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Possibility of a Mott-Hubbard ground state for the SiC(0001) surface

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The possibility that large electronic correlation effects produce a semiconducting surface-state spectrum for the Si-T_4 adatom model of the SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface is discussed. We argue that a Hubbard model, with parameters obtained from local-density calculations, provides a qualitatively correct account of the excitation spectra inferred from angle-resolved photoemission and inverse-photoemission experiments. The Hubbard U parameter obtained in local-density-functional calculations for the Si-adatom dangling bond on SiC(0001) is 1.6 eV. [S0163-1829(98)50608-X]

SiC is a wide-band-gap semiconductor with numerous technological applications in optoelectronics and in devices that require high-temperature or high-power operation. It has proven to be a viable substrate for growth of nitride-based light-emitting devices. An improved understanding of the surface chemistry and atomic structure could increase the capability to grow SiC at reduced cost and thereby enhance its value as a substrate for growth of nitride materials.

The SiC(0001) surface exhibits a well-ordered $\sqrt{3}\times\sqrt{3}$ reconstruction as one of its intrinsic surface phases.[1] This structure is not the most Si-rich phase or the most C-rich phase of SiC(0001). The addition of Si results in a transition to a 3×3 structure.[1] Heating to temperatures above 1250 °C results in a graphite overlayer above a 6×6 reconstruction.[2]

In a recent work, Owman and Martensson[3] performed scanning tunneling microscopy (STM) for SiC(0001) surfaces and, on the basis of the STM images, suggested that an adatom model was appropriate for the $\sqrt{3}\times\sqrt{3}$ reconstruction. In this structure there is one adatom bonded to three Si atoms in the plane below. First-principles total-energy calculations[4] indicated that the structural model with a Si adatom in the T_4 site was more stable than several other possible models. In particular, the Si-T_4 model was found to be stable with respect to three other adatom models: C-T_4, C-H_3, and Si-H_3. For the Si-T_4 adatom model the electronic band structure was calculated[4] in the local-density approximation. This one-electron theory would predict the existence of a half-filled band of Si dangling-bond states. The electronic states in this band, denoted the Σ_1 band, are localized on the Si adatoms, and the center of the band is located 1.2 eV above the valence-band maximum. Because the total width (W) of the Σ_1 band was quite small ($W=0.35$ eV) it was noted that correlation effects beyond the scope of the one-electron theory could be important.[4] In subsequent angle-resolved photoemission experiments,[5] a band of surface states was observed to be located about 1.0 eV above the valence-band maximum. The dispersion of this band was found to be quite similar to the calculated Σ_1 band, but in contrast to the predictions of one-electron theory, the band was found to be completely filled and located below the Fermi level. Thus, the angle-resolved photoemission experiment implies a semiconducting band structure. In subsequent inverse-photoemission experiments[6] an unoccupied band of surface states having a dispersion very close to the calculated Σ_1 band was identified, and again in contrast to one-electron theory, the band is completely empty. These two experiments lead to a picture in which the surface electronic structure is comprised of *two narrow* ($W\sim0.3$ eV) *bands* of surface states, *one occupied and one empty.* These experiments indicate that the surface is semiconducting, and if the symmetry of the surface is truly $\sqrt{3}\times\sqrt{3}$ then one must conclude that correlation effects are indeed present and strongly influence the surface electronic structure.

We point out that the existence of a half-filled band is a general feature of local-density calculations for the $\sqrt{3}\times\sqrt{3}$ adatom models. More generally, *all* structural models for the SiC(0001) surface having $\sqrt{3}\times\sqrt{3}$ translational symmetry will exhibit one or more partially occupied bands *within the local-density approximation (LDA).* The possibility that the semiconducting nature of the surface arises from a disordered surface having an equal number of Si and C adatoms is inconsistent with STM images showing a well-ordered surface.[3] We may also note that our LDA total-energy and electronic structure calculations[4] (which employed a plane-wave basis) have been confirmed recently by calculations in which a local-orbital basis was employed.[7] Based on prior calculations for Si(111) surfaces having dangling-bond surface states,[8–10] we expect that calculations employing the local *spin*-density approximation would predict a spin-polarized ground state and a gap between occupied and empty states for SiC(0001) $\sqrt{3}\times\sqrt{3}$. However, such calculations have not yet been performed for the $\sqrt{3}\times\sqrt{3}$ reconstruction of the SiC(0001) surface.

As already mentioned, first-principles total-energy calculations have been performed for various models appropriate for the $\sqrt{3}\times\sqrt{3}$ reconstruction. The results of those studies,[4] augmented by results obtained for several additional possible models are shown in Fig. 1. Only two of the possible $\sqrt{3}\times\sqrt{3}$ structures are stable at some point within the allowed range of chemical potential. Over most of the range the Si-T_4 adatom model is the most stable structure. However, in very Si-rich conditions a structure having a Si adatom on top of a Si adlayer becomes lower in energy. The structure may

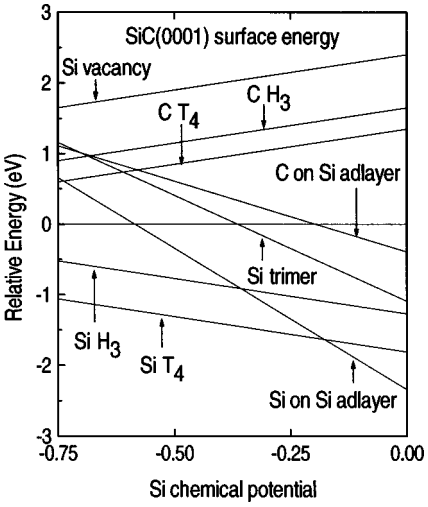

FIG. 1. Relative surface formation energies for possible models of the SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface. In addition to the results obtained in Ref. 4, energies for the Si adatom on Si adlayer and the C adatom on Si adlayer are shown. The energies are expressed relative to the energy of the 1×1 Si-terminated bilayer (relaxed).

be formed by bonding a monolayer of Si to the Si-terminated bilayer and then adding one additional Si atom per $\sqrt{3}\times\sqrt{3}$ cell above this adlayer. We may refer to the structure as a Si adatom on Si adlayer. The surface band structure for the Si adatom on Si adlayer was investigated and found to be completely incompatible with the angle-resolved photoemission measurement: It exhibits four bands of surface states in the gap, one of which has an energy dispersion greater than 3 eV. We may therefore eliminate it as a possible model on the basis of the photoemission[5] and inverse-photoemission[6] experiments. Moreover, this structure is probably less stable than the 3×3 surface under Si-rich conditions. The corresponding C-adatom on Si-adlayer structure is energetically unfavorable, as shown in Fig. 1. The Si-adatom on C-adlayer structure is extremely unstable and therefore does not appear within the energy range plotted in Fig. 1. We are left with one stable structure, the Si-T_4 adatom model, and we will argue that it can account for the experimental data.

In this paper we present a calculation of the surface-state dispersion for the Si-T_4 adatom model that includes correlation effects in the simplest possible model. The calculation is based on a Hubbard model in which the correlation energy of the Si dangling bond (U) is included as a parameter determined from local-density calculations for the various possible charge states of the Si-adatom dangling bond. We will show that the energy dispersions and positions calculated within this model for the occupied and empty surface states are consistent with the available photoemission and inverse-photoemission data.

The Hubbard model has been employed in several previous studies of two-dimensional ordered arrays of Si dangling bonds.[11–13] The model is specified by the one-electron dispersion relation of the dangling-bond band $\varepsilon(\mathbf{k})=\varepsilon_0+t(\mathbf{k})$ and the intra-atomic Coulomb interaction U. U is the energy required to remove an electron from an isolated adatom dangling bond and add it to another adatom. It is equal to the energy of the electronic transition:

$$2D^0\rightarrow D^+ + D^-, \tag{1}$$

where D represents the dangling bond associated with the Si adatom. When U is much larger than the width of the band, the quasiparticle energies are[14]

$$E_1(\mathbf{k})=\varepsilon_0+\tfrac{1}{2}t(\mathbf{k})+\tfrac{1}{2}U\{1-[1+t(\mathbf{k})^2U^2]^{1/2}\}\cong\varepsilon_0+\tfrac{1}{2}t(\mathbf{k}), \tag{2a}$$

$$E_2(\mathbf{k})=\varepsilon_0+\tfrac{1}{2}t(\mathbf{k})+\tfrac{1}{2}U\{1+[1+t(\mathbf{k})^2U^2]^{1/2}\}$$
$$\cong\varepsilon_0+\tfrac{1}{2}t(\mathbf{k})+U. \tag{2b}$$

In going from the one-electron model to the Hubbard model the doubly degenerate band is replaced by two narrower bands that are separated by the energy U. We take ε_0 and $t(\mathbf{k})$ from our previous LDA calculations.[4] These calculations indicate that ε_0 is 1.2 eV above the valence-band maximum and $t(\mathbf{k})$ is a smooth function of $\mathbf{k}$ with $t(\Gamma)=0.18$ eV, and $t(\mathbf{K})=-0.17$ eV.

To determine U we have calculated the energy of the reaction shown in Eq. (1) employing the charged supercell approach.[15] We have employed a cell containing a two-dimensional array of Si adatoms separated by a distance of about 9 Å. This is accomplished by placing one Si-T_4 adatom in each 3×3 cell of a SiC(0001) surface and saturating the remaining six Si dangling bonds with H atoms. A slab containing six layers is employed, and the C atoms on the other side of the slab are terminated with H atoms. The resulting cell contains 27 C atoms, 28 Si atoms, and 15 H atoms. Our purpose in choosing this geometry is to obtain the correlation energy for an isolated dangling bond. The calculations were performed with a 2 $\mathbf{k}$-point sampling scheme. The plane-wave cutoff was taken to be 30 Ry. Tests on thinner slabs indicate that U is not sensitive to the plane-wave cutoff. The charged dangling bonds are obtained by controlling the occupation of the Si dangling-bond orbital, which is occupied by two electrons for the negatively charged state, one electron for the neutral dangling bond, and zero electrons for the positively charged state. For the charged dangling bonds a uniform background of opposite charge is added to the supercell to obtain charge neutrality. This approach has been employed with considerable success to calculate charged point defect formation energies in bulk systems[16,17] and has recently been applied also to charged defects on surfaces.[18,19] With this procedure we calculate

$$U=E(+)+E(-)-2E(0), \tag{3}$$

and find a value equal to 1.4 eV. A spin-polarization energy correction for the neutral dangling bond is estimated to be -0.1 eV, as obtained in previous calculations.[10] The resulting value for the Hubbard U is then 1.6 eV with an uncertainty of several tenths of an eV coming from the nonphysical interaction between the charged dangling bond and the background. The value for U obtained here for the Si-*adatom* dangling bond is somewhat larger than the value (0.9 eV) obtained for the usual Si dangling bond on the Si(111) surface.[10] The larger value may reflect the reduction in screening on the SiC surface relative to that expected for the Si(111) surface: The bulk dielectric constant of SiC ($\sim$6.5) is lower than that of bulk Si ($\sim$12) by a factor of 2.

The quasiparticle energies obtained with the calculated values of U, ε_0, and $t(\mathbf{k})$ are plotted in Fig. 2 along with the experimental results.[20] Excellent agreement with the experi-

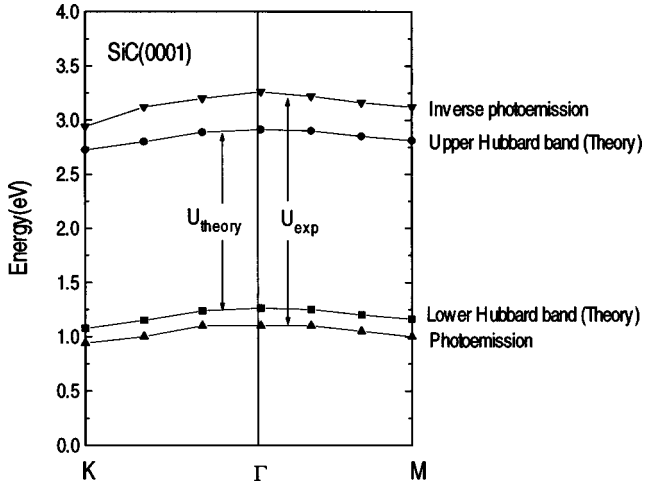

FIG. 2. The band structure for the SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface obtained by photoemission (Ref. 5) and inverse-photoemission experiments (Ref. 6) is compared with the theoretical band structure of the half-filled single band Hubbard model described in the text. The excitation energies are expressed relative to the valence-band maximum. The bulk band gap is approximately 2.9 eV for 6H-SiC.

mental results would be obtained within the Hubbard model simply by choosing U to be 2.1 eV, in reasonable agreement with the calculated value. This agreement, together with the total-energy calculations,[4,7] supports the view that the Si-T_4 adatom model[4] is the correct one, and that the semiconducting nature of the surface observed in the photoemission experiments arises from correlation effects.

We should emphasize that the quasiparticle band structure shown in Fig. 2 describes the single-particle excitations for a half-filled band and should be employed with great caution to describe the effects of doping. It seems likely that additional electrons (or holes) introduced by doping will couple strongly to the adatom positional coordinates, and this could lead to additional states near the Fermi level for doped surfaces.

There have been photoemission measurements of the shifts of the C 1s and Si 2p core levels.[21] These measurements indicate two types of energy shifts for both C and Si levels. Within the Si-T_4 adatom model the Si-related shifts to lower binding energy arise naturally from the Si adatom and the three equivalent Si atoms in the first layer. The remaining Si atoms reside in bulklike environments. The C-related shifts could arise from the two inequivalent types of C atoms in the second layer. One of these C atoms resides directly below the Si adatom and moves away from the surface while the other C atoms in this layer relax towards the surface. A quantitative theoretical study of the surface core-level shifts is required to provide clarification of this hypothesis.

There are a number of important issues that need to be addressed before the Mott-Hubbard model for SiC(0001)$\sqrt{3}\times\sqrt{3}$ can be regarded as firmly established. On the experimental side the most pressing issue is to obtain a definitive identification of the surface atomic structure. Low-energy electron diffraction, x-ray diffraction, or ion-scattering experiments could provide useful tests of the proposed atomic structure. Additional measurements of the surface band-gap energy, for example by tunneling spectroscopy, would also be interesting.

If the Mott-Hubbard model of the SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface can be established, then we will be presented with a well-defined system of interacting spins on a triangular lattice. Such a surface could provide an interesting test for theoretical models of magnetic ordering in two dimensions.[22,23]

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