Angle-Resolved-Photoemission Study of the Electronic Structure of the Si(001)$c(4\times2)$ Surface

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A wide-terrace single-domain Si(001)$c(4\times2)$ surface has been obtained by cooling a wide-terrace single-domain Si(001)2×1 surface to 200–80 K. Angle-resolved ultraviolet photoelectron spectra have been measured for the Si(001)$c(4\times2)$ surface at 200–100 K and compared with those for the Si(001)2×1 surface. The electronic structure of the Si(001)$c(4\times2)$ surface appears to be explained as that expected for "antiferromagnetic" order of asymmetric dimers of surface Si. The electronic structure of the Si(001)2×1 surface appears to be reminiscent of the $c(4\times2)$ surface.

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The Si(001)2×1 surface has been one of the simplest, but still most controversial, semiconductor surfaces. Although it is generally accepted that the origin of the 2×1 periodicity is due to pairing of the surface Si atoms, the actual configuration of the dimers remains unclear. The presence of asymmetric dimers was first suggested by Chadi[1] from an energy-minimization calculation of the electronic structure in order to explain the nonmetallic nature of the 2×1 surface revealed by photoemission.[2] Total-energy calculations showed later that an arrangement of asymmetric dimers is more stable than that of symmetric dimers.[3-5] Ihm *et al.*[6] and Saxena, Gawlinski, and Gunton[7] pointed out later that the 2×1 periodicity is not a ground state of the Si(001) surface and a higher-order periodicity should occur at about 250 K. A low-energy electron-diffraction (LEED) study has recently shown an order-disorder transition of the Si(001) surface between 2×1 and $c(4\times2)$ periodicities at about 200 K.[8] All these studies are consistent with the asymmetric-dimer model of the Si(001) surface.

However, recent scanning-tunneling-microscopy (STM) studies showed an arrangement of symmetric dimers in "ideal" parts of the surface.[9,10] Also, from photoemission spectra with a single surface-shifted Si $2p$ component for the 2×1 surface, it is concluded that there is no large and asymmetrical charge redistribution within each of the dimers.[11] Thus, an "antiferromagnetic" arrangement of spins of the dangling-bond electrons of the dimers has been introduced to overcome these controversies.[12]

From an experimental viewpoint of the electronic structure of the 2×1 surface, detailed information about the surface-state (SS) structure has been obtained by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS).[13] The ARUPS results are, in principle, consistent with those expected for the "ferromagnetic" arrangement of asymmetric dimers. Nevertheless, there remain additional surface bands that are not expected for an ideal ferromagnetic arrangement of asymmetric dimers. In a recent ARUPS study on a single-domain Si(001)2×1 surface, the additional SS bands were ascribed to $c(4\times2)$ and/or $p(2\times2)$ structures coexistent with the 2×1 periodicity.[14] In view of these circumstances, it is of great interest to measure ARUPS spectra of a single-domain Si(001)$c(4\times2)$ surface, and these are reported in this Letter.

The experiments were performed in a UHV chamber equipped with apparatus as described elsewhere.[15] The energy and angle resolutions of the ARUPS system were ~0.1 eV and ±1.5°, respectively. The sample was a mirror-polished Si(001) wafer ($25\times3.5\times0.38$ mm^3), whose surface normal was off from the [001] orientation by only ~3′ along a [110] direction and 0–~30″ along the other [110] direction. After the sample was preoxidized,[16] it was annealed (~1000 °C) and covered with Si epitaxial layers (~1000 Å) in the UHV chamber. After several cycles of annealing and epitaxial growth, LEED patterns changed from double-domain (DD) to single-domain (SD) 2×1 and the ratio of LEED-spot intensity for the major 2×1 domain to that for the minor domain reached more than 10:1 (cf. Fig. 1).

The sample was then cooled with copper-lead wires connected between a cold head of a helium cryogenic re-

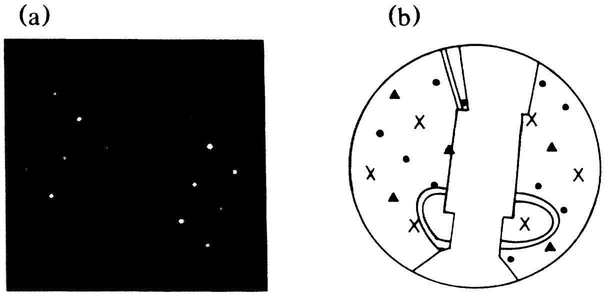

FIG. 1. (a) LEED pattern of the single-domain Si(001)$c(4\times2)$ surface at ~200 K and an electron energy of 50.5 eV. (b) Schematic of the LEED pattern; crosses are fundamental spots, triangles are half-order spots, and circles are quarter-order spots. Weak spots not shown in the schematic are due to the minor domain of $c(4\times2)$.

frigerator and a Mo sample holder. The sample temperature was monitored with a thermocouple attached to the sample holder and it decreased within 10 min to below $-75\,^\circ$C from the annealing temperature of $\sim 1000\,^\circ$C. The formation of a SD $c(4\times2)$ surface was confirmed from LEED patterns such as shown in Fig. 1. Sharp $c(4\times2)$ LEED spots were observed for the tested temperature range of 200–80 K. At ambient temperature, narrow half-order streak lines were noticed in LEED patterns as before[14] and changed to quarter-order spots as the temperature decreased. A clean and well-ordered substrate was needed to obtain a well-ordered $c(4\times2)$ surface. ARUPS spectra for the $c(4\times2)$ surface were measured at temperatures between 200 and 120 K. The Fermi level of the spectra was determined from the Fermi level of the Mo sample holder.

ARUPS spectra for the $c(4\times2)$ surface are shown in Fig. 2. The polar angle (θ) of photoelectron emission is changed so as to scan the symmetric axes of the surface Brillouin zone (SBZ) [cf. inset in Fig. 2(c)]. Unpolarized He I light (21.2 eV) was incident at 45° polar angle opposite to the photoelectron emission. For the $\bar{Y}$-$\bar{Y}'$ direction, the values in Å^{-1} of the surface component ($k_\parallel$) of the electron wave vector at binding energy (E_b) of ~ 1.0 eV are marked with respect to that for the $\bar{Y}'$ point. For the $\bar{\Gamma}$-$\bar{J}$ and $\bar{\Gamma}$-($\bar{J}'$) directions, ARUPS spectra for the SD 2×1 surface are overlaid; bulk peak positions ($E_b \gtrsim 4$ eV) are aligned by shifting the 2×1 spectra by 0.16 eV toward the lower-E_b side.

A dramatic change in the spectral profiles from the 2×1 to $c(4\times2)$ surfaces is found for the direction perpendicular to the dimer row ($\bar{\Gamma}$-$\bar{J}$ direction). For the $\bar{\Gamma}$-($\bar{J}'$) direction, most of the structures in the $c(4\times2)$ spectra are already visible in the 2×1 spectra although they are much sharper in the $c(4\times2)$ spectra. Along the $\bar{Y}$-$\bar{Y}'$ direction, one can notice dominant structures at $E_b \lesssim \sim 1.0$ eV which should be due to surface states.

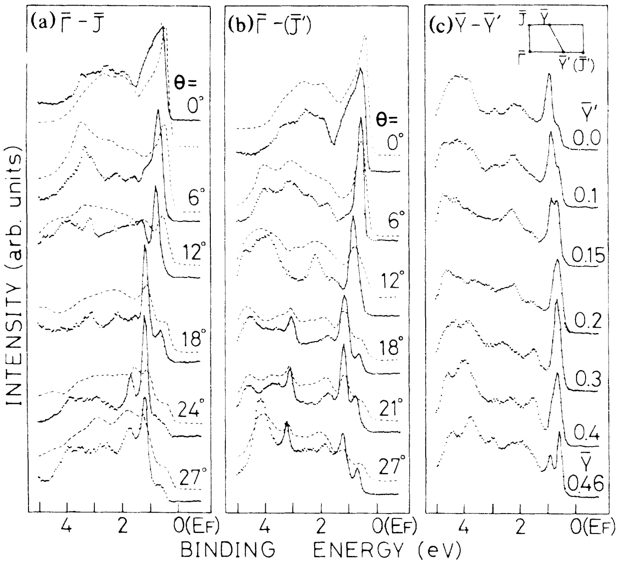

FIG. 2. He I ARUPS spectra of the SD Si(001)$c(4\times2)$ and 2×1 surfaces. Symmetric points in the surface Brillouin zones for the $c(4\times2)$ and 2×1 are indicated in the inset in (c). Dotted and dashed curves are for the $c(4\times2)$ and 2×1 surfaces, respectively; parts of the dotted curves are connected by solid lines for clarity: (a) along $\bar{\Gamma}$-$\bar{J}$, (b) along $\bar{\Gamma}$-($\bar{J}'$), and (c) along $\bar{Y}$-$\bar{Y}'$ lines.

E_b-$k_\parallel$ diagrams converted from the spectra in Fig. 2 and others are plotted in Fig. 3. The band A in Fig. 3(a) corresponds to the dispersion of dominant peaks in the spectra of Fig. 2(a). This band has been previously at-

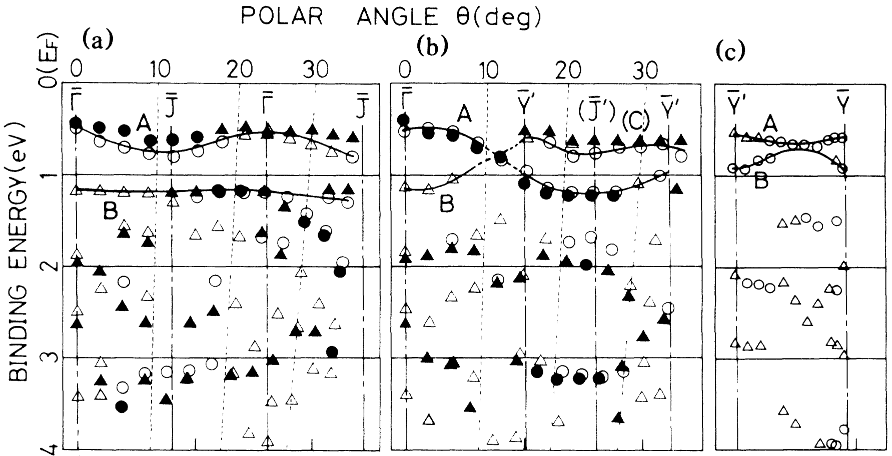

FIG. 3. E_b-$k_\parallel$ diagrams for the SD Si(001)$c(4\times2)$ and 2×1 surfaces. Open and solid symbols are for the $c(4\times2)$ and 2×1 surfaces, respectively. Circles stand for strong or clear peaks and triangles stand for weak or broad structures in the actual spectra. The E_b-$k_\parallel$ diagram for the 2×1 surface is shifted toward lower E_b by 0.16 eV in order to align bulk peaks at $E_b \gtrsim 4$ eV: (a) along $\bar{\Gamma}$-$\bar{J}$, (b) along $\bar{\Gamma}$-($\bar{J}'$), and (c) along $\bar{Y}$-$\bar{Y}'$ lines.

tributed to the dangling bond of the dimers for the 2×1 surface.[14] Peaks in the band A for the $c(4\times2)$ surface are dominant and disperse more than those for the 2×1 surface. The same band A is found along the $\bar{\Gamma}$-$\bar{Y}'$-($\bar{J}'$) direction in Fig. 3(b). This band disperses in almost the same manner as that for the 2×1 surface. A new surface band characteristic of the $c(4\times2)$ surface should appear in addition to the band A, since the area of the SBZ is half of that for the 2×1 surface. The additional band B is found as plotted in Fig. 3. Parts of this band have been already noticed for the 2×1 surface and attributed to partial $c(4\times2)$ and/or $p(2\times2)$ structures.[14] The dispersion of the two bands A and B along the $\bar{Y}$-$\bar{Y}'$ direction is traced in Fig. 3(c). Other possible surface bands due to dimer bonds and backbonds of the dimers, which may lie at $E_b \geq \sim 1.5$ eV, will not be discussed here.

Recently Zhu, Shima, and Tsukada made an *ab initio* calculation of the electronic structures for the 2×1, $p(2\times2)$, and $c(4\times2)$ surfaces based on the asymmetric (buckled) dimer model for the Si(001) surface.[17] For the $c(4\times2)$ surface, the electronic structures are calculated using two kinds of atomic positions of the "antiferromagnetically" ordered buckled-dimer model; one is an optimized structure with a total-energy minimization named geometry (a) here, and the other is a geometry modified from an optimized geometry provided by Yin and Cohen[18] named geometry (b) here. The calculated surface-state bands are compared with the present result in Fig. 4. The calculated bands are double, which is an artifact of the slab calculation. In the comparison, the experimental curves are shifted upward by 0.38 eV to obtain better agreement of overall dispersion. As seen in Fig. 4, very good agreement is obtained for the geometry (b). The theoretical dispersion for the geometry (a) gives qualitative agreement for the axes among the $\bar{J}$, $\bar{Y}$, and $\bar{Y}'$ points but the splitting of the experimental bands near the $\bar{\Gamma}$ point is not reproduced.

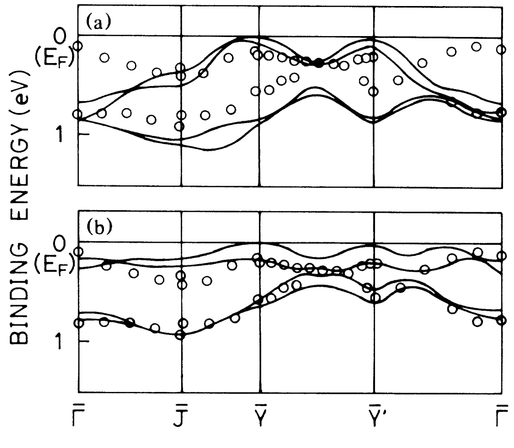

FIG. 4. Comparison of the present surface-state dispersion (circles) for the Si(001)$c(4\times2)$ surface with the results of recent *ab initio* calculations (Ref. 17) for two kinds of atomic positions in an "antiferromagnetically" ordered buckled-dimer model (solid lines).

Although the overall dispersion of the theoretical SS corresponds fairly well with that of experiment, absolute binding energies of the two do not match each other. In the experiment, E_b for the top of occupied SS band A is ~ 0.5 eV, whereas the band gaps of the theoretical SS for the two geometries (a) and (b) are both ~ 0.01 eV,[17] indicating the corresponding binding energy to be practically zero. One reason for this disagreement might be related to the self-energy correction of the SS which has been reported to open up the gap between the occupied and empty surface bands for the Ge(111)1×1-As surface.[19] Another point to be mentioned is the fact that the experimental bands are in better agreement with the calculated bands for the geometry (b), optimized for the 2×1 surface, than those for the geometry (a), optimized for the $c(4\times2)$ surface. Detailed theoretical analyses including the self-energy correction are needed to facilitate further quantitative comparison between theory and experiment.

On the basis of the present findings, we now discuss the controversy concerning the Si(001)2×1 surface. The unexpected structures B and C in the previous ARUPS study[14] and related unresolved structures[13,20] for the DD and SD Si(001)2×1 surfaces are explained as the correlation of buckled dimers. The correlation of buckled dimers within each of the dimer rows is indicated by the half-order streak lines in LEED.[14] In this case, structures similar to B and C can be expected.[21] A short-range correlation of buckled dimers among the dimer rows may be present locally and the dispersion of the structure A along the $\bar{\Gamma}$-$\bar{J}$ direction may appear. It is also possible that even with complete disorder of the buckling direction of dimers, some of the additional structures might appear in ARUPS spectra.

The symmetric dimer arrangement seen by STM in "ideal" parts of the surface[9,10] can be attributed to a time-averaged image of the buckled dimers. The buckle-flip frequency at a finite temperature is an important factor for the understanding of the properties of the Si(001)2×1 surface. It is also possible that the buckling direction may be flipped by a STM probe resulting in a STM image of seemingly symmetric dimers. A STM investigation on a Si(001)$c(4\times2)$ surface is, therefore, very desirable in this respect. A single surface Si $2p$ photoemission peak found previously[11] can be explained for the asymmetric-dimer model by taking into account the screening of core holes by dangling-bond electrons.[22] Antiferromagnetic arrangement of electron spins within the dimers[12] is not necessary and not likely; the $c(4\times2)$ LEED pattern proves the buckling of actual atoms.

In conclusion, a wide-terrace single-domain Si(001)-$c(4\times2)$ surface has been made from a SD Si(001)2×1 surface by cooling the sample to 200–80 K. Angle-resolved UPS spectra have been measured for the SD

Si(001)$c(4\times 2)$ surface at 200–100 K. The resulting surface-state bands are compared with those for the SD 2×1 surface together with those of *ab initio* calculations for the $c(4\times 2)$ surface based on antiferromagnetic order of buckled dimers. As a result, the following image of ideal parts of the Si(001) surface emerges. Namely, in the 2×1 surface at ambient temperature, the dimers are buckled and the buckling direction fluctuates with a tendency to the antiferromagnetic order within each of the dimer rows leading to a nominal "2×1" LEED pattern with weak half-order streak lines. ARUPS spectra for this surface consist of two kinds of dangling-bond surface-state bands: one, a band similar to the one expected from seemingly "ferromagnetically" buckled 2×1 surfaces, and other "additional" ones.[21] Below 200 K, the correlation of the buckling direction among dimer rows results to form the $c(4\times 2)$ arrangement. The dangling-bond surface-state bands for this surface appear to be in qualitative agreement with those of calculations by Zhu, Shima, and Tsukada,[17] although further theoretical studies are needed for quantitative argument.

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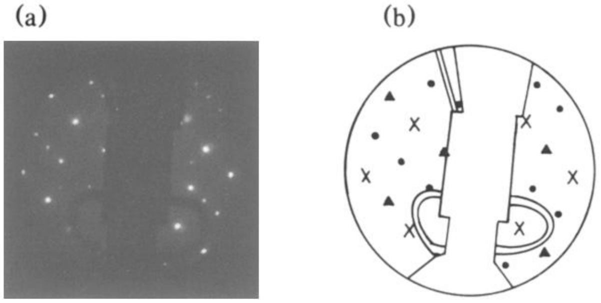

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