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# Evidence of asymmetric dimers down to 40 K at the clean Si(100) surface

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We have studied by synchrotron-radiation photoelectron spectroscopy the apparently $p(2\times1)$ structure recently imaged by scanning-tunneling microscopy at low temperatures in the form of seemingly symmetric dimers. Yet we demonstrate that the surface is semiconducting as in the $c(4\times2)$ phase and that most dimers remain asymmetric. The $p(2\times1)$ structure seen at low temperature may result either from a ferromagneticlike arrangement of static buckled dimers or, eventually, from an artifact of local tip-surface interactions.

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The silicon (100) surface has been extensively studied both experimentally and theoretically due to its major practical importance since most LSI devices are fabricated on this surface.[1] It is well established that at the (100) surface pairs of atoms form dimers along the $[01\overline{1}]$ direction to lower the surface energy by reducing the number of unsaturated dangling bonds. Following this dimerization a $p(2\times1)$ reconstruction is typically observed at room temperature.

These dimers are buckled and constitute the building blocks of different reconstruction; their origin and nature are among the most intensively discussed issues in surface physics. Symmetric dimers would lead to a metallic surface since the electronic bands derived from the dangling bonds at the two atoms of each dimer overlap in energy at the Fermi level. Buckling of the dimers leads to an energy gain of about 0.1 eV per unit cell by opening a Jahn-Teller-like gap between the surface-induced dangling-bond states.[2] Hence a semiconducting surface results, in agreement with experiment.[3]

The $p(2\times1)$ structure observed at room temperature (RT) is due to the thermal activated flip-flop motion of these asymmetric dimers between their two possible orientations. The surface dimer rows are maintained up to 1463 K, while the measured melting temperature is 1680 K.[4] Si $2p$ core-level spectra measured with synchrotron radiation show that the number of asymmetric dimers is conserved at high temperatures.[5] These buckled dimers seem to fluctuate between up and down positions with the same tilting angle, although the flipping frequency is higher at elevated temperatures.[6] Furthermore, the average time spent by instantaneous symmetric dimers does not change from RT up to 1100 K.[5]

At low temperatures, below about 200 K, the $p(2\times1)$ structure is reversibly transformed into the $c(4\times2)$ structure. The structural transformation is described as an order-disorder phase transition: the $c(4\times2)$ structure results from the freezing of the buckled dimers with alternated configurations of the tilt angles, as in a simple two-dimensional antiferromagnetic ordering, depicted in Fig. 1, in such a way as to reduce the stress in the back bonds. In scanning-tunneling microscopy (STM) images taken at about 100 K, the $c(4\times2)$ reconstructed surface appears as a zigzag pattern of dimer rows. This wiggling along the rows reflects the alternate orientations of the buckled dimers; it disappears above the phase-transition temperature: typically at RT the dimers look symmetric because only their time-average position can be observed upon STM imaging.

Until the beginning of 2000, this $c(4\times2)$ reconstruction was considered the ground-state structure, although practically degenerate with the $p(2\times2)$ configuration, which consists of an out-of-phase and an in-phase ordering of the buckled dimers along and perpendicular to the dimer rows.[7] It was thus quite a surprise to recover, upon further cooling the $c(4\times2)$ surface below about 100 K, a $p(2\times1)$ arrangement of, apparently, symmetric, unbuckled dimers in two independent STM observations at temperatures down to 5 K.[8,9] Indeed this recent discovery could eventually question the current common belief about the stability of the asymmetric dimers at the zero-temperature limit.

The two groups gave conflicting interpretations of this surprising observation. One interpretation was in terms of a

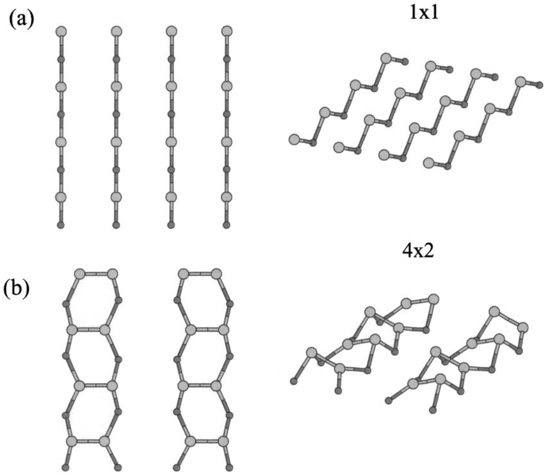

FIG. 1. Ball and stick bilayer model of (a) the unreconstructed Si(100)1×1 surface, and (b) the $c(4\times2)$ structure. Left panels: top views; right panels: side views. Large circles represent topmost surface atoms and small circles second layer atoms.

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sort of reentrant flipping motion of the *asymmetric* dimers because the potential barrier for the dimer buckling would have been reduced at low temperature (LT) by anharmonic potential effects in the subsurface layers giving a dynamically active surface phase, as at RT.[8] The other, on the contrary, gave evidence of the stabilization of static *symmetric* dimers.[9] Indeed symmetric dimers have not been completely excluded by theorists; they could be possibly stabilized either by an antiferromagnetic coupling between dimer spins[10] or by an electronic correlation between the dimers.[11]

Possibly, tip artefficts in STM imaging may play a key role; yet, here again, opposite arguments have been given. Some authors argue that the tip would tend to tie the atom under the tip into a down position (up position) for negative (positive) sample biases, hence the appearance of the $p(2\times1)$ phase below 80 K would be due to the absence of up-atom configurations, a phenomenon different from the appearance of the $p(2\times1)$ phase at RT.[12] Others, on the contrary, conclude that the influence of the tip is negligible at typical tunneling conditions.[9,13]

Hence we see that this discovery raises challenging questions: is the LT $p(2\times1)$ structure a new ground-state phase comprising *static symmetric* dimers, as concluded by Kondo *et al.*,[9] is it a dynamically active phase comprising *flipping asymmetric* dimers, as suggested in Ref. 8, or is it just an effect of strong tip-surface interactions as underlined in Ref. 12?

Experimentally this question must be addressed with a noninvasive technique; hence to solve this issue we used synchrotron-radiation photoemission. Valence-band photoemission shows that the surface electronic structure remains semiconducting at 40 K as in the ordered static $c(4\times2)$ phase. High-resolution core-level spectra reveal that the number of asymmetric dimers is essentially the same in both cases. The possible origin of the apparently symmetric dimers in STM imaging at LT is then discussed.

The experiment was performed at the VUV beam line of ELETTRA in Trieste, Italy. This beam line has a Dragon monochromator, which spans an energy range from 20 to 1000 eV with a resolving power better than 10 000. The silicon sample ($n$ type, 5.5 $\Omega$ cm, double domain), before insertion into the vacuum chamber, was degreased and etched according to the Ishizaka and Shiraki procedure.[14] In ultrahigh vacuum it was thoroughly outgased at 500 °C and then annealed at 850 °C for 10 min and flashed to 1100 °C. This cleaning procedure produces a sharp two-domain $2\times1$ diffraction pattern with low background in low-energy electron diffraction (LEED). Photoelectron spectra were acquired with two different analyzers at total-energy resolutions better than 50 meV: either an angle-resolved one with an acceptance of 2° or an angle-integrating one (acceptance cone of 16°). They were recorded after cooling to ~110 K for measurements on the $c(4\times2)$ phase, and then after further cooling at 40 K for measurement on the low-temperature $p(2\times1)$ structure: it is worth pointing out that, in our experimental setup, it was not possible to observe the LEED pattern at 40 K. This 40-K temperature was controlled by a platinum resistance attached to the sample holder. It was further checked by measuring the width of the Fermi step of a lead thin film evaporated *in situ* directly onto the sample.

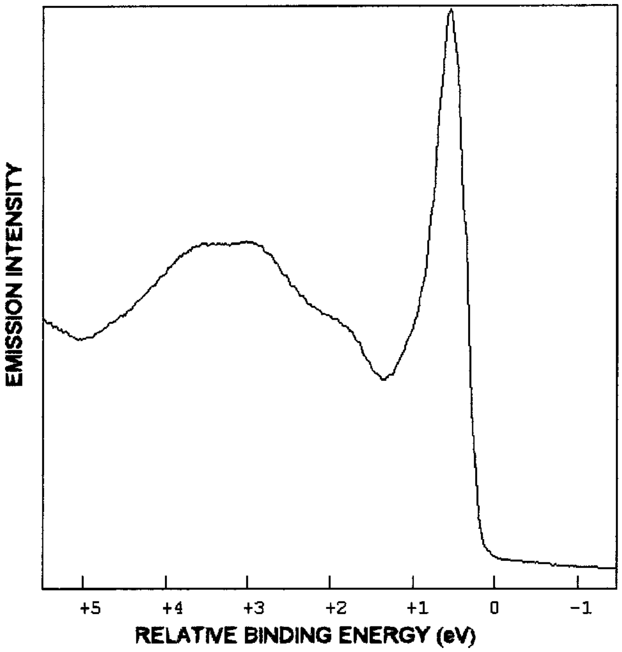

FIG. 2. Angle-integrated valence-band spectrum ($h\nu = 22.1$ eV) from the $2\times1$ structure at 40 K. The binding energy is referenced to the Fermi level.

Figure 2 presents an angle-integrated, normal-emission, valence-band (VB) spectrum from the double-domain surface collected at 40 K but corrected for an inevitable surface photovoltage effect (precisely determined from the Si $2p$ core-level shift at this low temperature). This spectrum shows that the surface is clearly semiconducting as is the case of the $c(4\times2)$ phase [as well as the $p(2\times1)$ phase at RT]. We further confirmed this semiconducting nature upon collecting with angle-resolved photoemission VB spectra (not shown here) along the $[01\bar{1}]$ direction, which is common to both $p(2\times1)$ and $p(1\times2)$ domains of our double-domain sample. The spectrum is dominated by a strong surface state at ~0.55-eV binding energy[15] that can be compared directly to the electronic state, which corresponds to the surface state derived from the occupied up-atom dangling bonds of the asymmetric dimers, are the building blocks of the $c(4\times2)$ phase (which we measured at 110 K) and of the $p(2\times1)$ phase at RT.[2,3] *Per se*, these results reveal that no significant increase of the number of *symmetric dimers* has occurred at 40 K: indeed, a dominant contribution of unbuckled dimers would instead give a metallic character to the surface electronic structure. It is worth noting that the valence band in Fig. 2 has been taken with an angle-integrated analyzer and is a strong indication of a very good quality for our surface since the surface-state band at +0.55 eV has a much stronger intensity as compared to the bulk structures around +2–4 eV. This figure can be compared with previous valence-band results of Refs. 3 or 15.

In Fig. 3, we compare high-resolution Si $2p$ core-level spectra, acquired with the angle-integrating analyzer in a very surface-sensitive mode. The experimental conditions

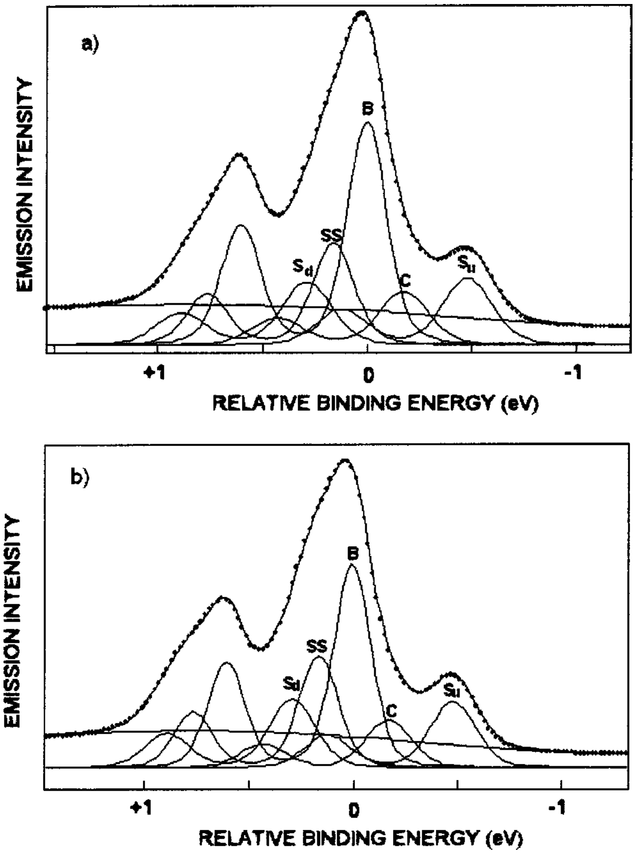

FIG. 3. Angle-integrated Si $2p$ core-level spectra ($h\nu = 138$ eV) acquired at (a) 110 K for the $c(4\times2)$ phase and at (b) 40 K for the $2\times1$ low-temperature structure. Fitting parameters at 110 K (40 K) for the different components: Gaussian full width at half maximum FWHM's of, respectively, 190(180), 200(190), and 244(230) meV for the bulk line *B*, the subsurface atoms *SS*, the up atoms $S_u$, and down atoms $S_d$ in the asymmetric dimers, the atoms in the symmetric dimers *C*, and relative energy shifts $-483(-485)$, $-177(-176)$, $+0.160(+0.160)$, and $+0.285(+0.285)$ for $S_u$, *C*, *SS*, and $S_d$; common to both spectra: identical spin-orbit splitting of 0.602 eV and Lorentzian FWHM of 0.056 eV, branching ratio of $0.52\pm0.02$ for each component, and polynomial background.

were practically identical, except for the temperatures of the measurements, respectively, of 110 and 40 K. The two spectra look pretty much the same, with just a slight narrowing of their constituent components at 40 K. Their similarity is confirmed by a detailed comparative deconvolution. To this end we use the most recent model function devised by Pi, Chang, and Hang.[16] This model function comprises four surface components in addition to the bulk line. For the $c(4\times2)$ phase, the two components at the lowest and highest binding energies are, respectively, assigned to the up and down atoms within the asymmetric dimers. The two other components on each side of the bulk line are associated with atoms in symmetric dimers, which are always observed by STM on the Si(100) surface, for the component on the low binding-energy side and on subsurface atoms for the component on the high binding-energy side. These assignments are in good agreement with the quasiparticle calculations of the surface core-level shifts of Rohlfing, Krüger, and Pollmann.[17] The comparison of the spectra and of their deconvolutions reveals just a ~10-meV narrowing of each component at 40 K. Note the high quality of the decompositions; using instead the original model function of Landemark *et al.*[18] gave poorer fits: this is particularly true near the valley around a relative binding energy of +0.4 eV, as also visible in Fig. 2(c) of Ref. 18. These parameter values are quite close to those of Pi, Cheng, and Hong;[16] we further stress that with essentially the same parameter values we could also fit the spectra acquired with the angle-resolving analyzer at different emission angles: normal, 30° and off-normal emission, 50°. We want to point out that the aim of the present work is not the fitting procedure of core levels and their deconvolution with the assignment of components to building blocks of the reconstruction, but that the core-level spectra taken at two different temperatures are very similar: in this sense the decompositions by Landemark *et al.* and Pi, Cheng, and Hong are both good, with the parameters from Pi, Cheng, and Hong closer to our own. Finally, the loss structures observed by Pi, Cheng, and Hong are not observed in our spectra and this can be due to a small contamination at the surface or to the presence of defected areas on the surface in the case of Pi, Cheng, and Hong's experiment. We observed similar structures in the case of the Si(110) surface for a surface kept in UHV for several hours[19] and in the case of C60 on Si(111)$\sqrt{3}\times\sqrt{3}$-Ag.[20]

The intensity ratio $C/S_u+S_d$ of the components attributed to atoms in symmetric ($C$) and asymmetric ($S_u+S_d$) dimers deduced from the fits gives directly an estimate of the corresponding coverages on the surface. We obtain a ~40% coverage by symmetric dimers at 110 K, which is compatible both with STM observations of the nominally $c(4\times2)$ surface[21] and decompositions of Si $2p$ core-level spectra[13,22] at similar temperatures. However, below 100 K, STM imaging reveals that most of the surface tends to be covered by apparently symmetric dimers in the low-temperature $p(2\times1)$ structure (areas of symmetric and asymmetric dimers are comparable at 80 K while asymmetric dimers are only visible near defects and step edges at 20 K).[8,9] If really symmetric dimers are involved in this $p(2\times1)$ structure, that would constitute, in such a case, a new static low-temperature phase; one would expect a strong increase of the ratio $C/S_u+S_d$ at 40 K. Instead we obtain a comparable (even slightly reduced) ratio of ~36%.

This rules out the possibility that static symmetric dimers form a new low-temperature $p(2\times1)$ phase. Together with the valence-band results described above, this indicates, on the contrary, that most of the apparently symmetric dimers are in fact really asymmetric.

Then what could be the origin of the low-temperature $p(2\times1)$ structure? One explanation proposed by Yokoyama and Takayanagi[8] is that the buckled static dimers in the $c(4\times2)$ phase start again at low temperature, as they do above 200 K, a flip-flop motion because of a reduction by anharmonic potential effects in the subsurface layers of the potential barrier for dimer buckling. In such a case one could possibly expect below 100 K a slight broadening of the $S_u$ and $S_d$ components in the Si $2p$ core-level spectra as a result of increasing dynamical disorder. This is not the case, instead we determine a 10-meV narrowing at 40 K in agreement with reduced phonon broadening. We noted also a marked increase of the intensity of the surface state associated with the up atoms in the valence-band spectra, hardly compatible also with an increasing disorder. Hence we believe that this explanation is rather unlikely.

A second explanation would be that instead of a dynamically active phase, as at RT where the buckled dimers are ‘‘paramagnetically’’ disordered, the $2\times1$ structure at low temperature really corresponds to a static new phase composed of asymmetric dimers arranged in a ferromagneticlike fashion.[23] However, on the one hand this is not supported by theoretical calculations, which instead predict a higher reconstruction, i.e., $p(2\times2)$ or $c(4\times2)$, as the ground-state structure[23,24] and, on the other hand, the appearance of static, ferromagnetically aligned, buckled dimers in STM images would be possibly different from symmetric ones.

A third explanation would be that the $p(2\times1)$ structures are images of ‘‘bulk states’’ instead of surface $\pi$ states. This would occur wherever electrons cannot be supplied into $\pi$ states or removed from $\pi^*$ states fast enough compared with the rate of the tunneling current. In such a case, the STM currents would unpin the surface states locally, especially at low temperatures; furthermore, the local depletion of the occupation of the surface states would reduce the Jahn-Teller-like distortion within each dimer, which could lower the activation energy for flipping.[12] Indeed this last explanation refers to tip-surface interactions, which, however, are denied by other STM groups.[9,13] The results presented here, obtained with photoemission, a noninvasive technique, are best compatible with these last two explanations. However, unfortunately, they do not allow to discriminate between them.

In conclusion we have studied, by synchrotron-radiation photoelectron spectroscopy, the origin of the $p(2\times1)$ structure observed by STM at low temperatures in the form of apparently symmetric dimers. We prove that most dimers remain asymmetric as in the $c(4\times2)$ phase. This means that the asymmetric dimers are the building blocks of all reconstructions from 40 up to 1000 K. The $p(2\times1)$ structure at low temperature may be due to a ferromagneticlike arrangement of static buckled dimers or may eventually result from an artifact of local tip-surface interactions. More refined calculations are needed to clarify this issue.

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