Kinetics and Reconstruction of Steps at the Si(001) Surface

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The stability ranges of monatomic and diatomic steps on the Si(001) surface are determined by high-resolution spot-profile analysis of low-energy diffracted electrons. Diatomic steps are predominantly observed at temperatures below 1200 K. With increasing annealing temperature the steps coagulate and we identify (113) facets stabilized by a (3×1) reconstruction. These facets are stable above 1200 K, and up to 1450 K. Annealing to higher temperatures results in the formation of monatomic steps with a terrace width above the experimental coherence length.

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Recently, scanning tunneling microscope (STM) results have renewed the discussion about the reconstruction of the Si(001) surface.[1] It has been determined previously[2-9] that a (2×1) reconstruction with scattering from two domains rotated by 90° is the origin of the Si(001) LEED patterns. Within these domains, the reconstruction is explained by the formation of symmetric and asymmetric dimers. These findings are in line with theoretical[2,3] and experimental results, such as photoelectron spectra,[4] surface core-level shifts,[5] and helium diffraction data.[6] Pandey's total-energy calculations, postulating a rough surface,[3] have led to several different models to characterize the type of the atomic roughness involved in the real structure of Si(001).

The existence of steps on the Si(001) surface was introduced quite early, to explain the observed two-domain LEED pattern, because steps act as boundaries between adjacent (2×1) domains. In general, direct experimental observation of steps is difficult.[7] On Si(111) surfaces monatomic steps are observed by STM,[1] low-energy electron microscopy,[8] and LEED.[9] The coexistence of monatomic and diatomic steps is reported for Os(0001) surfaces.[10] On the Si(001) vicinal surface the existence of monatomic steps is reported.[11] The existence of diatomic steps has also been deduced from the appearance of a single-domain (2×1) LEED pattern.[12] Their existence has been postulated on the basis of theoretical considerations[13] as well. Diatomic steps cause a single primitive sublattice on this surface that is of particular interest for epitaxial-growth applications.[13]

In the present work we determine the coexistence of monatomic and diatomic steps on the Si(001) surface. We also determine the kinetics of their formation and their stability ranges as a function of annealing temperature. We find that monatomic and diatomic steps coagulate towards large-size steps between 1250 and 1470 K. We observe (113) facets stabilized by a threefold reconstruction along the [110] direction. Annealing above 1470 K causes the (113) facets to disappear. The size of the (2×1) domains continues to increase with increasing temperature. The domain size exceeds our instrumental coherence length of 100 nm at about 1600 K.

The spot-profile-analysis–LEED instrument used in our studies is described in detail by Henzler and coworkers.[14] This instrument uses low-energy electrons impinging at near-normal incidence, and allows, with high dynamic range and with high resolution, the detection of coherently scattered electrons in k space not only for electrons in Bragg directions. Surface preparation is done as described earlier.[15,16] Thermally oxidized Si(001) wafers are used, and carbon contaminations are removed by soft Ne^+ sputtering followed by annealing

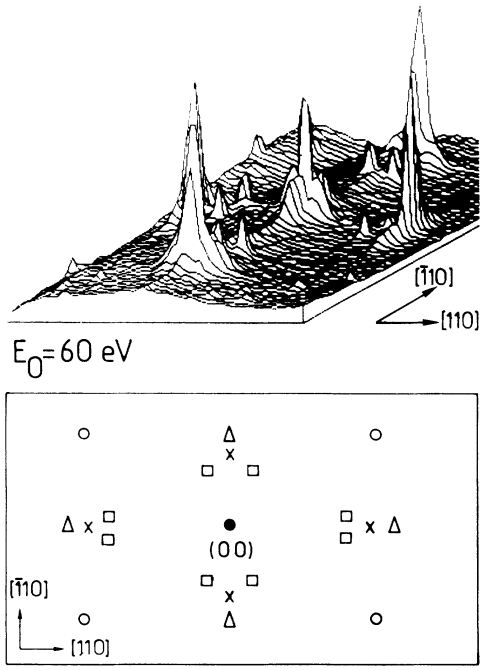

FIG. 1. Intensity contour for a primary electron energy of 60 eV; $T=1410$ K. The map is displayed schematically also: triangles, half order spots of Si(001) (2×1); crosses, integral order spots of Si(113) (3×1); squares, $\frac{1}{3}$ order spots of Si(113) (3×1); and circles, half-order spots of Si(001)p(2×2).

to remove the oxide layer. The intensity contours are always recorded at room temperature after annealing of the samples for 5 min. The sample temperature during annealing is determined with a pyrometer.

In this work, our main emphasis is on the observation of reconstructions even in steps, demonstrated on Si(001) as a prototype of a well-defined semiconductor surface. After annealing the surface to 1410 K, we observe characteristic intensity variations in k space. Figure 1 shows a typical intensity plot taken around the zero-order reflection at a primary energy of 60 eV. The assignment of the main features[17] is also visualized schematically. The main contributions around the (00) spot result from the half-order diffraction spots of the (2×1) reconstruction. We occasionally notice weak spots at $p(2\times2)$ positions.[6] Our main interest is focused on the spots that appear along the [110] and [$\bar{1}$10] directions (crosses), and the spots appearing next to these major axes (squares). All these extra spots arise from (113) facets, confirmed by the inclination angle of the observed reciprocal lattice rods and their distance in k space.[16] In particular, for primary energies between 60 and 75 eV, we notice the appearance of additional spots at the $\frac{1}{3}$ positions (squares). These spots do not result from an unreconstructed (113) facet, but rather indicate the existence of a superstructure with a threefold periodicity.

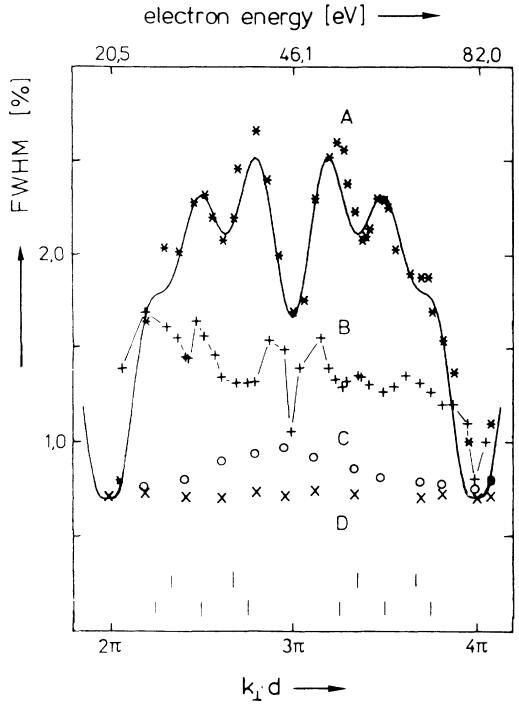

FIG. 2. Experimentally and theoretically (solid line) determined oscillations of the FWHM of the (00) spot as a function of $k_\perp d$ ($d = a_0/4$). The oscillations are recorded at room temperature, after annealing to 1320 K (curve A, asterisks), 1410 K (curve B, plusses), and 1600 (curve C, circles), respectively. Curve D (crosses) is taken after flashing a sample to 1600 K. The position of the minima characteristic for multiple step heights are indicated.

The intensity profiles of the integral-order spots vary characteristically with $k_\perp$ and contain information about the phase correlation from the different terraces involved. We have derived the FWHM of the (00), (10), and (11) spots along the [110] direction at energies between 20 and 260 eV. We concentrate on the oscillation of the FWHM of the (00) spot in the range between 15 and 85 eV in Fig. 2 (Ref. 16) as a characteristic result. We model these oscillations considering both the atomic displacements and the corresponding phase shifts of the scattering amplitudes, and taking into account steps of different heights. We performed a simple calculation of the scattering factors[18] including the phase shifts for step heights of $n(a_0/4)$ (Fig. 3), and the probabilities for their appearance per surface unit along the [110] direction. These probabilities are varied to achieve an optimal agreement with the experimental data (solid lines). The average (001) terrace width is also obtained from this. The calculations describe the different behavior of the FWHM oscillations of the (00), (10), and (11) spots.[16] In these calculations we follow strictly kinematic scattering arguments, and do not include multiple scattering at all. Although this implies a simplification, especially for small terraces,[19] the agreement between our model and the experimentally observed oscillations clearly shows that multiple scattering is not of importance under these conditions.

The data shown in Fig. 2 are taken after annealing of the sample to different temperatures. Evidently, the total amplitude of the oscillations is reduced with increasing temperature. The number of minima increases between 1320 K and 1410 K. Their positions indicate that the step heights elevate up to 6 or 8 monatomic steps. On the other hand, we have obtained very smooth variations of the FWHM of samples annealed to higher temperatures. As an example, curve C shows the behavior of a sample successively annealed to 1600 K, indicating the existence of monatomic steps only. For samples flashed to 1600 K without prolonged annealing at lower temperatures we do not find any oscillations (curve D). The

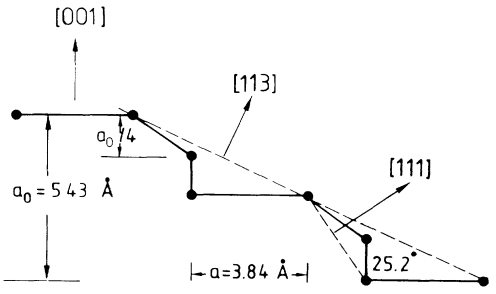

FIG. 3. Atomic arrangements of (113) facets on the Si(001) surface, projected on the (110) plane.

average terrace widths are also derived for all annealing temperatures. Their values increase from 7.3 (curve A) to 13.9 (curve B) to 38.4 nm (curve C), and exceed the experimental coherence length of 100 nm (curve D). All values are larger than those determined in a recent STM study.[1]

Our data show that rough Si(001) surfaces appear in a distinct temperature range and do contain multiatomic steps. We present the first experimental evidence for their coexistence. We not only derive information about the existence of steps on this surface, but also about their kinetics. Curves A and B in Fig. 2 indicate an increasing number of minima in these oscillations with increasing temperature. As well as identifying the existence of higher steps, we also identify the formation of (113) facets. The latter is evident from the inclination angle of 25.2° between the reciprocal lattice rods of the (001) and (113) surfaces, and from the distance in k space which reflects the distance between adjacent atomic rows on the (113) surface (0.64 nm). From the appearance of extra spots we deduce that these (113) facets are reconstructed and form a (3×1) superstructure. All these observations, the increasing number of the minima in Fig. 2, the increase of the average (001) terrace width, and as well the increasing intensities of (113) spots (Fig. 4), reflect the formation of larger steps within that temperature range. These large-scale steps result from the coagulation of hitherto separated monatomic and diatomic steps, forming (113) facets with an energetically more stable Si(113)-(3×1) reconstruction.

The Si(113) surface has been investigated before[20] and is described in the truncated bulk model as a regular

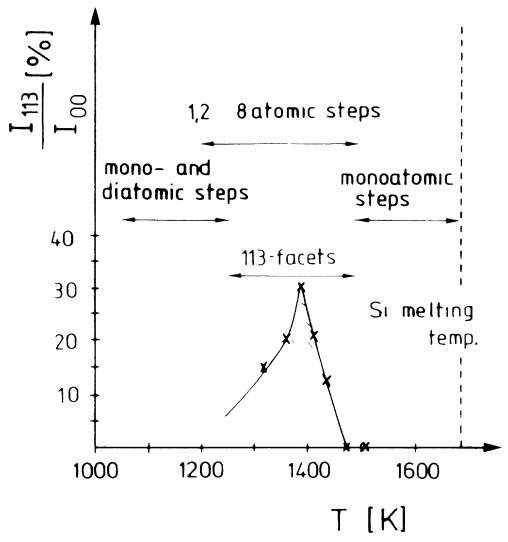

FIG. 4. Phase diagram for the existence of monatomic and diatomic steps, (113) facets, and multiatomic steps on the Si(001) surface. The appearance of (113) facets is monitored by the intensity of their integral superstructure reflexes at 65 eV, normalized to the (00) beam.

sequence of diatomic steps separated by a (001) terrace as shown in Fig. 3. A threefold reconstruction is characteristic for this regular sequence of (111) and (001) terraces.[20,21] As a consequence of that reconstruction, small (113) facets can be considered as multiatomic steps.

Generally, one might expect that a coagulation of steps ends with the formation of (111) facets. Obviously the (3×1) reconstruction of the (113) surface is strong enough to prevent the steps from further migration. This finding is in accordance with the observation of the work-function changes on a cylindrically shaped Si single crystal.[21] Starting from (001) orientation, the work function increases towards (111). However, near (113) it lowers considerably, although the appearance of two different work functions remains observable. The lower value can be understood by the formation of reconstructed (113) facets that reduce the work function whereas the higher values result from unreconstructed areas with a high step density. This interpretation is confirmed by the recent STM observation of (113) facets on a Si(112) surface.[22]

In Fig. 4 we have summarized the appearance of (113) facets measured by the intensity of the (113) spots relative to the integral order spots of the Si(001)-(2×1) surface. It is evident that these (113)-(3×1) facets show a distinct stability range around 1300-K annealing temperature. At lower temperatures the surface exhibits monatomic and diatomic steps with decreasing terrace widths. At temperatures above that range only monatomic steps with increasing terrace widths are observed.

During these experiments we noticed that the surfaces remained rough after prolonged annealing at 1200 K. The appearance of diatomic steps is observed under these conditions. Even by a following anneal to 1600 K, diatomic steps are still observable on a rather high diffuse background. In contrast, ideal Si(001) surfaces are regularly obtained when the wafers are flashed quickly to about 1600 K. After this pretreatment, the structure of the ideal surface can be reproduced repeatedly by annealing to 1600 K. It is obvious that the appearance of (3×1) reconstructed (113) facets can be avoided by a fast flash.

In the context of our results, the experimental studies on the microscopic structure of Si(001) surfaces should be reconsidered: Initiated by Pandey's theoretical work, a number of recent experiments deal with the roughness of this surface. Pandey found that an atomic displacement may lower the total energy of the dimeric reconstruction as the number of dangling bonds is reduced, albeit at the expense of elastic strain. Indeed, in a STM experiment,[1] pronounced atomic roughness is observed and discussed in terms of missing dimers. A regularly missing dimer that results in the formation of a $(2\times n)$ structure with $6 < n < 15$ is discussed.[23] However, our results indicate that surface roughness and average ter-

race width both depend critically on the sample preparation of Si(001) surfaces. This may cause different surface atom irregularities depending on the sample pretreatment. We have demonstrated that the annealing temperature sensitively determines the kinetics of step formation.

In summary, by using a spot profile analysis technique with high resolution in k space and high dynamic range we have investigated the stability ranges and kinetics of steps on the Si(001) surface. For the first time we show that the oscillations in the FWHM of the recorded spots allow us to distinguish between monatomic and diatomic steps as well as multiple arrangements of them. In particular, we describe the coexistence of multiatomic steps that coagulate and form microfacets of (113) orientation. Our work also gives the first experimental evidence that these (113) facets are reconstructed and form a (3×1) superstructure. This reconstruction explains the stability of these (113) facets and also explains the characteristic variations observed for phenomenological properties like work function and adsorption behavior.

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