Thermally stable Schottky contacts on $n$-type GaN using ZrB$_2$

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The electrical properties and thermal stability of ZrB$_2$ Schottky contacts deposited on $n$-type GaN have been studied. As-deposited contacts had a barrier height of 0.80 eV, which decreased to 0.7 eV after annealing at 300 °C, and to 0.6 eV after additional annealing at 400 °C in nitrogen for 20 min. However, the barrier height remained at about 0.6 eV even when the diodes were annealed at 600 °C for 20 min. The Rutherford backscattering spectra of annealed contacts showed no reaction at the ZrB$_2$/GaN interface. These results make ZrB$_2$/GaN Schottky contacts attractive for high temperature device applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2199611]

Over the past decade, rapid developments have been made in the growth and characterization of group III-nitride semiconductors (GaN, InN, AlN, and their alloys). A result of these developments has been the realization of several optoelectronic devices such as ultraviolet photodetectors, laser diodes (LDs), and light-emitting diodes (LEDs), as well as high-power/high-frequency electronic devices such as metal-semiconductor field-effect transistors (MESFETs), modulation doped field-effect transistors (MODFETs), and heterostructure field-effect transistors (HFETs).\textsuperscript{1,5} Schottky contacts with high Schottky barrier height (SBH), low leakage current, and good thermal stability play key roles in many of these devices. For instance, a large SBH greatly improves the breakdown voltage, maximum drain current, and transconductance of field-effect transistors, thus enhancing their noise and power performance. Improvements are being sought for Schottky diodes for operation in the terahertz frequency region.\textsuperscript{6} Investigations of Schottky contacts for $n$-type GaN indicate that the SBH varies approximately with the metal work function. High work function metals such as Ni, W, Pt, Pd, and Au have been used for Schottky contacts on Al$_x$Ga$_{1-x}$N materials, yielding zero-bias barrier heights and ideality factors in the ranges of 0.9–1.2 and 1.1–1.4 eV, respectively.\textsuperscript{7,8} However, subsequent thermal annealing above 500 °C resulted in a reaction between these metal films and the Al$_x$Ga$_{1-x}$N, greatly reducing the barrier heights to the point where the rectifying behavior was destroyed. Conducting oxides [e.g., indium tin oxide (ITO), RuO$_2$, and IrO$_2$] have also been studied with promising results, although significant diffusion of some of the oxide contacts into the nitride layer resulted in degraded electrical characteristics following 500 °C anneals.\textsuperscript{9} Rhenium has also been investigated as the gate electrode for AlGaN/GaN HFETs, but the contacts were found to degrade rapidly after annealing at 600 °C.\textsuperscript{10}

Transition metal borides have excellent electrical and thermal properties that make them candidates for thermally stable Schottky contacts. In particular, there is very close match in the thermal expansion coefficients of ZrB$_2$ and GaN (5.9 × 10$^{-6}$ and 5.6 × 10$^{-6}$ K$^{-1}$, respectively). The lattice mismatch between ZrB$_2$ and GaN on the basal plane is only about 0.6% compared to about 15% with sapphire. The close match in thermal expansion coefficient and lattice constant could lead to stress-free and thermally stable Schottky contacts. Indeed because of the close match, ZrB$_2$ has been investigated both theoretically and experimentally as a lattice-matched substrate for GaN epitaxy.\textsuperscript{11–13} Nitride epilayers grown on ZrB$_2$ were found to exhibit a reduction by two orders of magnitude in threading dislocation density.

TiB$_2$, ZrB$_2$, and W$_2$B make thermally stable Ohmic contacts and diffusion barrier layers on Si and GaAs.\textsuperscript{14,15} In addition, Ohmic contacts formed with Zn$_x$Zr$_{1-x}$B$_2$ bilayers on Mg-doped $p$-type GaN were found to exhibit very good thermal stability.\textsuperscript{16} Recently, Khanna and co-workers have characterized W$_2$B and Cr$_2$B Schottky contacts on $n$-type GaN and found that these contacts exhibit excellent thermal stability.\textsuperscript{17,18} In this letter, we report the successful fabrication and characterization of ZrB$_2$ Schottky diodes on $n$-type GaN.

The samples used in this investigation were Si-doped $n$-type GaN ($n = 1.8 \times 10^{18}$ cm$^{-3}$) grown by metal organic chemical vapor deposition on sapphire substrates. Standard chemical degreasing in acetone, isopropyl alcohol, and de-ionized water was used to prepare the samples for lithographic patterning. Prior to resist coating, the samples were sequentially dipped for 3 min in 1:1:5 of NH$_4$OH:H$_2$O$_2$:H$_2$O, 1:1:5 of HCl:H$_2$O$_2$:H$_2$O, and in buffered HF followed by rinsing in de-ionized water to remove native oxides on the surface. The diodes were fabricated using the donut configuration where the inner circles were the ZrB$_2$ Schottky contacts 30 nm thick with a diameter of 130 $\mu$m, and the outside rings were the Ohmic contacts. The gap between the Schottky and Ohmic contacts was 10 $\mu$m, which was small enough to reduce the series resistance. For the Ohmic contacts, we used Ni$_{0.9}$Ga$_{0.1}$/Au (50/75 nm) annealed in vacuum at 900 °C for 5 min. We found that this metallization scheme produced better Ohmic behavior compared to conventional Ti/Al contact. The metal films including ZrB$_2$ were deposited by dc magnetron sputtering at a...
base pressure of $2 \times 10^{-7}$ Torr and a substrate temperature of about 30 °C. The deposition was carried out at 50 mA current with an Ar flow rate and pressure of 2 SCCM (SCCM denotes cubic centimeter per minute at STP) and 20 mTorr, respectively. Electrical characterization of the Schottky diodes was carried out using a Keithley 2400 Source Meter for current-voltage (I-V) measurements. To investigate the thermal stability of the diodes, the samples were annealed in nitrogen at 300–600 °C in 100 °C increment for 20 min each using a rapid thermal processor (RTP). Additional samples with unpatterned ZrB$_2$ films were prepared under identical conditions for Rutherford backscattering spectrometry (RBS) physical analyses.

Figures 1(a) and 1(b) show the I-V data of the Schottky diodes on linear and semilogarithmic plots. The forward biased I-V was analyzed using the standard thermionic emission relation for electron transport from a metal to a semiconductor with low doping concentration,$^{19,20}$

$$I = A^{*}T^{2} \exp\left(-\frac{q\Phi_{b}}{kT}\right) \left[\exp\left(\frac{qV}{n kT}\right) - 1\right], \hspace{1cm} (1)$$

where $A$ is the area of the Schottky contact, $A^*$ is the effective Richardson constant (26.4 A cm$^{-2}$ K$^{-2}$), $\Phi_b$ is the zero-bias SBH, and $n$ is the ideality factor. From this expression, the plot of ln(I) versus applied voltage (V) gives a straight line (for values of $V \gg 3kT$) from whose slope the value of $n$ can be determined, and from which the intercept of $\Phi_b$ can be obtained. As shown in Fig. 1(b), the linear portion of the ln(I) vs V plot covers about four decades. Eight diodes were measured for the as-deposited ZrB$_2$ Schottky contacts, and the values of $\Phi_b$ ranged from 0.75 to 0.91 eV, with an average of 0.80 eV. This average value decreased slightly to 0.74 eV and to 0.60 eV after a 20 min rapid thermal anneal in nitrogen at 300 and 400 °C, respectively, as shown in Fig. 2. However, further annealing at 500 and 600 °C did not produce any additional decrease in the SBH, which remained at around 0.6 eV. The thermal stability of Schottky contacts is a very important factor in power electronic devices such as AlGaN/GaN high electron mobility transistors (HEMTs) that are used in power amplifiers for communication systems. The stability of ZrB$_2$ Schottky contacts demonstrated here for up to 20 min at 600 °C make these contacts attractive for such applications.

The decrease in $\Phi_b$ following annealing up to 400 °C could be due to the effect of temperature on defect sites in the nitride semiconductor (e.g., Ga and N vacancies) and to defects at the metal/nitride interface. The sputter deposition process could have generated additional defects even though an attempt to minimize sputter damage was made by using a much reduced deposition rate. These defects that act as electron acceptors or donors can diffuse into the GaN semiconductor during annealing, thus affecting the Schottky contact properties.$^{21}$

The average ideality factor ($n$) of 2.2 was calculated using the slope of the ln(I) vs V plot. This value also increased to 3–4 with annealing at 300–600 °C. A value of $n$ greater than one suggests that in addition to thermionic emission there are other carrier transport mechanisms for these diodes such as defect-assisted tunneling. For such nonideal Schottky diodes, it is more useful to determine the flat band barrier height ($\Phi_{BF}$) obtained by modifying the zero-bias barrier height ($\Phi_b$) according the expression$^{22,23}$

$$\Phi_{BF} = n\Phi_b - \frac{kT}{q} \ln \left(\frac{N_C}{N_D}\right), \hspace{1cm} (2)$$

where $N_C$ is the effective density of states in the conduction band, and $N_D$ is the donor concentration. The flat band SBH is independent of the current conduction mechanism; therefore it is a more general parameter that applies even for nonideal Schottky diodes. Theoretical and experimental studies have shown that the flat band SBH yields essentially the same SBH as that determined by the capacitance-voltage (C-V) method.$^{21–24}$ Using the relation

$$N_C = \frac{2}{3} \left(\frac{2 \pi m^*_e kT}{h^2}\right)^{3/2}, \hspace{1cm} (3)$$

we calculated the effective density of states for electrons in the conduction band to be $N_C = 2.6 \times 10^{18}$ cm$^{-3}$ using an effective electron mass $m^*_e = 0.22 m_0$. With this value, and using $\Phi_b = 0.8$ eV and $n = 2.2$, we calculated $\Phi_{BF}$ for the as-deposited ZrB$_2$ Schottky contact. An estimate of the series resistance of the as-deposited Schottky contacts was made using the relation

$$I = I_0 \exp\left[\frac{q(V - IR)}{n kT}\right]. \hspace{1cm} (4)$$

Differentiating this equation with respect to $I$ gives

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**FIG. 1.** (Color online) (a) Linear I-V plot of the diode with as-deposited ZrB$_2$ Schottky contact. (b) Semilogarithmic I-V plot of the diode with as-deposited ZrB$_2$ Schottky contact.

**FIG. 2.** (Color online) Annealing temperature dependence of the Schottky barrier height.
ing temperature observed for the front surface Ga signal of 600 °C/20 min anneal. The slight decreases with anneals from sample to sample.

This material is attractive for high temperature electronic device applications. Additional work to study the stability of this contact beyond 600 °C and to further compare its performance with other contacts such as Ni and Pt is underway.

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