Thin Films and Coatings

MS.5.P144
Polycrystalline to single crystalline, ALD deposited ZnO layers

B. Pecz[1], Z. Baji[1], Z. Lábadi[1], A. Kovács[2]

[1]Institute for Technical Physics and Matl. Sci., Research Centre for Natural Sciences, Hungarian Academy of Sciences, 1121 Budapest, Konkoly-Thege u. 29-33, Hungary, Budapest, Hungary
[2]Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons and Peter Grünberg Institute, Forschungszentrum Jülich, D-52425, Germany , Jülich, Germany

pecz.bela@ttk.mta.hu
Keywords: ZnO, atomic layer deposition, transmission electron microscopy

ZnO is a wide bandgap (~3.37 eV at room temperature) semiconductor and one of the transparent conductive oxides (TCO) that has recently gained interest in solar cells as a replacement of indium tin oxide. For these 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 vacuum chamber as separate pulses; therefore they only react with one another on the surface of the substrate, never in gas phase [1]. Consequently the growth can be controlled on an atomic level, and the grown layers are extremely conform and uniform. Due to this growth mechanism an epitaxial growth is quite straightforward although ALD is used most commonly for the deposition of oxides, nitrides, and other composite layers. ALD ZnO layers are usually deposited on Si and glass substrates, in which case the grown layers are polycrystalline. The crystalline structure and orientation of ALD ZnO depends on the deposition temperature and the substrate. The preferential orientation is typically (100) at lower deposition temperatures, and (002) above 220°C [2]. So far there have only been a few reports published on ALD deposited epitaxial ZnO layers [3-5] on GaN, or Al_2O_3 (sapphire). (In such a case the method is also called atomic layer epitaxy). In this work ZnO films are deposited using ALD on Si, 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 at 300°C and the nominal thickness of the layers was 40 nm. The grown layers are 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 (~ -15 µm) in order to enhance the contrast of the images. The TEM specimens were prepared using conventional method, namely mechanical polishing and Ar ion milling. The specimen preparation process was finished using low-energy (< 1 keV) Ar ion milling in order to reduce the surface damage. Figure 1 is a cross-sectional bright-field (BF) TEM image that shows a ZnO layer grown on (111) Si. The amorphous layer on the Si surface is a native oxide. The growth of ZnO on amorphous SiOx is very similar to the case that the ZnO film is deposited on glass substrate. One can see that grains of ZnO are nucleated with different orientation and the long columns are grown toward the surface. As the method utilises water as oxygen precursor it is very difficult (if not impossible) to get silicon/ZnO interface without an amorphous oxide strip at the interface. Figure 2 is a BF TEM image of ZnO film deposited on single crystalline sapphire. Interestingly the ZnO is polycrystalline again despite the fact that it was grown on single crystalline substrate. The random growth of ZnO grains can be explained this case by the large misfit (15 %) between ZnO and sapphire.Figure 3 is a BF TEM image of an ALD deposited ZnO layer on GaN, which is single crystalline proved by selected area diffraction pattern (not shown here). The Fourier image of this high resolution image also shows a single crystalline like diffraction pattern in which someone cannot distinguish the reflections of GaN and ZnO due to the very small (1.8%) misfit. This study shows, that ALD can provide ZnO layers which are always crystalline, but the epitaxial properties strongly depend on the substrate crystal.

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6. This work has been supported by the Hungarian National Scientific Research Fund (OTKA) under Grant No. K75735

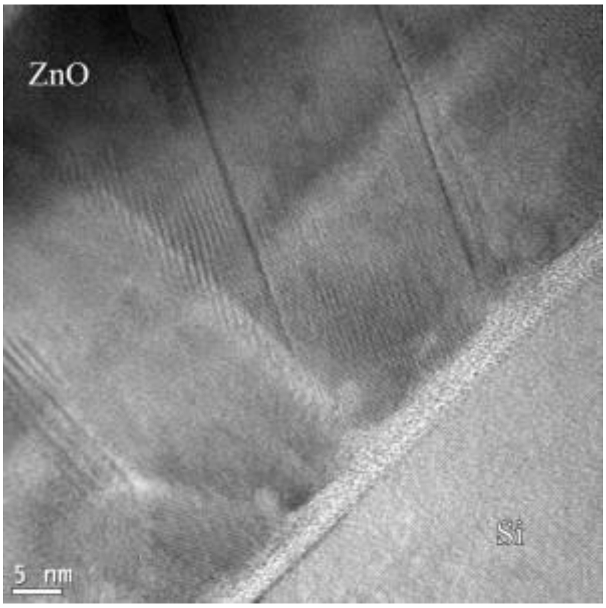

Figure 1. BF TEM image of ZnO deposited on (111) Si.

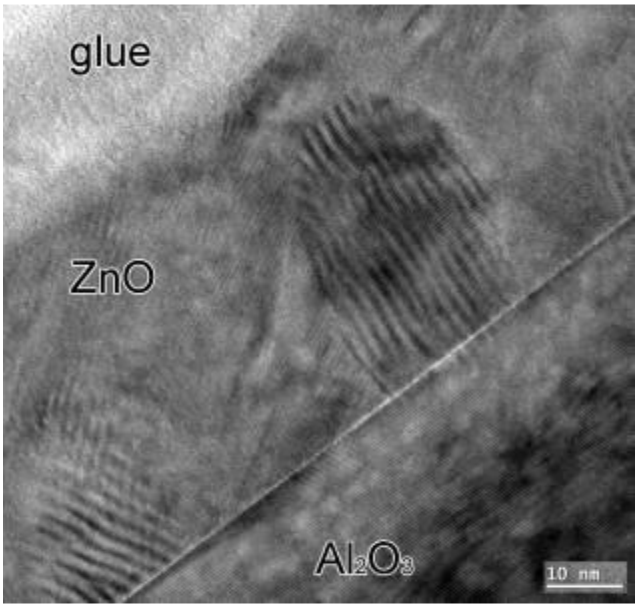

Figure 2. BF TEM image of ZnO deposited on (0001) Al_2O_3

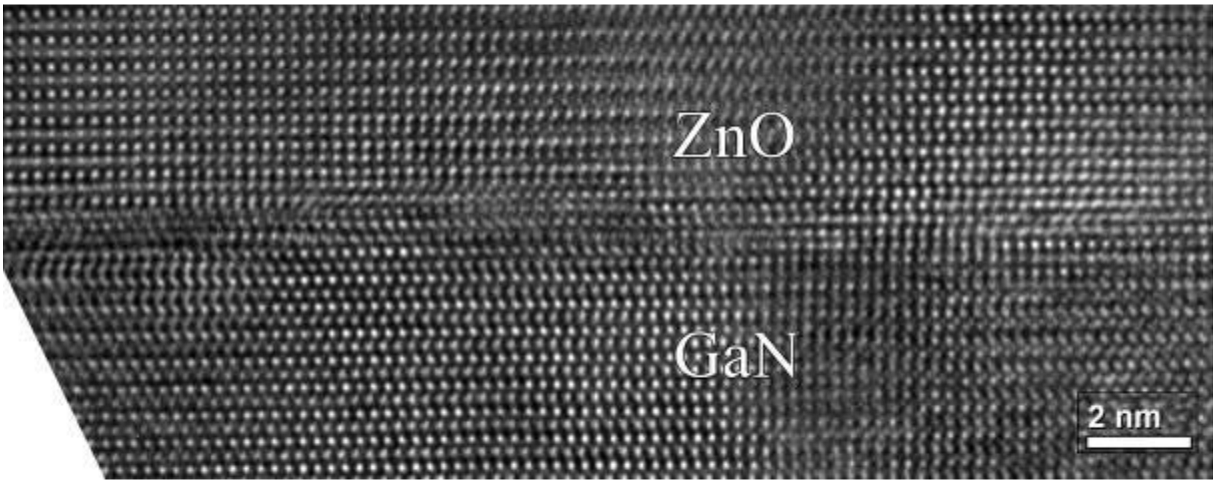

Figure 3. Aberration-corrected high-resolution TEM image showing an ALD grown ZnO on GaN.