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## Effects of interfacial oxides on Schottky barrier contacts to *n*- and *p*-type GaN

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Schottky contacts were formed on *n*- and *p*-type GaN after either a conventional surface cleaning step in solvents, HCl and HF or with an additional treatment in (NH<sub>4</sub>)<sub>2</sub>S to prevent reformation of the native oxide. Reductions in barrier height were observed with the latter treatment, but there was little change in diode ideality factor. A simple model suggests that an interfacial insulating oxide of thickness 1–2 nm was present after conventional cleaning. This oxide has a strong influence on the contact characteristics on both *n*- and *p*-type GaN and appears to be responsible for some of the wide spread in contact properties reported in the literature. © 1999 American Institute of Physics. [S0003-6951(99)03152-6]

One of the most important areas for GaN device technology is the development of reliable and reproducible contacts, as detailed in a number of recent review articles.<sup>1–6</sup> There is a need for rectifying contacts with a wider range of barrier heights and for ohmic contacts (especially on *p*-GaN) with lower specific resistance ( $\rho_c$ ). In the latter case, reports have appeared on the effect of annealing in O<sub>2</sub> ambient in reducing  $\rho_c$ ,<sup>7</sup> oxidation of Ni/Au metallization and its role in reducing  $\rho_c$ ,<sup>8</sup> the role of surface treatments in determining barrier heights,<sup>9–12</sup> and the use of Ta/Ti contacts with low, but unstable,  $\rho_c$  values.<sup>13</sup> In all of the work on contacts to GaN it is clear that two features are key in determining the electrical properties. The first is the islanded nature of the GaN growth on lattice-mismatched substrates. This can give rise to lateral variations in the local defect density and doping concentrations, which determine current transport. The second is the condition of the surface, since it is clear that the presence of native oxides can significantly affect carrier transport.<sup>1,9–12</sup>

In this letter we show that boiling *n*- and *p*-GaN in (NH<sub>4</sub>)<sub>2</sub>S solutions immediately prior to metal deposition reduces the barrier height for both conductivity types and explains why minimizing oxide formation at the metal/semiconductor interface improves ohmic contact resistance on GaN. An interfacial, insulating surface oxide provides an increased energy barrier for carrier injection into the GaN.

Three different types of samples were employed with *n*-type doping of either  $8 \times 10^{16}$ , or  $10^{18}$  cm<sup>-3</sup>, or *p*-type doping (hole concentration) of  $10^{17}$  cm<sup>-3</sup>. These GaN layers were 1–3 μm thick and were grown on *c*-plane Al<sub>2</sub>O<sub>3</sub> substrates by radio frequency plasma-assisted molecular beam epitaxy.<sup>14</sup> Each of the samples was treated in one of two different ways. The first involved a conventional cleaning process that involved sequential rinsing in acetone, isopropyl

alcohol, and de-ionized water prior to lithography for defining the contact areas. After lithography, the samples were rinsed 60 s in 30 HCl (25 °C) and 30 s in buffered HF to remove the native oxide and then immediately loaded into the *e*-beam evaporator. The second cleaning process was the same as the first, but the last step was a 20 min boil in (NH<sub>4</sub>)<sub>2</sub>S. This solution does not affect the photoresist mask. The (NH<sub>4</sub>)<sub>2</sub>S solution is effective in removing native oxide and prevention of immediate reoxidation, since a Ga–S monolayer is formed on the surface. This should be far less of a hindrance to current flow than the presence of a much thicker native oxide. The samples had Ti/Al or Ni/Au for ohmic contacts, each annealed at 750 °C for 30 s to produce low  $\rho_c$ . The Pt (400 Å)/Au (1500 Å) rectifying contacts were *e* beam deposited with diameters 50–200 μm. The effective barrier heights were obtained from the forward current–voltage (*I*–*V*) characteristics, according to the relation

$$J = A^{**} T^2 \exp\left(-\frac{\phi_b}{kT}\right) \exp\left(\frac{eV}{nkT}\right) \left[1 - \exp\left(-\frac{eV}{kT}\right)\right],$$

where *J* is the current density, *A*<sup>\*\*</sup> is the effective Richardson constant (26.4 A cm<sup>-2</sup> K<sup>-2</sup> for *n*-GaN, 96.1 A cm<sup>-2</sup> K<sup>-2</sup> for *p*-GaN),<sup>1–5</sup> *T* is the diode absolute temperature,  $\phi_b$  is the barrier height, *n* is the ideality factor, *k* is Boltzmann's constant and *e* is the electronic charge.

Figure 1 shows forward (top) and reverse (bottom) *I*–*V* characteristics from the *n*<sup>+</sup> GaN diodes, either with or without the (NH<sub>4</sub>)<sub>2</sub>S treatment prior to Schottky contact deposition. There are several key points in this data. First, the forward current increases as a result of the (NH<sub>4</sub>)<sub>2</sub>S treatment due to a decrease in barrier height from 0.81 eV on the control diode to 0.58 eV on the treated diode. Second, in the linear region of the forward characteristics, the scaling of current with contact diameter is much greater than a power of two. This suggests that there is a nonuniform concentra-

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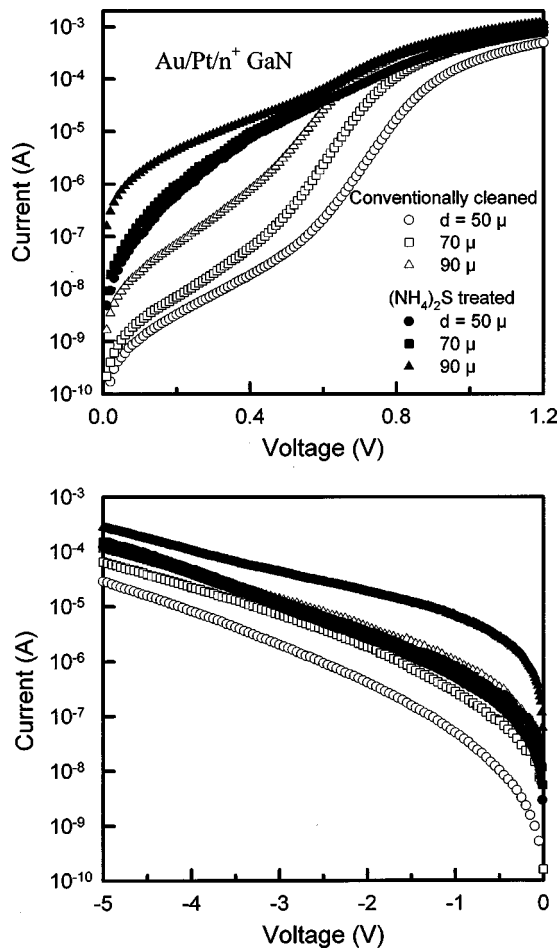


FIG. 1. Forward (top) and reverse (bottom)  $I$ - $V$  characteristics from Au/Pt/ $n^+$  GaN diodes of different diameters, either cleaned in a conventional fashion prior to metal deposition or boiled in  $(\text{NH}_4)_2\text{S}$ .

tion of defects, which are generation-recombination centers. Finally, the reverse leakage current is also increased by the  $(\text{NH}_4)_2\text{S}$  treatment.

Similar data is shown in Fig. 2 for the  $n$ -GaN diodes, at two different rectifying contact diameters. The average barrier height decreased from  $\sim 0.99$  eV on the control diodes to  $\sim 0.83$  eV on the  $(\text{NH}_4)_2\text{S}$  treated samples. Both the forward and reverse current increased as a result of the  $(\text{NH}_4)_2\text{S}$  step. The fact that the diode ideality factors did not improve suggests that  $(\text{NH}_4)_2\text{S}$  is not particularly effective in passivating the surface of GaN.

Figure 3 shows  $I$ - $V$  characteristics from the  $p$ -GaN diodes. These structures showed high currents due to the difficulty in forming high barriers to  $p$ -GaN. The control diodes showed average barrier heights of 0.49 eV, which was slightly reduced to 0.47 eV as a result of the  $(\text{NH}_4)_2\text{S}$  treatment. In these diodes the low bias current scaled with contact diameter, indicating that surface leakage is important. We did not passivate the perimeters of the devices in this work.

Table I shows a compilation of the barrier heights and ideality factors for the  $n^+$ ,  $n$ , and  $p$  diodes. The clear effect of the boiling  $(\text{NH}_4)_2\text{S}$  exposure is to decrease  $\phi_b$ , with less change in the ideality factors. Previous work on the effect of different surface treatments on the  $\rho_c$  of  $p$ -ohmic contacts on GaN has shown that wet chemical solutions that remove the native oxide improve the contact resistance.<sup>9,10,15</sup> For ex-

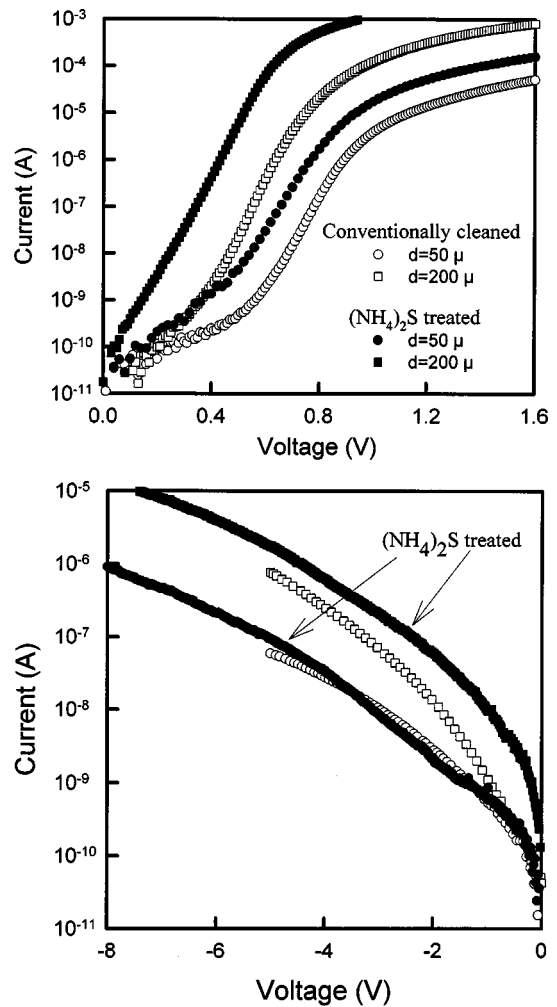


FIG. 2. Forward (top) and reverse (bottom)  $I$ - $V$  characteristics from Au/Pt/ $n$ -GaN diodes of different diameters, either cleaned in a conventional fashion prior to metal deposition or boiled in  $(\text{NH}_4)_2\text{S}$ .

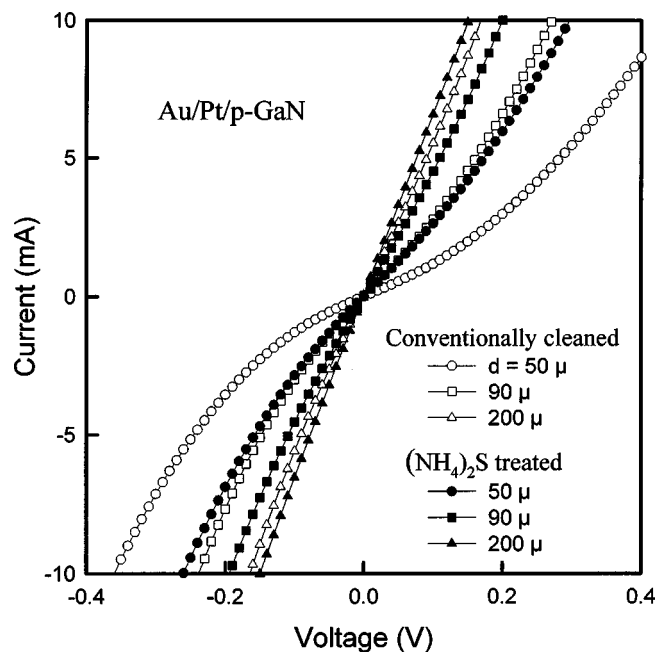


FIG. 3.  $I$ - $V$  characteristics from Au/Pt/ $p$ -GaN diodes of different diameters, either cleaned in a conventional fashion prior to metal deposition or boiled in  $(\text{NH}_4)_2\text{S}$ .

TABLE I. Summary of electrical data for test diodes.

| Sample              | $n$                    |                                           | $\phi_b$ (eV)          |                                           |
|---------------------|------------------------|-------------------------------------------|------------------------|-------------------------------------------|
|                     | Conventionally cleaned | (NH <sub>4</sub> ) <sub>2</sub> S treated | Conventionally cleaned | (NH <sub>4</sub> ) <sub>2</sub> S treated |
| AuPt/<br>$n^+$ -GaN | 1.6–1.8                | 1.8–1.9                                   | 0.81                   | 0.58                                      |
| AuPt/<br>$n$ -GaN   | 1.4–1.6                | 1.3–1.8                                   | 0.99                   | 0.83                                      |
| AuPt/<br>$p$ -GaN   | ~2                     | ~2                                        | 0.49                   | 0.47                                      |

ample, solutions of 1 HNO<sub>3</sub>:3 HCl were found to produce  $\rho_c$  values of  $4.1 \times 10^{-4} \Omega \text{ cm}^2$  for Pd/Au ohmic contacts on  $p$ -GaN, whereas untreated samples had values two orders of magnitude larger.<sup>10</sup> Similarly the use of buffered HF and boiling (NH<sub>4</sub>)<sub>2</sub>S, followed by a final dip in buffered HF prior to metal deposition was able to lower  $\rho_c$  by three orders of magnitude relative to untreated diodes.<sup>15</sup> Following previous treatments of the effect of an interfacial oxide layer of thickness  $\delta$  on the energy barrier for carrier injection, we can write the experimentally measured  $\phi_b$  as<sup>16,17</sup>

$$\phi_b = \phi_{b0} + \Delta\phi,$$

where  $\phi_{b0}$  is the barrier height without the interfacial layer and  $\Delta\phi$  is the additional barrier due to the oxide. The parameter  $\Delta\phi$  is given by  $2kT/\hbar (2m\chi)^{1/2}\delta$ , where  $\hbar$  is Planck's constant,  $m$  is the tunneling effective mass, and  $\chi$  is the mean tunneling barrier. In this work we typically observed  $\Delta\phi$  to be 0.16–0.23 eV for Pt/Au on  $n$ -GaN, which yields an estimate for oxide layer thickness of 1–2 nm on untreated GaN. Figure 4 shows the band diagrams for metal/ $n$  or  $n^+$  GaN structures either with an interfacial oxide (top) and after boiling in (NH<sub>4</sub>)<sub>2</sub>S to remove this oxide (bottom). In the case of  $n$ -GaN the dominant current conduction mechanism probably remains as thermionic field emission (albeit with low barrier height), while for  $n^+$  GaN there may also be a contribution from field emission. Alternative explanations for the increased current in (NH<sub>4</sub>)<sub>2</sub>S-treated samples would be an increase in contact area due to surface roughening or an increase in doping. However, atomic force microscopy and capacitance–voltage measurements showed no significant change in the root-mean-square surface roughness or near-surface doping in our samples.

In conclusion, we found that boiling  $n$ - and  $p$ -GaN in (NH<sub>4</sub>)<sub>2</sub>S prior to deposition of rectifying contacts produced much higher forward and reverse currents in diode structures, due to a decrease in barrier height. This reduction in  $\phi_b$  is correlated with removal of the native oxide that forms an interfacial insulating layer in untreated diodes. Our results show the strong influence of surface treatments on the electrical performance of metal contacts on GaN.

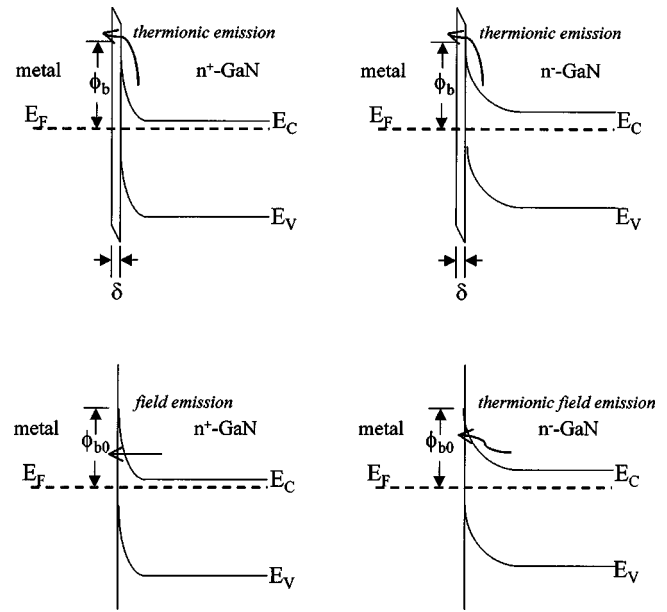


FIG. 4. Energy band diagrams of interface of  $n^+$  GaN or  $n$ -GaN with metal contacts either with the presence of an interfacial oxide (top) or without this layer (bottom).

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