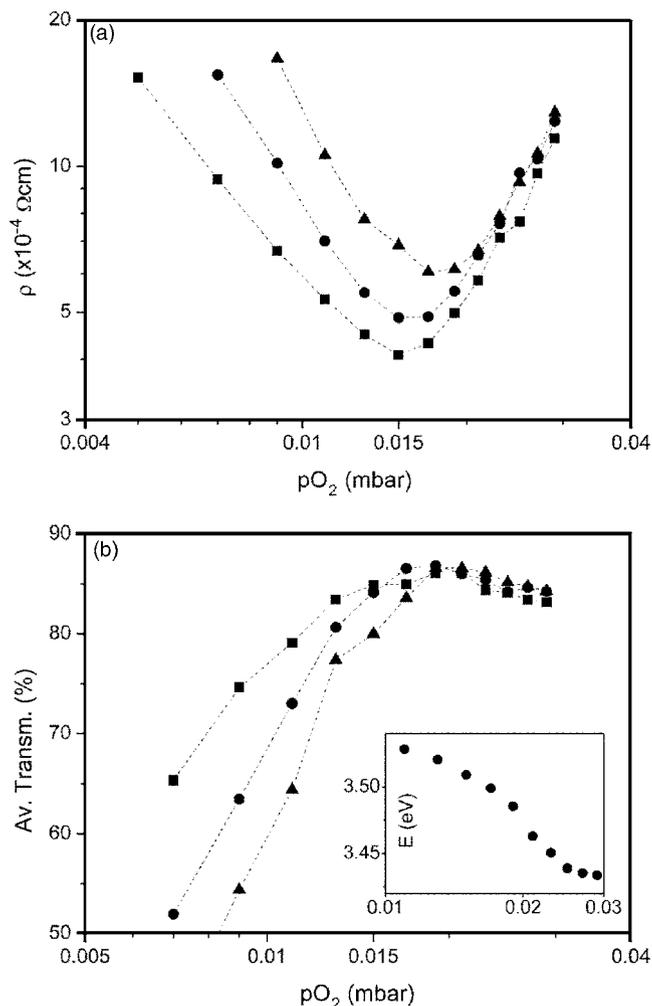


FIG. 1. Resistivity (a) and average transmission (400–700 nm) (b) of In_2O_3 films with 10 wt % (triangles), 5 wt % (circles), and 0 wt % (squares) Sn doping vs the oxygen deposition pressure. Inset in (b) shows the band gap energy and oxygen pressure relation.

films are yellowish, and the average transmittance is decreased. This is known to be caused by the Burstein-Moss (BM) shift,⁸ and is dependent on the carrier concentration. The measured band gap [inset in Fig. 1(b)] obeys the $n^{2/3}$ dependence as expected from BM theory.

In order to understand the resistivity data we performed Hall measurements to obtain the carrier density, and calculate the electron mobility. The results are plotted in Fig. 2 for

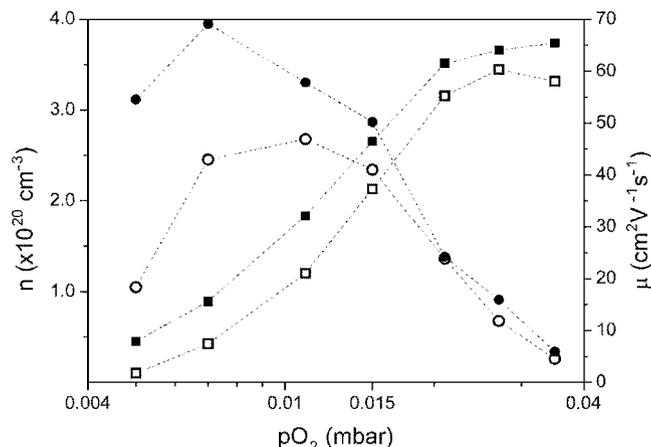


FIG. 2. Carrier concentration n (circles) and mobility μ (squares) of In_2O_3 (closed) and ITO 10% (open) vs the oxygen deposition pressure.

two compositions: pure In_2O_3 and ITO 10 wt %. As the oxygen pressure decreases, more oxygen vacancies are incorporated in the film, increasing the carrier density for both compositions. However, for ITO 10 wt % these values are somewhat lower than for pure In_2O_3 . In contrast to high temperature deposition, the addition of SnO_2 does not contribute to an increased carrier density, but it seems to deteriorate the film properties instead. The majority of Sn atoms are not thermally activated, i.e., substituting In^{3+} , and are believed to form neutral complexes with the oxygen anions.⁹ The charge carrier formation in ITO films grown at room temperature can therefore be mainly ascribed to oxygen vacancies. Note that when grown at high temperatures, the carrier density of SnO_2 doped In_2O_3 can be as high as 10^{21} cm^{-3} .

The mobility of the charge carriers is dependent on the scattering centers; in crystalline ITO films these are mainly ionized impurities.¹⁰ The number of ionized impurities (oxygen vacancies and Sn ions) is directly related to the carrier density. As oxygen deposition pressure increases, the amount of charge carriers decreases due to a smaller number of oxygen vacancies. As can be seen in Fig. 2, the total mobility is therefore higher since the number of ionized impurities decreases. However, independent of the difference in charge carrier concentration, the mobility for ITO films is considerably lower than for In_2O_3 for each deposition pressure. Apparently, in our amorphous/polycrystalline films, other scattering mechanisms play a role and are dependent on SnO_2

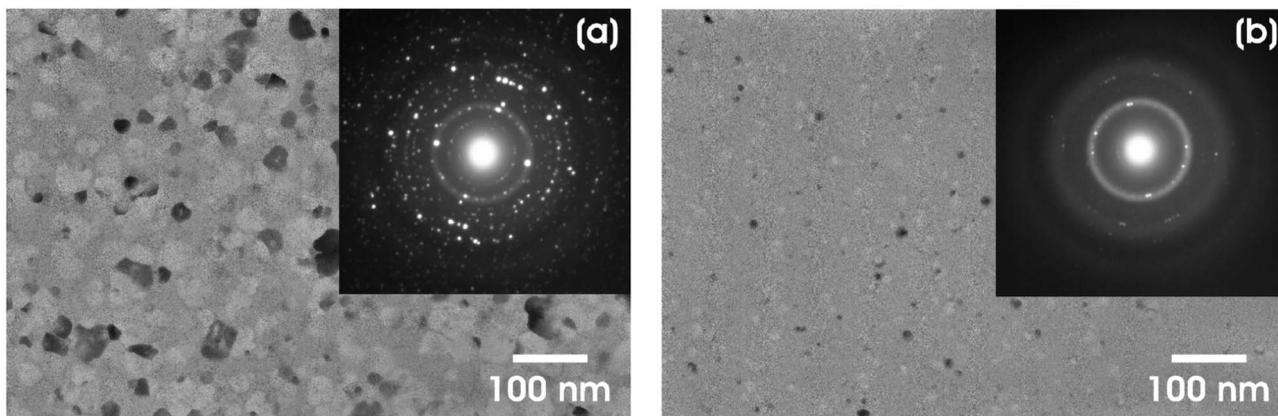


FIG. 3. TEM images and diffraction patterns of In_2O_3 (a) and ITO 10 wt % (b).

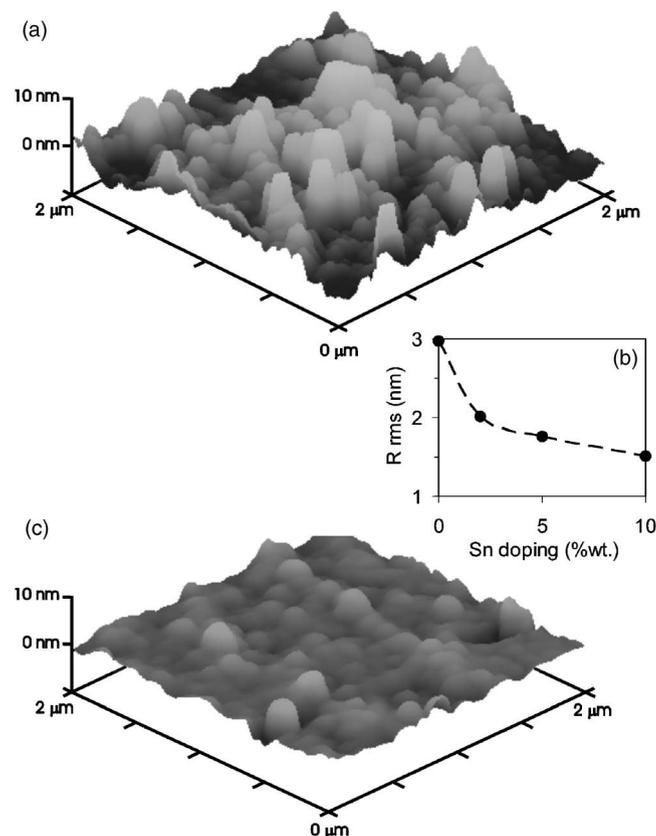


FIG. 4. AFM micrographs of In_2O_3 (a) and ITO 10 wt % (b) films. The relation between the rms surface roughness vs doping concentration (c).

doping. As mentioned earlier, Sn atoms can form neutral complexes and precipitates, acting as neutral scattering centers. The amount of neutral defects will be substantially higher in our room temperature grown films, and will no longer play a marginal role as stated by Hamberg and Cranqvist.¹¹ Moreover, the low crystallinity also induces scattering at grain boundaries,¹⁰ further lowering the mobility. By means of TEM the difference in grain sizes are investigated. Figure 3 shows transmission electron micrographs and diffraction patterns of undoped and doped In_2O_3 . A clear difference in structural properties can be seen. The ITO 10 wt % film has a nanocrystalline, nearly amorphous phase, confirmed by the hazy diffraction rings, whereas films of pure In_2O_3 clearly contain visible crystallites. The TEM micrographs of 2 and 5 wt % doping (not shown) are intermediate states complementing the trend of decreasing crystallinity as the doping level is increased. Although the size of

these crystallites is still too small to obtain conclusive x-ray diffraction (XRD) data, the surface morphology confirms the found relation between doping and crystallinity (Fig. 4). Not only the average particle size is larger at the surface of the undoped film, also the surface roughness is increased significantly, indicating a different growth mode for these compositions. Figure 4(c) illustrates the decreasing root mean square (rms) surface roughness for higher doping concentrations. Note that the average surface roughness of the polymer substrate is well below 1 nm. From the TEM and AFM data we observe that the grain size in room temperature grown films is decreasing on the addition of SnO_2 . We suppose that during PLD growth, Sn atoms act as nucleation sites. In Sn-doped In_2O_3 a larger amount of grain boundaries and increased structural disorder are observed, resulting in increased trapping of electrons and reduced mobility. Already in the initial growth stage, we observed a morphological difference between growth of doped and undoped In_2O_3 . At present, this effect is studied in more detail.¹²

In conclusion, films of ITO are grown at room temperature on polymer substrates by PLD. The deposition conditions are tuned carefully, resulting in films with electrical and optical properties comparable with high temperature deposited films. Sn-doped films are more resistive compared to pure In_2O_3 because of a structural difference. The presence of Sn during growth leads to the formation of smaller grains. The increased scattering and trapping of charge carriers deteriorate the electrical properties. For pure In_2O_3 films a lowest resistivity of $\rho = 4.1 \times 10^{-4} \Omega \text{ cm}$ is observed, and the optical transmittance well exceeds 85%.

This work has been supported by the Dutch Senter-IOP program (No. IOT00002).

- ¹F. Hanus, A. Jadin, and L. D. Laude, *Appl. Surf. Sci.* **96–98**, 807 (1996).
- ²H. Kim, J. S. Horwitz, A. Pique, C. M. Gilmore, and D. B. Chrisey, *Appl. Phys. A: Mater. Sci. Process.* **69**, S447 (1999).
- ³Sang Hyob Kim, Nae-Man Park, Tae Youb Kim, and Gun Yong Sung, *Thin Solid Films* **475**, 262 (2005).
- ⁴M. A. Morales-Paliza, M. B. Huang, and L. C. Feldman, *Thin Solid Films* **429**, 220 (2003).
- ⁵J. P. Zheng and H. S. Kwok, *Appl. Phys. Lett.* **63**, 1 (1993).
- ⁶M. A. Morales-Paliza, R. F. Haglund, and L. C. Feldman, *Appl. Phys. Lett.* **80**, 3757 (2002).
- ⁷Hiromichi Ohta, Masahiro Orita, Masahiro Hirano, Hiroaki Tanji, Hiroshi Kawazoe, and Hideo Hosono, *Appl. Phys. Lett.* **76**, 2740 (2000).
- ⁸E. Burstein, *Phys. Rev. Lett.* **93**, 632 (1954).
- ⁹G. Frank and H. Köstlin, *Appl. Phys. A: Solids Surf.* **27**, 197 (1982).
- ¹⁰Ho-Chul Lee and O. Ok Park, *Vacuum* **75**, 275 (2004).
- ¹¹I. Hamberg and C. G. Cranqvist, *J. Appl. Phys.* **60**, R123 (1986).
- ¹²J. Matthijn Dekkers, Guus Rijnders, and Dave H. A. Blank (unpublished).