Preparation of molybdenum-doped indium oxide thin films using reactive direct-current magnetron sputtering

Xifeng Li, Weina Miao, Qun Zhang,[a] Li Huang, Zhuangjian Zhang, and Zhongyi Hua
Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China

(Received 16 July 2004; accepted 3 January 2005)

High-mobility molybdenum-doped In_2O_3 films (IMO) were prepared on the normal glass substrate by reactive direct current magnetron sputtering from the molybdenum-embedded indium metal target. The effects of oxygen partial pressure, substrate temperature, and sputtering current on the optoelectrical properties of IMO films were investigated. The films with the highest carrier mobility of 50 $cm^2\ V^{-1}\ s^{-1}$, as well as the average visible transmission greater than 80% including the 1.2-mm-thick glass substrate, were obtained. The minimum resistivity of the films is 3.7×10^{-4} ohm cm. The properties of the IMO films are sensitive to the oxygen partial pressure in the sputtering environment. X-ray diffraction measurements indicate that the films show In_2O_3 crystal structure.

I. INTRODUCTION

Transparent conductive oxide (TCO) films with high electrical conductivity and high optical transparency have been widely used for many applications.[1,2] Of these films, In_2O_3:Sn (ITO), SnO_2:F, and ZnO:Al are the most commonly used materials because of their good optoelectrical properties and their industrial applicability at relatively low processing temperature. Generally, there are two ways to improve the electrical conductivity of the TCO thin films; one is by increasing the free-carrier concentration, and the other is by enhancing the carrier mobility. Until now, the electrical conductivity of the TCO thin films has been mainly improved by increasing the free-carrier concentration. However, the increase of the carrier concentration may lead to the degradation of the optical properties due to free carrier absorption,[3,4] whereas improving the electrical conductivity by increasing the carrier mobility can avoid sacrificing the optical properties. Consequently, carrier mobility enhancement is the more favorable alternative for high-quality TCO films.[5] Zhang's team first reported high-mobility molybdenum-doped In_2O_3 (IMO) films prepared by reactive evaporation[6–9] and thereby attracted much more attention,[10–15] not only because they represent a new way to explore the novel TCO materials, but also because TCO thin films with high mobility are of great significance in the development of transparent electronics due to high carrier mobility, which results in the high operation speeds in the transparent electronic devices.[16,17] A high valence difference of 3 between the dopant Mo ions and substituted In ions in IMO films with high carrier mobility and high visible transmission may be ascribed to the low dopant Mo concentrations and need to be further studied. Furthermore, the fabrication of high-quality IMO films by reactive direct current (dc) magnetron sputtering could be more cost effective than the other reported techniques.

In this study, reactive dc magnetron sputtering was used to deposit high-mobility IMO thin films with good crystallinity and optoelectrical properties on Mo-embedded In metal targets. The effects of oxygen partial pressure, substrate temperature, and sputtering current on the electrical and optical properties of IMO films were investigated and are discussed.

II. EXPERIMENTAL

A. Film preparation

The pure metal indium sputtering target embedded with 3 wt% pure metal molybdenum was fabricated in-house; its diameter was 51 mm and its thickness was 3 mm. The deposition chamber was evacuated by a turbo molecular pump to the base pressure of 2.0×10^{-3} Pa prior to deposition. The oxygen partial pressure was set using needle valves prior to throttling to the sputtering pressure of 1.7 Pa; both pressures were measured using an ion gauge with an yttrium oxide coated iridium cathode. The glass substrate was cleaned with ethanol and de-ionized water in an ultrasound bath for 20 min and set on the grounded bracket; its temperatures was measured using a thermocouple placed near the top of the

[a] Address all correspondence to this author.
e-mail: zhangqun@fudan.edu.cn
DOI: 10.1557/JMR.2005.0184

 © 2005 Materials Research Society

substrate and controlled by a differential control segment. The maximum temperature of the substrate was 350 °C due to limitations of the sputtering chamber. The distance between the sputtering source and the substrate was approximately 95 mm.

B. Measurements

The typical IMO film thickness of about 130 nm was measured by a stylus profilometer (Kosaka Lab. ET3000, Osaka, Japan) and calculated from the spectral transmission curves after deposition for about 15 min. The difference between measured thickness and calculated thickness was less than 5%. The sheet resistance measurements were performed using a four-point probe method. The resistivity was calculated using the sheet resistance and film thickness. The electron mobility and carrier concentration were obtained by Hall effect analysis using the van-der-Pauw method (in-house design). Optical transmission measurements from 300 to 900 nm were made with a spectrophotometer (Shimadzu UV2450, Tokyo, Japan). The crystallinities of the IMO film were examined with a Cu K_α X-ray diffractometer (Rigaku D/max-rB, Tokyo, Japan) with θ-2θ synchronous scan. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

The XRD patterns of IMO films formed at different substrate temperatures are shown in Fig. 1, in which amorphous halo peaks of glass substrates were subtracted. All the diffraction peaks were consistent with In_2O_3 polycrystalline structure, and no peaks pertinent to other crystalline structures were observed. When the substrate temperature increased from 300 to 350 °C, the intensity of diffraction peaks increased. The grain size of the films was evaluated from the half intensity width of the XRD peaks according to the Scherrer equation. The full widths at half-maximum (FWHMs) of 222 peaks for 300 and 350 °C were 0.76° and 0.40°, respectively. The average grain size evaluated from 222 peak increased from 10 to 19 nm with the increase of substrate temperature from 300 to 350 °C, which was ascribed to the improvement in the crystallinity of the films. The lattice parameters of IMO films evaluated from the 222 peaks are 1.005 nm at 300 °C and 1.007 nm at 350 °C, respectively, which are smaller than the lattice parameter of 1.0117 nm reported for In_2O_3. The decrease of lattice parameter in IMO films may be due to the incorporation of lattice defects. It also shows that lattice distortion is increased with the decrease of the substrate temperature.

Figure 2 shows the optical transmission for IMO films deposited under different oxygen partial pressures. From the figure, we know that when oxygen partial pressure is more than 1.8×10^{-2} Pa, the average visible transmission between 400 and 700 nm is over 80%, including 1.2-mm-thick normal glass substrate, showing the good transparency of the prepared films. It was noticed that the transmission of IMO films in the ultraviolet region (below 350 nm) increased slightly with the decrease of oxygen concentration when oxygen partial pressure is more than 1.8×10^{-2} Pa; then the transmission of IMO films deposited under oxygen partial pressure 1.5×10^{-2} Pa was relatively lower. However, the transmission in the near-ultraviolet region (wavelength between 350 and 400 nm) improved with the increase of oxygen concentration in the sputtering ambient.

The dependence of the average visible transmission of IMO films calculated from the transmission curve between 400 and 700 nm on oxygen partial pressure is shown in Fig. 3. For both substrate temperatures at 300 and 350 °C, the transmission decreases with decreasing oxygen partial pressure from 2.8×10^{-2} to 1.5×10^{-2} Pa.

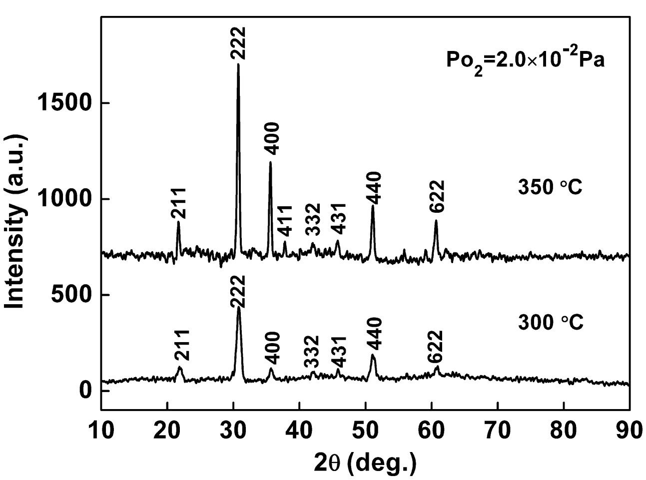

FIG. 1. θ-2θ XRD patterns of IMO films at substrate temperatures of 300 and 350 °C.

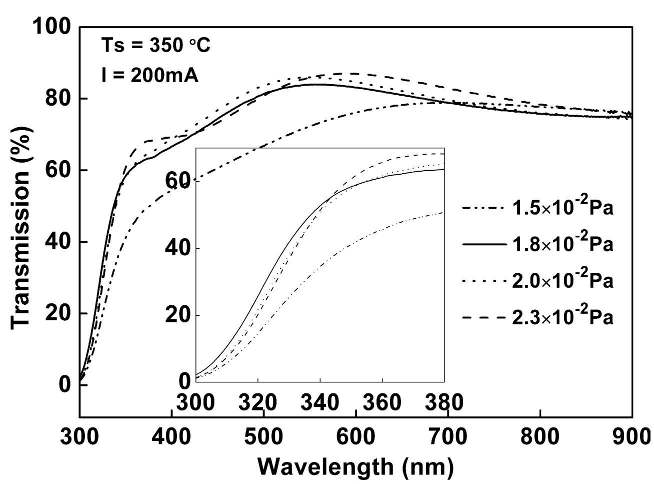

FIG. 2. Optical transmission spectra of IMO films deposited at different oxygen partial pressure; (inset) transmission spectra of IMO films between 300 and 380 nm.

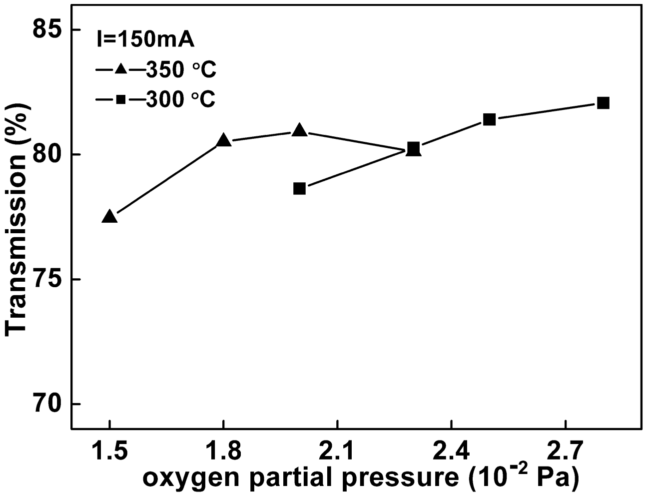

FIG. 3. Dependence of average visible transmission of IMO films on oxygen partial pressure at substrate temperatures of 300 and 350 °C.

The influence of the substrate temperature on average visible transmission is not remarkable between 300 and 350 °C. However, excessive low oxygen partial pressure will result in the drop of average visible transmission.

Figure 4 shows the resistivity of IMO films as a function of oxygen partial pressure. At substrate temperatures of 300 and 350 °C, the resistivity decreases monotonically with decreasing of oxygen partial pressure. Generally, conduction electrons in the transparent conductive oxide films are supplied from the native donor and doping donor. First, it is an overlap of an impurity band due to O^{2-} vacancies with the conduction band that provides two free electrons as a maximum.[18] Second, by randomly replacing the host cation with a doping cation, additional electron is provided to the conduction band. The resistivity ρ is proportional to the reciprocal of the carrier concentration n and the carrier mobility μ. As oxygen partial pressure decreases, the concentration of oxygen vacancies in the film also increases and accordingly causes the resistivity to drop. Figure 4 also indicates that high substrate temperature leads to lower resistivity of the IMO films at the same oxygen partial pressure. Grain boundary scattering is one of the important scattering mechanisms in polycrystalline semiconductors with small grain size.[19] XRD patterns show that higher substrate temperature is conducive to the growth of grain and improvement in crystallinity, which may be one of the reasons to reduce the grain boundary scattering and increase the carrier mobility. Therefore, the electrical resistivity decreases with increasing substrate temperature. This result suggests that higher substrate temperature may further reduce the electrical resistivity of the IMO films. This is in accordance with the result in Ref. 11.

Figure 5 shows the relationship of the resistivity of IMO films deposited at different sputtering current with the oxygen partial pressure. As shown in Fig. 5, for a fixed oxygen partial pressure, the electrical resistivity increases with the increase of sputtering current from 150 to 200 mA. In our experiment, the sputtering current was proportional to the sputtering voltage. At a low sputtering current, the energy of Ar^+ ions that collide with the target surface is low due to a low discharge voltage. Thus, the number of incident sputtered atoms on the film surface is small. Furthermore, because of the distance between the source and substrate, most of the adatoms will experience many collisions before they reached the film surface. Therefore, the properties of the deposited IMO films are impaired due to the bombardment of oxygen-related spicies such as ions and radicals. However, higher sputtering current could enhance the arrival rate of adatoms and reduce the O^{2-} ion bombardment. As a result, there an

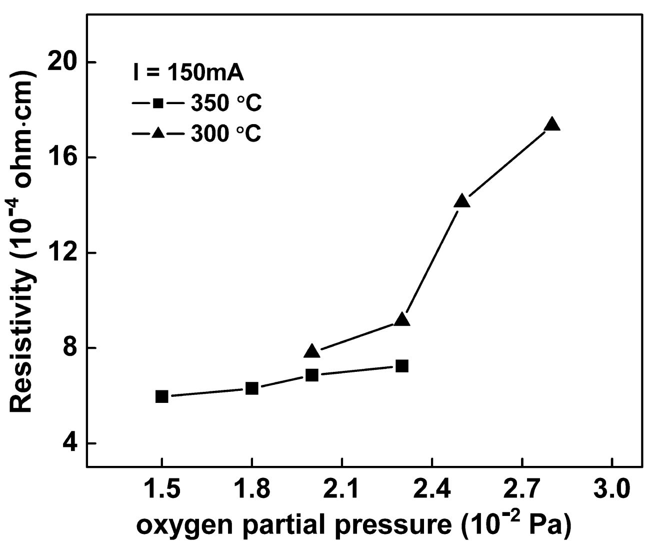

FIG. 4. Resistivity of IMO films as a function of oxygen partial pressure at different substrate temperatures.

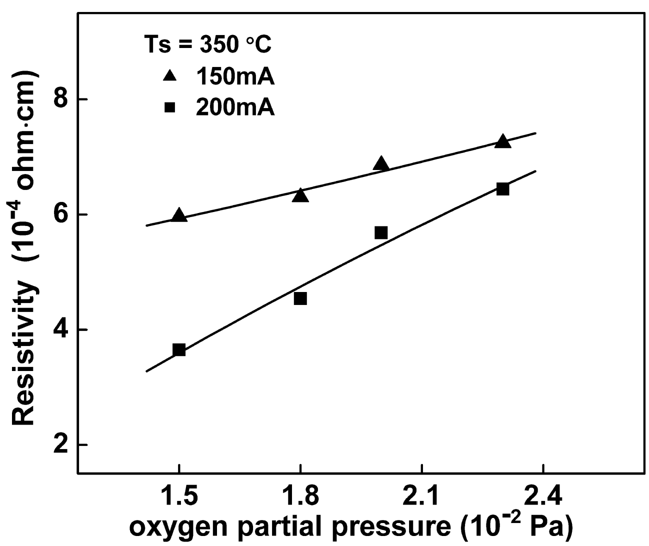

FIG. 5. Relationship of the resistivity of IMO films, deposited at different sputtering currents, to the oxygen partial pressure.

appropriate sputtering current exists at a certain oxygen partial pressure and substrate temperature, which could improve the electrical resistivity. From Fig. 5, it is shown that the best resistivity of IMO films prepared at sputtering current 200 mA and oxygen partial pressure 1.5×10^{-2} Pa is 3.7×10^{-4} ohm cm.

The dependence of carrier mobility and carrier concentration of IMO films grown at sputtering current 200 mA on the different oxygen partial pressure are shown in Fig. 6. It is obvious that the electrical properties of the films are sensitive to the amount of oxygen in the sputtering environment. With the change of the oxygen partial pressure from 1.5×10^{-2} to 2.3×10^{-2} Pa, the carrier concentration decreases from 4.0×10^{20} to 1.9×10^{20} cm^{-3} and the carrier mobility increases from 42 to 50 cm^2 V^{-1} s^{-1}. The results are almost the same as those of IMO films prepared by radio frequency (rf) sputtering, in which the best carrier mobility and the carrier concentration of the IMO films at the substrate temperature of 350 °C are 44 cm^2 V^{-1} s^{-1} and 1.3×10^{20} cm^{-3}, respectively.[11] This fact suggest that molybdenum-doped indium oxide thin films are promising TCO films.

The free electron concentration decreases with increasing oxygen partial pressure due to the decrease in oxygen vacancies. It has been reported that increasing the oxygen content in the ITO film should lead to augmentation in grain size.[20,21] Thus, the improvement in carrier mobilities is attributed to the larger grain sizes of IMO films due to the increase of oxygen partial pressure. Therefore, the fact of increasing the carrier mobility with increasing the oxygen partial pressure implies that high mobility may be limited by grain scattering.

IMO films prepared by evaporation,[6–9] rf sputtering,[11,12] and pulsed laser deposition[13,14] are also characteristic of high mobilities. Our previous study on IMO

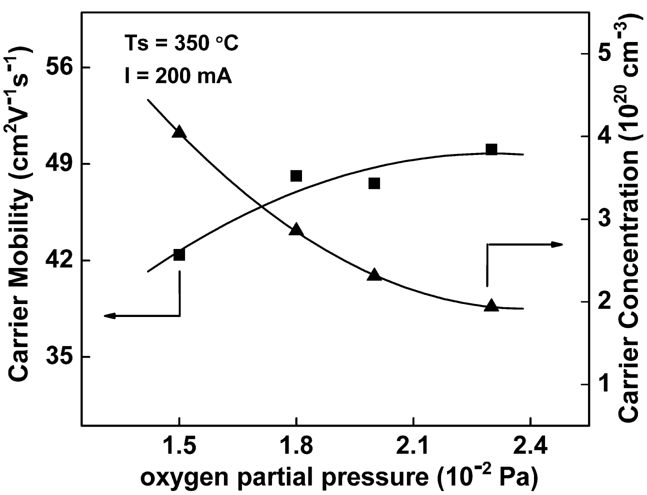

FIG. 6. Dependence of carrier mobility and carrier concentration of IMO films, grown at sputtering current 200 mA, on the different oxygen partial pressures.

shows that Mo^{6+} substituting for In^{3+} can supply three free carriers per substituting Mo ion and will contribute one carrier even after it associates with one interstitial O^{2-}. Scattering at ionized centers seems to be the greatest determining mechanism in the heavily doped TCO films. Therefore, the high valence difference between the dopant and substituted ion is of great advantage to TCO films with high carrier mobility. Yoshida et al. found that the optimally conducting IMO films is not Mo^{6+} but the mixture of Mo^{6+} and Mo^{4+}.[11] Warmsingh et al. considered that not all the doping Mo ions are activated, as is known to the case for Sn in ITO.[14] In short, molybdenum-doped indium oxide thin film is one of the promising new TCO films with high carrier mobility. The conducting mechanism of the IMO film is not yet completely understood and therefore needs to be studied further.

IV. CONCLUSION

Mo-doped In_2O_3 films were prepared by reactive dc magnetron sputtering, and the effects of oxygen partial pressure, substrate temperature, and sputtering current on the optoelectrical properties of IMO films were investigated. Films with the minimum resistivity of 3.7×10^{-4} ohm cm were obtained. The highest carrier mobility was 50 cm^2 V^{-1} s^{-1} while the average visible transmission between 400 and 700 nm was greater than 80%. High carrier mobility suggested that the IMO film could potentially be a highly transparent conductive oxide for the next generation of TCO films.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China under Grant No. 60376010.

REFERENCES

1. R.G. Gordon: Criteria for choosing transparent conductors. *MRS Bull.* **25**(8), 52 (2000).
2. D.S. Ginley and C. Bright: Transparent conducting oxides. *MRS Bull.* **25**(8), 15 (2000).
3. J.R. Bellingham, W.A. Phillips, and C.J. Adkins: Intrinsic performance limits in transparent conducting oxides. *J. Mater. Sci. Let.* **11,** 263 (1992).
4. I. Hamberg and C.G. Granqvist: Evaporated Sn-doped In_2O_3 films: Basic optical properties and applications to energy-efficient windows. *J. Appl. Phys.* **60,** R123 (1986).
5. T.J. Coutts, D.L. Young, and X. Li: Characterization of transparent conducting oxides. *MRS Bull.* **25**(8), 58 (2000).
6. Y. Meng, X.L. Yang, H.X. Chen, J. Shen, Y.M. Jiang, Z.J. Zhang, and Z.Y. Hua: New transparent conductive thin film In_2O_3:Mo. *Thin Solid Films* **394,** 218 (2001).
7. Y. Meng, X.L. Yang, H.X. Chen, J. Shen, Y.M. Jiang, Z.J. Zhang, and Z.Y. Hua: Molybdenum-doped indium oxide transparent conductive thin films. *J. Vac. Sci. Technol. A* **20,** 288 (2002).
8. Y. Meng, Z.J. Zhang, and Z.Y. Hua: Study on carrier mobility of

transparent conductive IMO films. *Vac. Sci. Technol.* **22,** 265 (2002), (in Chinese).

9. Y. Meng, X.L. Yang, H.X. Chen, J. Shen, Y.M. Jiang, and Z.J. Zhang: Transparent conductive oxide doped thin films with high valence difference between dopant and ion substituted. *Optoelectron. Technol.* **21,** 17 (2001), (in Chinese).
10. C.G. Granqvist and A. Hultåke: Transparent and conducting ITO films: New developments and applications. *Thin Solid Films* **411,** 1 (2002).
11. Y. Yoshidaa, T.A. Gessert, C.L. Perkins, and T.J. Coutts: Development of radio-frequency magnetron sputtered indium molybdenum oxide. *J. Vac. Sci. Technol. A* **21,** 1092 (2003).
12. Y. Yoshida, D.M. Wood, T.A. Gessert, and T.J. Coutts: High-mobility, sputtered films of indium oxide doped with molybdenum. *Appl. Phys. Lett.* **84,** 2097 (2004).
13. D. Ginley, B. Roy, A. Ode, C. Warmsingh, Y. Yoshida, P. Parilla, C. Teplin, T. Kaydanova, A. Miedaner, C. Curtis, A. Martinson, T. Coutts, D. Teadey, H. Hosono, and J. Perkins: Non-vacuum and PLD growth of next generation TCO materials. *Thin Solid Films* **445,** 193 (2003).
14. C. Warmsingh, Y. Yoshida, D.W. Readey, C.W. Teplin, J.D. Perkins, P.A. Parilla, L.M. Gedvilas, B.M. Keyes, and D.S. Ginley: High-mobility transparent conducting Mo-doped In_2O_3 thin films by pulsed laser deposition. *J. Appl. Phys.* **95,** 3831 (2004).
15. S-Y. Sun, J-L. Huang, and D-F. Lii: Effects of oxygen contents on the electrical and optical properties of indium molybdenum oxide films fabricated by high density plasma evaporation. *J. Vac. Sci. Technol. A* **22,** 1235 (2004).
16. J.F. Wager: Transparent electronics. *Science* **300,** 1245 (2003).
17. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono: Thin-film transistor fabricated in single-crystalline transparent oxide semiconductor. *Science* **300,** 1269 (2003).
18. R.B.H. Tahar, T. Ban, Y. Ohya, and A. Salehi: Annealing effects on opto-electronic properties of sputtered and thermally evaporated indium-tin-oxide films. *Thin Solid Films* **312,** 268 (1998).
19. M. Chen, Z.L. Pei, X. Wang, Y.H. Yu, X.H. Liu, C. Sun, and L.S. Wen: Intrinsic limit of electrical properties of transparent conductive oxide films. *J. Phys. D: Appl. Phys.* **33,** 2538 (2000).
20. T.J. Vink, W. Walravae, J.F.C. Daams, P.C. Baarslag, and J.E.A.M. Meerakker: On the homogeneity of sputter-deposited ITO films. Part I: Stress and microstructure. *Thin Solid Films* **266,** 145 (1995).
21. A.K. Kulkarni, K.H. Schulz, T.S. Lim, and M. Khan: Dependence of the sheet resistance of indium-tin-oxide thin films on grain size and grain orientation determined from x-ray diffraction techniques. *Thin Solid Films* **345,** 273 (1999).