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STRUCTURAL AND OPTICAL PROPERTIES OF ZnO THIN FILMS DEPOSITED USING ATOMIC LAYER DEPOSITION TECHNIQUE

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ABSTRACT

ZnO films have been successfully deposited by Atomic Layer Deposition (ALD) using Diethylzinc (DEZn) and water (H_2O) as precursors. These films had a smooth surface and high transmittance in the visible light region (e.g. film deposited at 145^{o}C had a small RMS roughness of 2.850 nm and 89.9±6.7% transmittance). Furthermore, the film resistivity measured by the Van der Pauw technique was 4.131x10^{-3} Ω.cm. This high transmittance and good conductive properties make the ALD deposited ZnO films suitable for transparent conducting oxide (TCO) applications such as transparent electrodes of solar cells. The preferred orientations of the films were found to be strongly dependent on the deposition temperature. (10.0) dominant ZnO films were grown in the temperature range of 155 to 220^{o}C, whereas (00.2) dominant ZnO films were formed between 220 to 300^{o}C. It is worth mentioning that ALD technique allowed ZnO films with preferred orientation, i.e. (00.2), to be deposited on both Si and glass substrates which have a large lattice mismatch to ZnO.

Keywords: ZnO, thin films, atomic layer deposition and crystal orientation

INTRODUCTION

ZnO is a wide band gap (E_g = 3.3 eV) semiconductor material with a large exciton binding energy (~ 60 meV) at room temperature. These properties have lead to many potential applications of this material such as piezoelectric transducers [1], ultraviolet light emitters [2], solar cells [3] and surface acoustic wave devices [4]. All the above applications require reproducible properties of this material such as specified crystal orientation, suitable optical and electrical properties.

High quality ZnO films are usually produced by pulsed laser deposition [5], molecular beam epitaxy [6] and radio-frequency magnetron sputtering [7]. However, these techniques require either a high growth temperature (>350^{o}C) or a post-annealing treatment. Atomic layer deposition (ALD) is one of the techniques that can produce highly conformal ZnO films with good reproducibility and nanoscale thickness control at temperature below 300^{o}C [8].

EXPERIMENTAL

In this work, the ALD was used to deposit ZnO thin films on Si substrates (p-type, (100)) and glasses. The substrates were cleaned by acetone/ deionized water / isopropanol. The substrates were then loaded into the ALD reactor (Cambridge Nanotech, Savannah 100). Diethylzinc (DEZn) and water (H_2O) were used as precursors for deposition of ZnO thin films. The ALD chamber was evacuated by a rotary pump (50 to 70 Pa) before the manual valve of the DEZn bubbler was turned on. The vapors of both precursors were purged alternately into the chamber through separate inlet lines. The opening and closing sequences of the high speed valves were controlled by a computer. A 3 s of evacuation time was used after each purging process to prevent mixing of DEZn vapor and H_2O vapor in the chamber during the deposition process. The deposition temperature was controlled from 60^{o}C to 300^{o}C. High purity nitrogen gas (N_2, 20 sccm) was used as carrier gas and for purging purposes.

RESULTS AND DISCUSSION

Fig. 1 shows the shows the XRD analysis of the crystal structure of thin film deposited at 145°C and 1200 cycles. The diffraction peaks matched well with the standard diffraction pattern of ZnO (JCP2.2CA. 01-079-2205), revealing that the as-deposited film was ZnO crystal with a wurtzite structure. No other phase or impurity was detected. The calculated crystal size of the film from Scherrer's equation was 17.7 nm.

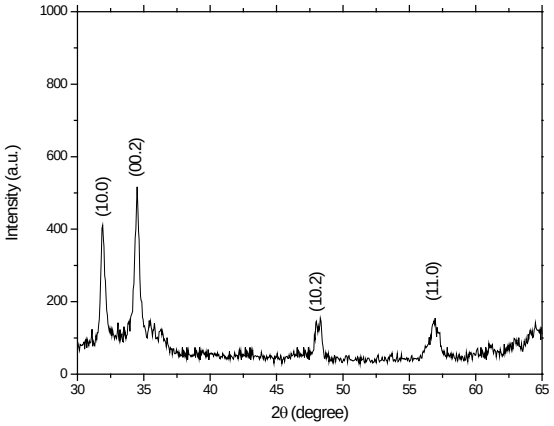

Fig. 1. The XRD diffraction peaks of ZnO film deposited at 145°C and 1200 cycles.

This ZnO film was highly transparent under visible light which could be seen from the coated glass substrate as shown in Fig. 2. The average transmittance of this ZnO film measured by UV-Vis spectroscope in the visible light region, i.e. 380 to 750 nm, was 89.9±6.7 %.

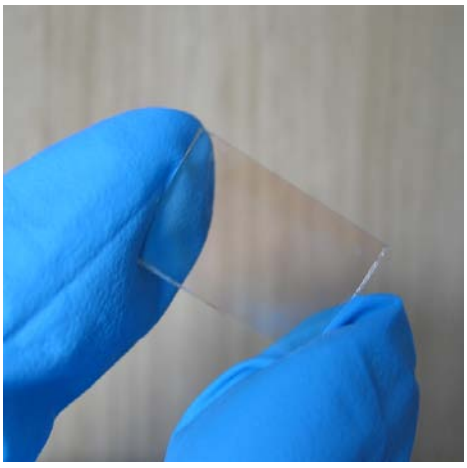

Fig. 2. Transparent ZnO film deposited on a glass slide at 145°C and 1200 process cycles.

The film resistivity measured by the Van der Pauw technique was 4.131×10^{-3} Ω.cm. The ZnO film had a smooth surface and composed of many tiny crystal grains as shown in Fig. 3. The RMS surface roughness of the ZnO film measured by AFM in contact mode was 2.850 nm.

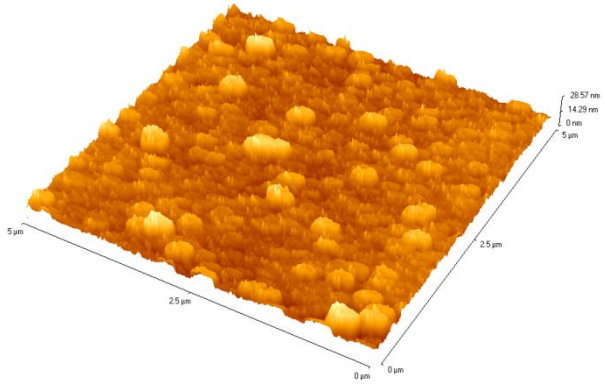

Fig. 3. Surface morphology of the ZnO film deposited at 145°C and 1200 cycles.

The effect of deposition temperature on the crystal orientation of ZnO films was studied. The ZnO films were deposited at various temperatures, ranging from 130 to 300°C. The DEZn and H_2O pulse rate were 0.015 s and 0.010 s, respectively. The ALD process cycles for all the experiments were 1200 cycles. As shown in Fig. 4, XRD peaks of films matched well with the standard diffraction pattern for wurtzite ZnO (JCP2.2CA. 01-079-2205) and for Zn (JCP2.2CA. 01-087-0713). The strong ZnO diffraction peaks revealed that the layers were mainly ZnO polycrystalline with a hexagonal wurtzite structure.

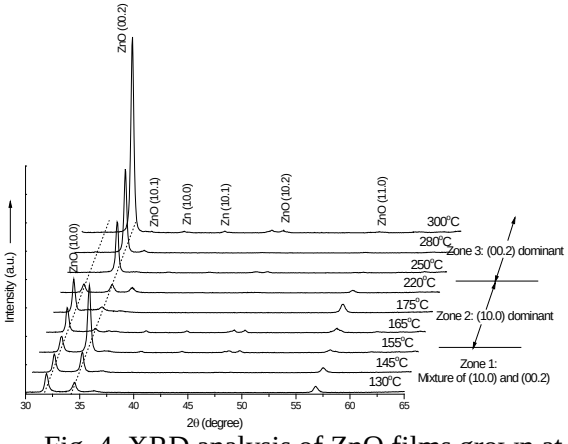

Fig. 4. XRD analysis of ZnO films grown at different deposition temperatures. Reproduced with permission [8].

Two dominant ZnO peaks were identified, i.e. ZnO (10.0) and ZnO (00.2). As depicted in Figure 4, it was clearly shown that the growth temperature played an important role in determining the crystal orientation of ZnO thin films. Three zones could be distinguished based on the dominance of ZnO (10.0) and ZnO (00.2), i.e. (a) zone 1: 130 to 155^{o}C, (b) zone 2: 155 to 220^{o}C, and (c) zone 3: 220 to 300^{o}C. In zone 1, the films were dominated by both ZnO (10.0) and ZnO (00.2)-oriented crystals. This indicated that the ZnO films were composed of a mixture of grains with the c-axis parallel and perpendicular to substrate surface. The XRD intensity of ZnO (10.0) and ZnO (00.2) peaks increased gradually with deposition temperature. This demonstrated that the crystallinity of ZnO films was likely to improve with increasing deposition temperature. A change of crystal orientation from the mixture of ZnO (10.0) and ZnO (00.2) to ZnO (10.0) dominant was observed in zone 2. It was noted that the suppression of crystal growth was only observed in ZnO (00.2) oriented crystals. The ZnO films grown at these temperatures contained crystal grains with c-axis mainly parallel to substrate surface. At high growth temperature range (220 to 300^{o}C), (00.2) oriented crystals were dominant in the ZnO films. The crystals growth direction, i.e. c-axis, was perpendicular to the substrate surface. The degree of crystallinity of ZnO films in the c-axis direction was also enhanced with increasing growth temperature.

It is worth mentioning that the preferred orientations of the ZnO films were found to be strongly dependent on the deposition temperature. Deposition parameters such as DEZn pulse rate, H_2O pulse rate and the number of ALD process cycles had limited effect on the preferred orientation of the ZnO films (results not shown).

Fig. 5 shows the film growth rate (= thickness/ALD cycles) as a function of deposition temperature. In this study, a fixed deposition condition, i.e. 1200 cycles, 0.015s DEZn pulse rate and 0.010s H_2O pulse rate was employed. At low deposition temperature such as 60^{o}C, the purged precursors might not have sufficient energy to chemically react with the surface functional groups in order to grow alternate layers of zinc and oxygen. Thus, a very low growth rate was observed. The purged precursors became more energetic and were able to react with more surface functional groups as the temperature increased. As a result, the growth rate increased with deposition temperature. The deposition of ZnO films was proposed to be chemical reaction limited at temperature below 125^{o}C due to the incomplete decomposition of the precursor materials. Similar observation and limiting mechanism (step) has been reported by Tapily *et al.* [9].

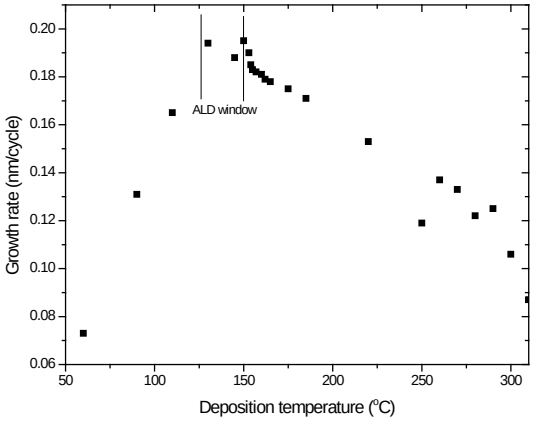

Fig. 5. The ZnO layer growth rate as a function of the deposition temperature. Reproduced with permission [8].

The growth rate remained constant between 125 to 150^{o}C, indicating that the self-limiting growth of ZnO films had occurred (ALD window). The growth rate in this ALD window was 0.194 nm/cycle. Theoretically, the deposition of ZnO layers in this temperature range should follow the chemical reactions as illustrated in equation (1) and (2).

$$ZnOH^* + Zn(CH_2CH_3)_2 \longrightarrow ZnOZn(CH_2CH_3)^* + C_2H_6 \quad (1)$$

$$Zn(CH_2CH_3)^* + H_2O \longrightarrow ZnOH^* + C_2H_6 \quad (2)$$

where the asterisks designate the surface species. The deposition rate did not depend on the deposition temperature in this temperature range. Thus, it was likely that the deposition was mass transport limited, i.e. controlled by the transport of DEZn and H_2O into or out of the system.

The growth rate decreased when the deposition temperature exceeded 150^{o}C. Two possible mechanisms might occur in this temperature range, i.e.

(i) desorption of Zn atoms from substrate surface, and/or
(ii) premature dissociation of the precursors by a pyrolysis process.

CONCLUSION

ZnO films have been successfully grown by ALD using DEZn and H_2O as precursors. These films had a smooth surface and high transmittance in the visible light region (e.g. film deposited at 145^{o}C had a small RMS roughness of 2.850 nm and 89.9±6.7% transmittance). Furthermore, the film resistivity measured by the Van der Pauw technique was $4.131x10^{-3}$ Ω.cm. The preferred orientations of the ZnO films were found to be strongly dependent on the deposition temperature. (10.0) dominant ZnO films were grown in the temperature range of 155 to 220^{o}C, whereas (00.2) dominant ZnO films were formed between 220 to 300^{o}C. Deposition parameters such as DEZn pulse rate, H_2O pulse rate and the number of ALD process cycles had limited effect on the preferred orientation of the ZnO films.

Acknowledgments

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