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Surface Oxidation Effect During high Temperature Vacuum Annealing on the Electrical Conductivity of ZnO thin Films Deposited by ALD

Jin Yong Kim, Yong-June Choi and Hyung-Ho Park†

Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea

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Abstract: The chemical, electrical, and optical properties of ZnO and Al-doped ZnO films after high temperature annealing were studied. The resistivity increased significantly after annealing at 600°C under 10^{-10} Torr atmosphere. The mechanism of the resistivity change was explored using photoemission spectroscopy and photoluminescence spectrometer. The results indicated that the amount of oxygen deficient region O–Zn bonds decreased and oxygen vacancy was decreased after the high temperature vacuum annealing. The increase in the resistivity of ZnO and Al-doped ZnO films was resulted from the decrease in carrier concentration due to a decrease in the amount of oxygen deficiency.

Keywords: ZnO, Al, ALD, high temperature vacuum annealing, PES, SIMS, PL

1. Introduction

Zinc oxide (ZnO) is possible candidate material for optical devices due to its wide band gap (3.37 eV at room temperature) and a high exciton binding energy of 60 meV.[1)] The electrical properties can be changed from insulator to n-type semiconductor through manipulating doping levels, while maintaining the optical transparency. This transparent and conductive properties make ZnO useful for using it as transparent electrode material in flat panel displays and solar cells.[2-4)]

A doping of Al to ZnO results in a marked increase in the electrical conductivity with the optical properties remaining excellent.[5)] Since the properties of Al-doped ZnO thin films depend on preparation conditions, a detailed understanding of relationships between the deposition process and the properties of thin films containing aluminum, zinc, and oxygen is of practical importance. In our previous work, we used unique atomic layer deposition (ALD) cycle to improve Al dopant uniformity in ZnO matrix and there were quite improvements.[6)] But, perfect dopant uniformity sometimes needs a post-heat treatment at high temperature because thermal treatment in different condition is an easy and effective way to change the atomic structure of ZnO.[7)]

However high temperature annealing treatment for uniform dopant distribution induces sometimes a degradation of the electrical property of doped-ZnO.[8,9)] Furthermore in the case of vacuum annealing, opposite results have been reported on the point of view of electrical conductivity and for a degradation of electrical conductivity, a decrease in oxygen deficiency was suggested as a main reason but it has not been clearly demonstrated yet.[10,11)]

In this work, high temperature annealing at 600°C under relatively high vacuum of 10^{-10} Torr was carried out on Al-doped ZnO films deposited using ALD and we investigated the electrical, chemical, and optical value changes in the films after this high temperature vacuum annealing.

2. Experimental Details

For a deposition of ZnO and Al-doped ZnO films, a traveling type ALD was used. Thin films were deposited on Si (001) wafer and glass (Fusion 1737) substrates. $Zn(CH_2CH_3)_2$, $Al(CH_3)_3$, and H_2O were used as starting precursor for zinc, aluminum, and oxygen, respectively. Hereafter, $Zn(CH_2CH_3)_2$ and $Al(CH_3)_3$ were renamed as DEZ and TMA, respectively. Temperature of DEZ and TMA was maintained at 10°C controlled by using individual chiller. In order to achieve an uniform dopant distribution, we used DTH (DEZ 0.1 sec – purge 10 sec – TMA 0.1 sec – purge 10 sec - H_2O 0.1 sec - purge 10 sec) cycle which was introduced in our previous work.[6)] Figure 1 (a) shows the typical ALD cycle for the synthesis of Al-doped ZnO films by a ZnO/Al_2O_3 nanolaminate structure. Figure 1 (b) shows our doping cycle procedure. Various doping concentration of Al in ZnO thin film was controlled by varying the combination of ZnO and DTH cycle such as 19ZnO-1 DTH cycle (19:1), 14 ZnO-1 DTH cycle (14:1), 9 ZnO-1 DTH cycle (9:1), and

†Corresponding author
E-mail: hhpark@yonsei.ac.kr

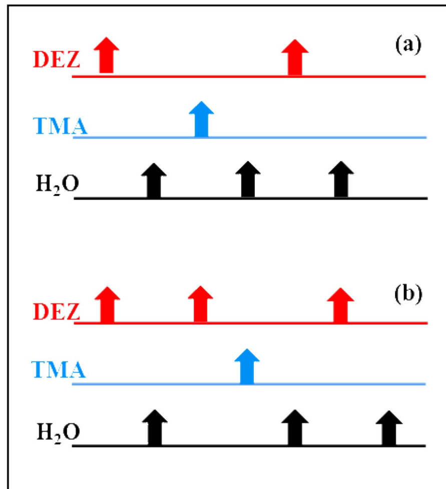

Fig. 1. ALD pulse sequence of (a) conventional ZnO/Al_2O_3 nanolaminate film and (b) modified DTH for Al-doped ZnO film.

4 ZnO-1 DTH cycle (4:1). The base pressure was 1.6×10^{-3} Torr and the growth temperature was maintained at 250°C. After the deposition of ZnO and Al-doped ZnO films, all films were post-annealed at 600°C for 1 hr under relatively high vacuum condition of 10^{-10} Torr. The phase and crystallinity of the films were monitored by using glancing angle X-ray diffraction (XRD) with Cu Kα radiation. The sheet resistance of the films was measured using four-point probe method and the optical transmittance measurements were performed using a UV-vis-NIR spectrophotometer. In order to investigate the doping uniformity, the films were surveyed by secondary ion mass spectrometry (SIMS) using O^{2-} ion source and chemical bonding state of ZnO thin films was investigated by photoemission spectroscopy (PES) at Pohang Accelerator Laboratory (PAL). And defect level was studied by photoluminescence spectrometer (PL).

3. Results and Discussion

Figure 2 represents the XRD pattern of the as-deposited and post-annealed ZnO and Al-doped ZnO thin films. Four diffraction peaks corresponding to the (100), (002), (101), and (110) of the hexagonal wurtzite structure were observed in the films. The undoped ZnO film exhibited a preferred orientation of (002) at 2θ = 34.4°. However, with increasing Al concentration, predominant peak changes from (002) to (100) were observed, corroborating the report by *Yousfi* et al.[12] This behavior was discussed in our previous work[6] with surface free energy changing due to the doping effect. Preferred orientation changing behavior was also observed in post-annealed samples. In this case, post-annealing couldn't

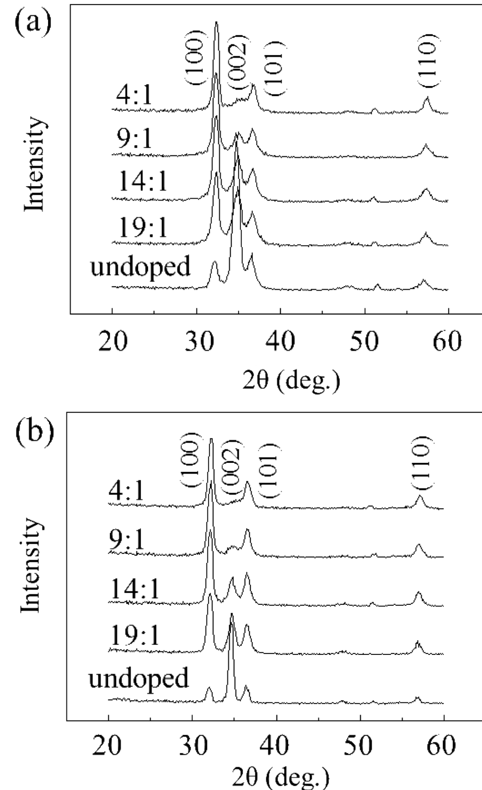

Fig. 2. Glancing angle XRD patterns of ZnO and Al-doped ZnO thin films: (a) as-deposited and (b) post-annealed samples.

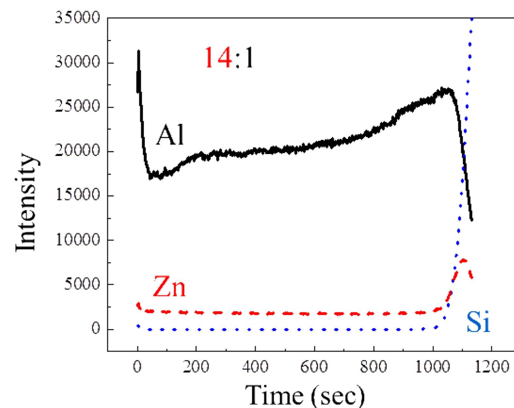

Fig. 3. Concentrations profiles of Al in the Al-doped ZnO film with ZnO:DTH cycle of 14:1 after post-annealing.

make up surface energy increasing due to the lattice distortion from the introduction of the Al-dopant.

In order to confirm the doping uniformity of Al in the ZnO thin film, dynamic SIMS analysis was executed with an O^{2-} ion beam. Figures 3 shows the depth profile results of post-annealed 14:1 sample. In our previous work, the SIMS intensity of Al in the before annealed ZnO film showed a sine curve form.[6] The post-annealed films on the other hand showed linear form. As a result, the annealed films could get more doping uniformity than the as-deposited films even

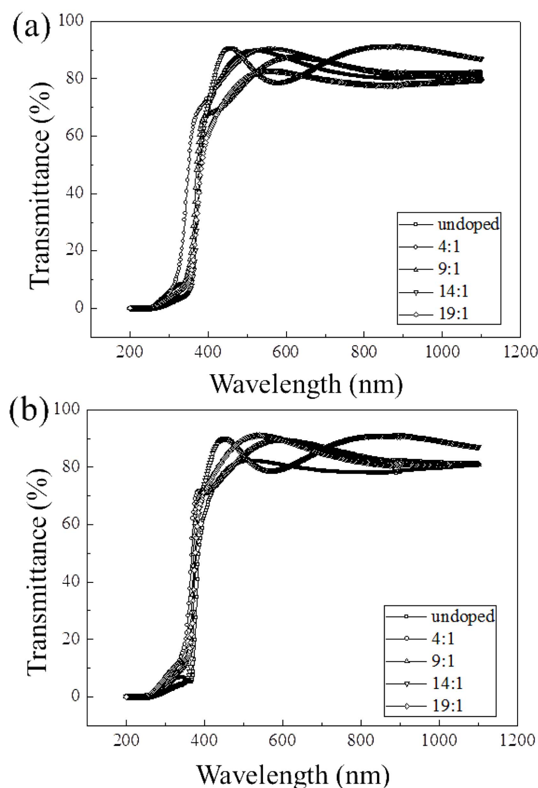

Fig. 4. Transmission spectra of (a) as-deposited and (b) post-annealed ZnO films.

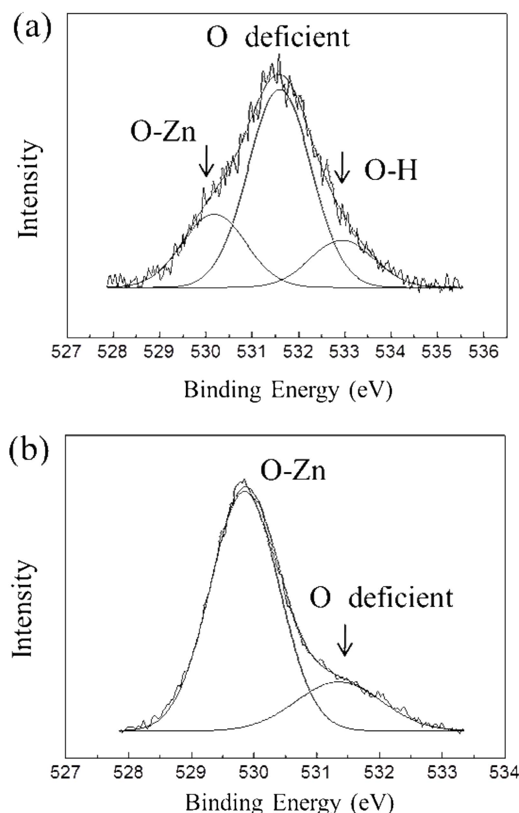

Fig. 6. PES spectra of O 1s of (a) as-deposited and (b) post-annealed ZnO films.

with the case of modified depositing sequence in ALD.

Optical transmittance spectra of the as-deposited and post-annealed ZnO and Al-doped ZnO thin films are shown in Fig. 4. All samples exhibited high optical transmittance above 80% in the wavelength range of 200 to 1100 nm. A change in the transmittance was not observed in our sample before and after post-annealing of the films, so the effect of post-annealing on the transmittance of ZnO and Al-doped ZnO films was found to be negligible.

The resistivities of the films before and after post-annealing are given in Fig. 5. In this figure, it was found that

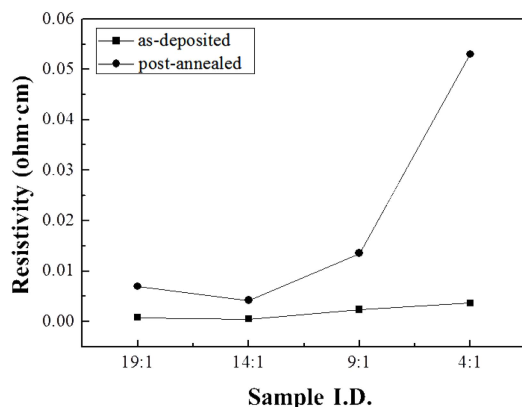

Fig. 5. Resistivity of as-deposited and post-annealed ZnO films.

the post-annealing under relatively high vacuum of 10^{-10} Torr induced an increase of the resistivity of the films. The post-annealed Al-doped ZnO films (synthesized with 14 ZnO-1 DTH cycle) exhibited the lowest resistivity (4.20×10^{-3} Ω·cm) among the films after post-annealing. However it is rather higher than those of as-deposited ZnO and Al-doped ZnO films. The increase of resistivity should be attributed to the increase in phase formation and bonding character of ZnO films. These increase induced a completion of stoichiometry between Zn and O as nearly 1, that is to say, a decrease in oxygen deficiency by oxidation of ZnO even in a relatively high vacuum condition of 10^{-10} Torr. Then it can be said that main conduction mechanism of ZnO is crystalline defect of oxygen in ZnO and this induces an increase of carrier concentration, finally an increase in the electrical conductivity. In order to examine conscientiously, we investigated chemical state and defect level by using PES and PL.

Figure 6 provides PES results of O 1s of (a) as-deposited and (b) post-annealed undoped ZnO films. In as-deposited film, three different bonding states including O–Zn bond (530.18 eV), O deficient O–Zn bond (531.60 eV), and O–H bond (532.94 eV) were found[13-15] and these bonding constituents have 23.0%, 62.2%, and 14.8% of relative area,

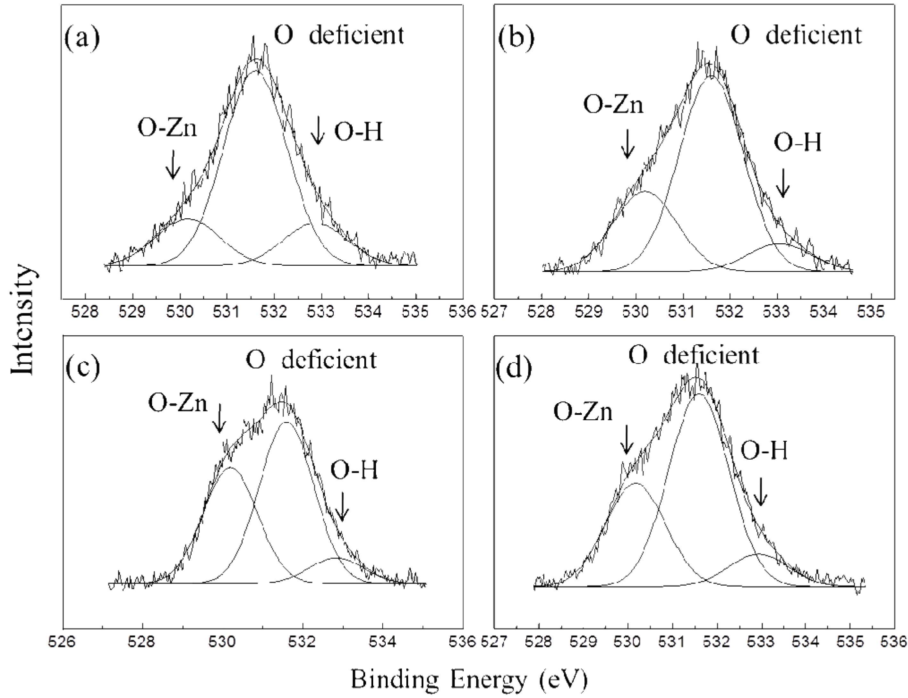

Fig. 7. O 1s PES spectra of as-deposited Al-doped ZnO films with ZnO:DTH cycle of (a) 19:1, (b) 14:1, (c) 9:1, and (d) 4:1.

respectively. The post-annealed film shows only two bonding states of O–Zn and O deficient O–Zn. However these relative bonding constituent area was remarkably changed as 79.8% of O–Zn and 20.2% of O deficient O–Zn. This phenomenon was also observed in the Al-doped ZnO films. Figures 7 and 8 shows PES results of O 1s of as-deposited and post-annealed Al-doped ZnO films, respectively. The undoped and Al-doped ZnO films showed almost same behavior of the oxygen deficiency before and after annealing. From the comparison of Figs. 5 to 8, it can be said that during the annealing at 600°C under 10^{-7} mTorr, the oxygen deficiencies in ZnO could be passivated with

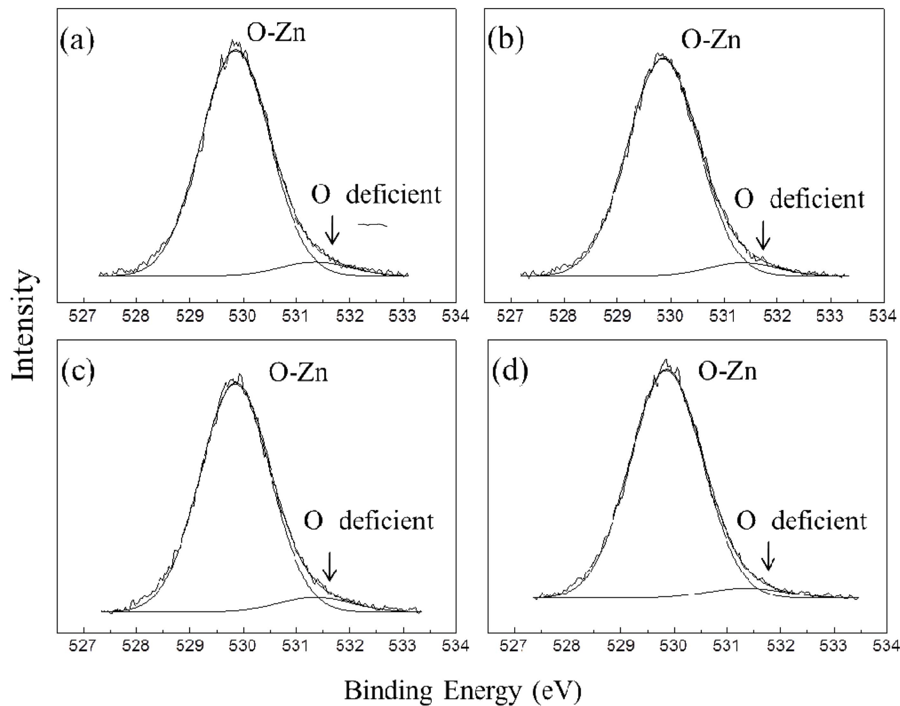

Fig. 8. O 1s PES spectra of Al-doped ZnO films with ZnO:DTH cycle of (a) 19:1, (b) 14:1, (c) 9:1, and (d) 4:1 after post-annealing.

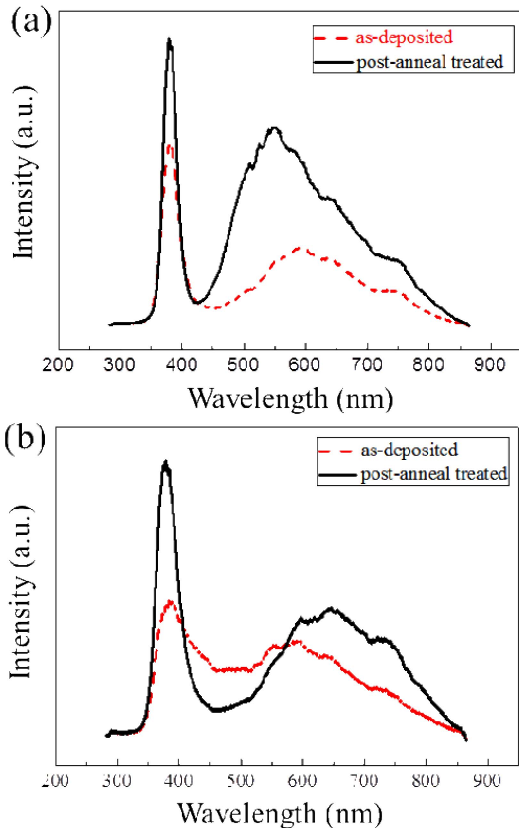

Fig. 9. PL spectra of as-deposited and post-annealed films: (a) undoped ZnO film and (b) Al-doped ZnO film with ZnO:DTH cycle of 9:1.

oxygen and this induced an increase of resistivity of ZnO. However Al dopant was still active after the post-annealinging, then the 14:1 Al-doped ZnO film showed the minimum resistivity as observed in our previous work.[6)]

Figure 9 shows PL results at room temperature of undoped ZnO and 9:1 Al-doped ZnO films before and after post-annealing. The increased intensity of post-annealed samples in the wavelength range of 375~385 nm might be attributed to an introduction of stoichiometry on Zn and O as nearly 1, which was demonstrated by PES observation as given in Figs. 6-8. The emission through 375~385 nm is due to near band edge (NBE) therefore we could assume that high temperature annealing under relatively high vacuum condition might increase a balance of stoichiometry.[2)]

4. Conclusions

We fabricated Al-doped ZnO thin films using DEZ and TMA at 250°C by thermal ALD. A DTH (DEZ 0.1 sec – purge 10 sec – TMA 0.1 sec – purge 10 sec - H_2O 0.1 sec - purge 10 sec) cycle was used. Post-annealing of ZnO and Al-doped ZnO films at 600°C under 10^{-10} Torr vacuum condition leads to an increase in electrical resistivity of the films. The glancing angle XRD showed that through the annealing at high temperature, predominant peak of the films was changed from (002) to (100). PES results showed that a completion of Zn–O bond was induced due to a crystallinity increase on the defective ZnO surface by high temperature annealing under relatively high vacuum condition. The average optical transmittance was calibrated to greater than 80% in the visible range without significant change by post-annealing. PL data showed an increase in the emission of NBE region through post-annealing.

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