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The effect of thickness on the properties of heavily Al-doped ZnO films by simultaneous rf and dc magnetron sputtering

Su-Shia Lin, Jow-Lay Huang*

Department of Material Science and Engineering, National Cheng-Kung University, Tainan 701, Taiwan, ROC

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Abstract

For heavily Al-doped ZnO (ZnO:Al) films, there was a tendency for the *c*-axis to be perpendicular to the substrate, and further increasing in crystallinity or degree of orientation by increasing the film thickness. The surface of ZnO:Al films exhibited the hillocks growth obviously with the decrease of film thickness. There was the close relation among the film thickness, surface roughness, and carrier mobility. Generally, the resistivity and visible transmission of film decreased with the increase of film thickness. However, in this work the proper film thickness could result in lower resistivity and visible transmission, respectively. With the increase of film thickness, the transmission in UV region decreased obviously. As the results, film thickness affected the properties of ZnO:Al films significantly.

Keywords: D. ZnO; Surface morphology; Thickness; Resistivity; Transmission

1. Introduction

Nowadays ZnO films have attracted much attention as the transparent conductive films because of their amenability to doping [1–3], low cost and non-toxicity [4]. Both stoichiometry and dopant impurities affect the electrical and optical characteristics to the point that ZnO can either be a near-insulator or a semi-metal [5]. For practical applications undoped ZnO films are inferior to indium- or tin-based oxide films. However, doped films can be made to have very stable electrical and optical properties.

In this study, the preparation of transparent conducting ZnO films was heavily doped with Al (ZnO:Al) by simultaneous rf magnetron sputtering of ZnO and dc magnetron sputtering of Al. The Al content was controlled by dc power of 40 W, and was 11.3 at.%. The characteristics of films are generally affected by preparation conditions, such as the deposition methods, working pressure, substrate temperature, types of substrates, and the thickness of films [6]. Among these factors, the direct influence of thickness on the characteristics of films is less noticed until now, although the thickness has been argued in most literatures. The direct influence of film thickness on the properties of ZnO:Al films was investigated in this work.

2. Experimental procedures

The ZnO:Al films were deposited by simultaneous rf magnetron sputtering of ZnO (99.99% purity, ∅ 3 in. × 0.25 in., Target Materials Inc., Columbus, OH) and dc magnetron sputtering of Al (99.999% purity, ∅ 3 in. × 0.25 in, Target Materials Inc.). The glass substrates (corning 1737F (Elecmat, CA)) were ultrasonically cleaned in acetone, rinsed in deionized water, and subsequently dried in flowing nitrogen gas before deposition.

The sputtering was performed in Ar atmosphere with a target-to-substrate distance of 5 cm. A cryo-pump coupled with a rotary pump was used to achieve 1×10^{-6} Torr pressure before introducing argon gas (99.9995%, Lien Hwa Gas Co., Hsin Chu, Taiwan). The substrate temperature was measured using a thermocouple gauge and a hot cathode gauge. The temperature was controlled using a feedback-controlled heater. The variation of the substrate temperature during deposition process was maintained within ±5 °C. For the ZnO:Al films deposition, the substrate were heated to 150 °C, the chamber was back-filled with Ar with a working pressure of 6×10^{-3} Torr. A typical rf

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* Corresponding author. Tel.: +886-6-2348188; fax: +886-6-2763586.
E-mail address: JLH888@mail.ncku.edu.tw (J.-L. Huang).

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power was 200 W, and dc power was 40 W. The Al content was controlled by dc power of 40 W, and was 11.3 at.%. The ZnO:Al films were deposited to the thickness in the range of 20–300 nm.

The film thickness was measured using a surface profiler (Alpha-Step 500, TENCOR, Santa Clara, CA) and the FE-SEM (XL-40FEG field emission scanning electron microscope, Eindhoven, The Netherlands). X-ray diffraction (XRD; Rigaku D/MAX2500, Tokyo, Japan) was used to study the crystallinity and crystal orientation of the films. The surface morphologies and surface roughness of ZnO:Al films were examined by atomic force microscopy (AFM; Digital Instruments Inc., NanoScope E, USA). The elemental compositions were investigated by X-ray photoemission spectroscopy (XPS; VG. ESCA 210, West Sussex, United Kingdom). The electrical resistivity, Hall mobility, and carrier concentration were measured by a Hall automatic measuring system (Bio-Rad HL 5500 PC, USA). The optical transmission spectra of films in the ultraviolet-visible-infrared (UV-Vis-IR) region were recorded by the ultraviolet (UV) spectrophotometer (HP Hewlett Packard 8452A diode array spectrophotometer, Palo Alto, CA).

3. Results and discussion

3.1. Structural characterization

According to the X-ray diffraction patterns, ZnO:Al films deposited to different thickness showed the (0 0 2), (1 0 2) and (1 0 3) peaks. The polycrystalline structure could be observed and there was a tendency for the *c*-axis to be perpendicular to the substrate. It led to further increase in crystallinity or degree of orientation by increasing the film thickness.

Fig. 1 shows the morphologies of ZnO:Al films with thickness of (a) 300 nm and (b) 80 nm. The surface of films exhibited the hillocks growth obviously with the decrease of film thickness. Ohring [7] reported that to consider electromigration, local mass flux divergences exist throughout the film because of varying grain size and orientation distributions. If more atoms enter a region such as a junction of grains than leave it, a mass pileup or growth can be expected [7]. For this reason, a uniform distribution of grain size is desirable in Fig. 1a. In Fig. 1b, mass-transport effects are manifested by void formation, mass pileups and hillocks [7]. Therefore, there may be more defects existing in ZnO:Al films with decreasing the film thickness. The development of root-mean-square (RMS) roughness values for films is shown in Fig. 2.

Fig. 2 shows the RMS roughness of ZnO:Al films with different thickness. The surface roughness increased by increasing the thickness of ZnO:Al films except 300 nm. Laukaitis et al. [8] reported that the roughness values were very close to the morphologies of growing films. It was probably why

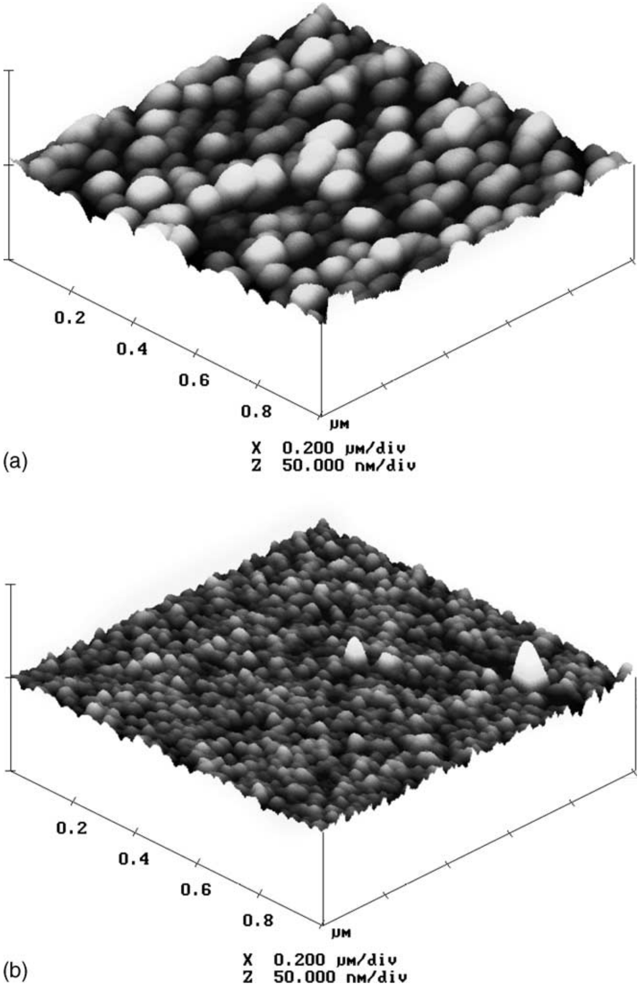

Fig. 1. The morphologies of ZnO:Al films with thickness of (a) 300 nm and (b) 80 nm.

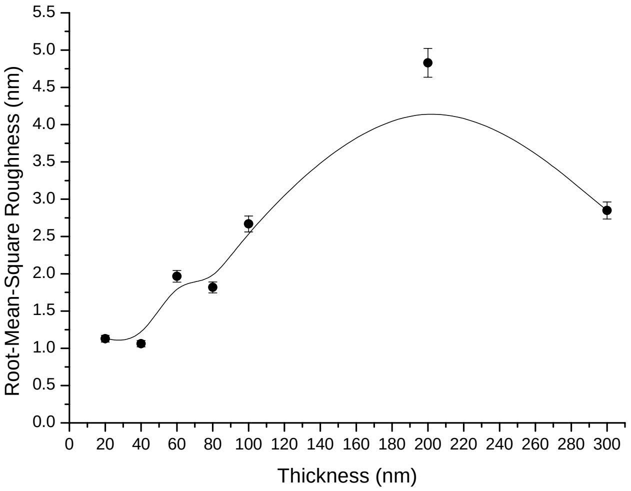

Fig. 2. The root-mean-square (RMS) roughness of ZnO:Al films with different thickness.

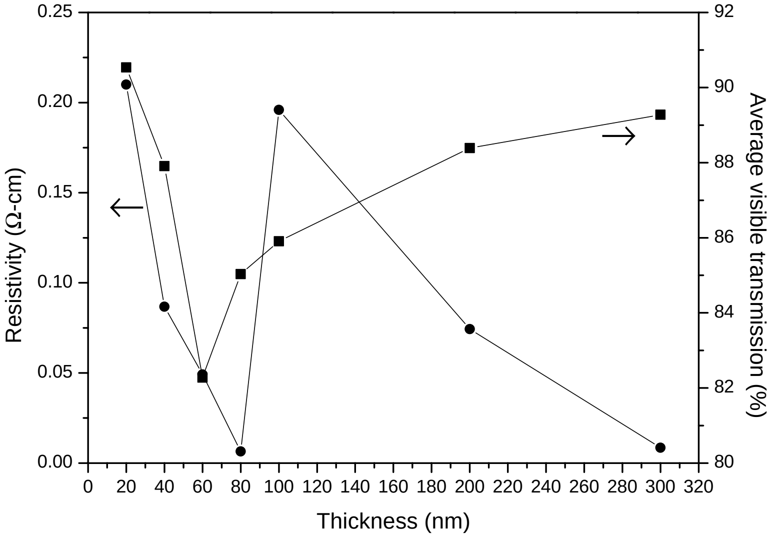

Fig. 3. The resistivity and average visible transmission of ZnO:Al films deposited to different thickness.

ZnO:Al films with 300 nm in thickness did not show the highest roughness.

The surface roughness could generally affect the carrier mobility [9]. The ratio of the surface area to the volume was large when the film thickness decreased, and resulted in more defects acting as scattering centers in the films. The electrons tend to be localized or trapped at these centers, and having very low mobilities [10]. It was in agreement with our results of Hall measurements. Therefore, the main scattering mechanism in the thin ZnO:Al films which limited the resistivity may be defects scattering [11]. However, the scattering mechanism in the thick ZnO:Al films was neutral impurity scattering, which was reported previously [12].

3.2. Electrical properties

Fig. 3 shows the resistivity and average visible transmission of ZnO:Al films deposited to different thickness. The resistivity decreased with the increase of film thickness first, but abruptly increased as the thickness of ZnO:Al film was 100 nm, and then the resistivity decreased with the increase of film thickness. ZnO:Al films showed similar tread for average visible transmission.

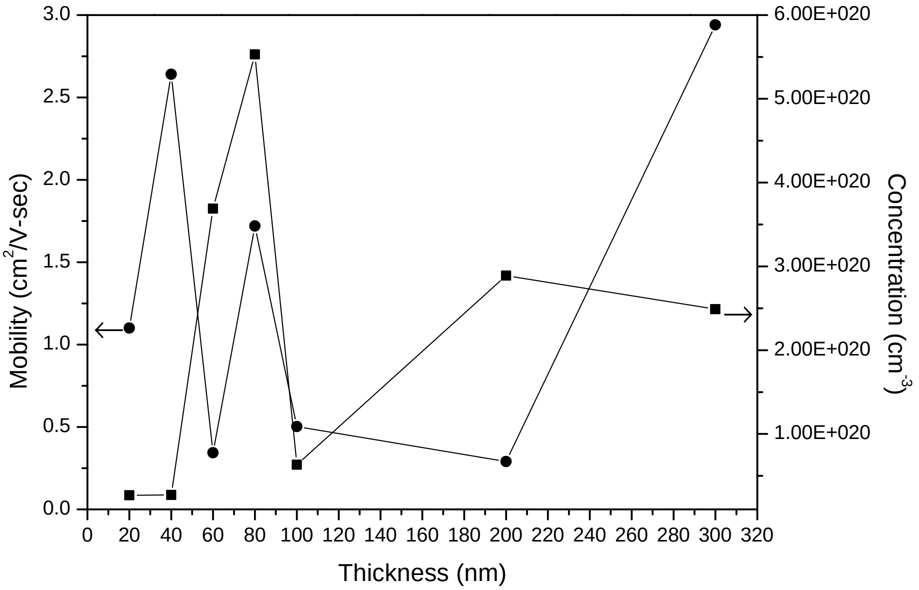

Fig. 4. The mobility and carrier concentration of ZnO:Al films deposited to different thickness.

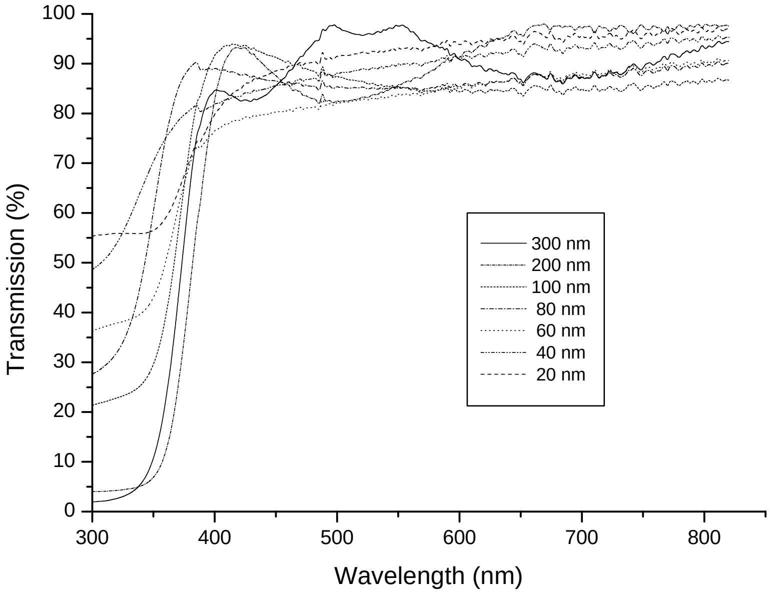

Fig. 5. The transmission spectra in the UV-Vis-IR region of ZnO:Al films deposited to different thickness.

Chiou et al. [13] reported that the resistivity of thick film and thin film could be expressed by Eqs. (1) and (2), respectively,

$$\frac{\rho_f}{\rho_o} = 1 + \frac{3}{8K}, \quad (K \gg 1) \tag{1}$$

$$\frac{\rho_f}{\rho_o} = \frac{4}{3K \ln 1/K}, \quad (K \ll 1) \tag{2}$$

Here ρ_f is the resistivity of thin film, ρ_o is the resistivity of bulk, and K is the reduced thickness ($K =$ the film thickness/the mean free path of the charge carrier in the bulk material). From Eqs. (1) and (2), it could be understood that the film thickness affected the resistivity of thin film more than thick film. In addition, the resistivity of film increased with the decrease of film thickness. However, the resistivity of ZnO:Al films in this study did not have the similar behavior. The ZnO:Al film with 80 nm in thickness had the lowest resistivity, $6.54 \times 10^{-3}\,\Omega\,\mathrm{cm}$. It suggested that the proper film thickness could result in the lowest resistivity.

Fig. 4 shows the mobility and carrier concentration of ZnO:Al films deposited to different thickness. In this work, the heavily Al-doped ZnO film in the incorporated state resulted in structural imperfection, and there actually be the high electron concentration [14]. The resistivity ρ is

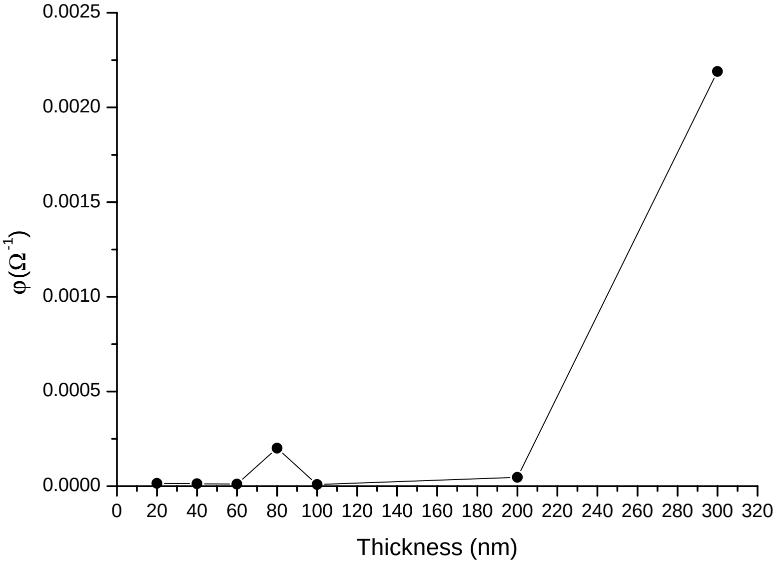

Fig. 6. A plot of the figure of merit vs. deposition thickness of the ZnO:Al films.

proportional to the reciprocal of the product of carrier concentration N and mobility μ by the following equation [15]:

$$\rho = \frac{1}{Ne\mu} \tag{3}$$

By comparing Fig. 3 with Fig. 4, the ZnO:Al film deposited to 80 nm thickness showed the lowest resistivity, which resulted from the highest product of carrier concentration N and mobility μ.

3.3. Optical properties

Fig. 5 shows the UV-Vis-IR transmission spectra of ZnO:Al films with different thickness. For films with different thickness, the optical transmission in the visible region all decreased substantially at short wavelengths near the ultraviolet range. The transmission in UV region decreased obviously with the increase of film thickness. Generally, the visible transmission of film decreased with the increase of film thickness. However, the films with proper thickness (60 nm) showed the lowest average visible transmission in this work (Fig. 3).

Fig. 6 shows a plot of the figure of merit versus deposition thickness for the ZnO:Al films. A figure of merit $\varphi = T^{10}/R_{\text{sh}}$, as defined by Haacke [16], which provides a criterion for the performance of a film. T is the optical transmittance and R_{sh} is the sheet resistance. In the visible region, the value of merit was higher for film thickness of 300 nm than the others. It was due to ZnO:Al films with 300 nm in thickness simultaneously had low sheet resistance ($2.84 \times 10^2\ \Omega$/sq) and high average visible transmission (~89%).

4. Conclusions

The crystallinity or degree of orientation was increased with the increase of film thickness. The surface of ZnO:Al films exhibited the hillocks growth obviously with the decrease of film thickness, which was probably due to the mass transport effects. The ZnO:Al film deposited to 80 nm thickness showed the lowest resistivity, $6.54 \times 10^{-3}\ \Omega$ cm. The transmission in the UV region decreased obviously with the increase of film thickness. In the visible region, the value of merit was higher for film thickness of 300 nm. This suggested that the application of thinner ZnO:Al film was limited.

Acknowledgements

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