

Summary Abstract: Mott insulator model of the Si(111)-(2×1) surface

Antonio Redondo, William A. Goddard III, and T. C. McGill

Arthur Amos Noyes Laboratory of Chemical Physics^{a)} and Harry G. Steele Laboratory of Electrical Sciences, California Institute of Technology, Pasadena, California 91125

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Results of fully correlated theoretical *ab initio* cluster calculations are reported¹ and compared with the following experiments: (i) Si(2*p*) core level shifts,^{2,3} (ii) the dispersion of dangling bond surface states,⁴ and (iii) angle-integrated ionization potentials (I.P.) from dangling bond orbitals.⁵

These comparisons show that very strong *electron correlation effects* at the surface lead to *singly occupied* dangling bond orbitals (one per surface atom) that are weakly coupled to yield a ground state for the surface having the form of a nondegenerate, nonmetallic *Mott insulator*.¹

Total energy geometry optimizations on Si₄H₉ and Si₆H₁₅ clusters, including nearest-neighbor interactions, lead to an optimum geometry with a (1×1) structure and a relaxation of $d_1 = -0.14$ Å (toward the bulk, with respect to the tetrahedral geometry), in excellent agreement with the value $d_1 = -0.16$ Å obtained from dynamic low-energy electron diffraction studies⁶ on Te-stabilized Si(111)-(1×1) surfaces. The energy associated with this relaxation is quite small (0.055 eV ≈ 1 kcal/mol).

At this optimum geometry for the neutral system, we calculate⁷ an I.P. for the dangling bond orbital of 5.71 eV. This is in excellent agreement with the experimental results⁵ for (2×1) structures (I.P. = 5.6–5.9 eV).

In addition, the observed core level shifts are consistent with no buckling of the Si(111)-(2×1) surface. Calculations on Si₄H₉ clusters show that the (1×1) structure with equivalent surface Si atoms would lead to four different Si(2*p*) surface core level ionizations¹ (ignoring spin-orbit coupling). Including the spin-orbit interaction, these four levels split up into eight levels: ¹σ₀(1) at +0.34, ¹π₁(2) at +0.23, ³π₀₋(1) at +0.18, ³π₀₊(1) at -0.24, ³π₁(2) at -0.33, ³π₂(2) at -0.38, ³σ₁(2) at -0.52, and ³σ₀(1) at -0.53 eV (weights are given in parentheses). The three levels with positive core shifts (given with respect to the calculated⁷ bulk value of 105.39 eV) are associated with the bulk 2*p*_{1/2} state, while the other five (³π₀₊, ³π₁, ³π₂, ³σ₁, and ³σ₀) are associated with the bulk 2*p*_{3/2} level. The total splitting between the 2*p*_{3/2} derived levels of 0.3 eV is in reasonable agreement with the experimental result of 0.53 eV of Himpsel *et al.*² The total splitting between the ¹σ₀ and ³σ₀ states is 0.9 eV, in good agreement with experimental results by Brennan *et al.*³ who obtain a width of ~0.9 eV.

In our model, the ground state of the surface consists of a singly occupied dangling bond orbital on each surface Si singlet-spin-paired to another such orbital.¹ To compare with angle-resolved photoemission spectra, we consider the final positive ion states obtained by removing an electron out of the ground state of the surface. There are two possible positive ion final states. One consists of an electron whose

orbital has the form of a symmetric combination ($\phi_l + \phi_r$). The other final state corresponds to the antisymmetric combination ($\phi_l - \phi_r$). These two final states lead to two different energy dispersion relationships. These are plotted in Fig. 1(b) and compared with experimental results of Himpsel and Eastman⁴ in Fig. 1(a).

We interpret¹ the results of Himpsel and Eastman as indicated in Fig. 1(a), leading to an experimental dispersion of 0.56 eV in the $\phi_l + \phi_r$ band. We calculate a dispersion of 1.28 eV in this band; however, these calculations only include nearest neighbor effects. At \bar{J} , the experimental separation of the $\phi_l + \phi_r$ and $\phi_l - \phi_r$ bands is 0.46 eV, in reasonable agreement with the theoretical value of 0.31 eV. Overall, the agreement between experiment and theory is good, providing experimental support for the notion that the Si(111)-(2×1) surface has singly occupied dangling bond orbitals and little distribution of the surface atoms.

Because of these large electron correlation effects, normal Hartree-Fock band calculations would tend to yield a buckled surface. This artifact of Hartree-Fock theory can be removed by calculating the ferromagnetic state of the surface or by carrying out an unrestricted Hartree-Fock (UHF) calculation.⁸ In that latter approach, the wavefunction leads to up-spin electrons in half the surface orbitals and down-spin electrons in the other half. The result is an apparently antiferromagnetic surface. This is an artifact of UHF theory, a lower energy being obtained when the proper spin eigenstate is calculated.⁹

The full-length paper¹ has previously been submitted to the Journal of Vacuum Science and Technology. This work

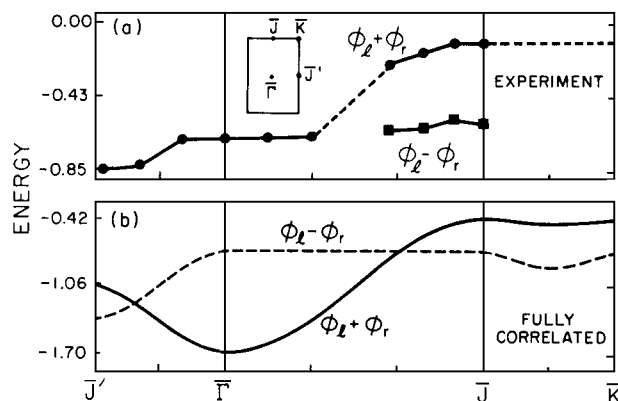


FIG. 1. Experimental and calculated energy band dispersions for surface states on Si(111)-(2×1). The calculated bands in (b) use parameters from *ab initio* cluster calculations. All energies are in eV, referenced to the valence-band maximum.

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¹A. Redondo, W. A. Goddard III, and T. C. McGill, *J. Vac. Sci. Technol.* **21**, 344 (1982).

²F. J. Himpsel, P. Heimann, T.-C. Chiang, and D. E. Eastman, *Phys. Rev. Lett.* **45**, 1112 (1980).

³S. Brennan, J. Stöhr, R. Jaeger, and J. E. Rowe, *Phys. Rev. Lett.* **45**, 1414 (1980).

⁴F. J. Himpsel, P. Heimann, and D. E. Eastman, *Phys. Rev. B* **24**, 2003

(1981); A. Redondo, W. A. Goddard III, T. C. McGill, F. J. Himpsel, and D. E. Eastman, *Phys. Rev. Lett.* (to be published).

⁵D. E. Eastman and W. D. Grobman, *Phys. Rev. Lett.* **28**, 1378 (1972); L. F. Wagner and W. E. Spicer, *ibid.* **28**, 1381 (1972).

⁶H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, *Phys. Rev. Lett.* **37**, 1622 (1976).

⁷A. Redondo, W. A. Goddard III, C. A. Swarts, and T. C. McGill, *J. Vac. Sci. Technol.* **19**, 498 (1981).

⁸R. Del Sole and D. J. Chadi, *Phys. Rev. B* **24**, 7431 (1981); J. E. Northrup, J. Ihm, and M. L. Cohen, *Phys. Rev. Lett.* **47**, 1910 (1981); C. B. Duke and W. K. Ford, *Surf. Sci.* **111**, L685 (1981).

⁹F. Sasaki and K. Ohno, *J. Math. Phys.* **4**, 1140 (1963).