Gold Schottky contacts on oxygen plasma-treated, *n*-type ZnO$(000\bar{1})$

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Reverse bias current–voltage measurements of $\sim$100-μm-diameter gold Schottky contacts deposited on as-received, *n*-type ZnO$(000\bar{1})$ wafers and those exposed for 30 min to a remote 20% O_2/80% He plasma at 525 ± 20 °C and cooled either in vacuum from 425 °C or the unignited plasma gas have been determined. Plasma cleaning resulted in highly ordered, stoichiometric, and smooth surfaces. Contacts on as-received material showed μA leakage currents and ideality factors >2. Contacts on plasma-cleaned wafers cooled in vacuum showed $\sim36\pm1$ nA leakage current to -4 V, a barrier height of 0.67 ± 0.05 eV, and an ideality factor of 1.86 ± 0.05. Cooling in the unignited plasma gas coupled with a 30 s exposure to the plasma at room temperature resulted in decreases in these parameters to $\sim$20 pA to -7 V, 0.60 ± 0.05 eV, and 1.03 ± 0.05, respectively. Differences in the measured and theoretical barrier heights indicate interface states. (0001) and $(000\bar{1})$ are used in this letter to designate the polar zinc- and oxygen-terminated surfaces, respectively. [DOI: 10.1063/1.1536264]

Zinc oxide (ZnO) commonly occurs in the hexagonal wurtzite crystal structure and possesses the direct band-gap energy of $\sim$3.4 eV at room temperature.[1] Applications commonly associated with powdered and bulk polycrystalline ZnO include paints, phosphors, surface acoustic wave devices, gas sensors, piezoelectric transducers, varistors, and transparent conducting films for the photovoltaic industry.[2] Recent research has focused on the electrical and optical properties of this material and the associated device applications, for example UV photodetectors.[3–5] Large-area substrates are also commercially available for growth of ZnO-based films. This material is typically *n*-type due to oxygen vacancies and/or zinc interstitials.[6] Several groups have reported the achievement of *p*-type ZnO[7,8] via several process routes. However, at this writing, no approach has been successfully duplicated in separate laboratories by different investigators. A review of the recent advances in ZnO materials and devices has recently been published.[1]

A prior determination of the Au Schottky barrier height (Φ_B) on chemically prepared ZnO crystals with an unspecified orientation resulted in a value of 0.66 eV by $I-V$, $C-V$, photoresponse, and thermal activation energy measurements; an ideality factor (n) of 1.05 was reported without specifying the reverse bias leakage current.[9] Fabricius *et al.*[3] measured $n=2.7$ for Au Schottky photodiodes fabricated on as-received polycrystalline ZnO, but did not indicate Φ_B nor leakage currents. This high value of n was reportedly influenced by recombination. Silver Schottky contacts with a Au cap have been fabricated on as-received ZnO$(11\bar{2}0)$ epilayers.[4,10] The values of Φ_B determined via $I-V$ and $C-V$ measurements were 0.89 and 0.92 eV, respectively. A leakage current of 0.1 nA at 1 V reverse bias and an ideality factor of 1.33 were also reported. The high ideality factor was attributed to an interfacial layer and/or surface states.

Investigations concerned with the properties of rectifying contacts deposited on as-received and cleaned surfaces of Si and GaAs have shown[11–13] that the ideality factors and the reverse bias leakage currents are both decreased in the contacts on the cleaned materials. In this regard, x-ray photoelectron spectroscopy (XPS) studies by Mintas and Filby[14] of the surfaces of as-received, sintered ZnO tablets revealed since hydrocarbons do not appear in the O 1*s* core level, but are still present, located 1.5–2 eV higher in binding energy than lattice oxygen. The complete removal of these contaminants was achieved via Ar^+ bombardment for 20 min at a potential and beam current of 6-kV ions and 40 μA, respectively. However, this process normally results in the chemical and physical alteration of the surface and the underlying layers via atomic mixing, vacancy formation, changes in oxidation state, and surface roughening, and thus disallows the achievement of rectifying contacts with optimum properties. Liang *et al.*[5] employed an oxygen plasma to clean ZnO$(11\bar{2}0)$ films before depositing Ag contacts, but neither the conditions of use nor the evidence of its effectiveness were reported.

2 mm-thick, single-crystal ZnO$(000\bar{1})$ wafers, diced from boules produced by seeded chemical vapor transport by Eagle-Picher Technologies, Inc.,[15] and chemomechanically polished on both sides, were employed in the present research. Grade I wafers were used, as they were essentially free of internal microvoids, which we determined produce highly ohmic behavior. Hall and $C-V$ measurements, the latter at 1×10^4 Hz, taken from the $(000\bar{1})$ surface, showed a bulk carrier concentration of $1\times10^{17}/\mathrm{cm}^3$ and a nominal effective donor concentration, (N_D-N_A), of $5\times10^{16}/\mathrm{cm}^3$, respectively, for the as-received samples. The wafers were

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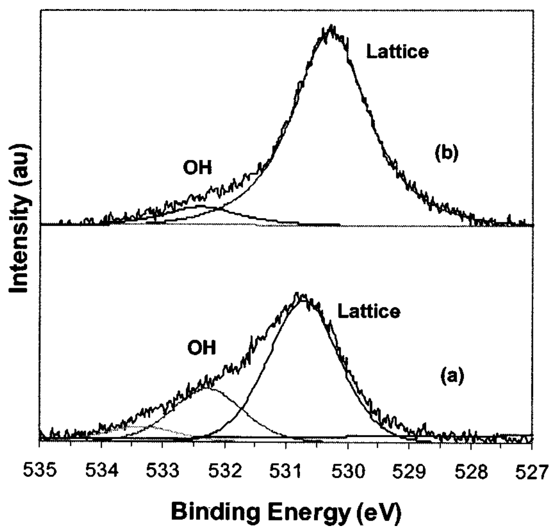

FIG. 1. XPS O 1s core level spectra acquired from ZnO(000$\overline{1}$) surfaces (a) in the as-received state and (b) after exposure to a 20-W remote 20% O_2/80% He plasma for 30 min at 525 °C and 0.050 Torr.

then cleaved into smaller pieces, rinsed *ex situ* in methanol for 5 s and dried in flowing nitrogen. A 40-nm-thick Ti film was subsequently deposited by electron beam evaporation on the entire (0001) face of each ZnO piece. This film served (1) to absorb radiation from the underlying Pt–Rh heater and to conduct heat into the wafer during the cleaning of the (000$\overline{1}$) face and (2) as an ohmic contact.

Low-energy electron diffraction (LEED) of the *ex situ* cleaned ZnO(000$\overline{1}$) surface showed only a bright background, indicative of an amorphous contamination layer. Deconvolution of the O 1s core level peak shown in Fig. 1(a), obtained via XPS studies, ($\pm$0.1 eV uncertainty) revealed that this surface contained 16 at. % [$\sim$1.6 monolayers (ML)] of OH^-, as determined by a peak at 532.3 eV, as well as weakly bound oxygen having a peak at 533.3 eV. One atomic percent of hydroxide is approximately equal to 0.1 ML. The resulting Zn/O atomic ratio was 0.7$\pm$0.1. Reverse bias $I-V$ measurements of the Au contacts on as-received ZnO(000$\overline{1}$) showed μA leakage currents and ideality factors >2, primarily due to the presence of the hydroxide, which increased the surface conductivity.

For all subsequent research, each ZnO(000$\overline{1}$) wafer was placed in an UHV chamber having a base pressure of 5×10^{-9} Torr, exposed to a 20-W remote plasma of 20% O_2/80% He for the optimized times, temperatures, and pressures of 30 min, 525$\pm$20 °C, and 0.050$\pm$0.001 Torr, respectively. In the initial experiments, each wafer was then cooled to 425 °C in the unignited plasma gas and further cooled to room temperature in vacuum. LEED studies revealed a sharp (1$\times$1) hexagonal pattern, while the XPS C 1s core level indicated the complete removal of all detectable carbon. A comparison of Figs. 1(a) and 1(b) reveals a shift in the lattice O core level peak from 530.7 to 530.3 eV due to band bending, which corresponds to a reduction in the OH^- concentration and an associated reduction in surface conductivity.[16,17] The XPS results in Fig. 1(b) also show the complete removal of all detectable weakly bound oxygen; 4$\pm$1 at. % ($\sim$0.4 ML) of the OH^- remained as the sole contaminant with a peak at 532.4 eV. This significant removal of $\sim$1.2 ML of the OH^- was critical for eliminating the proposed accumulation layer[16,17] and for generating a Zn/O atomic ratio of 1.0 $\pm$0.1. Atomic force microscopy studies revealed a rms surface roughness of 0.2$\pm$0.2 nm before and after the plasma clean.

Adsorbed oxygen species on ZnO act as electron acceptors, which lower the surface conductivity.[18,19] This is advantageous for subsequent Schottky barrier formation.[18,19] As such, the initial cooling procedure was altered such that each cleaned sample was cooled in the unignited plasma gas to $\sim$25 °C over 50 min and again exposed to the 20-W O_2/He plasma for 30 s. The final 30 s plasma exposure was found not to adsorb any more oxygen on the surface nor improve rectifying properties and has been deemed unnecessary.

Gold contacts having a thickness and diameter of $\sim$150 nm and $\sim$100 μm, respectively, and arranged in an 8$\times$8 array were subsequently deposited *in situ* via electron beam evaporation through a gold-coated molybdenum shadow mask. The resulting Au/ZnO/Ti structure allowed current to pass through the bulk wafer and reduced the need for complex isolation of the contacts. After removing from UHV, $I-V$ measurements were obtained for as-received, cleaned, and cleaned-and-oxidized samples.

For thermionic emission and V greater than $3kT/q$, the general diode equation in forward bias is

$$J=J_0 \exp\left(\frac{qV-IR}{nkT}\right), \tag{1}$$

where J is the current density, q is the charge of an electron, V is the voltage, I is the current, R is the series resistance, k is Boltzman's constant, and T is the absolute temperature. The saturation current density J_0 is given by $J_0 = A^*T^2 \exp(-\Phi_B/kT)$ where A^* is the Richardson constant. The theoretical value of $A^*=32\ \mathrm{A\,cm^{-2}\,K^{-2}}$ was used in this study.[20] The ideality factors were obtained by fitting the forward bias ln(J)–V curve between 0.1 and 0.2 V over several decades of current and correcting for the substrate series resistance measured directly by $C-V$. Soft breakdown was observed for all contacts presented, as evidenced by nonrepeatable low-leakage-current behavior after biasing to the breakdown voltage. The best results are presented and discussed for all sample types.

Room temperature ($\sim$293 K) $I-V$ measurements of the Au contacts on as-received ZnO(000$\overline{1}$) wafers revealed reverse-bias leakage currents below $\sim$4.6 μA to 4 V reverse bias, as shown in Fig. 2. The ideality factors were >2. These effects were primarily due to the presence of the hydroxide, which increased the surface conductivity. Soft breakdown occurred at $-$4.0 V. Significant improvements in the $I-V$ characteristics were obtained for the Au contacts on a plasma-cleaned ZnO(000$\overline{1}$) surface, as shown in Fig. 3. A barrier height of 0.67$\pm$0.05 eV was calculated based on $J_0 = 6.40\times10^{-5}$ A/cm^2 (2.40×10^{-4} cm^2 contact area). A 36 $\pm$1 nA leakage current was measured to 4 V reverse bias, with soft breakdown at $-$4.5 V. The value of the ideality factor was 1.86$\pm$0.05.

Cooling the cleaned surface in the unignited plasma gas coupled with the 30 s exposure to the plasma at room temperature resulted in a slightly smaller barrier height of 0.60 $\pm$0.05 eV, a higher saturation current density of 2.27×10^{-4} A/cm^2 (2.20×10^{-4} cm^2 contact area), lower values

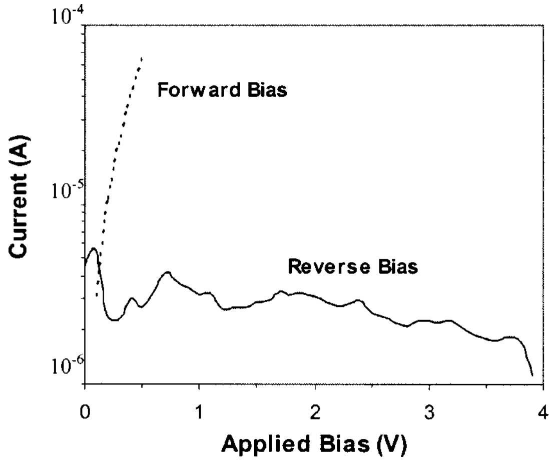

FIG. 2. I–V characteristics for a ~100-μm-diameter Au contact on as-received ZnO(000$\bar{1}$).

of $n=1.03\pm0.05$, a leakage current of ~20 pA to 7 V reverse bias and soft breakdown at this voltage, as observed in Fig. 3. The values of the barrier height correspond well with earlier results of 0.66 eV reported by Neville and Mead.[9] Thirty-three percent of these contacts exhibited leakage currents in the 10-nA range compared to 11% of the contacts that were cooled in vacuum from 425 °C.

Ultraviolet photoelectron spectroscopy measurements in the present research have shown that the electron affinity of a clean ZnO(000$\bar{1}$) surface is 4.1 eV.[21] Calculations of Φ_B for the metals (work functions) of Pt (5.7 eV), Au (5.3 eV), and

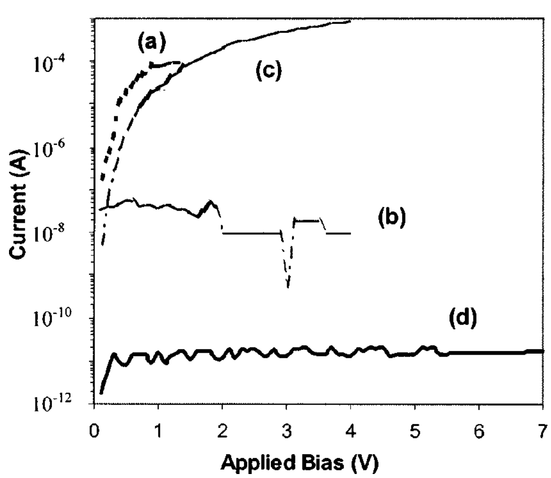

FIG. 3. I–V characteristics for a ~100-μm-diameter Au contact on plasma-cleaned ZnO(000$\bar{1}$) in (a) forward and (b) reverse bias and for a similar contact on a plasma-cleaned-and-oxidized ZnO(000$\bar{1}$) in (c) forward and (d) reverse bias.

Ag (4.4 eV)[22] from the Schottky–Mott model predict values of 1.7, 1.2, and 0.4 eV, respectively. A review of the values of this parameter obtained in this and prior research shows them to be markedly different from the theoretical values and therefore indicative of interface states.

In summary, clean, stoichiometric, highly ordered, and smooth ZnO(000$\bar{1}$) surfaces have been achieved via exposure to a remote O_2/He plasma. As a consequence, significant improvement in the I–V characteristics of as-deposited Au rectifying contacts was observed relative to those characteristics measured for similar contacts deposited on the same surfaces of as-received wafers. The best contact behavior was found for plasma-cleaned surfaces that were subsequently cooled to room temperature in the unignited plasma gas and subsequently exposed to the plasma for 30 s.

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[1] D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[2] F. D. Auret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, and D. C. Look, J. Phys.: Condens. Matter **13**, 1 (2001).
[3] H. Fabricius, T. Skettrup, and Paul Bisgaard, Appl. Opt. **25**, 2764 (1986).
[4] Y. Liu, C. R. Gorla, S. Liang, N. Emanetoglu, Y. Lu, H. Shen, and M. Wraback, J. Electron. Mater. **29**, 69 (2000).
[5] S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu, and H. Shen, J. Cryst. Growth **225**, 110 (2001).
[6] W. Göpel, L. J. Brillson, and C. F. Brucker, J. Vac. Sci. Technol. **17**, 894 (1980).
[7] T. Yamamoto and K. Yoshida, Jpn. J. Appl. Phys. **38**, L166 (1999).
[8] M. Joseph, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys. **38**, L1205 (1999).
[9] R. C. Neville and C. A. Mead, J. Appl. Phys. **41**, 3795 (1970).
[10] H. Sheng, S. Muthukumar, N. W. Emanetoglu, and Y. Lu, Appl. Phys. Lett. **80**, 2132 (2002).
[11] R. P. Vasquez, B. F. Lewis, and F. J. Grunthaner, Appl. Phys. Lett. **42**, 293 (1983).
[12] M. Yamada and Y. Ide, Jpn. J. Appl. Phys. **33**, L671 (1994).
[13] C. M. Rouleau and R. M. Park, J. Appl. Phys. **73**, 4610 (1993).
[14] M. Mintas and G. W. Filby, Z. Naturforsch. A **36A**, 140 (1981).
[15] D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, and W. C. Harsch, Solid State Commun. **105**, 399 (1998).
[16] G. Heiland and P. Kunstmann, Surf. Sci. **13**, 72 (1969).
[17] M. Nakagawa and H. Mitsudo, Surf. Sci. **175**, 157 (1986).
[18] E. Arijs, F. Cardon, and W. Maenhout-Van Der Vorst, Surf. Sci. **17**, 387 (1969).
[19] L. Lagowski, E. S. Sproles, Jr., and H. C. Gatos, J. Appl. Phys. **48**, 3566 (1977).
[20] S. M. Sze, *Physics of Semiconductors Devices* (Wiley, New York, 1981), p. 849.
[21] B. J. Coppa (unpublished).
[22] K. M. Tracy, Ph.D. dissertation, N. C. State University, Raleigh, NC, 2000.