DOI 10.1007/s11595-016-1324-9

Effect of Oxygen Partial Pressure on Epitaxial Growth and Properties of Laser-Ablated AZO Thin Films

WANG Chuanbin[1,2], LUO Sijun[1], SHEN Qiang[1], ZHANG Lianmeng[1*]

(1. State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China; 2. Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA)

Abstract: Al-doped ZnO (AZO) thin films were grown on *c*-sapphire substrates by laser ablation under different oxygen partial pressures (P_{O2}). The effect of P_{O2} on the crystal structure, preferred orientation as well as the electrical and optical properties of the films was investigated. The structure characterizations indicated that the as-grown films were single-phased with a wurtzite ZnO structure, showing a significant *c*-axis orientation. The films were well crystallized and exhibited better crystallinity and denser texture when deposited at higher P_{O2}. At the optimum oxygen partial pressures of 10 - 15 Pa, the AZO thin films were epitaxially grown on *c*-sapphire substrates with the (0001) plane parallel to the substrate surface, *i e,* the epitaxial relationship was AZO (000 1) // Al_2O_3 (000 1). With increasing P_{O2}, the value of Hall carrier mobility was increased remarkably while that of carrier concentration was decreased slightly, which led to an enhancement in electrical conductivity of the AZO thin films. All the films were highly transparent with an optical transmittance higher than 85 %.

Key words: AZO thin films; epitaxial growth; laser ablation; oxygen partial pressure; electrical and optical properties

1 Introduction

Transparent conductive oxide (TCO) thin films have been drawing great attention due to their outstanding optical and electrical properties including low resistivity and high transmittance in visible region. They can be widely used in various optical-electrical devices, for example, solar cells, display panels, organic light-emitting diodes, flexible thin film transistors and optical coatings, *etc*[1-4]. Typical TCO is indium tin oxide (ITO)[5], which has been by far most widely used because of its superb properties such as low resistivity (about 10^{-4} cm) and high transmittance (>80%). Unfortunately, indium is toxic, scarce and consequently expensive, which will limit the large-scale economical production of ITO films in the future. Among the possible alternatives, Al-doped zinc oxide (hereafter AZO)[6,7] has been regarded as one of the most promising TCOs to replace ITO due to its low manufacturing cost, non-toxicity, abundant source and similar electrical and optical properties to ITO. Therefore, the development of AZO thin films as the promising substitutes for indium-free transparent electrodes is extremely important, from the viewpoint of the massively growing market of transparent optoelectronics.

AZO thin films have been grown by a variety of deposition techniques[8-12], such as chemical vapor deposition, DC or RF magnetron sputtering, electron beam evaporation, pulsed laser deposition, metal organic chemical vapor deposition, and sol-gel. It was found that the electrical or/and optical properties of the as-grown AZO films were mostly affected by their structure (for example, microstructure, preferential orientation or surface morphology), while the structure could be modified by controlling the corresponding deposition process. Among those methods, laser ablation[13] is proposed to be a versatile technique for growing high-quality thin films. As for this method, the oxygen partial pressure (P_{O2}) is one of the key processing parameters, which has strong influence on

(Received: Oct. 20, 2015; Accepted: Nov. 4, 2015)

WANG Chuanbin (王传彬): Prof.; Ph D; E-mail: wangcb@whut.edu.cn

* Corresponding author: ZHANG Lianmeng (张联盟): Prof.; Ph D; E-mail: fgm@whut.edu.cn

Funded by National Natural Science Foundation of China (Nos.51272195, 51521001), 111 project (No.B13035), Hubei Provincial National Natural Science Foundation (No.2015CFB724), and Fundamental Research Funds for the Central Universities (Nos.2013-ZD-4, 2014-KF-3)

film growth[14].

In the present study, the epitaxial thin films of AZO were then grown by laser ablation under different oxygen partial pressures. The effect of P_{O2} on the epitaxial growth, electrical and optical properties of laser-ablated AZO thin films were investigated, for the purpose of further improving the electrical conductivity and optical transmittance by controlling their structures.

2 Experimental

The AZO thin films were grown on *c*-sapphire substrates by laser ablation of an Al (3 wt%) - doped ZnO ceramic target. A Q-switched Nd: YAG laser, operating at 355 nm wavelength with a pulse repetition of 10 Hz and pulse duration of 5 ns, was used for the deposition. The pulsed laser energy (laser fluence on target) and deposition temperature for growing AZO films were fixed at 3.4 J/cm^2 and 873 K, respectively. The deposition chamber was evacuated to about 1×10^{-4} Pa and then high-purity oxygen gas was injected into the chamber. The depositions took place for 15 min under different oxygen partial pressures, ranging from vacuum (about 10^{-4} Pa) to 15 Pa, respectively.

The crystal structure of the films was measured using X-ray diffraction (XRD $\theta/2\theta$ scan, Rigaku Ultima III) with Cu Kα radiation. The orientation relation of the AZO films with respect to the sapphire substrates was investigated by X-ray pole-figure (XRD ϕ scan, Rigaku RAD-2C). The surface morphology was observed by a scanning electron microscope (SEM, Hitachi S-4800). The electrical properties, including carrier mobility, concentration and electrical resistivity, were determined on a Hall measurement device (Accent Optical HL5500PC) by using the four-point probe method. The optical transmittance spectra were recorded by UV-visible-NIR spectrophotometer (Shimadzu UV-2550). All the measurements were carried out at room temperature.

3 Results and discussion

3.1 Structural characterization

Fig.1 shows the XRD patterns ($\theta/2\theta$ scan) of the AZO thin films grown on c-sapphire substrates under different oxygen partial pressures, *i e*, $P_{O2} = 10^{-4}$, 3, 6, 10, 13 and 15 Pa, respectively. We can see that besides the peaks from the sapphire substrates, only the characteristic diffraction patterns corresponding to the (000 2) AZO reflections are detected. This proves that the deposited films are single-phased in a wurtzite ZnO structure and with a *c*-axis orientation. With increasing P_{O2} from 10^{-4} to 15 Pa, the full width at half maximum (FWHM) of the (000 2) peaks decreases, indicating better crystallinity of the AZO thin films when prepared at higher oxygen partial pressures. The sharp (000 2) reflections of the AZO films grown at $P_{O2}\geqslant10$ Pa show that those films are well crystallized and highly *c*-axis oriented.

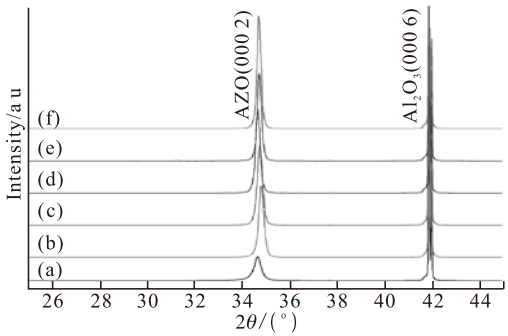

Fig.1 XRD patterns of AZO thin films grown at different P_{o2}:(a) 10^{-4}; (b) 3; (c) 6; (d) 10; (e) 13; (f) 15 Pa

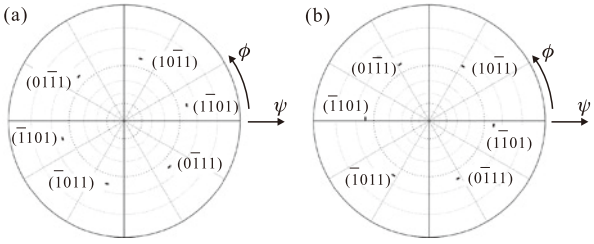

Fig.2 XRD pole figures (scan) for (10-11) plane of (000 1)-oriented AZO thin films grown at (a) P_{O2}=10 Pa and (b) P_{O2}=15 Pa

The XRD pole-figure characterization was performed by setting the diffraction angle (2θ) of AZO (10-11) plane to satisfy the Bragg law, so as to establish the in-plane orientation relationship between the as-grown (000 1)-oriented AZO thin films and the (000 1)-oriented Al_2O_3 (*c*-sapphire) substrates. The specimens were tilted (ψ-rotation) from 0 to 90 °, respectively, and then rotated by 360 ° (ψ-rotation) about the normal to the film surface at each value of ψ. Fig.2(a) and Fig.2(b) show the pole figures for (10-11) plane of the (000 1)-oriented AZO thin films grown at P_{O2} = 10 Pa and P_{O2} = 15 Pa, respectively. Six symmetrical poles resulted from AZO (10-11) reflections are identified at the tilting angle (ψ) of about 62 °, which is in agreement with the angle between the (000 1) plane and the diffracting (10-11) plane of AZO. The equally spaced reflections separated by 60° interval show that the AZO (10-11) plane is six-fold symmetry[15]. The pole-figure results confirm the

(000 1)-orientation of the AZO thin films, and further demonstrate the in-plane epitaxial relationship of the AZO films with respect to the *c*-sapphire substrates. That is, the AZO thin films were epitaxially grown on *c*-sapphire substrates with the (000 1) plane parallel to the substrate surface, *i e*, the epitaxial relationship was AZO (000 1) // Al_2O_3 (000 1).

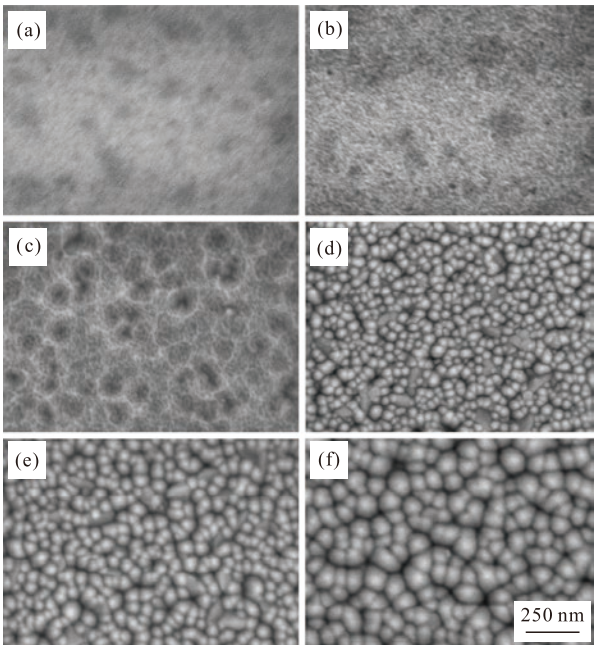

Fig.3 SEM images of surface morphology of AZO thin films grown at different P_{O2}: (a) 10^{-4}; (b) 3; (c) 6; (d) 10; (e) 13; (f) 15 Pa

The SEM images of surface morphology of the AZO thin films grown at different P_{O2} are shown in Fig.3. No well-crystallized grains can be observed in the AZO films prepared at lower oxygen partial pressures (vacuum or smaller than 10 Pa). With increasing P_{O2}, the films begin to be crystallized and the grain size is increased. The increasing in crystallite size might result from the enhancement in film's surface atomic mobility, which enables the thermodynamically favored grains to grow[16]. It can be seen from these figures that the AZO thin films deposited at P_{O2} = 10-15 Pa were well crystallized with uniform grains, showing a nearly dense texture and a smooth surface.

3.2 Electrical and optical properties

Fig.4 shows the room-temperature electrical properties of AZO thin films deposited at different P_{O2}. The value of electrical resistivity (the reciprocal of electrical conductivity) was derived from the product of carrier mobility (μ_H) and carrier concentration (N)[17]. It is noted that a close correlation between the conducting behavior and oxygen partial pressure does exist. For the AZO thin films prepared in vacuum or at lower P_{O2}, the carrier concentration N is high but begins to decrease slightly with increasing P_{O2} due to the reduction of oxygen vacancies. On the contrary, the carrier mobility H is increased remarkably with P_{O2}. As a result, the electrical resistivity of the AZO thin films is decreased with increasing P_{O2} to higher pressures until 13 Pa, but increases when P_{O2} is further evaluated to 15 Pa. A minimum value of electrical resistivity (6.52×10^{-4} cm) is obtained at P_{O2} = 13 Pa, indicating the best conductivity of AZO thin films if grown at the optimum oxygen partial pressure.

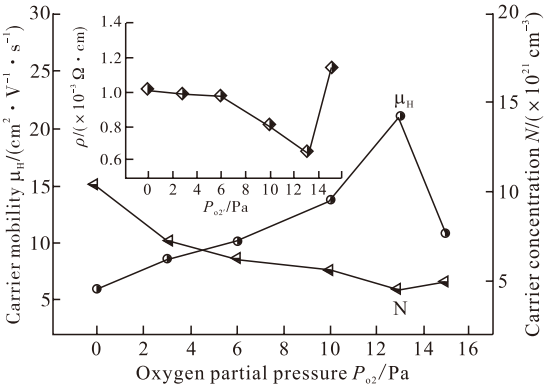

Fig.4 Electrical properties of AZO thin films as a function of P_{o2}

The variation of electrical resistivity of the AZO thin films as a function of oxygen partial pressure is mainly dependant on the changes in grain crystallinity and surface morphology at different P_{O2}. It is generally believed that better electrical conductivity could be attributed to the finer microstructure[18], including grain size and crystallinity. With increasing oxygen partial pressure, especially when P_{O2} = 10 Pa and P_{O2} = 13 Pa, the AZO grains are more crystallized and the film's surface is denser, which will improve the interconnectivity between grains and thus lead to a higher Hall carriers concentration. On the other hand, the grain size of the AZO thin films is also increased with P_{O2}. Therefore, the scattering from the grain boundaries will be weakened, which will result in a smaller grain-boundary-resistance. All those factors would be beneficial to the enhancement in electrical conductivity of the AZO thin films.

The measurement of UV-vis transmittance spectra was carried out to evaluate the potential applications for the AZO thin films in transparent optical-electrical devices. Fig.5 shows the optical transmittance spectra (200 - 800 nm) of the AZO thin films grown on the transparent c-sapphire substrates at different P_{O2} from 10^{-4} to 15 Pa, which are approximately 300 nm in thickness. It can be seen from the figure, all the AZO

films are highly transparent in the visible region with an optical transmittance higher than 85%. The sharp dropping in transmittance (so-called absorption edge) is observed in the UV region, due to the fundamental absorption resulted from ZnO. With increasing P_{O2}, the absorption edge shifts towards higher wavelengths, exhibiting a red-shifting characteristic because of the decreasing in carrier concentration[19].

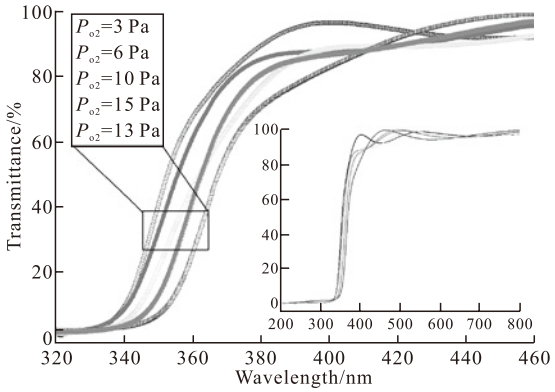

Fig.5 Optical transmittance of AZO thin films as a function of P_{O2}

From the above analyses, we can see that the epitaxially grown AZO thin films with good electrical and optical properties, resulting from high crystallinity and dense texture, could be obtained by choosing the optimum oxygen partial pressure. Our study would provide the possibility of the potential applications of the laser-ablated AZO thin films in optoelectronics.

4 Conclusions

Single-phased Al-doped ZnO (AZO) thin films with significant *c*-axis orientation were prepared by laser ablation. The films were well crystallized and exhibited better crystallinity as well as denser texture when deposited at higher oxygen partial pressures (P_{O2}). By choosing the optimum P_{O2} of 10 - 15 Pa, the AZO thin films could be epitaxially grown on *c*-sapphire substrates, and the epitaxial relationship of the films with respect to the substrates was found to be AZO (000 1) // Al_2O_3 (000 1). With increasing P_{O2}, the electrical resistivity of the AZO films was decreased, indicating better conductivity at higher oxygen partial pressures. All the films were highly transparent in the visible region with a high optical transmittance (> 85 %). The excellent electrical and optical properties of the laser-ablated AZO thin films were similar to those of ITO, which rendered them potential applications in optoelectronics.

References

[1] Zhu H, Hupkes J, Bunte E, *et al.* Influence of Working Pressure on ZnO:Al Films from Tube Targets for Silicon Thin Film Solar Cells[J]. *Thin Solid Films*, 2010, 518: 4 997-5 002

[2] Oh B Y, Jeong M C, Moon T H. Transparent Conductive Al-doped ZnO Films for Liquid Crystal Displays[J]. *J. Appl. Phys*., 2006, 99: 124 505-1-4

[3] Kim H, Gilmore C M, Horwitz J S. Transparent Conducting Aluminum-Doped Zinc Oxide Thin Films for Organic Light-Emetting Devices[J]. *J. Appl. Phys*., 1997, 81: 7 764-7 772

[4] Lee J, Park Y S. Characteristics of Al-doped ZnO Films Annealed at Various Temperatures for InGaZnO-Based Thin-Film Transistors[J]. *Thin Solid Films*, 2015, 587: 94-99

[5] Aouaj M A, Diaz R, Belayachi A, *et al.* Comparative Study of ITO and FTO Thin Films Grown by Spray Pyrolysis[J]. *Materials Research Bulletin*, 2009, 44: 1 458-1 461

[6] Özgür Ü, Alivov Y I, Liu C, *et al.* A Comprehensive Review of ZnO Materials and Devices[J]. *J. Appl. Phys*., 2005, 98: 041 301-1-103

[7] Zhu B L, Wang J, Zhu J, *et al.* Investigation of Structural, Electrical, and Optical Properties for Al-Doped ZnO Films Deposited at Different Substrate Temperatures and H_2 Ratios[J]. *J. Electrochem. Soc*., 2012, 159: H536-H544

[8] Kluth O, Schöpe G, Rech B, *et al.* Comparative Material Study on RF and DC Magnetron Sputtered ZnO:Al Films[J]. *Thin Solid Films*, 2006, 502: 311-316

[9] Kuroyanagi A. Properties of Aluminum-Doped ZnO Thin Films Grown by Electron Beam Evaporation[J]. *Jpn. J. Appl. Phys*., 1989, 28: 219-222

[10] Agura H, Suzuki A, Matsushita T, *et al.* Low Resistivity Transparent Conducting Al-doped ZnO films Prepared by Pulsed Laser Deposition[J]. *Thin Solid Films*, 2003, 445: 263-267

[11] Kuprenaite S, Murauskas T, Abrutis A, *et al.* Properties of In-, Ga-, and Al-doped ZnO Films Grown by Aerosol-Assisted MOCVD: Influence of Deposition Temperature, Doping Level and Annealing[J]. *Surf. & Coat. Tech*., 2015, 271: 156-164

[12] Tang W, Cameron D C. Aluminum-Doped Zinc Oxide Transparent Conductors Deposited by the Sol-Gel Process[J]. *Thin Solid Films*, 1994, 238: 83-87

[13] Willmott P R, Huber J R. Pulsed Laser Vaporization and Deposition[J]. *Rev. Mod. Phys*., 2000, 72: 315-328

[14] Luo S J, Zhang L M, Wang C B, *et al.* Preparation and Effect of Oxygen Annealing on the Electrical and Magnetic Properties of Epitaxial (000 1) $Zn_{1-x}Co_xO$ Thin Films[J]. *J. Wuhan Univ. Technol. -Mater. Sci. Ed*., 2013, 28: 893-897

[15] Narayan J, Dovidenko K, Sharma AK. Defects and Interfaces in Epitaxial ZnO/α-Al_2O_3 and AlN/ZnO/α-Al_2O_3 Heterostructures[J]. *J. Appl. Phys*., 1998, 84: 2 597-2 601

[16] Chen M S, Chen Z X, Tang S H, *et al.* Stress Effect on Raman Spectra of Ce-doped $BaTiO_3$ Films[J]. *J. Phys.: Condens. Matter*., 2000, 12: 7 013-7 023

[17] Takahashi M, Uosaki K, Kita H, *et al.* Resistivity, Carrier Concentration, and Carrier Mobility of Electrochemically Deposited CdTe Films[J]. *J. Appl. Phys*., 1986, 60: 2 046-2 049

[18] Wang C B, Shen Y J, Li L. Temperature Dependence of Transport Behavior and Thermochromic Property of Spark Plasma-Sintered (La,Sr)MnO_3 Bulk Ceramics[J]. *J. Mater. Sci*., 2015, 50: 5 593-5 598

[19] Gibbs Z M, LaLonde A, Snyder G J. Optical Band Gap and the Burstein-Moss Effect in Iodine Doped PbTe Using Diffuse Reflectance Infrared Fourier Transform Spectroscopy[J]. *New J. Phys*., 2013, 15: 075 020-1-18