Observations of conduction-band structure of 4*H*- and 6*H*-SiC

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Ballistic electron-emission spectroscopy (BEES) and photoluminescence are used to study conduction-band structure related transport properties of the 4*H* and 6*H* polytypes of SiC. A secondary energy threshold at 2.7 eV is observed in the BEES spectrum of 4*H*-SiC, in good agreement with a value of 2.8 eV deduced from reported *ab initio* calculations. The results from 6*H*-SiC, are suggested to be influenced by transport properties of other polytype inclusions, also supported by band-edge transitions evident in 6*H*-SiC photoluminescence spectra.

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Silicon carbide has received growing attention during the last decade for being the most mature and promising candidate material for high-temperature and high-power electronic device applications.[1,2] Of the large number of its possible polytypes, 4*H*- and 6*H*-SiC are commercially available in a quality considered appropriate for device applications. To utilize the unique characteristics of this family of materials, a knowledge base of their physical properties is required. Physical properties of some of the more common SiC polytypes have been calculated using various *ab initio* calculation methods.[3,4] Experimental data consists mostly of optical methods, which essentially are capable of resolving direct transitions, and, therefore, lend limited support to the existing theoretical results, especially in identifying the relative energy positions of conduction-band valleys.[5,6,7] Direct observations of conduction-band minima (CBM) were recently obtained using ballistic electron-emission spectroscopy (BEES).[8] However, these observations were restricted to energies close to the lowest conduction-band minimum. In this paper, we present experimental evidence for the energy positions of conduction-band minima in 4*H*- and 6*H*-SiC. Based mainly on BEES and augmented with photoluminescence (PL) spectroscopy, our results provide a wide energy-scale view while revealing the projection of a fundamental problem in present-day SiC material on the transport properties of 6*H*-SiC.

The SiC samples used in this study were cut from wafers purchased from CREE Research. All wafers were *n* type, 280 μm thick, with a 10-μm-thick *n*-type epilayer grown on its Si face. The substrates and the epilayers were doped with nitrogen to levels of $\sim 1\times 10^{18}/cm^3$ and $\sim 1\times 10^{16}/cm^3$, respectively. Prior to deposition, the samples were degreased in organic solvents in an ultrasonic bath (trichlorethylene, acetone, and methanol, sequentially). Following degreasing, the samples were placed in a 4:1 solution of standard concentrations of $H_2SO_4:H_2O_2$ at 80 °C for 40 min. Immediately prior to deposition the samples were etched in a 7:1 solution of standard concentrations of HF:NH_4F for 20 s and then rinsed in deionized water and blown dry with N_2 gas.

Metal contacts were deposited by electron-beam thermal evaporation in vacuum. The substrate holder was neither cooled nor heated externally. The evaporation system is equipped with a cryopump and a cryogenic baffle that yields a background pressure of 3×10^{-7} Torr prior to the deposition. A Ti(30 nm)\Pt(70 nm) scheme was used for the back contacts. After the deposition, the back contacts were heat treated in an evacuated tube furnace (5×10^{-7} Torr) at temperature of 800 °C for 15 min. The last etching step (HF:NH_4F) was then repeated once again, and the samples were introduced again to the vacuum chamber for Schottky contact deposition. 50-nm-thick Pt Schottky contacts were used throughout this study.

Ballistic electron-emission spectra were obtained at *room temperature* in *air* using model AIVTB-4 scanning tunneling microscope (STM) (Surface-Interface Inc.) with a gold tip. Details of the scanning tunneling microscope setup and operation were described elsewhere.[9] Tip voltages ranged from 1 V to as high a voltage the current stability allowed (2.9 V for 4*H*- and 2.5 V for 6*H*-SiC). The spectra were obtained in groups of 100 spectra collected and averaged at each point. During the acquisition at each point, the STM tip typically drifts while averaging spectra collected over a drifting range of ~10 nm. An ensemble of data obtained from ~100 such points is then compared and verified to possess the same features before being averaged to produce the final spectrum.[10] Derivatives were obtained using a 9th-order polynomial fit of the spectra without smoothing.[11] The overall error (a combination of the statistical and the fitting errors) is estimated to be 0.07 eV.

Photoluminescence was excited at room temperature using a He/Cd laser (325 nm, 12 mW). The emitted luminescence was monochromatized, filtered, and sensed using a GaAs photomultiplier tube. Wavelengths were scanned in 1 nm steps from 375 to 460 nm.

The cleaning and etching scheme used in this study was tested using Auger electron spectroscopy in ultrahigh vacuum and BEES. It was compared to a common scheme (same as above excluding the $H_2SO_4:H_2O_2$ step and with a final etch of HF only). For the same durations between cleaning and loading into the vacuum system (~20 min) the scheme used here was found to yield a surface clean of oxide while some oxide was observed with the other scheme. Ballistic electron-emission spectra showed a slightly higher Schottky barrier of ⟨6*H*-SiC⟩\Pt in the latter case as compared to the former (1.33 and 1.22 eV, respectively), as well as reduced collector current, and saturation of the current at

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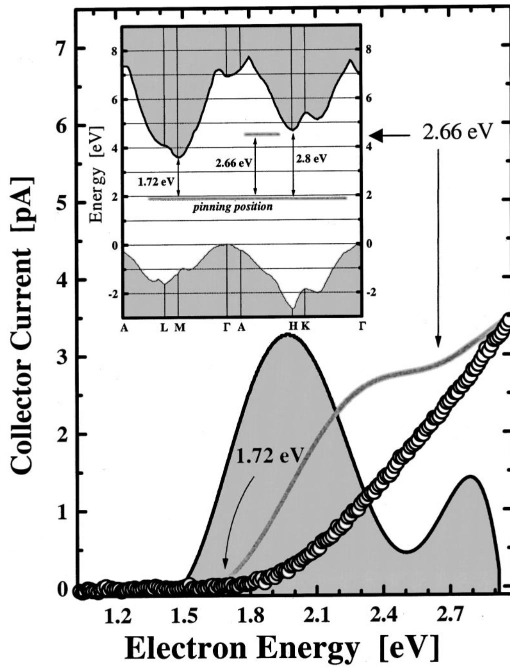

FIG. 1. Ballistic electron-emission spectrum of Pt Schottky contact 4H-SiC. The y-axis units relate to the collector current. The first and second derivatives are given in arbitrary units. The inset: Band structure of 4H-SiC calculated using quasiparticle *ab initio* method [from Wenzien *et al.* (Ref. 15)]. For clarity, only the lowest conduction band and the highest valence band are drawn.

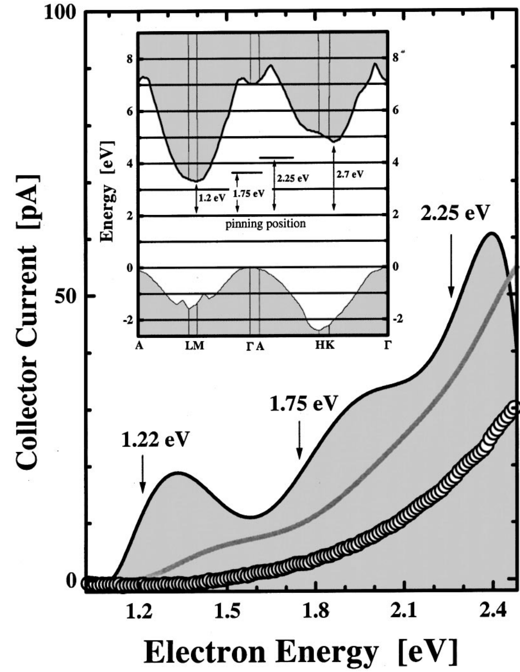

FIG. 2. Ballistic electron emission spectrum of Pt Schottky contact to 6H-SiC. The y-axis units relate to the collector current. The first and second derivatives are given in arbitrary units. The inset: Band structure of 6H-SiC calculated using quasiparticle *ab initio* method [from Wenzien *et al.* (Ref. 15)]. For clarity, only the lowest conduction band and the highest valence band are drawn.

high voltages. The effect of thin interfacial layers on Schottky-barrier heights is, however, well known and documented.[12]

Im *et al.* have also shown high-voltage BEES spectra from 4H- and 6H-SiC.[13] However, analysis of high-voltage thresholds was not offered, probably due to the observed differences at high voltages between Pd and Pt. These differences are often related to the attenuation of hot electrons in the metal due to their mean free path. As was shown in that paper, Pt does not show the electron attenuation effect at a thickness smaller than 10 nm. Hence, Pt is more suitable for this study.

Figure 1 shows ballistic electron-emission spectrum obtained from a $\langle 4H\text{-SiC}\rangle\backslash$Pt diode. First and second derivatives are shown in the same figure. Threshold currents were determined from the first derivative, whereas the second derivative is added to aid the eye in recognizing the features. The first current threshold is observed at ~1.72 eV, in agreement with forward IV measurements.[14] A second threshold is observed at ~2.66 eV. For comparison, we plot the band structure as calculated by Wenzien *et al.* using quasiparticle corrected density-functional theory in the local-density approximation method (Inset to Fig. 1).[15] For clarity, we draw only the lowest conduction band and the highest valence band. Based on our measurement of 1.72 eV of the Pt/4H-SiC Schottky-barrier height, a horizontal line representing the Fermi-level pinning position at the interface is plotted 1.7 eV below the lowest conduction valley at the M symmetry point. A minimum of the next conduction band appears about ~0.15 above it (not drawn). This minimum was observed in BEES by Kaczer *et al.* but not observed in our spectra, probably due to limited resolution. However, the next apparent valley at the H symmetry point, which was calculated by Wenzien *et al.* to be 1.12 eV above the M valley (2.82 eV above the observed pinning position) is in a good agreement with our measured value of ~2.66 eV. It should be pointed out that from the available calculations, it is not clear whether this is indeed a valley or a saddle point. However, both these features introduce a van Hove singularity in the density of states, and from the point of view of the BEES method, there is no fundamental difference between the two.

As opposed to the 4H-SiC polytype, results from the 6H-SiC polytype showed two high-energy thresholds, which could not be explained by the calculated 6H-SiC band structure. Figure 2 shows the BEES spectrum of Pt/6H-SiC and its first and second derivatives. Thresholds are observed at 1.22, 1.75, and 2.25 eV. These thresholds were observed in samples from two different wafers. The 1.22 eV threshold is well within the known range of Pt Schottky-barrier heights on 6H-SiC (1.06–1.33 eV).[2] The inset in Fig. 2 shows the relevant parts of the calculated band structure of 6H-SiC.[15] The pinning position at the metal semiconductor interface is indicated by a horizontal line positioned 1.2 eV below the lowest conduction-band minimum (between the M and the L symmetry points), while the other experimentally measured thresholds are shown relative to this line. As clearly noticed, the two upper thresholds fall between the conduction-band minimum and the next apparent valley (or saddle point) at the H point (1.6 eV above it and outside the range of our

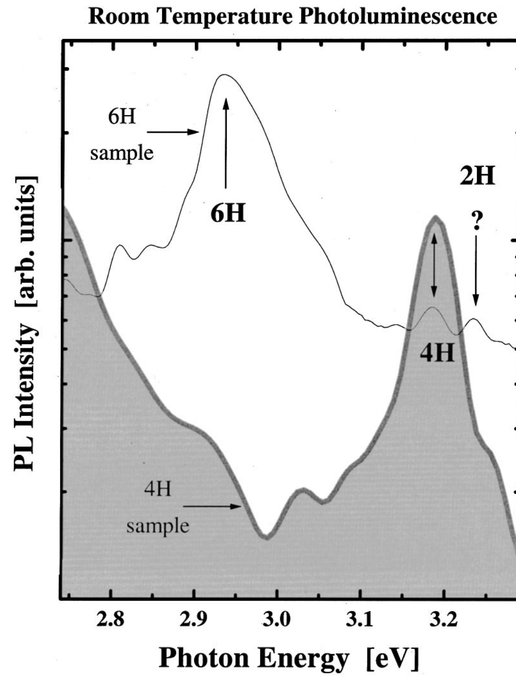

FIG. 3. Band-edge photoluminescence spectra of $4H$- and $6H$-SiC.

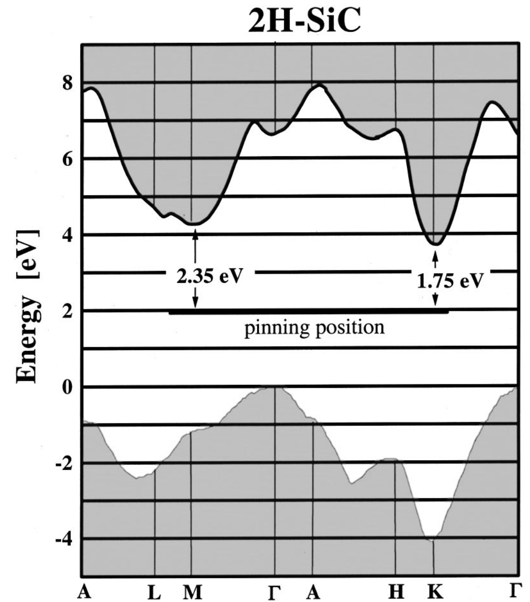

FIG. 4. Band structure of $2H$-SiC calculated using quasiparticle *ab initio* method [from Wenzien *et al.* (Ref. 15)]. For clarity, only the lowest conduction band and the highest valence band are drawn.

measurements). Hence, these thresholds cannot be related to conduction-band minima. Alternatively, they could be accounted for by additional Schottky barriers. Multiple Schottky barriers imply multiple metallic phases or multiple semiconducting phases. Since only Pt was deposited and no reaction seemed to have taken place, we sought for an explanation in the form of another semiconductor.[16] To examine this possibility, we conducted PL measurements. When different polytypes are present, their band-edge luminescence can be observed. For example, growth of $3C$-GaN sometimes results in additional $2H$-GaN inclusions (and also vice versa), which can be observed using room-temperature PL.[17]

Figure 3 shows band-edge PL spectra obtained from $4H$- and $6H$-SiC. The band-edge emission of $4H$- and $6H$-SiC are clearly observed at 3.18 and 2.93 eV, respectively. Additionally, two other emission peaks are observed in the $6H$-SiC spectrum. One clearly coincides with the energy position of the $4H$-SiC at 3.18 eV. The other is observed at 3.24 eV. These observations seem to suggest that small quantities of $4H$- and perhaps also $2H$-SiC were present in our $6H$-SiC samples. Inclusions of $4H$-SiC may indeed account for the 1.75-eV threshold in the $6H$-SiC BEES spectrum, which is very close to the value of 1.72 eV observed in our $4H$-SiC BEES spectra. To examine the possibility of $2H$-SiC inclusions, one must know the Pt Schottky-barrier height on that polytype. Unfortunately, such data do not exist. In the rare occasions where $2H$-SiC growth was reported, the material was below device quality.[18] However, if we could speculate, based on its very similar band gap to that of $4H$-SiC that the Pt Schottky barrier on $2H$-SiC is around the Pt Schottky-barrier height observed on $4H$-SiC, we would be able to explain the third threshold at 2.25 eV as belonging to the M valley in $2H$-SiC inclusions. This is supported by the calculated $2H$-SiC band structure (Fig. 4), where the M valley is positioned 0.6 eV above the K valley (CBM),[15] while our results give a slightly lower value of 0.5 eV (2.25–1.75). While the $2H$-SiC polytype is thermodynamically less favorable in bulk growth as compared to $6H$- and $4H$-SiC, it is still possible in epitaxial growth.[19] A BEES threshold of 1.79 eV was observed by Im *et al.* on a $15R$-SiC inclusion in a $6H$-SiC sample and was found to agree with full-potential linear muffin-tin orbital (LMTO) calculated band structure.[20] However, the identification method of that inclusion was not specified, and the inclusion was suggested not to be pure. Using LMTO, Limpijumnong *et al.* have also calculated a second conduction band at the M symmetry point of $6H$-SiC to be 1.2 eV above the first one, which could agree with the threshold observed by us at 2.25 eV.[21] However, this value was not quasiparticle corrected and probably underestimates the real value and does not agree with the value reported by Wenzien *et al.*[15]

Inclusions of other polytypes are a tenacious problem that persisted through the great progress made in the last years in the growth technology of SiC, especially in epilayers. Examination of x-ray powder diffraction files for the above three SiC polytypes shows that most of the intense diffraction peaks of one polytype can be found as weak peaks in spectra of the other polytypes.[22] These inclusions are generally assumed to be large enough to be readily identified and thus easily avoided. Our results suggest such inclusions may exist at *nanoscale sizes* as well.

In this paper, BEES and PL were used to identify conduction-band structure related transport thresholds in $4H$- and $6H$-SiC. Threshold energies in $4H$-SiC were found to match quasiparticle *ab initio* calculated band structure. Photoluminescence spectra show that our $6H$-SiC contains inclusions of $4H$ and possibly also $2H$-SiC or $15R$-SiC. Inclusions of these polytypes seem to provide a reasonable

account for the high energy thresholds observed in $6H$-SiC BEES spectra.

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