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Aluminum-doped zinc oxide film with gradient property deposited at oblique angle

Shan Peng Cao [a], Fei Ye [a,b,*], Bo Hou [a], Ai Yan Xu [a]

[a] School of Materials Science and Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, Liaoning 116024, China
[b] Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian 116024, China

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ABSTRACT

Aluminum-doped zinc oxide films were prepared using electron beam evaporation method at a series of oblique angles. It has been found out that the columnar structure in the films inclined with oblique angle. Moreover, the angle between the growth direction of the columnar structure and the substrate normal was essentially the same as the oblique angle. The film thickness, the average transmittance, the normalized absorption and the sheet resistance also varied as a function of angle. These properties also gradually varied along the film's surface. Then, the effects of oblique angle deposition on the film properties were discussed based on deposition speed and shadowing effect.

1. Introduction

Aluminum-doped zinc oxide (AZO) films are promising candidates for the applications such as transparent conductive electrodes of transparent organic light emitting diodes, UV/blue light emitters, photo detectors, and chemical sensors due to their excellent optical and electrical properties [1,2]. Various deposition methods have been used to prepare AZO films such as metal-organic chemical-vapor deposition [3], r.f. magnetron sputtering [4], reactive sputtering [5] and spray pyrolysis [6]. AZO films with a transmittance of about 90% and a resistivity of about $10^{-4}\,\Omega\cdot$cm can be obtained by using these deposition methods [7,8].

To meet the various requirements of the semiconductor industry, other deposition techniques have been proposed. Oblique angle deposition is a technique widely used for fabrication of metal, metal oxide and semiconductor thin films with inclined columnar structure [9–14]. In the case of zinc oxide films, the results of oblique angle deposition are conflicting. It was reported that inclined columnar structures in zinc oxide films were obtained by r.f. magnetron sputtering [16]. In contrast, it was observed that the inclined columnar structure in the film prepared by DC sputtering on glass substrate was not well defined because the columns contained stacks of small grains [15].

However, besides the formation of inclined columnar structure, the effects of oblique angle deposition on the optical and electrical properties of AZO films have not been systematically investigated. In other oxide materials, such as TiO_2 [17], it was observed that the porosity and surface roughness of the films increased with the increase of oblique angle due to the shadowing effect [17–19]. As a result, the photo catalytic property was enhanced with oblique angle up to 60°, while a further increase in the angle reduced the photo catalytic property due to lack of the crystalline phase. Therefore, the oblique angle deposition can significantly affect the film properties. On the other hand, the shadowing effect due to the oblique angle deposition may cause other phenomena such as the variation of crystal size, thickness, porosity and properties along the film's surface. However, such phenomena have not been considered in previous studies of zinc oxide films.

To address these issues, AZO films were prepared by electron beam evaporation method at a series of oblique angles in this work. The effects of oblique angle deposition on the microstructure, transmittance, and sheet resistance of AZO films were systematically investigated. Moreover, the property variation along the film's surface was considered. Then, the effects of oblique angle deposition on the film properties were discussed based on porosity and deposition speed.

2. Experimental details

AZO films were prepared by electron beam evaporated method (Shenyang technology instrument company, DZS-500). The targets were prepared by mixing ZnO (particle size: 1 μm, purity: 99.99%) and Al_2O_3 powders (particle size: 50 nm, purity: 99.9%). The procedure of the target preparation was optimized as follows. The mixture was pressed under 14 MPa followed by sintering at 1373 K for 6 h. The density of the targets was about 55% of the theoretical density. To maximize the transmittance and the conductivity of the film, the concentration of

* Corresponding author at: School of Materials Science and Engineering, Dalian University of Technology, 2 Linggong Road, Dalian, Liaoning 116024, China. Tel./fax: +86 411 84709230.
E-mail address: yefei@dlut.edu.cn (F. Ye).

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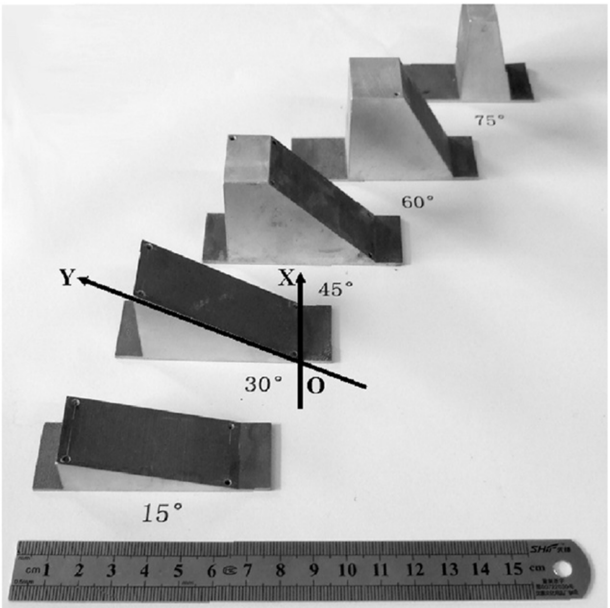

Fig. 1. Substrate tables with different tilt angles. The oblique angle for each substrate table is also given.

Al in the targets was optimized to 3 wt.%. Correspondingly, the concentration of Al in the film was about 1 wt.%.

Before deposition, the glass substrates (Sail Brand, CAT. NO. 7101) were ultrasonically cleaned by distilled alcohol and deionized water. Oblique angle deposition was achieved by preparing a series of substrate tables with different oblique angles using aluminum alloy. As shown in Fig. 1, the angles are 0°, 15°, 30°, 45°, 60°, and 75°, respectively. The samples deposited at these angles are hereafter referred to as T0, T15, T30, T45, T60, and T75, respectively. The height of the substrate tables is 4 cm except that of the T15 substrate table which is 2 cm. For convenience of the following discussion, a coordinate system is defined for each substrate table, as that shown on the T30 substrate table. Along the Y direction, which is named as relative position in the following text, the properties were measured at an interval of 0.5 cm.

The target/substrate distance was about 30 cm. Rotation speed of the substrate was 2 rad/min. After the electron-beam evaporator had been evacuated to a base pressure of 6.7×10^{-3} Pa, the films were deposited at a working gas pressure of 0.17 Pa. The gas was a mixture of Ar and O_2, whose flow rates were 18 and 25 ml/min, respectively. High voltage was 6.0 kV and the electron beam current was 25 mA. The deposition temperature was 250 °C and the deposition time was 1 h. After deposition, the samples were cooled to room temperature in the chamber.

The structure of the samples was examined by X-ray diffraction (XRD) using a Bruker, D8 Discover system with Cu K_α radiation ($\lambda =$ 1.540562 Å). The glancing angle was 0.5°, and the voltage was 40 keV. The microstructure and thickness of the AZO films were observed by scanning electron microscopy (SEM, Zeiss Supra 55) at a working voltage of 5 kV. The sheet resistance was tested by four-point probe method (4 Probes Tech, RTS-9) and the transmittance was examined by UV–Vis–NIR USB spectrophotometer (Ocean, MAYA2000PRO).

3. Results and discussion

XRD patterns of the samples deposited at different oblique angles are shown in Fig. 2. These films all have a hexagonal wurtzite structure, and the peaks of the sample T30 are indexed as an example. It can be seen that only (002) peak can be seen for the sample T0, indicating that the AZO films deposited at 0° have a highly c-axis vertically oriented structure, as widely observed in previous studies [20,21]. When the films are deposited at oblique angles between 15° and 60°, more peaks can be seen. It is possibly because the preferred orientation was destroyed by the oblique angle deposition.

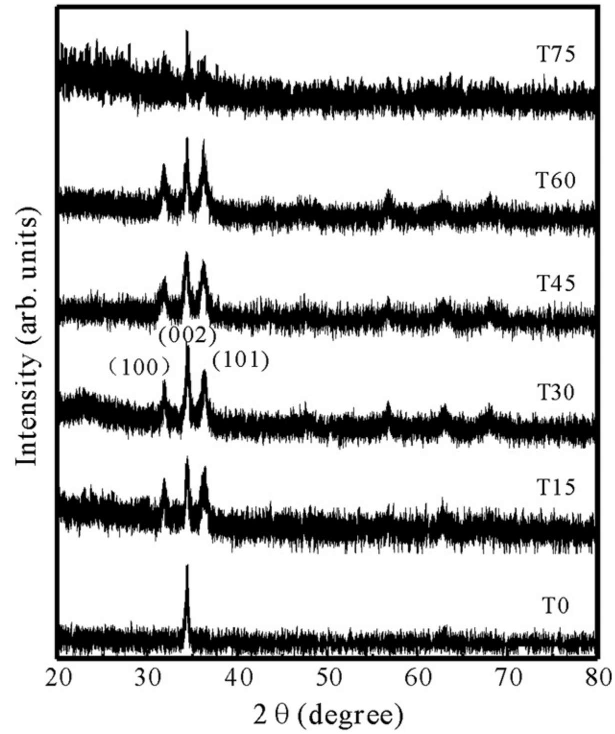

Fig. 2. XRD patterns of AZO samples deposited at different oblique angles.

The microstructures of the samples were observed by SEM (Fig. 3). When the samples are observed from the X direction as indicated in Fig. 3, columnar structures can be seen except in sample T75. It is possibly because the density of the film deposited at a higher oblique angle is lower. Some pores may be seen indistinctly in the SEM image of sample T75. In the case of samples T0, it is clear that the columnar structures are formed by stacks of small grains. It is interesting that the columnar structures are inclined due to the oblique angle deposition, and the inclined angles are essentially the same as the oblique angles of the substrate tables. Thus the growth direction of the columnar structures is parallel to the deposition direction. However, in the previous studies of Mukhtar et al. [22] and Hawkeye et al. [24], the inclined angle is smaller than the oblique angle due to the tangent rule, the origin of which is the flux directionality and the shadowing effect. For example, when the oblique angles are 30° and 60°, the inclined angles calculated using the tangent rule are 16.1° and 40.9°, respectively. The discrepancy is simply because of the difference in the deposition techniques. Comparing with the magnetron sputtering techniques used in the previous studies [22,23], the electron beam evaporation method in this work has a weaker directionality, and, hence, weaker shadowing effect, since the atoms evaporated by the electron beam have smaller kinetic energy and the working gas pressure was as high as 0.17 Pa. Thus, the growth direction of the columnar structures does not follow the tangent rule but are parallel to the deposition direction. The surface morphology was also observed by SEM. The effect of the oblique angle deposition on the grain size is not obvious, and all the samples have similar grain size at about 100 nm.

The film thickness is also influenced by the oblique angle deposition. In Fig. 4, it can be seen that the thickness of the film increases along the Y direction (relative position). Moreover, at the same relative position, the thickness increases with oblique angle, i.e. a larger oblique angle results in a higher deposition speed. This is possibly because at the same relative position, the target/substrate distance decreases with oblique angle and then leads to a higher deposition speed.