

Optical and electrical properties of aluminum-doped ZnO thin films grown by pulsed laser deposition

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Abstract

Transparent aluminum-doped zinc oxide (AZO) thin films were deposited on quartz glass substrates by pulsed laser deposition (PLD) from ablating Zn–Al metallic targets. The structural, electrical and optical properties of these films were characterized as a function of Al concentration (0–8 wt.%) in the target. Films were deposited at a low substrate temperature of 150 °C under 11 Pa of oxygen pressure. It was observed that 2 wt.% of Al in the target (or 1.37 wt.% of Al doped in the AZO film) is the optimum concentration to achieve the minimum film resistivity and strong ultraviolet emission. The presence of Al in the ZnO film changes the carrier concentration and the intrinsic defects.

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1. Introduction

In the last decade, transparent conducting oxides (TCO) materials have been actively studied [1]. Among these TCO materials, tin-doped indium oxide (ITO) film is the most commonly selected TCO electrode in flat panel displays including organic light-emitting diodes, liquid crystal displays and windows in solar cells due to its combined properties [2]. However, since indium is a rare and an expensive element, the cost of ITO films is very expensive. Recently, doped zinc oxide films (for example, ZnO films doped with impurities, such as B, Al, Ga and In) have been studied as alternate materials to replace ITO because they are non-toxic, inexpensive and abundant materials [3]. Among them, aluminium-doped ZnO film (AZO) is a wide band gap semiconductor, which shows good optical transmission in the visible wavelength regions (400–700 nm). Furthermore, AZO films have a lower electrical resistivity, which is similar to that of ITO film [4,5]. There were various methods to produce ZnO film, such as the metal-organic chemical vapor deposition (MOCVD) [1], the sol–gel method [6], spray hydrolysis [7], sputtering [8] and pulsed laser

deposition (PLD) [9]. In comparison with other techniques, PLD provides several advantages. For example, PLD films can crystallize at relatively low substrate temperatures due to the higher energy of the ablated particles in the laser-produced plume and relatively high deposition rates [10]. In some reports [11], ceramic targets prepared by sintering the mixture ZnO powder and Al₂O₃ powder was used. However, the expensive ceramic targets are usually brittle and would cause the cracking during deposition. In our previous work [12], ZnO film was deposited on Si(1 1 1) substrate by pulse laser ablation of Zn target in a controlled oxygen atmosphere, which is a simple method to produce oxide film by PLD. In this paper, Al-doped zinc oxide films will be deposited by pulse laser ablation of Zn–Al alloy targets onto glass substrates in an oxide atmosphere at a relatively low temperature (150 °C). The effects of aluminum concentration on the structural, electrical and optical properties of AZO films are investigated.

2. Experiments

The deposition of AZO film was performed in a vacuum chamber. The chamber was evacuated using a turbo-molecular pump to a base pressure of 5×10^{-4} Pa and then filled with oxygen (99.99 wt.% purity) at a fixed pressure of 11 Pa. This oxygen pressure is suitable for the growth of ZnO film along

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(0 0 2) orientation [10,12]. Metallic Zn–Al targets with different Al contents (0–8 wt.%) were ablated by an Nd:YAG pulsed laser with a wavelength of 1064 nm. The pulse duration of 100 ns and frequency of 10 Hz were used for all samples. Al-doped ZnO thin films were deposited on $2.5\text{ cm} \times 2.5\text{ cm}$ quartz glass at the substrate temperatures of 150°C . The target–substrate distance was kept at 2.3 cm and the deposition time of 50 min was maintained. Film thickness was determined by a surface roughness detector (DEKTAK). A low energy fluency of 11 J/cm^2 was set for all samples in order to avoid molten droplet [10].

X-ray diffraction (XRD, Rigaku Dymax) with a Cu target and a mono-chromator at 50 kV and 300 mA was used to analyze the crystal structure and the growth orientation of the films. The elemental compositions of the films were determined by the energy dispersive spectrometer (EDS). The optical properties of the AZO thin films were characterized by the photoluminescence with an Ar ion laser as a light source using an excitation wavelength of 325 nm. The electrical resistivity ρ and the Hall coefficient R_H were measured using the Van der Pauw method [11]. The carrier concentration N and the Hall mobility μ were calculated from the electrical resistivity and the Hall coefficient using the following relations [13]:

$$N = \frac{1}{eR_H} \quad (1)$$

$$\mu = \frac{1}{Ne\rho} \quad (2)$$

All measurements were done at room temperature.

3. Results and discussion

3.1. Structural properties

Doping of ZnO films with aluminum significantly affects the structural properties of the films. Fig. 1 shows the X-ray diffraction patterns taken on the Al-doped ZnO films ablated

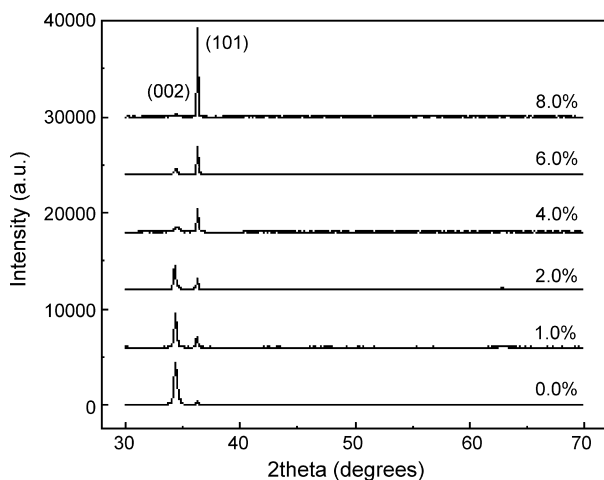


Fig. 1. XRD spectra obtained from Al-doped ZnO films deposited at the substrate temperature of 150°C , oxygen pressure of 11 Pa with different Al contents.

from the targets with different Al concentrations. They consist mainly of two peaks corresponding to (0 0 2) and (1 0 1) lattice plane diffraction of the hexagonal ZnO structure. No diffraction peaks of element Zn or Al are detected. Undoped ZnO film (0 wt.%) was observed to grow along the *c*-axis orientation of (0 0 2) [10,12]. However, as the increase of the Al concentration in the targets from 0 to about 4 wt.%, the diffraction intensity of (0 0 2) plane decreases and that of (1 0 1) plane increases, which indicates that the growth orientation of AZO changes from the *c*-axis orientation to the isotropic growth. When the concentration of Al in the target increases further from 4 to about 8 wt.%, the orientation growth along (1 0 1) plane was observed. Therefore, Al doping in ZnO cause a transformation of the preferred orientation of crystalline growth. The presence of Al in the ZnO film should change the diffusion rate of Zn and O at the surface during deposition. Then it will alter the energetic balance between (0 0 2) and (1 0 1) orientations and lead to the weakening of (0 0 2) orientation and the strengthening of preferred (1 0 1) texture in certain conditions.

Fig. 2 shows the EDS analysis of the AZO film with 2 wt.% doping of Al deposited at 150°C . The elements of O, Zn and Al were found on surface of the AZO film. The Al concentration in the AZO is about 1.37 wt.%, which is relatively low in comparison with the Al concentration of 2 wt.% in the target. The other Al concentrations of the AZO films are 0.79, 3.26, 5.08 and 7.44 wt.% corresponding to 1, 4, 6 and 8 wt.% Al concentration in targets, respectively. All the Al concentrations in the films are less than those in their corresponding targets. This may be attributed to the difference in melting temperatures of Zn and Al, the latter (660°C) is higher than the former (419.6°C). Under the same laser ablation energy fluency of 11 J/cm^2 , the element in the target that has lower melting temperature (Zn) is easy to be ablated out and deposited on the substrate. As a result, the concentration of Al in the AZO films are lower than those in their corresponding targets.

The mean crystallite size of the AZO films can be evaluated by the Scherrer formula [14]

$$D = \frac{0.94\lambda}{B \cos \theta}, \quad (3)$$

where λ , θ and B are the X-ray wavelength (0.15405 nm), the Bragg diffraction angle and the corrected peak width, respectively. The calculated crystallite sizes of the undoped (0 wt.%)

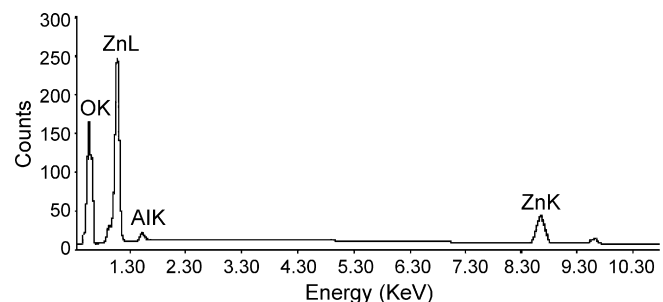


Fig. 2. The EDS analysis of ZnO film with 2 wt.% doping of Al deposited at the substrate temperature of 150°C .

ZnO film and the AZO films deposited from the targets with 1, 2, 4, 6 and 8 wt.% Al concentration are ~ 33 , ~ 29 , ~ 24 , ~ 23 and ~ 22 nm, respectively. The Al atoms doped in the ZnO film will replace of the crystal lattice of Zn. Because of the difference of atomic radius in Zn and Al, some quantity of Al atom prefers to locate in or near grain boundary regions, which would prevent grain growth. Therefore, it is seen that the grain size decreased as the increase of aluminum concentration doped in the film. The diffraction angle of the (0 0 2) peak ($2\theta = 34.47$ – 34.58°) is little larger than that of the standard ZnO crystal (34.45°). This may be due to the ionization of ZnO [15] or the residual stress parallel to the c -axis [16]. The c -axis lattice parameter, calculated from the XRD patterns for all AZO films, was in the range between 0.5084 and 0.5188 nm, which is smaller than the JCPDS value of 0.5195 nm for the ZnO powder. Since the ionic radius of Zn^{2+} and Al^{3+} are 72 and 53 pm, respectively [17], the length of the c -axis is expected to be shortened when Al atoms substitutes Zn atoms in the crystal. The result may be attributed to a self-arrangement effect, which is caused by the minimization of the crystal surface free energy favored already in the nucleation stage [18].

3.2. Electrical properties

The resistivity (ρ), carrier density (N) and Hall mobility (μ) of the films, as a function of Al concentration in the targets were measured and shown in Fig. 3. The resistivity of the AZO films is found to decrease initially with increasing the Al content up to 2 wt.%. This decrease in resistivity is due to the increase in free carrier concentrations as a result of the donor electrons from the Al dopant. Increase in carrier density in the AZO films maybe attributed to the substitutional replacement of Al^{3+} ions at Zn^{2+} cation sites or incorporation of Al ions in interstitial positions. However, the resistivity of the AZO films, after reaching a minimum (at 2 wt.% of Al), increase gradually with a further increase in the Al content up to 8 wt.%. In fact, when the Al concentration in the target is greater than 2 wt.% (or Al concentration in the ZnO film is larger than about 1.37 wt.%, which is similar to the result of 1.5 wt.% Al reported in ref. [19]), the excess Al atoms cannot be accommodated into ZnO

lattice due to the limited solid solubility of ZnO and therefore forms non-conducting Al_2O_3 clusters in the films causing crystal disorder, which act as carrier traps rather than electron donors [19,20]. It is also seen from Fig. 3 that the hall mobility of the AZO films decreases with increasing the Al concentration. This decrease in mobility may be attributed to with the decrease in grain size of the AZO films with increasing Al concentration. The decrease in grain size increases grain boundary scattering thus decreasing the mobility, therefore, the resistivity is expected to increase as observed in case of Al concentration in the target beyond 2 wt.%.

3.3. Photoluminescence

Fig. 4 shows the photoluminescence (PL) spectra obtained at room temperature for Al-doped ZnO thin films with different Al concentrations (0–8 wt.%). The PL spectra are found to be dependent on the Al concentration. When the Al concentration in the target is in the range of 0–2.0 wt.%, high strength UV emissions are observed. However, when Al concentration in the target increases to 4.0–8.0 wt.%, the intensity of the UV emission peak decreases rapidly. All the samples show UV emission of the near band edge (around 384 nm) with narrow full-width at half-maximum (FWHM).

Inset in Fig. 4 shows the intensities of the deep level emissions (DLEs). It is very interesting to note that all the AZO films with different Al concentrations observe only ultraviolet emission without notable DLEs. The strong UV emission without deep level emission was also observed recently from the ZnO film deposited on NiO buffered sapphire substrate by the laser molecular-beam-epitaxy at room temperature in an ultrahigh vacuum [21]. It is understood that [12,22,23] the deep level emission is probably relative to the variation of the intrinsic defects in ZnO films, different intrinsic defects correspond to various excited energies in deep level emission. According to the calculation, the energy interval for electronics transition from the bottom of the conduction band to the interstitial oxygen O_i level is 2.28 eV [12]. In our experiments,

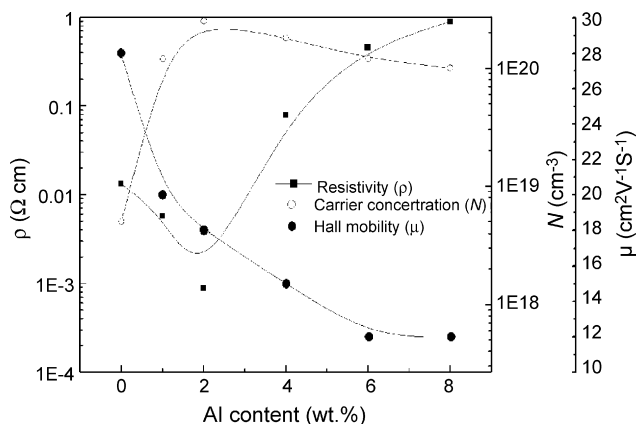


Fig. 3. Variation of resistivity (ρ), mobility (μ) and carrier concentration (N) of ZnO thin film with different Al contents.

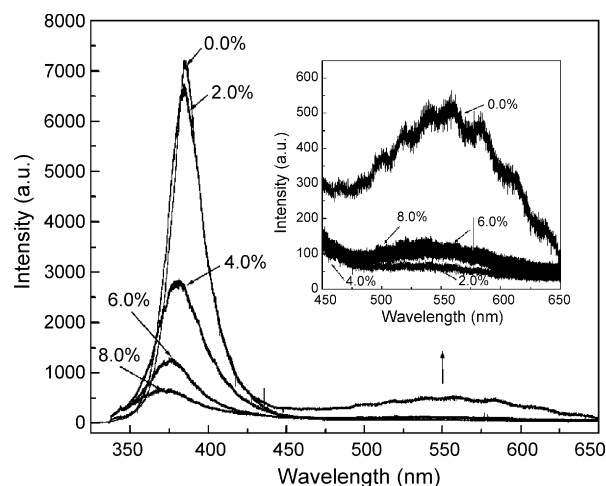


Fig. 4. Room temperature (298 K) photoluminescence spectra of Al-doped ZnO thin films on quartz glass grown by PLD with different Al contents.

the deep level emission centered at about 2.25 eV (or 550 nm) for the ZnO film without doped by Al, which implies that there should be interstitial oxygen defects in the films. As our experiment proceeded at a fixed partial-oxygen pressure of 11 Pa, when the deposited temperature is lower (150 °C), the oxidation reactive velocity maintains a lower level and the continuous supply of O atoms are sufficient to combine to ZnO with Zn ions, and there may be still residual O ions which may exist as O_i defects in ZnO films. As a result, the deep level emission centered around 550 nm is expected for the undoped ZnO film (0 wt.%). Because Al ions exists in Al^{3+} and Zn ions in Zn^{2+} , when Al element is doped in ZnO, Al ions will consume residual O ions and decrease the concentration of O_i defects in AZO films. As a result, intense UV emission with very slight or without deep-level emission were observed from the AZO films with different Al concentrations. Therefore, in our case of PLD of ZnO film under oxygen atmosphere, Al doping is a simple method to obtain ZnO film with only UV emission.

By comparison the results shown in Figs. 3 and 4, it is interesting to found that the AZO film with 1.37 wt.% doping of Al (or 2 wt.% Al in the target) observed high UV emission, nearly no deep level emission and very low electrical resistivity. This is the AZO film with expected optical and electrical properties, which may have the potential application in photo-electronic devices such as solar cells and displays. It should also be emphasized that in our experiments, both UV emission in PL spectrum and low electrical resistivity are observed from the Al-doped ZnO thin films deposited at a relatively low temperature (150 °C). This low temperature deposition is of considerable interest for practical applications such as depositing on polyimide (PI) substrates at a relatively low temperature.

4. Conclusions

Al-doped ZnO films were prepared on quartz glass substrates by PLD in oxygen atmosphere at a relatively lower temperature, by the pulse laser ablation of metallic Zn–Al targets with different Al concentrations (0–8.0 wt.%). The experimental results showed that both the ultraviolet emission in PL spectrum and the electrical properties are evidently influenced by the Al doping concentration. It was observed that

2 wt.% of Al in the target (or 1.37 wt.% Al doping in ZnO film) is the optimum doping amount to achieve the high UV emission and the minimum film resistivity. In the case of PLD of ZnO film under oxygen atmosphere, Al doping is also a simple method to obtain ZnO film with only UV emission.

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