Low-temperature deposition of transparent conducting Mn–W co-doped ZnO thin films*

Zhang Huafu(张化福)†, Liu Hanfa(刘汉法), Lei Chengxin(类成新), Zhou Aiping(周爱萍), and Yuan Changkun(袁长坤)

(School of Science, Shandong University of Technology, Zibo 255049, China)

Abstract: Mn–W co-doped ZnO (ZMWO) thin films with low resistivity and high transparency were successfully prepared on glass substrate by direct current (DC) magnetron sputtering at low temperature. The sputtering power was varied from 65 to 150 W. The crystallinity and resistivity of ZMWO films greatly depend on sputtering power while the optical transmittance and optical band gap are not sensitive to sputtering power. All the deposited films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. Considering the crystallinity and the electrical and optical properties, we suggest that the optimal sputtering power in this experiment is 90 W and, at this power, the ZMWO film has the lowest resistivity of 9.8×10^{-4} Ω·cm with a high transmittance of approximately 89% in the visible range.

Key words: Mn–W co-doped ZnO films; transparent conducting films; magnetron sputtering; sputtering power
DOI: 10.1088/1674-4926/31/8/083005 **PACC:** 6855; 8115C; 7360

1. Introduction

Transparent conducting oxides (TCO) are widely used in microelectronic devices such as liquid crystal displays, organic light-emitting diodes, and thin film solar cells[1, 2]. It is well known that tin-doped indium oxide (ITO) film is the most widely used TCO film due to its high transparency, low resistivity and high work function. However, since indium is a rare and expensive element, the cost of ITO film is very high. As a result, a stable supply of ITO may be difficult to achieve for the currently expanding market demands. Therefore, it is important to develop alternatives to the ITO thin film transparent electrodes used in liquid crystal displays[3], organic light-emitting diodes, thin film solar cells, etc. Presently, zinc oxide or impurity-doped (such as B, Al, Ga and Zr) zinc oxide films are being actively studied as alternate materials to replace ITO because they are non-toxic, inexpensive and abundant[4]. Moreover, they are also chemically stable under hydrogen plasma processes that are commonly used for the production of solar cells[5]. However, both the chemical and physical properties of currently utilized TCO besides impurity-doped ZnO are far from optimum. Improvement in the performance of TCO is desirable because their non-ideal properties will eventually ruin the complete device performance. For this purpose, the TCO community must either find better ways of optimizing the conventional TCO or explore more complex new materials with tailorable structural, physical and chemical properties. It is speculated that the latter case is more fruitful than the former because of the voluminous literature devoted to optimization of TCO film deposition without satisfying results[6]. However, to the best of our knowledge, no Mn–W co-doped zinc oxide (ZMWO) thin film has been reported yet. In our work, highly conducting and transparent ZMWO thin films were firstly deposited on glass substrate by DC magnetron sputtering, and the effect of sputtering power on the structural, electrical and optical properties of ZMWO thin films was investigated.

2. Experimental details

ZMWO films were deposited on glass substrates by DC magnetron sputtering at room temperature. Prior to the deposition, the glass substrates were ultrasonically cleaned in acetone for 10 min, immersed in alcohol for 30 min and washed by purified water. A sintered ceramic with a mixture of ZnO (99.99% purity), MnO_3 (99.99% purity) and WO_3 (99.99% purity) was employed as source material. The content of MnO_3 and WO_3 added to the ZnO target was 2.5 and 3.5 wt.%, respectively. During the process of deposition, the distance between target and substrate and the deposition pressure were controlled at 75 mm, 10 Pa respectively. The thickness of all the deposited films is in the range of 400–500 nm. In order to investigate the effects of sputtering power on the properties of ZMWO films, the power was varied from 65 to 150 W.

The structural properties of the films were analyzed with a D8 ADVANCE XRD using CuKα_1 radiation (λ = 0.15406 nm). The sheet resistance, film thickness and optical transmittance were measured with four-point probe measurements, an SGC-10 thin film thickness tester and UV-vis spectrophotometers at room temperature, respectively. The film resistivity was determined by taking the product of sheet resistance and film thickness.

3. Results and discussion

3.1. Growth rate of ZMWO films

Figure 1 shows the variation of growth rate with sputtering power. It is found that the growth rate increases nearly linearly

* Project supported by the Natural Science Foundation of Shandong Province, China (No. ZR2009GQ011).
† Corresponding author. Email: huafuzhang@126.com
Received 31 January 2010, revised manuscript received 5 April 2010

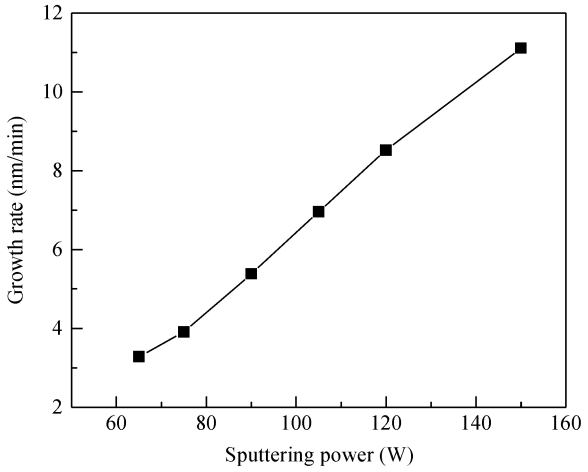

Fig. 1. Growth rate of ZMWO films as a function of sputtering power.

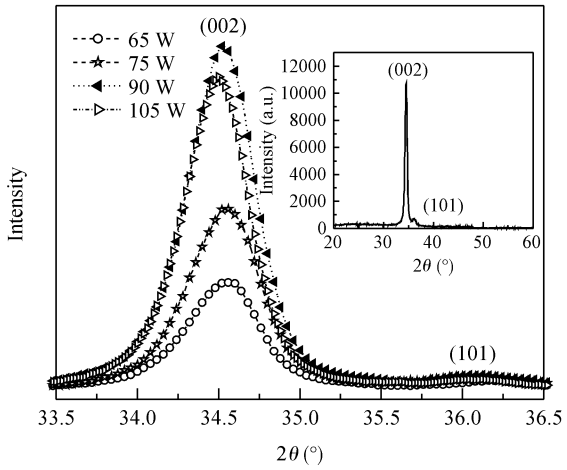

Fig. 2. XRD patterns of ZMWO films deposited at different sputtering powers. The inset shows the pattern of the film deposited at a power of 90 W.

from 3.3 to 11.1 nm when the sputtering power increases from 65 to 150 W. When the power increases, the self-polarization potential increases, leading to an increase in the kinetic energy of electrons and argon ions. The argon ion density in the neighborhood of the cathode and the sputtering yield increase; consequently the growth rate increases[7].

3.2. Structural characterization of ZMWO films

Figure 2 shows the XRD patterns of ZMWO films deposited by DC magnetron sputtering at different sputtering powers. The inset shows the pattern of the film deposited at the optimum power of 90 W. The θ–2θ scan datum of the ZMWO film exhibits a strong peak at about $2\theta = 34.5°$, which is close to the preferred orientation of the standard ZnO crystal (34.45°) and corresponds to the (002) peak. The ZnO (101) peak is also observed, but its intensity is much weaker than the (002) peak. This indicates that all the films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. We find that the position of the (002) peak changes within only a few tenths of degree while the intensity increases markedly with an increase in sputtering power up to 90 W, and above this power, the intensity decreases with further increase in sputtering power. This can be attributed to the improvement of the crystallinity when the sputtering power increased to 90 W. Similar results were also observed in ZnO:Zr films deposited by radio frequency magnetron sputtering[8]. The increase of sputtering power will lead to two effects: (1) The kinetic energy of the sputtered species increases leading to an increase of the particles' mobility in the surface of the film, which is in favor of an improvement of the crystallinity[8, 9]. (2) The surface damage caused by bombardment of the sputtered particles increases, which deteriorates the crystallinity[10]. In this experiment, as sputtering power increases from 65 to 90 W, the former effect dominates, leading to an improvement of the crystallinity. However, when the sputtering power further increases, the latter effect mentioned above is in the ascendant, leading to deterioration of the crystallinity.

Table 1. Data evaluated from XRD θ–2θ scans for the ZMWO thin films deposited at different sputtering powers.

Power (W)	FWHM (°)	Lattice constant *c* (nm)	Grain size (nm)
75	0.469	0.5187	17.5
90	0.435	0.5190	18.9
105	0.425	0.5196	19.3
120	0.429	0.5194	19.2
150	0.469	0.5209	17.5

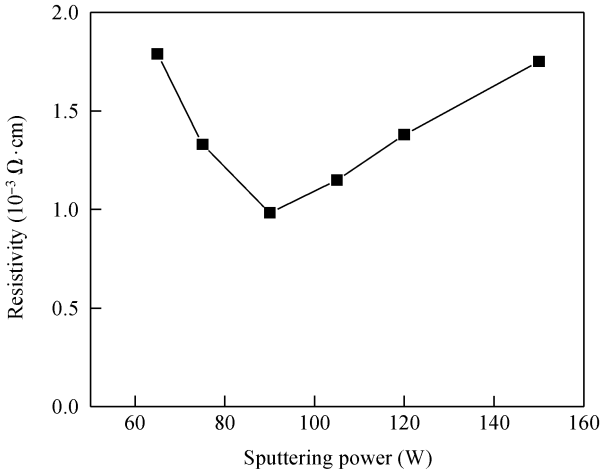

Fig. 3. Dependence of resistivity for ZMWO films on sputtering power.

From the full-width at half-maximum (FWHM) and the peak position of the (002) peak, the grain size is calculated. The grain size in the films can be estimated by the Scherrer formula. As shown in Table 1, the average grain size increases when the sputtering power increases to 105 W and then decreases with further increase in sputtering power. But the variation is small, which indicates that the grain size is not sensitive to sputtering power.

3.3. Electrical properties of ZMWO films

Figure 3 shows the dependence of the electrical resistivity of the ZMWO films on the sputtering power. With the increase of sputtering power, the electrical resistivity first decreases and

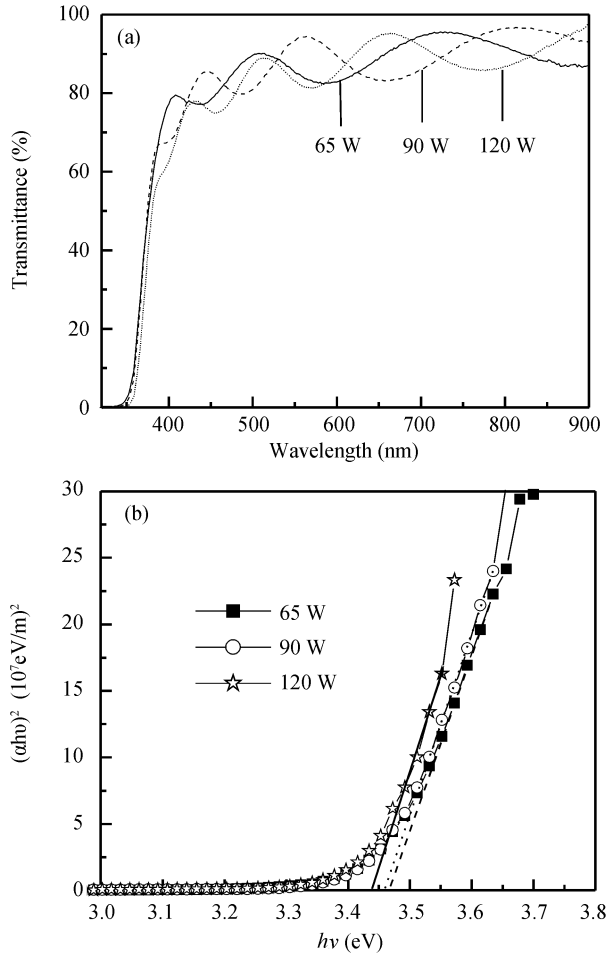

Fig. 4. (a) Effect of sputtering power on transmittance spectra for ZMWO films. (b) Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the ZMWO films deposited at 65, 90 and 120 W.

then increases. When the power is 90 W, it is obtained that the lowest resistivity of ZMWO films is 9.8×10^{-4} Ω·cm. The conductivity of the deposited films greatly depends on the film crystallinity[11−13]. As mentioned above, when the sputtering power increases up to 90 W, the crystallinity also increases with an associated decrease in the resistivity. However, with further increase in the sputtering power, the crystallinity decreases again which leads to an increase in the resistivity.

3.4. Optical properties of ZAZO films

Figure 4(a) shows the optical transmittance in the UV-vis region of ZMWO films deposited at different sputtering powers. When the power is 65, 90 and 120 W, the average transmittance of the ZMWO films in the visible range is 90, 89 and 88%, respectively. The average transmittance of ZMWO films is high and does not change much with the variation of the power.

The optical band gap was determined by extrapolation of the straight region of the plot of $(\alpha h\nu)^2$ versus $h\nu$[14]. As shown in Fig. 4(b), the optical band gap value is about 3.45 eV for the deposited films regardless of sputtering power. The optical band gap of ZMWO films is larger than that of ZnO films, which can be explained by the well-known Burstein–Moss (BM) effect. When Mn or W are deeply doped into ZnO films, the lower levels in the conduct band are occupied by electrons, leading to the increase of Fermi level and then the optical band gap widens.

4. Conclusions

ZMWO thin films with low resistivity and high transparency were successfully prepared on glass substrate by DC magnetron sputtering at low temperature. The experimental results indicate that sputtering power greatly influences the crystallinity and resistivity of ZMWO films. Considering the crystallinity, the electrical and optical properties, we suggest that the optimal sputtering power in this experiment is 90 W and, at this power, the ZMWO film has the lowest resistivity of 9.8×10^{-4} Ω·cm with a high transmittance of approximately 89% in the visible range. All experimental results indicate that ZMWO can be used to fabricate high performance TCO thin films.

References

[1] Ma H B, Cho J S, Park C H. A study of indium tin oxide thin film deposited at low temperature using facing target sputtering system. Surf Coat Technol, 2002, 153(2/3): 131
[2] Nisha M, Anusha S, Antony A, et al. Effect of substrate temperature on the growth of ITO thin films. Appl Surf Sci, 2005, 252(5): 1430
[3] Tadatsugu M. Present status of transparent conducting oxide thin-film development for indium-tin-oxide (ITO) substitutes. Thin Solid Films, 2008, 516(17): 5822
[4] Kim H, Horwitz J S, Kim W H, et al. Doped ZnO thin films as anode materials for organic light-emitting diodes. Thin Solid Films, 2002, 420/421: 539
[5] Ellmer K. Resistivity of polycrystalline zinc oxide films: current status and physical limit. J Phys D: Appl Phys, 2001, 34: 3097
[6] Cao H T, Pei Z L, Gong J, et al. Preparation and characterization of Al and Mn doped ZnO (ZnO:(Al, Mn)) transparent conducting oxide films. J Solid State Chem, 2004, 177(4/5): 1480
[7] Ben A S, Rogier B, Baud G, et al. Characterization of zirconia films deposited by r.f. magnetron sputtering. Mater Sci Eng B 1998, 57(1): 28
[8] Lv M S, Pang Z Y, Xiu X W, et al. Effect of RF power on the properties of transparent conducting zirconium-doped zinc oxide films prepared by RF magnetron sputtering. Chin Phys, 2007, 16(2): 548
[9] Zhang D H, Yang T L, Ma J, et al. Preparation of transparent conducting ZnO:Al films on polymer substrates by r.f. magnetron sputtering. Appl Surf Sci, 2000, 158(1/2): 43
[10] Shigesato Y, Paine D C. A microstructural study of low resistivity tin-doped indium oxide prepared by d.c. magnetron sputtering. Thin Solid Films, 1994, 238(1): 44
[11] Lv M S, Xiu X W, Pang Z Y, et al. Transparent conducting zirconium-doped zinc oxide films prepared by rf magnetron sputtering. Appl Surf Sci, 2005, 252(5): 2006
[12] Hao X T, Ma J, Zhang D H, et al. Thickness dependence of structural, optical and electrical properties of ZnO:Al films prepared on flexible substrates. Appl Surf Sci, 2001, 183(1/2): 137
[13] Zhang H F, Liu H F, Zhou A P, et al. Influence of the distance between target and substrate on the properties of transparent conducting Al–Zr co-doped zinc oxide thin films. Journal of Semiconductors, 2009, 30(11): 1130021
[14] Lin J M, Zhang Y Z, Ye Z Z, et al. Nb-doped ZnO transparent conducting films fabricated by pulsed laser deposition. Appl Surf Sci, 2009, 255(13/14): 6460