

Aluminum, magnesium, and gold contacts to contamination free *n*-GaN surfaces

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Current-voltage (*I*-*V*) characteristics of Al, Mg, and Au Schottky contacts to atomically clean *n*-GaN(0001)-1×1 surfaces prepared in an ultrahigh vacuum were investigated. The Al/*n*-GaN contact is rectifying at room temperature and becomes Ohmic after annealing at 500 °C. Coupled with previous photoemission spectroscopy data, this result demonstrates that the origin of the Ohmicity is the reaction-induced doping of the interface. For nonannealed interfaces, the Schottky barrier heights determined from *I*-*V* characteristics are in qualitative agreement with the results obtained by photoemission spectroscopy. We find that the ideality factor of the barrier is close to unity for the unreactive interface i.e. Au/GaN, but significantly higher for the reactive interfaces, i.e., Al/GaN and Mg/GaN. Our experimental results suggest that the reaction-induced defects and thermionic field emission play an important role in the electrical behavior of these interfaces.

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I. INTRODUCTION

III-*V* nitride semiconductors have been extensively investigated over the past few years in view of their applications in short-wavelength light emitting devices and high-temperature, high-power electronics.¹⁻³ Metal contacts to these materials are exceedingly important in nearly all applications, and have received a great deal of attention.⁴⁻¹² Unlike for other *III*-*V* (e.g. GaAs, InP) or *II*-*VI* (e.g., ZnSe) compounds, however, comparative studies of injection characteristics and interface electronic and chemical structures measured, e.g., via photoemission spectroscopy are still relatively scarce. Nitrides are wide band gap semiconductors that are supposed to exhibit reduced interface Fermi level pinning (with respect to lower gap *III*-*V*'s) and large dependence of Schottky barrier heights on the metal work function. Yet, these issues are still largely undecided. This rather surprising situation, given the technological importance of the materials, is due in most part to the lack of a "standard" starting nitride surface, which in turn results from the difficulties of preparing clean, stoichiometric, and ordered surfaces by conventional techniques.

An important, and related, issue concerning these materials, as well as most wide band gap semiconductors, is the fabrication of low resistivity stable Ohmic contacts to both *n*- and *p*-type materials. The problem has been satisfactorily solved for *n*-GaN, at least from an operative point of view. Resistivities as low as 10⁻⁸-10⁻⁹ Ω cm² have been obtained for Ti/Al based contacts annealed on *n*-type GaN.⁴ For *p*-GaN on the other hand, the lowest resistivities, obtained with Pd/Au, are typically limited to 10⁻⁴ Ω cm².⁵ However, the mechanism(s) leading to Ohmicity, in particular in the

Al/Ti case, is still being debated. It is still unclear whether the Ohmic contact with these relatively low work function metals results from a Schottky-type behavior, or from electron tunneling through a thin depletion region. The former argument is based on a Schottky-Mott view of metal-GaN interfaces according to which the Fermi level is not strongly pinned by interface states in the semiconductor gap, and the injection barrier results from a small difference between the metal work function and the semiconductor electron affinity.⁶ The transition between rectifying and Ohmic contacts, which is observed upon annealing the interface to temperatures above 400 °-600 °C, is then explained by the fact that the metal consumes the residual semiconductor surface oxide at high temperature, allowing intimate metal-semiconductor contact.⁷ The latter argument relies on a more practical view of metal-semiconductor interfaces according to which the "true" metal-GaN barrier is large, but the width of the depletion region in the semiconductor is considerably reduced by reaction-induced doping, and allows electrons to tunnel between the metal and the conduction band.

Initial studies involving in-vacuum preparation of clean nitride surfaces, controlled deposition of metals and subsequent treatment, e.g., annealing, coupled with an analysis of interface chemistry and electronic structure are bringing answers to these questions,⁸⁻¹⁰ and are suggesting that the simple Schottky-Mott picture is incorrect. However, Schottky barrier heights measured by current-voltage (*I*-*V*) characteristics of Al contacts on chemically prepared GaN samples^{11,12} do not agree with those obtained using photoemission spectroscopy on samples prepared in an ultrahigh vacuum (UHV).^{10,13} Whether these discrepancies reflect real differences in barrier heights or additional effects due to injection through a reacted interface (e.g., doped interface) is unknown. Combined *I*-*V* measurements and photoemission

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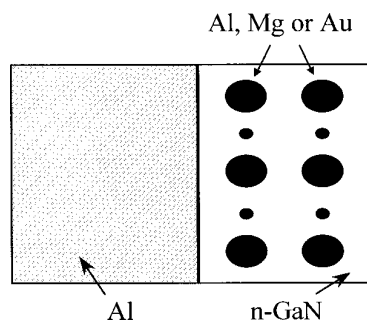


FIG. 1. The schematic diagram of the Schottky diodes used in this study. Only those circular metal contacts near by the Al pad (the first column) were tested.

spectroscopy experiments on identical UHV-prepared metal–GaN contacts are needed to answer these questions.

In the present study we specifically address this problem. We investigate the Al/*n*-GaN rectifying and Ohmic contacts by preparing Al–GaN diodes in UHV to eliminate all factors associated with residual oxygen or other contaminants. We also measure *I*–*V* characteristics on UHV-prepared Mg/ and Au/*n*-GaN Schottky diodes. The results are compared to those obtained from a previous photoemission spectroscopy investigation of interfaces formed under identical conditions.

II. EXPERIMENT

Si-doped ($xxx\text{ cm}^{-3}$) *n*-type, $xxx\text{ }\mu\text{m}$ thick GaN (0001) layers were grown by metal organic chemical vapor deposition on a sapphire at the Naval Research Laboratory. The samples were transported in air and loaded at Princeton University in an UHV system (base pressure 7×10^{-11} Torr) equipped with an ion sputtering gun, Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and a metal evaporation stage. The samples were cradled in tantalum foils that allowed resistive heating up to 1400 °C. Before metallization, the GaN surface was cleaned *in situ* by multiple cycles of nitrogen ion sputtering (0.5 kV) and annealing (900 °C), following precisely the method used to prepare surfaces for photoemission studies of Schottky barrier formation.¹⁰ This method, which is described in detail elsewhere,¹³ has been shown to produce clean surfaces with less than 0.1% of a monolayer of oxygen, as monitored by AES, and exhibiting a sharp (1×1) LEED pattern with low background intensity, indicating good atomic order.

Following the surface cleaning, an Ohmic contact was formed on each sample by depositing in an UHV a large Al pad covering about one-third of the surface (the shaded area in Fig. 1) and annealing the sample at 500 °C. The diodes were then formed by depositing the metal *in situ* (without exposing the surface to ambient) through a 1 and 0.1 mm circular opening in a mask positioned very close to the surface. The deposition was done by thermal evaporation from Al₂O₃ crucibles (Mg) or tungsten filaments (Al and Au) at rates of about 0.1 nm per second. The diode thickness was 100 nm and the diode area was verified with an optical microscope. The Al diodes were subjected to thermal treatment either in UHV or in forming gas. The current–voltage (*I*–*V*)

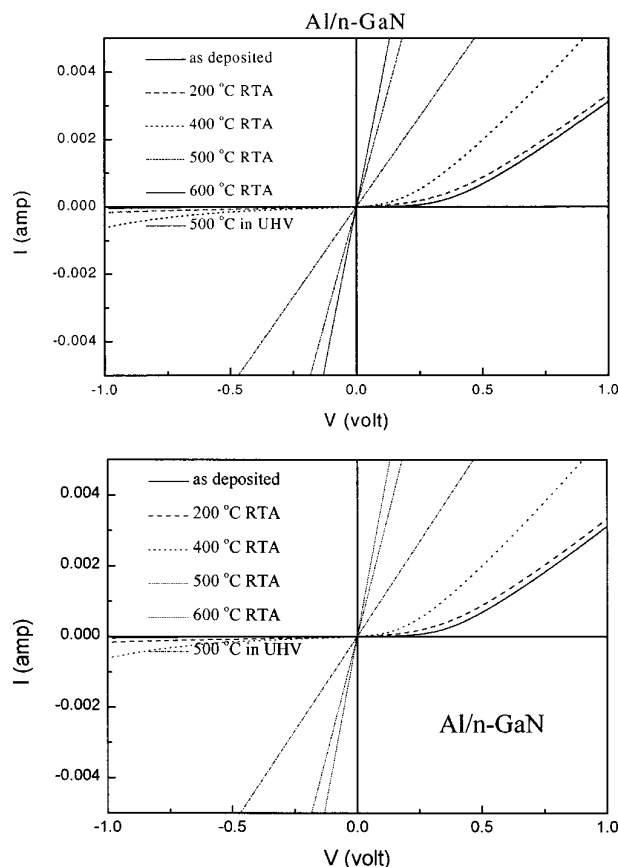


FIG. 2. The *I*–*V* characteristics of Al/*n*-GaN Schottky diodes with rapid thermal annealing at different temperatures.

characteristic curves were recorded outside the UHV system at room temperature with an HP4155A semiconductor parameter analyzer.

III. RESULTS AND DISCUSSION

A. Al Ohmic contact on *n*-GaN

The Al/*n*-GaN barrier was investigated first. Figure 1 shows the schematic diagram of the array of diodes. Because of the large series resistance between the Ohmic contact pad and the diodes, only the dots closest to the pad were investigated. Following the deposition of the Al diodes, the sample was annealed in UHV or taken out for rapid thermal annealing (RTA) in forming gas. Figure 2 shows the *I*–*V* characteristics of the Al/*n*-GaN Schottky diodes (1 mm diam) after a 1 min RTA in forming gas at increasingly higher temperatures. The *I*–*V* characteristics show a rectifying behavior for the as-deposited diodes and for annealing temperatures up to 400 °C. The contact becomes Ohmic at temperatures of 500 °C or above. Another set of experiments, which involved post-metallization annealing in UHV, produced similar results with differences in contact resistivity due to an inaccuracy in the UHV annealing temperature (Fig. 2). The forming gas plays therefore no significant role in the formation of the Ohmic contacts.

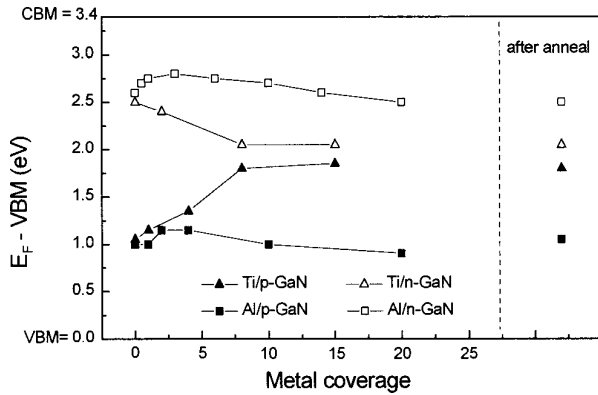


FIG. 3. Fermi level positions at the Al/n-GaN and Ti/n-GaN as a function of metal coverage and upon annealing (from Ref. 10).

These measurements unambiguously show that the reduction of an oxide and the formation of an intimate Al-GaN contact, previously mentioned as a possible mechanism for Ohmic contact formation,⁷ does not play any role in the process. Indeed, the initial GaN surface in our experiment is “oxide free” and the as-deposited contact is rectifying (Fig. 2). The “intimate” Al-GaN contact is therefore already rectifying (the analysis of the barrier height is presented below), in full agreement with two key results previously obtained via photoemission spectroscopy. First, the electron affinity of the GaN(0001)-1×1 has been carefully measured and found to be 3.2 ± 0.1 eV,^{13,14} and the Al work function is 4.2 ± 0.1 eV. Even if the Schottky-Mott model did apply to this interface, the barrier for electron injection would therefore be expected to be of the order of 0.8–1 eV. Second, our photoemission data on the formation of the Al/n-GaN interface show that the Fermi level is stabilized at about 0.8 eV below the conduction band minimum (Fig. 3), leading to a corresponding barrier height for electron injection and in accord with the rectifying nature of the contact. It is also interesting to note that the other constituent of the “technological” Ohmic contact, i.e., Ti, leads to an even larger barrier than Al, as determined via photoemission spectroscopy. The difference between the two barriers has been discussed in Ref. 10.

The photoemission experiments also provide the key to the mechanism of the formation of the Ohmic contact. First, the position of the Fermi level at the Al/n-GaN interface remains unchanged upon annealing above 500 °C (Fig. 3),¹⁰ i.e., the “true” barrier remains essentially unchanged. The same is true of the Ti/GaN interface. The transition to an Ohmic contact is therefore unrelated to any drastic modification of the barrier. Second, the x-ray photoemission data unambiguously show that Al reacts with the N of the lattice to form AlN or $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and that the reaction is greatly enhanced at high temperature (Ref. 10). Our data show that Al films at least 20 Å thick are entirely “consumed” by the high-temperature reaction. Given that the nitrogen used in the reaction originates from the near-interface region of the GaN, the process is believed to introduce a considerable amount of nitrogen vacancies that dope heavily the GaN near the interface. This, in turn, causes a collapse of the depletion

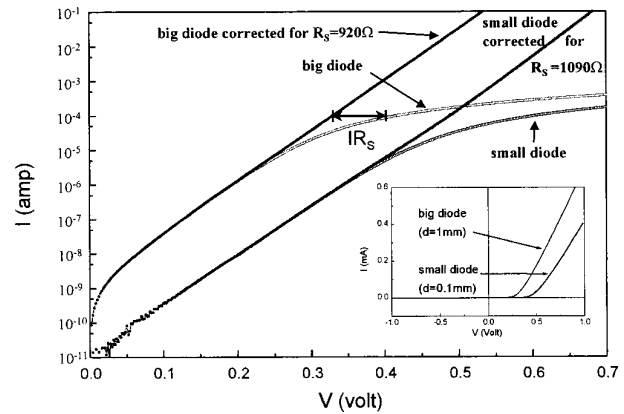


FIG. 4. The forward I - V characteristics of Au/n-GaN Schottky diodes plotted on a logarithmic scale. The dashed and dotted lines show the data after corrected by a series resistance, 920 and 1190 Ω for large and small diodes, respectively. Inset: The I - V characteristics of the Au/n-GaN Schottky diodes with 1 and 0.1 mm contact diameters.

region width that leads to increased electron tunneling through the barrier.

B. Al, Mg, and Au Schottky barriers on n -GaN

The Schottky barrier analysis for Au, Mg, and Al was done on diodes formed through the shadow mask on clean 1×1 surfaces on which the Al Ohmic pad had been previously deposited and annealed at 500 °C in UHV. I - V characteristics were obtained outside a vacuum at room temperature. From thermionic emission theory, the current-voltage characteristic of a diode is given by¹⁵

$$I = I_s \exp\left(\frac{q(V - IR_s)}{nkT}\right),$$

with

$$I_s = SA^{**}T^2 \exp\left(-\frac{\Phi_B}{kT}\right),$$

where I_s is the reverse-bias saturation current, R_s is the series resistance, k is the Boltzmann constant, T is the absolute temperature, n is the ideality factor, S is the area of the diodes, A^{**} is the effective Richardson constant, and Φ_B is the Schottky barrier height. The effective mass of electrons in GaN is $m^* = 0.22m_0$ (Ref. 16), which gives $A^{**} = 26.4 \text{ A/cm}^2 \text{ K}^2$.

The inset of Fig. 4 shows the I - V characteristics of a 1 mm and a 0.1 mm diam Au/n-GaN(0001) diode. These characteristics become approximately linear for a forward bias above 0.5–0.6 V, a result from the relatively high series resistance across the GaN between the diode and the Ohmic contact. From the characteristics and voltages larger than 0.7 V, the series resistances are estimated to be 920 and 1090 Ω for the large and small diodes, respectively. In order to obtain the Schottky barrier height and ideality factor, $\log(I)$ is plotted against the forward bias (Fig. 4). At voltages above 0.25 V for the large diode and 0.37 V for the small diode, the $\log(I)$ - V curves are no longer linear because the voltage dropped across the series resistance dominates the applied

TABLE I. Ideality factors (n) and Schottky barrier heights (Φ_B) measured in this work for Au, Al, and Mg on n -GaN. The Schottky barrier heights measured by photoemission spectroscopy (Ref. 10) are also listed.

	n	Φ_B (I - V) (eV)	Φ_B (PES) (eV)
Au	1.11	0.89	1.2
Al	1.58	0.60	0.8
Mg	1.61	0.62	0.8

voltage. This situation is corrected using the series resistance determined above and removing a voltage equal to IR_S . As shown in Fig. 4, the linear region is then extended over more than six decades of current. The Schottky barrier height and ideality factor are obtained from the intercept I_S for $V=0$ and slope, respectively. The Schottky barrier height is 0.89 eV and the ideality factor is 1.11 for the Au contacts on n -GaN. The same procedure was repeated for Mg and Al contacts. Table I summarizes the Schottky barrier heights and ideality factors obtained for these metals. The table also lists the barriers extracted from our previous photoemission measurements.¹⁰

It is important to recall that the photoemission investigations of metal/nitride interfaces demonstrated that both Al and Mg readily react at room temperature with GaN, whereas Au forms an abrupt and unreacted interface. The reported Schottky barrier height for Au on “practical” n -GaN surfaces, i.e., chemically etched, measured by either I - V or capacitance-voltage characteristics ranges between 0.8 and 1.2 eV,^{17–21} in close agreement with our results. No Schottky barrier I - V data have been reported for Mg/GaN and Al/GaN (all Al/GaN data were reported for annealed, and thus Ohmic, contacts). As listed in Table I, the ideality factor is close to unity for the unreacted Au contact, but is substantially greater than one in the other two cases. Several reasons can be invoked. First, the interfacial layer generated by the chemical reaction upon room temperature deposition is small but non-negligible and could affect the I - V characteristics.²² When the bias is applied, part of the voltage is dropped across the interfacial layers. Thus the barrier height becomes dependent on the bias voltage, leading to an ideality factor larger than one. Second, the current component resulting from carriers trapped and recombining in the depletion region also causes a large ideality factor. The recombination centers could correspond to (1) traps in the as-grown samples, (2) defects generated from the surface preparation, i.e., ion sputtering and high-temperature annealing, and (3) defects generated by an interface reaction. Given that the ideality factor for the unreacted Au contact, which is prepared under the same conditions and on the same samples than the other two, is much smaller, the recombination current is mostly the result of an interface reaction. Another reason for the large ideality factor is the increased tunneling current through the depletion region, which is more heavily doped by nitrogen vacancies in the Al and Mg cases.

The Schottky barrier heights measured from the I - V characteristics are in qualitative agreement with those measured via photoemission, although consistently lower by 0.2–0.3 eV for all the metal contacts investigated here. Such

discrepancies have been noted in the past for a number of semiconductor/metal systems,²³ and have several possible origins. First, there may be an intrinsic difference between barriers obtained with 30–40 Å metallic layers—the maximum thickness manageable with photoemission—and with thick (1000 Å) layers used in the diodes. This is particularly true for interfaces where intrinsic Schottky barrier formation mechanisms like metal-induced gap states compete with Fermi level pinning due to relatively large densities of extrinsic defects brought about by surface preparation and interface chemical reaction. Second, photoemission measured the relative position of energy levels, whereas I - V measurements look at transport across a barrier. The additional current components due to defects and tunneling are not specifically included in the formalism of the Schottky barrier analysis, and could account for a slightly lower barrier measured via transport. Finally, in the present case, the samples used for photoemission were grown on SiC and those used in the diode measurements were grown on a sapphire. Intrinsic differences between these materials, their surfaces, and their interfaces may contribute to the discrepancy. In particular, these factors might lead to different “bare-surface barrier height,” i.e., the energy difference between the Fermi level and the conduction band minimum at the surface prior to contact formation.²⁴ Further investigations will be needed to eventually resolve this issue.

IV. SUMMARY

We investigated Al, Mg, and Au contacts made on contamination-free, well-ordered n -GaN surfaces prepared in an UHV. Our combined I - V and photoemission measurements demonstrate that the Al/GaN Ohmic contact is formed above 500 °C as a result of heavy doping of the GaN depletion region by reaction-induced N vacancies, and not as a result of a lowering of the “true” barrier height. Au/, Al/, and Mg/ n -GaN Schottky barrier heights measured in this experiment are in qualitative agreement with the data obtained from photoemission spectroscopy. The unreacted and abrupt Au/GaN interface gives an ideality factor close to unity. A chemical reaction and resulting defects at the Mg/GaN and Al/GaN contacts lead to considerably larger ideality factors.

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