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Metal contacts on bulk ZnO crystal treated with remote oxygen plasma

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To study the quality of thin metal/ZnO Schottky contacts (SCs), temperature-dependent current-voltage (I - V), capacitance-voltage, deep level transient spectroscopy, and photoluminescence measurements were performed using bulk, vapor-phase ZnO, treated by remote oxygen plasma (ROP). Au/ZnO and Pd/ZnO contacts on both O and Zn faces are compared as a function of the ROP processing sequence and duration. We find that (i) as the duration of ROP treatment increases from 2 to 4 h, Au/ZnO contacts on the Zn face, *deposited before ROP treatment*, become rectifying, while those on the O face remain Ohmic; (ii) with long-term ROP treatments *prior to metallization*, both Au/ZnO and Pd/ZnO show high-quality SCs; however, their I - V characteristics can be significantly degraded by electric field and high temperatures; (iii) ROP treatment can cause more H removal on the Zn face than on the O face, resulting in a decrease in the near-surface carrier concentration for the Zn face only; (iv) in addition to the dominant bulk-trap E3, surface traps, E6/E7 and E8, and Es, can be observed in Au/ZnO and Pd/ZnO SCs, respectively, on the Zn face, with shorter ROP treatment; and (v) with long-term ROP treatment, E3 (or L2) significantly increases and shifts in Au/ZnO SCs on the Zn face. © 2009 American Vacuum Society. [DOI: 10.1116/1.3095814]

I. INTRODUCTION

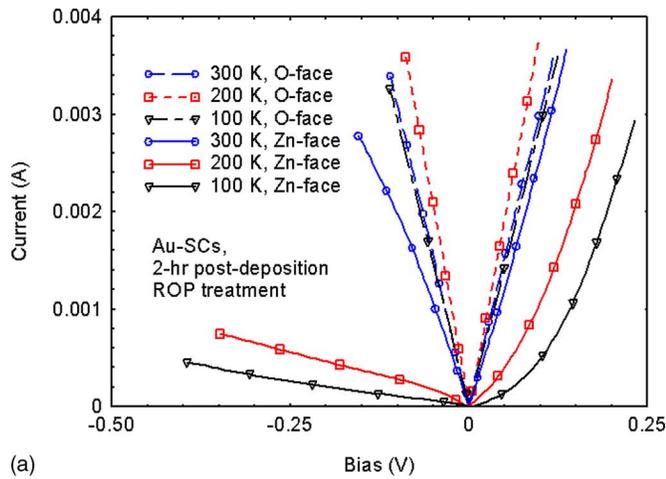
To realize the potential of high-performance ZnO-based optical and electronic devices, the formation of high-quality metal/ZnO Schottky contacts (SCs) is essential. Surface preparation prior to metal deposition is also important, and remote oxygen plasma (ROP) treatment has been found to be very effective to remove surface adsorbates and defects and to form good SCs.¹ The effects of near-surface or near-interface defects on the quality of ZnO Schottky barriers and Zn- and O-face polarity effects have been well characterized by applying depth-resolved cathodoluminescence spectroscopy (DRCLS) in conjunction with current-voltage (I - V) and capacitance-voltage (C - V) measurements.^{2,3} In addition to these optical studies, deep level transient spectroscopy (DLTS) has been used to observe a surface trap, Es (0.49 eV), in bulk vapor-phase (VP) grown ZnO, in addition to the well-known bulk traps E3 and E4.⁴ In this work, we perform temperature-dependent I - V , C - V , DLTS, and photoluminescence (PL) measurements on thin metal/ZnO SCs and ZnO surfaces. We compare Au and Pd SCs, on both the Zn and O faces, as a function of the duration of ROP treatment. We will present (i) temperature-dependent I - V characteristics of Au contacts, on both the Zn and O faces, deposited before and after ROP treatment; (ii) enhanced degradation of the I - V characteristics for Au and Pd SCs, by electric field and temperature; (iii) effects of ROP treatment and surface polarity on carrier concentration profiles in the SCs and hydrogen removal; and (iv) the effects of the ROP-

treatment duration and surface polarity on electrical properties of the Au and Pd SCs, bulk traps E3 and E4, and surface traps E6/E7 and E8

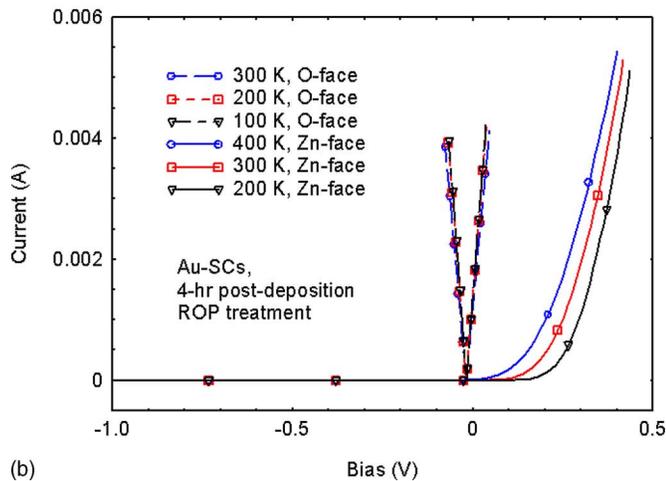
II. SAMPLE PREPARATION AND EXPERIMENT

Bulk, VP, ZnO samples grown by ZN Technology, Inc., which were chemomechanically polished on both (0001) Zn and (000-1) O faces, were used in this study. These samples typically exhibit room temperature (RT) carrier concentrations in the mid-to-high 10^{16} cm⁻³ range and a mobility of ~ 220 cm²/V s. To compare the effect of surface polarity, 5×5 mm² samples were cut in half, and oriented with O- and Zn-face up, respectively. The samples were cleaned with organic solvents and loaded into an ultrahigh vacuum chamber (base pressure of $\sim 5 \times 10^{-9}$ Torr) and processed with room temperature ROP (20% O₂-80% He and power of 40 W) treatment for 1, 2, or 4 h. Arrays of Au and Pd contacts (30 nm thick and 0.4 mm in diameter) were deposited *in situ* on the ROP-treated ZnO surfaces by electron beam evaporation using a removable mask. Au contacts were also deposited on the ZnO surfaces prior to ROP treatment. Thus, rectification of the Au contacts, deposited before and after the ROP treatment, can be compared. Finally, the back side of each sample was covered with a 40/60/30 nm Ohmic Ti/Ni/Au contact by e-beam evaporation. For the I - V and C - V measurements, Au probes were used to investigate individual Au and Pd contacts on the top surface. The C - V and DLTS measurements were performed with an Accent DL8000 spectrometer, operated at a frequency of 1 MHz. The I - V measurement was carried out with a current amplifier in the spectrometer. Carrier concentration profiles were determined from bias-dependent C - V data and the DLTS

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(a)



(b)

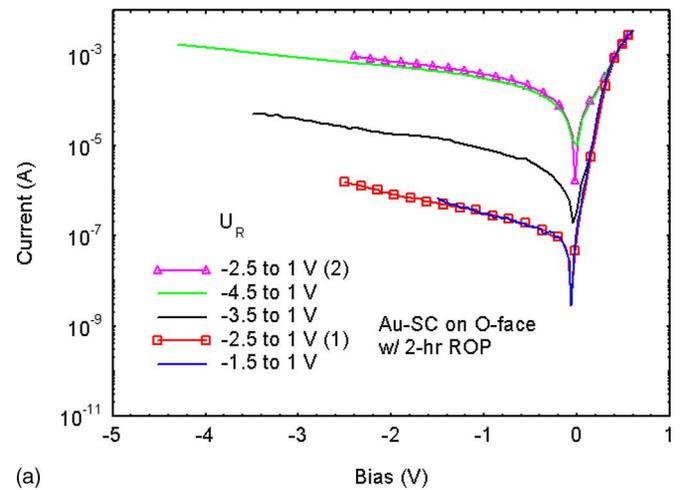
FIG. 1. (Color online) Temperature-dependent I - V characteristics, measured for Au contacts on O face and Zn face, with post deposition ROP treatment for (a) 2 h and (b) 4 h.

spectra were obtained from the Fourier transforms of capacitance transients as temperature was swept between 100 and 400 K. We used a technique that was developed previously to determine whether a particular trap originates in the bulk or near-surface regions.⁵ The DLTS spectrum is measured for different values of reverse bias while keeping the filling pulse height fixed. With increasing reverse bias (i.e., more negative value), the DLTS signal will increase for a bulk trap or decrease for a near-surface trap. PL at 4.2 K was measured on both O and Zn faces of the ZnO samples with different treatment durations of ROP using 325 nm line of a He-Cd laser.

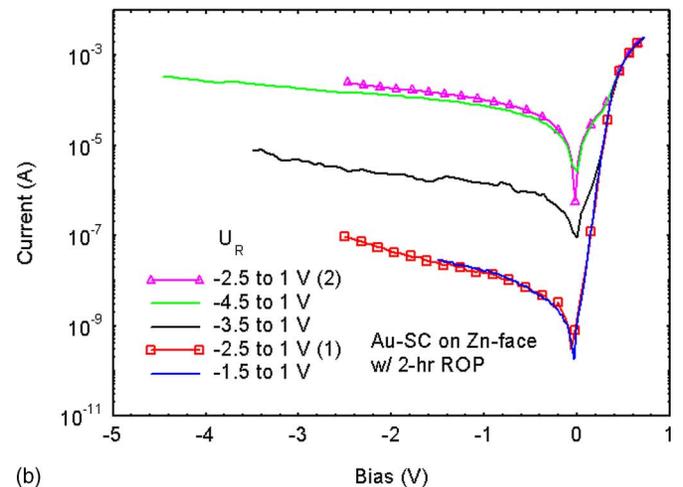
III. RESULTS AND DISCUSSION

A. Rectification and degradation of the I - V characteristics

Temperature-dependent I - V characteristics for Au contacts, deposited on the O and Zn faces and subjected to post-deposition ROP treatments for 2 or 4 h, are shown in Figs. 1(a) and 1(b), respectively. Both Au contacts on the O face are Ohmic at all temperatures. In contrast, the Au contact on



(a)



(b)

FIG. 2. (Color online) I - V characteristics, measured as a function of starting bias for Au-SCs on (a) O face and (b) Zn face, with 2 h prior-deposition ROP treatment. Curves (1) and (2) were measured under voltage swept from -2.5 to 1 V, following measurements at starting bias of -1.5 and -4.5 V, respectively.

the Zn face, with 2 h postdeposition ROP, is Ohmic only at 300 K and becomes rectifying at lower temperatures. However, the Au contact on the Zn face, with 4 h postdeposition ROP treatment exhibits good rectifying ratios at all temperatures. On the other hand, likely because of the removal of OH radicals and adsorbed carbon,¹ Au contacts deposited after ROP treatment are good SCs. Both reverse and forward currents of these SCs decrease with increasing duration of the ROP treatment, especially those on the Zn face [compare I - V curves measured at lower biases in Figs. 2(a) and 2(b)]. We checked the stability of the I - V characteristics for these Au-SCs at 300 K and found significant electric-field-enhanced degradation. 300 K I - V curves of Au-SCs on the O and Zn faces, both with 2 h ROP treatment, measured as a function of initial bias (U_R), are pictured in Figs. 2(a) and 2(b), respectively. It is clearly seen that for Au-SCs on O and Zn faces, (i) for measurements started at $U_R = -1.5$ or -2.5 V, the I - V curves were not affected by U_R , (ii) as the initial value of U_R increases from -2.5 to -4.5 V, both the reverse and forward currents increase, and (iii) a permanent

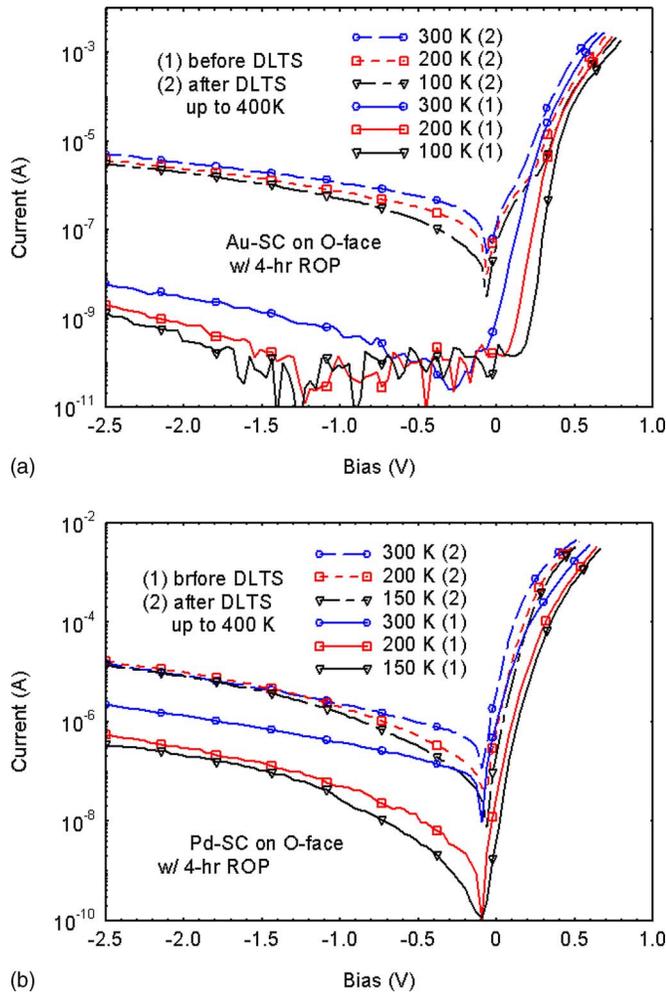


Fig. 3. (Color online) Temperature-dependent I - V characteristics, measured before and after DLTS measurements, for (a) Au-SC and (b) Pd-SC on O face, with 4 h ROP treatment.

increase of the forward and reverse currents was observed for I - V measurements starting at $U_R = -2.5$ V following measurement initiated at $U_R = -4.5$ V. Since C - V characteristics and carrier concentration profiles at 300 K do not change in the measurements until the initial value of U_R increases to -4.5 V (not shown here), we believe that the increased currents probably flow through localized current paths.

In general, the electrical quality of Pd-SCs was found to be poorer than that of Au-SCs, possibly due to higher carrier concentrations in the former caused by hydrogen diffusion through the thin Pd layers.^{3,4} Electric-field-enhanced degradation was also observed on Pd-SCs on both O and Zn faces, with 2 h ROP treatment (not shown here). Degradation of the I - V characteristics, produced by exposure to high temperatures, for both Au- and Pd-SCs, was often found after DLTS measurements up to 400 K, as shown in Figs. 3(a) and 3(b), respectively. In Fig. 3(a), very good quality Au-SCs, with leakage currents of 10^{-9} – 10^{-8} A at $U_R = -2.5$ V, are observed in the first measurements after mounting the sample in vacuum. However, after subsequent DLTS measurements up to 400 K, the Au-SC degrades, with the leakage currents increasing to 10^{-6} – 10^{-5} A. The forward currents at lower

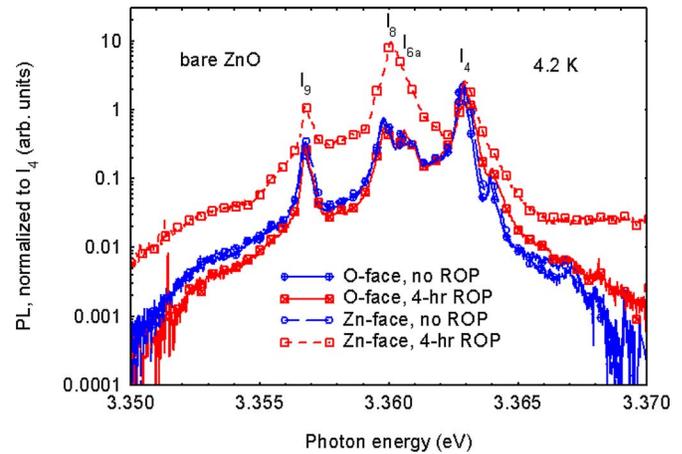


Fig. 4. (Color online) Normalized 4.2 K PL spectra measured on O face and Zn face, with 0 or 4 h ROP treatment.

biases are also affected. Similarly, in Fig. 3(b), the Pd-SC initially is fairly good, with leakage currents of 3×10^{-7} – 2×10^{-6} A at $U_R = -2.5$ V, but degrades, with leakage currents of $\sim 10^{-5}$ A, after subsequent DLTS measurements. As compared to the data measured before DLTS, the I - V characteristics measured after DLTS show much less temperature dependence, indicating possible tunneling conduction or the presence of localized current paths.

Observations of the Ohmic-Schottky conversion, facilitated by an increase in the postdeposition ROP duration, and the degradation of the I - V characteristics, enhanced by electric field and high temperatures imply that a mobile species, such as hydrogen, might play an important role in the formation of high-quality metal/ZnO SCs. Hydrogen incorporation by the application of electrical current (under higher voltage sweep) in annealed hydrothermal ZnO has been reported.⁶ Degradation of the I - V characteristics following DLTS measurements (up to 400 K) could be accelerated by long-term current-driven hydrogen incorporation at high temperatures. Indeed, bulk hydrogen was detected in our VP-ZnO samples, as described below.

B. Photoluminescence and carrier concentration profiles

PL spectra measured at 4.2 K on the O and Zn faces, for untreated samples or those that received a 4 h ROP treatment, are shown in Fig. 4. Donor bound exciton lines, I_4 (3.3628 eV), I_{6a} (3.3604 eV), I_8 (3.3598 eV), and I_9 (3.3567 eV), have been identified using the spectral positions published by Meyer *et al.*⁷ The lines I_4 , I_{6a} , I_8 , and I_9 are assigned to H, Al, Ga, and In, respectively. It should be noted that (i) the two PL spectra for O and Zn faces, without ROP treatment, are almost identical and are dominated by I_4 (H donor), (ii) the 4 h ROP treatment on the O face did not produce any meaningful change in PL features (H donor still dominant), and (iii) the 4 h ROP treatment on the Zn face did cause a significant increase in the relative peak intensities of I_8 and I_{6a} over I_4 . These results reveal a reduction in near-surface H donors (i.e., H removal) by ROP treatment on the

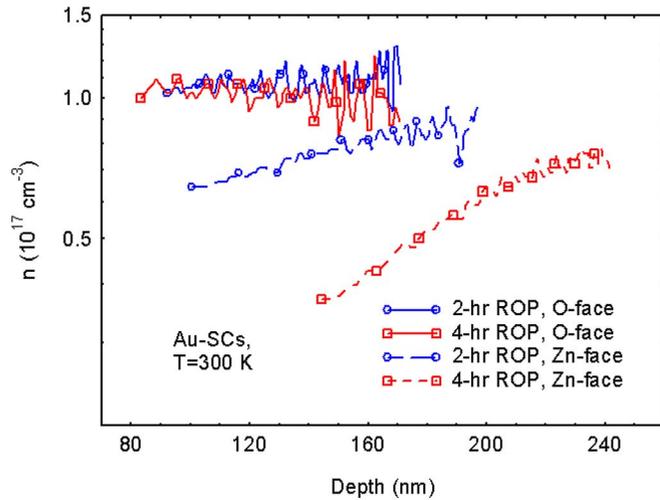
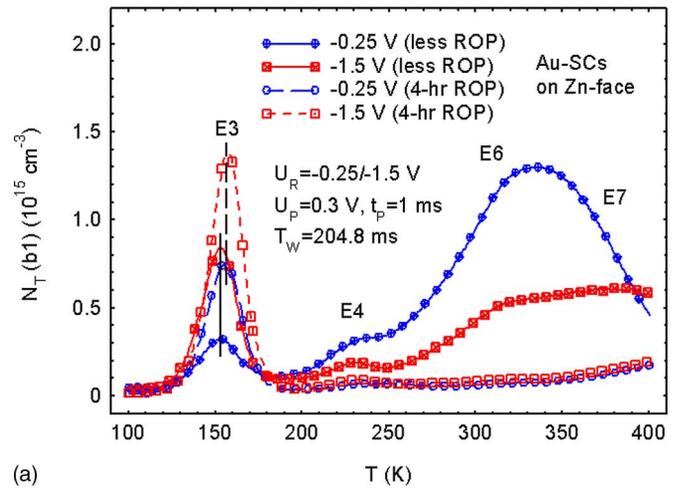


FIG. 5. (Color online) Carrier concentration profiles for Au-SCs on O-face and Zn face, with 2 or 4 h ROP treatment.

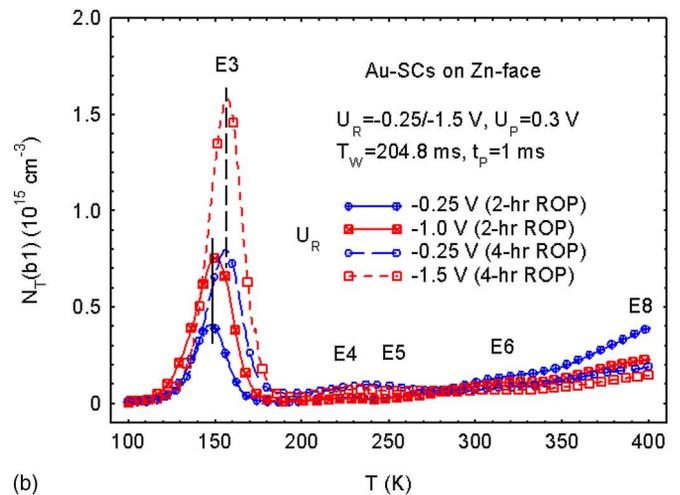
Zn face (similar to observations in a previous report¹), but not on the O face. Interestingly, carrier concentration profiles, deduced from C - V measurements with U_R swept from -2.5 to 0 V, behave differently for Au-SCs on the two polar faces for different durations of ROP treatment. As shown in Fig. 5, Au-SCs on the O face that were exposed to ROP for 2 or 4 h exhibit almost identical, flat carrier concentration profiles of $\sim 1 \times 10^{17} \text{ cm}^{-3}$. However, carrier concentration profiles for Au-SCs on the Zn face were found to decrease towards the surface with a larger decrease seen for longer ROP treatment. This sharp contrast in carrier concentration profiles (flat on O face versus a decrease in the Zn face with a larger drop for longer ROP treatment) was also found in the Pd-SCs (not shown). We believe that the decrease of carrier concentration on the Zn face with increasing ROP-treatment duration is mainly due to H removal, consistent with the observation of a ROP-induced reduction in I_4 . It seems that there exists a barrier on the O face to prevent hydrogen out-diffusion. Further study is needed to understand the mechanism of the H removal from ZnO by ROP treatment at RT and the difference between the two polarities.

C. Observation of surface traps on Zn face

DLTS spectra measured at different reverse bias (U_R) values for Au-SCs on the Zn face, with different ROP treatments, are shown in Figs. 6(a) and 6(b), respectively. Figure 6(a) compares DLTS spectra for Au-SCs deposited before or after a 4 h ROP treatment. As U_R increases from -0.25 to -1.5 V, the trap E3 increases (for both ROP treatments), indicating its bulk nature. However, the Au-SC deposited before the 4 h ROP (having only a postdeposition ROP treatment, i.e., less ROP), shows strong traps E6/E7, which must be surface-related because they significantly decrease as U_R is made increasingly negative. The U_R dependence indicates that these traps are confined to a depth less than about 90 nm below the Au/ZnO interface. Furthermore, the DLTS signal of traps E6/E7 depends strongly on filling pulse width (not



(a)



(b)

FIG. 6. (Color online) DLTS spectra, measured as a function of U_R , for Au-SCs on Zn face, with (a) post-deposition (or less) ROP vs 4 h ROP and (b) 2 h ROP vs 4 h ROP. Measurement conditions: reverse bias $U_R = -0.25/-1.5$ V; filling pulse height $U_p = 0.3$ V; filling pulse width $t_p = 1$ ms; and transient period $T_W = 205$ ms.

shown), indicating their association with extended defects [similar to the case of Es (Ref. 4)]. Figure 6(b) shows a comparison of DLTS spectra for Au-SCs, deposited after either a 2 h or 4 h ROP treatment. Again, observing the dependence of signal strength on U_R we find that the dominant E3 trap is bulklike for both Au-SCs. In addition, for both Au-SCs, a surface trap E8 peaked at $T \geq 400$ K is observed. With increasing ROP duration, E8 becomes weaker. For Pd-SCs on the Zn face, we see a similar behavior. For a 1 h ROP, a surface trap Es is observed,⁴ while for a 2 h ROP, Es disappears, leaving a larger E3 peak and a very weak E4 trap (not shown). As reported previously,⁴ Es (0.49 eV) is located at depths less than about 95 nm below the Pd/ZnO interface and shows an electron capture behavior indicative of extended defects. Thus, from the comparisons presented above, we can conclude that a long ROP treatment is effective at removing extended-defect-related surface traps on the Zn face of ZnO. It is interesting to note that E3 can be affected by the ROP treatment. With increasing duration of the ROP treatment, the trap density of E3 increases by approximately

two times, and its peak shifts to higher temperatures by a few degrees (sometimes ~ 10 K). According to previous DLTS studies on bulk ZnO,^{8–10} E3 (or L2), with $E_T = 0.28\text{--}0.32$ eV, has tentatively been assigned to a defect related to oxygen vacancies (V_O). Since the ROP treatment causes significant H removal on the Zn face, we speculate that (i) there might exist complexes of V_O with H in the surface region of VP-ZnO, and (ii) the increase in E3 might result from the dissociation of the $V_O\text{--}H$ complexes. The peak temperature shift of E3 might be related to the electric-field related Poole–Frenkel effect. As seen in Fig. 5, 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. However, in addition to the commonly observed trap E3 (0.3 eV), another close lying peak E3' (0.37 eV) was reported by using high resolution Laplace-transform DLTS in ZnO grown by pulsed-laser deposition.¹¹ An increase in the concentration of E3' after annealing in oxygen suggested that this new trap could be associated with oxygen incorporation. In that study, however, E3' was not found in any bulk-grown ZnO (serving as a reference). Here, we cannot rule out that the increase and shift of E3 observed in the Au-SCs, with 4 h ROP treatment, could be due to existence of E3' since more oxygen can be produced by a ROP treatment. Further study would be needed to determine whether or not there really exists an E3/E3' feature in vapor-phase grown ZnO treated by long-term ROP.

D. Observation of traps on O face

Here, we present the effects of ROP on the traps in the SCs on the O face. DLTS spectra measured at different reverse bias (U_R) values for Au- and Pd-SCs with 2 h and 4 h ROP treatments, are shown in Figs. 7(a) and 7(b), respectively. For the Au-SC, with a 2 h ROP treatment, we observe traps E3, E4, E5, E6, and E8, which are all bulk traps. However, for the 4 h ROP treated Au-SC, we find an increase in E3 and the appearance of surface trap E8. Since the carrier concentrations in the near-surface region for both ROP treatments are about the same (Fig. 5), there is little electric-field related shift of E3. In both Pd-SCs [Fig. 7(b)], we observe E3, E4, E6, and E8, which are all bulk traps. However, in the Pd-SC, with a 4 h ROP treatment, we find an increase in E4, E6, and E8, but not in E3. The trap densities of E3 in the Pd-SCs appear to be lower than those in the Au-SCs, which could be related to the higher carrier concentrations in the near-surface region for the Pd-SCs. Once again, the electric-field related shift of E3 is not significant, because of the flat carrier concentration profiles. Or, there might exist much less E3' in the SCs on the O face. By using the “maximum evaluation” method, the activation energies and capture cross sections for traps E3, E4, and E6 in the Pd-SC were determined

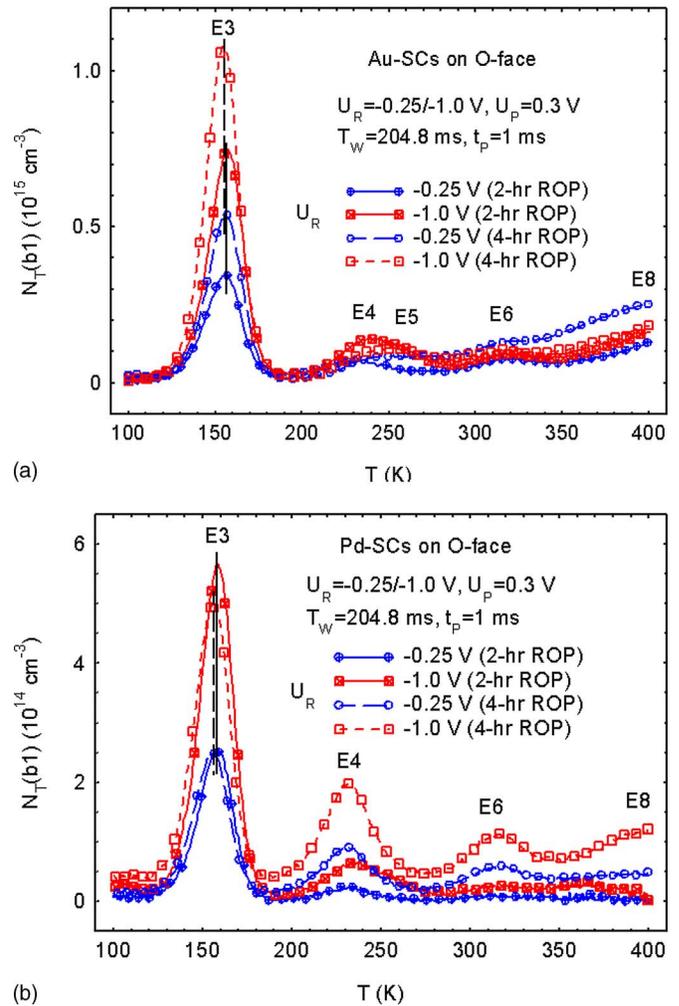


Fig. 7. (Color online) DLTS spectra measured as a function of U_R for (a) Au-SCs and (b) Pd-SCs on O face with 2 or 4 h ROP treatments. Measurement conditions: reverse bias $U_R = -0.25\text{--}1.0$ V; filling pulse height $U_p = 0.3$ V; filling pulse width $t_p = 1$ ms; and transient period $T_w = 205$ ms.

to be 0.22 eV and 1.2×10^{-17} cm²; 0.49 eV and 2×10^{-15} cm²; and 0.71 eV and 5×10^{-15} cm², respectively.

IV. CONCLUSIONS

To study the quality of thin metal/ZnO SCs, temperature-dependent I - V , C - V , DLTS, and PL measurements were performed, using bulk, VP ZnO samples, treated by ROP. We have compared Au- and Pd-SCs, on both O and Zn faces, as a function of the ROP processing sequence and duration. It is found that (i) as ROP-treatment duration increases from 2 to 4 h, Au/ZnO contacts deposited on the Zn face without pre-ROP treatment, become rectifying, while those on O-face remain ohmic; (ii) long-term ROP treatments prior to metalization, produce high-quality Au/ZnO and Pd/ZnO SCs; however, degradation of their I - V characteristics can be significantly enhanced by electric-field and high-temperatures; (iii) ROP-treatment promotes more H removal on the Zn face than on the O face, resulting in a decrease in carrier concentration towards the surface on Zn face; (iv) surface traps, E6/E7 and E8, and Es, can be observed in Au/ZnO and

Pd/ZnO SCs, respectively, on the Zn face, for shorter ROP treatments; and (v) long-term ROP treatment significantly increases and shifts E3 (or L2) for Au/ZnO SCs on the Zn face.

Further study is needed to correlate these surface traps with deep level defects (such as the 2.45– eV “green band”) observed in the surface region by DRCLS.

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