

## Schottky barrier between 6H-SiC and graphite: Implications for metal/SiC contact formation

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Using photoelectron spectroscopy we have determined the Schottky barrier between 6H-SiC(0001) and graphite layers grown by solid state graphitization. For *n*-type 6H-SiC(0001) we find a low Schottky barrier of  $\phi_{bn}=0.3\pm 0.1$  eV. For *p*-type SiC(0001) a rather large value of  $\phi_{bp}=2.7\pm 0.1$  eV was determined. It is proposed that these extreme values are likely to have an impact on the electrical behavior of metal/SiC contacts subjected to postdeposition anneals. © 2006 American Institute of Physics. [DOI: 10.1063/1.2213928]

Silicon carbide is a large band gap semiconductor suitable for power electronic devices.<sup>1</sup> Contacts to SiC are an important technological issue.<sup>2,3</sup> In general, as-deposited metals form Schottky contacts.<sup>2</sup> Ohmic contact behavior is usually obtained by deposition of the metal on a heavily doped *n*- or *p*-type region followed by postdeposition annealing (PDA) at temperatures of around 950 °C. This PDA induces chemical reactions between the SiC substrate and the metal deposit. The use of a high doping concentration leads to a thin Schottky barrier which the electrons can overcome by field emission, i.e., by tunneling through the thin barrier.

The interfacial reaction between the contact material and the SiC substrate is undoubtedly of great importance. According to several studies (see Refs. 2 and 3 and references therein), the chemical reaction results in the formation of metal silicides. This can only be accomplished by a dissociation of SiC which also sets free carbon. Accordingly, the observation of graphitic carbon was also reported. Following this line of argument it seems natural to ask the question: What is the nature of an interface between SiC and graphite? Therefore we have used photoelectron spectroscopy to determine the electronic structure of the graphite/SiC(0001) heterointerface.

Graphite layers on SiC(0001) surfaces were grown by solid state graphitization.<sup>4,5</sup> First the sample is annealed at 950 °C in a flux of Si which yields the Si-rich (3×3) structure, thereby removing oxygen from the surface. Part of the Si is desorbed from the surface by further annealing at 1050 °C *in vacuo* which leads to the Si-rich ( $\sqrt{3}\times\sqrt{3}$ )R30° structure. Alternatively, the first step can be skipped and the sample can be annealed at 1050 °C in Si flux. Next, the sample is annealed at 1150 °C which results in the formation of the carbon-rich ( $6\sqrt{3}\times 6\sqrt{3}$ )R30° structure. Finally growth of well ordered graphite layers occurs during annealing at temperatures above 1400 °C

The surfaces were investigated *in situ* by low-energy electron diffraction (LEED), synchrotron radiation induced x-ray photoelectron spectroscopy (SXPS), and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). Additional structural information was gathered by scanning tunneling microscopy (STM) in UHV and by atomic force

microscopy (AFM) at atmospheric pressure.<sup>6</sup> Here we focus on the core level spectra obtained from *n*-type and *p*-type 6H-SiC(0001). The *n*-type samples were nitrogen doped, on-axis oriented 6H-SiC(0001) substrates from SiCrystal AG with a doping concentration of  $5\times 10^{18}$  cm<sup>3</sup>. The *p*-type sample was a 3.5° off-axis oriented epitaxial layer from Cree Research, Inc. with an Al doping concentration of  $1\times 10^{16}$  cm<sup>3</sup>.

Figure 1 displays C 1s and Si 2p core level spectra of a *n*-type SiC(0001) sample taken after the individual preparation steps outlined above. A photon energy of 510 eV was chosen so that the spectra were rather bulk sensitive. Note that the spectra are normalized so that they have the same amplitude in the figure. The line shape varies due to different surface components caused by the individual surface reconstructions.<sup>7,8</sup> What is important in the context of the present letter are the changes in the binding energies of the bulk Si 2p and C 1s lines as traced by the dashed lines in Fig. 1. Both change by the same amounts. Since all binding energies are referenced to the Fermi level  $E_F$ , this indicates a variation in band bending brought about by different pinning centers associated with different surface structures. After annealing at 1400 °C the formation of graphite is witnessed by the appearance of an asymmetric peak at  $284.46\pm 0.05$  eV in the C 1s core level spectrum. Increasing the bulk sensitivity by applying a higher photon energy [dashed curve in Fig. 1(a)] reveals the C 1s core level of the SiC bulk located at  $283.75\pm 0.07$  eV. The Si 2p core level spectrum shows a single doublet at  $101.45\pm 0.07$  eV due to the underlying SiC. A graphite overlayer thickness of  $2.0\pm 0.25$  nm is estimated from the intensity ratio between the C 1s bulk line and the graphite signal.<sup>6</sup>

Figure 2 summarizes the Si 2p and C 1s bulk core level binding energies  $E_b^{\text{Si } 2p}$  and  $E_b^{\text{C } 1s}$  observed for two *n*-type samples and one *p*-type sample as obtained by a least squares fit. The accuracy of the values is judged from the spread of fitting results obtained for measurements with different photon energies on the same sample. It amounts to  $\pm 0.07$  eV. The error arises from the inaccuracy of the fitting and from the error in determining the exact photon energy, which was carried out by measuring the Fermi edge of the Mo sample holder. The fact that C 1s and Si 2p bulk core level shifts run parallel to each other proves that the variation of the binding energy is due to changes in the surface band bending caused

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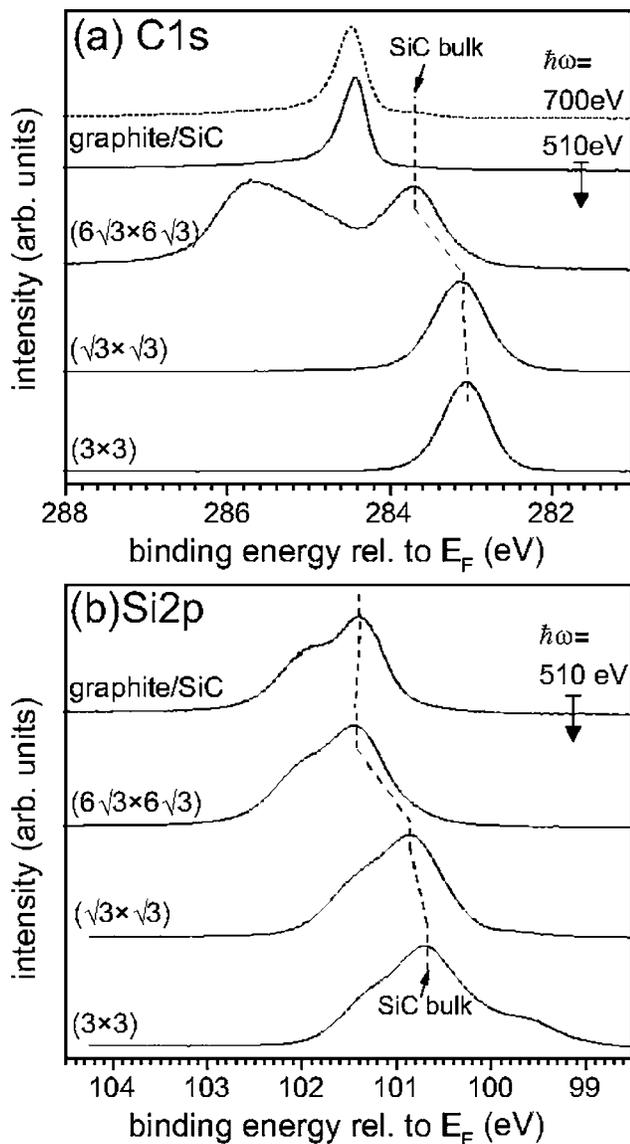


FIG. 1. C 1s (a) and Si 2p (b) photoelectron spectra of on-axis oriented 6H-SiC(0001) (sample 1) after the four preparation steps mentioned in the text. All spectra are normalized to the same amplitude.

by a pinning of the surface Fermi level  $E_F^s$  at different surface states.

The energy difference between the bulk C 1s core level and the valence band maximum of 6H-SiC amounts to  $281.0 \pm 0.1$  eV.<sup>9,10</sup> Therefore, the position of the surface Fermi level  $E_F^s$  with respect to the valence band maximum  $E_v$  is given by  $E_F^s - E_v = E_b^{C\ 1s} - 281.0$  eV with an overall error of the order of  $\pm 0.1$  eV. The numerical values for  $E_F^s - E_v$  can be read off from the graph in Fig. 2 by using the scale on the right side. The bulk Fermi level position  $E_F^b$  of our *n*-type and *p*-type samples is calculated<sup>9</sup> to be at 0.10 eV below the conduction band minimum  $E_c$  and 0.23 eV above the valence band maximum  $E_v$ , respectively. This is indicated in Fig. 2 by two horizontal dashed lines. The surface band bending is simply the difference between the bulk Fermi level and the surface Fermi level.

In the case of the Si-rich  $(3 \times 3)$  and  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structures,  $E_F^s$  is pinned at particular surface states which are caused by residual dangling bonds on the surface (see Refs. 11 and 12 and references therein). For the

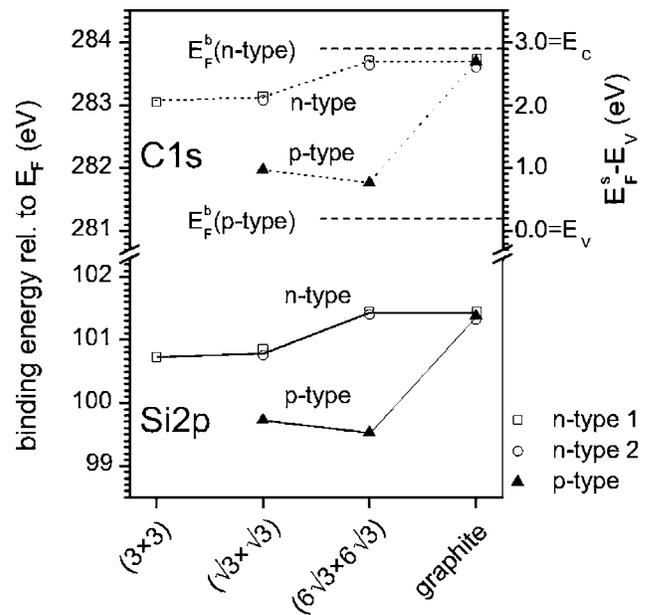


FIG. 2. The C 1s and Si 2p core level binding energies of the bulk component as a function of preparation and sample doping. The scale on the right hand side gives the position of the surface Fermi level  $E_F^s$  with respect to the valence band maximum  $E_v$ . The C 1s flatband binding energy of *n*-type/*p*-type 6H-SiC amounts to 283.9 eV/281.2 eV.

$(\sqrt{3} \times \sqrt{3})R30^\circ$  structure  $E_F^s - E_v$  is 2.1 and 1.0 eV for *n*- and *p*-type 6H-SiC(0001), respectively, which correspond to a respective upward/downward surface band bending of 0.8 eV. The  $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$  structure is a carbon-rich structure.<sup>13,14</sup> In this case, for *n*-type 6H-SiC(0001),  $E_F^s - E_v = 2.7$  eV, i.e., the surface Fermi level is close to  $E_F^b$ . However, on *p*-type 6H-SiC(0001),  $E_F^s - E_v$  is 0.85 eV. The surface electronic structure of this phase is presently unknown. Thus we can say nothing about the nature of the pinning centers.

Finally and most importantly, after growth of the graphite layers,  $E_F^s - E_v$  amounts to 2.7 eV for both *n*-type and *p*-type 6H-SiC(0001). This translates into a small (0.2 eV) upward band bending on *n*-type 6H-SiC(0001) and a quite large (2.5 eV) downward band bending on the *p*-type substrate. From these experimental observations, the band lineup is derived as shown in Fig. 3. The Schottky barrier between graphite and 6H-SiC(0001) amounts to  $\phi_{bn} = 0.3 \pm 0.1$  eV on *n*-type material and  $\phi_{bp} = 2.7 \pm 0.1$  eV on *p*-type material, respectively. Thus we observe a rather small barrier height on *n*-type 6H-SiC and a huge barrier on *p*-type material.

The dramatic difference between the Schottky barriers observed here may have serious consequences for metal contacts formed on SiC. Schottky contacts on *n*-type SiC may degrade if graphite is formed at the interface, but Ohmic contacts would not be influenced negatively. In fact, graphitic carbon may actually be beneficial for Ohmic contacts on *n*-type SiC. This is corroborated by reports of Lu *et al.*<sup>15</sup> who studied the contact behavior of metal/carbon/SiC stacks annealed to 800 °C. They observed Ohmic behavior for Ni and Co which also led to the formation of graphite. For W, Mo, Au, and Al no graphite was observed after annealing and the contacts were rectifying. Lu *et al.*<sup>16</sup> also reported Ohmic behavior of carbon contacts on *n*-type 4H-SiC(0001) annealed at 1150–1300 °C. This could be explained by the small Schottky barrier between SiC and graphite. Lundberg

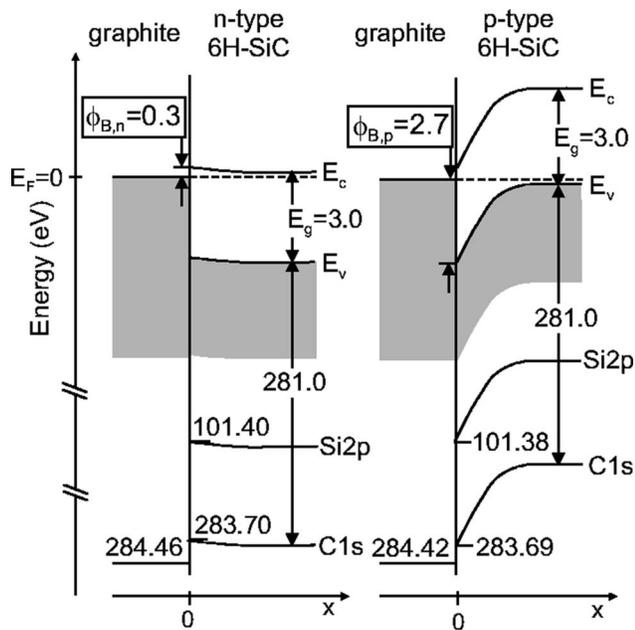


FIG. 3. Band lineup at the interface between graphite and *n*-type 6H-SiC(0001) (left) and *p*-type 6H-SiC(0001) (right).

and Östling<sup>17</sup> demonstrated that Co/SiC Schottky contacts turned into Ohmic contacts after annealing at 900 °C. They reported the formation of Co<sub>2</sub>Si and a buildup of carbon in the contact layer. Consequently, for Schottky contacts to *n*-type SiC, metals are recommended which form carbides or which have a high solubility for carbon.

On the other hand, on *p*-type SiC, a graphitic interface is likely to be detrimental for Ohmic contacts and unproblematic for rectifying contacts. Accordingly, Lundberg and Östling<sup>18</sup> reported that Si/Co/SiC contacts annealed at 900 C showed an Ohmic behavior superior to Co/SiC contacts treated in the same way. This can be explained by considering that in the Si/Co/SiC structure, cobalt silicide formation can occur without SiC decomposition, thus avoiding graphite formation. In the case of the simple Co/SiC contacts, annealing and subsequent silicidation will undoubtedly produce graphite which will have a negative effect on the Ohmic contact properties. Thus, for Ohmic contacts on *p*-type SiC, metals should be preferred which form stable carbides or which have a high solubility for carbon.

In conclusion, we have determined the Schottky barriers between graphite and *n*- and *p*-type 6H-SiC(0001). While we find a rather small value of  $\phi_{bn}=0.3\pm 0.1$  eV on *n*-type 6H-SiC, the Schottky barrier on *p*-type SiC is extremely large  $\phi_{bp}=2.7\pm 0.1$  eV. In the light of experimental evidence for PDA induced graphite formation, we stress that the large difference between the Schottky barriers on *n*-type and *p*-type SiC is bound to have a considerable impact on the electrical behavior of metal/SiC interfaces.

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