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Thickness-dependent Electrical, Structural, and Optical Properties of ALD-grown ZnO Films

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Abstract: The thickness dependent electrical, structural, and optical properties of ZnO films grown by atomic layer deposition (ALD) at various growth temperatures were investigated. In order to deposit ZnO films, diethylzinc and deionized water were used as metal precursor and reactant, respectively. ALD process window was found at the growth temperature range from 150°C to 250°C with a growth rate of about 1.7 Å/cycle. The electrical properties were studied by using van der Pauw method with Hall effect measurement. The structural and optical properties of ZnO films were analyzed by using X-ray diffraction, field emission scanning electron microscopy, and UV-visible spectrometry as a function of thickness values of ZnO films, which were selected by the lowest electrical resistivity. Finally, the figure of merit of ZnO films could be estimated as a function of the film thickness. As a result, this investigation of thickness dependent electrical, structural, and optical properties of ZnO films can provide proper information when applying to optoelectronic devices, such as organic light-emitting diodes and solar cells.

Keywords: Zinc Oxide, Atomic Layer Deposition, Thickness, Transmittance, Resistivity

1. Introduction

Recent years, next-generation optoelectronic devices have been intensively investigated in order to use displays, solar cells, and smart phones. These optoelectronic devices are generally composed with glass substrate, transparent contact layer, active layer, and electrode. Among these parts, transparent conducting oxide (TCO) layer is the most important to operate the optoelectronic devices with high optical and electrical performances. TCOs are oxide semiconductors, which provide broad controllability of electrical conductivity and transparency in the visible region. The combination of high electrical conductivity with high optical transparency of TCOs allows the use of transparent electrode for the aforementioned next-generation optoelectronic applications. Among TCO materials, indium tin oxide (ITO) has been the TCO most widely used for transparent conductors in optoelectronic devices due to its excellent transparency and high conductivity. However, there are many problems regarding to the use of ITO, such as high costs due to the rarity of indium, environmental pollution, and high crystalline temperature.[1)] Therefore, it is necessary to identity indium-free TCO materials, such as tin dioxide (SnO_2)[2)] and zinc oxide (ZnO).[3)] Especially, ZnO, which is an n-type semiconductor with direct and wide band gap (3.3 eV), is widely attractive material for alternating to ITO because ZnO is non-toxicity, low cost, high abundance, and especially stable in the hydrogen plasma when comparing with ITO. It has, therefore, been considered promising transparent electrodes for the development of optoelectronic devices such as organic light emitting diodes (OLEDs)[4)] and organic photovoltaics (OPVs).[5)] Many techniques have been investigated for the deposition of ZnO films, such as sol-gel,[6)] photochemical metal-organic deposition,[7)] sputtering,[8)] e-beam,[9)] pulsed laser deposition,[10)] chemical vapor deposition,[11)] and atomic layer deposition (ALD).[12,13)] Specifically, ALD is an advanced growth method that enables growth of high quality thin films. The ALD method is a thin film growth method employing self-limiting surface chemistry comparing repeating process of pulses and purges with precursors in which the source materials are kept separate during the deposition process. Therefore ALD allows for low temperature growth, better step coverage, good uniformity and controllability of thickness. Moreover, separate dosing

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of the precursors prevents gas phase reactions, which allows the use of highly reactive precursors and provides sufficient time for each reaction step to reach completion. These excellent properties of ALD technique permit the deposition of transparent oxide semiconductors in electronic devices with complex structures at relatively low temperatures, facilitating the use of flexible substrates.

The thickness of films is important to apply them to the transparent electrodes in optoelectronic devices such as OLEDs and OPVs, because the optical and electrical properties of ZnO film are dependent to the thicknesses of the films and the properties dependent on the thickness play an important role for device performances. In this work, therefore, we studied the thickness dependent optical and electrical properties of ALD-grown ZnO films in order to find an effective figure of merit depending on the thickness of the film when applying them to the transparent contact layer in optoelectronic devices.

2. Experimental Details

ZnO films were deposited on LCD glasses and Si (100) substrates by ALD using a traveling wave type Lucida D100 system (NCD Technology, Inc. Korea) at various deposition temperatures of 50, 100, 150, 180, 200, and 250°C and a working pressure of 3 to 3.3 Torr. Diethylzinc (DEZ, Hansol Chemical Co., Ltd., Korea) and deionized water (H_2O) were used as the Zn precursor and a reactant, respectively. DEZ and H_2O were delivered into the chamber with a high purity N_2 (99.999%) carrier gas flow of 20 sccm (standard cubic centimeters per minute). The ZnO films were typically deposited by DEZ-H_2O cycles with following sequence: DEZ pulse 0.1 s $\rightarrow$ N_2 purge 10 s $\rightarrow$ H_2O pulse 0.1 s $\rightarrow$ N_2 purge 10 s and the total ALD cycles were controlled 100, 200, 250, 500 and 1000 cycles in order to give a variation of film thickness. Field emission scanning electron microscopy (FE-SEM; JEOL, JSM 7001F) was used to observe the thickness and morphology of the films. The electrical resistivity was obtained by the van der Pauw method at room temperature using a Hall effect measurement system (Ecopia HMS3000) without the use of metal soldering for the electrical contacts in the magnetic field up to 0.57 T (Tesla). The phase and crystallinity of the films were monitored by thin film X-ray diffraction (XRD; Rigaku Ultima IV) with Cu Ká radiation ($\lambda = 1.5418$ Å). The optical transmittance spectra were monitored using an ultraviolet-visible-near infrared (UV-vis-NIR) spectrophotometer (V-570, JASCO) in the range of 200 to 1000 nm wavelength.

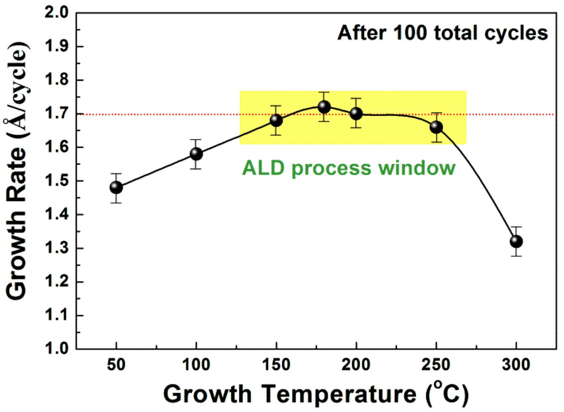

Fig. 1. The growth rate of ZnO films after 100 ALD cycles and the yellow highlighted region indicated by ALD process window.

3. Results and Discussion

In order to confirm the ALD growth window, ZnO films are grown at different growth temperatures ranging from 50°C to 300°C by ALD. Figure 1 shows the ALD process window of ZnO films after 100 total cycles at various growth temperatures. The growth rate was calculated by using a simple equation of [thickness of the sample / number of cycles]. Therefore, the thickness can be estimated from multiplying the number of cycles by growth rate of ZnO films in further discussion with regard to their properties as a function of cycle number. The growth rate of ZnO films were increased with an increase of growth temperature up to 150°C and then, almost constant at the temperatures ranging from 150°C to 250°C as about 1.7 Å/cycle. With further increase of the growth temperature over 250°C, the growth rate of ZnO films was dramatically decreased to 1.3 Å/cycle. From this result, it was suggested that the ALD process window is 100°C to 250°C and the self-limiting growth of ZnO films can be expected at this condition.

Figure 2 shows the resistivity values of ZnO films deposited by ALD at various growth temperatures as a function of number of ALD cycles. The resistivity of samples was the highest values through all the thicknesses when the films were grown at 50°C and 100°C. This could be suggested that the growth of films were not satisfied with the self-limiting condition as shown in Fig. 1. In the case of the films grown in the ALD process window, the resistivity values were lower than the films grown at low temperatures. The lowest resistivity was obtained by 4.225×10^{-3} Ω cm in the ZnO films grown at 200°C. Therefore, further analysis about the structural and optical properties of ZnO films as a

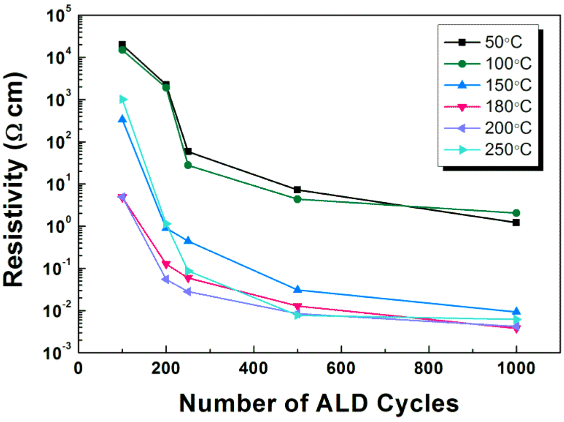

Fig. 2. The resistivity values of ZnO films deposited by ALD at various growth temperatures as a function of number of cycles.

function of thickness was conducted with the 200°C-grown-samples.

Figure 3 shows the thin film XRD patterns of ZnO films grown by ALD at 200°C as a function of thickness. The thicknesses of films were 17, 34, 43, 85, and 170 nm for 100, 200, 250, 500, and 1000 cycles, respectively. The 100-cycles-samples seem to have an amorphous nature due to relatively thin thickness with initial ALD growth stage. With an increase of thickness, the crystallinity of ZnO films was increased and they showed hexagonal wurtzite structure with (100), (002), and (101) diffraction peaks. The (100) preferred orientation was observed. In order to check the grain growth of the films with an increase of the number of cycles, surface morphologies of the ZnO films grown by ALD at 200°C as a function of thickness were observed using FE-SEM as shown in Fig. 4. The grain sizes of the films were obviously increased according to an increase of the number of ALD cycles. This result might be caused by further growth of ZnO crystals with an increase of ALD cycles and thus the thickness-dependent structural properties of ALD-grown ZnO films were clearly shown from the growth of grains with well-matched XRD results.

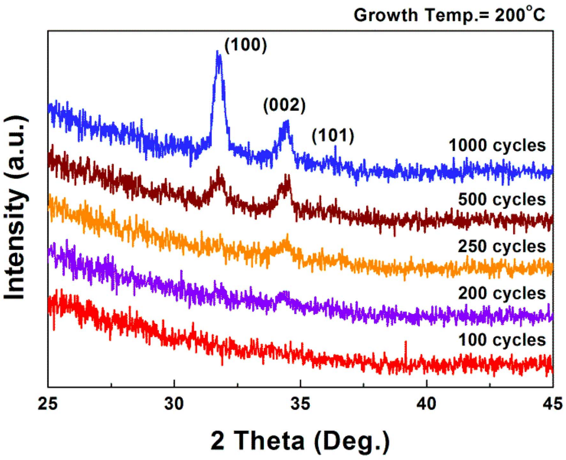

Fig. 3. The thin film XRD patterns of ZnO films grown by ALD at 200°C as a function of number of ALD cycles.

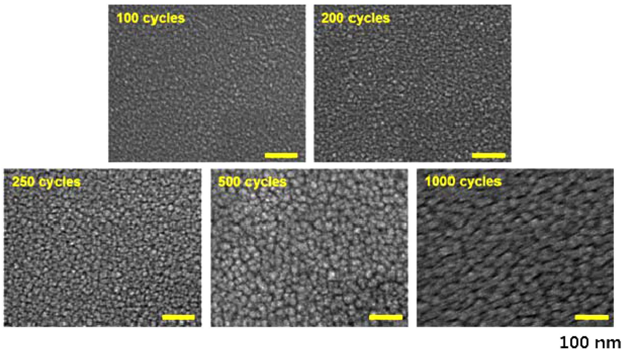

Fig. 4. Top view FE-SEM images of ZnO films grown by ALD at 200°C as a function of the number of ALD cycles. (All scale bars represent 100 nm).

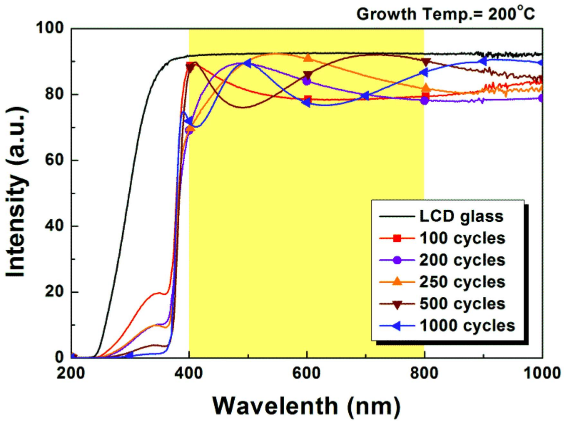

Fig. 5. The optical transmittances of ZnO films with various number of ALD cycles.

The optical transmittances of ZnO films with various number of ALD cycles were shown in Fig. 5. The band edge absorption in the near UV region (300 nm to 400 nm) was increased. This phenomenon was induced due to an increase of carrier concentration from an increase of thickness and this result was well matched with a decrease in the resistivity according to an increase of film thickness. All films showed good transmittance in visible region (yellow heighted region). The average transmittances in visible range (400 nm to 800 nm) were 83.53, 84.98, 86.20, 85.79, and 81.96% for the ZnO films with 100, 200, 250, 500, and 1000 ALD cycles, respectively. The factors influenced to transmittance of the films might be grain boundary scattering with the crystallinity of the films, optical band gap shift related with carrier concentration, and also thickness of the films. From the combinational properties of those factors, 250-cycles-ZnO

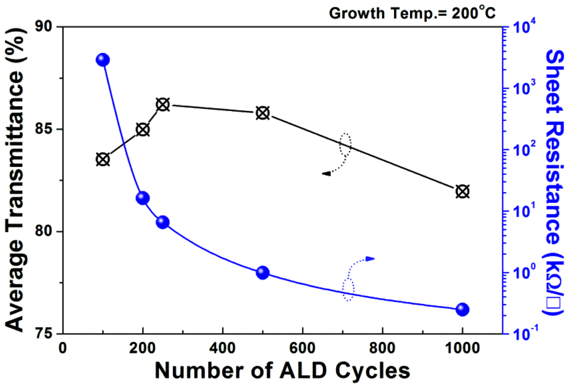

Fig. 6. The average transmittance in the visible region versus sheet resistance values of ZnO films as a function of number of cycles.

films had the highest average transmittance in visible range.

In order to estimate the TCO figure of merit, the average transmittances of ZnO films were plotted with the resistivity. Figure 6 shows the average transmittance of ZnO versus the sheet resistance of ZnO films as a function of ALD cycle number. Sheet resistance values were obtained by converting from the electrical resistivity using a simple division of the resistivity by the thickness of the films. The obtained values were 2.90×10^{3}, 1.62×10^{1}, 6.53, 9.88×10^{-1}, and 2.49×10^{-1} kΩ/□ for the ZnO films with 100, 200, 250, 500, and 1000 ALD cycles, respectively. The figure of merit is an important evaluating factor in TCO application for optoelectronic devices such as OPVs and OLEDs. In order to compare the performances of various transparent electrodes, the most commonly used figure of merit, as first defined by Haacke,[14] is

$$\varphi = T_r^{10} / R_s$$

where T_r is the transmittance at λ =550 nm (the wavelength at which solar power conversion is maximized) and R_s is the sheet resistance. In this work, however, T_r was replaced by the average transmittance in visible region to expand the solar cell application to all the optoelectronic applications. The evaluated values of figure of merit (φ) as a function of number of ALD cycles were 5.70×10^{-5}, 1.21×10^{-2}, 3.47×10^{-2}, 2.19×10^{-1}, and 5.50×10^{-1} Ω^{-1} with the order of an increase of thickness. Therefore, in our experimental condition, the highest figure of merit was obtained for the ZnO film with a thickness of about 170 nm.

4. Conclusions

We investigated the ALD-grown ZnO films as a function of thickness. First, the ALD process window was confirmed from the growth rate of films deposited at various temperatures and the resistivities of ZnO films as a function of growth temperature were measured by Hall effect measurement in order to find the proper growth temperature with the lowest resistivity. In selected growth temperature (200°C), the structural and optical properties, and also TCO figure of merit could be analyzed as a function of film thickness. As a result, 1000-cycles ZnO samples presented the best figure of merit value as 5.50×10^{-1} Ω^{-1} with the average optical transmittance of 81.96% and 2.49×10^{-1} kΩ/□ of sheet resistance.

Acknowledgements

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