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Growth process optimization of ZnO thin film using atomic layer deposition

Binbin Weng[1,4], Jingyu Wang[2,4], Preston Larson[3] and Yingtao Liu[2]

[1] School of Electrical & Computer Engineering, University of Oklahoma, Norman 73019, USA
[2] School of Aerospace & Mechanical Engineering, University of Oklahoma, Norman 73019, USA
[3] Samuel Roberts Noble Microscopy Laboratory, University of Oklahoma, Norman 73019, USA
[4] These two authors contribute equally in this work.

E-mail: binbinweng@ou.edu

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Abstract

The work reports experimental studies of ZnO thin films grown on Si(100) wafers using a customized thermal atomic layer deposition. The impact of growth parameters including H_2O/DiethylZinc (DEZn) dose ratio, background pressure, and temperature are investigated. The imaging results of scanning electron microscopy and atomic force microscopy reveal that the dose ratio is critical to the surface morphology. To achieve high uniformity, the H_2O dose amount needs to be at least twice that of DEZn per each cycle. If the background pressure drops below 400 mTorr, a large amount of nanoflower-like ZnO grains would emerge and increase surface roughness significantly. In addition, the growth temperature range between 200 °C and 250 °C is found to be the optimal growth window. And the crystal structures and orientations are also strongly correlated to the temperature as proved by electron back-scattering diffraction and x-ray diffraction results.

1. Introduction

In recent years, ZnO is one of the most intensively investigated semiconductor materials due to its wide direct bandgap (~3.3 eV), large exciton binding energy (~60 meV), and excellent piezoelectric properties [1]. Significant interest has been attracted in view of its broad range of research and industrial applications, including light emitting diodes [2], UV laser diodes [3, 4], photon detectors [5], solar cells [6], pressure sensors [7], transparent conductive materials [8], and also interfacial coatings for fiber strength enhancement [9], etc.

Common techniques used to grow relatively good quality ZnO thin films are physical vapor deposition (PVD) systems, such as magnetron sputtering [10, 11], e-beam evaporation [12], and pulsed laser deposition [13]. However, these high energy PVD methods typically result in broad material interface damage, significant stoichiometric non-uniformity in films, and commonly existing structure imperfections including micro pin-holes and point-defects. With the continual trend towards scaling modern novel electronic devices down to micro- and nano-scale levels, such issues become even more severe and degrade the material quality tremendously. In contrast to these PVD methods, ALD is well-known as a promising alternative deposition method with numerous advantages, such as good uniformity and conformality, atomic-scale thickness controllability, perfect stoichiometric uniformity and low impurity contamination at lower growth temperatures from 400 °C down to as low as 50 °C [14, 15]. In addition to the improvement of the structural property, this technique also has strong capabilities to enhance the electric, optical and mechanical characteristics [16, 17] of the ALD-derived thin films, including Hall mobility, electrical resistivity, light transparency, photoluminescence, hardness and Young's modulus. Moreover, in recent years, rapidly growing research attention has been paid to growing semiconductor thin films onto lightweight, flexible and mechanically strong plastic films [18]. Generally, such organic substrates can not withstand high processing temperature (e.g. PET $\leqslant$ 150 °C [19], Kapton Polyimide $\leqslant$400 °C [20]).

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Table 1. The relationship between pulse time and pressure spike of H_2O source.

Pulse time	0.1 s	0.2 s	0.3 s
Pressure spike (ΔP)	100 mTorr	180 mTorr	250 mTorr

Note: pulse time and pressure spike for DEZn were set at 0.3 s and 120 mTorr.

Therefore, it becomes increasingly advantageous to study ZnO thin film growth using ALD at lower temperature ranges under these considerations. It is noted that there are a few efforts that have already been made in this area, with different research emphasis including growth rate, crystal quality, and optical and electronic properties [21, 22].

In this work, our efforts focus on developing a thermal ALD process to optimize the morphology and structural properties of as-grown ZnO thin films. Major growth factors including the H_2O/DiethylZinc (DEZn) dose ratio, background base pressure and growth temperature are investigated systematically. When some growth factors are tuned out of certain ranges, a high density of flower-like nanostructures were observed for the first time in ALD growth research works. Such limitations for using thermal ALD to deliver high quality ZnO thin films are reported in this work. It is believed that the findings reported in this paper will offer unique and valuable guidelines for researchers to grow high quality ZnO thin films by ALD method.

2. Methodology

ZnO thin films were grown on (100) silicon substrates by an ALD method under various growth conditions. Prior to the growth step, all 2×2 cm^2 Si substrates were degreased by dipping into Trichloroethylene (TCE), Acetone, and Methanol solvents respectively for 5 min (mins) each under ultrasonic agitation, followed by cleaning the substrates under running deionized water (DI) for 10 min before finally purge-drying by ultrahigh purity (UHP) N_2 gas. A customized 3' thermal ALD system was then used to perform the ZnO growth on the cleaned Si wafers. In the reaction process, we adopted a double-exchange chemical vapor reaction between DI water and DEZn precursors. The dose time was controlled by computer driven pneumatic valves, and N_2 gas carried these vaporized sources to the reaction chamber. The H_2O and DEZn were alternately distributed, and a 10 s (s) UHP N_2 purge period was carried out after each dosing process. It is noted that this period was enough to ensure that the pressure returned to its base level before the next pulse.

In order to find a suitable growth window and optimize the deposition procedure, three major growth factors including H_2O/DEZn distribution ratio, background base pressure, and growth temperature were investigated. Three H_2O/DEZn dose ratios of 0.8, 1.5, and 2.0 were studied by tuning the DI H_2O pulse time while fixing the pulse for the DEZn precursor. To investigate the impact of the base pressure conditions, ZnO films were grown under 0.5, 0.4, 0.3 and 0.2 Torr respectively by adjusting the feeding UHP N_2 amount. For both H_2O/DEZn dose ratio and base pressure studies, the growth temperatures were all set at 150 °C. For the temperature impact study, the growth temperatures were adjusted from 100 °C to 300 °C, in steps of 50 °C. It is worth noting that 300 growth cycles were carried out to ensure sufficient film thicknesses for characterization.

After the series of growth processes, thin films were characterized by a high resolution Zeiss Neon EsB FESEM with Oxford EBSD capabilities, an Asylum atomic force microscope (AFM), a KLA Tencor D500 stylus profiler, and a Rigaku powder x-ray diffraction (XRD) system.

3. Results and discussion

During the ALD process, precursor chemistry plays a vital role. Different precursors have different chemical properties such as volatility and thermal stability. Therefore, finding a good balance between the H_2O and DEZn precursors is the most critical step in order to achieve successful ZnO ALD growth. With this consideration, the effect of dose ratio between the H_2O/DEZn precursors was studied first. With the change of pulse time of H_2O from 0.1 s to 0.3 s, the resulting pressure spikes (ΔP) were increased consequently, as shown in table 1. The top-view morphologies of feeding ratio dependent as-grown ZnO films are demonstrated in figures 1(a)–(c). As can be seen in figures 1(a) and (b), when the H_2O source was not sufficiently supplied, nanoflower-like structures were formed on top of the thin films. Such random structures increase the surface roughness and play a role as irregular seeds that will adversely affect film quality in subsequent growth processes, such as fast growth speed, and irregular orientations of grains. It is believed that the nano-flower formation results from the unbalanced H_2O/DEZn dose ratio. With a decreasing amount of H_2O, the DEZn was overdosed relatively, which results in a

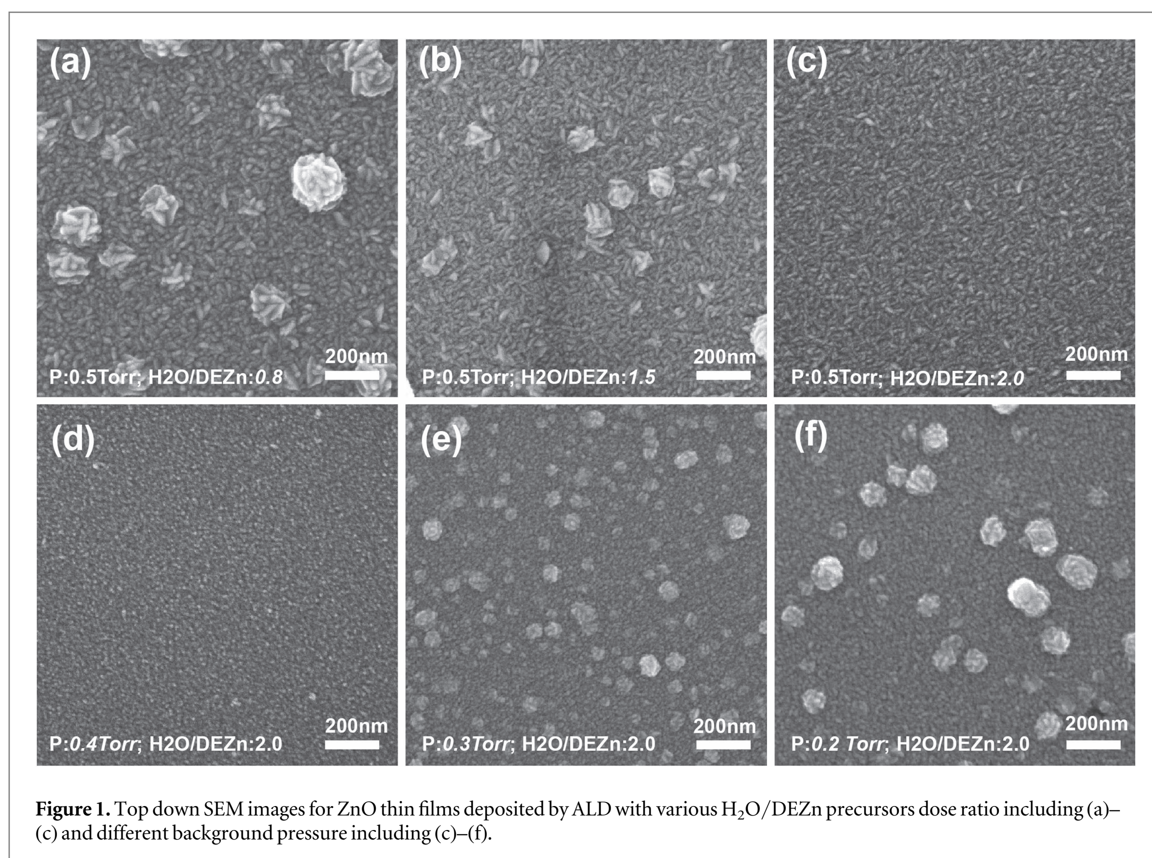

Figure 1. Top down SEM images for ZnO thin films deposited by ALD with various $H_2O/DEZn$ precursors dose ratio including (a)–(c) and different background pressure including (c)–(f).

process more like chemical vapor deposition (CVD) rather than an ALD process. Therefore, in order to eliminate the formation of those nano-flowers, it is necessary to keep the $H_2O/DEZn$ dose ratio over a certain level to prevent a DEZn over-dose situation. In our system, to deliver successful ZnO growth, the H_2O dose amount needs to be close to or higher than 2 times of DEZn, as shown in figures 1(c).

ALD is a self-limiting chemical reaction process that can provide an equilibrium state between adsorption and desorption of precursors within each reaction cycles. Since background pressure is directly related to the surface adsorption or residence time of a precursor, without a suitable base pressure, the equilibrium state will be hard to maintain resulting in an uncontrollable growth process. Therefore, even if $H_2O/DEZn$ dose ratio is at a balanced range, similar nanoflower-like random grains can still form when the base pressure falls below 0.3 Torr, as shown in figures 1(e) and (f). It is believed that a similar CVD process might be happening under this condition. Specifically, too low of a base pressure results in desorption of DEZn precursors that originally bonded on the ZnO thin film. Consequently, those precursors react with H_2O molecules and redeposit on the surface creating nanoflower-like grains. As a result, the surface roughness is found to be strongly dependent on both the $H_2O/DEZn$ dose ratio and base pressure parameters. In order to perform a controllable and uniform ZnO ALD deposition, both dose ratio and base pressure during the reaction process have to be tuned to a suitable window as shown in figures 1(c) and (d).

It is well known that ALD is a thermally activated process that produces self-limiting reactions on the surface of a substrate. Therefore, a suitable temperature window can be identified for ZnO thin film deposition based on the constant growth rate of the ALD process. To study the effect of deposition temperature for ZnO thin films, five different deposition temperatures were tested from 100 °C up to 300 °C as mentioned before. Other conditions followed the optimized parameters discussed in previous sections: $H_2O/DEZn = 2$, $P_{base} = 0.5$ Torr and cycle $= 300$.

Figure 2 shows the average growth rate as a function of the growth temperature. As shown, the growth rate increases from 100 °C to 150 °C. This is due to the fact that the reactant is unable to fully overcome the necessary activation energy to chemisorb on the substrate at lower temperatures (~100 °C). It is known that H_2O is a highly polar molecule that tends to condense or physisorb on to the surface and lead to a partial CVD process with an unwanted higher growth rate. High temperature can help to minimize this issue, therefore the growth rate decreases after the temperature rises from 150 °C to 200 °C. From 200 °C to 250 °C, a relatively stable growth rate is achieved. The range is believed as the good ALD growth window for deposition of ZnO thin films. However, extremely high temperatures will lead to decomposition or desorption of adsorbates before the reaction. This explains why the growth rate quickly decreases from 250 °C to 300 °C.

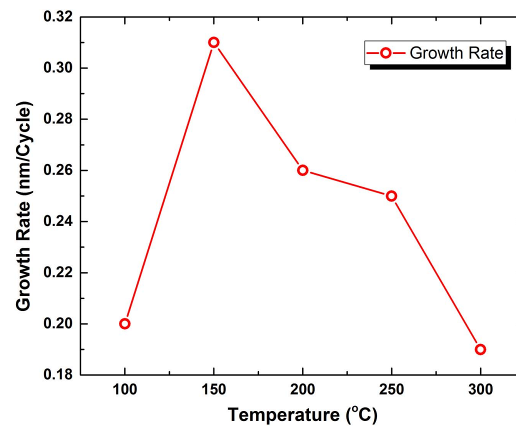

Figure 2. Growth temperature dependent deposition rate of ZnO thin films on Si wafers.

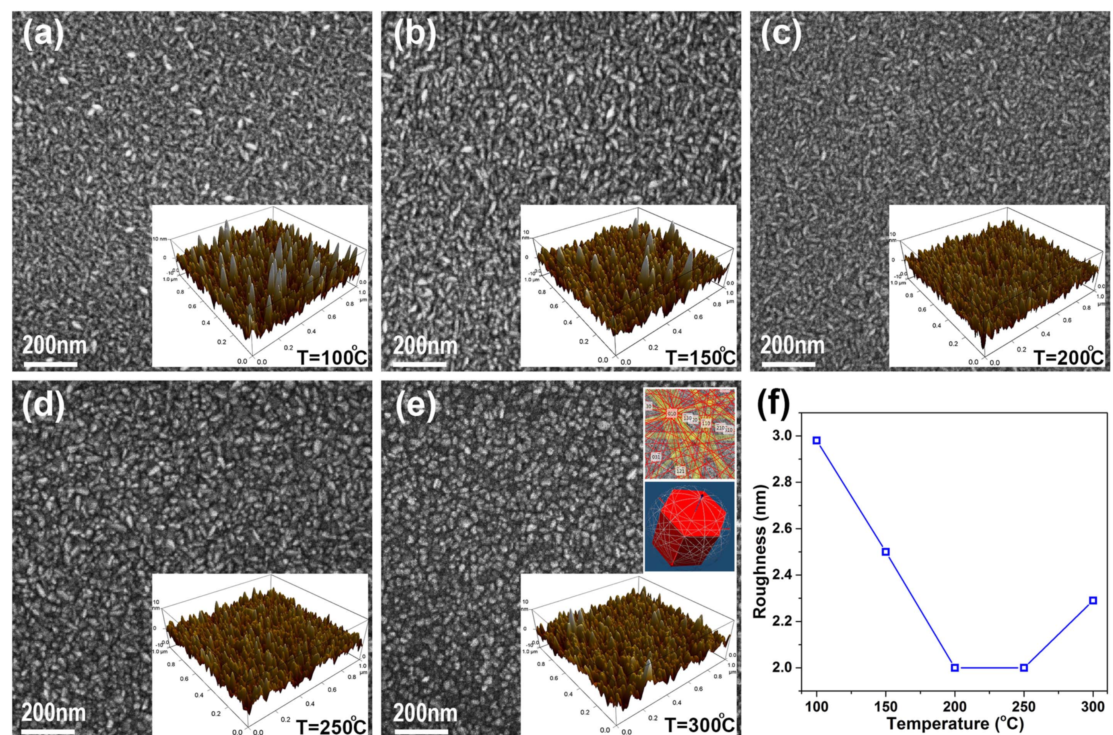

Figure 3. Temperature dependent morphologies of ZnO films by ALD: (a)–(e) top down SEM pictures with 3D AFM insets; (f) surface roughness as a function of growth temperature. (Note: extra small insets in (e) are indexed Kikuchi pattern and EBSD resolved wurtzite structure.)

The surface morphologies of ZnO films grown under different temperatures were also characterized by SEM and AFM tools as presented in figures 3(a)–(e). The root mean square (RMS) of surface roughness was obtained from the AFM image with an accuracy of 0.1 nm. The relationship between RMS and growth temperature is also shown in figure 3(f). As shown in the 3D AFM images, with an increase in the growth temperature from 100 °C to 200 °C, the surface morphology is steadily improved. At 100 °C and 150 °C, the growth process is either due to insufficient chemisorbtion energy or involved with a partial CVD mechanism due to the H_2O condensation issues as mentioned. Therefore, the growth is not primarily through ALD's self-limiting reaction condition and consequently we observe rough growth surfaces. This also explains why the RMS value goes up when the growth temperature increases to 300 °C, since this region can lead to very poor absorption of reactants on the substrate as explained previously. Finally, for growth temperatures at 200 °C and 250 °C, the RMS values of 2 nm suggest that the ZnO film grown by our customized ALD system is able to achieve atomic flatness under optimized growth conditions. In addition, it is worth noting that the ZnO grains have changed from rice-like to rock-shaped microstructures when the temperature goes to 300 °C, while the films grown at 250 °C is at a transition

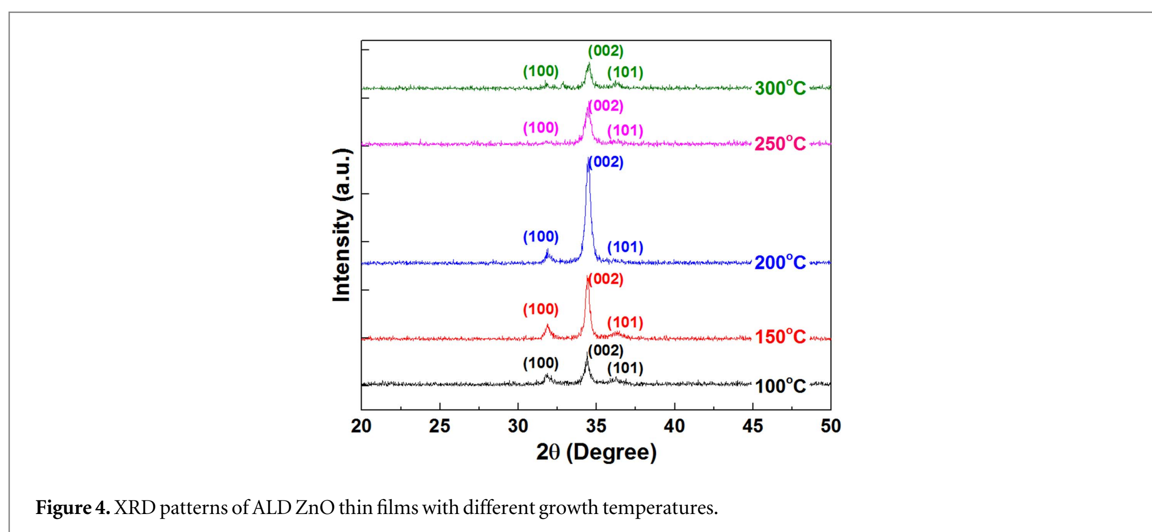

Figure 4. XRD patterns of ALD ZnO thin films with different growth temperatures.

state having grains with both formations, as shown in the SEM images in figures 4(d) and (e). EBSD was used to investigate the crystallographic change of the microstructures where it was observed that rice-like grains randomly contains both zinc blende and wurtzite crystal structures. On the contrary, rock-shaped grains primarily have a wurtzite crystal structure whose indexed Kikuchi pattern and the resolved wurtzite formation are displayed as insets in figure 3(e).

Furthermore, in order to investigate the crystal quality of these films grown under different temperatures, XRD data was collected through a Rigaku powder XRD tool. XRD scans were performed from 20° to 50°, and the spectra are shown in figure 4. It is found that ZnO films can be poly-crystallized even at the lowest growth temperature of 100 °C, as ZnO peaks can still be observed at this level. With an increase in temperature, we found the intensity of the (002) peak increased strongly, but the (100) and (101) peaks become weaker. The strongest (002) peak is observed at 200 °C which indicates the films were primarily grown in the *c*-axis orientation. However, after the temperature is over 200 °C, the (002) peak goes weaker indicating the films are no longer dominated by a *c*-axis. The reason could be due to the fact that crystal structures start transforming at this stage. Similar results were also observed in other studies [23, 24].

4. Conclusion

In this work, the thermal ALD growth process of ZnO thin films on silicon is systematically studied and optimized through a customized ALD system using alternating pulses of DEZn and H_2O. The impact of three ALD growth factors include H_2O/DEZn precursors dose ratio, background base pressure and growth temperature have been studied. In order to perform a controllable and uniform ZnO ALD deposition, it is found that both dose ratio and base pressure during the reaction process have to be tuned to a suitable window for highly uniform deposition: the H_2O/DEZn ratio needs to be controlled close to or above 2, and 0.4 Torr is the bottom limit base pressure for our customized ALD system. On the other hand, the study of the temperature impact suggests that the suitable temperature window for growth should stay within 200 °C–250 °C.

Acknowledgments

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