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Scanning Tunneling Spectroscopy of Oxidized 6H-SiC Surfaces

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Abstract. Scanning tunneling microscopy and spectroscopy has been used to study the electronic states of oxidized 6H-SiC interfaces. The SiC surfaces were oxidized by annealing in an ultra-high vacuum chamber at 600–800ºC under 1×10^{-7} Torr pressure of molecular oxygen. Tunneling spectra revealed two dominant states at –1.8 and 1.5 eV relative to the Fermi level, which lie outside the band gap region but are inhomogeneously broadened such that they extend into the gap, together with additional features within the band gap.

Introduction

Silicon carbide is a promising wide band gap compound semiconductor suitable for demanding applications such as high temperature, high voltage and/or high power devices and sensors. SiO_2/SiC interfaces formed by high temperature oxidation permit field-effect transistor operation. However, it appears that SiO_2/SiC interface has generally poor properties because of the presence of carbon. Conventional oxidation results in mixed oxidation products including carbon, as well as rough interfaces, with high densities of fixed charges and interface trap states [1-5].

Measurements on SiC/SiO_2 interface states in prior work [5-8] revealed distinct donor peaks at E_v+0.3eV [6] and E_v+1.1eV [5], where E_v denotes the valence band edge. There are acceptor peaks at E_v+1.8eV [7] (believed to correspond to a $(C\text{-}C_i)_C$ defect near a V_cO_2 unit [9]), at E_v+2.1eV (associated with interface states having very long charging and discharging times [8]), and at E_v+2.56V [6]. To some extent the interface states of 6H-SiC and 4H-SiC is similar [9], but the interface state density in 4H-SiC is about an order of magnitude higher than that of 6H-SiC [6].

In this work, the thermal oxidation of 6H-SiC (0001) surface has been investigated. Scanning tunneling spectroscopy (STS) was used to examine the electronic states of the oxidized surface. STS is sensitive to states not only in the band gap but also outside the gap. We observe states that are peaked outside the gap but have tails extending into the gap, together with various additional states at energies within the gap.

Experimental

The n-type 6H-SiC (0001) samples studied in this work were cut from a wafer purchased from Cree, Inc. The wafer was miscut 3.5° towards $(11\bar{2}0)$ and had resistivity of 0.057 ohm-cm. Samples were cleaned by acetone, methanol, and de-ionized (DI) water. After the cleaning process they were soaked in 10% HF solution for 10 minutes followed by a rinse with DI water. The samples were then dried by flowing nitrogen. They were transferred to an ultra-high vacuum (UHV) chamber ($<10^{-10}$ Torr) and degassed at 400°C for 2 hours. Oxidation was performed in pure oxygen (99.998%) of 1×10^{-7} Torr at temperatures in the range 600–800°C for 4 hours. Auger electron spectroscopy, performed after various oxidation times, revealed the formation of a saturated surface oxide after 0.5 hour, with thickness of about 1.2 ML (ML = monolayer = 1.217×10^{15} atoms/cm^2).

Commercial Pt-Ir probe tips were used to perform STS measurements. Topographic images were acquired at a constant current of 0.1 nA. For spectroscopy, the differential conductance dI/dV was

measured using a lock-in amplifier with modulation voltage of 50 mV. Normalization of the spectra to obtain $(\mathrm{d}I/\mathrm{d}V)/\overline{(I/V)}$ was performed with broadening of 2 V [10]. Measurements of dI/ds were performed similarly, using a modulation on s of 0.02 nm.

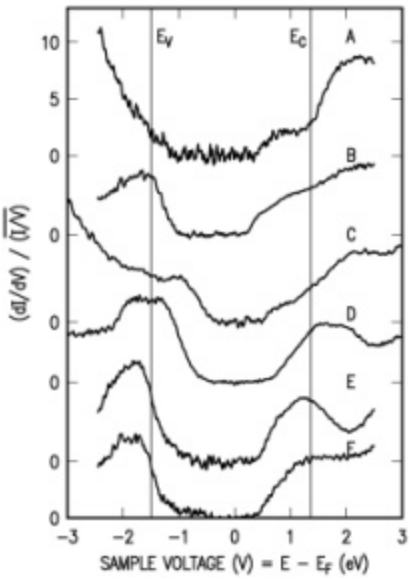

Fig. 1. Typical spectra acquired at various positions on an oxidized SiC(0001) surface. Valence and conduction band edges are indicated.

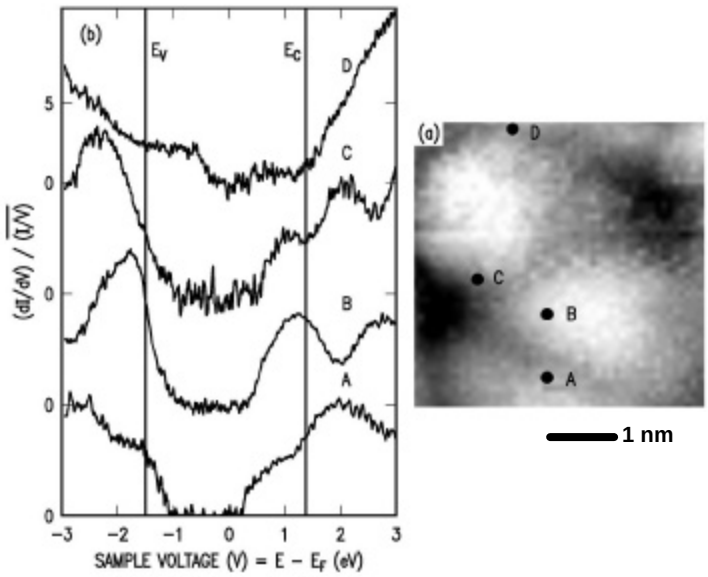

Fig. 2. Spatially-dependent tunneling spectra: (a) Topography of the surface, acquired at sample voltage of –3V, and displayed with a gray scale range of 2.5 Å; (b) tunnel-ing spectra acquired at the locations indicated in (a).

Results

Figure 1 shows typical tunneling spectra acquired from the oxidized surface. The horizontal axis corresponds to the energy of a state relative to the Fermi-level. The Fermi-level for oxidized 6H-SiC is located at about E_v+1.5 eV [5], and using the indirect band gap of 2.86 eV we position the bulk band edges as shown in the figure. States at –1.8 and +1.5 eV relative to the Fermi-level dominate the spectra. The positions and magnitude of these two dominant states vary with location on the surface. Additional states within the gap are also observed, such as the one at +0.8 eV and –0.8 eV seen in Fig. 1 A and C.

Spatial dependence of the results is shown in Fig. 2. Figure 2(a) shows the topography of the surface, with dots indicating the locations at which the spectra in Fig. 2(b) were acquired. Every spectrum in Fig. 2(b) is an average of 3 to 5 spectra taken near (within 0.2 nm) of the specific dot indicated in Fig. 2(a). From the spectra it is clear that magnitude of features at –2, +1.2, and +2 V change with respect to location. To further examine this spatial dependence we acquired current images from the same surface region. In such measurements, the tunnel current is measured at specific voltages at each pixel in the image. These results are shown in Figs. 3(b)-(f), with the constant-current topograph shown in Fig. 3(a). A white shade in the current images represents large current while a black shade represents low (or zero) current. Examining the results, the dominant states at about –1.8 and +1.2 V in spectrum B of Fig. 2(b) are seen to give rise to the high current values observed in Figs. 3(c) and (d); these states are found to be spatially localized at a specific region, near a minimum in the topography in this case. From similar measurements at other surface regions we find that these two states are always localized at overlapping spatial locations, although such locations are not always topographic minima.

To further probe the nature of the states observed in the spectra we have performed measurements of the dependence of the tunnel current on sample-tip separation, s. In general this dependence is given by $I \propto \exp(-2ks)$, so that $k = -0.5 d \ln I / ds$. For an ideal tunnel junction k is given by

$\sqrt{2m(\bar{f} - e|V|/2)/\hbar^2}$ [11], where $\bar{f}$ is the average work function of sample and tip. From this dependence we expect a gradually decreasing k at high voltages. Comparing to the data of Fig. 4, this gradual decrease at high voltages is possibly seen in the data, but a much larger effect is the dramatic decrease as the voltage approaches small values. That behavior begins at voltage of about –2 and +2 V, roughly coinciding with the locations of the bulk band edges. We interpret this behavior as indicative of limited transport of carrier through states near the band edge (and also within the band gap), similar to that previously observed for the SiC(0001)$\sqrt{3}\times\sqrt{3}$-30° surface [14]. Limited transport of the carriers over the surface leads to a buildup of surface charge, which in turn produces band bending in the semiconductor in such a way to decrease the current. Thus, the observed k values become relatively small, in agreement with Fig. 4.

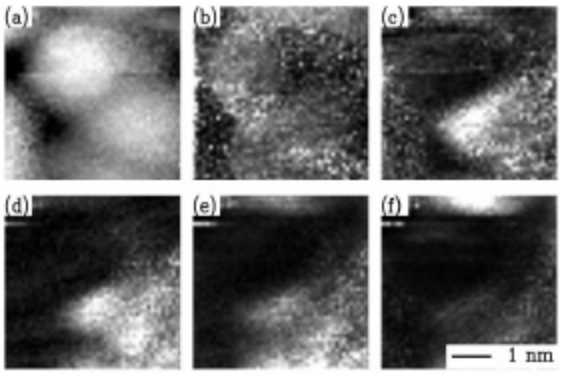

Fig. 3. Current imaging of oxidized SiC (0001) surface. (a) Topography acquired at sample voltage of –3 V and current of 0.1nA. Gray scale range is 2.5 Å. (b-f) current images acquired at sample voltage of -3, -2, 1.4, 2, 2.8V, respectively.

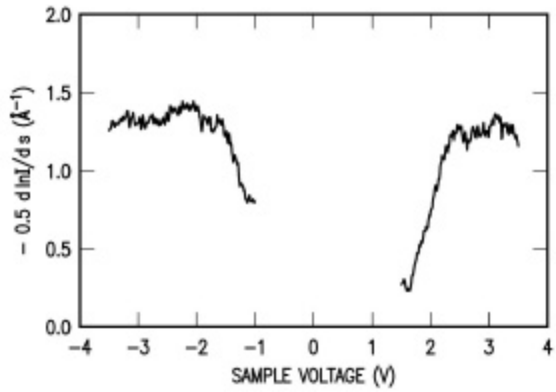

Fig. 4. Local barrier height at oxidized SiC(0001) surface.

Discussion

Let us consider how the states observed in our STS spectra compare with those seen in prior studies of SiC/SiO_2 interfaces [5,7,9,13]. As summarized by Knaup et al. [9], there are various discrete interface states (labeled D_1–D_4) observed to lie within the SiC band gap. The spectrum of these states appears to have the form of a continuous distribution of states, rising towards the band edges. We interpret this distribution below in terms of tails of states extending out of the valence band (VB) and conduction band (CB). Excess carbon, in the form of small defect complexes or larger clusters is generally thought to produce some or all of these states, although definitive identification of the underlying structure and chemical identity giving rise to the states is lacking.

The dominant states seen in our spectra, at energies of about E_v – 0.3 and E_v + 3.0 eV, lie slightly outside of the 6H-SiC band gap region as shown in Fig. 1. These states do display substantial broadening however, which we attribute to inhomogeneous broadening arising from the disorder (structural, and chemical) at the interface, and tails of these states extend into the gap region. Such tails are consistent with the prior observations of interface states just discussed [5]. We cannot offer any direct identification of the defects giving rise to the states based on our work, but our results do demonstrate that there are specific (albeit broadened) states, located just outside the gap region for 6H-SiC, that produce the observed tails. Perhaps these features arise from carbon clusters, as previously suggested [5], and we note in this regard that the recent theoretical work of Knaup does report the existence of states within the VB associated with clusters larger than pairs of C atoms [9].

Our interpretation is supported by the fact that the distribution of interface states extending out from the CB is much less intense for 3C-SiC than for 4H or 6H material [5]. Assuming that the states are all tied to

the VB maximum (an assumption that is known to work reasonably well for the various polytypes of SiC) [5,12] so that the E_v+3.0 eV state we observe would be at the same energy in 3C material, then the downwards shift of the CB edge for 3C-SiC compared to the other polytypes would give rise to a greatly reduced number of these states, consistent with the data and the arguments of Ref. [5].

We also observed additional features in our spectra that are associated with states lying within the gap region. In Fig. 1, spectrum B shows a feature at E_v+2.1 eV, similar in energy to the slow interface states previously reported [8]. Both spectrum A and B in Fig. 1 show a peak close in energy to the previously observed state at E_v+2.56 eV [6]. A donor state at E_v+0.8eV and an acceptor states at E_v+2.0eV are also seen in spectrum D of Fig. 2, similar to the states attributed to a $(C\text{-}C_i)_C$ defect near a V_cO_2 unit [9].

Conclusion

We have investigated the interface states on oxidized 6H-SiC by spatially-resolved scanning tunneling spectroscopy. Relative to the VB maximum, we observe dominant states at E_v – 0.3 and E_v + 3.0 eV. These states lie just outside the band gap and have tails (arising from inhomogenous broadening) extending into the gap region. We also observe discrete donor and acceptor states within the band gap, consistent with those found in prior works.

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