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ZnO layers deposited by Atomic Layer Deposition

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Abstract. The structure of 40 nm thick epitaxial ZnO layers grown on single crystalline sapphire and GaN substrates by atomic layer deposition has been studied using transmission electron microscopy. The growth is carried out between 150°C and 300°C without any buffer layer using di-ethyl zinc and water precursors. The ZnO layer on sapphire is found to be polycrystalline, which is probably due to the large misfit (~15 %) and the relatively low deposition temperature. However, the small misfit (~1.8 %) between the ZnO layer that is deposited on GaN at 300°C resulted in a high quality single crystalline layer.

1. Introduction

ZnO is a wide band gap (~3.37 eV at room temperature) semiconductor and one of the transparent conductive oxides (TCO) that has recently gained interest for solar cells as a replacement of indium tin oxide partly for safety, partly for low cost reasons. For this kind of applications, the polycrystalline ZnO thin film is usually sputter deposited, but other deposition methods such as metalorganic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE) and atomic layer deposition (ALD) are applied when ZnO is to be used as a semiconducting layer. The principle of the ALD process is that the precursors are introduced into the reaction chamber as time-separated pulses; therefore their reactions can take place only at the gas-solid interface, and never in the gas phase [1]. Consequently the growth can be controlled on an atomic level, and the grown layers are extremely conformal and uniform. The ALD growth, however, is time consuming since several cycles are needed to deposit a complete monolayer. However, due to this growth mechanism a well-controlled epitaxial growth is possible although ALD is used most commonly for the deposition of oxides, nitrides, and other polycrystalline composite layers.

ALD ZnO layers are usually deposited on Si and glass substrates, in which case the grown layers are polycrystalline. There are a few reports published on ALD deposited epitaxial ZnO layers [2-4] on GaN, or Al₂O₃ (sapphire). (In such a case the method is also called atomic layer epitaxy).

2. Experimental

In this work ZnO films are deposited using ALD on sapphire and GaN substrates in a Picosun Sunale R-100 type ALD reactor. Di-ethyl zinc (DEZ) and water were used as precursors for growth of ZnO.



The deposition was carried out in the temperature range of 150 - 300°C. 500 ALD cycles were done, which gave a layer with thickness of about 40 nm. The deposited layers were studied using conventional and aberration-corrected transmission electron microscopy (TEM). High-resolution TEM images were taken in a JEOL 3010 microscope at 300 kV, while the aberration-corrected TEM images were recorded in a FEI Titan microscope operated at 300 kV. The aberration functions were corrected up to fourth order. The spherical aberration function (Cs) was set up to be negative ($\sim -15 \mu\text{m}$) in order to enhance the contrast of the images. The TEM specimens were prepared using conventional methods, namely mechanical polishing and Ar ion milling. The specimen preparation process was finished using low-energy ($< 1 \text{ keV}$) Ar ion milling in order to reduce the surface damage.

3. Results

3.1 ZnO on sapphire

Figure 1 shows a cross section of a ZnO layer grown on sapphire at 300°C. The image shows ZnO columns with different orientations. X-ray diffraction results also showed a very small (10 $\bar{1}$ 1) ZnO peak beside the strong (0002) peak [5].

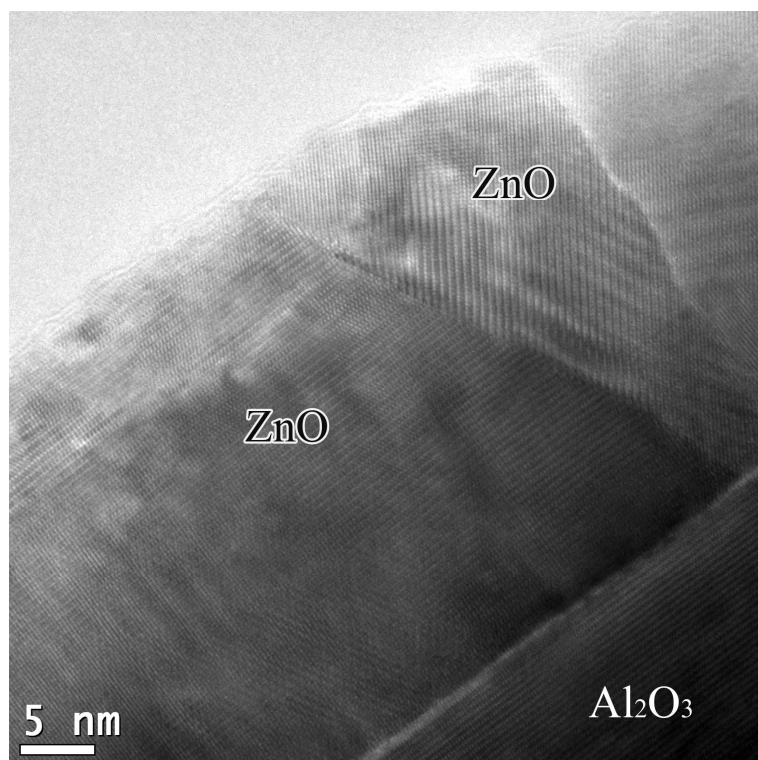


Figure 1. High-resolution cross-sectional TEM image of ZnO/sapphire. One can see crystalline grains in ZnO with different orientations.

The same sample was investigated in plan-view as well. Figures 2 and 3 show the bright field (BF) TEM and the dark field (DF) TEM images, respectively. The morphology, the contrast and the moiré fringes all confirmed a polycrystalline ZnO layer formation. The grain size values are measured in the 10-50 nm range. The selected area diffraction (SAED) pattern is shown in Figure 4 and one can see immediately that some of the grains are oriented with respect to the single crystalline substrate, while other grains give diffraction rings due to their random orientation. Reflections of the Al₂O₃ substrate are marked with dots and indexed with hexagonal indexes. The ZnO diffraction rings are indexed with italic style. One should note that the ZnO is highly textured. The intensity along the 10 $\bar{1}$ 0 ring has 6 maxima close to Al₂O₃ reflections indicating that most of the ZnO is nearly in epitaxial orientation (ϵ s (11 $\bar{2}$ 0) Al₂O₃ \parallel (10 $\bar{1}$ 0) ZnO AND (0001) Al₂O₃ \parallel (0001) ZnO). Double diffraction can also be seen forming a hexagon around the Al₂O₃ reflections.

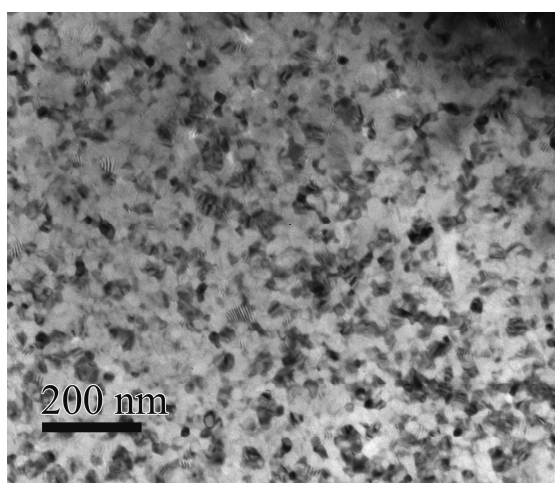


Figure 2. BF TEM image taken on a plan view ZnO/sapphire sample.



Figure 3. DF TEM image of ZnO grains.

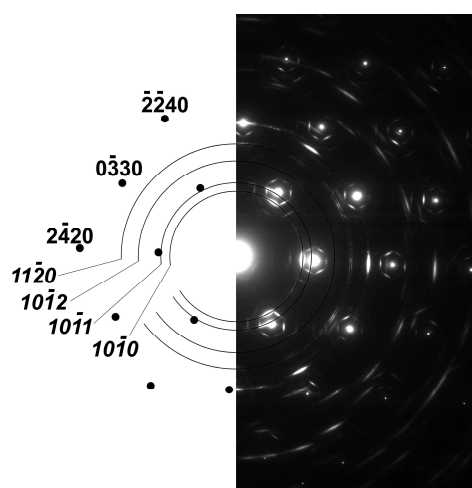


Figure 4. Indexed SAED pattern taken on a plan view ZnO/ Al_2O_3 sample grown at 300°C. Al_2O_3 reflections are marked with dots and indexed with hexagonal indexes. The ZnO diffraction rings are indexed with italic style.

3.2 ZnO on GaN

ZnO is deposited onto GaN as well and the structural properties have been investigated using cross-sectional TEM. X-ray diffraction results showed a dominant (0002) peak of ZnO, and a (10 $\bar{1}$ 1) also appears in the layer that was deposited at low temperature [5]. However, the (10 $\bar{1}$ 1) peak is not observed in the case of the ZnO layer deposited at 300°C. X-ray results [5] indicate a single crystalline ZnO layer, epitaxial to the GaN substrate. Indeed, the high resolution TEM image in Fig. 5 confirmed the epitaxial growth of ZnO on GaN. The inset is a Fast Fourier transformation (FFT) of the experimental image that shows one set of single crystalline diffraction pattern, as they are not separated due to the very low (1.8%) misfit. Figure 6 shows a plan-view BF TEM image of the same sample showing a network of moiré fringes. The moiré fringe periodicity is ~ 15.5 nm, which agrees well with the calculated value, when we consider the overlapping of (10 $\bar{1}$ 0) lattices in ZnO and GaN. However, taking SAED patterns in different regions (of about 5 μm area) sometimes we observed extra spots in them, which we could identify definitely as (10 $\bar{1}$ 1) reflections. Therefore we concluded that ZnO grains with different orientations can be traced in some regions despite X-ray diffraction measurements that suggested a completely single crystalline nature of ZnO.

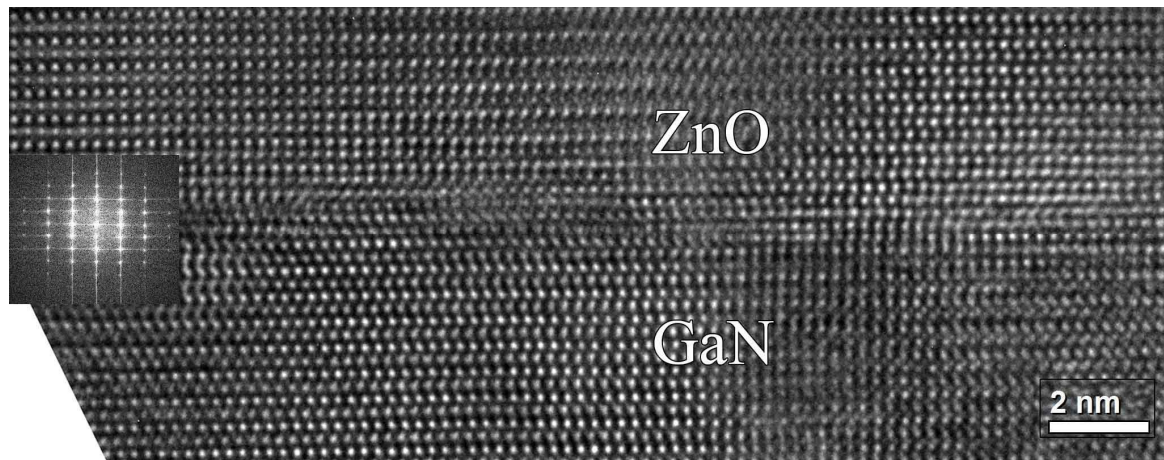


Figure 5. High resolution TEM image showing the ZnO/GaN interface. The inset is an FFT pattern recorded from the interface region.

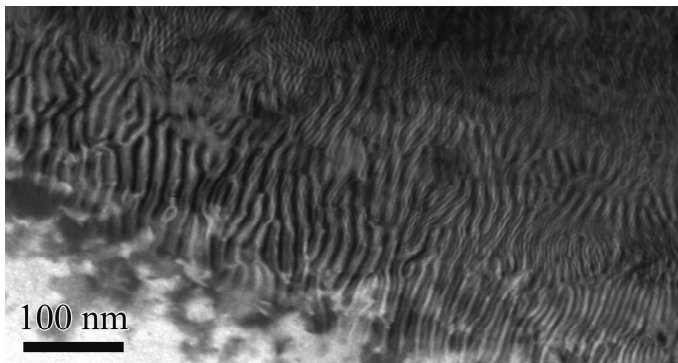


Figure 6. Plan view TEM image of ZnO/GaN showing a moiré pattern.

4. Conclusions

The ZnO layer on sapphire was found to be polycrystalline, which is explained by the large misfit and by the relatively low deposition temperature. ZnO deposited on GaN is single crystalline due to the low misfit. However, occasionally ZnO domains with different orientations were traced by selected area diffraction images, showing again that SAED is more sensitive for detecting small grains than X-ray analysis.

Acknowledgments

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References

- [1] Leskela M, and Ritala M 2002 *Thin Solid Films* **409** 138
- [2] Chen HC, Chen MJ, Liu TC, Yang JR and Shiojiri M 2010 *Thin Solid Films* **519** 536
- [3] Wachnicki L, Krajewski T, Luka G, Witkowski B, Kowalski B, Kopalko K, Domagala JZ, Guziewicz M, Godlewski M and Guziewicz E 2010 *Thin Solid Films* **518** 4556
- [4] Ku CS, Huang JM, Lin CM and Lee HY 2010 *Thin Solid Films* **518** 1373
- [5] Baji Zs, Lábadi Z, Horváth ZsE, Molnár Gy, Volk J, Bársony I and Barna PB 2012 *Cryst. Growth Des.* **12** 5615