Orientations of Polycrystalline ZnO at the Buried Interface of Oxide Thin Film Transistors (TFTs): A Grazing Incidence X-ray Diffraction Study

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Characterization of crystal structures and their orientations at the interfacial region has been of great interest for many researchers both in fundamental sciences and various application areas. Due to the importance of understanding the potential impacts of key parameters (*e.g.*, crystallinity, crystal orientation, grain size, defect density and morphology) controlling performance of devices involving thin-layered films (*e.g.*, thin film transistors, solar cells and display devices), various analytical techniques, such as high-resolution transmission electron microscopy (HR-TEM), secondary ion mass spectrometry (SIMS) and grazing-incidence x-ray analysis (GIXA) methods, have been applied for the characterization of thin films and their interfaces. Among these tools, due to the benefits of GIXA methods, such as sensitivity for near surface or buried interface regions and nondestructive nature of x-rays, GIXA studies has been extensively performed for the study of interfacial regions of various layered materials, especially on organic thin film transistors.[1-3]

In this study, ZnO thin films grown by plasma enhanced Atomic Layer Deposition (ALD) methods on a Al_2O_3/Si substrate were investigated using synchrotron-based grazing incidence x-ray diffraction (GI-XRD) technique combined with x-ray reflectivity (XRR) measurements (see supporting information for detailed experimental setup and XRR analysis results). Our study particularly focused on the distribution ZnO crystal orientations at the interfacial region with Al_2O_3 layer to understand its structure-property relationship with the observed characteristics of TFT device (*e.g.*, charge-carrier mobility).

In Figure 1(a), cross sectioned diagram of typical bottom-gate type oxide Thin Film Transister(TFT) is presented, in which ZnO is frequently used as an active layer deposited over insulator substrate (Al_2O_3). However, as shown in the TEM image of the cross sectioned ZnO/Al_2O_3/Si sample (see Figure 1(b)), the crystallinity, crystal orientation and grain size observed at the interfacial region of ZnO with Al_2O_3 substrate seems different from that of bulk ZnO film region. For instance, the interfacial region seems to have smaller grain size, more randomly oriented crystals, while ZnO grains far from the interfacial region have larger and columnar grains with growth direction perpendicular from the surface, although it is not easy to confirm these observed

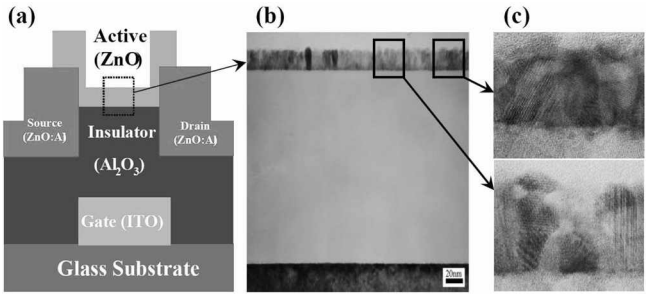

Figure 1. (a) Cross sectioned view of typical bottom-gate type oxide Thin Film Transistor, (b) TEM image of cross-sectioned ZnO/Al_2O_3/Si sample grown by ALD method and (c) zoomed TEM images of rectangled areas in (b).

trends from TEM images only (see Figure 1(c)). Recently, Park *et al.*[4] have reported fabrication of transparent AM-OLED panel driven by ALD grown ZnO-TFT and suggested that the key characteristics of TFT device (*e.g.*, charge-carrier mobility) are closely associated with the physical properties (*e.g.*, grain size, crystallinity, crystal orientation, defect concentration and morphology) of ZnO interfacial region with the gate insulator. Therefore, for the understanding of device characteristics and improving performances of oxide TFTs, characterization of the physicochemical properties of the interfacial region, rather than those of the whole ZnO film, could be more critical.[5]

GI-XRD data collected for two PEALD grown ZnO thin films with different thickness are presented in Figure 2. These data were further deconvoluted into three gaussian type peak components representing ZnO (100), (002) and (101) and presented in Table 1. As shown in Figure 2(a) and 2(b), for the relatively thick sample (P100, 17.1 nm), small but significant differences were observed in the relative intensities of ZnO (100), (002) and (101) peaks. Peak deconvolution results in Table 1 clearly showed that, when the incidence angle is changed from lower angle (θ_i = 0.2) to higher angle (θ_i = 1.0), significant increase in the contribution of (002) phase (22.5% → 33.0%) and decrease in the contribution of (100) (45.5% → 37.7%)were observed, while contribution from (101) phase stayed almost same (31.9% → 29.4%). Measured and fitted data for P75 sample (see Table 1) also show similar trends, although the differ-

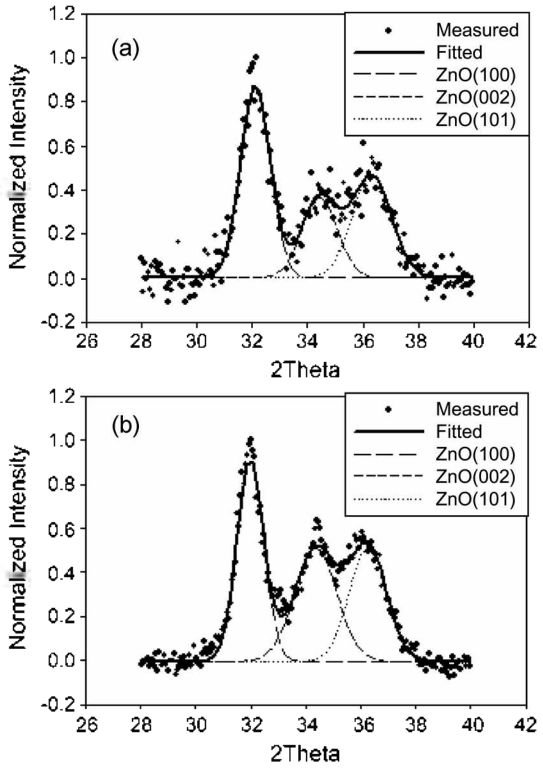

Figure 2. Measured and Fitted GI-XRD data for (a) P100 above critical angle (b) P100 below critical angle.

ences are less significant (35.5% → 39.0 % for (002) phase; 33.9% → 31.1% for (100) phase; 30.6% → 29.9% for (101) phase). The followings can be inferred from above observations: Under given growth condition (*i.e.*, plasma enhance ALD at 100 °C), ZnO grows in polycrystaline form with preference in (002) direction near the ZnO/Al_2O_3 interface and (100) direction in the bulk ZnO film region, while ZnO (101) phase have no significant preference for the interfacial or film regions. In addition, considering the significant differences between the two incidence angles of P100 and P75 sample, we roughly estimate the thickness of the interfacial region as ~10 nm, which agree with the TEM image shown in Figure 1(b). Above observations on preferred growth of ZnO in (002) direction at the ZnO/Al_2O_3 interfacial region was further confirmed by the comparison between P75 and P100 XRD data measured above the critical angle (Figure 2(b)) Thinner ZnO film (P75, 13.6 nm), which should have more contribution from the interfacial ZnO grains, shows higher contribution from the (002) phase (39.0% compared to 33.0% for P100 sample), while thicker ZnO film (P100, 17.1 nm) show enhanced contribution from the (100) phase (37.7% compared to 31.1% of P75 sample). The observation of preferential growth of ZnO in (002) direction at the interfacial region is quite interesting, since it has been known that (100) phase is preferred in the case of bulk ZnO films at lower temperature and (002) phase is only preferred above 150 °C. From our observations, it is inferred that the crystal orientation of the interfacial grain is less

Table 1. GI-XRD peak deconvolution results for $ZnO/Al_2O_3/Si$ samples

Sample	degree	100(%)	002(%)	101(%)
P100	$\theta_i < \theta_c$	45.5	22.5	31.9
	$\theta_i > \theta_c$	37.7	33.0	29.4
P75	$\theta_i < \theta_c$	33.9	35.5	30.6
	$\theta_i > \theta_c$	31.1	39.0	29.9

dependent on the growth temperature and rather controlled by the other parameters (*e.g.*, surface properties of the substrate).

In this GIXA study on ZnO thin films, we have shown that the ZnO crystal orientations at the interfacial region can be quite different from those of bulk ZnO films, which was previously observed in various organic TFTs involving pentacene.[3] Similar to the case of organic TFTs, this observation will also have significant impacts on future studies to improve device performances of oxide TFTs, since the charge-carrier mobility in the channel between the source and drain is thought to be closely related with the physicochemical properties of the interfacial region and the crystal orientations and grain sizes near the interfaces are considered as key parameters controlling device characteristics. Although simple prediction model for the structure-property relationship in the oxide TFT device is not currently available yet, considering capabilities of GIXA methods demonstrated in many other applications (*e.g.*, conjugated polymer TFTs[1-3]), further GIXA studies being performed in our group based on this study will help us for better understanding of device characteristics and improving performances of oxide TFTs.

Supporting Information. Detailed description of experimental and data analysis procedures are available online.

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