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Low temperature method to passivate oxygen vacancies in un-doped ZnO films using atomic layer deposition

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ABSTRACT

Owing to oxygen vacancies, the as-prepared ZnO normally shows n-type semiconducting characteristic. This has restricted the preparation of high-quality p-type ZnO and the application of ZnO optoelectronic devices. Therefore, we studied a method of using H_2O_2 as an oxygen source to passivate oxygen vacancies (V_o) in ZnO films via atomic layer deposition (ALD). The temperature range for the self-limited growth of crystalline ZnO thin films by ALD using diethylzinc and H_2O_2 was found to be in the range of 80 to 150 °C. Our results show that the use of H_2O_2 as an oxygen source can provide an O-rich condition (instead of H_2O) for the growth of ZnO film, with a total preferential (002) orientation of the growth plane and decreased grain size. Further, the O-rich growth environment can suppress the formation of V_o and zinc interstitials and decrease the carrier concentration in ZnO (from $2.525 \times 10^{19}\,cm^{-3}$ to $1.695 \times 10^{12}\,cm^{-3}$). This can lead to an increase in the film resistivity from $1.717 \times 10^{-2}\,\Omega{\cdot}cm$ for a ZnO film prepared using H_2O to $1.348 \times 10^{4}\,\Omega{\cdot}cm$ for a ZnO film prepared using H_2O_2. Thus, H_2O_2 could be used to passivate V_o in ZnO at a low temperature, and it could be beneficial for the preparation of p-type ZnO films.

1. Introduction

ZnO film is a transparent semiconductor material with a direct band gap of 3.37 eV, outstanding optoelectronic properties, and high exciton binding energy of 60 meV which is higher than that of GaN (24 meV) [1–3]. Owing to these properties, ZnO has potential applications in short wavelength optoelectronic devices such as ultraviolet-blue light emitting diodes and laser diodes [4–6]. However, the as-grown ZnO film usually has some native defects, such as oxygen vacancies (V_o), oxygen interstitials (O_i), oxygen antisites (O_{Zn}), zinc vacancies (V_{Zn}), zinc interstitials (Zn_i), and zinc antisites (Zn_o). Among these defects, in general, the donor defect, V_o is the dominant one in as-grown ZnO films and usually results in n-type semiconducting behavior [7,8]. Moreover, V_o can also counteract the acceptor dopants in ZnO, and it is one of the main reasons why p-type ZnO with a high carrier concentration is difficult to prepare [7–9]. This issue is a bottleneck in the application of ZnO devices. Therefore, to accelerate the application of ZnO-based optoelectronic devices, it is important to carry out focused studies on passivating the donor defects, V_o in ZnO films, to enable the fabrication of p-type ZnO films with a high carrier concentration. The often-used method to decrease V_o in ZnO is the post-annealing of the as-prepared ZnO in oxygen atmosphere at a high temperature (~500–1000 °C) [10–13]. Previous experimental studies have shown that the doping of F and Cl can fill V_o and decrease the V_o concentration in ZnO films [14,15]. However, both F and Cl are n-type dopants that could also counteract the acceptor dopants in ZnO. Previous theoretical works have indicated that V_o can be easily formed under zinc-rich (Zn-rich) growth condition; in contrast, V_o can be passivated in an oxygen-rich (O-rich) growth environment [7,16,17]. Previous works also predict that when ZnO thin films are prepared by metal-organic vapor phase epitaxy, higher oxygen partial pressure lead to lesser V_o [18]. However, there are no detailed experimental studies on how the oxygen condition (O-rich or oxygen-deficient) influences the V_o in ZnO film prepared by atomic layer deposition (ALD). Therefore, in this work, we used ALD to study the passivation of V_o in ZnO film at a low temperature by preparing the ZnO film in an O-rich environment. The deposition mechanism of ALD is a self-limiting chemical reaction with a single pulse of the precursor leading to the formation of only one atomic layer and the film was deposited by alternative pulses of each separated precursor. Therefore, the film thickness could be controlled according to deposition cycle number. Moreover, ALD also provides an excellent step coverage and uniformity, and can enable deposition of a uniform film with outstanding properties on substrates with complex structures [19–21]. For ALD prepared ZnO films, H_2O was generally used as oxygen source, H_2O_2 and O_3 also were used as oxygen source in a small amount of research [22–24]. Park et al. studied the preparation of ZnO

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using both H_2O_2 and O_3 as oxygen source via ALD, and found the growth rate of ZnO using H_2O_2 is higher than using O_3 [22]. It is because H_2O_2 can provides a better surface adsorption of the DEZ precursor molecules, however, the using of O_3 is more like a thermally activated process which means the growth rate increases with substrate temperature. And the study of Park et al. also showed the resistivity has a decrease because of the increase of carrier concentration with the increase of substrate temperature in both ZnO film prepared using H_2O_2 and O_3 [22]. The study of Kim et al. indicated the ALD prepared ZnO using O_3 on SiO_2/Si substrate at high temperature can induce the diffusion of Si into ZnO and increase the resistivity [23]. When H_2O_2 was used as oxygen source, the ZnO film prepared via ALD method has a (002) preferential growth orientation, which is different from the using of H_2O as oxygen source [14,15,24]. In this work, H_2O_2 (50% in H_2O) with a higher stoichiometric ratio of oxygen was used as the oxygen source, which is required for providing more oxygen atoms than H_2O for the preparation of ZnO and suppress the generation of V_o. As a reference, H_2O was also used as an oxygen source to prepare ZnO films in combination with DEZ. The ALD temperature window for the preparation of ZnO thin films using DEZ and H_2O_2 was first investigated, and then the properties of the ZnO thin films prepared at different deposition temperatures within the range of the ALD window were evaluated.

2. Experiment method

The ALD of ZnO thin films was carried out with a traveling wave type Lucida D100 system (NCD Technology, Inc., Korea), and ZnO film was deposited on both liquid crystal display glass (Fusion 1737) and Si substrates for measuring different properties. Diethylzinc (DEZ) (Hansol Chemical Co., Ltd., Korea) was used as the Zn source and H_2O and H_2O_2 (50% in H_2O, Sigma-Aldrich) were used as the O sources. A high-purity N_2 (99.999%) gas with a flow rate of 20 standard cubic centimeters per minute (sccm) was used both as the purge gas and transport gas to carry DEZ, H_2O, and H_2O_2 into the deposition chamber. The ALD dosing sequence of the precursors for the preparation of ZnO thin films is as follows: DEZ (0.1 s) $\rightarrow$ N_2 (10 s) $\rightarrow$ H_2O/H_2O_2 (0.1 s) $\rightarrow$ N_2 (10 s).

X-ray diffraction (XRD, D/MAX-2000, Rigaku) was used to analyze the crystal structure of ZnO thin films using Cu-$K\alpha$ radiation ($\lambda = 0.154$ nm) at 30 mA and 40 kV. Field emission scanning electron microscopy (FE-SEM, JEOL, JSM 7001F) was used to investigate the surface morphology and film thickness of ZnO films at an operating voltage of 15.0 kV, and energy-dispersive X-ray spectroscopy (EDS) was used at 15.0 kV for the quantitative analysis of the elements in the ZnO film. Photoluminescence (PL) spectroscopy (LabRam Aramis, Horriba Jovin Yvon) was carried out with 325 nm laser excitation at room temperature. The O 1s near edge X-ray absorption fine structure (NEXAFS) was investigated using the Pohang Accelerator Laboratory (PLS) 4D beam line. Hall effect measurements (Ecopia HMS3000) based on van der Pauw method was used to measure the resistivity (ρ), mobility (μ), and carrier concentration (n) of ZnO films at room temperature.

3. Results and discussion

3.1. ALD window

The influence of the deposition temperature on the growth rate was examined at first. Fig. 1 shows the growth rate of a ZnO film prepared using H_2O (ZnO-H_2O film) at 140 °C, and the growth rate of a ZnO film prepared using H_2O_2 (ZnO-H_2O_2 film) at temperatures ranging from 60 to 200 °C. From 60 to 150 °C, the growth rate of ZnO-H_2O_2 film remained in the range of 0.108 nm/cycle (at 60 °C) to 0.088 nm/cycle (at 80 °C), without noteworthy influence of the temperature. When the temperature was increased to 160 °C and 200 °C, the ZnO-H_2O_2 film growth rate shows a visible increase owing to the decomposition of the precursor on the substrate surface due to the high temperature. Therefore, the ideal temperature (ALD window) for the self-limited growth of ZnO-H_2O_2 film by ALD is in the range of 60 to 150 °C. Previous studies have indicated that the ALD window for the preparation of ZnO-H_2O film is normally in the range of 100–180 °C [25–27]. Therefore, by comparing with the results obtained using H_2O as the oxygen precursor, the ZnO deposition temperature using ALD can be decreased to as low as 60 °C when using H_2O_2 as the oxygen source. The growth rate of a ZnO-H_2O film at 140 °C is 0.21 nm/cycle, which agrees with previous results which indicate the growth rate of ZnO-H_2O film ranging from 0.18 nm/cycle to 0.27 nm/cycle within the ALD window [25,27]. Fig. 1 also shows that the growth rate of a ZnO-H_2O_2 film between 60 and 150 °C is notably lower than that of a ZnO-H_2O film at 140 °C. The growth rates of ZnO-H_2O and ZnO-H_2O_2 films were compared from the average grain sizes of ZnO-H_2O and ZnO-H_2O_2 films obtained, using the Scherrer equation [28]. The calculated average crystalline sizes are given in Table 1. The average crystalline size of the ZnO-H_2O film is 29.1 nm and 29.3 nm, as calculated from the (100) and (002) diffraction peaks, respectively. However, for ZnO-H_2O_2 film an obviously decreased average grain sizes in the range of 15.7 to 23.5 nm is observed according to the variation in the deposition temperature from 60 to 150 °C. The smaller grain size of the ZnO-H_2O_2 film than those of ZnO-H_2O films could be attributed to the increased number of nuclei per unit area in the former (a discussion in detail in next section).

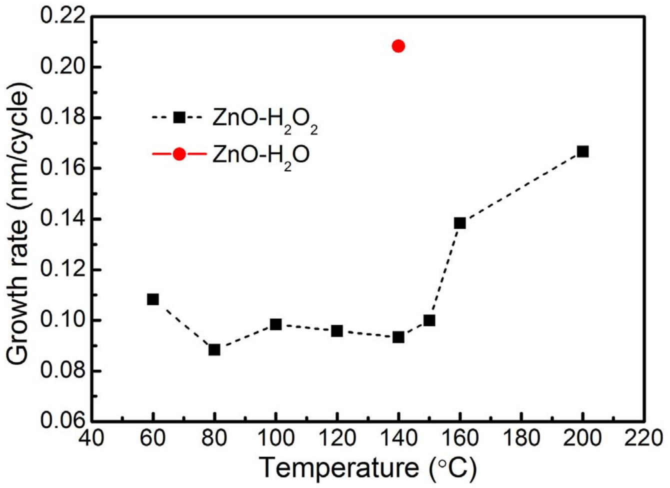

Fig. 1. The growth rate of ZnO-H_2O film prepared at 140 °C and ZnO-H_2O_2 film prepared at temperatures ranging from 60 to 200 °C.

3.2. *Growth orientation and surface morphology of ZnO-H_2O_2 film*

Depending on the ALD window of ZnO-H_2O_2 film, the properties of ZnO-H_2O_2 film deposited within the ALD window at 60 °C (ZnO-H_2O_2-60), 80 °C (ZnO-H_2O_2-80), 100 °C (ZnO-H_2O_2-100), 120 °C (ZnO-H_2O_2-120), 140 °C (ZnO-H_2O_2-140), and 150 °C (ZnO-H_2O_2-150) were studied along with ZnO-H_2O film deposited at 140 °C (ZnO-H_2O-140) for comparison. The crystal structures of the ZnO-H_2O and ZnO-H_2O_2 films were studied using XRD and the results are listed in Fig. 2. As shown in Fig. 2, three diffraction peaks of ZnO-H_2O film corresponding to the 100, 002, and 110 planes are observed at 2θ values of 31.93°, 34.54°, and 56.76°, respectively, and this indicates that ZnO-H_2O has a hexagonal wurtzite structure. However, all the ZnO-H_2O_2 film deposited within the temperature range of 60 to 150 °C only have one diffraction peak corresponding to the 002 plane. The diffraction peak intensity of 002 is very weak for ZnO-H_2O_2-60 because of its poor crystallinity due to the low temperature growth. When the deposition temperature is above 80 °C, the intensity of the 002 diffraction peak of ZnO-H_2O_2 film is very strong without dramatic change, implying that these films have good crystallinity. Upon changing the oxygen precursor from H_2O to