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Valence band structure and band offset of 3C- and 4H-SiC studied by ballistic hole emission microscopy

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p-type Schottky barriers in Pt/3C-SiC contacts have been measured using ballistic hole emission microscopy (BHEM) and estimated to be ~ 0.06 eV higher than identically prepared Pt/*p*-type 4H-SiC contacts. This indicates the 3C-SiC valence band maximum (VBM) is ~ 0.06 eV below the 4H-SiC VBM, consistent with the calculated ~ 0.05 eV type-II valence band offset between these polytypes. We also observe no evidence of an additional VBM in 3C-SiC, which supports the proposal that the second VBM observed in BHEM spectra on 4H-SiC is a crystal-field split VBM located ~ 110 meV below the highest VBM. © 2006 American Institute of Physics.

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Silicon carbide (SiC) is a unique material, known to have more than 200 polytypes with different stacking sequences of essentially identical Si-C bilayers.¹ Its superior thermal, mechanical, chemical, and electronic properties are of great interest for high temperature, high power, and high-frequency electronic device applications,² which has led to extensive experimental and theoretical investigation. Of particular interest is the large (up to ~ 1 eV) variation of SiC band gap with polytype,³⁻⁹ which offers the possibility of making unique quantum-well heterostructures and two-dimensional electron gas devices that are based only on the stacking sequence of pure SiC.^{10,11} A number of first-principle calculations³⁻⁷ have indicated that most of the band gap variation between polytypes is in the energy of the conduction band minimum (CBM), with only ~ 0 – 130 meV offset in the valence band maximum (VBM) between different polytypes. Calculations also indicate that spontaneous polarization exists in hexagonal SiC polytypes, but not in the (cubic) 3C-SiC polytype.¹² This should produce a small (< 200 meV) crystal-field splitting in the valence band of the hexagonal polytypes that is absent in 3C-SiC.^{3,6,7}

It has been found¹³⁻¹⁵ that differences in the *n*-type Schottky barrier heights (SBHs) measured using ballistic electron emission microscopy¹⁶ (BEEM) on *n*-type 4H-, 6H-, and 15R-SiC closely track the corresponding difference in band gap. This suggests that measured differences in SBH can be used to track the corresponding bulk conduction band offsets. This conclusion is supported by a recent study of *n*-type 4H-SiC samples containing thin planar 3C inclusions¹⁷ which found that the inclusions greatly reduced the measured SBH [as determined from conventional diode current-voltage (*I*-*V*) and capacitance-voltage (*C*-*V*) measurements]¹⁸ but did not affect the *interface-state* pinning strength that was measured when different metals were used to make the Schottky contacts. If the interface-state electric dipole is the same (for a given metal) on all polytypes, then the measured *n*-type SBH should indeed track the conduction band energy. These studies^{13-15,17} also showed

that BEEM could detect the presence and energy splitting of higher conduction bands in 4H- and 15R-SiC. This past work indicates that it should be possible to use SBH measurements on *p*-type SiC to measure the *valence band* offsets between SiC polytypes, and also to investigate the possible existence of a crystal-field split valence band in hexagonal SiC polytypes.

Here we compare local SBH measurements on *p*-type 3C-SiC and 4H-SiC using ballistic *hole* emission microscopy¹⁹ (BHEM) to investigate possible differences in valence band structure between these polytypes. We find that the measured intrinsic *p*-type SBH on 3C is ~ 0.06 eV larger than 4H, implying that the VBM of 3C is lower than 4H by this same amount. This is very close to the theoretically calculated value of ~ 0.05 eV, and confirms the calculated type-II energy band alignment between 3C-SiC and hexagonal SiC polytypes. We also show that BHEM spectra on 3C-SiC can be fitted reasonably well using a single “BHEM threshold,” while two thresholds are needed for 4H-SiC. This supports the report²⁰ of a crystal-field split VBM in 4H-SiC, located ~ 110 meV below the highest VBM.

The *p*-type 3C sample used in this study is composed of the 3C epilayers grown on step-free 4H mesa structures, as described previously.²¹ The sample was unintentionally boron-doped during growth with an estimated dopant density of $1\text{--}5 \times 10^{17} \text{ cm}^{-3}$. After growth, the sample was thermally dry oxidized at 1150°C to form a thick SiO₂ protective top layer. Figure 1 shows a schematic cross-sectional view of the final sample structure and electrical connections used for BHEM measurements. 27 circular openings (0.17 mm diameter) each isolated completely on top of a 3C mesa were fabricated by etching through the top oxide layer. The exposed 3C surfaces were then cleaned with one cycle of 30 min ultraviolet ozone (UVO) room-temperature oxidation followed by 10 s HF (1:10 diluted) dip and methanol rinse. This HF etch was long enough to remove the thin UVO oxide over the holes, but not the surrounding thick thermal oxide. The sample was then introduced into an UHV sample preparation chamber (base pressure: $\sim 1 \times 10^{-10}$ torr) and outgassed mildly overnight at $< 230^\circ\text{C}$. 5 nm thick Pt Schottky diodes of ~ 0.5 mm diameter were formed *in situ*

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FIG. 1. Schematic sample cross-section and electrical connections for BHEM measurements. The Pt dot (~ 0.5 mm diameter) can completely cover the ~ 0.17 mm circular opening through the oxide on top of the mesa. One sidewall of the mesas may not be covered by Pt due to shadowing during evaporation.

using e-beam evaporation through a shadow mask at room temperature. After evaporation, the sample was transferred in UHV to an adjacent scanning tunneling microscope (STM) chamber for BHEM measurements. A BHEM measurements were done on the Pt dots that happened to overlap the oxide openings on the 3C-SiC mesas. The sample preparation and BHEM measurements for the *p*-type 4H-SiC sample have been reported previously.²⁰ Identical equipment and procedures were used in sample preparation and measurement for both the *p*-type 3C- and 4H-SiC samples.

BHEM (Ref. 19) and BEEM (Ref. 16) are variants of STM that can be used to investigate hole- or electron-carrier transport property through buried M/S interfaces with nanometer-scale spatial resolution (estimated to be ~ 7 nm for a 4 nm top Pt film^{17,22}) and high energy resolution. In BEEM,¹⁶ “hot” electrons are injected by vacuum tunneling from the STM tip into the metal overlayer of a Schottky contact with a negative tip bias $-V_T$ and the BEEM “collector” electron current (I_c) is measured from the semiconductor substrate. By monitoring the threshold voltage in a “BEEM spectrum,” (which is a plot of I_c vs V_T) at which hot electrons start to flow into the semiconductor substrate, the local (*n*-type) SBH and the energy of additional CBMs can be measured. In BHEM (Ref. 19) hot holes are injected into the metal base at positive tip bias, with the collector hole current measured from the substrate. In the same manner as BEEM, the *p*-type local SBH and additional VBM information can be obtained from the BHEM spectra thresholds.

Figure 2(a) shows a typical BHEM spectrum averaged over ~ 100 individual spectra taken on one of the *p*-type 3C-SiC mesas covered by the Pt dots at the tunnel current of 20 nA. For comparison, Fig. 2(b) shows a previously reported²⁰ BHEM spectrum on a Pt/*p*-type 4H-SiC using the same equipment and sample preparation procedures. The solid lines in Fig. 2 are the best fits of the near-threshold data using the standard Bell-Kaiser (BK) model¹⁶ with one threshold for 3C and two thresholds for 4H. These fits were used to extract the BHEM thresholds on the 3C- and 4H-SiC samples. While a BK model with a single threshold was sufficient to describe the data for *p*-type 3C-SiC, two thresholds were required to reasonably fit the *p*-type 4H-SiC data. The dashed line in the inset of Fig. 2(b) shows a close-up of a single-threshold fit on 4H-SiC, which is a poor fit just above threshold. In contrast, the inset of Fig. 2(a) shows that a single threshold is quite sufficient for 3C-SiC. On *n*-type Schottky contacts it is well documented that a second BEEM threshold may indicate the existence of

FIG. 2. Typical BHEM spectra averaged over ~ 100 individual I_c - V_T curves taken on (a) Pt/3C-SiC and (b) Pt/4H-SiC contacts. Solid lines are fits to Bell-Kaiser Model with fitted thresholds indicated by arrows. Insets show close-ups of the near-threshold data points, and show that the 3C spectrum is well fit with one threshold, while the 4H spectrum requires two thresholds. The dashed line in the inset of (b) shows that a single-threshold fit on 4H-SiC noticeably misses the measured data.

a second CBM at higher energy than the lowest CBM,^{13–17} and by analogy a second BHEM threshold on *p*-type Schottky contacts suggests the presence of a second VBM at slightly lower energy than the highest VBM. We will return to this point later.

The best-fit threshold for this 3C-SiC sample was found to be 1.58 ± 0.01 V. However, to get the true “intrinsic” SBH, one must correct for the effects of image force lowering,²³ which reduces the SBH measured by conventional macroscopic diode I - V curves and by BEEM/BHEM. Using the standard theory²³ for image force lowering and the estimated doping range (1 – 5×10^{17} cm⁻³) of the 3C-SiC sample, the intrinsic *p*-type SBH of the Pt/3C-SiC contact is estimated to be 1.67 ± 0.02 eV. For the 4H-SiC sample, the measured SBH was 1.45 ± 0.01 eV. Including the image force effect (using the larger $\sim 5 \times 10^{18}$ cm⁻³ doping of this sample,²⁰) the estimated intrinsic SBH of the Pt/4H-SiC was 1.61 ± 0.01 eV, which is $\sim 0.06 \pm 0.02$ eV lower than the intrinsic SBH on the Pt/3C-SiC sample. We here note that the 3C sample has on-axis surface orientation while the 4H sample was 8° miscut from the basal plane. However, previous BEEM measurements on *n*-type 4H-SiC samples with different sample miscut [one on-axis *c*-face (0001) orientation,^{13–15} two with 8° miscut from the [0001] direction,^{17,20} and one *a* face (11–20) orientation²⁴] had measured intrinsic SBHs (with the image force correction) that were all in the range of 1.60–1.63 eV. Since sample miscut does not significantly affect the SBH on *n*-type 4H-SiC, we do not believe that the 8° miscut of the *p*-type 4H-SiC sample affects the comparison to the on-axis *p*-type 3C-SiC sample.

As discussed above, one would expect that differences in the measured SBHs between different *p*-type SiC polytypes should be approximately equal to the corresponding valance

FIG. 3. The schematic representation of the energy band lineup of a 3C/4H heterostructure. Our BHEM measurements suggest a type-II heterostructure interface with valence and conduction band offsets that are consistent with theoretical calculations.

band offsets. This is indeed consistent with our measured 0.06 ± 0.02 eV larger intrinsic SBH on *p*-type 3C-SiC than on 4H-SiC, which is close to the calculated⁶ ~ 0.05 eV lower bulk VBM for 3C-SiC. Together with previous measurements on *n*-type SiC polytypes, this work indicates that careful measurements of SBHs on SiC can be used to determine the corresponding conduction and valence band offsets between different SiC polytypes.

Figure 3 is a schematic representation of the estimated bulk energy band alignments between 3C- and 4H-SiC, based on our measured valence band offset and the known band gaps of 3C- and 4H-SiC. These measured alignments show a type-II band alignment between 3C- and 4H-SiC, with band offset values that are in excellent agreement with calculations.^{6,12} We note that Fig. 3 does not reflect possible effects of the different spontaneous polarization expected between 3C- and 4H-SiC, which would produce electric fields in the vicinity of an actual 3C/4H interface.^{11,25}

We next return to the *shapes* of the measured BHEM spectra on 3C- and 4H-SiC. As discussed above, the 4H spectra require two thresholds to be fitted adequately. For all spectra measured at six different randomly selected locations on the 4H sample, the second threshold is observed to be on average $\sim 0.11 \pm 0.01$ eV larger than the first one. This strongly suggests that on 4H-SiC a second VBM exists at ~ 0.11 eV below the highest VBM. It has, in fact, been calculated that the highest valence bands in hexagonal SiC are split due to the crystal field that exists in hexagonal polytypes. Crystal-field splitting is not expected in 3C-SiC because of its cubic symmetry. Several groups^{3,6,7} have calculated this crystal-field splitting for 4H-SiC with predicted values of 56–130 meV, depending on the calculation method. We believe that the second threshold observed in the BHEM spectra on the 4H sample represents this crystal-field split band because (1) the measured splitting is consistent with theoretically calculated values and (2) we do not observe a second threshold on *p*-type 3C-SiC. We note that another type of valence band splitting due to the spin-orbit interaction has been calculated to exist⁷ for both 3C- and 4H-SiC, but is expected to be very small (< 10 meV). This would be very difficult to observe in room-temperature BHEM measurements because it is less than the ~ 25 meV thermal smearing of the metal Fermi energy.

In summary, the intrinsic Pt/*p*-type 3C-SiC SBH measured with BHEM is found to be ~ 0.06 eV larger than intrinsic Pt/*p*-type 4H-SiC SBH for contacts prepared in the same way. This SBH difference directly implies that the highest VBM on 3C-SiC is ~ 0.06 eV lower than that on 4H-SiC, consistent with the calculated value of ~ 0.05 eV. We have also shown that the BHEM I_c - V_T curves on 3C-SiC are well described assuming one-threshold while those on 4H-SiC exhibit two-threshold behavior. The second threshold in the 4H spectra indicates the existence of an additional VBM ~ 0.11 eV below the highest VBM, likely due to crystal-field splitting in hexagonal SiC polytypes.

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