Influence of the distance between target and substrate on the properties of transparent conducting Al–Zr co-doped zinc oxide thin films

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

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

Abstract: Highly transparent and conducting Al–Zr co-doped zinc oxide (ZAZO) thin films were successfully prepared on glass substrate by direct current (DC) magnetron sputtering at room temperature. The distance between target and substrate was varied from 45 to 70 mm. All the deposited films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. The crystallinity increases obviously and the electrical resistivity decreases when the distance between target and substrate decreases from 70 to 50 mm. However, as the distance decreases further, the crystallinity decreases and the electrical resistivity increases. When the distance between target and substrate is 50 mm, it is found that the lowest resistivity is 6.9×10^{-4} Ω·cm. All the deposited films show a high average transmittance of above 92% in the visible range.

Key words: Al-Zr co-doped zinc oxide films; transparent conducting films; magnetron sputtering; distance between target and substrate

DOI: 10.1088/1674-4926/30/11/113002 **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[1−3]. 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 films is very high. As a result, a stable supply of ITO may be difficult to achieve for the recently expanding market demands. Therefore, it is important to develop alternatives to the ITO thin film transparent electrodes used in LCD, etc[4]. Currently, 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[5]. Moreover, they are also chemically stable under the hydrogen plasma processes that are commonly used for the production of solar cells[6]. To further improve ZnO film properties, the co-doping effect of some impurity and Al^{3+} has been studied before[7−9]. However, to the best of our knowledge, the co-doping effect of Zr^{4+} and Al^{3+} has rarely been reported before. Furthermore, zirconium dioxide (ZrO_2) has lots of unique properties such as a high refractive index, wide optical band gap, low absorption, high chemical and thermal stabilities[10], and was selected as a dopant and expected to improve the transmittance and transport properties for ZnO film. In this study, we successfully prepare highly conducting and transparent ZnO thin films using the aluminum and zirconium co-doping method by the DC magnetron sputtering technique, and the effects of distance between target and substrate on the structural, electrical and optical properties of ZAZO thin films are investigated. This report may give an added impetus to the applications of this technologically important material and give newer alternatives to ITO in applications.

2. Experimental details

ZAZO 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 15 min, marinated in alcohol for 10 min and washed by purified water. A sintered ceramic with a mixture of ZnO (99.99% purity), Al_2O_3 (99.99% purity) and ZrO_2 (99.99% purity) was employed as a source material. The optimum content of Al_2O_3 and ZrO_2 added to the ZnO target was 1.5 and 2.5 wt%, respectively, which will be reported on elsewhere. During the process of deposition, the DC sputtering power, deposition pressure and deposition time were controlled at 75 W, 2.0 Pa and 20 min, respectively. In order to investigate the effects of distance between target and substrate on the properties of ZAZO films, the distance was varied from 45 to 70 mm.

The structural properties of the films were analyzed with a D8 ADVANCE XRD using CuKα_1 radiation (λ = 0.15406 nm) and their surface morphologies were analyzed using a Sirion 200 SEM. The sheet resistance and optical transmittance were measured with four-point probe measurements and UV-vis spectrophotometers at room temperature, respectively. The thickness l of the films was measured using a SGC-10 thin film thickness tester. The film resistivity was determined

† Corresponding author. Email: huafuzhang@126.com

Received 25 May 2009, revised manuscript received 16 June 2009

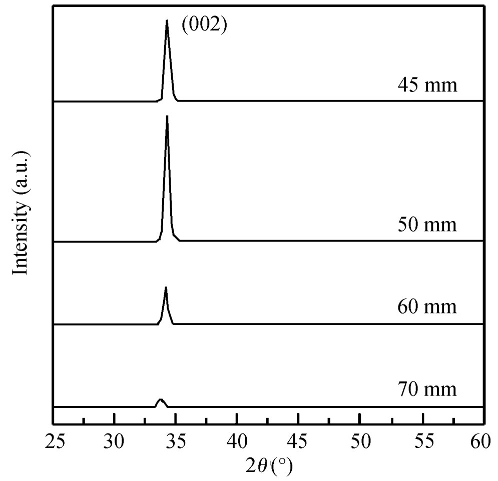

Fig. 1. X-ray diffraction patterns of ZAZO films deposited at different distances between target and substrate.

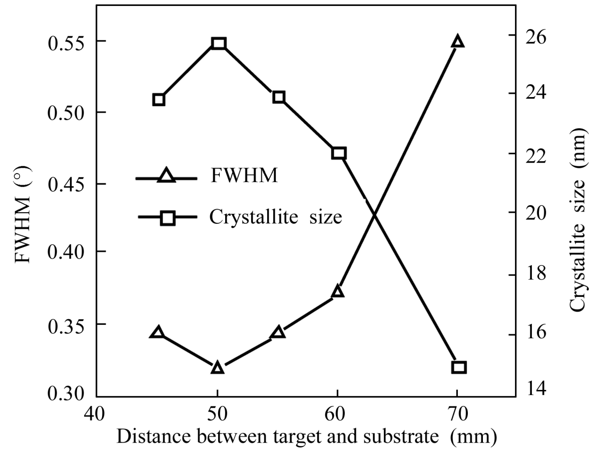

Fig. 2. FWHM and crystallite size of ZAZO films as a function of distance between target and substrate.

by taking the product of sheet resistance and film thickness.

3. Results and discussion

3.1. Structural characterization of ZAZO films

Figure 1 shows the XRD patterns of ZAZO films deposited by DC magnetron sputtering at different distances between target and substrate. The θ–2θ scan datum of the ZAZO film only exhibits a strong peak at about $2\theta = 34.1°$, which is close to the preferred orientation of the standard ZnO crystal (34.45°) and corresponds to 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. No other phases were detected from the XRD patterns. This may be due to zirconium and aluminum replacing zinc substitutionally in the hexagonal lattice or zirconium and aluminum segregating to the non-crystalline region in the grain boundary. As the distance between target and substrate decreases from 70 to 50 mm, the intensity of the (002) peak increases significantly while the full-width at half-maximum (FWHM) decreases, suggesting an improvement of the crystallinity and an increase in the crystallite size. However, as the distance decreases further to 45 mm, the peak intensity decreases while the FWHM increases, indicating a deterioration of the crystallinity and a decrease of the crystallite size.

The decrease of the distance between target and substrate will lead to three effects: (1) For smaller distances between target and substrate, the sputtered species undergo fewer collisions between the substrate and the target, and hence the kinetic energy of the sputtered species increases, which causes an increase of the particles' mobility in the surface of the film. The particles (including molecules, atoms, ions and their clusters) under a larger driving force can migrate to more suitable lattice sites and adjust their own bond direction and length to obtain optimum bonding to the adjacent ones, which are helpful for nucleation and growth, and consequently the crystallinity is improved and the crystallite size is increased[11]. (2) The surface damage caused by bombardment of the sputtered particles increases. It is proposed that the kinetic energy of the particles increases on decreasing the distance between target and substrate, so smaller distances can enhance the lattice damage by the high-energy particles, which deteriorates the crystallinity[12]. (3) The uniformity of the deposited films deteriorates with the decrease of the distance as shown in Fig. 3. The uniformity of the particles absorbed by film surfaces decreases due to the decrease of the particle collisions between substrate and target with decreasing distance, which does not favor crystallinity. In this experiment, as the distance between target and substrate decreases from 70 to 50 mm, the first effect dominates, leading to an improvement in crystallinity and an increase in the crystallite size. However, when the distance is below 50 mm, the second and third effects mentioned above are in the ascendant, resulting in a decrease of film quality.

Figure 2 shows the FWHM and crystallite size of ZAZO films as a function of the distance between target and substrate. As the distance decreases from 70 to 50 mm, the FWHM decreases from 0.549° to 0.319° while the crystallite size (evaluated by Scherrer's formula) increases from 14.9 to 25.8 nm. However, as the distance decreases further, the FWHM increases from 0.319° to 0.344° while the crystallite size decreases from 25.8 to 23.9 nm. In this study, the crystallite quality changes obviously with the variation of the distance between target and substrate.

Figure 3 shows SEM images of ZAZO films deposited at different distances between target and substrate at room temperature. From the micrographs, an obvious increase of grain size is observed when the distance decreases from 70 to 50 mm, and the surface roughness also increases simultaneously. However, with a further decrease in distance, the grain size shows a small decrease. It can also be seen that the ZAZO film structure consists of some columnar structured grains, representing c-axis oriented grains. These results agree well with

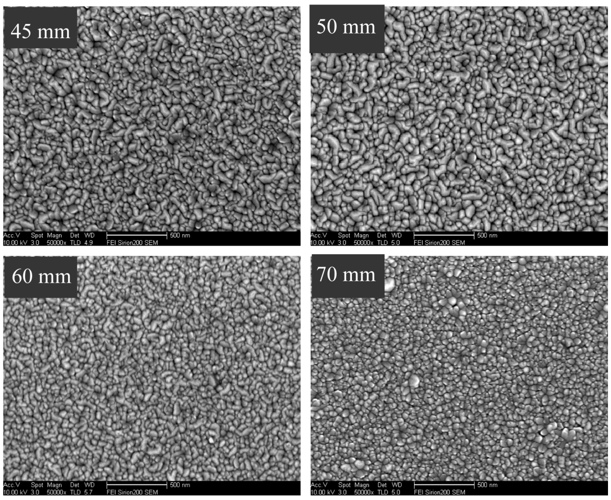

Fig. 3. SEM images of ZAZO films deposited at different distances between target and substrate.

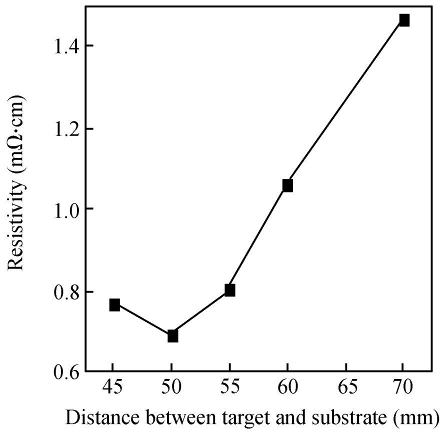

Fig. 4. Dependence of resistivity of ZAZO films on distance between target and substrate.

the XRD analysis mentioned above.

3.2. Electrical properties of ZAZO films

Figure 4 shows the dependence of the electrical resistivity of the ZAZO films on the distance between target and substrate. With the decrease of the distance, the electrical resistivity first decreases significantly and then increases a little. The increase of conductivity can be attributed to the improvement of crystallinity and an increase in the crystallite size. A larger crystallite size results in a lower density of grain boundaries, which behave as traps for free carriers and barriers for carrier transport. Hence, an increase in the crystallite size can cause a decrease in grain-boundary scattering and an increase of carrier lifetime and carrier concentration[13], and consequently leads to an increase of both the carrier concentration and Hall mobility, and therefore the electrical resistivity decreases. With the improvement of crystallinity, the concentration of electrically active donor sites is improved, which can also increase the carrier concentration[14]. As mentioned above, when the distance decreases from 70 to 50 mm, the crystallite size increases obviously leading to a decrease in the

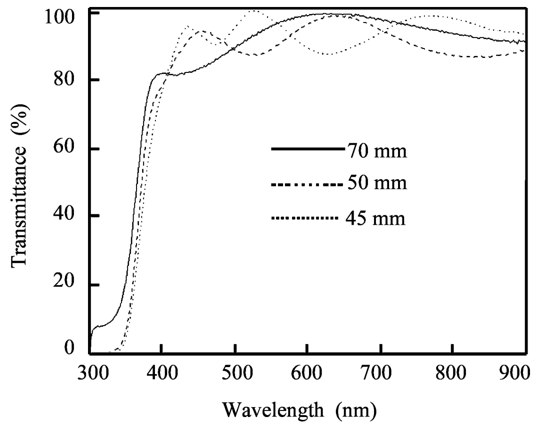

Fig. 5. Transmittance spectra of ZAZO films deposited at different distances between target and substrate.

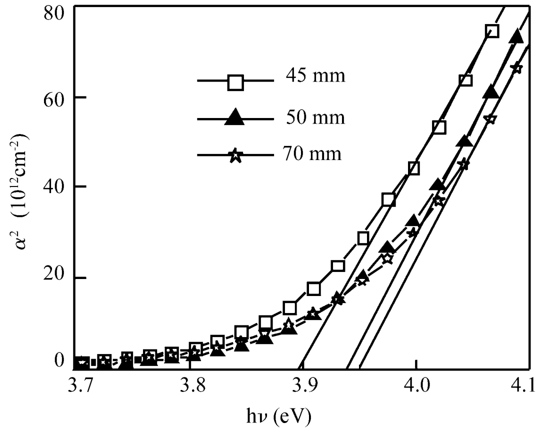

Fig. 6. Square of the absorption coefficient as a function of photon energy at different distances between target and substrate.

electrical resistivity. When the distance decreases from 50 to 45 mm, the crystallite size decreases, resulting in an increase in electrical resistivity. When the distance is 50 mm, it is found that the lowest resistivity of ZAZO films is 6.9×10^{-4} Ω·cm.

3.3. Optical properties of ZAZO films

Figure 5 shows the optical transmittance in the UV-vis region of ZAZO films deposited at different distances between target and substrate. When the distance is 70, 50 and 45 mm, the average transmittance of the ZAZO films in the visible range is 93.5%, 93.2% and 92.6%, respectively. The average transmittance of the ZAZO films is high and does not change much with variation in the distance.

The optical band gap (E_g) was determined by extrapolation of the straight region of the plot of the square of the absorption coefficient (α^2) versus photon energy ($h\nu$)[5]. As shown in Fig. 6, the optical band gap value is about 3.93 eV for all the films regardless of distance. The optical band gap of the ZAZO films is much larger than that of ZnO films, which can be explained by the well-known Burstein–Moss (BM) effect. When Zr^{4+} or Al^{3+} ions are deeply doped into ZnO films, the lower levels in the conduct band are occupied by electrons, leading to an increase in the Fermi level and widening of the optical band gap.

4. Conclusions

Highly transparent and conducting ZAZO thin films were successfully prepared on glass substrate by DC magnetron sputtering at room temperature. The effect of the distance between target and substrate on the structural, morphological, electrical and optical properties of ZAZO films was investigated in detail. All the deposited films are polycrystalline with a hexagonal structure and have a preferred orientation along the *c*-axis perpendicular to the substrate. As the distance between target and substrate decreases, the electrical resistivity of the ZAZO films initially decreases and then increases, while the crystallinity first increases and then decreases. When the distance between target and substrate is 50 mm, it is found that the lowest resistivity is 6.9×10^{-4} Ω·cm. All the deposited films show a high average transmittance of above 92% in the visible range. All experimental results indicate that ZAZO 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] Meng Z G, Peng H J, Wu C Y, et al. Room temperature deposition of thin-film indium-tin oxide on micro-fabricated color filters and its application to flat-panel displays. Journal of Optoelectronics·Laser, 2005, 16(2): 140

[4] Tadatsugu M. Present status of transparent conducting oxide thin-film development for indium-tin-oxide (ITO) substitutes. Thin Solid Films, 2008, 516(17): 5822

[5] 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

[6] Ellmer K. Resistivity of polycrystalline zinc oxide films: current status and physical limit. J Phys D: Appl Phys, 2001, 34: 3097

[7] Lin W, Ma R X, Shao W, et al. Structural, electrical and optical properties of Gd doped and undoped ZnO:Al (ZAO) thin films prepared by RF magnetron sputtering. Appl Surf Sci, 2007, 253(11): 5179

[8] Minami T, Suzuki S, Miyata T. Transparent conducting impurity-co-doped ZnO:Al thin films prepared by magnetron sputtering. Thin Solid Films, 2001, 398/399: 53

[9] Jiang M H, Liu X Y. Structural, electrical and optical properties of Al–Ti codoped ZnO (ZATO) thin films prepared by RF magnetron sputtering. Appl Surf Sci, 2008, 255(5): 3175

[10] Liang L P, Xu Y, Wu D, et al. A simple sol–gel route to ZrO_2 films with high optical performances. Mater Chem Phys, 2009, 114(1): 252

[11] 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

[12] 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

[13] 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

[14] Juang Y S, Seo J Y, Lee D W, et al. Influence of DC magnetron sputtering parameters on the properties of amorphous indium zinc oxide thin film. Thin Solid Films, 2003, 445(1): 63