

Transparent conductive Al doped ZnO thin films produced by pulsed laser deposition*

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Highly textured pure and Al-doped ZnO thin films have been produced by pulsed laser deposition, for applications such as transparent electrodes. The crystalline quality, optical transmission and electrical properties of the films strongly depended on the presence of the Al dopants. All the films showed 82 – 90% optical transparency in the visible (VIS) and near infrared (IR) spectral ranges. The films prepared at 300 °C substrate temperature and 0.05 mbar oxygen pressure, maintained during deposition, had a resistivity of $2.4 \times 10^{-4} \Omega \text{ cm}$.

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1. Introduction

Highly transparent and conductive thin films are important components of large-area electronic applications, such as transparent electrodes in flat panel displays, thin film transistors and solar cells [1]. The requirements for the transparent conducting thin films in these applications are: light transmission in the visible wavelength region higher than 80%; resistivity as low as $10^{-4} \Omega \text{ cm}$; and ability to withstand high temperatures and a reducing chemical environment.

Doped zinc oxide (ZnO) thin films have been proposed as a transparent conducting material [2-5]. In particular, aluminum- and gallium-doped ZnO films have attracted considerable attention for such applications, in place of indium tin oxide (ITO), because of their high conductivity, good optical transmittance and low cost of fabrication [2,3,5]. Doped ZnO films have been prepared by a number of techniques, including chemical vapor deposition, reactive magnetron sputtering, electron-beam evaporation and pulsed laser deposition (PLD). [2-7]. Compared to sputtering and evaporation, laser ablation provides some advantages. The film's composition is quite close to that of the target, even for a multicomponent target. Also, the films may crystallize at a lower substrate temperature due to the high excitation energy of the ionized and ejected species in the laser-produced plasma.

In this paper, we report the electrical and optical properties of ZnO films doped with aluminum oxide, prepared by PLD for applications such as transparent electrodes.

2. Experimental

The ZnO thin films were prepared using a standard on-axis PLD setup. The experiments were performed using a XeCl excimer laser (308 nm, pulse duration of 30 ns, repetition rate of 2 Hz). The laser fluence was kept at 2 J/cm^2 . Home-made pure and Al_2O_3 doped ceramic ZnO targets were used for ablation. A ceramic target with an Al_2O_3 concentration of 2 wt% was prepared and used. This target was made from 99.99 % purity ZnO and Al_2O_3 powders which were mixed, homogenized, and pressed at 6 MPa. The as-prepared targets (pure and Al_2O_3 doped) were calcified at 500 °C for 4 h and then sintered at 1150 °C for 12 h. The target-to-substrate distance was kept constant at 4 cm. (001) SiO_2 was used as substrates, because of its high transparency in the visible and near infrared ranges. All experiments were performed in an oxygen atmosphere at a pressure of 0.05 mbar. The films were grown at a substrate temperature of 300 °C.

X-ray diffraction (XRD) measurements with $\text{Cu K}\alpha$ radiation in the θ -2 θ Bragg-Brentano geometry were performed to study the phase composition and crystalline structure of the films. The Scherrer equation was used for estimation of the “apparent crystallite size”. A correction

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for instrumental broadening was introduced. Stress broadening was assumed to be zero, since the sources of microdeformations are numerous and their particular contribution could not be estimated. Atomic force microscopy (AFM) was applied, in order to characterize the thin film surface and to measure the film roughness. Optical transmission through the films at normal incidence was measured with a double-beam spectrophotometer (CARY 5E) in the UV-VIS-NIR ranges of the spectrum. All optical measurements were performed in air. The film thickness was also analysed using a conventional step height detector. The electrical resistivity of the films was measured at room temperature, using a standard four-point probe.

3. Results and discussion

It is well known that the electrical and optical properties of ZnO films strongly depend on their crystallinity [3,5,8]. Our previous studies of the crystalline structure of pure ZnO films have shown that increasing the substrate temperature enhances the diffraction peak intensity, which has mainly to do with the mobility of the atoms in the films at different temperatures [9]. Craciun et al. [10] also reported that the degree of the film crystallinity of pure ZnO films deposited by PLD was improved by increasing the substrate temperature from 150 to 350 °C, but this tendency was reversed for temperatures higher than 400 °C. At the same time, the highest intensity peak was obtained at oxygen pressures in the range 0.05 – 0.1 mbar [9]. This is why we chose a substrate temperature of 300 °C and an oxygen pressure of 0.05 mbar as optimal experimental conditions for growing high quality ZnO films.

Fig. 1 presents typical XRD spectra for pure and Al-doped ZnO films. Only ZnO-related peaks such as (002) and (004) were observed. Al₂O₃ or Al-related peaks were not detected. This leads us to the conclusion that the excess concentration of Al or Al₂O₃, if any, exists in the form of an amorphous phase. As is clearly seen in Figs. 1a and b, the films have a preferred orientation of ZnO (002), indicating a perpendicular alignment of the c-axis of the grains. This means that the wurtzite structure of ZnO is conserved after doping with Al, at the doping level used.

For pure ZnO films, the (002) peak was observed at a slightly larger angle (Fig. 1a) than that of the bulk material (JCPDS #36-1451), which is probably due to the residual stress stemming from the different expansion coefficients of the film and the substrate.

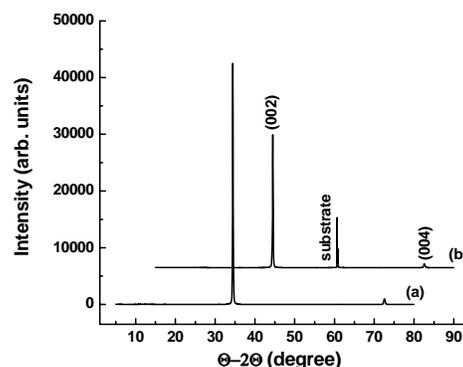
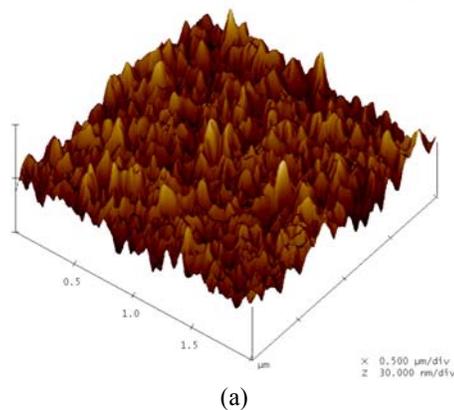


Fig. 1. XRD spectra of ZnO films prepared at a 300 °C substrate temperature and 0.05 mbar oxygen pressure: (a) pure; (b) Al-doped.

The (002) peak was also observed to be shifted towards higher diffraction angles for Al-doped ZnO films (Fig. 1b). This is probably due to the contraction of the unit cell occurring as Al ions with radius 0.51 Å replace Zn ions of larger radius, 0.74 Å. The line width of the (002) peak, 0.18° for pure ZnO films, increased slightly with Al doping and reached 0.21°, which implies that the grain size in the ZnO films is reduced as it is doped with Al. The result is in line with our previous studies [11]. The average grain size is around 130 nm for the pure sample and 105 nm for the doped one. As was reported by Zeng et al. [8], a larger grain size of the films results in a lower resistivity of the films.

The morphology of the transparent conductive films is an important characteristic for optical applications. A droplet-free smooth surface is necessary to ensure minimum optical losses. Fig. 2 presents AFM images taken from a 2×2 μm² area of pure and Al-doped ZnO films. It should be pointed out that the use of doped target increases the roughness of the films. The roughness mean square (RMS) value of the films deposited from a 2 wt% Al₂O₃ doped ZnO target is 6-9 nm, which is slightly higher than the one of the film deposited from the pure ZnO target, 5 nm. In other words, the films possess an optical quality higher than λ/20 in the visible and infrared ranges of the spectrum.



(a)

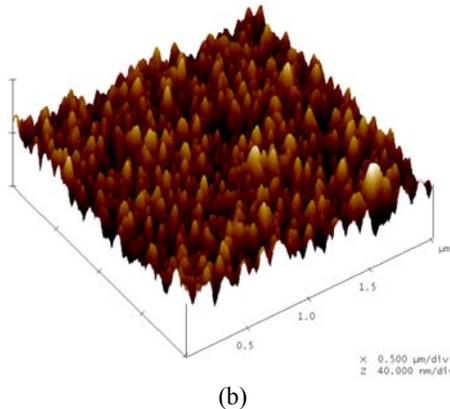


Fig. 2. AFM images of ZnO films prepared at a 300 °C substrate temperature and 0.05 mbar oxygen pressure from: (a) pure; (b) 2 wt% Al₂O₃ doped.

Optical transmission spectra of pure and doped films are presented in Fig. 3. It should be pointed out that these spectra include the losses from surface reflection of the glass substrate itself. The oscillations in the spectra in Fig. 3. are connected with the film thickness and, consequently, with interference in the film.

All the films (pure and Al-doped) are transparent in the VIS and IR ranges. The pure ZnO films show 90 % optical transmission in the visible range. As is clearly seen, the transparency of the films decreases when the dopants are added. The result is in good agreement with previously reported data [11].

The optical band gap (E_g) was determined from the transmission curve's second derivative [12]. The band gap energies of the Al-doped ZnO films are larger than that of pure ZnO films. ZnO is naturally an n-type material and the Fermi level will fall in the conduction band when it is heavily doped. Since the states below are filled, the optical band gap should be increased to higher energies [13]. This means that the absorption edge of the Al-doped films will be shifted to shorter wavelengths compared to that of pure ZnO films, as seen in Fig. 3. The optical band gaps of the Al-doped films are estimated to be 3.25 eV, while 3.22 eV is obtained for pure ZnO samples, which confirms the results previously reported [11,13].

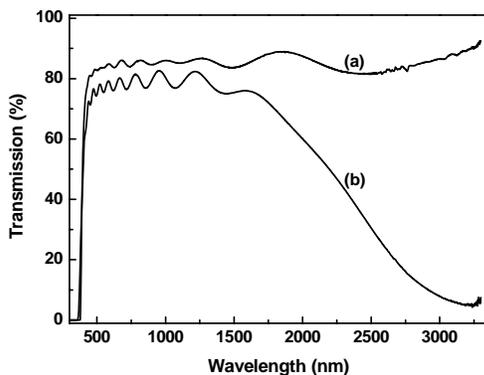


Fig. 3. Transmission spectra of ZnO films prepared at a 300 °C substrate temperature and 0.05 mbar oxygen pressure: (a) pure; (b) Al-doped.

It is well known that the resistivity of ZnO films depends on the concentration of oxygen, because the free carriers are mainly due to oxygen vacancies [3,5,6]. The oxygen content of the films is determined by the oxygen originating from the target itself, and the oxygen maintained during deposition. During laser deposition, oxygen molecules are dissociated or ionized to oxygen atoms or ions in the laser plume. When the films are prepared at a higher temperature, such as 300 °C, the atoms and ions impinging on the substrate have a high mobility on the film surface and are easily incorporated into the films. This results in a decrease in the number of oxygen vacancies and an enhancement of the film crystallinity on the one hand, and an increase in the resistivity of the films, on the other. The resistivity of the pure ZnO films was measured to be $2.8 \times 10^{-3} \Omega \cdot \text{cm}$. It was seen that the resistivity of the films decreases with Al doping. A value of $2.4 \times 10^{-4} \Omega \cdot \text{cm}$ was obtained for the films produced from a 2 wt% Al₂O₃ doped ZnO target. The results are in agreement with previous reports [3,5].

In order to investigate the ability of the films to operate as transparent electrodes, a voltage in the range of 0 to 20 V was applied to the films. No electrical current was detected in the pure ZnO sample. When the voltage was applied to the Al-doped sample, an electrical current was measured to flow through the film. This result is evidence of the presence of Al in the ZnO films.

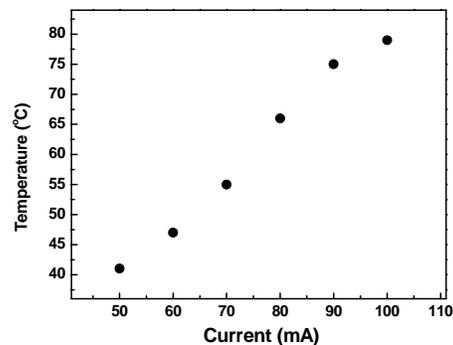


Fig. 4. Temperature dependence of an Al-doped ZnO film on the current passing through it.

Fig. 4. presents the dependence of the current passing through the Al-doped ZnO film on the film temperature. This means that Al-doped ZnO films prepared by PLD may be used for such engineering applications as transparent heating coatings for Rb cells [14].

4. Conclusion

Transparent, low resistivity, c-axis highly oriented pure and Al-doped ZnO thin films were grown by PLD. The crystallinity, optical transmission and electrical properties strongly depended on the presence of the Al dopant. An Al-doped ZnO sample produced at a 300 °C substrate temperature and 0.05 mbar oxygen pressure during deposition showed a low resistivity value of $2.4 \times 10^{-4} \Omega \text{ cm}$, and a transmission of about 82 % in the VIS and near IR ranges, which makes it a possible candidate for transparent heating coatings.

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