

Improved Schottky Contacts on *n*-Type 4H-SiC Using ZrB₂ Deposited at High Temperatures

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We report on improved electrical properties and thermal stability of ZrB₂ Schottky contacts deposited on *n*-type 4H-SiC at temperatures between 20°C and 800°C. The Schottky barrier heights (SBHs) determined by current-voltage measurements increased with deposition temperature, from 0.87 eV for contacts deposited at 20°C to 1.07 eV for those deposited at 600°C. The Rutherford backscattering spectroscopy (RBS) spectra of these contacts revealed a decrease in oxygen peak with an increase in the deposition temperature and showed no reaction at the ZrB₂/SiC interface. These results indicate improved electrical and thermal properties of ZrB₂/SiC Schottky contacts, making them attractive for high-temperature applications.

Key words: Schottky contacts, Schottky barrier height (SBH), *n*-type 4H-SiC, thermal stability

INTRODUCTION

The materials properties of SiC such as its wide band gap, high thermal conductivity, high electron saturation velocity, and high breakdown field have made it one of the most promising materials for many high-power and high-temperature electronic device applications.^{1–4} Consequently, a great deal of research effort has been put into the study of this material in the past 20 years, leading to the demonstration of new electronic device structures with remarkable performance. The maturation of the SiC technology will significantly impact both civilian and military sectors. Application areas include wireless technologies for commercial and military needs, high efficiency switches for power distribution, harsh environment sensors, and uses in the automobile industry.

At the present time, one of the major limitations to the full performance of SiC-based devices is the Schottky and ohmic metal contacts. In particular,

Schottky contacts with high Schottky barrier height (SBH) and good thermal stability are essential for operations involving high temperature, high gain, and low power consumption.^{5,6} Selection of Schottky contact metals is generally guided by the reaction chemistry at the metal/semiconductor interface and by the Schottky–Mott theory, which predicts the energy barrier Φ_b (barrier height) to the flow of electrons to be given by the relation

$$q\Phi_b = \phi_m - \chi_S \quad (1)$$

where χ_S is the electron affinity of the semiconductor and ϕ_m is the work function of the metal. For this reason, several high work function metals such as Pt, Ni, Au, and Pd have been investigated as Schottky contacts to *n*-type SiC.^{7–9} Although technological advancement has led to the commercial availability of SiC-based Schottky diodes, their performances still require further improvement especially to ensure reproducibility and reduced reverse bias currents of the devices.

Ni and Ti are the metals most widely used in the fabrication of SiC Schottky diodes.^{9–12} However;

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Ni/SiC Schottky diodes have been shown to produce nonideal current-voltage (I-V) characteristics accompanied by dependence of SBH on the surface preparation conditions.¹²⁻¹⁴ Such contacts were improved by sintering the Ni between 500°C and 600°C to form nickel silicide (Ni₂Si). In the process of interfacial solid-state reaction, some SiC material is consumed.¹⁴ However, this process could be undesirable in submicrometer device structures, and Ni/SiC Schottky contacts change to ohmic contact when annealed at ~800°C for 2 min. The formation of silicides or carbides by several refractory metals (e.g., Co, Ni, Cr, Fe, Pt, Pd, and W), including the interdiffusion of other metals such as Pt and Au noted at temperatures as low as 450°C, is indicative of poor thermal stability, which could eventually lead to the degradation of the Schottky characteristics.¹⁵⁻¹⁸ Oxides of Ir and Ru formed by annealing the metals in O₂ have been reported to improve the Schottky barrier heights and thermal stability of the contacts to *n*-type 4H-SiC.¹⁰ The use of refractory metal borides could provide an alternative solution to the problem of interdiffusion and poor thermal stability for Schottky contacts to *n*-type SiC. Refractory metal borides are stoichiometric compounds with narrow composition ranges in contrast to their nitrides and carbides. They possess extended networks of covalently bonded boron atoms resulting in very high hardness, very high melting points, excellent chemical resistance, and yet very low electrical resistance.¹⁹⁻²² In particular, ZrB₂ possesses a very low electrical resistivity of 4.6 μΩ-cm and a high melting point of about 3,220°C for the bulk material, which make it more attractive than its parent metal Zr with resistivity 42 μΩ-cm and melting point 1,852°C.^{23,24} The refractory nature of the borides offers a very attractive advantage as contact metallization for high-temperature device applications. While refractory borides have been investigated for contact and diffusion barrier metallizations on Si and GaAs,²⁵⁻²⁹ there is very little reporting on the investigation of their suitability for Schottky contacts on SiC. Boltovets et al. investigated Schottky contacts on *n*-type 6H-SiC using TiB₂ and found them to have very stable electrical properties under thermal stressing at 1,000°C for 2 min, where the barrier height remained around 0.7 eV and the ideality at 1.5.³⁰ In this report, we present the results of the fabrication and characterization of ZrB₂ Schottky diodes on *n*-type 4H-SiC. Of particular note is the improvement we found in the Schottky barrier characteristics as the substrate temperature during deposition was increased. The SBHs, determined by I-V measurements, increased with the deposition temperature from an average value of 0.87 eV for contacts deposited at 20°C to 1.07 eV for those deposited at 600°C. Physical analysis of the contacts performed using Rutherford backscattering spectroscopy (RBS) revealed a substantial decrease in oxygen with increase of the deposition temperature and showed no reaction at the ZrB₂/SiC interface.

The Schottky contact characteristics have been observed to be strongly dependent on the quality of the metal/semiconductor interface, normally controlled by chemical cleaning.^{31,32} Our results indicate improved electrical characteristics and thermal stability of ZrB₂/SiC Schottky contacts using high-temperature metal deposition, and this makes ZrB₂ a very attractive contact metallization for high-temperature applications.

EXPERIMENT

The samples used in this investigation were from an *n*-type 4H-SiC wafer purchased from Cree Research, Inc. (Durham, North Carolina, USA) and diced into 5 mm × 5 mm squares. The wafer consisted of a 4.6-μm-thick *n*-type epilayer ($N_d \sim 1 \times 10^{16} \text{ cm}^{-3}$) grown 8° off the basal (0001) plane of a 400-μm-thick *n*-type substrate of resistivity 0.019 Ω-cm. The samples were cleaned in boiling acetone and isopropyl alcohol and rinsed in deionized water. After this, a 30-nm-thick sacrificial layer of SiO₂ was grown at 1,150°C and later stripped with buffered hydrofluoric acid followed by rinsing in deionized water. Metal deposition was performed by direct current (DC) magnetron sputtering in a vacuum system with a base pressure of 2×10^{-7} Torr. During the deposition, the Ar plasma was maintained at a pressure of 2 mTorr, a flow rate of 20 standard cubic centimeters per minute, and a current of 50 mA. Ohmic contact was formed on the unpatterned back side of the samples by depositing Ti (25 nm)/Ni_{0.9}Ga_{0.1}(65 nm)/Ti (10 nm) followed by annealing in a flowing nitrogen atmosphere at 950°C for 2 min using a rapid thermal processor (RTP). The Schottky contacts were then fabricated by depositing about 20-nm-thick ZrB₂ films on the epilayer side of the sample, a process that took about 90 min. Prior to deposition of the ZrB₂ Schottky contacts, thermal adsorption was carried out on each sample by vacuum heating at 800°C for 1 hour. In order to study the effect of deposition temperature, five separate samples were prepared and deposited at 20°C, 200°C, 400°C, 600°C, and 800°C. Heating was achieved using a pair of 500-W halogen lamps. A photolithographic technique was used to make circular patterns on the deposited films, and the unwanted ZrB₂ film was acid-etched by a 3-min dip in 3:1 of HCl:HNO₃. The resulting Schottky contacts were circles of diameters varying from 140 to 200 μm. The electrical characterization of the Schottky diodes was performed using current-voltage and capacitance-voltage (C-V) measurements, while RBS was used for physical characterization of the ZrB₂/SiC contacts. Samples for RBS analyses were prepared by depositing the ZrB₂ films on unpatterned SiC samples under identical conditions described previously. To investigate the thermal stability of the diodes, the samples were annealed in nitrogen at 200°C to 600°C in 100°C increments for 20 min each using the RTP.

RESULTS AND DISCUSSION

Figure 1a shows a semilogarithmic plot of the I-V data of the diodes with the Schottky contacts deposited at various temperatures. 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:^{33,34}

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

where A is the area of the Schottky contact, A^* is the effective Richardson constant ($146 \text{ A}\cdot\text{cm}^{-2}\cdot\text{K}^{-2}$), 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 determined. The C-V measurements were

performed on samples deposited at 200°C, 400°C, and 600°C. The capacitance (C) of each Schottky diode as a function of the reverse voltage bias (V) was measured by superposing a small alternating voltage (10 to 20 mV at 1 MHz) on the reverse DC bias. This was then analyzed using the relation

$$\frac{C}{A} = \sqrt{\frac{q\epsilon_S|N_D - N_A|}{2(V_{bi} + |V| - kT/q)}} \quad (3)$$

that can be rewritten as

$$\left(\frac{A}{C}\right)^2 = \frac{2(V_{bi} - kT/q)}{q\epsilon_S N_D} + \frac{2|V|}{q\epsilon_S N_D} \quad (4)$$

where A is the area of the Schottky contact, V_{bi} is the built-in potential, ϵ_S is the semiconductor dielectric constant (9.66 for 4H-SiC), N_D is the doping concentration of the semiconductor, and kT is the thermal energy.³³⁻³⁵ By plotting $(A/C)^2$ versus V , a straight line graph is obtained whose slope is $2/q\epsilon_S N_D$ and the intercept on the V -axis is $V_i = -V_{bi} + kT/q$. From the relation of the SBH and the built-in potential, we obtain

$$\Phi_b = V_i + \frac{kT}{q} \left[1 + \ln\left(\frac{N_o}{N_D}\right) \right] \quad (5)$$

and the value $N_o = 1.69 \times 10^{19} \text{ cm}^{-3}$ was used for the effective density of state for 4H-SiC.³⁶ A typical plot of $(A/C)^2$ versus V for one of our diodes is shown in Fig. 1b. The average value of N_D obtained from these plots was $1.23 \times 10^{16} \text{ cm}^{-3}$, which is close to $1 \times 10^{16} \text{ cm}^{-3}$, the value specified by Cree, Inc., for these samples.

In the determination of the SBH by I-V and C-V methods, five diodes were characterized and the average of the values was used. Figure 2a shows a plot of the SBH versus the deposition temperature of the ZrB₂/SiC Schottky contacts. As can be seen from this figure, there is a remarkable increase of the SBH from 0.87 eV for a deposition temperature of 20°C to 1.07 eV for a deposition temperature of 600°C from the I-V measurements ($\Delta\Phi_b = 0.20 \text{ eV}$). The C-V measurements revealed a similar trend with slightly higher values for the SBH of 1.05 eV for contacts deposited at 200°C to 1.17 eV for contacts deposited at 600°C. Figure 2b shows the variation of the ideality factor (n) with the deposition temperature. It is seen here that the ideality factor decreases from 2.91 for contacts deposited at 20°C to 1.06 for contacts deposited at 600°C, indicating improvement of the interface homogeneity. A non-ideal Schottky diode with ideality factor greater than 1 suggests the presence of other carrier transport mechanisms in addition to thermionic emission. For such a diode, the flat band Schottky barrier height, independent of the current conduction mechanism, provides a more representative value. Thus, for the results of our I-V measurements shown in Fig. 2a and b, the larger ideality factors at

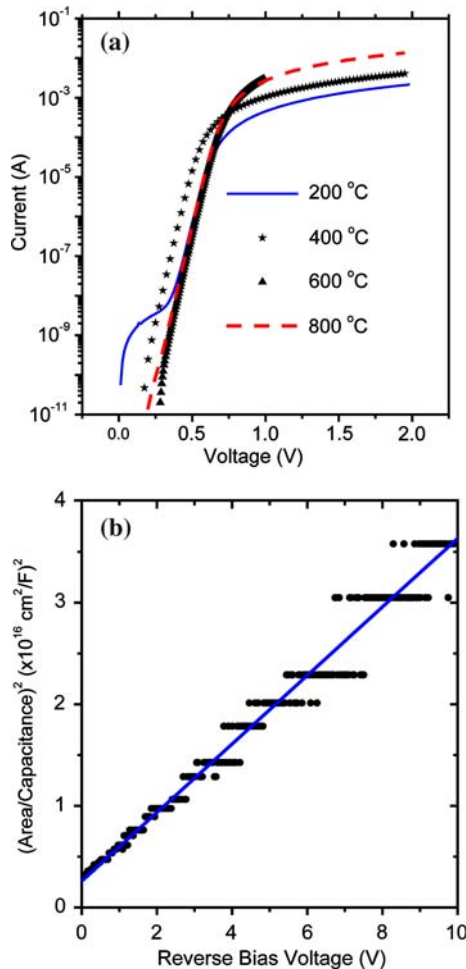


Fig. 1. (a) A semilogarithmic plot of the I-V data of the ZrB₂/SiC diodes with the Schottky contacts deposited at various temperatures. (b) (Color) A typical plot of $(A/C)^2$ versus V for one of the ZrB₂/SiC diodes. The straight line drawn is the least-squares fit of the data points.

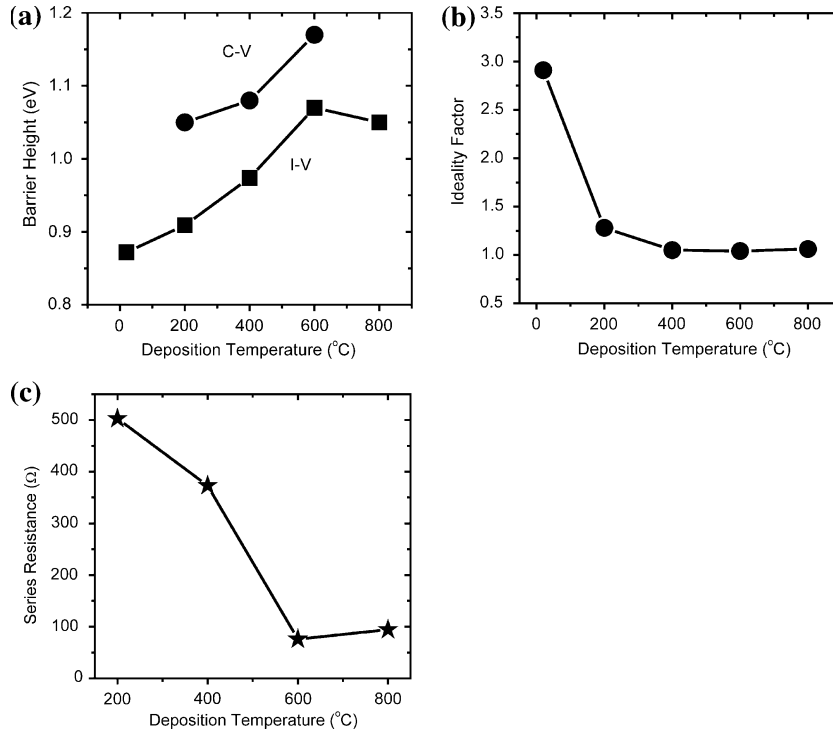


Fig. 2. The variation of the (a) Schottky barrier heights, (b) ideality factor, and (c) series resistance with the deposition temperature of the ZrB₂/SiC Schottky contacts. The barrier heights in (a) were determined by C-V and I-V measurements, as indicated.

lower deposition temperatures result in underestimated barrier heights that can reduce the trend of SBH increase with increasing deposition temperature. However, theoretical and experimental studies have shown that SBH determined by the C-V method essentially matches the flat band SBH.^{37,38} The values of the SBH we determined by C-V measurements shown in Fig. 2a confirm the trend of increasing SBH with the deposition temperature. An estimate of the series resistance (R_S) of the as-deposited Schottky contacts was made using the procedure discussed in Reference 39. Figure 2c shows the variation of the average values of R_S with the deposition temperature. As can be seen here, there is a decrease in the value of R_S from about 502 Ω to 76 Ω as the deposition temperature was varied from 200°C to 600°C and slightly rising to about 94 Ω for contacts deposited at 800°C. The value of R_S for the contacts deposited on the unheated substrate could not be determined accurately and is therefore not reported.

Investigation of the physical structure at the ZrB₂/SiC interface was performed by the Rutherford backscattering spectroscopy analysis of two samples, one with the ZrB₂ Schottky contact deposited at 20°C and the second one with the contact deposited at 600°C. The spectra from these samples are shown in Fig. 3a and b, and the inset in Fig. 3b is an expanded view of the spectra at the location of the oxygen backscatter signal. As can be seen in these spectra, there is a remarkable decrease in the

oxygen content in the film deposited at 600°C (Fig. 3b) compared to the film deposited at 20°C (Fig. 3a). These results imply that a substantial amount of oxygen was removed from the ZrB₂/SiC by heating the substrate during deposition.

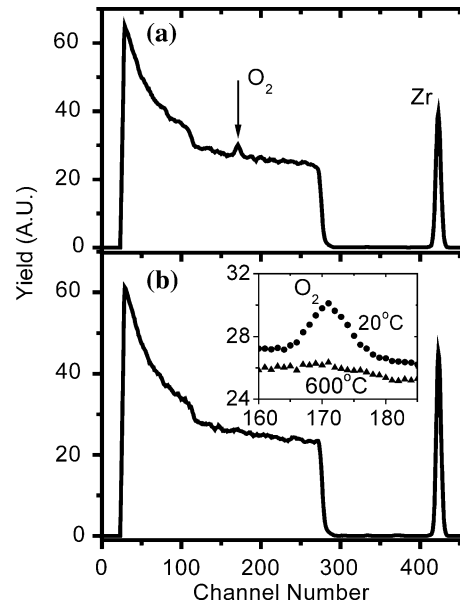


Fig. 3. The spectra from the Rutherford backscattering spectroscopy measurements of two samples with the ZrB₂ contact deposited at (a) 20°C and (b) 600°C. The inset in (b) is an expanded view showing the oxygen content in spectra (a) and (b).

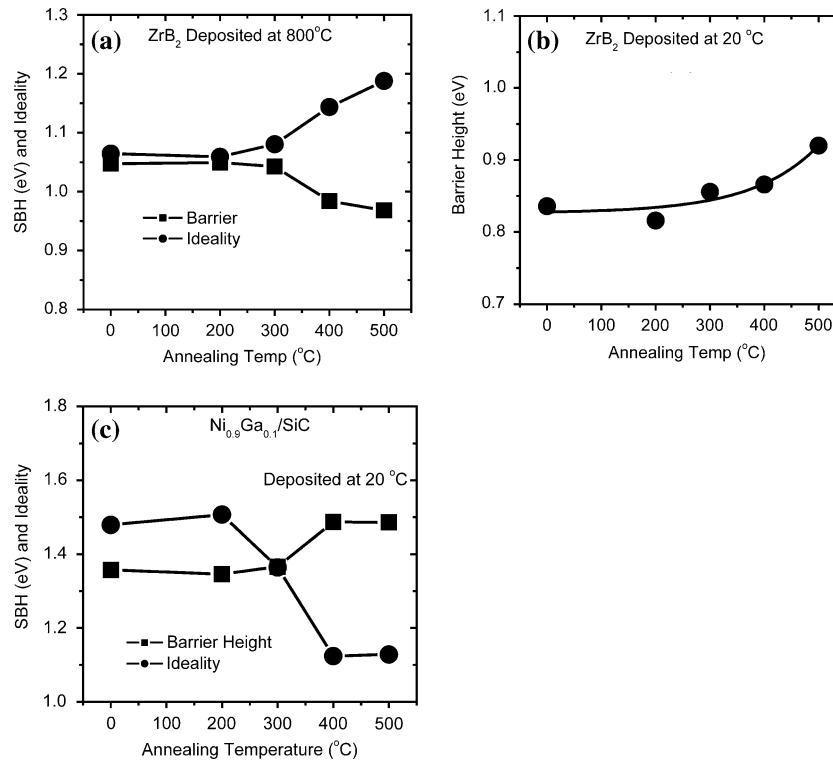


Fig. 4. (a) The plot of SBH and the ideality factor (*n*) as a function of annealing temperature for ZrB₂/SiC contacts deposited at 800°C and later sequentially annealed by RTP in nitrogen for 20 min each time. (b) The plot of SBH as a function of annealing temperature for ZrB₂/SiC contacts deposited at 20°C and later sequentially annealed by RTP in nitrogen for 20 min each time. (c) The plot of SBH and the ideality factor (*n*) as a function of annealing temperature for Ni_{0.9}Ga_{0.1}/SiC contacts deposited at 20°C and later sequentially annealed by RTP in nitrogen for 20 min each time.

In the investigation of thermally stable ohmic contact to *p*-type SiC using CrB₂, Oder et al. reported the removal of a significant amount of O₂ from the CrB₂/SiC interface in the form of volatile B₂O₃ following high-temperature annealing.^{40,41} Similar removal of O₂ was also reported during the intentional oxidation of TiB₂, where B₂O₃ was observed to form and evaporate rapidly at high temperatures.⁴² We believe that the removal of O₂ from the ZrB₂/SiC interface similarly occurs in the form of oxides such as B₂O₃ or H₃BO₃ known to be volatile at 300°C.⁴³

As the presence of impurities such as O₂ at the interface is known to contribute to undesirable electrical characteristics, this removal of O₂ is possibly the main reason for the improvement of the Schottky characteristics we have observed. In addition, Zr is known to be quite reactive with oxygen, and in this case, it may also be getting oxygen from the heated SiC surface.^{44,45} The RBS spectra further reveal an absence of any substantial reaction between the ZrB₂ film and the SiC, indicating the thermal stability of this contact. However, a minimal interaction with possible silicide or carbide formation cannot be completely ruled out from these spectra, and additional analysis is underway to further study the interface chemistry of the ZrB₂/SiC contact deposited at elevated tem-

peratures. Contamination or inhomogeneities at the interfacial region during device processing are usually the cause of deviations from the ideal behavior in the electrical characteristics of Schottky contacts on SiC. Thus, the control of the interface quality through an effective surface preparation prior to metal deposition, or by postdeposition annealing, helps to improve the quality of the Schottky contacts.

To further study the thermal stability of the ZrB₂/SiC Schottky contact, the diodes deposited at 20°C and at 800°C were annealed for 20 min in a nitrogen environment from 200°C to 500°C at intervals of 100°C. At each interval, I-V measurements were carried out to obtain the SBH and ideality factor. As shown in Fig. 4a, the SBH of the diodes deposited at 800°C stays constant at 1.05 eV when annealed up to 300°C and then decreases slightly to 0.97 eV ($\Delta\Phi_b = 0.08$ eV) after sequential annealing up to 500°C. On the other hand, the SBH of the diodes deposited at 20°C indicates a slight increase in the SBH from 0.85 eV to about 0.92 eV ($\Delta\Phi_b = 0.07$ eV) (Fig. 4b), with the ideality factor (not shown) decreasing on average from 3.1 to 2.0 after sequential annealing up to 500°C. The minimal change in the SBH during the sequential annealing up to 500°C, which may be accounted for by the large values of the ideality factors, shows that

ZrB₂/SiC Schottky contacts exhibit good thermal stability. ZrB₂-based contacts have recently been shown to exhibit better thermal stability when used as ohmic or Schottky contacts on GaN and ZnO materials in comparison to conventional contacts.^{39,44,46,47} For comparison, we fabricated Schottky contacts using Ni_{0.9}Ga_{0.1} deposited on unheated SiC cut from the same wafer used for the ZrB₂ contacts. When annealed under the conditions described previously, it was found that the SBH determined by I-V increased from 1.36 eV to 1.49 eV and the ideality factor decreased from 1.5 to 1.1 after sequential annealing up to 500°C (Fig. 4c).

CONCLUSIONS

In conclusion, we have investigated the Schottky characteristics of ZrB₂ deposited on 4H *n*-type SiC. The SBH was found to increase with the deposition temperature, from 0.87 eV for unheated substrate to 1.07 eV when the substrate was kept at 600°C during deposition. The RBS spectra showed a significant decrease in the oxygen content of ZrB₂/SiC when the SiC substrate was heated during deposition. The SBH however was found to vary only by 0.08 eV when the contact was subjected to annealing from 200°C to 500°C for 20 min. Our results not only demonstrate the thermal stability of ZrB₂, but also provide a method that could be used to remove unwanted contaminations at a metal/semiconductor interface to ensure an intimate contact with good electrical characteristics.

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