

Surface Stress as a Driving Force for Interfacial Mixing

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Displacive adsorption of As on vicinal Si(001) surfaces has in the past been attributed to reduction of step-related (extrinsic) surface stress. Here we show images of As adsorption on flat Si(001), obtained with *in situ* low-energy electron microscopy, and with scanning tunneling microscopy. We find displacive adsorption even on micron-size terraces, on which steps play no significant role. These new results reveal the role of intrinsic surface stress as a driving force for interfacial mixing.

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The adsorption of As on Si(001) has been a subject of considerable interest in recent years. Bringans *et al.* used angle-resolved ultraviolet photoelectron spectroscopy to show that the dangling-bond states characteristic of clean Si surfaces are removed by As adsorption and replaced by a lone-pair state well below the Fermi level [1]. Naively, one would expect the As dimers to adsorb on top of the Si surface, breaking the existing Si dimers, which would lead to a rotation of the dimer orientation on (2×1) terraces to (1×2) and vice versa. Using scanning tunneling microscopy (STM) Becker, Klitsner, and Vickers observed this at relatively low adsorption temperatures (less than 500°C) on large-miscut surfaces with double-height steps and a single domain orientation [2]. Surprisingly, they found that at higher temperatures a single domain (2×1) reconstruction remains unrotated after As adsorption, or breaks up into a mixture of (2×1) and (1×2) . This phenomenon can only be understood if Si atoms in the outer monolayer are displaced during the As adsorption process. Becker, Klitsner, and Vickers suggested that this phenomenon may be due to "surface strain effects," but they did not discuss the detailed nature and origin of such strains. Additional support for the possible role of surface stress came from Alerhand *et al.* who calculated that the energy of a Si(001) surface with double-height steps is lower when the dimer orientation does not rotate upon As adsorption [3]. Although no explicit stress calculations were performed, the authors argued that this is due to a reduction in surface stress at the step edges, and that therefore the step edges play an essential role in the displacement of Si by As.

In this Letter we present an experimental study that reveals the role of *intrinsic* (i.e., non-step-related) surface stress in the displacive adsorption of As on Si(001). We show that displacive adsorption not only occurs on densely stepped Si(001) surfaces, but also on flat, step-free terraces of micron size. During As adsorption, Si atoms are displaced from the outer monolayer and migrate over the surface to the nearest step edge. Eventually 2D As islands nucleate on top of the terrace as well, until coverage saturates at ~ 1 monolayer [1 monolayer (ML) = 6.78×10^{14} atoms/cm²]. During subsequent annealing at higher temperature, the 2D As islands desorb as ex-

pected. Additionally, 2D holes open up on the terraces due to desorption of As atoms that have displaced Si atoms during the adsorption process. Since the step density on our Si samples is very low, step edge relaxation cannot be invoked to explain these results. Instead, we argue that Si displacement is driven by a reduction of intrinsic surface stress.

The type of displacements considered here is different from that commonly observed in cases where an adsorbate gives rise to surface reconstruction, displacing *some, but not all*, of the metal surface atoms in the reconstructed unit cell. A good example would be the missing-row surface reconstruction induced by oxygen adsorption on Ni(110) [4]. In the displacive reactions considered here, the resulting surface structure at full As coverage does not depend on the displacive nature of the adsorption and is identical to As dimers adsorbed on top of the terraces, except for a 90° rotation of the dimer orientation on a given terrace.

We have studied the As adsorption-desorption process using low-energy electron microscopy (LEEM), a technique pioneered by Telieps and Bauer [5]. Briefly, a 15-keV electron beam is focused in the backfocal plane of an immersion-type objective lens and decelerated to a few eV at the sample. There the electrons undergo conventional low-energy electron diffraction (LEED), and are accelerated back into the objective lens. A focused LEED pattern is formed in the backfocal plane, while a Gaussian image of the surface is formed at larger distance. A contrast aperture in the backfocal plane (or a conjugate plane further down in the projector lens system, as in our microscope) selects a particular diffracted beam for image formation. On a Si(001) surface alternating terraces may be imaged black and white in a dark-field imaging mode by selecting a $(\frac{1}{2}, 0)$ beam. To optimize resolution the illuminating beam is incident off-normal, allowing the half-order beam to exit along the electro-optical axis, minimizing image degradation due to spherical aberration. Experimentally we obtain a lateral resolution of $\sim 150 \text{ \AA}$. A more detailed description of our microscope has been published elsewhere [6]. Additional studies were made with a scanning tunneling microscope as described earlier [7].

For the LEEM experiments Si(001) samples (n -type, 2 m Ω cm, miscut $<0.5^\circ$) were cut into disks (8.5 mm diam) and mounted in a molybdenum cap at the end of an alumina tube. Sample heating was accomplished by electron bombardment from behind. A clean Si(001) surface was obtained by repeated heating to 1200–1250°C. After flashing, the sample was cooled to the As adsorption temperature, and imaged in the microscope. Exposure to As was started within 5 min of surface cleaning. As₄ was evaporated from a quartz Knudsen cell, surrounded by a liquid-nitrogen-cooled shroud. The As₄ flux was controlled by a shutter. During As₄ exposure the chamber pressure increased to $(1-2)\times 10^{-8}$ Torr, and dropped immediately upon closing the shutter. The base pressure of the microscope was 5×10^{-10} Torr. For the STM experiments the samples were cut into strips (5×15 mm²), and mounted between Ta and Si clamps, and cleaned by resistive heating to 1250°C. As₄ exposure was done with the same As cell used previously for the LEEM experiments. The base pressure in the STM chamber was $<1\times 10^{-10}$ Torr.

Figure 1 shows a sequence of LEEM images obtained (at high temperature) on the clean Si(001) surface, during subsequent adsorption at 630°C and during desorption at 800°C. Image (a) was obtained on the clean Si(001) surface, prior to As adsorption. Only the $(\frac{1}{2}, 0)$ beam was used for dark-field imaging. Domains that diffract into that beam are imaged white, and domains diffracting into the $(0, \frac{1}{2})$ beam are black. [The contrast can be inverted by forming the image with the $(0, \frac{1}{2})$ beam.] Black and white terraces are separated by single-height atomic steps. The surface height increases

from the upper left to the lower right. The round feature marked with a cross is a 2D hole on the large black terrace and was formed during surface cleaning. After adsorption of ~ 0.5 ML As the positions and shapes of the steps have changed, but no contrast differences are observed to distinguish As- and Si-terminated areas [Fig. 1(b)]. Image (c) shows the saturated surface, at a coverage of 1 ML. Now, islands have formed on the largest terraces. The black-white contrast of the terraces and the 2D islands only tells us the (2×1) domain orientation, not the chemical composition of the domains. Clearly, the large terraces have predominantly the same domain orientations as in image (a), before As adsorption. If As dimers had adsorbed on top of the terraces seen in (a), this would have resulted in rotation from (2×1) to (1×2) domains and vice versa, giving rise to inversion of the contrast seen in (a), without motion of the atomic steps [8]. In numerous As adsorption experiments under similar conditions in a medium-energy ion scattering (MEIS) setup it was found that the As coverage saturates at ~ 0.95 ML, without detectable incorporation of As in the substrate [9]. Thus, given the fact that the surface is fully terminated with As, we must assume that both the 2D islands as well as the areas between the 2D islands have an outer atomic layer of As. This, and the obvious absence of simple contrast reversal, immediately implies that displacive adsorption of As has occurred on the terraces, between the 2D islands.

Additional information may be obtained by desorbing the As monolayer at higher temperature. Image (d) shows the surface after the onset of desorption. The 2D islands have almost disappeared, confirming that these

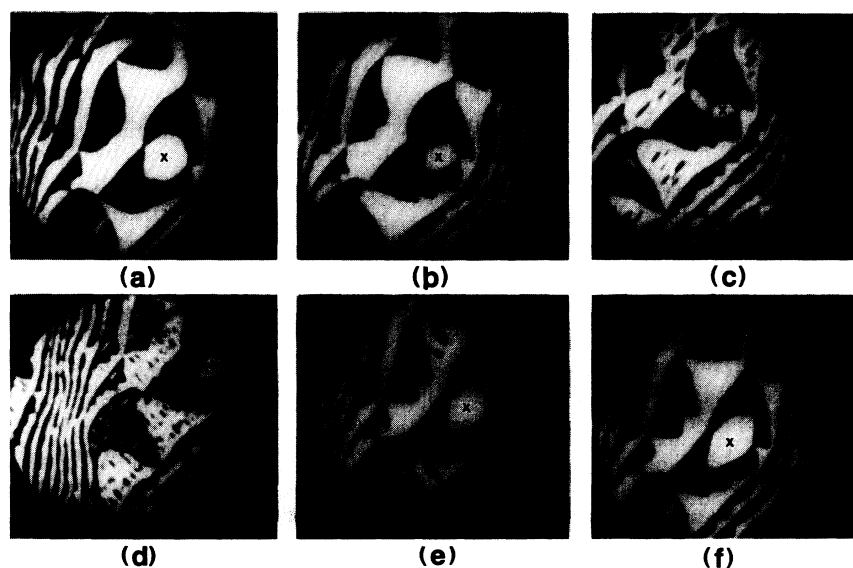


FIG. 1. Clean Si(001) surface; (b) 0.5 ML of As; (c) 1 ML of As; (d) immediately after onset of desorption; (e) 2 min after (d); (f) 2 min after (e). Field of view in all images is 4 μ m. Image shifts are due to drift and mechanical displacements. A fixed point in all images is indicated by a cross.

are indeed As islands, since the sample temperature is too low for Si evaporation, and the time scale too short for significant Si surface diffusion. At the same time a large number of holes have opened up on the terraces, due to desorption of As atoms that had displaced Si atoms during adsorption. Image (e) was taken 2 min later, showing that the holes undergo coarsening. That these features are holes and not 2D islands can be deduced from two observations. First, the elongated football-like shape is rotated 90° relative to the equilibrium shape of 2D Si islands on this surface. The equilibrium shape of a 2D Si island is determined by the step energies of its boundaries. STM [10] and LEEM [11] experiments have shown that such Si islands are elliptical in shape, with the long direction of the ellipse running parallel to the low-energy *A*-type step edges. If a *hole* is formed on a terrace (instead of an island), the equilibrium shape of the hole is determined by the same step energies, but since the *A*-type step edges rotate 90° between island and hole, the elliptical shape of the holes is rotated 90° relative to that of islands. Second, upon repeated As adsorption these features shrink, as expected for holes. At the As desorption temperature, there is an equilibrium 2D pressure of Si dimers (or atoms) on the clean Si surface. Thus one would expect the holes to slowly disappear during prolonged annealing. This is shown in image (f) where most of the holes are gone, and the surface looks very similar to the starting surface [image (a)]. If, on the other hand, the temperature is increased further to induce significant evaporation of Si, the holes may grow in size and eventually "consume" the entire terrace on which they were formed. The formation of holes during desorption is another indication of displacive adsorption of As on the large Si(001) terraces shown here, far away from step edges.

More detailed information on the initial stages of As adsorption may be obtained from STM images taken at different bias voltages. Figure 2 shows two such images, after adsorption of ~ 0.5 ML of As (coverage measured with medium-energy ion scattering) at 700°C , at -2 V [2(a)] and -1.5 V [2(b)] sample voltage, with the tip grounded. Under these bias conditions the STM probes the filled surface states of the sample. Since the surface state energy of the As-terminated surface is lower than that of the Si-terminated surface [1], Si- and As-terminated areas can be distinguished by varying the tunneling bias voltage. Image 2(a) shows a regular dimer-reconstructed Si(001) surface, with a single-height atomic step traversing the field of view. At this bias voltage the adsorbed As is not apparent. Image 2(b), however, obtained immediately after 2(a) shows many dark patches over all the terraces. Since tunneling from the As-related surface states is strongly quenched at bias voltages closer to the Fermi level, we identify the dark patches as As terminated. As seen in 2(b), As adsorbs in small areas, all over the terraces. No preferential adsorption of As is observed at the step edges, in agreement

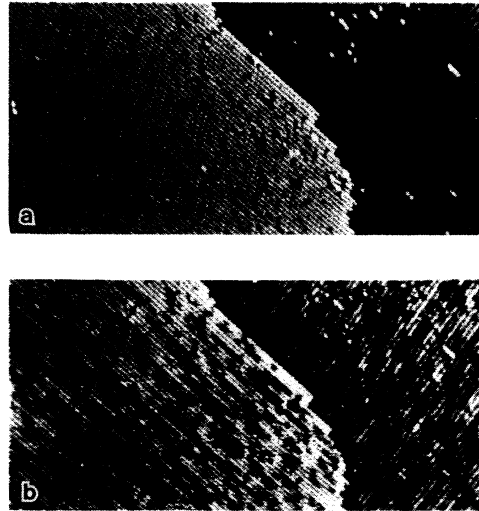


FIG. 2. STM images obtained at (a) -2 and (b) -1.5 V bias (tip grounded), on a Si(001) surface with ~ 0.5 ML As adsorbed at 700°C . As-terminated regions show up darker in (b). Both Si- and As-terminated areas are dimer reconstructed as seen in (a). Image size is $600 \times 300 \text{ \AA}^2$.

with the LEEM observations, and the step edges appear to play no significant role in the As adsorption process. Image 2(b) shows that the As-terminated areas are dimerized, with the As dimers coplanar with the Si dimers. Furthermore, the As areas are too small to be resolved in the LEEM experiments, explaining the lack of contrast changes between Figs. 1(a) and 1(b). After annealing we have observed holes on the terraces, similar to those observed in the LEEM experiments [Figs. 1(d) and 1(e)].

We find that displacive adsorption of As takes place on the terraces, and that the surface steps play no role in this process, in contrast to previous suggestions. A simple explanation is presented in the following. First-principles calculations of the surface stress tensor for clean Si(001) have shown that the surface stress is tensile in one direction (parallel with the surface dimers), and compressive in the other (perpendicular to the dimers) [12]. At small-miscut angles (where step energies play an insignificant role) the surface prefers an alternation of domain orientations, preventing the buildup of a large macroscopic compressive or tensile stress on the sample. (Conversely, application of external strain will favor one domain over the other [13], illustrating the interplay between surface stress and substrate strain in determining surface geometry.) The surface stress tensor for an As-terminated Si(001) surface, however, is qualitatively different, with tensile stress occurring both parallel with and normal to the As dimers [12]. Experimentally it was found that the As-terminated surface is under tensile stress relative to the clean surface, in agreement with these theoretical results [14]. On a given terrace, at an As coverage below 1 ML (as one necessarily encounters

during As adsorption), the surface stress can be reduced by displacive adsorption of As: In the surface plane, the compressive stress in the Si dimers can be alternated with the tensile As stress. By exchanging a Si dimer with an As dimer, the number of dangling bonds stays constant, but the surface stress is reduced. The As dimer is embedded in the surface plane, and the displaced Si dimer sits on top of the terrace, 90° rotated from its original orientation, and thus also rotating its stress tensor by 90° , helping to reduce the local stress even further. This reduction of surface stress will lead to a reduction of a substrate strain and associated strain energy [15]. In addition, the Si dimer will diffuse and eventually adhere to a step edge, lowering the energy further. (On very large terraces the displaced Si dimers may also nucleate 2D islands.) At some point the displacement of Si dimers with As dimers becomes less favorable, as the balance shifts from a net compressive to a net tensile stress. At this point 2D As islands start to grow on top of the terraces, until complete coverage has been achieved. Adsorption at higher temperature and/or slower deposition rate results in a smaller number of 2D As islands. At full monolayer coverage the presence of these islands is energetically unfavorable due to the island step energies involved, but due to kinetic limitations it is difficult to obtain an island-free surface.

While step energies and relaxation of surface stress at step edges may play some role on vicinal surfaces, these results raise two key issues to be considered even with high step density: (1) Displacive adsorption can lower surface stress on the terraces, away from step edges; and (2) it is insufficient to consider only the energetics of fully As-terminated surfaces, since these can only be prepared by passing through lower coverage intermediate structures that may throw the surface permanently out of thermodynamic equilibrium. In a recent study of step rearrangement on Si(001) by As adsorption, Bringans, Biegelsen, and Swartz's remark [16] that "It is possible that As atoms (or dimers) could replace Si atoms (or dimers) in the center of terraces. It is difficult to see how this would have a lower energy than As atoms bonded on top of the Si atoms on the terraces, but our data cannot rule out such a mechanism." In this study we have shown that occurrence of just such midterrace displacive adsorption of As on low step density Si(001), explained by a reduction of intrinsic surface stress. Stress relaxation at

surface steps plays no role in this process. Recent theoretical and experimental studies have also addressed displacive adsorption in metallic systems. Field ion microscopy experiments by Kellogg give direct evidence for displacive adsorption of Pt on Ni(110) [17]. Indeed, one may suspect that this phenomenon is quite common, and that surface stress plays an important role. In general, reduction of surface stress by the mechanism discussed here may be a driving force for interfacial mixing during the initial stages of heteroepitaxial growth.

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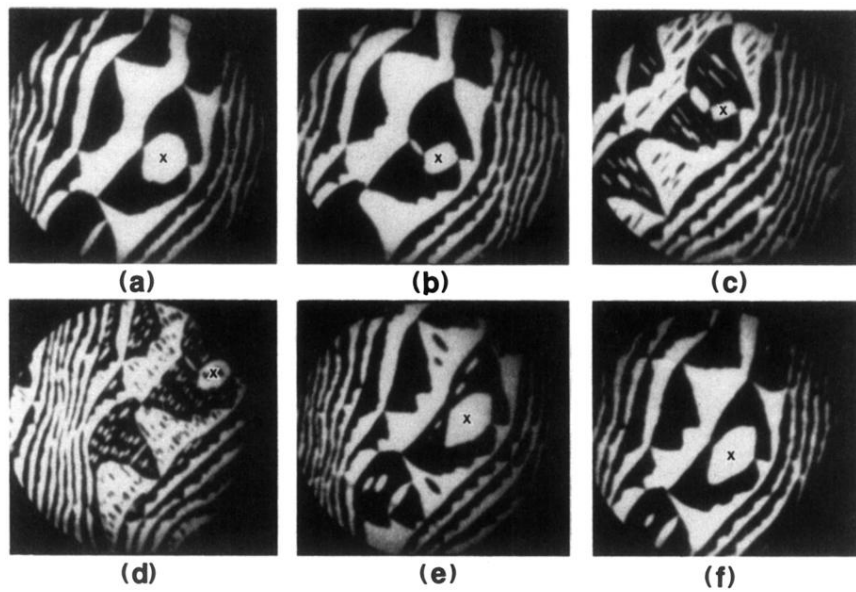


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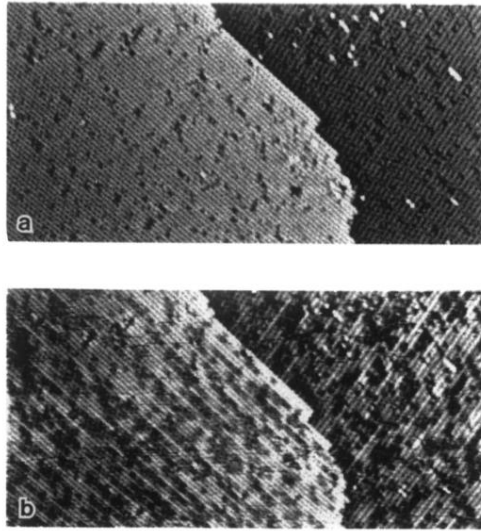


FIG. 2. STM images obtained at (a) -2 and (b) -1.5 V bias (tip grounded), on a Si(001) surface with ~ 0.5 ML As adsorbed at 700°C . As-terminated regions show up darker in (b). Both Si- and As-terminated areas are dimer reconstructed as seen in (a). Image size is $600 \times 300 \text{ \AA}^2$.