Impurity distribution and microstructure of Ga-doped ZnO films grown by molecular beam epitaxy

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We report microstructural characterization of heavily Ga-doped ZnO (GZO) thin films on GaN and sapphire by aberration-corrected scanning transmission electron microscopy. Growth under oxygen-rich and metal-rich growth conditions leads to changes in the GZO polarity and different extended defects. For GZO layers on sapphire, the primary extended defects are voids, inversion domain boundaries, and low-angle grain boundaries. Ga doping of ZnO grown under metal-rich conditions causes a switch from pure oxygen polarity to mixed oxygen and zinc polarity in small domains. Electron energy loss spectroscopy and *energy dispersive spectroscopy* spectrum imaging show that Ga is homogeneous, but other residual impurities tend to accumulate at the GZO surface and at extended defects. GZO grown on GaN on c-plane sapphire has Zn polarity and no voids. There are misfit dislocations at the interfaces between GZO and an undoped ZnO buffer layer and at the buffer/GaN interface. Low-angle grain boundaries are the only threading microstructural defects. The potential effects of different extended defects and impurity distributions on free carrier scattering are discussed. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4769801>]

INTRODUCTION

Ga and Al doped ZnO (GZO and AZO) films are alternative materials to indium tin oxide (ITO) for high-performance n-type transparent conducting oxide (TCO) applications in solar cells, flat screen displays, and light-emitting devices.^{1–5} Low cost AZO is suitable for large-area applications such as displays and solar cells, while GZO is finding applications in solid-state optoelectronics due to higher performance. GZO has very low stress-strain constraints on doping compared to AZO and ITO, because the Ga-O bond length, 1.88 Å, is very close to the Zn-O bond length, 1.97 Å,⁶ resulting in potentially higher mobility and carrier concentration. GZO and GaN both have wurtzite (WZ) crystal structure, with close in-plane lattice parameters (1.8% lattice mismatch).⁷ As we show below, unlike Al, Ga does not have a tendency to segregate to surfaces, interfaces, and extended defects. This could be crucial for applications requiring fine control over the impurity distribution including small structures where the effect of surface layers could drastically affect performance.

We have investigated the effects of Ga doping on extended defect formation in high quality structures grown under well-controlled conditions by plasma assisted molecular beam epitaxy (MBE). Although this method has limited throughput, it is well suited to grow model structures under well-controlled conditions in order to reveal the detailed, and in our case unusual, extended defects in GZO.

The growth mechanism and adatom surface diffusion for many ionic wurtzite materials depend on the surface polarity.^{8,9} The different bond energy of atoms on surfaces of different polarity results in differences in surface hardness and chemistry, which strongly affect epitaxial growth. For example, sublimation of Zn from the Zn-terminated basal

surface of ZnO begins at 380 °C, while sublimation of Zn on the O-surface takes place at only 600 °C.¹⁰ The differences of the two polar surfaces are also revealed in experiments of electron irradiation damage.¹¹ The threshold energy required to displace Zn atoms on the surface layer of the Zn-face surface is 0.5 MeV lower than that on the O-face surface. Many aspects of the effect of surface polarity on the growth and microstructure of ZnO on the two most commonly used substrates, GaN and sapphire, have been thoroughly studied elsewhere.^{9,12} However, as we demonstrate, Ga doping of ZnO leads to noticeably different crystal structure with some unusual consequences.

Several scattering mechanisms compete in AZO and GZO at e^- concentrations of 10^{19} – 10^{21} cm⁻³, so the mobility often depends on the crystal quality.¹³ In general, extended defects, ionized impurities, and native defects can be responsible for electron scattering. Microstructural characterization of extended defects in GZO, XRD data, and electrical measurements enable us to elucidate the role of various extended defects in carrier scattering in our films. In the same samples studied here, we previously found that the electrical properties of GZO layers are strongly dependent on growth mode, which varies with metal-rich and oxygen-rich conditions.¹³ Structures grown under Zn-rich conditions had excellent properties, including low resistivity ($<3 \times 10^{-4}$ Ω cm), high carrier concentrations (up to 1.5×10^{21} cm⁻³), high mobility (from 20 to 80 cm²/V s, depending on the carrier concentration), uniform depth distribution of free carriers, and high optical transparency ($>95\%$ in the visible spectral region). Structures grown in oxygen-rich condition required thermal activation of the dopants and even then had relatively low carrier concentration and mobility compared to structures grown under Zn-rich conditions.¹⁴

EXPERIMENTAL DETAILS

A MBE system equipped with a RF oxygen plasma source and effusion cells for Zn and Ga was employed to grow GZO layers. The plasma power was 400 W and Zn cell temperature was 350 °C for all the layers. The substrate temperature T_{sub} of all samples characterized in this study was 400 °C, the Ga cell temperature T_{Ga} , which controls the Ga flux, was 600 °C. The effects of varying the substrate temperature^{14,15} and the Ga cell temperature¹⁶ on electrical and structural characteristics were published elsewhere. The flux of reactive oxygen was varied. It was controlled by passing O_2 through a mass-flow controller prior to the plasma source and measured by the corresponding pressure in the chamber, P_{O_2} , during growth. We used $P_{\text{O}_2} = 4.5 \times 10^{-6}$, 8.0×10^{-6} , and 1.5×10^{-5} Torr, which correspond to metal (Zn + Ga) rich, near stoichiometric (reactive oxygen to incorporated Zn ratio $\approx 1:1$), and oxygen-rich conditions, respectively.^{13,14} The reactive oxygen-to-incorporated Zn ratios were assessed from the growth rate vs. oxygen pressure dependence. Rapid thermal annealing at ~ 600 °C in nitrogen was used for the oxygen-rich and stoichiometry samples. GaN(0001) templates grown on c-plane sapphire by metal-organic chemical vapor deposition and a-plane sapphire wafers were used as substrates. The GZO layers were grown on nominally undoped ZnO seed layers.¹³

TEM samples were prepared by mechanical wedge polishing with diamond lapping films in the $[11\bar{2}0]$ cross-section projection and by dimpling. Both types of samples were ion milled in a Fischione 1010 low angle ion mill and then in a Fischione low energy Nanomill. Scanning transmission electron microscopy (STEM) experiments were performed on a FEI Titan microscope with a CEOS probe aberration-corrector operated at 200 keV. STEM images were collected with a 24.5 mrad probe semi-angle, 25 pA probe current, and STEM resolution of 0.8 Å. High angle annular dark field (HAADF) images, which suppress diffraction contrast in favor of atomic number (Z) contrast were acquired with a detector subtending 54 to 270 mrad. Annular bright field (ABF) STEM images, which are dominated by diffraction, were collected with a detector subtending 4.0 to 8.8 mrad, smaller than other ABF STEM images.¹⁷ STEM

electron energy loss spectroscopy (EELS) spectrum images (SIs) were acquired using a 24.5 mrad probe semi-angle, spectrometer collection angle of 82 mrad, 400 pA probe current, and STEM resolution of 2.1 Å. *Energy dispersive spectroscopy (EDS) measurements were done at probe current 800 pA.* Position averaged convergent beam electron diffraction (PACBED)¹⁷ was used to confirm the polarity of the GZO films.¹⁸ PACBED patterns are acquired while scanning the electron probe across a 2 nm $\times$ 2 nm image area. Conventional TEM measurements were done on Philips CM200UT and Titan microscopes, both operating at 200 keV.

Experiments have shown that our Titan microscope vacuum causes no measurable buildup of hydrocarbons on the sample even though the typical pressure near the sample is $\sim 7 \times 10^{-7}$ Torr.¹⁶ We are confident that carbon microanalysis reflects the state of the sample and not the accumulation of carbon due to the microscope vacuum.

RESULTS

TEM images (not shown) indicate that the main defects in the ZnO seed layer on sapphire are low-angle grain boundaries, mostly perpendicular to the ZnO/sapphire interface. Selected area diffraction (SAD) taken from both the substrate and ZnO seed layer indicates good epitaxial relationship between sapphire and ZnO: $(0001)_{\text{ZnO}} // (11\bar{2}0)_{\text{Sapphire}}$ and $[11\bar{2}0]_{\text{ZnO}} // [0001]_{\text{Sapphire}}$ in the plane. However, the ZnO grains were textured, with a misorientation range of 8°–10°.

GZO growth on a-plane sapphire under oxygen-rich conditions

Gallium doping of ZnO grown under oxygen-rich conditions leads to instability of WZ crystal structure. Figure 1 shows phase switching from WZ structure (bottom part of layer) to zinc blend (ZB, top part of layer). The image was taken in strong-beam condition in central dark-field mode ($\mathbf{g}, -3\mathbf{g}$) with the $[111]$ $\mathbf{g}$ vector of the ZB structure. Under these conditions, bright grains on Figure 1 have the ZB structure, and the WZ phase exhibits darker, fine-scale contrast. In many cases, there are additional reflections in the SAD patterns that correspond to a mirror symmetry about the

FIG. 1. Strong beam dark-field image with the $[111]$ $\mathbf{g}$ vector of the ZB structure. (a) SAD pattern of one grain in the ZB top layer. (b) SAD pattern from the bottom WZ part of the GZO layer and (c) a region with both WZ and ZB. Additional reflections in the mixed phase layer are caused by double diffraction and multiple twins in the ZB phase. The SAD patterns are taken at the $[0110]$ zone axis for WZ and the $[110]$ zone axis for ZB. The angle between the grain boundaries in the top and bottom layers corresponds to angle between $[0001]_{\text{WZ}}$ and $[2\bar{2}0]_{\text{ZB}}$.

FIG. 2. (a) HAADF STEM image of a GZO/undoped ZnO/sapphire structure grown under oxygen-rich conditions. The image was taken close to the $[1\bar{1}00]$ zone axis for GZO. (b) EDS spectra profiles for host elements and impurities in ZnO/Sapphire acquired in the box in (a).

(220) axis that related with twin boundaries and reflections related to multiple diffraction in $\{111\}$ directions. The growth direction changes from $[0001]$ in WZ ZnO to $[02\bar{2}]$ in ZB ZnO instead of keeping the same growth orientation of $[0001]_{\text{WZ}} \parallel [11\bar{1}]_{\text{ZB}}$. The grain boundaries in the ZB GZO are tilted by 24° from the direction perpendicular to the substrate surface. This direction coincides with $[2\bar{2}0]_{\text{ZB}}$, which means that the two possible fast growth directions, $[11\bar{1}]_{\text{ZB}}$ and $[1\bar{1}1]_{\text{ZB}}$, compete each other. That indicates a 3D growth mechanism for the ZB GZO.

Figure 2 shows a HAADF STEM image of a GZO/undoped ZnO/sapphire structure taken on the $[1\bar{1}00]$ zone axis of the GZO. On top of the GZO is another layer 15–20 nm thick. Figure 2(b) shows the composition of the layers from EDS spectrum profiling. The modified surface layer is aluminum oxide. TEM and STEM nanodiffraction (not shown) show that this layer is amorphous. Ga has an almost homogeneous depth distribution. The Al depth distribution suggests diffusion from substrate through the entire structure with a strong tendency to accumulate on the surface. The SIMS profiles in Figure 3 (measured by Evans Analytical Group) confirm the surface segregation of Al. Figure 3 shows that Al has a higher concentration in GZO layer grown in oxygen-rich conditions compare to Al concentration in the layer grown in metal-rich condition. If we consider sapphire substrate as major source for Al incorporation to GZO films, Al diffusion coefficient should be correspondingly higher in

FIG. 3. SIMS profiles for Zn (dashed lines) and Al (dotted lines) for GZO grown under metal-rich and oxygen-rich growth conditions.

GZO grown in oxygen-rich conditions. Al concentration profile reveals depletion depth coincided with the formation of mixed ZB/WZ structure on these GZO layers.

GZO growth on a-plane sapphire under Zn-rich conditions

Metal-rich growth conditions give rise to a GZO layer that is much closer to single-crystal material than the textured structure of GZO grown under oxygen-rich conditions. SAD (not shown) taken along $[01\bar{1}1]_{\text{Sapph}}/[01\bar{1}0]_{\text{ZnO}}$ for the whole structure shows very good epitaxial relationship between GZO and substrate. However, the films are porous, as shown in Figure 4. The voids in GZO grown under metal-rich conditions occur at very high density (up to $\sim 2 \times 10^{17} \text{ cm}^{-3}$) in various shapes. Pyramid-like voids and basal plane stacking faults or basal-plane inversion domain boundaries (IDBs) are the most common defects. However, we also observe other shapes of faceted voids in the GZO layer. The size of the pyramid-like voids ranges from 1 to 20 nm. Due to the extraordinarily high concentration of these defects, we often found overlapping chains of voids forming larger pores. Most of the voids have $\{0001\}$ base facets perpendicular to the growth direction. With respect to the growth direction, the pyramids are either point up or point down. Similar voids (point up or down) group together into nanoscale domains, examples of which are shown in Figure 4.

Figure 5 shows that nucleation of the pores starts at the seed layer/GZO interface, right when the Ga flux is turned on. There are no voids in the nominally undoped seed ZnO layer. At the interface between the seed ZnO and GZO layers, we found a set of point down pyramids. This is followed by ~ 20 nm thick intermediate layer that does not contain any voids. Finally, in the top GZO, a very complex void/pore structure is formed. Most of the voids are point up pyramids clustered together in large domains. The other areas contain mostly basal-plane defects and smaller, point down pyramid voids.

Figure 6 shows that the pyramid voids at the interface between the undoped ZnO layer and GZO are the origin of

FIG. 4. HAADF STEM images of two areas inside the porous, metal-rich conditions GZO. In (a), point up pyramid shaped voids prevail. In (b), point down pyramid shaped voids prevail. We propose that the two regions have different polarities.

IDBs. Most of these boundaries are terminated by pores within 25 nm of the seed layer. However, some of them propagate up to the surface of the GZO layer. IDBs inclined to the beam direction are dark lines indicated with arrows in Figure 5(b) and shown in Figure 6(a). The inversion domains form columnar structures. The basal-plane defects and the point up pyramidal voids occur within some columns and point down pyramidal voids are formed in other columns, so they occur in domains of opposite polarity.

We confirmed the change in polarity from one column to another using PACBED¹⁸ measurements and simulations, shown in Figure 7. Details of the PACBED pattern simulations for ZnO are given elsewhere.¹⁹ Both patterns come from the GZO layer. Figure 7(a) is O-polar GZO, and Figure 7(b) is Zn-polar GZO. Further, PACBED measurements (not shown) show that the ZnO seed layer on sapphire is O-polar, and ZnO grown on GaN is Zn-polar.

In addition to IDBs and voids, the metal-rich GZO films contain low angle grain boundaries. By decreasing the collection angles in HAADF STEM, we observed increased strain contrasts from grain boundaries, which are almost invisible in images taken at high collection angles, where they masking by strong pore contrast. Measurements by electron nanodiffraction in points on both sides of grain boundaries confirm conclusion about nature of these extended defects (these measurements are not shown here). The grain boundaries simply propagate through GZO film from the seed layer. The grain size varies from 30 to 90 nm.

Figure 8 shows an EELS SI of host elements and impurities around a void in GZO/sapphire grown under metal-rich conditions. The SI was de-noised using principle component

FIG. 5. (a) HAADF STEM image of GZO grown under metal-rich growth conditions on top of an undoped ZnO seed layer on sapphire. (b) ABF STEM image, taken from the rectangle in (a). A indicates the undoped seed ZnO layer, B indicates the layer where Ga doping starts and a line of pyramid voids is visible, and C indicates the layer of intensive formation of IDBs. Arrows indicate dark lines, which are IDBs inclined to the electron beam direction. These images were taken in $[2\bar{1}1]0$ zone axis for ZnO.

analysis, keeping 5 principle components. As expected, the concentration of host elements (Zn and O) inside the pores is at a minimum. Two common residual impurities, carbon and fluorine, accumulate inside the pores. Gallium does not segregate inside the pores. In general, we found that Ga does not accumulate at any detected extended defect, interface, or surface.

GZO grown under Zn-rich conditions on GaN substrate

Due to the excellent lattice match, ZnO layers on GaN have a much smaller concentration of extended defects than on sapphire. A GaN substrate is also not a source of Al

FIG. 6. High resolution STEM images of the interface between undoped ZnO seed layer and GZO grown under metal-rich conditions. (a) ABF STEM image. IDBs terminated by voids are clearly visible; (b) HAADF STEM image, in which IDB contrast is weak.

impurities. Figures 9(a) and 9(b) show HAADF STEM images of GZO grown on a GaN template under metal-rich conditions. There are no voids. Epitaxial GZO grown on an ~ 4 nm thick undoped ZnO buffer on GaN has atomically sharp interfaces. In Figure 9, there are two rows of defects near the ZnO/GaN interface, marked A and B in Figure 9(b).

FIG. 7. Experimental PACBED patterns taken in different domains in metal-rich conditions GZO (outside images) and simulated PACBED patterns (central images). (a) O surface polarity, (b) Zn surface polarity. Areas marked by arrows are matched with simulated $[11\bar{2}0]$ O-polar and Zn-polar ZnO models using the frozen-phonon multislice algorithm.

FIG. 8. EELS spectrum images showing the distribution of host elements and impurities around a void in GZO/sapphire grown under metal-rich conditions. The color maps show the integrated intensity of each edge after background subtraction, normalized to O K-edge.

“A” defects are exactly at the interface between GaN and the ZnO buffer layer, and their strain-induced contrast slightly extends into the GaN template. These defects are conventional misfit dislocations with Burgers vectors $1/3[1\bar{2}10]$, $1/3[2\bar{1}10]$, and $1/2[1\bar{1}00]$. Their density is high enough to compensate most of the interface strain at the growth temperature ($\sim 0.8\%$ at 350°C , accounting for the differences in thermal expansion). “B” defects are 3–4 nm away from the interface inside the ZnO seed layer and have relatively diffuse strain-induced contrast. They are misfit dislocations at the ZnO seed layer/GZO interface. Two rows of misfit dislocations located on the GZO/undoped ZnO and undoped ZnO/GaN interfaces indicate that the ZnO seed layer thickness is smaller than the critical thickness for strain relaxation. When the combined GZO and undoped ZnO seed layer thickness reaches the critical thickness during GZO growth, misfit dislocations are generated at both interfaces simultaneously. The residual stress due to differences of thermal expansion coefficient for ZnO(GZO) and GaN is compensated by threading extended defects inside the ZnO/GZO layer.

Low-angle grain boundaries are the prevailing large scale defects in these GZO structures, as shown in Figure 9(a). The grain size varies from 50 to 80 nm depending on the growth conditions. Because the dislocations are localized at the interfaces, the low-angle grain boundaries are the major extended defects responsible for free carrier scattering.

FIG. 9. HAADF STEM images of (a) the entire composite structure of GZO grown on GaN template; (b) two rows of defects near the interface between GaN and ZnO; (c) high resolution HAADF STEM image of both interfaces. There are misfit dislocations between GaN and ZnO seed layer and between the ZnO seed layer and the GZO. The images were taken in $[2\bar{1}10]$ zone axis for both materials.

EDS spectrum imaging (not shown) did not reveal any irregularity in the concentration vs. depth profile of major impurity and host elements. We found a flat distribution profile for Ga in GZO, and there is no accumulation on the surface or the interfaces.

DISCUSSION

Our results give a thorough picture of the formation of extended defects in Ga-doped ZnO. The surface polarity of ZnO determines the formation of interface and extended defects.^{8,12} GZO layers grown on a ZnO seed layer on sapphire have a columnar structure of mixed oxygen and zinc polarities. Point down pyramid defects nucleate IDBs. After just 2 nm of GZO growth, the surface polarity mostly switches from oxygen to zinc, with the exception of narrow columns. These columns propagate through the whole GZO layer, with a tendency to become wider and wider as growth

progresses. The two types of columns have different extended defects. Point up pyramid voids dominate in the Zn-polar columns, while point down pyramid voids and basal plane defects dominate in the O-polar columns.

Ga doping does not affect the stability of ZnO surface polarity on GaN substrate. However, GZO grown on O-polar surface of an undoped ZnO seed layer grown on sapphire exhibits polarity instabilities. We suggest that Ga doping of oxygen-polarity ZnO leads to the accumulation of Ga species on the surface of the film during MBE growth. The surface Ga then modifies the dangling bond configuration on the surface, leading to a change in the surface adsorption/evaporation coefficient for Zn- and O-species, and finally switching the surface polarity from O to Zn. This process could be laterally inhomogeneous due to surface fluctuations of the Ga concentration at the nanoscale. When GZO is composed of columns having different surface polarities, the system keeps a mixed surface polarity. We propose that further switching to the more favorable polarity does not occur because Ga species do not accumulate on the oxygen-polar surface, instead diffusing to the neighboring columns having Zn surface polarity.

The distribution of Al in GZO on sapphire shown in Figures 2 and 3 and the flat distribution of Ga suggest different microscopic diffusion mechanisms for Al and Ga even though they both are group III elements widely used for n-type doping of ZnO. We always observe increased concentration of Al in GZO having oxygen surface polarity, so we suggest that the mechanism of Al diffusion (but not Ga diffusion) depends on the electrical charge of the surface, implying electromigration of Al in ZnO. A high electromigration coefficient for Al in ZnO could limit the applications of AZO in some devices that require a homogeneous dopant distribution and high applied field, such as integrated circuits using a TCO based on ZnO. The Ga concentration is flat and Ga does not have a tendency to accumulate on extended defects, which is another positive attribute of Ga as a donor dopant in ZnO in comparison with Al.

Gallium does not segregate inside the pores in contrary to two common residual impurities, carbon and fluorine, which accumulate inside these voids as was shown in Figure 8. Our results suggest that oxygen deficiency may enhance graphitic cluster formation during growth, similar to previous reports.²⁰ The role of carbon in ZnO grown under different conditions is controversial.^{21,22} Fluorine is considered to be a shallow donor.²³

In the cases of GZO/a-sapphire grown under oxygen-rich conditions and GZO/GaN grown under metal-rich conditions, low-angle grain boundaries are the major defects which impact electron scattering and electron mobility. The grain boundary inclination of 24° for GZO on sapphire grown under oxygen-rich conditions should strongly affect the carrier scattering. An inclined grain boundary has a strong associated polar field in highly ionic ZnO, giving rise to a Coulombic interaction with free carriers and reducing electron mobility. Our previous investigations compare the grain size derived from XRD and STEM to the electron mobility.^{14,16} There are sufficiently good correlations with grain size from STEM data and XRD data in the whole range of

grain boundary sizes to show a significant contribution of grain-boundary scattering for our samples.¹⁶ Careful analysis of the electrical data reveals a significant effect of ionized impurities and polar optical phonon scattering, especially for samples with large grains and thus relatively high carrier mobility.¹⁴

However, the formation of numerous voids and IDBs in GZO films grown on a-sapphire under metal-rich conditions means that electron mobilities could be limited by scattering at other extended defects as well. The pores must also reduce the conductance of the film because they reduce the current-carrying cross-sectional area, but that effect may be more than compensated by the decrease in defect density. The small pores (with sizes much smaller than the wavelength of visible light) also increase the optical transparency.

CONCLUSIONS

We have investigated the microstructure of Ga doped ZnO (GZO) grown under metal and oxygen-rich conditions by molecular beam epitaxy on GaN templates and sapphire substrates, motivated by its application as a transparent conducting oxide. All GZO layers grown on a-sapphire and GaN show relatively good epitaxial relationship with the substrate. Their structural characteristics strongly depend on the oxygen-rich and metal-rich growth conditions.

When grown under metal-rich conditions, GZO films on a-sapphire have good crystal quality with slightly textured grains as large as 90 nm, but they are porous. Inside the grains, there are mixture of domains having O- and Zn-polarity and an extremely high concentration of voids, most of which have clear facets. The porous GZO grows on top of a non-porous ZnO seed layer. We suggest that Ga doping of ZnO with O-polarity leads to the accumulation of Ga species on the growing surface at the nanoscale, eventually switching the surface polarity from O to Zn. The final structure is a GZO layer with mixed polarity in columns. Further optimization of growth parameters is needed to avoid polarity switching in GZO/a-sapphire structures grown under metal-rich conditions. Residual impurities such as carbon and fluorine segregate inside the voids. Ga does not tend to accumulate inside the voids or at any other defect site.

GZO grown on GaN under similar growth conditions has Zn-polarity and does not contain voids. A network of misfit dislocations at the GZO/substrate interface relaxes most of the residual stress between the thin layers and the substrate. Threading low-angle grain boundaries are the major microstructural defects which limit the carrier mobility when the electron concentration is relatively low.

Ga doping of ZnO grown under O-rich conditions on a-sapphire substrates leads to instability of the wurtzite crystal structure. We observed phase switching from wurtzite structure on the bottom part of GZO layer to zinc blende structure on the top part of the layer. The grain boundaries in the top zincblende layer of GZO are along the [022] direction for the zinc blend phase, which is tilted $\sim 24^\circ$ from the [0001] growth direction of the wurtzite layer. This inclination could

noticeably affect the carrier scattering because an inclined grain boundary has a strong polar field in highly ionic ZnO resulting in Coulombic interaction between free carriers and grain boundaries. Al diffuses out from the sapphire substrate and accumulates on the surface. Ga is uniformly distributed within all our structures, which means that GZO potentially has more predictable optical and electrical properties than Al-doped ZnO.

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