Observation of an intrinsic 5×5 reconstruction on the clean Si(111) surface

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Low-temperature annealing of the cleaved Si(111)2×1 surface revealed the existence of an *intrinsic* 5×5 reconstruction on the clean Si(111) surface. The electronic structure of the Si(111)5×5 surface, obtained with angle-resolved photoemission, is almost identical to that of the 7×7 reconstruction. This is strong evidence that the 5×5 reconstruction is also of the dimer–adatom–stacking-fault (DAS)-type. The experimental observation of a 5×5 reconstruction supports recent theoretical results that the 7×7 and 5×5 DAS models are very close in total surface energy.

In this paper we report the existence of a 5×5 reconstruction on the clean Si(111) surface obtained by low-temperature annealing of the cleaved Si(111)2×1 surface. So far, the 7×7 reconstruction is the only ordered surface structure that has been reported for annealed Si(111) surfaces. An important reason for this is probably that most sample preparation techniques involve high-temperature annealing (generally higher than ≈800 °C) in order to restore the crystalline order after sputter cleaning or to remove the oxide after an etching-oxidation pretreatment of the sample. In this study we have carefully examined the 2×1-to-7×7 structural transition on cleaved Si(111) surfaces which occurs at much lower temperatures (250–350 °C) than is normally used to create the Si(111)7×7 surface. These studies revealed the existence of an intermediate 5×5 reconstruction on *macroscopic* areas of the sample. The existence of 5×5 unit cells on a disordered Si(111) surface prepared by a combination of laser and thermal annealing has been reported earlier in a scanning-tunneling-microscopy study.[1] However, only a few 5×5 unit cells were observed on that kind of surface. The transformation of the 2×1 reconstruction to a 5×5 reconstruction reported here depends on the detailed structure of the cleaved surface. It is interesting to note that the 5×5 reconstruction was observed on areas which initially showed the sharpest, single-domain, 2×1 low-energy electron-diffraction (LEED) pattern. The discovery of an intrinsic 5×5 reconstruction on the clean Si(111) surface provides new important information on the energetics of the reconstruction mechanisms, supporting recent total-surface-energy calculations which find the 5×5 and 7×7 dimer–adatom–stacking-fault (DAS) models to be very close in energy.[2–5]

The electronic structure of the 5×5 surface, obtained by angle-resolved photoemission, is here compared to the results for the clean Si(111)7×7 surface and the Ge-induced Si(111)7×7:Ge and Si(111)5×5:Ge surfaces.[6,7]

Si(111) bars with a cross section of 8×8 mm^2 (p type, ρ=43 Ω cm) were cleaved in ultrahigh vacuum (≈6×10^{-11} Torr) and the resulting surfaces were characterized with low-energy electron diffraction and angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). The change in surface reconstruction of the cleaved Si(111)2×1 surface was studied at successively higher annealing temperatures with LEED. The LEED pattern first changed from a 2×1 to an apparent "1×1" pattern at ≈250 °C. At higher temperatures (≈300 °C) streaks and weak diffraction spots indicative of a transition to a 7×7 reconstruction started to appear. However, careful analysis of the LEED pattern revealed the existence of 5×5 spots in the diffraction pattern. Further annealing of the sample at 350–400 °C for 5 min caused a large part of the surface (≈3×3 mm^2) to transform into a 5×5 reconstruction. The resulting LEED pattern is presented in Fig. 1. The quality of the 5×5 pattern is comparable to the best 7×7 patterns obtained with this specific LEED apparatus. The rest of the sample showed predominantly a 7×7 pattern with some mixed 5×5 and 7×7 areas. The stability of the 5×5 reconstruction with respect to annealing temperature was tested on a second cleave. Also this cleave showed a 5×5 LEED pattern, after annealing, on the part of the crystal which initially showed the sharpest 2×1 pattern. No change of the 5×5 LEED pattern was detected up to ≈550 °C. After annealing at higher temperatures the 7×7 diffraction spots became visible, and after annealing at 600–650 °C the surface had completely transformed into the 7×7 reconstruction.

Angle-resolved photoemission spectra probing the $\bar{\Gamma}$-$\bar{K}$ line in the 1×1 surface Brillouin zone are shown in Fig. 2 for the Si(111)5×5 surface. A reference spectrum from the initial, cleaved, 2×1 surface is displayed in Fig. 3(a). The spectrum shows the high-intensity dangling-bond state, characteristic of a well-ordered 2×1 surface, at the $\bar{J}$ point in the 2×1 surface Brillouin zone. After transformation into the 5×5 reconstruction, the surface exhibits three surface states which are very similar to those observed on the 7×7 surface (see Fig. 2). Structure S_1 is located ≈0.2 eV below the Fermi level E_F and shows a characteristic increase in intensity at $k_\parallel$ values corresponding to the boundary of a 2×2 surface Brillouin zone. The second surface state (S_2) is observed at ≈0.8 eV below E_F for all emission angles, while S_3 located at

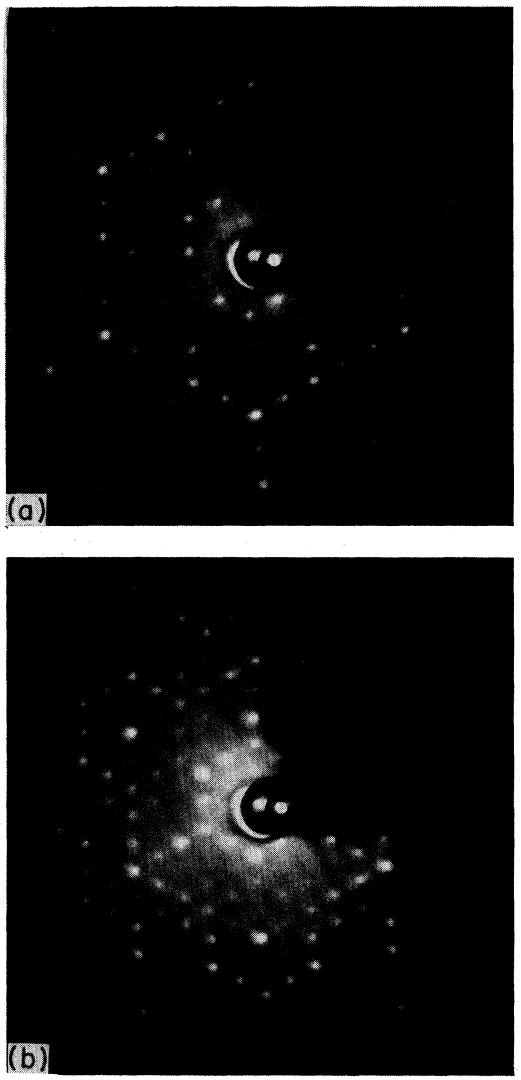

FIG. 1. LEED patterns from the Si(111)5×5 surface obtained by low-temperature annealing of a cleaved Si(111)2×1 surface. The electron energy used in (a) was 60 eV and in (b) 85 eV. The upper right-hand parts of the LEED patterns are hidden behind the electron analyzer.

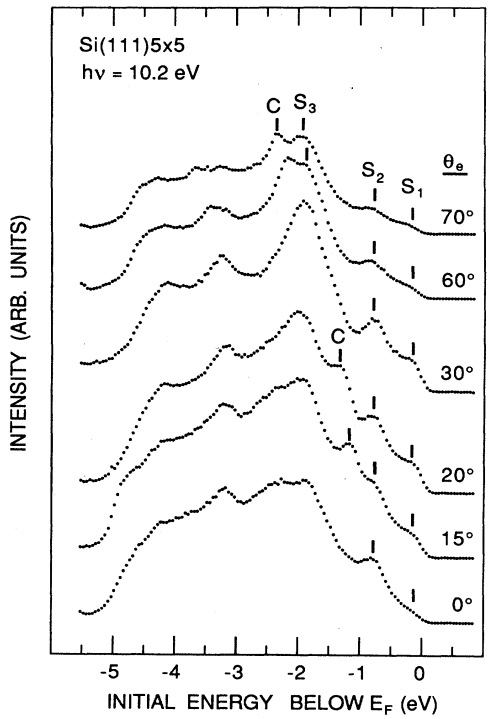

FIG. 2. Angle-resolved photoemission spectra ($\theta_i = 45°$) from the Si(111)5×5 surface for different emission angles along the $\bar{\Gamma}$-$\bar{K}$ line of the 1×1 surface Brillouin zone. Structures S_1–S_3 correspond to surface-state emission. Structure C corresponds to a bulk direct transition.

≈ 1.8 eV below E_F can only be identified at higher emission angles for the photon energy (10.2 eV) used in this experiment.

The surface-state structure of the 5×5 surface is found in this experiment to be almost indistinguishable from that obtained from the Si(111)7×7 surface.[6] There exists, however, a clear difference in the emission associated with direct bulk transitions. Structure C corresponds to a direct transition from the uppermost valence band. In an earlier study[8] it was found that the initial energy dispersion of this bulk structure, both as a function of photon energy and $\bar{k}_{\parallel}$, could be accurately described by a free-electron dispersion of the final band. The intensity of structure C for the 5×5 surface is significantly higher than that of the 7×7 surface (but lower than that of the 2×1 surface). The clear difference in the visibility of the bulk structure C could be due to differences in the surface scattering and/or differences in subsurface distortion caused by the reconstructions. The polarization dependence of the intensity of structures S_1, S_2, and C is obtained by comparing Fig. 3(b) with the corresponding spectrum ($\theta_e = 15°$) in Fig. 2. The surface-state structures S_1 and S_2 are highly reduced for normal light incidence, which is consistent with the dangling-bond character of these states, while the emission from the bulk structure C is slightly increased.

Outside the 5×5 area, the sample showed a 7×7 LEED pattern with some admixture of 5×5 spots. The LEED pattern in these areas was not as sharp as in the good 5×5 region. A photoemission spectrum obtained at $\theta_e = 30°$ from the "7×7" part is shown in Fig. 3(c). The main difference observed is that the surface state S_1 is not at all developed. The surface state S_2, on the other hand, has an intensity comparable to that of either the 5×5 or a well-ordered 7×7 surface. The S_1 and S_2 surface states have been identified with dangling-bond states on the adatoms and the rest atoms of the DAS model, respectively.[9,10] It can thus be concluded that the 7×7 areas do not have a fully developed adatom structure at these rather low annealing temperatures (≈ 400 °C). It is worth noting that laser-annealed "1×1" surfaces have a similar surface electronic structure to this underdeveloped 7×7 part of the crystal.[11] The laser-annealed surfaces also lack the adatom surface state, S_1.

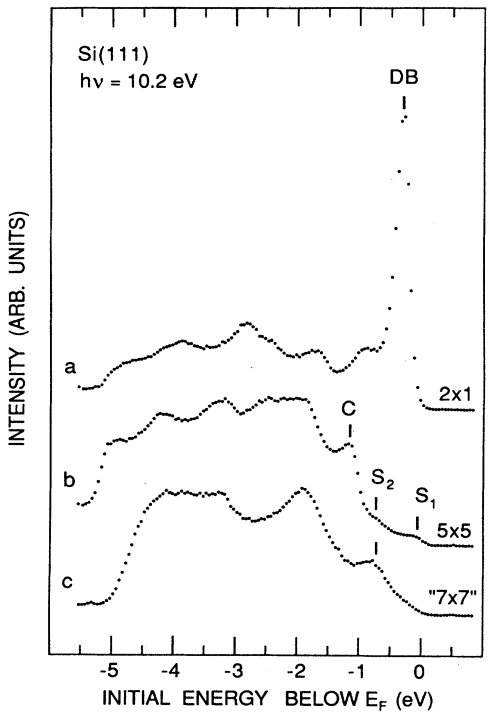

FIG. 3. (a) Angle-resolved photoemission spectrum ($\theta_i = 45°$) showing the dangling-bond emission (DB) at the $\bar{J}$ point, in the 2×1 surface Brillouin zone, from the initial, cleaved, Si(111)2×1 surface. (b) Photoemission spectrum obtained at $\theta_e = 15°$ from the Si(111)5×5 surface for normal light incidence ($\theta_i = 0°$). The emission from the surface states S_1-S_2 is strongly reduced compared to $\theta_i = 45°$ (compare with Fig. 2). The direct transition structure C is slightly enhanced for $\theta_i = 0°$. (c) Photoemission spectrum obtained at $\theta_e = 30°$ from the "7×7" part of the crystal. The adatom dangling-bond state S_1 is missing in the spectrum which indicates that the decoration of the terraces with adatoms is incomplete at the lower annealing temperatures used here (350–400 °C).

It is interesting to compare the surface electronic structure of the intrinsic Si(111)5×5 reconstruction to that of Si(111)7×7, Si(111)7×7:Ge, and the *strain-induced* Si(111)5×5:Ge surfaces which have recently been studied in detail with ARUPS by Mårtensson *et al.* at 10.2-eV (Ref. 6) and 21.2-eV (Ref. 7) photon energy. Both the Si(111)7×7:Ge and Si(111)5×5:Ge surfaces were reported to have surface states quite similar to the S_1 and S_3 surface states on the clean Si(111)7×7 surface. The surface states corresponding to S_3 were shifted, however, towards E_F by 0.25 and 0.45 eV for the 7×7:Ge and 5×5:Ge surfaces, respectively. The main difference in the surface electronic structure between the clean 7×7 surface and the Ge induced reconstructions was found for the surface state corresponding to S_2. Besides a shift in initial energy by ≈ 0.2 eV towards higher binding energies, this surface state was difficult to identify in the spectra. This problem was most evident in the Si(111) 5×5:Ge spectra obtained at 10.2-eV photon energy for which this second surface state could not be identified at all in the spectra. For the 5×5 reconstruction on the clean Si(111) surface reported in the present study the identification of S_2 is not a problem. The rest-atom state S_2 is easily observed over the whole range of emission angles at the same initial energy as for the Si(111)7×7 surface. This clearly demonstrates that the energy shift observed for the Si(111)5×5:Ge surface[6] is due to the presence of Ge atoms on the surface and not caused by the change in surface periodicity.

A very successful research effort in recent years has resulted in a widely accepted model for the clean reconstructed Si(111) surfaces, i.e., the π-bonded chain model for the 2×1 reconstruction[12] and the dimer–adatom–stacking-fault model for the 7×7 reconstruction.[13] The latter model can easily be generalized to $(2n+1)\times(2n+1)$ models which all show the main features of the dimer–adatom–stacking-fault model. One very important puzzle that remains to be solved is why the Si(111) surface prefers the 7×7 periodicity instead of a 5×5 or 9×9 or any other periodicity. The energetics of the DAS model leading to a 7×7 periodicity have been addressed in some recent theoretical studies.[2–5] The surface periodicity is determined by a balance of energies associated with the different features of the DAS model, i.e., dimer, adatom, corner-hole, rest-atom, and stacking-fault energies. In a tight-binding calculation by Qian and Chadi[2,3] the 7×7 reconstruction was indeed found to have the lowest energy of the $(2n+1)\times(2n+1)$ DAS models. The major factors which yield the low energy were reported to be the adatoms and the reduction of the number of surface atoms because of the stacking fault and the dimers. The surface energy for the 7×7 DAS model was reported to be 0.403 eV lower per 1×1 surface unit cell than the ideal, unrelaxed surface using the semiempirical tight-binding method.[2] This energy value is even lower than the 0.36-eV reduction per 1×1 cell obtained by the same authors for the π-bonded chain model of the Si(111) 2×1 surface.

A different mechanism for the formation of the 7×7 reconstruction was proposed by Vanderbilt.[4,5] In this study the main driving force was suggested to be dangling-bond reduction due to the formation of dimer domain walls between the faulted parts of the 7×7 cell, while the adatoms were concluded to be only of secondary importance for the formation of the 7×7 reconstruction. The periodicity of the DAS-type reconstruction was found to depend on the relative magnitude of the domain wall and corner-hole energies (with or without adatoms).

A result common to the two different theoretical studies is that they both find the 7×7 and 5×5 DAS models to be rather close in energy, e.g., the results obtained for the decrease in surface energy in the semiempirical tight-binding calculation[2] were -0.403 eV (7×7) and -0.395 eV (5×5) relative to the unrelaxed 1×1 surface. The surface energies calculated for the adatom-free analogs of the DAS model in Ref. 4 were 1.427 and 1.428 eV/(1×1 cell) for the 7×7 and 5×5 periodicities, respectively. From the calculations in Ref. 4 of the surface energy of the adatom-free analogs of the DAS structures it was also concluded that a compressive strain will lead to a transition from a 7×7 to a 5×5 periodicity. The calculations

gave an equal surface energy for the 5×5 and 7×7 surfaces at a compressive strain of $\approx0.1\%$. Since the 5×5 and 7×7 surfaces are calculated to be very close in energy, we find that strain fields induced by the cleavage process[14] are most likely to be the major factor that determines whether a specific part of the 2×1 surface will transform into a 5×5 or 7×7 reconstruction at the lower annealing temperatures used here.

In summary, the discovery of an intrinsic 5×5 reconstruction on the clean Si(111) surface gives strong support to recent calculations which find the 5×5 and 7×7 DAS models to be very close in surface energy. Whether the Si(111)2×1 surface will transform into a 5×5 or 7×7 reconstruction seems to depend critically on the detailed structure of the cleaved surface. It is quite interesting to note that the 5×5 reconstruction was obtained at the areas which initially showed the sharpest, single-domain, 2×1 LEED pattern. The fact that the surface state S_1 is missing on the low-temperature "7×7" surface shows that the decoration of the terraces with adatoms is incomplete, which supports the idea that the adatoms are of secondary importance for the *formation* of the 7×7 reconstruction. From the very close resemblance between the electronic structure of the 5×5 and 7×7 surfaces it can be concluded that the two reconstructions are most likely of the same type, i.e., the DAS model which now seems to be generally accepted for the 7×7 surface.

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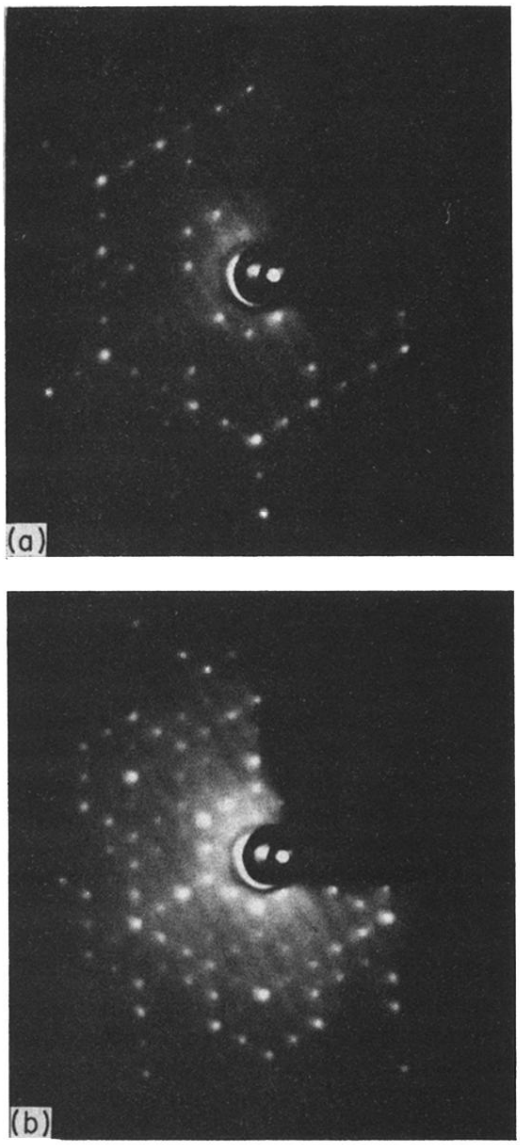

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