

## Optical and electrical characterizations of ZnO film grown on c-plane sapphire by using atomic layer deposition

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Optical and electrical properties of ZnO films were investigated by the photoluminescence (PL) and hall measurements. Thin films of ZnO were deposited by atomic layer deposition (ALD) with the different feed times of DEZn and H<sub>2</sub>O precursor. As the feed times of DEZn and H<sub>2</sub>O precursors increased, the intrinsic carrier concentration of ZnO film decreased from  $6.29 \times 10^{19}$  to  $4.13 \times 10^{19}/\text{cm}^3$ . Room temperature PL spectra of ZnO films represented two emission bands which consisted of the near bandedge ( $\sim 380$  nm) and the deep level emissions ( $\sim 510$  nm). The deep level emission was thought be ascribed to the native defects such as Zn vacancy ( $V_{\text{Zn}}$ ) and oxygen vacancy ( $V_{\text{O}}$ ), etc. With increasing the feed time of diethylzinc (DEZn,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ ) and H<sub>2</sub>O, PL intensity of near bandedge emission was increased, while that of deep level emission was decreased. These results respects that the native defects such as  $V_{\text{Zn}}$  and  $V_{\text{O}}$  were significantly reduced by the feed time of DEZn and H<sub>2</sub>O, resulting in the low intrinsic carrier concentration as well as the elimination of deep level transition.

**Key words:** ZnO, ALD, PL, HR-XRD, Hall.

### Introduction

Zinc oxide (ZnO) semiconductor has attracted much attention for optoelectronic materials such as light emitting diode and transparent conducting oxide (TCO), etc. Due to its wide band gap ( $\sim 3.37$  eV at room temperature) and large exciton binding energy of  $\sim 60$  meV, ZnO becomes an excellent semiconductor material for optoelectronic applications as the substitute of GaN. Recently, many growth techniques have been studied to achieve high quality ZnO thin film, such as sol-gel, sputtering, chemical vapor deposition (CVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE), and atomic layer deposition (ALD), etc [1-5]. Among these growth methods, ALD is one of promising deposition techniques since it has several practical benefits for high accuracy, simple thickness control, large capability, good conformality and reproducibility [16]. In addition, ALD system has been used for achieving high quality Ga-, B-, and Al- doped ZnO films as a TCO material.

However, un-doped ZnO thin films have typically exhibited n-type conduction with intrinsic carrier concentration as high as  $\sim 10^{20} \text{ cm}^{-3}$ . It has been believed by the deviation of stoichiometry due to the native defects such as oxygen vacancies ( $V_{\text{O}}$ ), oxygen interstitial, Zn interstitial [6-8] and the presence of hydrogen [9]. It is often reported that the native defects had been observed by the photoluminescence (PL) spectrum

whose emission energy of  $\sim 2.45$  eV and  $\sim 2.38$  eV would be attributed to  $V_{\text{O}}$  and  $O_{\text{Zn}}$ , respectively [10-13]. In addition, Zn vacancy ( $V_{\text{Zn}}$ ) [8, 14] and Zn interstitial ( $\text{Zn}_i$ ) were one of candidates for this deep level emission [1]. However, there are only a few reports on intrinsic ZnO films grown by ALD system [15]. This work aims to investigate the effect of the feed time of DEZn and H<sub>2</sub>O on the optical and the electrical properties of intrinsic ZnO films grown on c-plane sapphire substrate.

### Experimental procedure

25 ~ 30 nm-thick ZnO thin films were grown on (0001) sapphire substrates by an ALD technique. The film growth temperature was fixed at 300 °C. Diethylzinc (DEZn,  $\text{Zn}(\text{C}_2\text{H}_5)_2$ ) and distilled water (H<sub>2</sub>O) were used as precursors of Zn and O, respectively. DEZn and H<sub>2</sub>O were fed into the chamber through separate inlet lines and purged by N<sub>2</sub> gas in an ALD cycle as shown in Fig. 1. The opening and the closing sequences of the valves were controlled by a computer. The reactants were supplied by a pulse flow sequence (1cycle) of DEZn - N<sub>2</sub> purge - H<sub>2</sub>O - N<sub>2</sub> purge. All samples were performed by the growth of 200 cycles. Two series of sample were prepared. One is the DEZn feed time from 0.5 to 1.0 second under the constant H<sub>2</sub>O feeding time of 0.5 second, the other is the H<sub>2</sub>O feed time from 0.5 to 1.2 second under the constant DEZn feed time of 0.5 second. The N<sub>2</sub> purging time and the N<sub>2</sub> flow rate of all samples were fixed at 1.0 second and 1600 sccm.

X-ray reflectivity analyses were performed to evaluate the thickness of ZnO thin films. The crystal quality and

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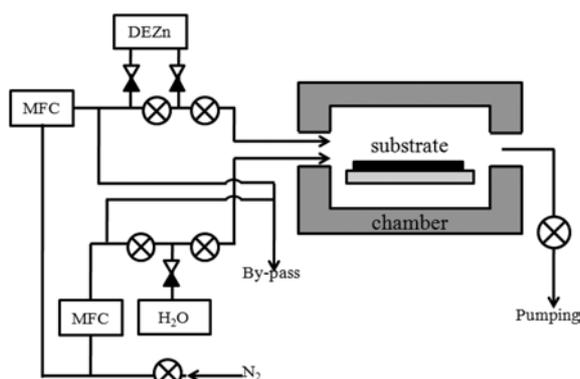


Fig. 1. A schematic diagram of the ALD system.

the orientations of ZnO were measured by high resolution X-ray diffraction (HR-XRD). Room temperature photoluminescence (PL) analysis was performed to observe the optical qualities of ZnO thin films such as bandedge emission and impurity-related green emission. For PL measurements, all samples were focused by the 325 nm line of He-Cd laser with the beam diameter of 20  $\mu\text{m}$  and the excitation power of 1.0  $\text{kW}/\text{cm}^2$ . The PL results were compared with the electrical properties obtained by Hall measurements. All samples were analyzed by van der Pauw method to estimate the carrier concentration and the resistivity of ZnO films with different growth conditions.

## Results and Discussion

Figs. 2 (a) and (b) showed the growth rate of ZnO thin films grown on c-plane sapphire as a function of the feed times of DEZn and H<sub>2</sub>O sources under the constant H<sub>2</sub>O and DEZn feeding time of 0.5 second, respectively. The growth rates of ZnO were increased by the feed time of DEZn or H<sub>2</sub>O. It implied that growth conditions were to be the deficient condition of zinc and oxygen. Assuming the growth condition of ZnO was in the deficient condition of zinc and oxygen, the possible defects with different feed times of DEZn or H<sub>2</sub>O would be described as the followings;  $[V_{\text{O}}] \propto t_{\text{DEZn}}$ ,  $[Zn_{\text{i}}] \propto t_{\text{DEZn}}$ ,  $[V_{\text{Zn}}]^{-1} \propto t_{\text{DEZn}}$ ,  $[O_{\text{i}}]^{-1} \propto t_{\text{DEZn}}$ ,  $[V_{\text{Zn}}] \propto t_{\text{H}_2\text{O}}$ ,  $[O_{\text{i}}] \propto t_{\text{H}_2\text{O}}$ ,  $[V_{\text{O}}]^{-1} \propto t_{\text{H}_2\text{O}}$ ,  $[Zn_{\text{i}}]^{-1} \propto t_{\text{H}_2\text{O}}$ , etc. It is believed that long feed time of DEZn could increase oxygen vacancy ( $V_{\text{O}}$ ) or zinc interstitials ( $Zn_{\text{i}}$ ) and that long feed time of H<sub>2</sub>O could increase Zn vacancy ( $V_{\text{Zn}}$ ) or O interstitials ( $O_{\text{i}}$ ).

Fig. 3(a) showed the room temperature PL spectra of ZnO thin films with increasing the feed time of DEZn. All samples represented two emission peaks. One was the near bandedge emission at the wavelength of  $\sim 380$  nm which was caused by free excitation recombination, and the other was the green-band emission around  $\sim 500$  nm. The PL intensities of both peaks of ZnO were increased with the feed time of DEZn as shown in Fig. 3(a). The increase of near bandedge emission was caused by forming stable stoichiometry due to the increase of the

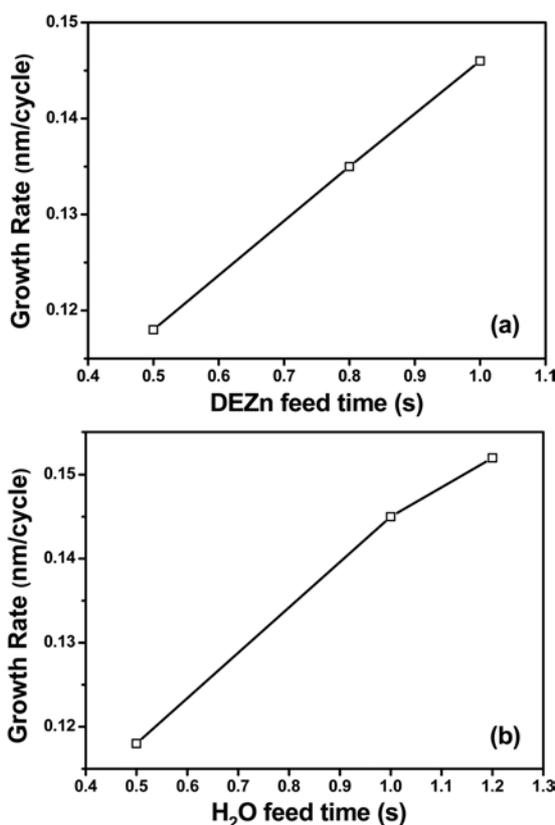
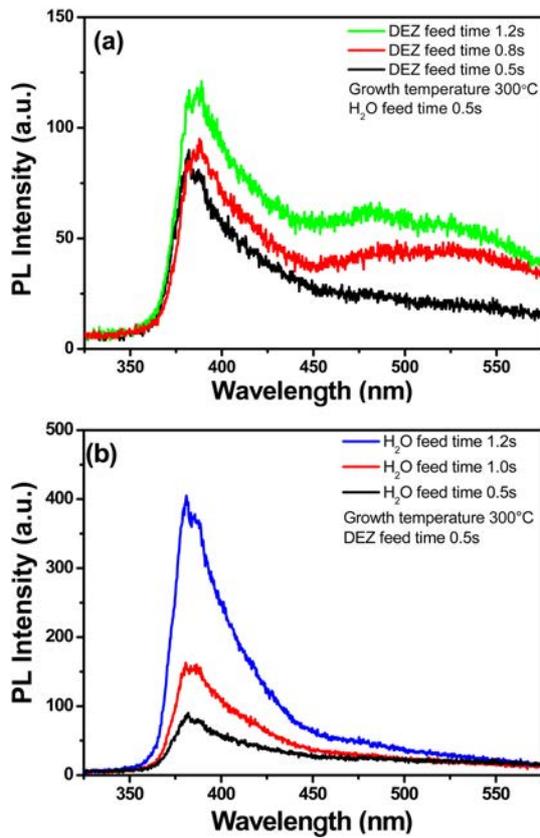


Fig. 2. The growth rate of ZnO film as a function of the feed time of (a) DEZ and (b) H<sub>2</sub>O precursor under the constant feed time of 0.5 s for H<sub>2</sub>O and DEZn precursors, respectively.

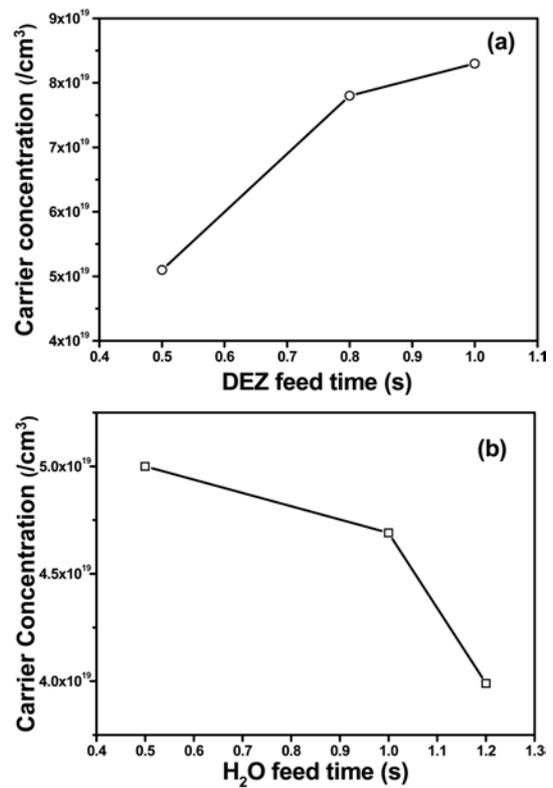
ratio of O to Zn [17]. Regarding green band emission, it has been known that the origin of green-band emission is mainly due to the oxygen vacancies [10-12]. If the deep level emission is related to radiative transition from the conduction band to oxygen vacancy level [16] or from an oxygen vacancy level to the valence band [10], the deep level emission should increase with oxygen vacancies. As previously mentioned, it could be explained that the longer feeding time of DEZn resulted in an increase of oxygen vacancy instead of Zn interstitials. Therefore, one can see that the increase of green band emission was caused by the increase of oxygen vacancy due to the increase of Zn precursors under constant H<sub>2</sub>O precursors. Fig. 3(b) showed the room temperature PL spectra of ZnO thin films with increasing the feed time of H<sub>2</sub>O precursor. On the contrary with Fig. 3(a), PL spectra represented only one emission peak without green band emission. It was thought that those peaks around 380 nm were near bandedge emission with low energy tails. PL intensity of near bandedge emission was increased with the ratio O to Zn, which was similar trend with the increase of DEZn feed time. Although an increase of H<sub>2</sub>O feed time would generate a lots Zn vacancy, green band emission was not observed but broader bandedge emission (380  $\sim$  410 nm) by increasing the feed time of H<sub>2</sub>O. A few research groups reported that deep level-related



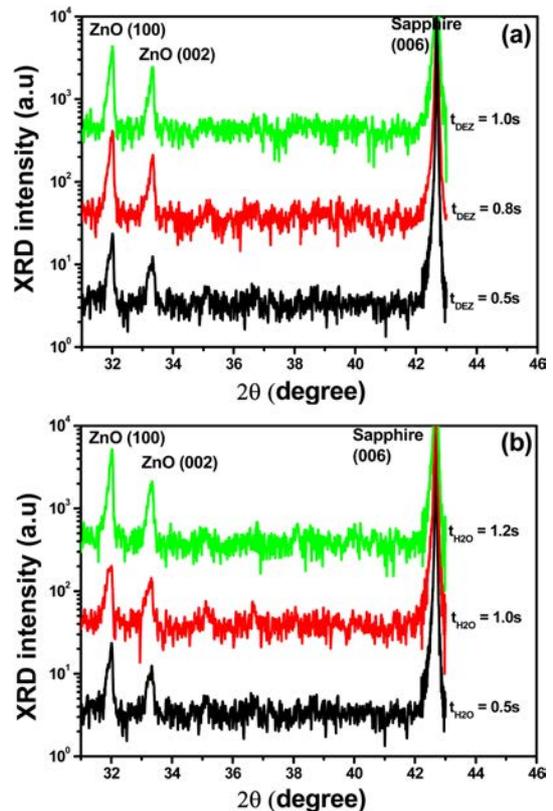
**Fig. 3.** Room-temperature PL spectra of ZnO with different feed times of (a) DEZn and (b) H<sub>2</sub>O precursors under the constant feed time of 0.5 s for H<sub>2</sub>O and DEZn precursors, respectively.

emission peaks of ZnO could be slightly formed around 410 nm which might be originated from the formation of Zn vacancy [7]. Using full-potential linear muffin-tin orbital method, Sun *et al.* calculated the energy levels of the intrinsic defects in ZnO films [17]. They reported that the energy gap from conduction band to the Zn vacancy level was 3.06 eV. Therefore, we believed that near bandedge emission with low energy tails would be generated by Zn vacancy with increasing the feed time of H<sub>2</sub>O.

Fig. 4 (a) showed the intrinsic carrier concentration of ZnO thin films with an increase of DEZn feed time under the constant H<sub>2</sub>O feed time of 0.5 s. The carrier concentration was slightly increased from  $5.0 \times 10^{19}$  to  $6.62 \times 10^{19} / \text{cm}^3$  with increasing the DEZn feed time. In general, un-doped ZnO thin films have typically exhibited n-type conduction with background electron concentration due to Zn interstitial and oxygen vacancies. In general, ZnO contains large voids which can easily accommodate interstitial atoms [18]. These Zn interstitials are easily ionized, and electrons produced by ionized Zn interstitials contribute to electrical conductivity [19]. Therefore, it was caused by the increase of oxygen vacancy and Zn interstitial due to increase of Zn precursors, which was consistent with the increase of PL green-band emission. However, the carrier concentration of ZnO thin films was slightly decreased from  $5.0 \times 10^{19}$  to  $3.9 \times 10^{19} /$



**Fig. 4.** Intrinsic carrier concentration of ZnO film as a function of the feed time of (a) DEZn and (b) H<sub>2</sub>O precursors under the constant feed time of 0.5 s for H<sub>2</sub>O and DEZn precursors, respectively.



**Fig. 5.** XRD patterns of ZnO thin films with an increase the feed time of (a) DEZn and (b) H<sub>2</sub>O precursors under the constant feed time of 0.5 s for H<sub>2</sub>O and DEZn precursors, respectively. ( $t_{\text{Zn}}$  : DEZn feed time,  $t_{\text{H}_2\text{O}}$  : H<sub>2</sub>O feed time)

cm<sup>3</sup> with increasing of the H<sub>2</sub>O feed time, as shown in Fig. 4(b). It may be caused by the reduction of Zn interstitials and oxygen vacancy due to the increase of H<sub>2</sub>O precursors.

Figs. 5(a) and (b) show the XRD pattern of ZnO thin films with increasing the feed time of DEZn or H<sub>2</sub>O precursors. Two peaks were clearly observed by all samples regardless of growth conditions. The angles of both peaks were positioned at 31.7° and 34.4° which corresponded to (100) and (002) diffraction of hexagonal wurtzite ZnO structure, respectively. It implied that the ZnO films would be polycrystalline consisting of major two oriented crystal plane of (100) and (002). It is known that the relative intensities of low angle reflections of the ALD-ZnO film obtained with the DEZ precursor depend on growth temperature and film thickness [20-21]. The XRD intensities of (100) and (002) diffraction peak were increased with increasing of DEZ and H<sub>2</sub>O feed time due to the increase of film thickness. In particular, the intensity ratio of (100) to (002) diffraction peaks was not affected by increasing the feed time of DEZn, while ratio of (100) to (002) diffraction peaks was increased with the feed time of H<sub>2</sub>O. It indicated that H<sub>2</sub>O precursor would be one of major factors to form (100) plane by reducing oxygen vacancy.

### Conclusion

Optical and electrical properties of ZnO thin films grown on c-plane (0001) sapphire were investigated with increasing the feed times of DEZ and H<sub>2</sub>O precursors. The growth conditions were deficient of zinc and oxygen and therefore the growth rate of ZnO was increased with the feed time of DEZn and H<sub>2</sub>O, resulting in the increase of PL bandedge emission as well as defect-related green band or low energy tailed emission. In addition, the intrinsic carrier concentration of ZnO increased with the feed time of DEZn, while that of ZnO decreased with the feed time of H<sub>2</sub>O. These results suggest that H<sub>2</sub>O precursor would be one of major factors to achieve high quality ZnO thin film.

### Acknowledgement

This research was supported by the IT R&D program of MKE/KEIT [10039151, the development of 200 mW

level high power green (525 nm) LED for full color display] and Core Corporation Research Program (2010-0026523) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

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