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Effects of oxygen concentration on the electrical properties of ZnO films

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Abstract

In this paper, electrical characteristics by various oxygen content in ZnO films were studied. To control the oxygen content of ZnO films, post-thermal annealing was performed in N_2 and air ambient, led to improve crystallinity and optical properties of ZnO films. The oxygen concentration was measured by Auger electron spectroscopy. The ZnO films having the deficiency of oxygen showed the electron concentrations between 10^{21} and mid 6×10^{17} cm^{-3} and resistivity at 10^{-3}–10^{-1} Ω cm. On the other hand, when the oxygen concentration of the ZnO films was up to the stoichiometry with Zn, the ZnO films showed low electron concentration at -10^{17} cm^{-3} and resistivity at 10 Ω cm.

Keywords: A. Films; C. Electrical property; D. ZnO; Oxygen content

1. Introduction

Zinc oxide (ZnO) is currently considered as a promising material for very bright ultraviolet and blue optical devices, like light-emitting diodes (LED), laser diodes (LD), and photo-diodes (PD) [1], because of its interesting characteristics, such as a large direct band gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV, which is 2.4 times higher than that of GaN. Furthermore, it is widely applied in transparent conductive contact and thin-film gas sensors, varistors, solar cells, and other devices. In practice, ZnO films can be deposited by various deposition techniques including molecular beam epitaxy (MBE), chemical vapor phase deposition (CVD), pulse laser deposition (PLD) and sputtering [2–5]. However, most of the deposited ZnO films tend to show many point defects, such as oxygen vacancy, zinc interstitial, zinc vacancy, interstitial oxygen, and antisite oxygen. These point defects have an influence on structural, optical, and electrical properties of ZnO films [6–8]. Especially, the oxygen vacancies generate the free electrons in ZnO films due to oxygen nonstoichiometry [9] and are responsible for natural n-type of ZnO. Thus, it is of great significance to understand the properties of ZnO films with oxygen contents.

In this paper, the effects of oxygen content in ZnO films on the electrical properties of ZnO films were reported. To control oxygen concentration of ZnO films, several kinds of post-thermal annealing in N_2 and air ambient were preformed. The relationship between the electrical characteristics and oxygen content of ZnO films was investigated.

2. Experimental procedure

ZnO films were deposited on SiO_2/Si (1 0 0) substrates at room temperature by RF sputtering system. ZnO (4N) was used as the target. The vacuum chamber was evacuated to 10^{-5} Torr, then Ar (50 sccm) gas was introduced through mass flow

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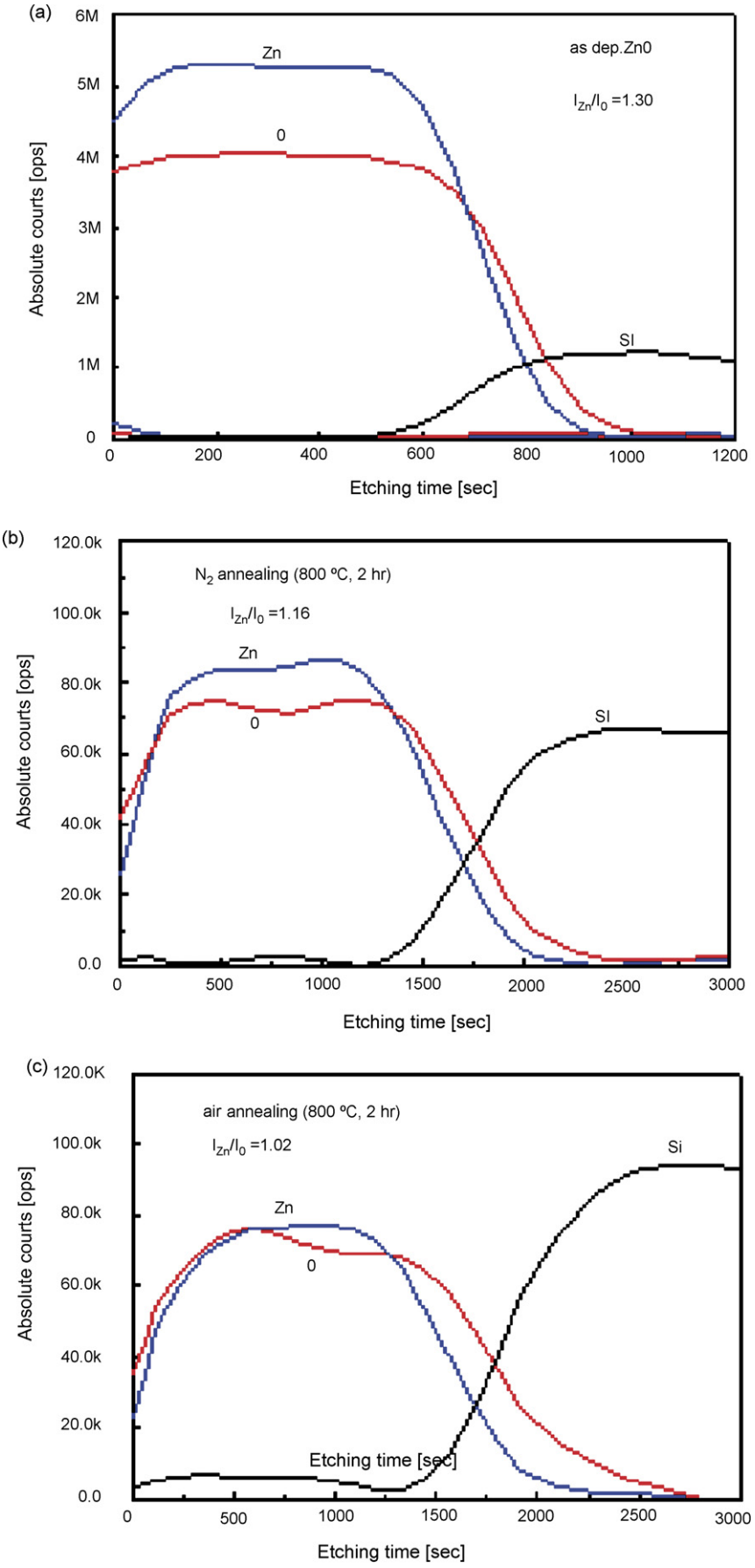

Fig. 1. Auger depth profiles of ZnO films with different annealing ambient. (a) *as dep.* ZnO (b) in N_2 ambient, (c) in air ambient at 800 °C for 2 h.

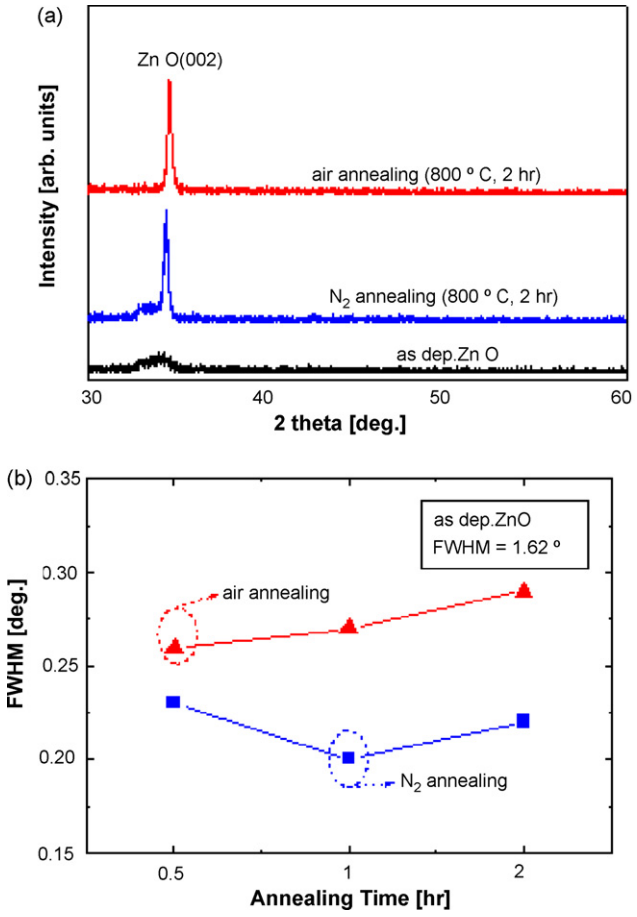

Fig. 2. (a) The $\theta - 2\theta$ XRD patterns of the *as dep.* ZnO and ZnO films annealed in N_2 and air ambient at 800 °C for 2 h. (b) The FWHM of the (0 0 2) plane of ZnO films according to annealing condition.

controllers (MFC). The total pressure was controlled at 5 mTorr. The sputtering time was 40 min and the RF power was 200 W. The thickness of the deposited ZnO films was approximately 260 nm. After deposition, the films were annealed in a thermal furnace under N_2 and air ambient at 800 °C for 2 h. The structural properties were investigated by X-ray diffraction (XRD, Rigaku D/max 2100H) with a CuK_α radiation ($\lambda = 0.1542$ nm). Optical properties were investigated by Photoluminescence (PL) measurements at room temperature using a 325 nm line of He–Cd laser as an excitation source. To investigate the oxygen concentration of the ZnO films, Auger electron spectroscopy (AES) was used. The electrical properties were measured by Hall-effect measurement in the van der Pauw configuration using a magnetic field of 0.51 T at room temperature. To form the Ohmic contact, $In_{0.95}Sn_{0.05}$ was used.

3. Results and discussion

To confirm the variation of oxygen content by annealing, Auger spectra of *as dep.* ZnO and ZnO films annealed in N_2 and air ambient at 800 °C for 2 h are shown in Fig. 1. In the case of *as dep.* ZnO, oxygen concentration was much lower than zinc concentration and the ratio of zinc to oxygen (I_{Zn}/I_O) was 1.30. It revealed that deposited ZnO films included many oxygen vacancies (V_O). The deficiency of oxygen was still present in ZnO films annealed in N_2 ambient. However, I_{Zn}/I_O was 1.16, which means that oxygen concentration slightly increased. On the other hand, ZnO films annealed in air ambient had almost the same level of oxygen and zinc content.

Fig. 2(a) shows the $\theta - 2\theta$ XRD patterns of the *as dep.* ZnO and ZnO films annealed in N_2 and air ambient at 800 °C for 2 h. The *as dep.* ZnO and ZnO films annealed had only a peak of 34.4° at 2θ, which corresponds to the (0 0 2) plane of hexagonal ZnO crystal structure and ZnO films exhibit (0 0 2) preferential

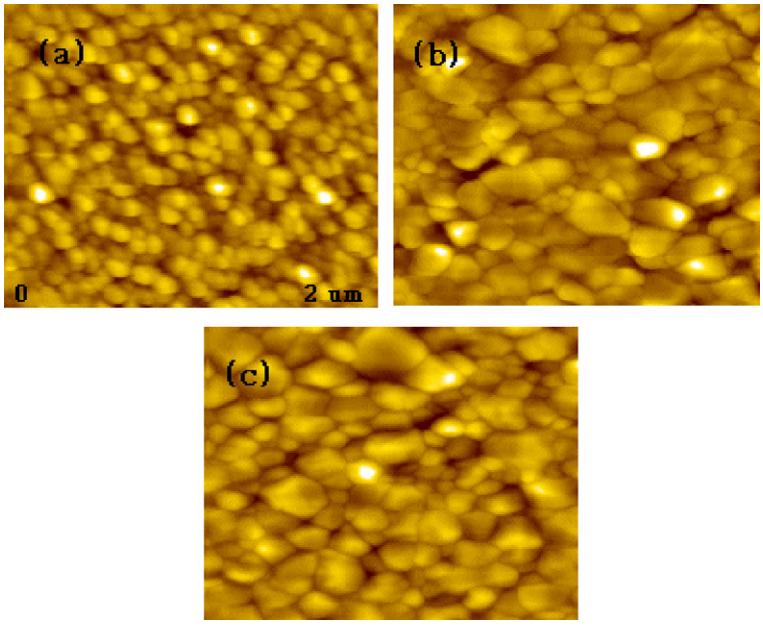

Fig. 3. AFM surface images of ZnO films with different annealing ambients (a) *as-dep.* ZnO, (b) in N_2, and (c) air at 800 °C for 2 h.

orientation with the *c*-axis perpendicular to the substrate. After post-thermal annealing, the intensity of the diffraction peak of ZnO (0 0 2) strongly increased and the peak width was narrow. Fig. 2(b) shows the FWHM of the (0 0 2) plane of ZnO films according to annealing condition. While the FWHM of the *as dep.* ZnO was 1.62°, that of annealed ZnO films was decreased between 0.3° and 0.2°. Especially, when the ZnO films were annealed in N_2 ambient for 1 h, the films showed the narrowest peak width of only 0.2°. With post-thermal annealing, the intensity of the peak of ZnO (0 0 2) plane increased, while the FWHM decreased. This implies that the crystallinity of ZnO films was improved during annealing in both ambient. Also the grain size of ZnO films increased from 130 nm to over 200 nm after annealing, as shown in Fig. 3.

Fig. 4 shows PL spectra at room temperature of ZnO films annealed in N_2 and air ambient at 800 °C for 2 h. Generally, ZnO films display a UV near-band-edge emission peak around 3.2 eV, a green emission around 2.4 eV, a yellow emission around 2.1 eV, and a red emission around 1.9 eV [10,11]. The origin of the green and red emissions that are called by deep-level emission is attributed to defect levels associated with oxygen vacancy (V_O) or zinc interstitial (Zn_i) [12,13]. The relative PL intensity ratio of the UV emission to the deep-level emission (I_{UV}:$I_{deep\text{-}level}$) were compared. For ZnO films annealed in N_2, air ambient, the ratio was 2.5:1, 5.4:1, respectively. This indicates that the concentration of oxygen vacancy or zinc interstitial of the air annealed ZnO film, which is generally incurred by the deficiency of oxygen in the ZnO films, is lower than that of the N_2 annealed ZnO film. This is similar to the result of AES.

It is generally recognized that during annealing, the variation of the intrinsic defects in ZnO film, such as oxygen vacancy (V_O), zinc vacancy (V_{Zn}), interstitial oxygen (O_i), and antisite oxygen (O_{Zn}), with oxygen pressure (p_{O_2}) can be expressed as follows [14]:

$$\tfrac{1}{2}O_2 + V_O = O_O, \quad [VO] \propto p_{O_2}^{-1/2} \tag{1}$$

$$\tfrac{1}{2}O_2 + V_{Zn} = O_O, \quad [V_{Zn}] \propto p_{O_2}^{1/2} \tag{2}$$

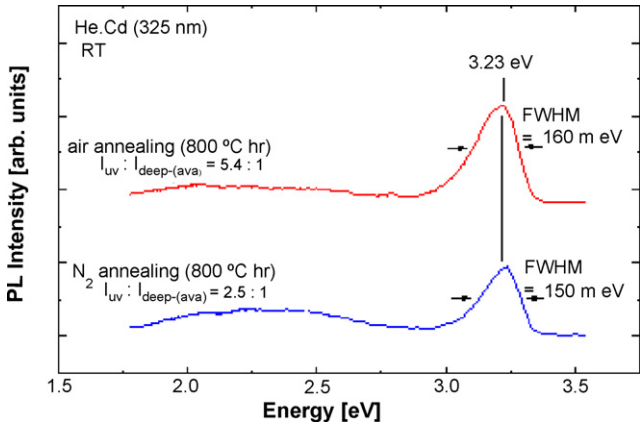

Fig. 4. PL spectra at room temperature of ZnO films annealed in N_2 and air ambient at 800 °C for 2 h.

$$Zn_i + \tfrac{1}{2}O_2 = Zn_{Zn} + O_O, \quad [Zn_i] \propto p_{O_2}^{-1/2} \tag{3}$$

$$\tfrac{1}{2}O_2 = O_i, \quad [O_i] \propto p_{O_2}^{1/2} \tag{4}$$

$$\tfrac{1}{2}O_2 + V_{Zn} = O_{Zn}, \quad [O_{Zn}] \propto p_{O_2}^{1/2}[V_{Zn}] \tag{5}$$

Here, $[V_O]$ and $[V_{Zn}]$ are the concentrations of the nonionized vacancies of oxygen and zinc, respectively. $[Zn_i]$, $[O_i]$, and $[O_{Zn}]$ are the concentrations of the interstitial zinc, interstitial oxygen, and antisite oxygen, respectively. Eqs. (1) and (3) indicate that concentrations of the V_O and Zn_i have to decrease with an increase of oxygen pressure p_o, while Eqs. (2), (4) and (5) reveal that V_{Zn}, O_i, and O_{Zn} could be increased with an increase of oxygen pressure p_o. Thus, annealing with oxygen source ambient can decrease V_o and Zn_i.

Now, the effects of oxygen content in ZnO films on the electrical properties of the ZnO films are discussed. To investigate the electrical properties according to oxygen content, Hall-effect measurements were carried out at room temperature. In the case of *as dep.* ZnO, it had high carrier concentration of 10^{21} cm^{-3} and low resistivity of 10^{-3} Ω cm. On the other hand, ZnO films annealed in N_2 ambient showed a carrier concentration of mid 4×10^{18} cm^{-3} and a resistivity of approximately 10^{-1} Ω cm and ZnO films annealed in air ambient showed a carrier concentration of high 8×10^{16} cm^{-3} to low 2×10^{17} cm^{-3} and a resistivity of approximately 10 Ω cm. Compared with the AES results, with increasing oxygen content of ZnO films, the carrier concentration

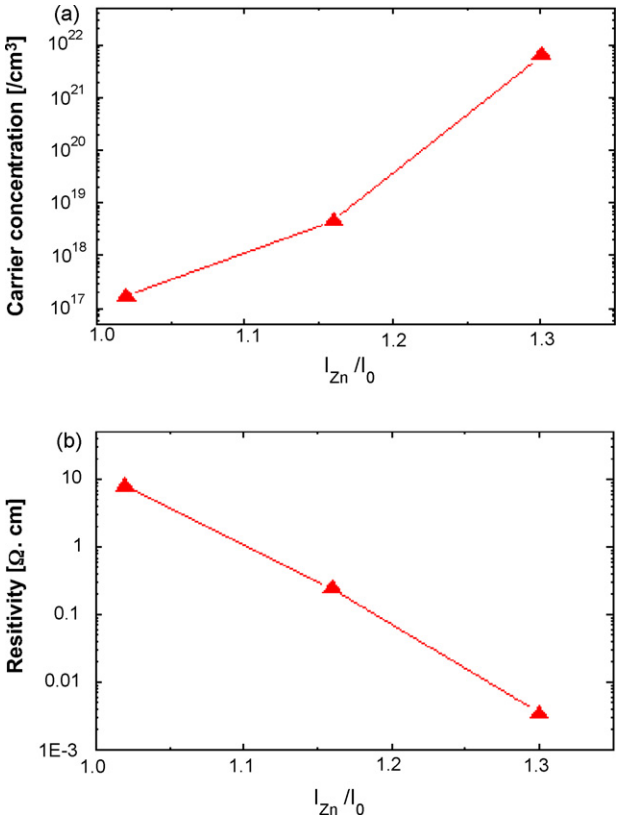

Fig. 5. The variation of (a) carrier concentration and (b) resistivity with change of oxygen content.

decreased and the resistivity increased. This is because the oxygen vacancies generating the free electrons decreased by diffusing the oxygen in films. However, note that we could not get carrier concentration with under mid -1×10^{16} cm^{-3} even the excess of oxygen in ZnO films. Fig. 5 shows the variation of carrier concentration and resistivity with oxygen content.

4. Conclusions

In this paper, the effects of oxygen content in ZnO films on the electrical properties of ZnO films were reported. To control the oxygen content, post-thermal annealing in N_2 and air ambient were performed, which improved crystallinity and optical properties of ZnO films. The oxygen concentration was measured by Auger electron spectroscopy. In ZnO films annealed in N_2 ambient, the deficiency of oxygen was still present and it showed stable n-type conduction. On the other hand, ZnO films annealed in air ambient had almost the same level of oxygen and showed the decrease in carrier concentration to 10^{17} cm^{-3} and increase in resistivity. This results show that the electrical properties can be controlled with oxygen content by post thermal annealing in oxygen source ambient.

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