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).[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.[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 $Al_xGa_{1-x}N$ materials, yielding zero-bias barrier heights and ideality factors in the ranges of 0.9–1.2 and 1.1–1.4 eV, respectively.[7,8] However, subsequent thermal annealing above 500 °C resulted in a reaction between these metal films and the $Al_xGa_{1-x}N$, 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.[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.[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.[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_2B make thermally stable Ohmic contacts and diffusion barrier layers on Si and GaAs.[14,15] In addition, Ohmic contacts formed with ZrN/ZrB_2 bilayers on Mg-doped *p*-type GaN were found to exhibit very good thermal stablility.[16] Recently, Khanna and co-workers have characterized W_2B and CrB_2 Schottky contacts on *n*-type GaN and found that these contacts exhibit excellent thermal stability.[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 ($n\sim1.8\times10^{18}$ cm^{-3}) grown by metal organic chemical vapor deposition on sapphire substrates. Standard chemical degreasing in acetone, isopropyl alcohol, and deionized 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 $NH_4OH:H_2O_2:H_2O$, 1:1:5 of $HCl:H_2O_2:H_2O$, 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 μm, and the outside rings were the Ohmic contacts. The gap between the Schottky and Ohmic contacts was 10 μm, 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

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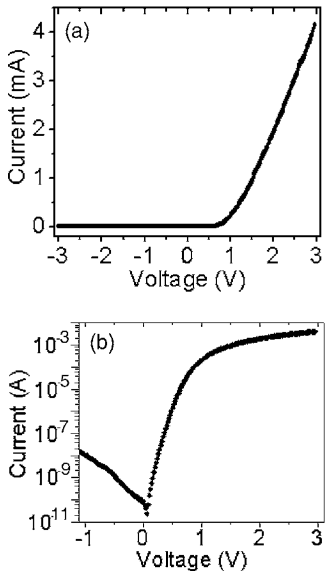

FIG. 1. (Color online) (a) Linear *I-V* plot of the diode with as-deposited ZrB_2 Schottky contact. (b) Semilogarithmic *I-V* plot of the diode with as-deposited ZrB_2 Schottky contact.

base pressure of 2×10^{-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]

$$I = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right)\left[\exp\left(\frac{qV}{nkT}\right)-1\right], \tag{1}$$

where A is the area of the Schottky contact, A^* is the effective Richardson constant (26.4 A cm^{-2}), Φ_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 whose intercept the value of Φ_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 Φ_b ranged from 0.75 to 0.91 eV, with an average of 0.80 eV. This average value decreased slightly to 0.70 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)

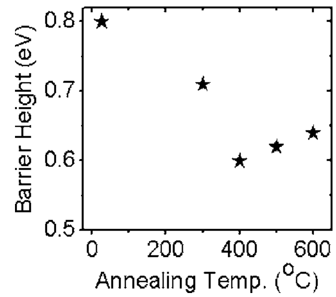

FIG. 2. (Color online) Annealing temperature dependence of the Schottky barrier height.

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 Φ_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/semiconductor 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 (Φ_{BF}) obtained by modifying the zero-bias barrier height (Φ_B) according the expression[22,23]

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

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

$$N_C = 2\left[\frac{2\pi m_n^* kT}{h^2}\right]^{3/2}, \tag{3}$$

we calculated the effective density of states for electrons in the conduction band to be $N_C = 2.6\times10^{18}\ \mathrm{cm}^{-3}$ using an effective electron mass $m_n^* = 0.22 m_o$. With this value, and using $\Phi_B = 0.8$ eV and $n = 2.2$, we calculated Φ_{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

$$I = I_0 \exp\left[\frac{q(V-IR)}{nkT}\right]. \tag{4}$$

Differentiating this equation with respect to I gives

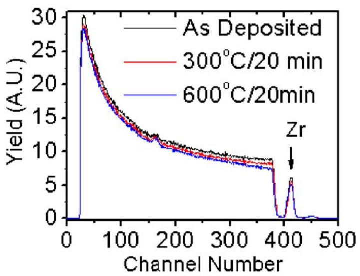

FIG. 3. (Color online) Rutherford backscattering spectroscopy of the ZrB_2/GaN contact.

$$I = \frac{1}{R}\left(\frac{dV}{d\ln(I)}\right) - \left(\frac{kT}{q}\right)\left(\frac{n}{R}\right). \tag{5}$$

The value of R can be obtained when I is plotted against $dV/d\ln(I)$. This procedure gave us values of the series resistance in the range $R=110-350\ \Omega$ for the as-deposited ZrB_2 Schottky contacts.

Figure 3 shows the RBS spectra of the as-deposited and annealed ZrB_2 contacts. As can be seen, there is no evidence of interfacial interactions between the ZrB_2 films and the GaN substrates, which is indicative of thermal stability for the 600 °C/20 min anneal. The slight decreases with annealing temperature observed for the front surface Ga signal (channel number 380) and the Zr signal (channel number 410) are likely the result of beam current integration variations from sample to sample.

The effective Schottky barrier height of 1.75 eV obtained herein for ZrB_2/GaN can be compared with published results for the metals Pt and Ni that are commonly used as Schottky contacts for $Al_xGa_{1-x}N$. As-deposited Pt/GaN and Ni/GaN contacts had an ideality factors of 1.0–1.6 and SBHs of 1.04–1.46 eV.[7,8,25] In addition, the rectifying properties of Pt and Ni contacts were found to deteriorate significantly after anneals at 300–500 °C, with SBH decreasing to 0.47 eV. In contrast, the rectifying properties of the ZrB_2 contacts are not significantly degraded after short anneals at 600 °C.

In conclusion, we have investigated the electrical properties and thermal stability of ZrB_2 Schottky contacts on *n*-type GaN. The zero-bias barrier height for the as-deposited contact was 0.80 eV with a flat band barrier height of 1.75 eV. The barrier height initially decreased during anneals at up to 400 °C, but became stable at around 0.6 eV and remain so for subsequent anneals at 600 °C for 20 min in N_2. The thermal stability of ZrB_2 demonstrated here makes this material 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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[1] S. N. Mohammad, A. Salvador, and H. Morkoc, Proc. IEEE **83**, 1306 (1995).
[2] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Heidelberg, 1997).
[3] N. Stath, V. Harle, and J. Wagner, Mater. Sci. Eng., B **80**, 224 (2001).
[4] S. C. Binari, K. Doverspike, G. Kelner, H. B. Dietrich, and A. E. Wickenden, Solid-State Electron. **41**, 177 (1997).
[5] W. Gu, S. J. Chua, X. H. Zhang, M. S. Hao, J. Zhang, W. Wang, and W. Liu, Phys. Status Solidi A **188**, 329 (2001).
[6] N. Biyikli, I. Kimukin, T. Kartaloglu, O. Aytur, and E. Ozbay, Appl. Phys. Lett. **82**, 2344 (2003).
[7] E. Monroy, F. Calle, T. Palacios, J. Sánchez-Osorio, M. Verdú, F. J. Sánchez, M. T. Montojo, F. Omnès, Z. Bougrioua, I. Moerman, and P. Ruterana, Phys. Status Solidi A **188**, 367 (2001).
[8] D. Qiao, L. S. Yu, S. S. Lau, J. M. Redwing, J. Y. Lin, and H. X. Jiang, J. Appl. Phys. **87**, 801 (2000).
[9] C. M. Jeon and J. L. Lee, J. Appl. Phys. **95**, 698 (2004).
[10] L. Zhou, F. A. Khan, G. Cueva, V. Kumar, I. Adesida, M. R. Sardela, and F. D. Auret, Appl. Phys. Lett. **81**, 1624 (2002).
[11] J. I. Iwata, K. Shiraishi, and A. Oshiyama, Appl. Phys. Lett. **83**, 2560 (2003).
[12] H. Kinoshita, S. Otani, S. Kamiyama, H. Amano, I. Akasaki, J. Suda, and H. Matsunami, Jpn. J. Appl. Phys., Part 2 **40**, L1280 (2001).
[13] R. Liu, A. Bell, F. A. Ponce, S. Kamiyama, H. Amano, and I. Akasaki, Appl. Phys. Lett. **81**, 3182 (2002).
[14] Y. F. Venger, V. V. Milenin, I. B. Ermolovich, R. V. Konakova, D. I. Voitsikhovskiy, I. Hotovy, and V. N. Ivanov, Semicond. Phys., Quantum Electron. Optoelectron. **2**, 124 (1999).
[15] M. Guziewicz, A. Piotrowska, E. Kamińska, K. Gołaszewska, A. Turos, E. Mizera, A. Winiarski, and J. Szade, Solid-State Electron. **43**, 1055 (1999).
[16] E. Kaminska, A. Piotrowska, A. Barcz, D. Bour, M. Zielinski, and J. Jasinski, Mater. Sci. Eng., B **82**, 265 (2001).
[17] R. Khanna, S. J. Pearton, F. Ren, and I. Kravchenko, J. Electrochem. Soc. **152**, G804 (2005).
[18] R. Khanna, S. J. Pearton, F. Ren, I. Kravchenko, C. J. Kao, and G. C. Chi, Appl. Phys. Lett. **87**, 052110 (2005).
[19] E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts* (Clarendon, Oxford, 1988).
[20] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981).
[21] P. Revva, J. M. Langer, M. Missous, and A. R. Peaker, J. Appl. Phys. **74**, 416 (1993).
[22] H. Sheng, S. Muthukumar, N. W. Emanetoglu, and Y. Lu, Appl. Phys. Lett. **80**, 2132 (2002).
[23] L. F. Wanger, R. W. Young, and A. Sugerman, IEEE Electron Device Lett. **4**, 320 (1983).
[24] Vincent W. L. Chin, Martin A. Green, and John W. V. Storey, J. Appl. Phys. **68**, 3470 (1990).
[25] J. K. Kim, H. W. Jang, and J. L. Lee, J. Appl. Phys. **94**, 7201 (2003).