Scanning Tunneling Spectroscopy of Mott-Hubbard States on the 6*H*-SiC(0001)$\sqrt{3} \times \sqrt{3}$ Surface

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Scanning tunneling spectra have been measured on the 6*H*-SiC(0001)$\sqrt{3} \times \sqrt{3}$ surface for both *p*- and *n*-type materials. With the use of exceptionally low tunnel currents, the tunneling spectra reveal distinct bands of empty and filled states, separated by 2.0 eV. The states are located at the same spatial position, thereby supporting a silicon adatom model which predicts a Mott-Hubbard-type density of states. [S0031-9007(98)08314-8]

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Silicon carbide is a wide band gap semiconductor with properties that make it useful in high temperature electronics and other areas. SiC crystals exist with various stacking arrangements of the atomic planes; of particular interest are the cubic 3*C* polytype and hexagonal 4*H* and 6*H* polytypes. Much work has been done on characterizing the 6*H*-SiC(0001) surface as a surface suitable for epitaxy and device development. Several workers have studied the atomic structure of the surface using the scanning tunneling microscope (STM) [1,2]. A set of reconstructions of the Si terminated (0001) surface has been discovered, one of which, the $\sqrt{3} \times \sqrt{3}$, has evoked much experimental [3–5] and theoretical [6–9] interest.

Theoretically, the lowest energy model for this reconstruction consists of Si adatoms at T_4 positions on a Si terminated bulk crystal. Here, three of the Si adatom bonding orbitals are back-bonded to Si atoms. The fourth bonding orbital extends into vacuum with only one electron in it. Local density functional calculations for this structural model [6,8] predict a half-filled and hence metallic band arising from the dangling bond. More refined computations [7] performed after the photoemission [4] and inverse photoemission [5] spectra became available employed a two-dimensional Hubbard model. These calculations indicate that the energy levels of this surface consist of a filled band and an empty band, separated by a Hubbard gap of $U = 1.6$ eV, thus producing a semiconducting density of states (DOS). Such a surface would have at each site a single localized electron, forming a 2D system of spins which can take two values on a triangular lattice. This problem is of great theoretical interest because such systems can be frustrated and form 2D spin glasses. This structure has been questioned in the literature, and several alternatives have been proposed [1,3,10,11], but experimental results to date are unable to distinguish between these models.

Photoemission spectroscopy (PES) experiments on *n*-type 6*H*-SiC(0001) wafers which show a $\sqrt{3} \times \sqrt{3}$ low energy electron diffraction (LEED) pattern reveal a fully filled band 1.2 eV below the Fermi level [4]. Inverse photoemission spectroscopy (IPES) [5] on the same surface shows an empty surface state 1.1 eV above the Fermi level. Both these results are in moderate agreement with recent theoretical predictions of a Mott-Hubbard ground state for this surface [7] as mentioned above. Scanning tunneling spectroscopy (STS) has a great advantage over PES and IPES in that a single tunneling spectrum can show surface states both above and below the Fermi level simultaneously, at the same spatial location. In this work we measure tunneling spectra for the $\sqrt{3} \times \sqrt{3}$ structure for both *p*-type and *n*-type 6*H*-SiC. We find that at typical tip-sample separations given by a tunneling current set point of 100 pA, the tunneling spectra show no resemblance to the PES and IPES results. But as the tip is retracted from the surface by reducing the tunnel current set point, features of the density of states seen in these other experiments begin to appear and several other strong features that are seen only in the high current tunneling spectra get suppressed. We have measured tunneling spectra over 4 orders of magnitude of current set-point values going down to as low as 0.5 pA in some cases, and we have traced the evolution of the density of states through them. We observe a remarkable evolution of the spectra with current. At high currents we see the appearance of doping-dependent features in the spectra which we attribute to tip-induced band bending. Using exceptionally low currents, we observe a filled state 1 eV below the Fermi level and an empty state 1 eV above, in agreement with both prior experiment and theory. Although Hubbard *U* effects have been associated with defect related states in several previous STS studies [12,13], this is the first STS observation of such effects for an intrinsic surface state band. Most importantly, STM images of the surface taken when tunneling into the empty state or out of the filled state show that both the empty and filled states are localized at the same spatial point, further supporting a Mott-Hubbard-type band structure for the surface.

SiC(0001) surfaces for our experiments are prepared from polished wafers by hydrogen etching [14]. This technique is known to produce large, flat areas on the

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wafer suitable for conducting STM experiments on. We have used both n-type and p-type materials, with resistivities of 0.1 and 7 Ω cm, respectively. Following etching, the sample is loaded into an ultrahigh vacuum chamber (base pressure less than 1×10^{-10} Torr) equipped with a STM, LEED apparatus and Si electron beam evaporation source. After outgassing the sample, Si is deposited on it at room temperature. Finally, the sample is heated at about 1000 °C till a $(\sqrt{3} \times \sqrt{3})R30°$ LEED pattern is obtained. Tunneling spectra are obtained by measuring the derivative of the tunnel current I with respect to the voltage V across the tunnel junction as a function of V. Normalization of the spectra is performed as described in Ref. [15], using parameters $a' \approx 0.5\ \mathrm{V}^{-1}$ and $\Delta V \approx 2$ V (the locations of the features in the spectra are all very insensitive to the choice of these parameters).

In Fig. 1(a), we show a spectrum obtained on n-type 6H-SiC [16], acquired with a tunnel current set point of 100 pA, a value which is typical of STM experiments. (The current set point corresponds to the constant current used prior to acquiring the spectrum, which generally is close to the value of tunnel current at the positive and/or negative end of the spectrum. Measurable values of the current in the spectra presented here range over 2–3 orders of magnitude below the set point.) In Fig. 1(b) we show the main features of the PES and IPES results on the $\sqrt{3} \times \sqrt{3}$ surface. It is apparent that the agreement between the STS and PES/IPES results is poor. The tunneling spectrum shows a small band gap of about 0.6 eV, compared to 2.3 eV in the combined PES/IPES spectra. The tunneling spectrum is almost featureless in the range where the surface states are expected, and at more negative voltages we see a large feature D_1 which has no counterpart in the PES spectrum. Because of the increased barrier to tunneling from states below the Fermi level, tunneling spectra features at negative V should be suppressed, but remarkably this feature seems to be very strong. Nearly identical spectra at similar set-point values have been obtained by other workers [17].

Figures 2(a) and 2(b) show a series of spectra acquired with varying current set points for (a) n-type material and (b) p-type material. As the set point is reduced and the STM tip withdrawn, several dramatic effects are noticed. For n-type material, the large feature D_1 at negative voltages diminishes. Two new states appear above the Fermi level, at $E - E_F = +0.9$ and $+1.9$ eV, and a state also appears below the Fermi level at $E - E_F = -1.1$ eV. The states at about 1 eV above and below the Fermi level we identify with those seen in PES and IPES. The origin of the state observed at 1.9 eV above E_F is not clear at present, although it may be associated with one of the many surface resonances which occur on this surface [8]. For p-type material, at large currents we again see

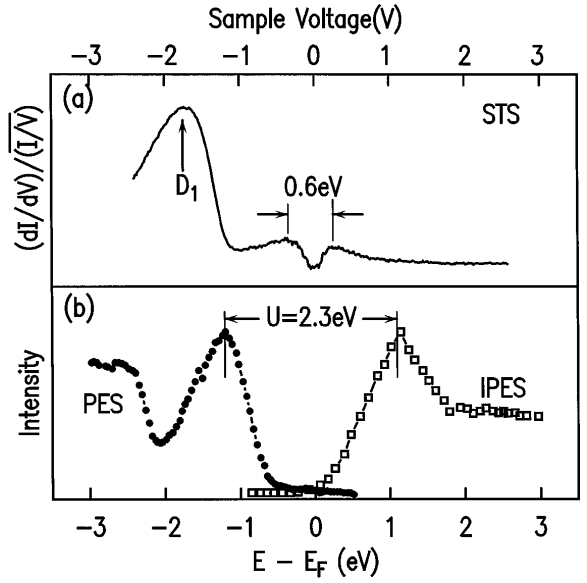

FIG. 1. (a) Tunnel spectrum at a current set point of 100 pA (measurable values of the tunnel current in the spectrum range over 2–3 orders of magnitude below the set point). (b) Results of PES and IPES experiments, taken from Refs. [3] and [4], respectively. The zero level for $(dI/dV)/(\overline{I/V})$ in (a) is given by the horizontal line separating panels (a) and (b).

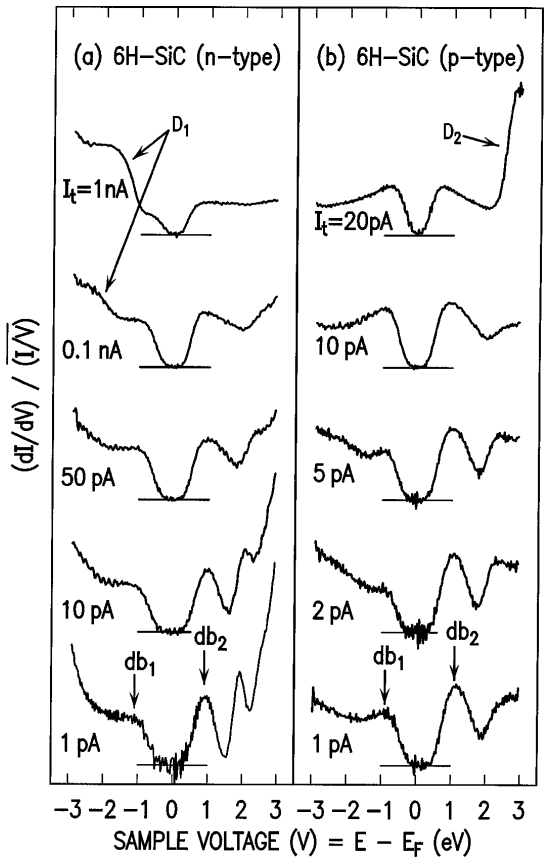

FIG. 2. (a) A series of tunneling spectra with varying current set points (I_t) taken on n-type 6H-SiC. (b) A similar series taken on p-type material. The dopant induced current components, D_1 and D_2, are labeled, as are the two states arising from the Si dangling bonds, db_1 and db_2.

a mostly featureless spectrum with a strong feature D_2 at large positive voltages. As the tip is retracted, this distinctive feature vanishes and the two states at positive voltages and one at about -1 V appear. The position of these states is shifted by 0.2 eV relative to the n-type results due to a shift in the surface Fermi level position, which is clearly evident by comparing the 1 pA spectra in Figs. 2(a) and 2(b).

Clearly, at large tunnel currents the spectra obtained are not intrinsic properties of the surface itself but arise from effects of the STM probe tip on the surface. These observed effects scale with tunnel current, and we attribute them to a type of "spreading resistance" in the transport of carriers to (or from) the localized surface states [18]. Such transport may occur through subsurface bulk states or through surface states, but in either case it appears from the data that at the relatively large current values, limited mobility of carriers results in the formation of a voltage drop on the surface region below the tip apex, as illustrated in Fig. 3. Evidence of such a voltage drop can be seen in Fig. 2; the state at $+2$ V in the 1 pA spectrum of Fig. 2(a) shifts to higher voltages as the set point increases, and the states at $+1$ and -1 V broaden. We note that the transition from high-current to low-current spectra is tip dependent, which is to be expected since a spreading resistance effect scales with current *density* rather than just current itself. Also, at a given current set point, we find the spreading resistance effects to be more severe in the p-type compared to the n-type material, consistent with the higher resistivity of the former.

Explanation of the high voltage, doping dependent features D_1 and D_2 requires additional considerations. First we recall the occurrence of the "dopant-induced" components of tunneling in semiconductors with no surface states, in which, at negative sample bias for n-type material, electrons in the conduction band can tunnel out of the material, and similarly for holes in the valence band seen for positive voltage in p-type material [19]. Such features are not expected (and have never been reported) when a significant number of surface states are present, since the states generally pin the surface Fermi level position at a midgap position thereby pinching off these dopant-induced components [19]. However, with the spreading resistance type of effect described above, the surface Fermi level position will be *different* than that in the bulk, so that the bulk bands can flatten out and produce this source of current. This situation is illustrated in Fig. 3(c). For the case of SiC(0001)$\sqrt{3} \times \sqrt{3}$, the surface Fermi level (at zero tunnel current) is pinned at a location 0.6 ± 0.2 eV below the conduction band edge for n-type material [4]. We then expect, in the limit of large tunnel current, that a dopant-induced component will be seen for negative voltage with magnitude larger than 0.6 ± 0.2 V. This result is close to that seen in the 1 nA spectra of Fig. 2(a) in which the onset of

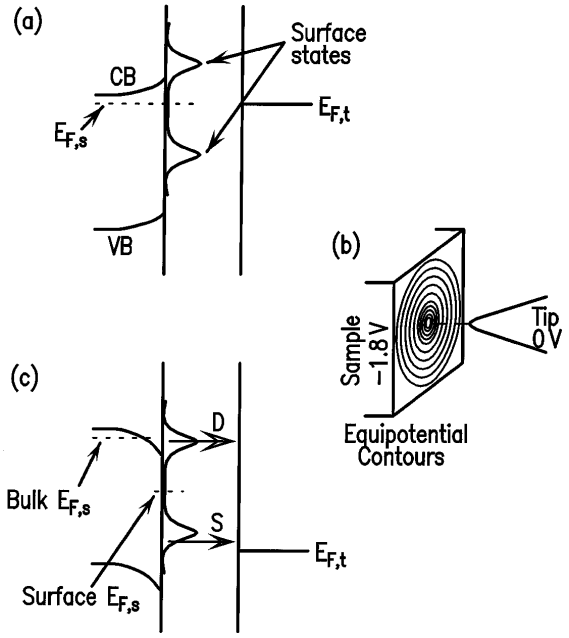

FIG. 3. (a) Zero sample bias band structure for 6H-SiC (0001)$\sqrt{3} \times \sqrt{3}$ structure. CB and VB represent the conduction band and valence band, respectively. $E_{F,s}$ and $E_{F,t}$ denote the sample and tip Fermi levels. (b) Constant potential contours (with potential rising towards the center) on the 6H-SiC(0001)$\sqrt{3} \times \sqrt{3}$ surface in the vicinity of the tip arising from spreading resistance. The surface bands and Fermi level follow these contours. (c) At large negative sample bias, bending of bulk bands leads to dopant induced tunnel current (D), whose magnitude exceeds the conventional tunnel current from occupied surface states (S).

the D_1 component is at about -1 V. Similarly, for p-type material with a pinning position of 0.8 ± 0.2 eV below the conduction band edge, and using the band gap of 2.9 eV, we expect a dopant-induced component at positive voltage greater than 2.1 ± 0.2 V. This result again agrees with the onset of D_2 at $+2.2$ V in Fig. 2(b).

Based on our spectra, we conclude that, in agreement with PES and IPES experiments, we see surface states at about the same energies as predicted by theory. The strong appearance of spreading resistance effects also shows that carrier transport is very limited and so these surface bands are indeed narrow. However, it is important to realize that an electronic band structure alone cannot unambiguously determine the actual surface structure (many semiconductor surfaces show a gap in the surface DOS). Along with the acquisition of spectra, voltage dependent imaging of the surface is necessary to determine the spatial location of these states. In Fig. 4, we show topographic views of the 6H-SiC(0001)$\sqrt{3} \times \sqrt{3}$ reconstruction on n-type material. Figure 4(a) was acquired at a sample voltage of -1.2 V and a current set point of 100 pA. Imaging at positive voltages at this set point was very unstable, as expected from the absence of features in the spectra above the Fermi level. Figures 4(b) and 4(c) were acquired simultaneously (alternating line

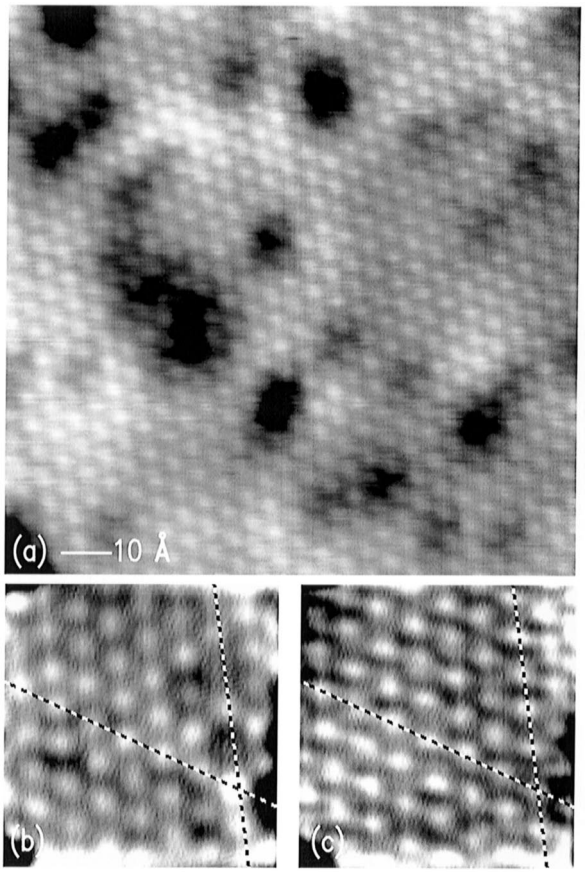

FIG. 4. (a) Surface topograph of the $6H$-SiC(0001)$\sqrt{3} \times \sqrt{3}$ surface taken at sample voltage of -1.2 V and 100 pA current set point. The grey scale ranges from 0 (black) to 0.6 Å (white). (b) and (c): Surface topographs 40 Å $\times$ 40 Å in size taken at -1 V and $+1$ V, respectively. Grey-scale range is 0.15 Å and current set point was 10 pA. The two dashed intersecting lines are drawn over two intersecting rows of topographic maxima, occurring at identical locations in the two images.

scans) at -1 V and $+1$ V, respectively, with a set point of 10 pA. As seen there, the topographic maxima at both polarities are at the same spatial location, thus demonstrating that the states corresponding to both the band 1 V above the Fermi level and the band 1 V below the Fermi level are located at the same position on the surface. Similar results are obtained for sample voltages with magnitudes in the range 0.8–2.0 V. This combination of tunneling spectra and surface topography is clearly consistent with what is expected for a T_4 Si adatom model. Furthermore, it is inconsistent with other models of the surface which involve vacancies [3], trimers [1,8], or more complicated entities since there we would expect either metallic bands or the empty and filled states at different spatial locations or both. Our results are unable to distinguish between Si and C adatoms, T_4 and H_3 adatoms, or discern rearrangements of the bulk layers beneath the adatoms but nevertheless are strongly in favor of a Mott-Hubbard model since the empty and filled states are spatially coincident.

In summary, we have measured tunneling spectra on the $6H$-SiC(0001)$\sqrt{3} \times \sqrt{3}$ surface. Tunneling experiments performed with moderate or high current levels are found to produce artifacts in the spectra, which are explained in terms of spreading resistance effects. At very low currents, the spectra are seen to agree with PES and IPES experiments, with a semiconducting DOS having a state about 1 eV above the Fermi level and another state 1 eV below the Fermi level. STM images of the surface taken at positive and negative polarities show that these two states are localized in the same spatial area, supporting a silicon adatom model which predicts a Mott-Hubbard-type density of states.

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