Influence of post-deposition annealing on the electrical properties of zinc oxide thin films

Hui Kyung Park, Jaeseung Jo, Hee Kyeung Hong, Jaeyeong Heo *

Department of Materials Science and Engineering, and Optoelectronics Convergence Research Center, Chonnam National University, Gwangju 500-757, Republic of Korea

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1. Introduction

Transparent but electrically conducting oxide thin films have been the focus of scientific and technological attention in recent years [1,2]. Zinc oxide (ZnO) is one of the most popular transparent conducting oxide thin films [3]. The applications of ZnO include solar cells, light emitting diodes, energy saving windows, gas sensors, and transparent substrates [17–20]. Among these methods, ALD has been highlighted due to the self-limiting reaction between the precursor and the reactant on the surface of growing thin films [21–23]. There are several ways to form ZnO thin films, which include sputtering [7–9], evaporation [10], electrodeposition [11], solution-process [12], and atomic layer deposition (ALD) [13–15]. Among these methods, ALD has been highlighted due to the self-limiting reaction between the precursor and the reactant on substrates [17–19], which is well-suited for the formation of various nanostructures required in many applications.

There are numerous reports regarding the growth of ZnO by ALD [15,16,20–25]. However, due to their relatively low growth temperature (<300 °C), the properties of the ZnO thin films are inferior compared to the films processed at high temperature and under high vacuum. Electrical conductivity (or resistivity) of ZnO films is strongly related to the defect states; as a result, the control of defect states is of great importance. One of the ways to improve the quality of the ALD-ZnO thin films is through post-deposition annealing (PDA). The selection of the gas ambient and annealing temperature is critical for determining the final properties of the ZnO films especially for electronic properties.

In this work, ZnO films of different preferred orientations and resistivities were prepared by varying the deposition temperature (120–300 °C) and/or adding a molecular oxygen pulse. The PDA temperature was varied from 200 to 400 °C, and the ambient gas was set to either an oxidizing (air) or a reducing (N2/H2) environment. The use of PDA in general led to the increase in resistivity, but certain films grown at 300 °C exhibited a reduction in the resistivity when annealed at 200 to 300 °C. The defect states modified via PDA were analyzed by photoluminescence (PL) at room temperature, and the possible correlation between the resistivity of the ZnO films and the broad red emission band centered at ~630 nm (~1.97 eV) from photoluminescence was examined.

2. Experimental details

ZnO thin films were deposited using a laminar-flow thermal ALD reactor (CN1, Atomic Classic, Rep. of Korea) at various substrate temperatures ranging from 120 to 300 °C. Diethylzinc (DEZ, Zn(C2H5)2, UP Chemical, Rep. of Korea) and H2O were used as the Zn precursor and oxidant gases, respectively. One ZnO growth cycle consists of four steps: DEZ pulse (0.05 s), N2 purge (7 s), H2O pulse (0.2 s), and N2 purge (20 s). The flow rate for the N2 purge was 200 sccm. Detailed information on the ZnO growth was reported elsewhere [24]. Three out of four different samples were prepared in this study, primarily by changing the growth temperature: 120 °C, 170 °C, and 300 °C. The growth at 300 °C, which is considered to be a slightly higher growth temperature for ALD-ZnO [25,26], was intentionally attempted to widen the spans of the properties of the investigated ZnO films. For convenience, these films grown at 120 °C, 170 °C, and 300 °C will be called “ZnO-A,” “ZnO-B,” and “ZnO-C,” respectively. The last sample, “ZnO-D,” was...
deposited at 300 °C with a modified pulse sequence: exposure of molecular oxygen (O2) for 7 s was carried out prior to the last N2 purge step, i.e., DEZ/N2/H2O/O2/N2 represents one growth cycle for ZnO-D. As discussed later in X-ray diffraction (XRD) analysis, this O2 pulse changes the preferred orientation of the grown ZnO film to be highly (002)-oriented [27]. The total film thickness was set to ~80 nm based on the observed growth-per-cycle (GPC). Information on the as-deposited ZnO films with basic physical properties is summarized in Table 1. The growth was performed on quartz and on Si substrates.

To investigate how the annealing conditions affect the ZnO films, the PDA temperature (200–400 °C) and ambient gas (air or 95% N2/5% H2, N2/H2 hereafter) were varied. A conventional quartz tube furnace was used for the PDA, and the ramp rate of heating was 20 to 25 °C/min. Annealing was performed for 30 min, after which the sample was naturally cooled.

The ZnO film thickness and the refractive index were measured using an ellipsometer (Gaertner, Stokes Ellipsometer LSE). The optical properties were measured via transmittance measurement using a UV-vis spectrophotometer (Agilent, Cary-100). The crystallinity of the film was examined using XRD (PAAnalytical, X’Pert Pro MPD) with Cu Kα radiation (λ = 1.542 Å) using theta–2theta scan. A four-point probe (Veeco, FPP-5000) was used for the electrical measurements and Hall measurements (Lakeshore, 7504) were carried out on selected samples. The resistivity values of the films were correlated with the defect states determined by PL (Accent optical technology, RPM2000 rapid photoluminescence) at room temperature. An He–Cd laser operating at 325 nm with an output power of 13 mW was used.

### 3. Results and discussion

First, the optical properties of the as-deposited ZnO-A to ZnO-D films were investigated via transmittance measurements. Fig. 1a shows the transmittance spectra of the four samples grown on quartz substrates. All these samples exhibit high transparency for the visible range from 400 to 700 nm. The average transmittance is ~83 to 86% (Table 1). The optical bandgap of the as-deposited ZnO films was extracted based on the transmittance data of Fig. 1a. Fig. 1b shows the corresponding direct-band Tauc plot of the four as-deposited films [25]. The extracted bandgap was in the range of 3.26–3.29 eV. The transmittance was also recorded for the ZnO films annealed in various temperature/ambient conditions, but a prominent change was not noted among the films. Fig. 1c shows the representative transmittance spectra for the ZnO-C films.

The crystallinity of the ZnO films was investigated by XRD. Fig. 2a shows the XRD patterns of the four as-deposited ZnO films. The plot at the bottom shows the powder XRD result with their relative intensities (JCPDS #00-005-0664). First, the formation of a polycrystalline wurtzite ZnO structure is confirmed by the patterns. The ZnO-A film grown at 120 °C exhibits a (100)-preferred orientation, while the other three films exhibit a (002)-preferred orientation. Note that the ZnO-D film, for which O2 was additionally pulsed after the H2O pulse, has the most (002)-oriented structure among all the samples considered in this study [27]. When ZnO-B and ZnO-C are compared, ZnO-B is more (002)-oriented than ZnO-C. This result indicates that the preferred orientation changes from (100) to (002), and finally to a slightly random orientation, as the growth temperature changes from 120 °C to 170 °C and up to 300 °C. Both annealing in air and in N2/H2 ambient led to the slight improvement in crystallinity for all four samples. Fig. 2b shows the representative XRD patterns of the as-deposited and the 300 °C-PDA ZnO-B films. The grain size estimated by the Scherrer formula was 16 to 19 nm for all the as-deposited and the annealed films. No clear trend was observed.

Meanwhile, the electrical properties of the ZnO thin films were highly dependent on the annealing conditions. Fig. 3 shows the summarized resistivity of the ZnO films before and after PDA. Here, closed and open symbols represent the ZnO films annealed in air and N2/H2, respectively. The resistivity of the as-deposited ZnO films is ~2–5 × 10−2 Ω·cm, except for the one grown at 170 °C (ZnO-B, 7.4 × 10−3 Ω·cm). The resistivity of as-deposited ZnO films shows sensitive dependence on growth temperature [28–31]. Notably, the resistivity of the ZnO films exhibits strong dependence both on the annealing temperature and on the ambient gas used. When the annealing ambient gases are compared, annealing in air generally caused the film to be more resistive compared to that of the N2/H2 annealing. In the cases of the ZnO-A and ZnO-B films, both the case of annealing in air and of annealing in N2/H2 result in an increase in the resistivity compared to those of the as-deposited films. In the cases of ZnO-C and ZnO-D, annealing at 200 °C and 300 °C reduces the resistivity of the films. For ZnO-C, annealing in air at 200 °C slightly decreases the resistivity from 5.2 to 8.5 × 10−1 Ω·cm, and both 300 °C- and 400 °C-annealing again increase the resistivity to 13.3 Ω·cm and 469 Ω·cm, respectively.

However, annealing at 200 °C and 300 °C in N2/H2 ambient largely decreases the resistivity to ~5 × 10−2 Ω·cm. ZnO-D also exhibits a similar trend as that of ZnO-C. Annealing in N2/H2 at 200 °C and 300 °C decreases the resistivity, but the drop (1.7 Ω·cm and 4.4 × 10−2 Ω·cm for 200 °C and 300 °C, respectively) is not as dramatic as that for ZnO-C. For

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**Table 1**

Sample information of the as-deposited ZnO films and their physical properties. (Tsub, growth temperature, Tavg: average transmittance in visible range, Eg: extracted direct-band Tauc plot of the four as-deposited films [25]. The extracted bandgap was in the range of 3.26–3.29 eV. The transmittance was also recorded for the ZnO films annealed in various temperature/ambient conditions, but a prominent change was not noted among the films. Fig. 1c shows the representative transmittance spectra for the ZnO-C films.

<table>
<thead>
<tr>
<th>Film</th>
<th>Tsub (°C)</th>
<th>O2 flow</th>
<th>GPC (nm cycle−1)</th>
<th>Ref. index</th>
<th>Resistivity (Ω·cm) Tavg (%)</th>
<th>Eg (eV)</th>
</tr>
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<tr>
<td>ZnO-A</td>
<td>120</td>
<td>X</td>
<td>0.18</td>
<td>1.96</td>
<td>2.8</td>
<td>83.0</td>
</tr>
<tr>
<td>ZnO-B</td>
<td>170</td>
<td>X</td>
<td>0.21</td>
<td>1.96</td>
<td>7.4 × 10−3</td>
<td>83.3</td>
</tr>
<tr>
<td>ZnO-C</td>
<td>300</td>
<td>X</td>
<td>0.14</td>
<td>1.98</td>
<td>5.2</td>
<td>85.9</td>
</tr>
<tr>
<td>ZnO-D</td>
<td>300</td>
<td>O</td>
<td>0.18</td>
<td>1.98</td>
<td>3.2</td>
<td>84.3</td>
</tr>
</tbody>
</table>

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**Fig. 1.** (a) Transmittance of the four as-deposited ZnO films (ZnO-A to ZnO-D). (b) Tauc plots of the corresponding as-deposited ZnO films assuming direct band transitions. (c) The representative transmittance spectra of the as-deposited and the annealed ZnO-C films.
all cases, the resistivity of the ZnO films annealed in N₂/H₂ ambient exhibits a lower value than those of the ZnO films annealed in air ambient. This result suggests that the oxidizing or reducing ambient from air or N₂/H₂ strongly influences the defect states of the ZnO films.

Hall measurements were further carried out on as-deposited and some annealed films and the results suggested that the change in resistivity mainly comes from large variation in carrier concentrations (\(10^{19} - 10^{21} \text{ cm}^{-3}\)).

The changes in the defect states of the ZnO films were investigated by PL measurements. Figs. 4 and 5 show the PL spectra of ZnO-A–ZnO-D annealed in various conditions including as-deposited films. The left and right panels correspond to the spectra from the ZnO films annealed in air and N₂/H₂, respectively. Fig. 4a shows the PL spectra for the ZnO-A films annealed in air. The as-deposited ZnO-A film exhibits a broad red emission PL band centered at ~630 nm (~1.97 eV), which is attributed to oxygen vacancy or interstitial [32,33]. The PL band dramatically increases for 200 °C annealing and gradually decreases with increasing annealing temperature up to 400 °C. In contrast, a slight increase in the broad PL band is observed for the annealing in N₂/H₂ ambient at elevated temperature, as shown in Fig. 4b.

When the ZnO film was grown at 170 °C, as shown in Fig. 4c, a strong peak at ~400 nm is observed, which is due to the near-band-edge emission [33]. With annealing at 200–400 °C, the near-band-edge emission almost disappears. Notably, the PL for as-deposited ZnO-B exhibits a green emission band centering at ~550 nm (~2.25 eV), which is also attributed to oxygen vacancy or interstitial [34]. However, it quickly disappears after annealing in air. Instead, the PL band center returns to ~630 nm and gradually increases with the annealing temperature. A similar trend is observed for the ZnO films annealed in N₂/H₂, as shown in Fig. 4d. The intensity of the broad visible PL band at each annealing temperature is lower than those of the ZnO films annealed in air.

The PL spectra for ZnO-C and ZnO-D are plotted in Fig. 5. For these ZnO films, the 400–C annealed samples exhibit a slight increase in the broad visible PL band. Interestingly, decreases in the broad PL band are noted for the ZnO-C films annealed at 200 °C and 300 °C in N₂/H₂, as shown in Fig. 5b. Such decreases in the PL peaks are closely related with the decrease in the resistivity of the films. As manifested in Fig. 3, 200–C and 300–C annealed ZnO-C films in N₂/H₂ exhibit the decrease in resistivity by approximately two orders of magnitude compared to the as-deposited film. The observation from Figs. 4 and 5 suggests that the electrical resistivity of the ZnO films is associated with this broad PL band.

To determine the relationship between the resistivity of the films and the PL spectra, each area of the broad PL bands from 430 to 1000 nm was calculated. Fig. 6 shows the integrated area of the PL bands as a function of the measured resistivity of the corresponding films. This plot clearly suggests that the area of the PL bands which mainly consist of the red emission peak centering at ~630 nm is related to the electrical resistivity of the ZnO films: the increase in the resistivity of the film leads to the increase in the broad PL band. Similar relationship between film’s electrical resistivity and visible PL peaks was also reported for ZnO films prepared by ultrasonic spray pyrolysis [35] and by ion plating [36].

Unintentional n-type conductivity in ZnO has often been attributed to oxygen vacancy. However, recent first-principle calculations suggest that oxygen vacancy is indeed a deep donor and cannot contribute to n-type conductivity [3,37]. Instead, incorporated hydrogen forming a strong bond with oxygen in ZnO was identified to be a shallow donor [3]. The exact origin of the PL band in the visible range is still controversial, but generally the red emission peak at ~630 nm is attributed to the oxygen-related defects (vacancy or interstitial). Our results suggest that the oxygen-related defects that increased during high-temperature PDA appear to act as trap states, increasing the resistivity of the ZnO film.

Possible other factors that could affect electrical resistivity include film density and change in preferred orientation (morphology) [35]. The refractive indexes of all as-deposited and annealed ZnO films up to 400 °C were within 1.95–2.00 range. From this observation, no significant change in film density is estimated, which excludes the possible contribution of film density on electrical resistivity. As confirmed by the representative XRD patterns of ZnO-B (Fig. 2b), the change in preferred orientation before and after annealing was not noted as well. Taking these into account, the main contribution to the increased electrical resistivity of the ZnO films after thermal annealing appears to be the increased oxygen-related defects.
4. Conclusions

Various ZnO thin films with different structural and electrical properties were deposited by atomic layer deposition after changing the growth conditions. PDA at 200 to 400 °C was performed in air and N$_2$/H$_2$ ambient, and the properties of the films were compared. No obvious change in the optical properties was observed. From the XRD measurements, slight improvement in the crystallinity was noted. In contrast, the electrical properties were highly dependent on the PDA conditions. Annealing at higher temperature led to the increase in the
resistivity, and the use of reducing N2/H2 ambient gases delayed such an increase compared to the use of oxidizing air ambient. The increase in the electrical resistivities was correlated with the increase in the defect states, presumably oxygen vacancies or interstitial acting as deep traps, as demonstrated by PL analysis.

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References


"Fig. 6. The integrated area of the PL bands (430–1000 nm) as a function of the resistivity of the film, plotted in a semi-log plot."