Adsorbate Induced Change of Equilibrium Surface during Crystal Growth: Si on Si(111)/H

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Surface termination of Si(111) with atomic hydrogen changes the homoepitaxial growth from a layer-by-layer mode (bare surface) to a faceting of the whole surface. This decomposition of the planar surface into a "hill-and-valley" structure is explained by a change of the surface free energy during Si deposition and H termination. This favors the growth of facets, which are stable as long as the surface is covered with H. The effect is reversible, with the growth mode returning to layer by layer after H desorption.

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The physical and chemical properties of a surface can be altered drastically by monolayer adsorption of an additional element. For example, the surface free energy, the mobility of diffusing adatoms, and their nucleation behavior is affected. This is of critical importance during crystal growth. For growth mode engineering of heteroepitaxial systems, the use of adsorbates (surfactants) has recently attracted much attention [1–4]: Instead of cluster formation, the growth of continuous heteroepitaxial films can be observed. The surfactant strongly lowers the surface free energy by saturating the dangling bonds as in the case of semiconductors, which leads to strong segregation of the surfactant and the incorporation of the growing species.

These lattice mismatched heteroepitaxial films exhibit a pronounced microroughness during the coherent stage of growth [5] (prior to the generation of dislocations), which allows strain relaxation by partial elastic deformation. The reversible change of the surface morphology of strained heteroepitaxial films has been ascribed to the influence of the surfactant on the surface free energy [6].

The formation of an increasingly rough growth front is also known for homoepitaxial systems far from equilibrium conditions and with a barrier for diffusion across step edges (Ehrlich-Schwoebel step edge barrier) [7]. Here the use of adsorbates influences the mobility and the nucleation process and results in layer-by-layer growth [8].

However, growth of homoepitaxial films without kinetic limitations usually proceeds in the Frank–Van der Merwe (layer-by-layer) mode (which is the typical example for this growth mode) or by step propagation. This is because the low index planes usually have the lowest surface free energies. Formation of small areas with different surface planes (facets or step bunching) is expected for vicinal surfaces and has been observed [9,10]. Adsorbates can also change the surface free energy and can induce the decomposition of a planar surface into a "hill-and-valley" structure, exposing facets of other (often low index) orientations [9].

In this Letter we demonstrate another new and unexpected mechanism of adsorbate induced changes in surface morphology during growth. For temperatures above 400 °C homoepitaxial growth of Si(111) proceeds either in a layer-by-layer fashion or by step propagation, and results in a planar surface with (111) orientation [12]. Adsorption of H without deposition of Si passivates the surface by saturation of the dangling bonds. This changes the equilibrium surface reconstruction of the (111) surface from (7×7) to (1×1), the surface with the lowest free energy.

Adsorption of H *during* Si(111) molecular beam homoepitaxy, however, changes the growth mode and causes film roughness, although strain is not a driving force in this case. The complete disappearance of planar (111) areas, the formation of well developed facets with orientations ranging from [113] to [779], and a typical size of ~100 Å (hill-and-valley structure) is explained by a change of the surface free energy *during Si deposition and H termination of the surface:* The energetically more favorable orientations develop during growth.

Without further Si deposition, those facets are stable as long as the surface is H terminated. A continuous dosing with atomic H is required to compensate for desorption. The effect is reversible, with the growth mode returning to layer by layer after desorption of H from the surface (after turning off the H flux). The facets immediately dissolve and the surface smooths again.

We have used high resolution electron diffraction (spot profile analysis low energy electron diffraction [13]) to determine the surface morphology during Si deposition and H adsorption and desorption. With a second electron gun in glancing angle geometry, there was ample space for the Si and atomic H sources, which allowed Si deposition and H termination during measurements [11].

Si was grown above 500 °C. At these temperatures H desorption is already significant. To keep the surface H terminated a continuous flux of atomic H was provided, by flowing H_2 through a tungsten tube, which is heated by an *e* beam to 2000 °C [14]. The flux was controlled by the background pressure of H_2 in the chamber. This type of effusion pipe provides a concentrated beam of atomic H and avoids flooding the whole chamber with H_2 (when using a hot tungsten wire for H_2 dissociation). H fluxes of

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up to ~2 monolayers/s or 2×10^{15} H atoms $cm^{-2}\,s^{-1}$ at a background pressure of 5×10^{-6} mbar were possible.

Without H and for temperatures between 500 and 600 °C homoepitaxial growth on Si(111) proceeds in a layer-by-layer mode as could easily be observed in periodic, undamped low energy electron diffraction (LEED) intensity oscillations [12,14]. With H termination during Si growth layer growth with a bilayer (monolayer: 1 ML = 7.8×10^{14} atoms/cm^2, bilayer: 1 BL = 2 ML) period is still observed, as shown by the pronounced intensity oscillations in Fig. 1. The strong (and initially exponential) decay of the oscillation maxima, however, reflects a buildup of surface roughness during growth [15]. The LEED pattern (Fig. 1) after deposition of 40 BL of Si at 520 °C is completely different from the patterns observed for growth at lower temperatures [12] or without H [14]: All integer order spots exhibit a starlike shape with a threefold symmetry. The appearance of sharp central spikes at three integral order spot positions (arrow) reflects excellent epitaxial growth without formation of stacking faults (which would produce sixfold symmetric LEED patterns). We would like to emphasize that the adsorption of atomic H without Si deposition does not produce facets at the surface, even at temperatures up to 650 °C and H fluxes of 10 ML/s.

The shape of those threefold "stars" varies with electron energy. Depending on the scattering condition, the elongated spots (which form a star) move towards or away from the central spikes. The position in reciprocal space of one set of those spots is plotted in Fig. 2 as a function of the vertical scattering vector k_z. The linear dependence of the spot position on the vertical scattering vector identifies them as facet spots [16] with an average facet plane orientation of [557]. The facets are composed of dihydride-terminated steps in the $[\bar{1}\,\bar{1}2]$ direction. The width of the ovals in Fig. 2 corresponds to the intensity and the length of the ovals to the extension of the spots in reciprocal space. The facet spots become much broader with increasing distance from the integral order spot positions (also clearly seen in Fig. 1). This behavior indicates the formation of an irregular step train, i.e., not well ordered facets. The steps, however, are straight according to the narrow shape of the facet spots, which points to an increased mobility of the deposited Si along the step edge.

From the finite width of the facet spots close to the Bragg conditions of scattering, an average size of ~100 Å

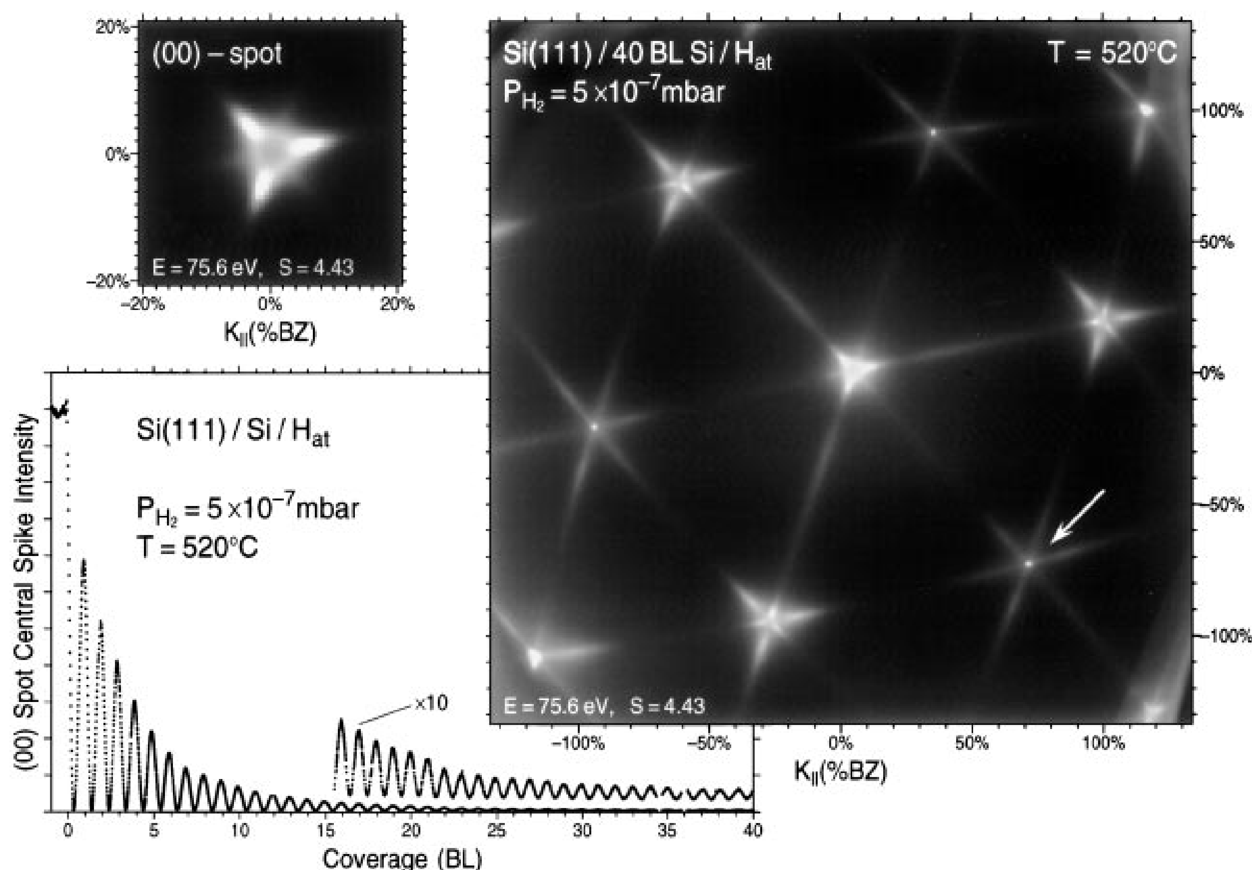

FIG. 1. Exponentially decaying LEED intensity oscillations reflects a buildup of surface roughness during epitaxial growth. After deposition of 40 BL Si all integer order spots in the LEED pattern were split into starlike shaped facet spots (shown right in a logarithmic intensity to grey scale representation). Sharp central spikes at three integral order spot positions (arrow) reflect excellent epitaxial growth without formation of stacking faults. The complete lack of the (00)-spot central spike (left pattern in a linear intensity representation) indicates that the whole surface is completely covered by facets.

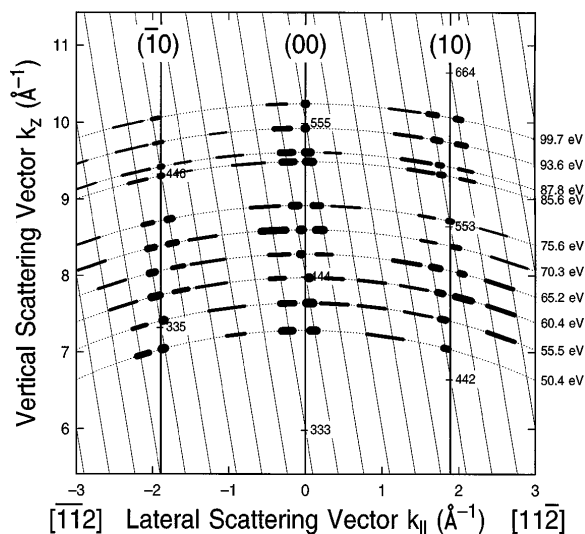

FIG. 2. The facet spots move in reciprocal space on rods perpendicular to the facet plane. The mean facet orientation of [557] is plotted with thin lines. The width of the ovals corresponds to the intensity, the length to the extension of the spots in reciprocal space.

is estimated for this film with 40 BL coverage [17]. The complete lack of the (00)-spot central spike at the out-of-phase or anti-Bragg condition (see inset of Fig. 1) indicates that the whole surface is completely covered by facets, without any remaining (111) face.

Figure 3 shows the growth behavior before and during H adsorption, and after H desorption at 540 °C. The undamped oscillations of Si homoepitaxial growth on the bare surface (Si has been deposited with 1 BL/min) are decreasing exponentially after H termination (a rough estimation for the H flux yields 0.5 ML/s). Since the period of oscillation stays constant during H exposure, we can conclude that all deposited Si atoms are immediately incorporated into the adsorbate layer and stick to the surface (and do not desorb again). We also can exclude any H related etching processes. After 13 additional BLs of Si the H has been turned off and the undamped LEED intensity oscillations recovered immediately. The LEED pattern shows a mixture of (7×7) and (5×5) spots, which is typical for growth on the bare Si(111) surface. Obviously the H is desorbed. First, this shows that we can exclude any form of contamination originating from the H source as the reason for faceting. Second, there is no generation of bulk defects as observed for growth below 500 °C [14].

After interruption of the Si deposition the facets are stable under continuous H flux. Although the driving force for the faceting (the depositon of Si atoms) is turned off, the diffusion of the Si out of subadsorbate sites seems to be kinetically hindered [4] due to the strength of the H-Si bond with a binding energy of 3.1 eV [18–20]. A minimum flux of atomic H is necessary for facetting and stabilization of the facets. This minimum flux depends on the temperature of growth and compensates for H desorption. A value roughly twice the critical value has been chosen for the experiments.

The decomposition of the facets upon desorption of the H proves that the facets are a phase stabilized by the adsorbate. This process has been monitored during H desorption by the intensity decay of one of the facet spots. Figure 4 shows this decay for various temperatures after the H flux has been turned off. Increasing the temperature by only 60 °C yields a change of the decay time constant τ by a factor of 20. Considering the decay as an activated process, an energy of $E_a = 2.3$ eV and a pre-exponential factor of $\nu_0 = 10^{13}$ s^{-1} result. From excellent agreement with parameters found in the literature [19] we conclude the desorption of H is the dominant process in the decomposition of the facets. The smoothing of the facets is driven by Si diffusion, which cannot be the limiting process and must happen on a much faster time scale.

Chemical vapor deposition (CVD) of disilane at high fluxes (flooding the chamber, $p_{Si_2H_6} > 1 \times 10^{-4}$ mbar)

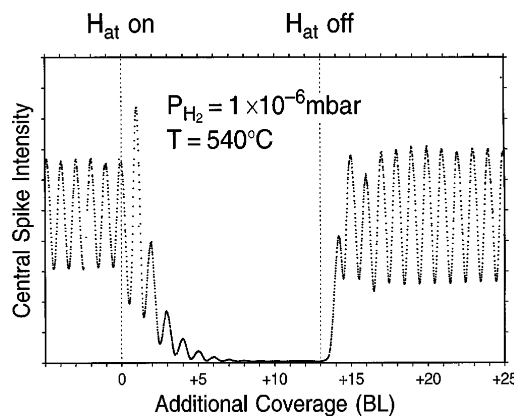

FIG. 3. Growth behavior before and during H adsorption, and after H desorption at 540 °C. The exponential decay after H adsorption reflects the faceting. After H desorption the surface smoothened and the undamped LEED intensity oscillations immediately recovered again.

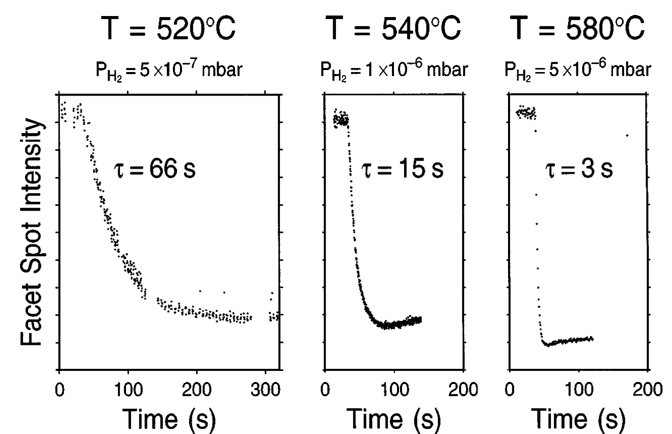

FIG. 4. The decreasing intensity of one facet spot during desorption of H at different temperatures reflects the temperature dependence of the decay of the facets and the smoothening of the surface. An activation energy of $E_a = 2.3$ eV and a pre-exponential factor of $\nu_0 = 10^{13}$ s^{-1} can be derived.

results in identical LEED patterns [21]. Triangular pyramids have also been observed for CVD by scanning tunneling microscopy [22]. The faceting is therefore independent of the adsorption and reaction processes of the disilane to Si-H. During CVD Si-H radicals are present at the surface [23]. With increasing H coverage the mobility seems to be strongly reduced (a transition from layer-by-layer growth or step propagation to faceting is also observed) resulting in a supersaturation of Si-H radicals. During CVD the Si growth is intimately connected to the ad- and desorption of H. In our experiment we were able to independently adjust the Si and H fluxes which has offered the variety of experiments presented here.

The decomposition of the planar (111) surface and the formation of facets is thus explained in terms of an adatom gas induced increase of the free energy of the low index surface: It is very likely that the ideally H terminated Si(111) surface still has the lowest free energy. Only by the additional deposition of Si atoms the surface energy increases, because the Si atoms could not occupy regular lattice sites and remain as supersaturated lattice gas of weakly bonded Si monohydrides as for CVD [23]. We argue that the mobility of these monohydrides is reduced, because they are embedded in the H layer, which is strongly bonded with 3.1 eV [18–20].

At step edges the geometry and the strength of the H-Si bond is different and the weakly bonded monohydrides could exchange easier with H and occupy regular binding sites to the Si substrate without generation of defects as observed for lower growth temperatures [14]. Under these conditions (together with the reduction of mobility) only the formation of steps strongly reduces the number of Si-H monohydrides and thus lowers the surface free energy. This reduction of the surface free energy is the precondition for the decomposition of the planar surface into a hill-and-valley structure [9]. It is, however, also possible that the faceted surface could be thermodynamically stable in the H environment. Then the driving force for faceting may be to maximize the number of Si-H bonds without much reduction in Si-Si bonds. In this case kinetic barriers might prevent the spontaneous faceting of the (111) surface.

In conclusion, we have shown that adsorption of H can strongly affect homoepitaxial growth of Si(111) just by a subtle change of the surface free energies *during deposition*. Initially H reduces the surface free energy and passivates the Si surface. We suggest that the addition of Si to such a surface actually raises the free energy by creating a weakly bonded gas of Si monohydrides. This favors the decomposition of the planar low index surface and causes the formation of (557)-like facets during growth. With desorption of H the facets immediately dissolve and the surface smooths again, with the growth mode returning to layer by layer.

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