

Proposal for Symmetric Dimers at the Si(100)-2×1 Surface

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(Received 25 January 1989)

Total-energy and core-level-shift calculations in clusters of atoms and a simple model strongly support a symmetric configuration of the dimers at the Si(100)-2×1 surface. The spin arrangement within the dimer is found to be antiferromagnetic lowering the total energy and opening a gap in the surface bands. Different experimental results are examined and found to be fully compatible with this model.

PACS numbers: 68.35.Bs, 71.45.Nt, 73.20.At

The problem of the reconstruction of semiconductor surfaces is beginning to be solved due to the appearance of both new experimental techniques and more powerful calculation methods. Among the experimental techniques, we can mention scanning tunneling microscopy (STM), He scattering, electron microscopy, etc. In spite of these new tools the 2×1 reconstruction of the (100) silicon surface is still controversial. It is generally accepted that the origin of the new periodicity is due to pairing of the atoms at the surface to make rows of dimers. Nevertheless, the actual configuration of the dimers remains unclear. Total-energy calculations using the closed-shell formalism with tight-binding,¹ local-density,^{2,3} or cluster approximation⁴ show that the stable configuration is that of asymmetric dimers. In addition, these calculations^{1,2} show that unless the dimers are asymmetric the surface is metallic contrary to the experimental findings.⁵ However, recent STM^{6,7} measurements show a symmetric dimer arrangement in the clean parts of the surface. Moreover, some experiments are compatible with both symmetric and asymmetric dimers.

In this Letter we show that the symmetric configuration for the dimers is the more stable one, this configuration being fully consistent with all the available experimental data. The key idea to reach this conclusion is that an antiferromagnetic arrangement of the spins within the dimer, not included in previous surface calculations, can substantially lower the total energy making the symmetric dimer the stable one and at the same time open a gap in the surface-state bands making the surface semiconducting.

We first look at the core levels of the silicon surface atoms. If the dimers are asymmetric, there is some charge transfer that should be reflected in the binding energy of the core levels. We have calculated the 2*p* energy level in a cluster with nine silicon atoms simulating a dimer and part of the first layers of the silicon crystal. The rest of it is simulated by appropriate saturators. We have performed an *ab initio* all electron Hartree-Fock calculation with a single- ζ basis. Each basis orbital is expanded in four Gaussian functions.

For the symmetric dimer we obtain that the 2*p* silicon levels corresponding to the dimer shift +0.55 eV towards lower binding energies with respect to the bulk

level (see Table I) without distinction between the atoms. However, in the case of the asymmetric dimer we get the "up" silicon atom with a shift of +1.50 eV in the 2*p* levels, whereas for the "down" atom they shift -0.52 eV (see Table I). This difference is essentially due to a charge transfer of 0.14 electron between the atoms forming the dimer. Experimentally only one peak in the photoemission spectra has been associated with the surface⁸⁻¹⁰ and it is shifted about +0.5 eV towards lower binding energies, in agreement with our calculation for the symmetric dimer. Using a novel calibration technique Rich, Miller, and Chiang¹⁰ stated that both atoms in the dimer are responsible for the emission of this peak. All this gives us the first strong indication in favor of the symmetric bonding.

We have also calculated total energies for both symmetric and asymmetric dimers. In the closed-shell approximation, where no spin correlation is allowed, there is a gain of 0.4 eV/dimer when allowing the dimer to be asymmetric, in agreement with most total-energy calculations using this approximation.¹⁻⁴ However, in the restricted open-shell approximation¹¹ and for the most stable triplet state, we have found that the lowest total energy corresponds to the symmetric configuration. In this case the total energy is 1.3 eV/dimer below the lowest energy obtained in the closed-shell approximation (asymmetric dimer). With other calculation techniques, Redondo and Goddard¹² found a correlated singlet as being the ground state of the system. We are not able to

TABLE I. Core-level shifts associated to the six 2*p* states both in a symmetric and in an asymmetric dimer referred to the bulk value. Shift towards lower (higher) binding energy is represented with a plus (minus) sign. The absolute value of the bulk 2*p* level is -116.63 eV.

Symmetric	Asymmetric
+0.51	-0.54
+0.51	-0.53
+0.54	-0.50
+0.55	+1.49
+0.55	+1.49
+0.57	+1.54

calculate the total energy of such a state, but, in order to compare with their results, we have also performed the above calculations using the unrestricted Hartree-Fock approximation, obtaining that the ground state presents an antiferromagnetic spin arrangement within the dimer, which means that a correlated singlet would be even lower in energy than the triplet referred to above. All these results indicate that the closed-shell approximation and its extensions are not appropriate to handle the problem and that the spin arrangement plays an important role.

Because of the difficulty of a realistic *ab initio* spin-dependent calculation in an infinite system we have sorted out a simple model to study the effect of the spin arrangement in the surface band structure. We have assumed a simple two-dimensional lattice formed by the dangling bonds at the Si(100)- 2×1 surface. We assume symmetric dimers and a tight-binding Hamiltonian that gives the bands shown in Fig. 1(a), which are very similar to those of Chadi.¹ To study the effect of spin arrangement we take the Hubbard Hamiltonian

$$H = H_0 + U \sum_i n_i \uparrow n_i \downarrow,$$

such that H_0 is the tight-binding Hamiltonian and U is

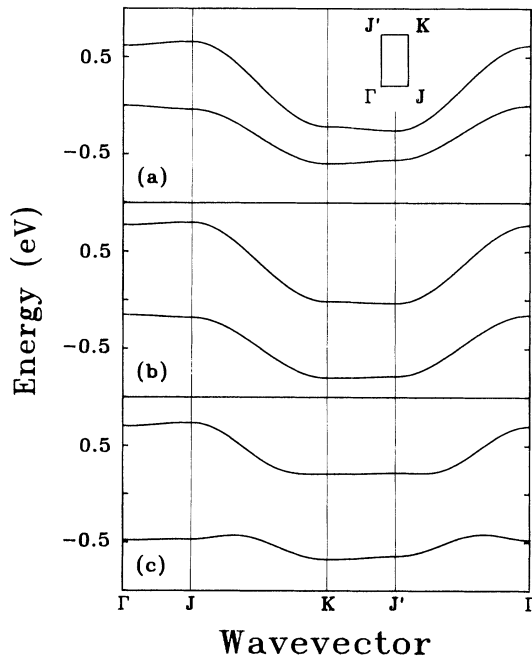


FIG. 1. Surface-state bands near the valence-band maximum in the case of symmetric dimers for three different spin arrangements: (a) no spin ordering (tight-binding Hamiltonian), (b) layered antiferromagnetic, and (c) antiferromagnetic. Inset: Irreducible Brillouin zone for the 2×1 periodicity. In case (c), with a magnetic $p(2\times 2)$ periodicity, there would correspond an irreducible Brillouin zone half as large as the one presented. The bands have been unfolded in order to make them comparable with cases (a) and (b).

the intrasite Coulomb electron-electron interaction which accounts for the spin correlation within the dimers. Before solving the above Hamiltonian it should be pointed out that, considering a standard value of U for bidimensional systems¹³ and a hopping interaction within the dimer (t) consistent with the surface bands in the literature,^{1,2} the ratio t^2/U is much less than 1 eV, as expected from the results obtained in the cluster calculations.

Although it is not essential in the present study, it should be noticed that the ground state associated with the proposed Hamiltonian is not expected to present spin long-range ordering. The interdimer versus intradimer effective magnetic interaction ratio lies below the value for which a transition to Néel ordering occurs¹⁴ and, in addition, the interaction between rows of dimers is rather weak. Therefore, the ground state will be an adiabatic continuation of the state associated to the isolated-dimer limit.

We have solved the above Hamiltonian in the spin-polarized mean-field approximation self-consistently. We have assumed magnetic long-range ordering in order to get the band structure. Therefore, stressing the paramount importance of the spin arrangement within the dimer, we have considered the following magnetic orderings: (i) All the atoms have the same magnetic momentum (ferromagnetic). (ii) The momenta at the atoms of the dimer are equal but oppositely oriented. Nearest neighbors in the direction normal to the dimers have the same momentum (layered antiferromagnetic). (iii) The ordering of the atomic momenta is antiferromagnetic. The first arrangement would correspond to a triplet state for an isolated dimer. It has by far the highest energy and therefore will not be considered here. The band structure obtained for arrangements of (ii) and (iii) is shown in Fig. 1 for $U=0.85$ eV. Similar results are indeed obtained with other values of U . It should be noticed that in the antiferromagnetic case the surface is an atomic (2×1) and a magnetic $p(2\times 2)$, while the layered antiferromagnetic is (2×1) in both senses. We have not studied different orderings between rows due to the very weak effective interaction between them. For the sake of simplicity we have assumed antiferromagnetic ordering in the direction parallel to the dimers for cases (ii) and (iii), which excludes structures like the $c(4\times 2)$.

The main result of Fig. 1 is that the inclusion of the spin arrangement opens a gap at the Fermi level similar to the case of the asymmetric dimers. Within this model the antiferromagnetic arrangement has a total energy of 0.1 eV per atom lower than the layered antiferromagnetic one. It should be stressed that with the inclusion of spin arrangement the occupied band in Fig. 1(a) transforms to a band in fair agreement with experiments.

In Fig. 2 we show the densities of states for the four atoms in the $p(2\times 2)$ unit cell in the antiferromagnetic case. There is a strong spin asymmetry in each atom,

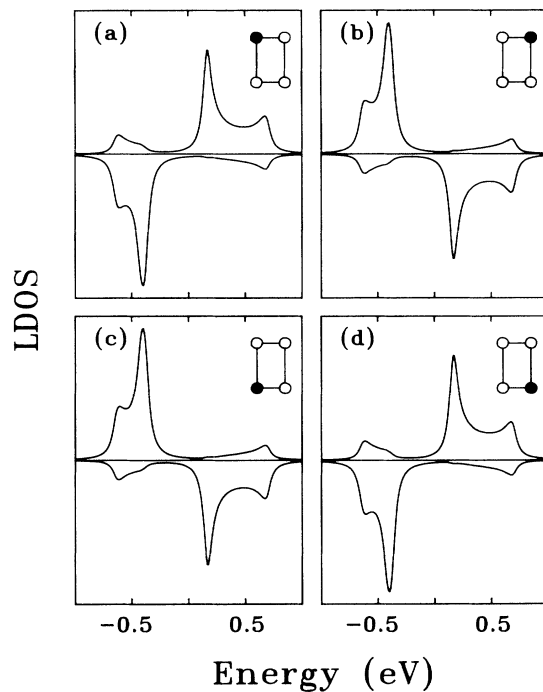


FIG. 2. Local densities of states (LDOS) associated to the four atoms included in a $p(2 \times 2)$ unit cell for the antiferromagnetic ordering. Positive (negative) LDOS corresponds to spin up (down) states. For computational purposes an imaginary contribution to the energy of 0.04 eV has been included in the calculation.

which gives non-negligible magnetic moments on them. Expressing them in terms of $|\langle n_{i\uparrow} \rangle - \langle n_{i\downarrow} \rangle|$ we get 0.76 and 0.81 electron for the antiferromagnetic and layered antiferromagnetic cases, respectively.

The above calculations strongly support the symmetric dimer configuration. This configuration is compatible with the following experimental results.

(i) STM topographs made by Hamers, Tromp, and Demuth^{6,7} clearly show the surface studied here as having a dimerized structure with the dimers being along rows. The surface presents some missing dimers (around 10%), as qualitatively predicted by Pandey.¹⁵ Near defects the dimers buckle forming little domains with $p(2 \times 2)$ or $c(4 \times 2)$ structure. Nevertheless, on the larger regular parts of the surface the dimers are seen to be clearly nonbuckled. This is in full agreement with our proposal that dimers are essentially symmetric; i.e., the minimum potential energy for the nuclei is in the non-buckled position far from defects. The reason why they buckle near defects is beyond the scope of this study.

(ii) Diffraction experiments with low-energy electrons¹⁶⁻¹⁸ and He atoms¹⁹ show a fundamental 2×1 pattern with traces of secondary reconstructions of the $p(2 \times 2)$ and $c(4 \times 2)$ types, which is fully compatible with the view of the surface given by STM topographs presenting these extra reconstructions as stabilized only

in little domains around defects. LEED I - V studies have not led to reliable results on this surface: Jona *et al.*¹⁷ found best agreement of their data with a conjugated chain model which was later found to be very unlikely;⁷ Yang, Jona, and Marcus¹⁸ obtained lateral twisting of the dimers, which was not seen in STM topographs⁷ and is incompatible with low-energy ion-scattering experiments.²⁰

(iii) Medium-energy²¹ and low-energy²⁰ ion-scattering experiments both support the dimerized surface, but they do not distinguish whether dimers are buckled or not.

(iv) There is a considerable amount of experimental information about the surface states of the system under consideration.²²⁻²⁹ Nevertheless, the situation considering unoccupied surface states, defect states, and possible umklapp processes remain quite unclear. However, it is the nonmetallic character of the surface that is generally accepted.⁵ The dispersion of the occupied surface state shown in Fig. 1(c) along the Γ - J' line is in good agreement with the experimental findings.^{22,24} To get a better fit an improved calculation should be done including a real semi-infinite crystal and a correct description of the weak spin correlation between dimers.

(v) The work-function decrease due to hydrogenation of the surface reported by Mönch and co-workers²³ is explained assuming a surface dipole on the clean reconstructed surface. It is not necessary to have buckling to get such a dipole; it may be due to charge transfer from the inner layers to the dimers. Indeed, our cluster calculations give an extra charge of 0.09 electron on each surface atom.

(vi) Core-level photoemission experiments are naturally interpreted assuming a symmetric dimer arrangement as discussed above.

However, an interpretation of the order-disorder transition seen by Tabata, Aruga, and Murata³⁰ based on our findings would not be compatible with the predictions by Ihm *et al.*³¹ in terms of differently oriented asymmetric dimers.

We believe that we have presented conclusive evidence to show that the dimers at the Si(100)- 2×1 surface are essentially symmetric with a strong spin correlation within them. To support these conclusions more experiments and calculations have to be performed. We propose that careful analysis of the core levels and spin-dependent probes would help to clarify the problem.

Detailed calculations of semi-infinite crystals taking into account spin arrangement are in progress.

We are indebted to Dr. R. Ramirez who brought our attention to this problem. Fruitful discussions with Dr. E. G. Michel, Dr. L. Seijo, Dr. L. Miláns del Bosch, and Dr. G. Gómez-Santos are fully acknowledged. Part of this work has been supported by a Comisión Asesora de Investigación Científica y Técnica grant.

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