Spatial Analysis of ZnO Thin Films Prepared by Vertically Aligned MOCVD

Prakash Mishra, Rahi Patel, Babar Hussain*, Justin Stansell, Bahadir Kucukgok, M. Yasin Raja, Na Lu, and Ian T. Ferguson
Electrical and Computer Engineering Department and Center for STEM Education
University of North Caroline at Charlotte
Charlotte, NC
*bhussai1@uncc.edu

***Abstract*—Zinc Oxide thin films were grown using a homemade metallorganic chemical vapor deposition apparatus with a non-centrosymmetric groove for the substrate. Films grown with relatively constant thickness and varying temperatures were tested using photoluminescence spectrometry, *ex-situ* spectral reflectance, and *ex-situ* transmittance measurements at five distinct points. Results are analyzed to evaluate the spatial consistency in thickness and optical characteristics of the ZnO films.**

***Index Terms*—MOCVD, zinc oxide, thin film, transmission, photoluminescence, spatial analysis, spectral reflectance.**

I. Introduction

Over the last decade or so, there has been a renewed interest in cheaper, more efficient materials and processes for the production of energy. Zinc Oxide is a wide bandgap semiconductor, which has a wurtzite crystal structure. ZnO has a bandgap of 3.34 eV, though the bandgap is highly versatile, able to be tuned from 2.8eV to 4 eV [1–2]. ZnO thus provides one of the most promising methods of supplying clean energy through photovoltaic cells with a higher degree of efficiency and cost effectiveness than previously seen. In addition to use in photovoltaic cells, ZnO has numerous potential applications in the fields of optoelectronic and electronic devices such as UV LEDs [3–4].

Metal organic chemical vapor deposition (MOCVD) can be used to grow ZnO films at different temperatures and pressures, allowing the relatively fast growth of ZnO film in highly controlled and desirable conditions. A carrier gas (mostly nitrogen) carries diethylzinc (DEZn) vapors into a heated, vacuum-control chamber and reacts with oxygen, which enters the reaction chamber via different lines. Compared to other methods of ZnO growth such as RF sputtering, laser ablation and deposition, and Molecular Beam Epitaxy, MOCVD provides the prospect of higher quality ZnO films with fewer defects and impurities, thus increasing the crystal quality of ZnO [4–5]. Furthermore, the MOCVD process is very easy to upsize, able to produce large samples on a variety of substrate materials for various industrial applications and mass production.

In literature, various variables such as temperature, pressure, rotation speed, and flow rates have been optimized in an effort to determine the optimal conditions to improve the quality of ZnO [6–8]. Uniformity in optical, electrical, and structural properties over the surface of the film is critical to fabricate efficient devices from the wafers. Therefore, in this paper, we experimentally study the spatial consistency of ZnO growth using MOCVD process. It is investigated whether basic properties of ZnO thin films are maintained as one deviates from the center of the film (as the center is the locus of most measurements). An axial approach was taken to observe the variation in the properties of ZnO. In this fashion, properties such as Photoluminescence (PL), Transmittance, and Spectral Reflectance were measured along an arbitrary x-y plane.

II. Materials and Methods

Deposition was performed by a custom made MOCVD reactor in which the susceptor rotates clockwise. The substrate is positioned so that it is not rotating on its own axis, but is rather placed in an indent in one quadrant of the susceptor. The MOCVD reactor is vertically oriented, so reactant gases come from a shower-like plate above the susceptor. The flow flange picture is shown in Fig. 1.

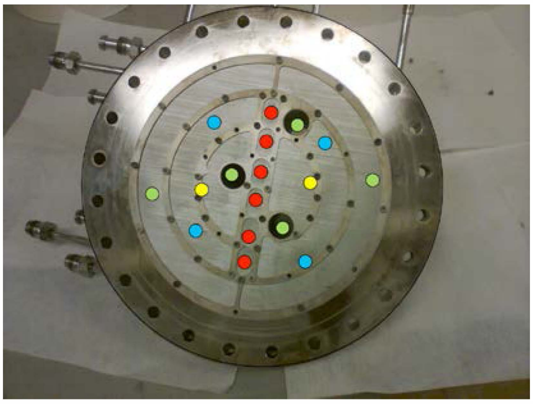

Fig 1. Flow flange for gas entrance into chamber. Red dots show DEZn entry points, blue for oxygen, green for nitrogen, and yellow for trimethylgallium for doping (not used).

Sapphire substrates with 2” diameter were used. They were placed in the groove with a cleaved end facing outward, used as a reference for the development of a Cartesian system on the substrate. Five measurement points were selected, marked front, back, left, right, and center (Fig. 2 (a)), each 0.5” from the center of the Sapphire substrate. Reaction chamber temperature was varied from 300 to 600 °C at intervals of 50 °C. Chamber pressure was kept at a constant 3 torr. The oxygen and carrier

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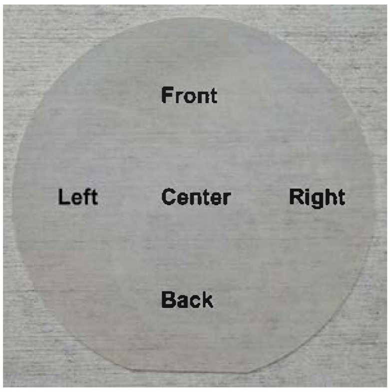
gas had flow rates of 1000 and 100 sccm respectively. The metallorganic precursor had a bubbler pressure of 180 torr at 5 °C, resulting in a VI/II ratio of 330 [6]. PL was conducted by a PL/Raman spectrophotometer from Photon Systems. Transmittance and spectral reflectance are measured by UV-vis Hamamatsu light source and a FILMetrics spectrophotometer. Substrates were cleaned with acetone, methanol, isopropanol, and distilled water before being placed on a graphite susceptor. The rotation speed during growth was 800 rpm [9]. All the samples were around 500 nm thick, with the exception of the sample grown at 300 °C which was unable to grow past 358 nm due to very small growth rate because of lack of energy to overcome molecular bonds [6].



(a)

(b)

Fig. 2. (a) Substrate with regions labeled. Cleaved end at front was placed on outer edge of groove towards edge of the susceptor. (b) Susceptor inside the MOCVD reactor with grooves to place substrates.

III. Results and Discussion

The effect of temperature on MOCVD growth is explained somewhere else, where the optimal growth temperature was discovered to be 550 °C [6]. To prevent any deviations based on temperature, we used an average across temperature for all presented data. When normalized with respect to temperature, data showed no significant deviation.

A. Photoluminescence

Photoluminescence was used to characterize defect concentration and determine spatial crystal behaviors. PL spectra have two quintessential characters; the height of their main, or exciton emission, peak, and the narrowness thereof. The larger the height and the narrower the peak (the sharper), the better the crystal quality is [6, 8, 10–12]. The results of PL spectrum analysis of the ten samples can be seen in Fig. 3. This figure demonstrates the full width at half maximum (FWHM) at each of the five points on the substrate. The crystal structure of the front of the crystal displays a much higher quality than the rest of the film. FWHM seems to vary more along the back-front axis than it does along the left-right axis. For reference, Fig. 4 provides a photoluminescence spectrum for one of the samples, grown at 600 °C. From this figure, we note a general consistency of PL spectra across the spatial gradient. No auxiliary peaks or deviations from existing peaks in the centre were noted; the only deviation to note was a difference in crystal quality from Fig. 3.

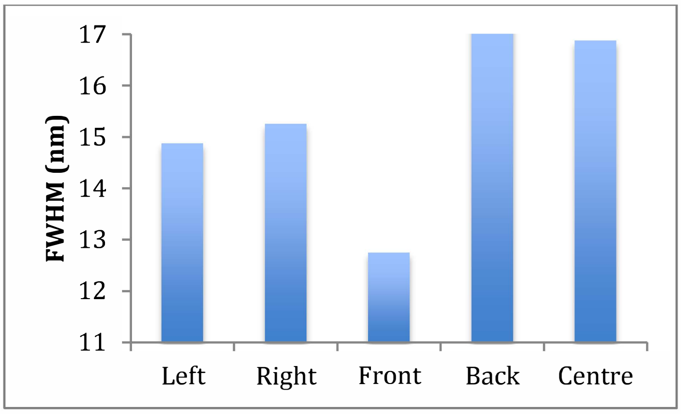


Fig. 3. Full width at half-maximum of the PL spectra at each of 5 points measured at room temperature.

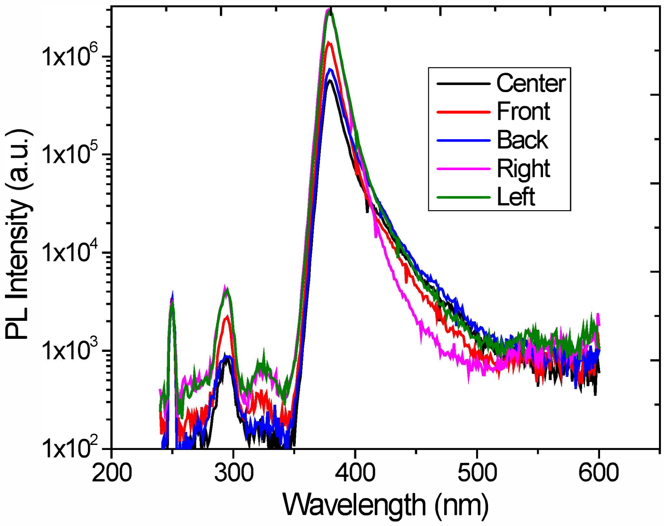


Fig. 4. Photoluminescence spectra at five different points for a sample grown at 600 °C.

B. Spectral Reflectance

Spectral reflectance data is used by Filmetrics tool in an algorithm to calculate three values: the thickness of the sample, the roughness at the surface of the sample, and the fitting accuracy of the algorithm. All accuracies are above 95%. The roughness and thickness values are presented in Fig. 5.

Roughness of the samples is visibly consistent across the substrate. Thickness deviations are marginal (~20 nm) for all regions but the front, which had a deviation of nearly 70 nm.

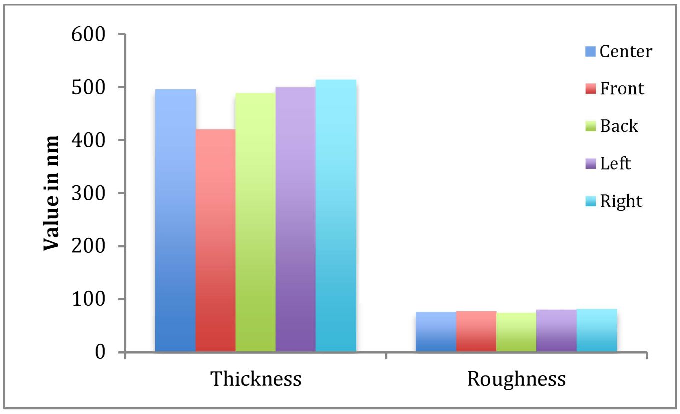
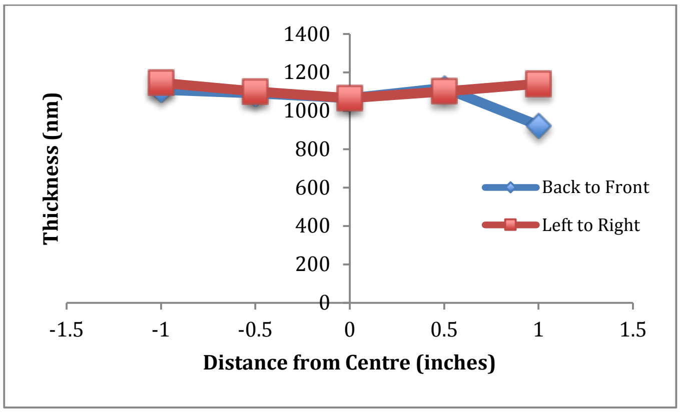
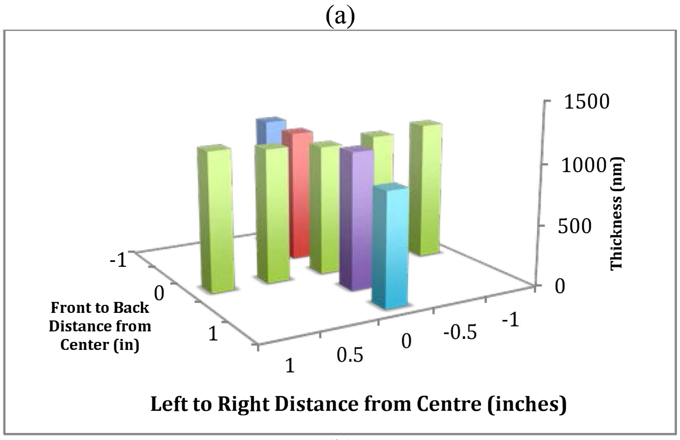


Fig. 5. Values of thickness and root mean square roughness as obtained by spectral reflectance by spatial positioning.



(a)



(b)

Fig. 6. (a) Thickness at 5 points along each axes left-to-right and back-to-front. Gradients visible in all four cardinal directions in a positive direction, with the exception of the negative gradient in the frontward direction. (b) A 3D histogram representation of the thicknesses on the area of the substrate. **in**: inch

To understand the nature of these thickness variations, we further investigated an additional two points on each axis, intermediary with respect to the measured points and the center on one of the substrates. These results are plotted in Fig. 6 (a). The same results are visualized in 3D histogram in Fig. 6 (b). From the figure, we can see a clear gradient-style activity along both axes emanating from the center. The only area to show a decrease with emanation distance is the front-side of the back-to-front axis, attributed to the fact that it is distal with relation to the sources of the gas (placed near the outer edge of the susceptor).

C. Transmittance

Transmittance spectra for all samples were relatively consistent. The average transmittances at the five points over the wavelength range of 390 – 1100 nm are plotted in Fig. 7. Transmittance for the average photocell window layer is >80% [13], which is a criterion met by the front, back, right, and center regions of the samples measured on average. However, the left region show lower rates of transmittance through the film. As the thicknesses are relatively consistent across the substrate, the lower transmittance of the left region can be attributed to the crystal quality of the ZnO film.

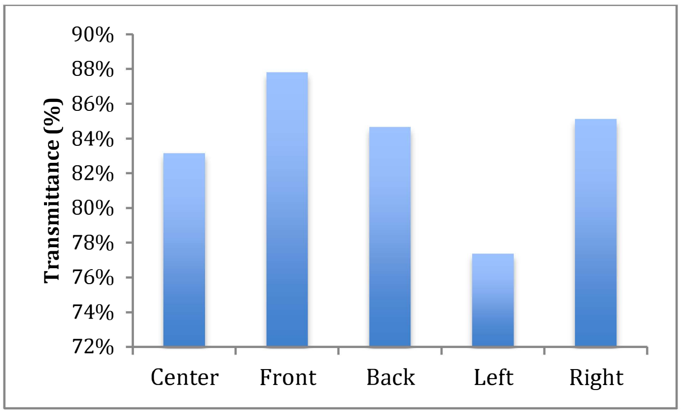


Fig. 7. Average transmittance values from wavelengths 390 nm to 1100 nm.

D. Framework for Spatial Behavior

All of the characteristics discussed above can be attributed to the position of the substrate on the susceptor in MOCVD reactor. The standard deviation of the measured values at different point on the substrate are summarized in Table 1. The standard deviation of the values across the substrate are not substantial, but are enough to warrant scrutiny of a certain behaviors along the axes. The substrate is not positioned in the center of the susceptor, but rather positioned to the side of the susceptor so the substrate does not turn on its own axis (Fig. 2(b)). Due to this positioning, some areas of the substrate receive uneven coating of reactive gases in the chamber. For example, looking at the front-back, or y-, axis, we observe a decreased thickness in the front because it is farther removed from the source of the gas which is primarily received in the center of the susceptor, also, explaining its abnormally high transmittance.

Table 1. The average of all PL-FWHM, transmittances, and thicknesses over the five measured points on the substrates

	Average	Standard Deviation
PL-FWHM (nm)	15.40	1.797
Transmittance (%)	83.61	3.878
Thickness (nm)	483.4	36.62

As shown in Fig. 8, upon entry into the chamber, the gas follows a path radiating outward, with inflection opposing the direction of susceptor motion. However, the gas reaches the outside region of the susceptor and follows the direction of motion. On the outside rim of the susceptor, the susceptor's need for traction overtakes the motion of the direction of gas. In other words, the clockwise motion of the susceptor induces opposing counterclockwise motion of the surrounding atmosphere. Thus, the gas seems to follow a hook-like path along the outside region of the susceptor.

Adsorption of adatoms occurs upon contact between the gas and the substrate. This can explain the y-axis gradient (along the front and back). Thus, as the back is proximally positioned to the center of the susceptor it receives the brunt of reactant gas. Therefore, the same stress argument can be used to explain the high-to-low FWHM y-axis gradient. The back is pressured by a large influx of reactant gas whereas the front can undergo more steady and ordered growth. On the x-axis, the left-to-right increase in transmittance is again directly tied to the hooking motion of the gas on the outside rim. The efflux of reactants is towards the left end of the substrate, which in turn produces a stress gradient towards the left, causing lower transmittance due to haphazard stress-induced growth [14].

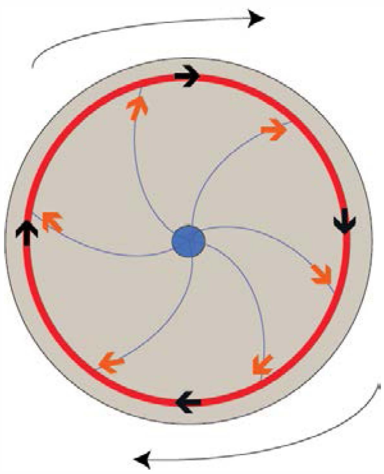


Fig. 8. Paths followed by the reactant gases above the susceptor.

IV. Conclusion

In this paper, we experimentally studied the spatial consistency of ZnO thin film deposition by MOCVD on a sapphire substrate with oxygen and diethylzinc precursors at an average thickness of about 500 nm. Measurements were made on various points on the film to compare transmittance, photoluminescence, thickness, and roughness. The samples were grown at a range of temperatures to make sure that growth temperature does not play significant role in large-scale spatial consistency of the film. We explained the gradients through the asymmetric stress applied by reactant gas in the chamber as well as the fact that the substrate does not spin on its own axis but on that of the susceptor. The inconsistency can potentially be reduced by using substrate grooves in the center of the susceptor. Further work is in progress to evaluate electrical, structural and morphological uniformity on the films [6,15].

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