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

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ABSTRACT

The influence of the post-deposition annealing (PDA) temperature and the use of different ambient gases on the structural and electrical properties of zinc oxide thin films grown by atomic layer deposition were investigated. The PDA did not change the optical properties of the films, but a slight improvement in the crystallinity was observed. The PDA strongly affected the electrical properties of the ZnO films. High-temperature annealing in air ambient led to the increase in resistivity, and high-temperature annealing in reducing N_2/H_2 ambient delayed such an increase. The increase in resistivity was correlated with the generation of deep-level trap states, as manifested by the increase of the red emission band centered at ~630 nm (~1.97 eV) from photoluminescence.

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 thin-film transistors [4–6]. 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) [13–16]. 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 be either an oxidizing (air) or a reducing (N_2/H_2) 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 centering at ~630 nm (~1.97 eV) 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, $Zn(C_2H_5)_2$, UP Chemical, Rep. of Korea) and H_2O were used as the Zn precursor and oxidant gases, respectively. One ZnO growth cycle consists of four steps: DEZ pulse (0.05 s), N_2 purge (7 s), H_2O pulse (0.2 s), and N_2 purge (20 s). The flow rate for the N_2 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

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Table 1
Sample information of the as-deposited ZnO films and their physical properties. (T_{sub}: growth temperature, T_{avg}: average transmittance in visible range, E_g: extracted optical bandgap).

Film	T_{sub} (°C)	O_2 flow	GPC (nm cycle^{-1})	Ref. index	Resistivity (Ω·cm)	T_{avg} (%)	E_g (eV)
ZnO-A	120	X	0.18	1.96	2.8	83.0	3.26
ZnO-B	170	X	0.21	1.96	7.4×10^{-3}	83.3	3.29
ZnO-C	300	X	0.14	1.98	5.2	85.9	3.28
ZnO-D	300	O	0.18	1.98	3.2	84.3	3.27

deposited at 300 °C with a modified pulse sequence: exposure of molecular oxygen (O_2) for 7 s was carried out prior to the last N_2 purge step, i.e., DEZ/N_2/H_2O/O_2/N_2 represents one growth cycle for ZnO-D. As discussed later in X-ray diffraction (XRD) analysis, this O_2 pulse changes the preferred orientation of the grown ZnO film to be highly (002)-oriented [27]. The total film thickness was set to be ~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%-N_2/5%-H_2, N_2/H_2 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 (PANalytical, 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 O_2 was additionally pulsed after the H_2O 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 N_2/H_2 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 N_2/H_2, respectively. The resistivity of the as-deposited ZnO films is ~2–5 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 for the N_2/H_2 annealing. In the cases of the ZnO-A and ZnO-B films, both the case of annealing in air and of annealing in N_2/H_2 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 N_2/H_2 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 N_2/H_2 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

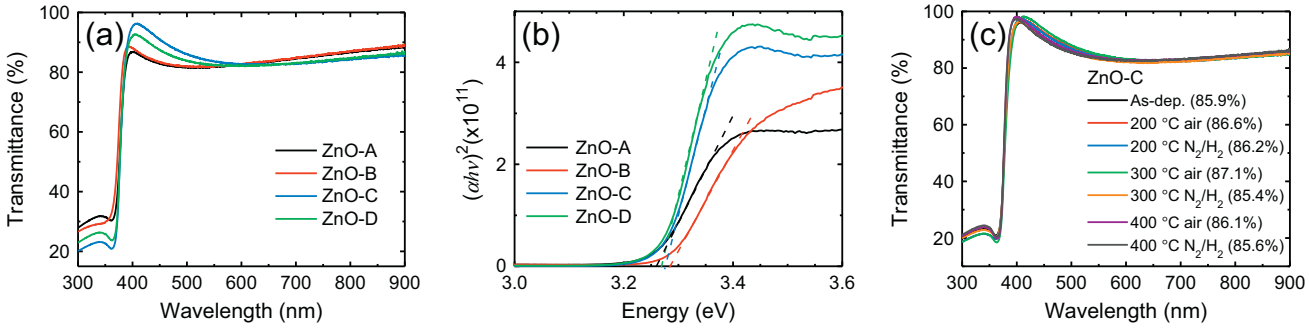

Fig. 1. (a) Transmittance of the four as-deposited ZnO films (ZnO-A to ZnO-D). (b) Tauc plots of the corresponding as-deposited ZnO films assuming direct band transitions. (c) The representative transmittance spectra of the as-deposited and the annealed ZnO-C films.