Atomic and Electronic Structure of the 7×7 Reconstructed Si(111) Surface

D. J. Chadi, R. S. Bauer, R. H. Williams,[a] G. V. Hansson, R. Z. Bachrach, and J. C. Mikkelsen, Jr.
Xerox Palo Alto Research Center, Palo Alto, California 94304

and

F. Houzay,[b] G. M. Guichar,[c] R. Pinchaux,[c] and Y. Pétroff
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud, Orsay F-91405, France

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It is suggested that the 2×1 and 7×7 reconstructions of Si(111) surfaces are inherently quite similar and propose a 7×7 structure based on ringlike arrangements of positively and negatively charged surface atoms. High-resolution angle-resolved photoemission data are shown to provide strong support for the buckled, (2×1)-like nature of the 7×7 surface.

The 2×1 and 7×7 reconstructions of Si(111) surfaces have been extensively studied.[1-26] The generally accepted description for the 2×1 reconstruction[1-10] is that rows of surface atoms are alternately raised and lowered. This is accompanied by charge transfer between inequivalent atoms and by a metal-semiconductor transition at the surface. Because of the greater complexity of the 7×7 surface no comparable understanding of its atomic and electronic structure has been obtained yet. In this paper we present arguments based on high-resolution angle-resolved photoemission experiments, empirical energy-minimization calculations, and other considerations to suggest that the 7×7 and 2×1 reconstructions are similar in character. We propose a new model based on ringlike arrangements of raised and lowered atoms for the 7×7 surface and use it to interpret various experimental results and to make predictions on the nature of the surface electronic states.

The most extensively studied model for the 7×7 surface has been the Lander vacancy model.[13-15,24,25] A number of arguments have been given in the past in support of this model. These arguments, which are discussed and reexamined below, are based on the following observations:

(i) *A relatively high transition temperature of 700 °C for 2×1 to 7×7 conversion.* Lander[13] inferred that atomic mobilities became large at 700 °C, leading to vacancy formation. Recent measurements[16] have shown, however, that the transition temperature is as low as 200 °C for low-step-density surfaces.

(ii) *A sharp drop of 0.6 eV in the work function[17] in a narrow temperature range separating the 2×1 and 7×7 surfaces.* Rowe and Phillips have argued[19] that this would imply significant differences between 2×1 and 7×7 surface structures. More recent measurements by one of the authors[27,28] indicate, however, that the work function varies smoothly from the 2×1 to the 7×7 surface, there being no large drop in the work function.

(iii) *The different surface reactivities of the 2×1 and 7×7 structures.* Chlorine[29,30] and hydrogen[31,32] chemisorption studies have shown that 2×1 structure transforms relatively easily into a 1×1 structure, whereas the 7×7 surface is much more stable. The stability of the 7×7 surface has been taken as strong evidence for the vacancy model. The presence of only one vacancy (or adatom, or some other internal feature) could inhibit the 7×7 to 1×1 conversion, and such a possibility cannot be ruled out. However, an alternative explanation for the greater chemical reactivity of the 2×1 surface should also be considered. This is related to the presence of steps on cleaved surfaces. It has been shown[33] that the sticking coefficient of oxygen on the (111) surface increases *exponentially*[34] with the step density at the surface. Steps could also play a crucial role in facilitating the chemisorption of chlorine and hydrogen on the 2×1 surface.

Low-energy-electron-diffraction (LEED) studies[25] have shown that the 7×7 surface has threefold rotational symmetry. At low incident electron energies ($E \simeq 40$ eV), when only the top layer of surface atoms contributes effectively to the scattering, a sixfold rotational symmetry is observed. Kinematical analyses[25,26] of LEED data have led to the conclusion that vacancy[13] and adatom[6] models are inadequate and that rippled or buckled surfaces are more suitable. Dynamical studies are, however, necessary before the LEED results can be used with certainty for structural determination. Our model for the 7×7 surface which incorporates the symmetries required from LEED is shown in Fig. 1(a). There are 25 raised (open circles) and 24 (dark circles) atoms per

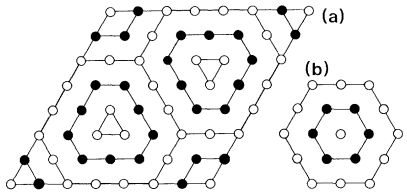

FIG. 1. (a) Proposed model for the 7×7 surface of Si(111). (b) The hexagonal symmetry of the surface atoms around the corner atom of the unit cell. Raised and lowered surface atoms are represented by open and dark circles, respectively.

unit cell. The lines connecting the surface atoms are intended to show the nearly ringlike arrangements of the atoms as compared to the linear patterns of the 2×1 surface. The atomic arrangements of the first two rings around a corner atom of the unit cell are shown in Fig. 1(b). We assume that as on the 2×1 surface, raised and lowered atoms become negatively and positively charged, respectively. For the 7×7 structure the vertical displacements of surface atoms, as discussed below, are calculated to be nearly identical to those on the 2×1 structure, except for the corner atom which is raised less (by $\simeq 0.05$–0.1 Å) than the other "up" atoms. Bond-length as well as bond-angle variations on the two surfaces are also found to be very similar.

The relaxed atomic positions of the first double layer at the surface were determined from an empirical force-constant model. The model involves the use of a Keating-type[35] elastic energy term augmented by a term U which was taken to have the form

$$U=\sum_i[-k_1(\Delta z_i)^2+k_2(\Delta z_i)^4]. \quad (1)$$

In Eq. (1) the sum is over the top layer of surface atoms with Δz_i representing displacements normal to the surface. The term U is necessary; otherwise a minimization of the elastic energy for the Keating model will always lead to an unrelaxed 1×1 surface. The coefficients k_1 and k_2 in Eq. (1) were chosen such that a reasonable description of the 2×1 reconstruction of Si(111) was obtained through energy minimization. The term $k_2(\Delta z_i)^4$ was found to be needed since for k_2 equal to zero the surface remains 1×1 when k_1 is small and it becomes unstable when k_1 is large. To start the calculations surface atoms were raised or lowered by an arbitrary amount and the surface was then allowed to relax. For the 7×7 surface ringlike geometries of raised and lowered atoms were tested. The innermost rings of three atoms in Fig. 1(a) are required by the rotational and translational symmetries of the surface. The atomic relaxations were not constrained to be consistent with threefold or sixfold (for the top layer) rotational symmetries but these were obtained as a result of the calculations. Within the context of the empirical model used we estimate the "elastic" energy of the 7×7 surface to be slightly (0.02 eV per surface atom) lower than that of the 2×1 surface. Assuming similar charge transfers (of about 0.3 electron) on the 2×1 and 7×7 surfaces and ignoring screening effects, the difference in the surface Coulombic energies of the two surfaces is calculated to be small ($\simeq 0.01$ eV/atom).

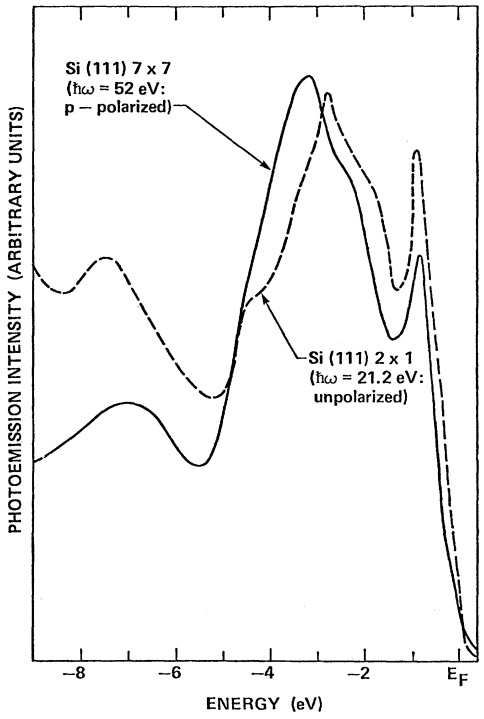

FIG. 2. Normal-emission spectra for 2×1 and 7×7 surfaces. The photoemission measurements for the 7×7 surface were performed at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, at the Orsay Synchrotron Radiation Center (Ref. 24). The 2×1 results are from Ref. 20.

Strong evidence for the (2×1)-like (i.e., buckled) nature of the 7×7 surface is provided by our high-resolution angle-resolved photoemission measurements. Normal-emission spectra for the 2×1 and 7×7 surfaces obtained from two independent experiments on different samples are shown in Fig. 2. The 2×1 sample was n type (10-Ω-cm resistivity) and was one of several prepared by cleavage.[20] The 7×7 sample (also n type with

a 0.005-Ω-cm resistivity) was prepared[24] by flashing and was characterized by LEED and Auger spectroscopy. The photoemission measurements for the 7×7 surface were performed[24] for photon energies $\hbar\omega$ in the range $18 \leq \hbar\omega \leq 120$ eV at the Orsay Synchrotron Radiation Center. The energy resolution (monochromator + analyzer) was ≥ 250 meV and the angular resolution was ± 0.5°. A detailed discussion of the results will be presented elsewhere.[24]

The most interesting feature of the normal emission spectra shown in Fig. 2 is that the dangling-bond states on the 2×1 and the 7×7 surfaces occur at nearly the same energy (≃ − 0.8 eV) with respect to the Fermi energy E_F. For the 7×7 surface the angle-resolved measurements show that maximum emission intensity occurs at normal emission for p-polarized light, leaving no doubt as to the dangling-bond character of this state. No dispersion with polar angle was found. Another intesting feature revealed by our measurements is that the intensities of the surface states, in particular of the − 0.8-eV state, exhibit an *oscillatory* behavior[36] as a function of $\hbar\omega$. Previous angle-resolved measurements[21,22] as well as our own measurements done at low photon energies ($\hbar\omega \leq 25$ eV) show a weak peak at − 0.8 eV. We find that this structure becomes sharply peaked at $\hbar\omega \simeq 50$ eV as shown in Fig. 2. Overall, the normal-emission spectra for the 2×1 and 7×7 surfaces are quite similar. Recent measurements[24] on the 2×1 surface using synchrotron radiation show that the maximum emission intensity for the dangling-bond state of this surface also occurs at normal emission, for a photon energy near 50 eV and for p-polarized light. The back-bonding surface states on the 7×7 surface appear to be broadened as compared to those of the 2×1 surface, most probably because of the greater variety of back-bonding geometries on the 7×7 surface.

At the present time a calculation of the electronic structure of the 7×7 surface for comparison to the experimental results is too difficult to carry out. However, on the basis of our structural model the electronic states at the metallic edge are expected to be dangling bond in character. The 25 up atoms in Fig. 1(a) give rise to dangling-bond surface bands that can be occupied fully by 50 electrons; with only 49 dangling bonds present these bands are 98% full, forcing the empty states to be at the upper end of the dangling-bond density-of-states distribution, resulting in a small density of states at E_F.

Internal-reflection[9,10] measurements and electron-loss spectroscopy,[12] in combination with photoemission measurements, have given evidence for the presence of empty surface states in the band gap of the 2×1 surface but not[10,12] of the 7×7 surface. More precisely, the internal-reflection measurements[10] for the 7×7 surface show some evidence for a metallic surface with Drude-like absorption, but strong absorption corresponding to excitations between filled and empty surface states seems to be absent. The buckled model of Fig. 1 would lead to the expectation that the empty dangling-bond states of the 2×1 and 7×7 surfaces should be at approximately the same energy. For the 7×7 surface, empty states in the bandgap have been observed in surface photoconductivity measurements by Mönch.[17,37] For the 2×1 surface his results are in good agreement[37] with the internal-reflection measurements of Chiarotti, *et al.*[10,11] The sensitivity of the photoconductivity measurements is much higher[38] than that achieved in internal reflection. The differences in the results of the two measurements could be caused by the presence of an indirect gap[33] (in the extended Brillouin zone) on the 7×7 surface. Evidence for the presence of empty surface states in the band gap has also been obtained recently by surface photovoltage spectroscopy.[39]

An analysis of the similarities and differences between the 2×1 and 7×7 surface reconstructions in terms of "frozen-in" surface phonons[40] will be discussed elsewhere.[41]

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[a]Permanent address: School of Physical Sciences, New University of Ulster, Coleraine, Northern Ireland.

[b]Also at Centre National d'Etudes des Télécommunications, Grenoble, France.

[c]Also at Université Pierre et Marie Curie, F-75230 Paris 05, France.

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