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# STRUCTURAL, ELECTRICAL, AND OPTICAL PROPERTIES OF ZnO FILMS GROWN BY ATOMIC LAYER DEPOSITION AT LOW TEMPERATURE

Zinc oxide (ZnO) is a prominent n-type semiconductor material used in optoelectronic devices owing to the wide bandgap and transparency. The low-temperature growth of ZnO thin films expands diverse applications, such as growth on glass and organic materials, and it is also cost effective. However, the optical and electrical properties of ZnO films grown at low temperatures may be inferior owing to their low crystallinity and impurities. In this study, ZnO thin films were prepared by atomic layer deposition on $SiO_2$ and glass substrates in the temperature range of 46-141°C. All films had a hexagonal würtzite structure. The carrier concentration and electrical conductivity were also investigated. The low-temperature grown films showed similar carrier concentration (a few $10^{19}$ cm$^{-3}$ at 141°C), but possessed lower electrical conductivity compared to high-temperature (>200°C) grown films. The optical transmittance of 20 nm thin ZnO film reached approximately 90% under visible light irradiation. Additionally, bandgap energies in the range of 3.23-3.28 eV were determined from the Tauc plot. Overall, the optical properties were comparable to those of ZnO films grown at high temperature.

*Keywords:* Zinc Oxide (ZnO); Atomic layer deposition; Low temperature growth; Optoelectronic properties

## 1. Introduction

Zinc oxide (ZnO), which has a wide-bandgap, is a chemically and thermally stable material. It exhibits interesting dielectric, piezoelectric, and transparent properties, making it a promising candidate for functional electronics. [1] Recently, research on the low-temperature (LT) growth of ZnO films has garnered attention because of the low thermal budget and expanding diverse applications, such as glass, organic, and biomaterials. [2] The LT deposition process of the ZnO film could be time- and cost-effective because the fluctuating time and energy costs required for the high-temperature manufacturing process could be saved. LT-grown ZnO films are widely used in optoelectronic and photovoltaic applications, such as transparent conducting oxides, transparent thin-film transistors [3], solar cells [4], thermoelectric devices [5], and light-emitting diodes. [6]

In this study, we investigated whether ZnO thin films deposited in the LT regime (46-141°C) possess similar properties to those deposited at higher temperatures (above 200°C). Guziewicz et al. reported on the electrical properties of ZnO films grown on $SiO_2$/Si substrates at 90-200°C. [7] The carrier concentration of films can reach up to $10^{20}$ cm$^{-3}$, and the

mobility of electrons is between 20 and 50 cm$^2$ V$^{-1}$ s$^{-1}$. Kim et al. reported that ZnO thin films were grown on $SiO_2$/Si substrates using $Zn(C_2H_5)_2$ at substrate temperatures of 230-300°C by thermal atomic layer deposition (ALD). [8] ZnO films grown using the $H_2O$ reactant exhibited higher carrier concentration and lower resistivity. In the aforementioned studies, high electrical conductivity was achieved without intentional doping. Although many studies have been conducted on substrate temperatures above 100°C, the temperature range below 100°C has not been actively studied. Therefore, we wanted to investigate the characteristics of the thin film grown at low temperatures compared to those grown at higher temperatures. In this study, ZnO thin films were grown by thermal ALD, which is a promising technology for thin-film deposition. [9] This technology is useful to produce uniform thin films that are few nanometers thick with fewer voids and pinholes. Additionally, self-limiting property of ALD gives films outstanding step coverage and uniformity. ZnO thin films were deposited using diethylzinc (DEZ; $Zn(C_2H_5)_2$) and water ($H_2O$) as precursors. The ZnO thin films were grown on $SiO_2$ and glass substrates. The structural, electrical, and optical properties of the obtained films were analyzed in this study.

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## 2. Experiment

ZnO thin films were grown by thermal ALD (atomic-shell, CN-1 Co., Korea). ALD was performed using DEZ, $H_2O$, and nitrogen gas ($N_2$) at a flow rate of 500 sccm. The pulse sequences for the ZnO thin films were as follows; DEZ: 0.2 s; $N_2$: 15 s; $H_2O$: 0.1 s; $N_2$: 15 s. The base pressure was $6.7 \times 10^{-2}$ Torr and the deposition was processed under 1.4 Torr. ZnO films were deposited for 100, 200, and 300 cycles on $SiO_2$ and glass substrates at substrate temperatures of 46, 73, 96, 119, and 141°C. The $SiO_2$ substrates were made of 1 μm $SiO_2$ film grown on a Si wafer. We used soda-lime glass slides (CORNING 2947) w. The glass substrates were ultrasonically cleaned in isopropyl alcohol for 5 min and then washed twice in deionized water for 5 min. They were dried by blowing pure nitrogen gas.

The thickness of the ZnO films was measured using ellipsometry (FS-1, Film Sense, USA). To measure the film thickness, we deposited ZnO thin films on Si (100) substrates with $SiO_2$ and glass, simultaneously. The crystallinity of the films was observed via X-ray diffraction (XRD: Dmax2500/ PC, Rigaku, Japan) in the glancing angle mode. The 200 cycle-deposited films grown on $SiO_2$ substrates were used for this purpose. The electrical properties of ZnO films, such as carrier concentration and conductivity, were analyzed using Hall measurements (HMS-3000, ECOPIA, Korea). Indium was soldered onto the substrates for performing Hall measurements. The transmittance and absorbance were examined using UV-visible spectroscopy (UV-vis: UV-2600i, Shimadzu, Japan). The bandgap energy was derived from the Tauc plot using the absorbance spectra.

## 3. Results and discussion

Fig. 1(a) shows the thickness of the ZnO film as a function of the number of ALD cycles at each substrate temperature. The growth rate or growth-per-cycle (GPC) of ZnO films was estimated from the slope of the linear fitting of the thickness values, as shown in Fig. 1(b). As the substrate temperature increased, GPC increased monotonically. When the temperature was below 96°C, the fitting line decreased gradually, i.e., nucleation delay increased. Thermal energy was insufficient to overcome
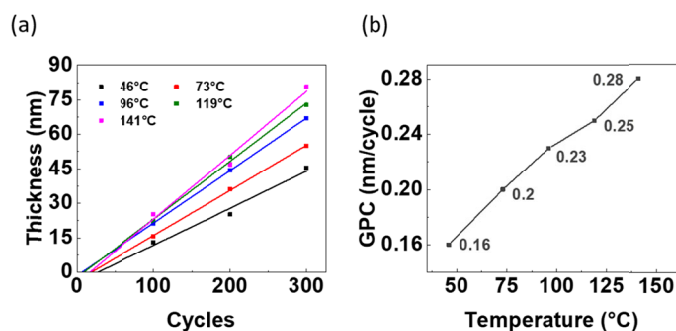


Fig. 1. (a) Film thickness as a function of the number of cycles at each temperature, (b) Growth-per-cycle of ZnO film according to the substrate temperatures

nucleation on the initial surface in the LT regime. Meanwhile, in the temperature range of 96-141°C, the starting points of the fitting lines were similar and close to zero, indicating that facile nucleation could occur because sufficient energy and active sites were available.

The crystallinity of the 200-cycle-deposited ZnO thin films on the $SiO_2$ substrate was examined using XRD analysis. Fig. 2 shows multiple diffraction peaks corresponding to the reference data of the hexagonal würtzite structure. Moreover, the diffraction patterns indicate that all peaks shifted to a higher angle. These shifts were considered to be caused by an increase in the internal stress generated by the non-uniform crystals and defects. According to the XRD spectra, the (002) direction was the dominant peak for the films grown at 46°C and 73°C. As the substrate temperature increased, the (100) direction became stronger and dominant in the films deposited at 96°C and 119°C. At 141°C, the (002) and (100) directions exhibited higher intensities. This shows that the (002) direction, which has low surface energy, can grow rapidly even at extremely low temperatures, and the (100) direction requires more energy to grow at higher temperatures. We estimated the crystallite size using Scherrer's formula and considered only the main peak of each film. The grain sizes of the films grown at 46, 73, 96, 119, and 141°C were 16.25, 15.67, 13.70, 14.64, and 16.26 nm, respectively, with the average grain size being 15.31 nm.
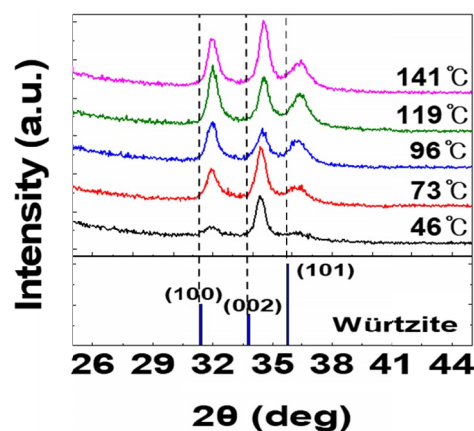


Fig. 2. XRD patterns of ZnO thin films deposited in 200 cycles with different deposition temperatures

The electrical properties, including carrier concentration and electrical conductivity, were examined by Hall effect measurements at room temperature. ZnO thin films with thicknesses of ~20 nm (precisely 16-25 nm) and ~50 nm (44-55 nm) were grouped as 20T and 50T at each growth temperature, respectively. Fig. 3 shows the n-type carrier concentration and electrical conductivity of the 20T and 50T films deposited on $SiO_2$ and glass substrates as a function of the substrate temperature. We noticed that the electrical properties of thinner (20T) and thicker (50T) ZnO films on glass substrates were more similar to each other than those on $SiO_2$ substrates. The carrier concentration and electrical conductivity of the films grown on glass substrates exhibited few differences up to 119°C. Both parameters increased

significantly in the film grown at 141°C. On the other hand, a greater fluctuation of electrical parameters was observed in the films grown on SiO$_2$ substrates.
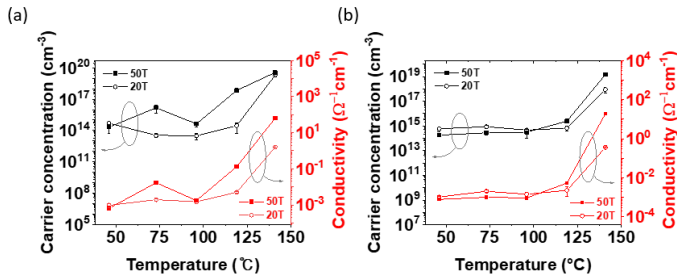


Fig. 3. Hall-effect measurement results of the ZnO films deposited with different substrate temperatures of 46, 73, 96, 119, and 141°C; n-type carrier concentration and electrical conductivity of (a) SiO$_2$ and (b) glass substrates

The carrier concentration on SiO$_2$ and glass substrates were $3.2 \times 10^{13}$-$6.8 \times 10^{17}$ cm$^{-3}$ and $1.8 \times 10^{14}$-$2.4 \times 10^{15}$ cm$^{-3}$ up to 119°C, and the maximum values, $2 \times 10^{19}$-$3.6 \times 10^{19}$ cm$^{-3}$ and $9 \times 10^{17}$-$1.5 \times 10^{19}$ cm$^{-3}$, were recorded at 141°C, respectively. The electrical conductivity also had a maximum value at 141 °C. The lower conductivity of the films on SiO$_2$ and glass substrates were found to be $6.6 \times 10^{-4}$-$1.3 \times 10^{-1}$ W$^{-1}$ cm$^{-1}$ and $7.9 \times 10^{-4}$-$5 \times 10^{-3}$ W$^{-1}$ cm$^{-1}$ up to 119°C, while the higher conductivities of 1.6-63 W$^{-1}$ cm$^{-1}$ and 0.4-19 W$^{-1}$ cm$^{-1}$ were observed at 141°C, respectively. It is considered that the electrical properties could have been affected by crystallinity, film density, and film thickness. The gas molecules become more reactive at higher growth temperatures where sufficient thermal energy for surface reactions is provided; thus, higher crystallinity and film density can be achieved. Crystallinity was confirmed by XRD analysis, as mentioned previously. Furthermore, the film density also increased with increasing temperature, as determined from the refractive index (data not shown) of the films.

The electrical parameters of HT-grown ZnO have been discussed in other studies. Mishra et al. [10] demonstrated that the carrier concentration of a ZnO thin film deposited on an α-Al$_2$O$_3$ substrate at 300°C was $4.7 \times 10^{19}$ cm$^{-3}$. Min et al. [11] reported that ZnO films on SiO$_2$ (100 nm)/Si substrates at 300°C had almost over $1 \times 10^{20}$ cm$^{-3}$. Regarding electrical conductivity, Kim et al. [12] found that the conductivities of films on glass substrates at 200°C and 250°C were $10^2$ W$^{-1}$ cm$^{-1}$ and over 30 W$^{-1}$ cm$^{-1}$, respectively. Considering the carrier concentration, the maximum results of the LT-grown films in our study seem to be comparable to the reference data from HT-grown films, whereas the electrical conductivity of LT-ZnO seems to be at most half.

The optical properties of the LT-grown ZnO thin films were measured in the near-infrared (900 nm) to ultraviolet (300 nm) range using UV-vis. Figs. 4(a) and (b) present the transmittances of the 20T and 50T films deposited on glass substrates at 46-141°C. An absorption edge shift toward longer wavelengths can be observed with increasing growth temperature. The transmittance was significantly dependent on the film thickness. In the

visible region, the optical transmittance of 20T reaches almost 90%, whereas that of 50T is lower at ~80% or higher. Maeng et al. [13] demonstrated that films of approximately 35 nm grown at 250°C exceed 80% transmittance. Figs. 4(c) and (d) show the Tauc plots for the absorbance of 20T and 50T, respectively. They presented the relationship between $(\alpha h v)^2$ and photon energy ($hv$). The direct bandgap energies ($E_g$) were obtained from the Tauc plot. [14] The x-intercept of the trend line at the slope of the straight range indicates $E_g$. $E_g$ of LT-ZnO was estimated to be between 3.23 and 3.28 eV. $E_g$ decreased slightly as the substrate temperature increased. It was estimated that the dominant orientation from the XRD analysis at each temperature may affect the change in $E_g$. The $E_g$ values corresponded to the reference values in other studies at higher growth temperatures. Yuan et al. [15] obtained the $E_g$ of the films on a glass substrate as 3.27 eV. Under identical temperature conditions, Pal et al. [16] revealed that the value for the film on the SiO$_2$ substrate was 3.2 eV. Therefore, similar ranges of transmittance and $E_g$ are found in LT-ZnO and HT-ZnO films in the literature.
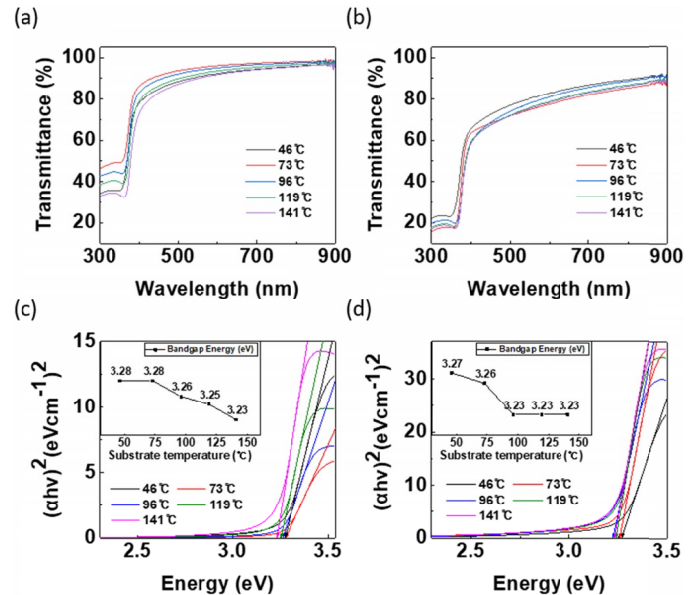


Fig. 4. Transmittance spectra with varying deposition temperatures of (a) 20T and (b) 50T films. Tauc plots from absorbance spectra of ZnO thin films for (c) 20T and (d) 50T

## 4. Conclusions

ZnO thin films were deposited on SiO$_2$ and glass substrates at 46-141°C using thermal ALD, and their structural, electrical, and optical properties were examined for comparison with films grown at higher temperatures (>200°C). The growth rate of the films was increased from 0.16 to 0.28 nm/cycle with increasing growth temperature. The films were well-crystallized with a hexagonal würtzite structure. There was a transition of the dominant diffraction peaks with varied substrate temperatures, but the crystallite size seemed to be constant. The LT-grown ZnO films were more conductive, and the highest conductivity was observed in the film grown at 141°C. Compared to the HT-ZnO

films reported in other studies, the maximum results obtained for LT-grown films in our study were similar that in terms of carrier concentration. However, the electrical conductivity was comparatively relatively low. Transmittance was approximately 90% for the 20T films and over 80% for the 50T films. The bandgap energies of the LT-ZnO films varied from 3.23 to 3.28 eV. The optical characteristics of LT-ZnO agreed well with the reference data for the ZnO film grown under HT growth conditions.

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