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Citation: *Journal of Applied Physics* **104**, 073706 (2008); doi: 10.1063/1.2987472

View online: <http://dx.doi.org/10.1063/1.2987472>

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Reversible change in electrical and optical properties in epitaxially grown Al-doped ZnO thin films

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(Received 5 March 2008; accepted 5 August 2008; published online 2 October 2008)

Aluminum-doped ZnO (AZO) films were epitaxially grown on sapphire (0001) substrates using pulsed laser deposition. As-deposited AZO films had a low resistivity of $8.01 \times 10^{-4} \Omega \text{ cm}$. However, after annealing at 450 °C in air, the electrical resistivity of the AZO films increased to $1.97 \times 10^{-1} \Omega \text{ cm}$ because of a decrease in the carrier concentration. Subsequent annealing of the air-annealed AZO films in H₂ recovered the electrical conductivity of the AZO films. In addition, the conductivity change was reversible upon repeated air and H₂ annealing. A photoluminescence study showed that oxygen interstitial (O_i') is a critical material parameter allowing for the reversible control of the electrical conducting properties of AZO films. © 2008 American Institute of Physics. [DOI: 10.1063/1.2987472]

I. INTRODUCTION

Transparent conducting ZnO films have received a great deal of attention due to their wide applications in various optoelectronic devices.¹ A commonly used method to control the electrical properties of the ZnO films for use as a transparent conducting oxide (TCO) film is to incorporate a small amount of *n*-type donors. Among several donor-doped ZnO films, aluminum-doped zinc oxide (AZO) films have been extensively explored as a TCO material. The low manufacturing cost and nontoxicity of the AZO films make them more suitable for TCO applications than relatively expensive ITO (In₂O₃:Sn) films.^{2,3}

Thermal annealing of TCO films at temperatures as low as 400 °C in air has been widely adopted in the manufacturing processes of optoelectronic devices. The air annealing of TCO films generally increases their resistivity by changing the defect concentration of the films. The electrical conductivity of pure ZnO is controlled by intrinsic defects such as oxygen vacancies and/or zinc interstitials, which act as *n*-type donors. When Al is doped into ZnO, excess electrons compensating the positive charge of Al in Zn sites play a critical role in increasing its conductivity.⁴ The increase in resistivity by air annealing is more pronounced for AZO films than for other TCO films such as indium tin oxide (ITO), fluorine tin oxide (FTO) (SnO₂:F), and SnO₂:Sb.⁵ The thermal degradation in the resistivity is a very serious problem in the application of AZO films as electrodes because it decreases the energy conversion efficiency or the electric signal transfer speed of the optoelectronic devices employing the AZO films.⁶ In previous studies, the thermal

degradation in polycrystalline AZO films has been simply attributed to oxygen adsorption on the grain boundary surface.^{4,7,8} Moreover, a poor understanding of the degradation mechanism has delayed the development of a method to reversibly heal the electrical properties of degraded AZO films. While a significant increase in the resistivity of polycrystalline AZO films by air annealing has been experimentally confirmed and estimated, a systematic investigation of the degradation and recovery mechanisms has yet to be performed.⁷ Studenikin *et al.*⁹ reported only that electrical properties of undoped polycrystalline ZnO could be changed reversibly through air and hydrogen annealing.

In the present study, we investigated the degradation behaviors of Al (1.6 at. %)-doped ZnO films epitaxially grown by pulsed laser deposition (PLD) as well as the underlying physics of thermal annealing effects on the reversible change in electrical properties. Based on the explored degradation mechanism, we also propose a way to recover thermally degraded AZO films.

II. EXPERIMENTAL PROCEDURE

Pure ZnO and AZO films were grown on sapphire (0001) substrates at 400 °C and 1.0×10^{-1} torr of oxygen pressure from pure ZnO and Al (1.6 at. %)-doped ZnO targets using the PLD technique with a KrF (248 nm) excimer laser with a pulse energy density of 2 J/cm² and a repetition rate of 5 Hz. To study the thermal stability of the electrical properties, a portion of the films was annealed in air at 450 °C for 1 h. Subsequent annealing at 450 °C for 1 h in a pure hydrogen atmosphere was performed to recover the electrical properties of the air-annealed films. The crystallinity of the films was characterized by x-ray diffraction (XRD) using Cu K α radiation. The resistivity, carrier concentration

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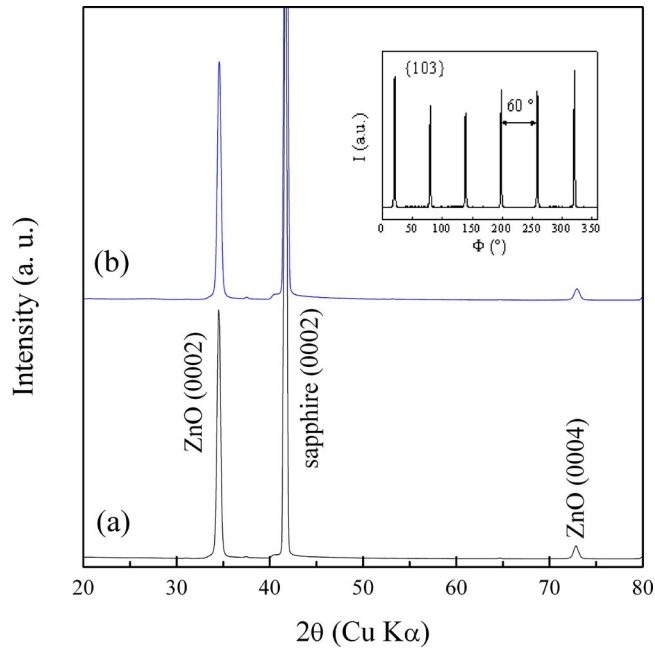


FIG. 1. (Color online) XRD θ - 2θ scan of (a) the as-deposited and (b) the air-annealed AZO films. The inset shows the result of an in-plane Φ scan for the as-deposited AZO film.

(n), and Hall mobility (μ) of the films were measured using the van der Pauw method. Optical absorbance was measured by ultraviolet-visible spectrophotometry. Photoluminescence (PL) was measured at room temperature using a He-Cd laser operating at 325 nm and a charge coupled device detector.

III. RESULTS AND DISCUSSION

Figure 1 shows XRD θ - 2θ scan results of both as-deposited and air-annealed AZO films on sapphire (0001) substrates. In both films, only ZnO (0002) and (0004) peaks were observed without any other secondary phase peaks, indicating that aluminum ions are well incorporated into the ZnO matrix. The sixfold symmetry of the Φ scan for ZnO (103) in the inset of Fig. 1 indicates that the AZO films were grown epitaxially on the sapphire substrates. The ZnO (0002) peaks in the θ - 2θ scan and the full width at half maximum of the rocking curves (not presented) were identi-

cal for both as-deposited and air-annealed AZO films. This implies that the thermal annealing process did not change the crystallinity or the doping behavior of the epitaxial AZO films. As a result, the well known increase in the resistivity of the air-annealed AZO films cannot be attributed to a structural change in the AZO films such as decreased crystallinity or the formation of secondary phases.

The electrical properties of the AZO films before and after being subjected to air annealing, subsequent H_2 annealing, and repeated air and hydrogen annealing (six cycles) are summarized in Table I. As-deposited AZO films have a low resistivity (ρ) of $8.01 \times 10^{-4} \Omega \text{ cm}$ with a large carrier concentration (n) of $1.72 \times 10^{20} \text{ cm}^{-3}$ and a high mobility (μ) of $45.4 \text{ cm}^2/\text{V s}$. An annealing of AZO films in air increased the resistivity by more than two orders of magnitude. The thermal treatment in a reducing atmosphere recovered the resistivity of the as-grown AZO films, which indicates that the change in the electrical properties of the AZO films is reversible. Table I also shows that the change in electrical resistivity during the annealing atmosphere is due mainly to the change in the carrier concentration. We confirmed the effect of the thermal treatment on the electrical properties of AZO films by measuring the optical band gap. Figure 2 shows the band gap of the as-deposited ZnO film as well as the as-deposited and air-annealed AZO films. Because ZnO is a direct band gap semiconductor, the optical band gap (E_g) was obtained from the plot of the optical absorption coefficient as a function of $h\nu$ as in Eq. (1).

$$\alpha = (h\nu - E_g)^{1/2}. \quad (1)$$

Here, h is Planck's constant and ν is the frequency of the incident photon.¹⁰ The decrease in the band gap from 3.35 to 3.25 eV can be explained by the Burstein–Moss effect.¹¹ An air annealing of degenerate AZO films removes surplus electrons occupying the energy states above the bottom of the conduction band, thereby decreasing both the optical band gap and electron concentration. The increase in the optical band gap with the increase in electron concentration is related to the following relation given by Burstein:¹²

TABLE I. The electrical properties of as-deposited, air-annealed, and subsequently H_2 -annealed AZO films as well as AZO films subjected to repeated air and hydrogen annealing (six cycles). ρ is the resistivity, n is the carrier concentration, μ_T is the total mobility, μ_I and μ_N are mobilities caused by ionized and neutral impurity scattering, respectively, and N_I and N_N are the concentrations of ionized and neutral impurity scattering centers, respectively. Assuming that electrons of AZO films are mainly produced by singly ionized Al in Zn sites, the electron concentration (n) is the same as the concentration of ionized impurities and not the combined acceptor (N_I).

	ρ ($\Omega \text{ cm}$)	n ($=N_I$) (cm^{-3})	μ_T ($\text{cm}^2/\text{V s}$)	μ_I ($\text{cm}^2/\text{V s}$)	μ_N ($\text{cm}^2/\text{V s}$)	N_N (cm^{-3})
As-deposited film	8.01×10^{-4}	1.72×10^{20}	45.4	123	71.8	8.78×10^{19}
Air-annealed film	1.97×10^{-1}	2.13×10^{18}	14.9	401	15.5	4.07×10^{20}
Subsequently H_2 -annealed film	1.65×10^{-3}	1.13×10^{20}	33.5	134	44.6	1.41×10^{20}
Sixth air-annealed film	1.10×10^{-1}	3.60×10^{18}	15.8	336	16.6	3.80×10^{20}
Sixth subsequently H_2 -annealed film	9.58×10^{-4}	1.78×10^{20}	36.6	122	52.2	1.21×10^{20}

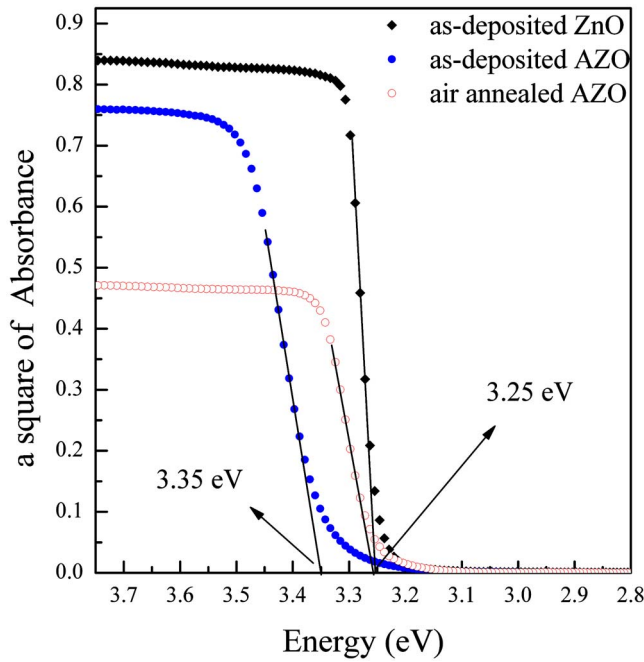


FIG. 2. (Color online) Square of absorbance as a function of photon energy for the as-deposited ZnO and AZO films and the air-annealed AZO film.

$$\Delta E_g \approx \frac{h^2}{8m^*} \left(\frac{3}{\pi} \right)^{2/3} n^{2/3}, \quad (2)$$

In Eq. (2), ΔE_g is the energy band gap widening, n is carrier concentration, h is Planck's constant, and m^* is the electron effective mass in the conduction band. Equation (2) predicts that the difference in the band gap between the air-annealed AZO and the as-deposited AZO film is about 0.38 eV, which is the same order of magnitude as the experimental observation.

In Table I, it is noted that the mobility (μ_T) of the air-annealed AZO films is three times smaller than that of as-grown AZO films. This is contrary to general semiconductors. In most degenerated semiconductors, the increase in the carrier concentration promotes scattering between carriers, leading to a decrease in mobility.¹³ The mobility in ZnO films is determined mainly by scattering centers such as grain boundaries, ionized impurities, and neutral impurities. Given that the AZO films in this study are epitaxial films, the reduction in the mobility after annealing in air is not attributed to the grain boundary effect. Based on and neutral and ionized impurity scattering mechanism by Erginsoy¹⁴ and Dingle¹⁵ we analyzed the change in the films. In Erginsoy and Dingle's mechanism, the scatterings of carriers at ionized dopants and neutral dopants contribute to the mobility of carriers; and their individual effect is determined by the following relation:

$$\mu_N = (m^* e^3) / (20 \epsilon_0 \epsilon_r \hbar^3 N_N), \quad (3)$$

$$\mu_I = [24 \pi^3 (\epsilon_0 \epsilon_r)^2 \hbar^3 n] / [e^3 m^{*2} g(x) z^2 N_I]. \quad (4)$$

Here, μ_N and μ_I are the mobilities due to neutral and ionized impurities, respectively, N_N and N_I are the concentrations of neutral and ionized impurities, respectively, that play a role as a scattering center, m^* ($=0.28m_0$ for AZO) (Ref. 16) is the

effective mass of the free electrons, ϵ_0 is the permittivity of free space, ϵ_r ($=8.0$ for AZO) is the relative permittivity, z is the charge of the ionized centers, and n is the carrier concentration. In Eq. (3), $g(x)$ is a screening function calculated as follows:

$$g(x) = \text{Ln}(1 + 4/x) - (1 + x/4)^{-1},$$

and

$$x = (4e^2 m^*) / [4 \pi \epsilon_0 \epsilon_r \hbar^2 (3 \pi^5)^{1/3} n^{1/3}].$$

Then, the total mobility μ_T measured by a Hall measurement is expressed by the harmonic mean of the mobilities determined by neutral and ionized impurities.

$$\mu_T^{-1} = \mu_N^{-1} + \mu_I^{-1}. \quad (5)$$

The electron concentration (n) equals the difference in the concentration of the singly charged Al dopants (N_I) and that of the charged acceptors, e.g., the concentration of singly ionized Al in Zn sites, which are neither combined with nor compensated by acceptors. μ_I can be obtained by calculating $g(x)$ in Eq. (4). Then, μ_N and N_I can be determined using Eqs. (3) and (5). The analysis of the mobility of the films is also summarized in Table I. Thermal annealing drastically increases the concentration of neutral scattering centers of the AZO film, while it moderately decreases the concentration of the ionized scattering centers. H_2 gas treatment of air-annealed AZO films almost completely nullifies the effect of the air annealing; and recovers the concentration of the scattering centers. The reduction and oxidation experiments were repeated six times to see if variations of the carrier concentration and mobility by the thermal annealing are reversible. The results are summarized in Table I and reveal that the electrical properties changed reversibly by controlling the annealing atmosphere and temperature. No substantial degradations were observed after six repeated hydrogen-air annealing cycles.

In the mobility analysis of Table I, the large increase in the concentration of the neutral scattering centers suggests that the positively ionized impurity (Al_{Zn}^+) is neutralized by the appearance of acceptors during annealing in air. A clue to explain the physics underlying the neutralization of the defects can be found in recent studies conducted with Sn-doped In_2O_3 (ITO) films. It has been shown that the oxygen interstitials are formed near the positively charged tin ions (Sn_{In}^+) and that two oppositely charged impurities form the defect complexes.^{17,18}

To probe the origin of the increase in the neutral scattering centers by the air annealing, we measured the PL of the films. Figure 3 shows the PL spectra. The near band edge (NBE) emission of the AZO films at 3.37 eV is larger than that of pure ZnO, which is 3.28 eV. This is consistent with the increase in the optical band gap of the AZO films, which is traced to the Burstein–Moss effect. After air annealing, the energy of the NBE emission peak returns to that of the as-deposited ZnO films at 3.28 eV. Subsequent H_2 annealing of the air-annealed AZO film shows a blueshift of the NBE emission once again. This is consistent with the results of conductivity measurements showing a reversible change in the carrier concentration. The NBE emission of the thermally

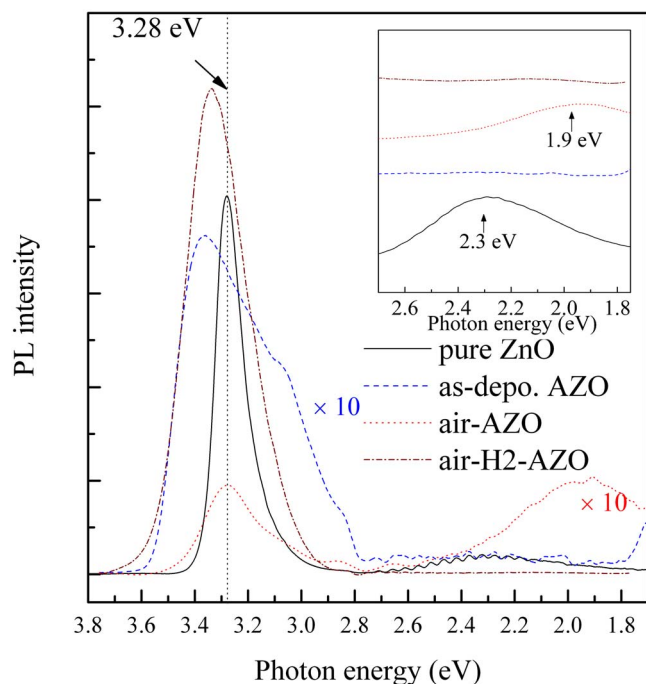


FIG. 3. (Color online) PL of as-deposited ZnO (as-depo. ZnO), as-deposited AZO (as-depo. AZO), air-annealed AZO (air-AZO), and air-annealed and subsequently hydrogen-annealed AZO films (air-H₂-AZO). All data were measured at room temperature. The inset shows the deep level emission of the films.

annealed AZO films in conjunction with the conductivity data indicates that the change in the optical properties of the AZO films is due to the change in the carrier concentration.

A remaining question is which material parameter causes the reversible control of the carrier concentration. In general, a change in carrier concentration should accompany a change in the concentration of donor defects in *n*-type ZnO. A PL measurement in the visible range is a very powerful tool to qualitatively investigate the presence of defects in ZnO. In this study, we examined the deep level transition of several films to explore the origin of the conductivity change. The inset in Fig. 3 presents deep level emissions of the films, as discussed above. The as-deposited ZnO film showed a broad green emission with a center position of 2.3 eV. This indicates that a fair amount of donor defects, such as oxygen vacancies and zinc interstitials, are formed during the deposition of pure ZnO films.^{1,19} In the as-deposited AZO film, the intensity of the green emission is far lower than that of as-deposited ZnO, which indicates that the incorporation of Al into ZnO suppresses the formation of intrinsic defects such as oxygen vacancies or zinc interstitials. Since Al₂O₃ dopants contain excess oxygen compared to ZnO, the excess oxygen may compensate the oxygen vacancies or zinc interstitials in the ZnO matrix. Therefore, in as-deposited AZO films, the main conductional carriers are electrons produced by Al substituting Zn (Al_{Zn}[•]+e[']) and not intrinsic electrons produced by intrinsic defects.

After annealing AZO films in air, the PL data show a very strong orange emission centered at 1.9 eV. Though the origin of the orange emission is controversial, the overall consensus of previous studies is that a singly and negatively

charged interstitial oxygen, O_i['], plays an important role in emitting the orange light in ZnO.²⁰⁻²³ The orange emission of the air-annealed AZO films proves that air annealing of the AZO films incorporates oxygen into AZO; and produces a great amount of O_i['] in AZO. O_i['] acts as an acceptor in ZnO and occupies 1 electron/interstitial. Therefore, the formation of O_i['] during air annealing reduces the electron concentration and decreases the conductivity of the AZO films. We did not observe an orange emission in air-annealed pure ZnO films at 450 °C (not shown). The orange emission was observed in a pure ZnO film annealed in air or oxygen at a much higher temperature. The pronounced effect of air annealing on the orange emission in AZO films is explained by the fact that Al doping decreases the base level of the oxygen vacancy, which suppresses the formation of O_i['] at 450 °C. When H₂ annealing followed air annealing, the AZO films no longer showed a green or orange emission. The disappearance of the orange emission in Fig. 3 means that the O_i['] produced by air annealing can be reversibly eliminated by H₂ annealing. This explains why the AZO films recovered their initial carrier concentration after H₂ annealing, as shown in Table I.

IV. CONCLUSIONS

The electrical and optical properties of epitaxially grown AZO films were investigated as a function of the annealing atmosphere. The change in the resistivity of the AZO films was found to result mainly from the change in carrier concentration and the increase in scattering centers. An air annealing of the AZO films increased the resistivity by more than two orders of magnitude. Subsequent H₂ annealing recovered the initial carrier concentration of the AZO films. The PL study revealed that the degradation and recovery of electrical properties in AZO films are strongly related to the formation of the oxygen interstitial O_i['], which is the acceptor in ZnO. This study shows that the electrical degradation of the AZO films is due to the formation of oxygen interstitials; and that annealing in proper ambient atmospheres can reversibly control the electrical properties of the AZO films.

ACKNOWLEDGMENTS

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy, Republic of Korea (RIAM).

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