Schottky-barrier behavior of metals on *n*- and *p*-type 6*H*-SiC

M. O. Aboelfotoh

Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7907

C. Fröjdh and C. S. Petersson

The Royal Institute of Technology, Solid State Electronics, P.O. Box E229, S-164 40 Kista-Stockholm, Sweden

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The Schottky-barrier height of a number of metals (Ti, Ni, Cu, and Au) on *n*- and *p*-type Si-terminated 6H-SiC has been measured in the temperature range 150–500 K. It is found that the barrier height to *n*-type 6H-SiC does not exhibit a temperature dependence, while for *p*-type 6H-SiC the change in the barrier height with temperature follows very closely the change in the indirect energy gap in 6H-SiC. These results are inconsistent with models of Schottky-barrier formation based on the concept of a charge neutrality level. Furthermore, the present results cannot be reconciled with a defect pinning mechanism, contrary to the conclusions of earlier studies on III-V compound semiconductors. We suggest that chemical bonding at the metal-semiconductor interface plays an important role in determining the Schottky-barrier height.

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I. INTRODUCTION

Metal-silicon carbide (SiC) interfaces play very important roles in many high-performance devices in optoelectronic, high-temperature, high-frequency, and power applications. Understanding Schottky-barrier formation at these interfaces on a fundamental basis is therefore of great interest. Experimentally, Schottky-barrier heights (SBHs) on most covalent semiconductors are found to depend weakly on the metal work function, i.e., the Fermi level is pinned relative to the semiconductor. Theoretical models have been based largely on the pinning mechanisms of the intrinsic metal-induced gap (MIG) states¹ or the native defects.² The role of MIG states and defects in the formation of Schottky barriers at the interfaces with group-IV and III-V semiconductors has been discussed by several authors.^{3,4}

One approach to distinguish between the MIG states and defect models, however, is to use temperature as a perturbation under which the charge neutrality level and the defect levels would behave differently. The charge neutrality level reflects an average of the whole band structure, and therefore its shift with the temperature is expected to be small. Thus, if the charge neutrality level (MIG states) model is valid, the temperature dependence of the barrier height on n- and *p*-type semiconductor should reflect the individual temperature shift of the conduction and the valence band, respectively. On the other hand, it has been argued,⁵ based on a thermodynamic concept introduced by Van Vechten and Thurmond,⁶ that if defects govern the Fermi-level pinning, then the ionization entropy of the defects would control the temperature dependence of the barrier height. Van Vechten and Thurmond⁶ noted that a nonzero ionization entropy ΔS_{I} comes from a change of the lattice vibration frequencies in the vicinity of the defect upon ionization (from ω to ω'): $\Delta S_I = -k \Sigma_i \ln(\omega_i'/\omega_i)$. Consider now the case of a Fermi level pinned by a defect whose ground-state wave function is of a bonding type. The ionization of such a defect involves the release of a free carrier, and is nothing but a bond breaking, similar to that occurring during the creation of an

electron-hole pair. The softening of the vibrational modes of the lattice which results when an electron-hole pair is excited across the band gap is the same as the one which results when an electron is excited from the defect bonding state.⁶ The latter results in similar ionization entropies for both excitations, and as a consequence, in an *n*-type semiconductor the barrier height will have a temperature dependence comparable to the temperature dependence of the energy gap. In the opposite case of a pinning by an antibonding defect state, the *n*-type barrier height will be largely independent of temperature. Here a small ΔS_I is expected for the ionization of the antibonding defect state.⁶ Thus a consequence of Fermilevel pinning by defect levels is that the temperature dependence of the barrier height will depend upon the nature of the defect.

To access the validity of the proposed models, we have measured the dependence of the barrier height on temperature for a number of metals (Ti, Ni, Cu, and Au) on n- and p-type Si-terminated 6H-SiC in the temperature range 150-500 K. We find that the barrier height to *n*-type 6*H*-SiC does not exhibit a temperature dependence, while for *p*-type 6H-SiC the change in the barrier height with temperature follows very closely the change in the indirect energy gap in 6H-SiC. The same type of behavior was observed earlier for metal-Si (Refs. 7 and 8) and metal-group III-V semiconductor⁵ interfaces, and was interpreted in terms of Fermi-level pinning by defect levels.⁵ Our results cannot, however, be reconciled with defect pinning. Furthermore, our results are inconsistent with the charge neutrality level (MIG states) model of the Schottky barriers. We suggest that chemical bonding at the metal-semiconductor interface plays an important role in the formation of the Schottky barrier.

II. EXPERIMENTAL PROCEDURE

A. Sample preparation

The nitrogen and aluminum doped $\sim 5-\mu$ m-thick *n*- and *p*-type 6*H*-SiC epitaxial layers used in this study were grown on Si-terminated (0001) surfaces of vicinal (3°-4° off

(0001) toward [11 $\overline{2}$ 0]) n^+ and p^+ 6H-SiC substrates by chemical vapor deposition.⁹ The epitaxial layers, ranging in impurity concentration from $\sim 2 \times 10^{16}$ to 1×10^{17} cm⁻³. were subsequently thermally oxidized to a thickness of ~ 75 nm. To prepare the surface the samples were cleaned in sequence using a 10% hydrofluoric acid solution to remove the oxide layer and a thermal desorption at 700 °C for 15 min in ultrahigh vacuum ($\sim 1 \times 10^{-9}$ Torr), after which the sample surface exhibited a 1×1 reflection high-energy electron diffraction pattern. X-ray photoemission spectroscopy (XPS) analysis¹⁰ revealed that such a cleaning procedure leaves $\sim \frac{3}{4}$ ML of oxygen on the Si-terminated surface and that the oxygen is bonded primarily as SiO_x. Schottky diodes were then prepared by deposition of \sim 100-nm-thick Ti, Ni, Cu, or Au films on the samples. The metal films were deposited using electron-beam evaporation in a pressure of 1 $\times 10^{-9}$ Torr at a rate of 1 nm/s, with the samples kept at room temperature. For current-voltage (I-V) and capacitance-voltage (C-V) measurements the deposition was made through a metal mask defining diodes of 200 and 400 μ m in diameter. The samples were subsequently annealed for 20 min at temperatures up to 400 °C in an atmosphere of pure nitrogen.

B. Schottky-barrier height determination

Schottky-barrier heights for *n*- and *p*-type 6*H*-SiC(0001) were determined using I-V measurements at temperatures in the range 200-400 K. The I-V data were analyzed in terms of the thermionic emission theory:¹¹ $J = J_0 \exp(qV/nkT)$ [1] $-\exp(-qV/kT)$], where the ideality factor n and the saturation current density J_{ρ} were found by a least-squares fit. The low ideality factors and the fact that the ideality factors were independent of temperature showed that the current transport in our diodes is well described by the thermionic emission theory. The barrier height Φ_B was then extracted from J_a = $A^* T^2 \exp(-q\Phi_B/kT)$, where A^* is the effective Richardson constant. The barrier height and the Richardson constant A^* were also determined from the activation energy analysis¹¹ of $\ln(J_{\rho}/T^2)$ versus 1/T. The barrier heights for nand *p*-type 6H-SiC(0001) were also determined from the C-V characteristics by a linear extrapolation to the intercept on the voltage axis of the C^{-2} versus the voltage plot.¹¹ The measurements were carried out at frequencies ranging from 1 kHz to 1 MHz, and with the samples held at temperatures in the range 150-500 K. The barrier height was also measured with the use of the internal photoemission (IPE) technique. In these measurements, light from an Oriel 1/8-m monochromator equipped with a 150-W xenon arc lamp was incident on the diode through the SiC (back illumination). The photocurrent without application of an external bias voltage was detected by using the lock-in technique and was normalized with respect to the incident photon flux as measured by an optometer with a calibrated Si photodiode. The experimental setup has been described in detail elsewhere.¹² The Fowler plot, i.e., the square root of normalized photocurrent versus photon energy (from 0.9 to 2.7 eV) then yielded a direct determination of SBHs by a linear extrapolation of the curve to zero current.⁷ Although this paper deals mostly with Siterminated interfaces, results for *C*-terminated interfaces are reported to emphasize the effect of interface atomic structure on the barrier height.

III. RESULTS

A. *n*-type 6*H*-SiC(0001)

In Fig. 1(a) we show, as an example, the forward I-Vcharacteristics obtained at 295 K for Ti and Ni on *n*-type 6H-SiC(0001) after a 400 °C anneal. The I-V characteristics yield ideality factors of 1.04-1.06 and SBHs, using a Richardson constant of $A^* = 194 \text{ A cm}^{-2} \text{ K}^{-2}$,¹³ of 0.96 and 1.08 eV for Ti and Ni, respectively. In Fig. 2(a) the roomtemperature Fowler plots are shown for Ti and Ni on *n*-type 6H-SiC(0001). The plots are linear over an energy range of almost 1 eV above the threshold and yield SBHs which are in very good agreement with those deduced from the I-Vmeasurements (see Table I). Note that the 6H-SiC conduction band has a single minimum close to the M point at the zone edge,¹⁴ which contributes to the photocurrent. For Ti and Ni in the as-deposited state the SBHs deduced from the I-V and IPE measurements at 295 K are 0.86 and 1.07 eV, respectively. It should be noted that the SBH values are given here without any image force lowering correction (which for these contacts is calculated to be 0.03-0.04 eV). Waldrop and Grant,¹⁰ using x-ray photoemission spectroscopy, showed that for Ti on Si-terminated 6H-SiC, roomtemperature deposition leads to an interfacial chemical reaction with the formation of TiC and TiSi_x and to a chemical reduction of SiC_r , and that annealing at 400 °C increases the interface chemical reactivity. The above results thus indicate that the increase in interface reactivity during the 400 °C anneal results in an increase of ~ 0.1 eV in the SBH of Ti. For Ni on Si-terminated 6H-SiC, on the other hand, no chemical reaction occurs at room temperature and the interface remains inert during a 400 °C anneal.

The forward I-V characteristics obtained for Ti on n-type 6H-SiC(0001) as a function of temperature are shown in Fig. 1(b). The results clearly show that the ideality factor and the barrier height are independent of temperature (results for Ni, Cu, and Au are very similar). Moreover, the dependence of $\ln(J_o/T^2)$ on 1/T is linear in the temperature range 200– 400 K, as shown in Fig. 1(c), with a slope giving a barrierheight value at 0 K of 0.97 eV. Assuming that the temperature dependence of the barrier height is of the form $\Phi_{Bn}(T) = \Phi_{Bn}(0) - \alpha T$, where α is the temperature coefficient of the barrier height, the intercept of the straight line with the ordinate in Fig. 1(c) is then $\ln A^* + (q\alpha/k)$.¹¹ For $\alpha = 0$ the intercept yields a value for the Richardson constant $(187 \text{ A cm}^{-2} \text{ K}^{-2})$ in good agreement with the A* related to the 6H-SiC conduction-band minimum.13 Furthermore, the shift of the Fowler plots in Fig. 2(a) with temperature is found to be negligible.¹⁵

In Fig. 3 we show typical C-V characteristics obtained at 295 K for Ti, Ni, and Cu on *n*-type 6*H*-SiC(0001) after a 400°C anneal. In the calculation of the energy difference between the bottom of the conduction band and the Fermi level in the bulk we have used a value for the effective den-



FIG. 1. (a) Forward current-voltage characteristics at 295 K of Ti and Ni on *n*-type Si-terminated 6*H*-SiC after a 400 °C anneal. (b) Forward current-voltage characteristics of Ti on *n*-type Si-terminated 6*H*-SiC as a function of temperature. (c) Temperature dependence of the forward current measured at zero applied voltage. The diode diameter is 400 μ m.

sity of states in the conduction band (which is proportional to $T^{3/2}$) of 1.23×10^{19} cm⁻³ at 300 K.¹⁶ The data in Fig. 3 then yield SBHs which agree well with those deduced from the *I-V* measurements (Table I) and are again independent of temperature, as shown in Fig. 4.

B. *p*-type 6*H*-SiC(0001)

Figure 5(a) shows typical C-V characteristics obtained at 295 K as a function of frequency for Ti on p-type 6H-SiC(0001) after a 400 °C anneal (data for Ni, Cu, and Au are very similar). At frequencies ranging from 1 to 10 kHz no frequency dependence of the C-V curves is observed, indicating that the C-V curves are free from deep

level effects.¹⁷ Quintanilla *et al.*,¹⁸ using admittance spectroscopy, reported a value for the emission rate of the Al impurity level (~0.23 eV above the top of the valence band) of 3×10^5 s⁻¹ at 172 K, which is sufficiently high that the impurity level is able to follow a small signal with frequencies in the range of 1 to 10 kHz at and above 172 K. Using a value for the effective density of states in the valence band of 4.8×10^{18} cm⁻³ at 300 K,¹⁶ the data obtained at 1 kHz yield a SBH of 2.04 eV for Ti, in very good agreement with the value reported by Waldrop¹⁹ using XPS measurements. On the other hand, at higher frequencies (1 MHz) and 295 K not all of the impurity level charge participate in the small-signal measurement, resulting in a decrease in capacitance¹⁸ and a shift of the intercept on the voltage axis in a direction



FIG. 2. (a) Square root of the photocurrent vs photon energy at 295 K for Ti and Ni on *n*-type Si-terminated 6H-SiC. The Fowler plot gives SBHs of 0.98 and 1.06 eV, respectively. (b) Square root of the photocurrent vs photon energy at 295 K for Ti and Ni on *p*-type Si-terminated 6H-SiC. The Fowler plot gives SBHs of 2.04 and 1.85 eV, respectively.

characteristic of higher apparent barrier height. However, as can be seen from Fig. 5(b), at 440 K the impurity level emission rate becomes sufficiently high that the C-V curve measured at 1 MHz lies near the low-frequency curves, and, at 500 K, it is coincident with and extrapolates to yield the same barrier height as the low frequency curves. Thus it is clear that reliable values for the *p*-type barrier height can be obtained over a wide range of temperature only at low frequencies.

In Fig. 5(c) we show typical C-V characteristics obtained at 1 kHz as a function of temperature for Ni on p-type 6H-SiC(0001). The data yield a SBH of 1.54 eV at 295 K, in very good agreement with the value deduced from XPS



FIG. 3. Capacitance-voltage characteristics of Ti, Ni, and Cu on *n*-type Si-terminated 6*H*-SiC after a 400 °C anneal. Measurements are performed at 295 K at a frequency of 1 MHz. The diode diameter is 400 μ m.

measurements.¹⁹ It is also clear from the data in Fig. 4 that the barrier height decreases with increasing temperature with a coefficient almost equal to that of the indirect energy gap in 6H-SiC.²⁰ The temperature variation of the barrier height for Ti, Cu, and Au is very similar. In Fig. 2(b) the roomtemperature Fowler plots are also shown for Ti and Ni on p-type 6H-SiC(0001). Again, the plots are linear over an energy range of 0.8 eV above the threshold and yield SBHs which agree well with those deduced from the C-V and I-Vmeasurements (see Table I). In addition, the temperature shift of the Fowler plots is found to be almost equal to the shift of the 6*H*-SiC energy gap.¹⁵ Values of the *n*- and *p*-type SBHs (Φ_{Bn}, Φ_{Bn}) at 295 K for the metals studied here are summarized in Table I. Also listed are the SBH values reported by Waldrop and Grant¹⁰ and Waldrop¹⁹ using XPS measurements.

IV. DISCUSSION

The SBH data in Fig. 4 clearly demonstrate that for all metals studied here, the *n*-type SBH does not exhibit a temperature dependence, and that the change in the *p*-type SBH with temperature follows very closely the change in the indirect energy gap in 6H-SiC. As mentioned earlier, the same type of behavior was observed in a study of the temperature dependence of the barrier height on Si (Refs. 7 and 8) and on III-V compound semiconductors,⁵ which Revva *et al.*⁵ interpreted in terms of Fermi-level pinning by defect levels.

TABLE I. Values of SBHs at 295 K for Ti, Ni, Cu, and Au on n- and p-type Si-terminated 6H-SiC.

Barrier height (eV)								
Metal	$\Phi_{{\scriptscriptstyle B}n}^{ m IV}$ a	$\Phi_{Bn}^{\mathrm{IPE}\ \mathrm{a}}$	$\Phi_{Bn}^{ m CV}$	$\Phi_{Bn}^{ ext{XPS b}}$	$\Phi_{Bp}^{ m IV}$ a	$\Phi_{Bp}^{\mathrm{IPE}\ \mathrm{a}}$	$\Phi^{ m CV}_{{\it Bp}}$	$\Phi_{{\it B}p}^{ m XPS \ b}$
Ti	0.96	0.98	0.97	0.97	2.02	2.04	2.04	2.16
Ni	1.08	1.06	1.12	1.24	1.63	1.85	1.54	1.56
Cu	1.18	1.12	1.23		1.53	1.60	1.53	•••
Au	1.41	1.42	1.43	1.42	1.43	1.45	1.43	1.45

^aValues are not corrected for image force lowering.

^bValues from Refs. 10 and 19.



FIG. 4. Temperature variation of barrier heights of Ti, Ni, Cu, and Au on n- and p-type Si-terminated 6H-SiC. The solid (and dashed) curve shows the temperature variation of the barrier height calculated on the assumption that it is entirely due to the temperature dependence of the indirect energy gap in 6H-SiC with the barrier-height value at 295 K as a reference.

However, defects such as the antisites do not have electronic states in the SiC band gap,²¹ and even if carbon or silicon vacancies were to be created near, for example, the reactive Ti/Si terminated interfaces, their dangling-bond energy levels²² do not correlate with the observed pinning position of the Fermi level. Theoretical studies²³ have shown that interface states occur in the SiC band gap with the creation of a metal (A1)/SiC interface, and that the distribution of these gap states depends strongly on the atomic structure of the SiC surface. This distribution reflects the particular type of bonding (i.e., whether the bonding is metalliclike or covalentlike) that occurs at the interface. This finding is inconsistent with a basic assumption of the MIG states model, that the MIG states are only a property of the bulk semiconductor band structure. Furthermore, the dependence of the barrier height on temperature is difficult to reconcile with the MIG states model. We therefore suggest that the interface dipole which arises from chemical bonding plays an important role in determining the barrier height. Tung²⁴ recently pointed out that the polarization of the chemical bonds at metalsemiconductor interface leads to a tendency for the SBH to converge toward one-half of the band gap, because of minimum total energy considerations. This is in agreement with the results for Au on Si-terminated 6*H*-SiC (see Table I). We note that the Fermi level shifts to above the midgap position for metals with lower electronegativity than the semiconductor. Thus, this shift may be attributed, at least in part, to the difference in electronegativity.²⁴



FIG. 5. (a) Capacitance-voltage characteristics at 295 K of Ti on p-type Si-terminated 6*H*-SiC as a function of frequency. (b) Capacitance-voltage characteristics at 440 K of Cu on p-type Si-terminated 6*H*-SiC as a function of frequency. (c) Capacitance-voltage characteristics of Ni on p-type Si-terminated 6*H*-SiC as a function of temperature. Measurements are performed at a frequency of 1 kHz. The diode diameter is 400 μ m.

barrier height. Our results can be understood if the Fermi level position is determined by the interface gap states which occur as a result of bonding.²³ For the Si-terminated interface, these gap states have been shown to contain the contri-

bution from not only the Si p orbitals, but from C orbitals as well.²³ Here the thermodynamic concept introduced by Van Vechten and Thurmond⁶ can in principle be also applied to these gap states. The ionization of such gap states involves the release of a free carrier, and because the presence of either a hole or electron usually softens the local vibrational modes of the lattice, the ionization entropy $\Delta S_{n(p)}(T)$ is positive⁶ above T = 0 K and according to the thermodynamic definition given by $\Delta S_{n(p)}(T) = -\partial \Delta E_{n(p)}(T)/\partial T$, where $\Delta E_{n(p)}(T)$ is the free energy for electron (n) or hole (p) excitation from the gap states. $\Delta E_{n(p)}(T)$ can then be decomposed into the enthalpy of ionization and the entropy of ionization, $\Delta E_{n(p)}(T) = \Delta H_{n(p)}(T) - T\Delta S_{n(p)}(T)$. Since we are dealing here with a thermally activated process, it is the enthalpy that is measured. Our results show that ΔH_n is a constant, independent of the temperature, and therefore, we can conclude that the Fermi level is pinned to the conduction band. This means that vibrational related entropy involved in electron excitation is negligible, i.e., $\Delta S_n = 0$. For this result to be coherent with thermodynamic requirements,⁶ the entropy change when exciting a hole from the gap states to the valence band, $\Delta S_p(T)$, must be equal to the entropy $\Delta S_{cv}(T)$ of creation of an electron-hole pair in 6*H*-SiC. Consequently, the temperature dependence of the *p*-type SBH will be the same as that of the energy gap. Some complication may arise if the ionization of the gap states is accompanied by a large lattice relaxation. In this case, additional contribution from a change in configuration (configurational entropy) must be added. However, as pointed out by Langer and Revva,⁵ this entropy factor is usually small.

Theoretical studies²³ have shown that very different types of bonding occur at Si- and C-terminated interfaces. These studies also predict a large difference in the SBHs of these two interfaces. Our results for metals forming abrupt unreactive interfaces with 6*H*-SiC (Ref. 19) at room temperature corroborate these findings. For example, we find that for Ni and Pd (Ref. 15) on *n*-type 6*H*-SiC, the SBH is higher for C-terminated than for Si-terminated interfaces by ~0.4 eV. This is attributed to the large charge transfer between the metal and the interface carbon atoms, creating an interfacial dipole which shifts the electrostatic potential of the metal downward. For Au on C-terminated 6*H*-SiC, on the other hand, the Fermi level remains close to the midgap position, which, in the context of the chemical bonding approach of Tung,²⁴ corresponds to the minimum of the total energy of the system. It has also been argued that the charge neutrality level which has been postulated to be a reference point for metal-induced gap states pinning of the Fermi level should fall at or near the middle of the indirect band gap.²⁵ This helps explain why these different approaches yield similar results. However, the temperature dependence of the SBH raises doubt concerning the validity of the charge-neutrality level argument.

We now examine the interface parameter $S = \partial \Phi_{Bn} / \partial \chi_m$, where χ_m is the metal electronegativity, which is a measure of how effectively the interfacial dipole is screened. From our SBH data and those reported for other metals^{10,19} on Si-terminated 6*H*-SiC, a value of $S_{\phi} = S/A = 0.4$, where $A \approx 2.27 \text{ eV}$,²⁶ is obtained. This S_{ϕ} value is much larger than the value estimated from the bulk dielectric properties of 6*H*-SiC ($S_{\phi} \approx 0.08$), and thus finds no explanation in a MIG states model. However, this S_{ϕ} value is in good agreement with the value predicted from the analysis of Tung,²⁴ providing further support for the chemical bonding picture of Fermi-level pinning.

V. SUMMARY

The Schottky-barrier height of a number of metals (Ti, Ni, Cu, and Au) on *n*- and *p*-type Si-terminated 6H-SiC has been measured in the temperature range 150-500 K. The barrier height for the *n*-type material does not exhibit a temperature dependence, while for the *p*-type material the change in the barrier height with temperature follows very closely the change in the indirect energy gap in 6H-SiC. These results are inconsistent with models of Schottky-barrier formation based on the concept of a charge neutrality level. Furthermore, the present results cannot be reconciled with a defect model. We suggest that chemical bonding at the metal-6H-SiC interface plays an important role in the formation of the Schottky barrier.

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