Microstructures of ZnO Films Deposited on (0001) and r-cut α-Al_2O_3 Using Metal Organic Chemical Vapor Deposition

CM Wang[a], LV Saraf[a], and Y Qiang[b]

(a) EMSL, Richland, Washington
(b) University of Idaho, Moscow, Idaho

ZnO is a wide-bandgap semiconductor material with wide application in the field of optoelectronics, spintronics, piezoelectric transducers, and ultraviolet optoelectronics (Fan and Liu 2005). Considerable research effort has been made for modifying the properties of the ZnO through tailoring of the structure of the material, typically such as doping, grown ZnO into different dimensional structures (dots, thin film, and bulk materials). One of most useful forms of ZnO is the thin film. The key challenge for growing ZnO into a thin film is the control of defect structure in the film, because defects influence the optical and electrical properties of the film. Selection of the substrate and the control of the defect across the interface between the substrate and the film play an important role on the quality of the grown film. This research addresses the defect structure of the ZnO thin film grown on a sapphire substrate.

ZnO grown on (0001) sapphire will generally be oriented such that α-Al_2O_3 (0001)//ZnO(0001). Variable in-plane orientation may lead to two domains such that: α -Al_2O_3 [11-20]//ZnO[11-20] and α -Al_2O_3 [11-20]//ZnO[10-10]. The first mode corresponds to the hexagon-on-hexagon growth and the second mode corresponds to a 30-degree in-plane rotation of the ZnO relative to the α -Al_2O_3. Since it is difficult to obtain an ideal sapphire surface with a well-defined surface structure, various rotation domains, such as the 30-degree rotation domains and a recently reported 21.8-degree rotation domain, may coexist. A previous study shows that by using gallium pre-deposition to modify the sapphire (0001) surface, rotated domains can be completely eliminated. Another growth parameter that could be controlled is the selection of the orientation of the substrate. It has been generally realized that ZnO grown on r-cut sapphire possesses a high quality. However, there is no direct comparison of the film quality grown on both r-cut and c-plane oriented sapphire under an identical growth condition.

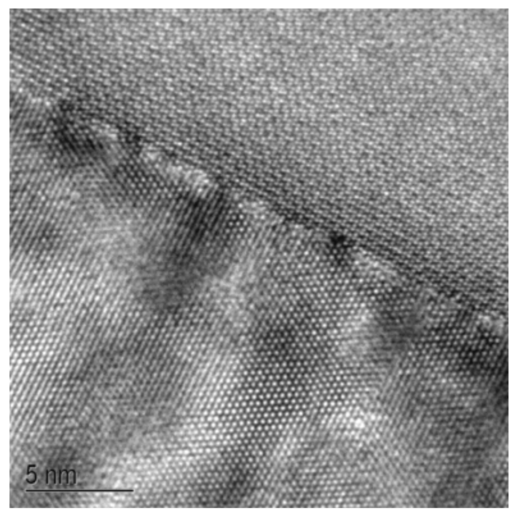

Figure 1. *High-resolution transmission electron microscopy image showing the interface between α -Al_2O_3 and ZnO with the film grown on r-cut α -Al_2O_3.*

In this paper, we report a comparison of the structural features of ZnO thin films grown on both r-cut and c-plane sapphire using metal organic chemical vapor deposition (MOCVD) under identical growth conditions (Wang et al. 2008). It has been found that the film grown on r-cut sapphire shows high-quality single crystals. Film grown on the c-plane shows a range of domains, one that corresponds to the classic growth mode. At the same time, a new growth mode was observed following the deposition of

ZnO thin film on α -Al_2O_3 (0001). In this new growth mode, α -Al_2O_3 [11-20]//ZnO[10-10], but the (0001) plane of ZnO is tilted relative to the (0001) plane of α -Al_2O_3 such that ZnO(0001) is almost parallel to the α -Al_2O_3 (-1104) plane.

Growth of the film was performed using a three-source EMCORE MOCVD reactor. The precursor preparation was done by dissolving $Zn(C_{11}H_{19}O_2)_2$-Bis(2,2,6,6-tetramethyl-3,5-heptanedionato) zinc powder in tetrahydrofuran at a concentration of 0.025 M. During the depositions, the substrates were rotated at 500 rpm and the substrate temperature was varied between 450 ºC to 600 ºC. The carrier gas pressure during the growth was kept at 0.28 MPa with a zinc precursor flow rate of 100 g/hr. The operating pressure was kept at 10 Torr with mixed gases of oxygen and argon flows of 500 sccm and 2000 sccm, respectively. Single crystals of α -Al_2O_3 (0001) and r-cut α -Al_2O_3 were used as substrates.

The film grown on r-cut α -Al_2O_3 possesses a single orientation with respect to the substrate. The interface shows some contrast features that are related to the mismatch dislocations. This feature is further revealed by the high-resolution transmission electron microscopy image illustrated in Figure 1. The interface was featured by very high density of misfit dislocations. The dislocation is not evenly distanced along the interface. Rather, it appears that the dislocation is coupled, leading to a pattern of two dislocations forming a pair. The physical reason for this must be studied. Across the interface, on average, every sixth of α -Al_2O_3 (-12-10) plane terminates at the interface. This result is consistent with that when the film grown on the α -Al_2O_3 (0001) plane. However, the dislocation appears to be uniformly distributed when grown on the (0001) direction. Using the α -Al_2O_3 (-12-10) lattice plane space of 2.3794 Å as an internal standard, the ZnO (01-10) lattice plane space was determined to be 2.773 Å. This will lead to a lattice constant for ZnO to be 3.202 Å, which is slightly smaller than the literature data of 3.249 Å.

ZnO films grown by MOCVD on α -Al_2O_3 (0001) using the Zn $(TMHD)_2$ precursor show granular structures and the grains possess different orientations. Based on electron diffraction and high-resolution transmission electron microscopy imaging, at least two distinct orientations have been identified. One corresponds to the classic 30-degree in-plane rotational domain. The other also includes the 30-degree rotational domain, but, instead of the ZnO (0001) plane being parallel to the (0001) plane of α -Al_2O_3, the (0001) plane of ZnO is tilted ~ 38-degrees in such a way that the (0001) plane of ZnO is approximately parallel with the (-1104) plane of α -Al_2O_3. This tilting of the (0001) plane results in a reduction of interface lattice mismatch from ~18 percent to ~ 2 percent in one direction. Therefore, the tilted growth mode was driven by minimization of interfacial energy. The film grown on r-cut α -Al_2O_3 showed a single crystalline structure and the interface was featured by a high density of mismatch dislocations.

Citations

Fan Z, and JG Lu. 2005. "Zinc Oxide Nanostructures: Synthesis and Properties." *Journal of Nanoscience and Nanotechnology* 5(12):1561-1573.

Wang CM, LV Saraf, TL Hubler, and P Nachimuthu. 2008. "Tilted Domain Growth of Metalorganic Chemical Vapor (MOCVD)-Grown ZnO(0001) on α-Al_2O_3(0001)." *Journal of MaterialsResearch* 23(1):13-17.