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Defects at oxygen plasma cleaned ZnO polar surfaces

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Depth-resolved cathodoluminescence spectroscopy (DRCLS) reveals the evolution of surface and near surface defects at polar surfaces with remote oxygen plasma (ROP) treatment. Furthermore, this evolution exhibits significant differences that depend on surface polarity. ROP decreased the predominant 2.5 eV defect emission related to oxygen vacancies on the O face, while creating a new 2.1 eV defect emission on the Zn face that increases with ROP time. The surface-located 2.1 eV emission correlates with carrier profiles from capacitance-voltage measurements and a shift of the E3 trap to higher binding energy from deep level transient spectroscopy (DLTS). This result suggests that ROP generates Zn vacancies on the Zn face which act as compensating acceptors at the surface and in the near surface region. Secondary ion mass spectrometry (SIMS) shows no polarity dependence due to impurities. We conclude that the near-surface deep level optical emissions and free carrier densities of ZnO depend strongly on the ROP modulation of native defects related to Zn or O vacancies. © 2010 American Institute of Physics. [doi:10.1063/1.3514102]

I. INTRODUCTION

ZnO has attracted extensive study due to its large band gap and exciton binding energy, which have the potential to enable numerous optoelectronic applications.^{1,2} Despite ZnO's long history of research and thousands of publications, many fundamental issues remain unresolved. One key issue centers on the difficulty of doping ZnO p-type, which has been attributed to the compensation of acceptors by native defect donors.³ Oxygen vacancies,⁴ Zn interstitial-related complexes,⁵ impurities and hydrogen⁶ have been suggested as the origin of native donors in ZnO, while Zn vacancies and complexes were considered as acceptors.⁷ In spite of the importance of native defects as important native donors and acceptors, many of the fundamental physical properties of native defects in ZnO are unknown. For example, it is still a challenge to correlate the red and green luminescence emissions with native defects.⁸

Our previous studies on ZnO surfaces and metal/ZnO interfaces have revealed the important role of polarity, surface adsorbates, near surface native defects, and thermally induced interface chemical interactions on the electrical and optical properties of single crystal ZnO and related devices.^{9–12} The 2.5 eV green luminescence predominant in most ZnO luminescent spectra has been associated with oxygen vacancies.¹³ However, the origin of this and other deep level emissions, the role of native defects, and their correlation with optical and electrical properties are still subjects of controversy. For example, the origin of the green luminescence is still a matter of debate and it has also been attributed to either impurities or Zn vacancies.² In particular, there are

few studies on the polarity dependence of such native defects and their correlation with ZnO physical properties. Here we use depth-resolved cathodoluminescence spectroscopy (DRCLS),¹⁴ current-voltage and capacitance-voltage measurements, atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS) and deep level transient spectroscopy (DLTS) to probe the physical properties of surface and near surface defects at (0001) Zn- and (000 $\bar{1}$) O-polar surfaces of remote oxygen plasma (ROP) cleaned ZnO.

II. EXPERIMENTS

The single crystal ZnO samples we used in this study were grown by a vapor-phase process at ZN Technology Inc. and polished chemomechanically on both the (0001) and (000 $\bar{1}$) faces. They have mid- 10^{16} cm⁻³ carrier concentration and 220 cm²/V s Hall mobility at 300 K. The $5 \times 5 \times 0.42$ mm³ pieces were cut into halves, chemically cleaned, treated with a remote oxygen plasma (ROP), and deposited with metal *in situ* for Schottky contacts in the same plasma chamber under 1×10^{-9} Torr base pressure. The detailed procedures are described elsewhere.¹⁵ The *ex situ* CL measurements were performed at 10 K employing a JEOL 7800F scanning electron microprobe equipped with a hemispherical electron analyzer and Oxford CLS optical train. Current-voltage characteristics for the metal diodes was measured at room temperatures.

III. RESULTS AND DISCUSSION

Figure 1 shows 10 K CL spectra at 2 keV for as-received and ROP-cleaned Zn and O faces. The high quality single crystal ZnO samples exhibit dominant near band edge emis-

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FIG. 1. (Color online) CL spectra at 2 keV for as-received, 2 h, and 4 h ROP cleaned Zn face. The inset shows the CL spectra for as-received and 4h ROP cleaned O face. ROP generates 2.1 eV emission on the Zn face, increasing with ROP time.

sion (NBE) from neutral donor-bound excitons and their longitudinal optical (LO) photon replicas, along with a broad visible emission whose intensity was three orders of magnitude lower than the NBE peak. Both as-received Zn and O surfaces show a single 2.5 eV defect emission peak that dominates the spectra. However, with ROP treatment, the Zn face shows an additional 2.1 eV emission, whose intensity increases with ROP time. In contrast, ROP treatment generates no new emission on the O-face. Instead, it decreases the intrinsic 2.5 eV emission. The 2.5 eV emission is due to defects associated with O vacancies (V_O),¹¹ which can pin the surface Fermi level as well as degrade the quality of Schottky diodes.¹⁶ Therefore, ROP cleaning improves the rectifying behavior of Schottky diodes on O-face ZnO.

The time dependence of ROP effects on the Zn face is more complex. The 2.5 eV emission first slightly decreases, then slightly increases, while the newly generated 2.1 eV emission continues to increase. These differences do not appear related to surface morphology. AFM images show that room mean square (rms) surface roughness increases only slightly for both faces, from 0.4 to 0.6 nm for O face and from 0.2 to 0.5 nm for Zn face after 4 h ROP treatment.

Figure 2 shows the comparison of CL spectra for 4 h ROP treated Zn and O faces, CL spectra were normalized to a constant NBE emission intensity. The O face has relatively strong LO phonon replicas. This is consistent with PL spectra for similar samples and suggests different local crystal environments near the two polar surfaces.¹⁷ The broad defect emission for Zn face spectra can be decomposed into two Gaussian peaks, at 2.1 and 2.5 eV respectively, while the O face contains only one Gaussian peak at 2.5 eV. The inset in Fig. 2 shows the relative defect intensity (defect emission divided by NBE intensity ratio) of 2.1 and 2.5 eV emissions on the Zn face as a function of incident electron beam energy E_B . The electron cascade and thereby the primary excitation depth on a nanometer scale increases with E_B .¹³ The intrinsic 2.5 eV emission has higher density in the surface region, which is consistent with our previous results,¹² suggesting more V_O -related defects in the surface region. The ROP-

FIG. 2. (Color online) CL spectra at 2 keV for Zn and O faces with 4 h ROP: generation of 2.1 eV defect emission only on the Zn face. The inset shows the depth distribution of relative defect density for the Zn face.

generated 2.1 eV emission is found to be mainly localized in the surface and near surface region (<100 nm).

Significant polarity-related electrical differences were found for Au diodes on the two polar surfaces cleaned by ROP. The Au diodes deposited on both as-received surfaces are strongly ohmic. With ROP through the diodes, those diodes on the Zn face that were originally Ohmic gradually become rectifying, while those on the O face change little. We refer to these “ROP-post” diodes as “Au I.” Au diodes deposited on surfaces first cleaned by ROP are referred to as “Au II.” The duration of ROP treatment varied from 1 h to 4 h. All the Au II diodes were rectifying. The degree of rectification for Au II diodes on the O face increased significantly with increasing ROP time. For Au II diodes on the Zn face, the reverse current decreases by a two orders magnitude from 1h to 2 h ROP. However, increasing ROP treatment to 4h does not decrease reverse currents of these Au Schottky diodes further.

To correlate the optical emissions to electrical properties, we measured CL spectra for Au I and II diodes on the Zn- and O-faces as shown in Figs. 3(a) and 3(b) respectively and compared them to capacitance-voltage (C-V) profiles of the same diodes. The inset shows the corresponding carrier profiles derived from C-V data. Since Au I diodes on the O face are Ohmic, C-V measurements were not possible. Of chief importance, CL revealed that only Au II diode on the Zn face displays the ROP-generated 2.1 eV emission. All the other three diodes, Au I on the Zn face, and both Au diodes on the O face, exhibit only the intrinsic 2.5 eV emission. Corresponding to the 2.1 eV emission, the carrier profile for Au II on the Zn face decreases approaching the surface, which directly indicates the correlation of ROP-generated 2.1 eV emission with a compensating acceptor-type defect.

The surface defects generated by ROP on the Zn face are most likely Zn vacancies (V_{Zn}). Thermodynamically, Zn vacancies have the lowest and the only negative formation energy in bulk ZnO in an oxygen rich atmosphere, compared with other possible native defects such as oxygen interstitials.^{3,18} This is especially true with the Fermi level close to the conduction band and, in our case, E_C-E_F

FIG. 3. (Color online) Comparison of CL spectra for Au I and II diodes on Zn and O faces. The corresponding CV carrier profiles appear in the inset.

$=0.1$ eV in bulk. In order to understand the differences in polarity and why the V_{Zn} is introduced only on the Zn face, the thermodynamic stability of ZnO polar surfaces in the oxygen plasma atmosphere must be considered. Although the stabilization mechanisms of ZnO polar surfaces are still controversial,¹⁹ it is well known that adsorbates cover the air-exposed ZnO surfaces, e.g., C, H, or OH groups, that induce an accumulation layer and increase its conductivity.²⁰ ROP can effectively remove the surface conductive layer without causing noticeable surface deterioration.^{9,12} However, after ROP, the stabilized Zn-ZnO termination of Zn face and O-ZnO termination of O face should be quite different based on the arguments of thermodynamic stability for polar oxide surfaces over a large oxygen and hydrogen chemical potential.²¹ Thus for the Zn-ZnO termination, hydroxyl groups are removed and roughly 1/4 of the surface Zn ions are missing to stabilize the polar surface;²² while for the O-ZnO termination, the most stable surface structure is that with 1/2 monolayer H coverage.²³ Our photoluminescence (PL) results support this scenario by showing a decreased H donor bound exciton peak ($I_4=3.3628$ eV) only on ROP cleaned Zn face.²⁴ Considering the near-surface region, ROP generates V_{Zn} on the Zn face while only depressing V_{O} -related defects on the O face.

Our most recent study on ion-implanted ZnO combining DRCLS and positron annihilation spectroscopy (PAS) demonstrate that 2.1 emission is related to V_{Zn} or clusters.²⁵ V_{Zn} is a deep acceptor (1.6–2.1 eV below conduction band, depending on the degree of vacancy clustering) and acts as compensating centers in n-ZnO, while V_{O} -related defects act as deep donors and have no significant impact on the CV carrier profiles. Therefore, we observed the generation of 2.1

eV emission, accompanied by a decreased carrier profile on the Zn face, while the constant carrier profiles are independent of the 2.5 eV emission for both faces.

Figure 4 shows representative deep level transient spectroscopy (DLTS) spectra for Au II diodes on 4 h ROP-cleaned polar surfaces. E3 is the dominant trap for both surfaces. However, a shift of E3 trap to higher temperatures (E3') was found on the Zn face with ROP-treatment. In addition, the trap density of E3 trap is much higher for the Zn vs. O face and increases with increasing ROP-treatment time on both faces.²² The E3 trap is commonly observed for most bulk and thin film ZnO. Earlier studies suggest its association with V_{O} . However, this is still under discussion.²⁶ A

FIG. 4. (Color online) DLTS spectra for Au SBDs on Zn- and O-surfaces with 4 h ROP. The DLTS parameters, bias U_R , filling pulse height U_P , filling pulse width t_P , and transient period T_W are shown.

shift of the E3 trap to higher temperatures has also been found for oxygen-annealed ZnO which was associated with oxygen incorporation.²⁷ Since V_{Zn} is too deep (2.1 eV below conduction band) to be detected by DLTS, E3 should not be directly associated with V_{Zn} defects. However, whether or not the E3 is related to a di-vacancy, i.e., $V_{\text{O}}\text{-}V_{\text{Zn}}$, requires further study. By virtue of its near-midgap energy, V_{Zn} defects can act as compensating acceptors and decrease near surface carrier concentration. The peak temperature shift of the E3 trap corresponding to an increased binding energy may be related to the electric field-related Poole–Frenkel effect.²⁴ The carrier concentration in the near-surface region on the Zn-face decreases with increasing ROP duration. This decrease in carrier concentration can lead to a lower electric-field in the depletion region, resulting in a shift of E3 to higher temperatures.

Finally, the impurity asymmetry on the polar surfaces was evaluated by SIMS. While pronounced segregation differences were reported for annealed bulk ZnO wafers,²⁸ we found only trace accumulation (below 10 ppm) of Al, In, and Ga on both as-received and ROP cleaned surfaces, and no significant difference in impurity level was observed between the two polar surfaces. While impurity diffusion was found to be affected by substrate surface polarity in ZnO homoepitaxial growth,²⁹ impurities have no significant contributions to the observed polarity effects on ROP cleaned surfaces.

IV. CONCLUSIONS

In summary, ROP treatment generates Zn vacancies on the Zn face and decreases oxygen vacancies on the O face which results in significant optical and electrical polarity-dependence. The ROP-generated V_{Zn} corresponds to a 2.1 eV deep level emission and may also be attributed to decreasing carrier profiles on ROP-treated Zn-face, which results in the shift of E3 trap to a higher temperature due to an electric field related Poole–Frenkel effect. Our findings demonstrate the importance of polar effects and oxygen plasma treatment on forming surface and near-surface defects that control the physical properties of ZnO.

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