

## Surface stress and interface formation

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We discuss the role of surface stress during the initial stages of adsorption of As and Ge on Si(001). At submonolayer coverages the adsorbing species displaces Si atoms from the terraces, driven by a reduction of surface stress, leading to mixed terrace composition. As the coverage increases to one monolayer, chemical effects become dominant, leading to complete termination with Ge or As atoms. Depending on kinetic limitations, the surface at one-monolayer coverage may be smooth or rough. The reduction of surface stress by displacive adsorption provides a lower-energy pathway than growth by simple step flow and may play a role in the formation of a wide variety of (epitaxial) interfaces.

The role of surface stress in the initial stages of interface formation has not received much attention.<sup>1,2</sup> In a recent paper we pointed out its role in the adsorption of As on Si(001).<sup>2</sup> The clean Si(001) surface, reconstructed in rows of dimers to eliminate half of its dangling bonds, has an anisotropic stress tensor: tensile along the dimer bond, compressive normal to it.<sup>3,4</sup> The As terminated surface is also dimer reconstructed, but has a much more isotropic stress tensor, tensile both along and normal to the dimer bond.<sup>3,4</sup> At submonolayer As coverage the Si surface can lower its energy by dispersive incorporation of As dimers on the terraces, alternating the compressive component of the Si-dimer stress with the tensile As-dimer stress.<sup>2</sup> In order to achieve this, As dimers displace Si dimers from the terraces. The Si dimers can diffuse to a step edge (if the temperature is sufficiently high), or else form two-dimensional (2D) islands on the terraces. As the coverage approaches one monolayer (ML) chemical effects start to dominate. As termination removes all dangling bonds from the surface, resulting in a very large reduction in surface free energy.<sup>6</sup> Thus, at 1-ML coverage, the surface is completely terminated with As. If the temperature is high, the terraces may evolve from a mixed composition to full As composition, without becoming rough. But at lower temperatures many islands will form on the terraces, resulting in high step density.<sup>7</sup>

Here we discuss a very similar effect occurring during the adsorption of Ge on Si(001) at coverages up to 1 ML. The adsorption of Ge in this coverage range has been studied by various techniques, including low-energy electron microscopy (LEEM),<sup>8</sup> low-energy electron diffraction (LEED),<sup>9</sup> scanning tunneling microscopy (STM),<sup>9-11</sup> reflection electron microscopy,<sup>12</sup> medium energy ion scattering (MEIS),<sup>13</sup> and surface stress-induced optical deflection (SSIOD).<sup>5</sup> The combined results of these studies present a clear picture of dispersive adsorption, with Ge displacing Si from the terraces at submonolayer coverages, but leading to full Ge termination at 1 ML.

Tromp and Reuter<sup>8</sup> studied the adsorption of Ge on Si(001) both without and with a monolayer of As present on the sample prior to Ge growth. Here we only concen-

trate on the As-free case. At first glance these observations appear simple: up to 1 ML the steps advance with increasing coverage (at a growth temperature of 610°C), apparently indicative of step-flow growth. However, upon further consideration it is rather striking that no contrast is found on the atomic terraces between Ge-terminated regions (supposedly formed as the steps advance by Ge adhesion), and Si-terminated regions (where the original terraces are still intact). Certainly, Ge termination would give rise to a change in the LEED  $I$ - $V$  curves, at least at *some* energies, so that a contrast difference between Si- and Ge-terminated areas should be observable. No such contrast differences were observed over a range of electron energies, indicating that purely Ge-terminated regions—if they exist—are smaller than the resolution limit of the microscopy ( $\sim 150$  Å), and therefore smaller than the distances over which step flow is observed (several thousand Å).<sup>8</sup> Inspection of the LEED pattern during LEEM microscopy shows that Ge adsorption is accompanied with a gradual change in LEED pattern, from a two-domain ( $2 \times 1$ ) pattern to a two-domain ( $2 \times n$ ) pattern, where  $n$  is initially large and not well defined at  $\sim 0.5$  ML, but decreases to  $\sim 12$  at 1 ML, and to  $\sim 8$  at 2 ML. At this point the  $n$ th-order beams are quite sharp, indicating good order.

Similar changes have been observed in STM studies.<sup>9-11</sup> The adsorption of Ge is accompanied by the appearance of missing dimers on the terraces. At low coverage the missing dimers are far apart, and not particularly well ordered. As the coverage increases the missing dimers line up in bands (perpendicular to the basic dimer rows). There is a strong repulsion between these missing dimer bands, resulting in good ordering. Tersoff has shown that the missing dimers help relieve the 4.3% lattice mismatch strain between Si and Ge, with an optimum calculated missing dimer density (at monolayer coverage) in agreement with the observations.<sup>14</sup> Again, the gradual nature of the ( $2 \times n$ ) formation is striking. If the Ge atoms would adhere to the step edges, forming large contiguous areas of Ge-terminated Si that expand with coverage, one would expect *immediate* formation of a well-defined ( $2 \times n$ ) structure in those areas, coexisting with the clean Si-terminated ( $2 \times 1$ ) structure below 1

ML. Instead, poorly ordered ( $2 \times n$ ) structures are formed first, all over the terraces, where  $n$  decreases with coverage.

MEIS was used to determine the depth distribution of Ge on Si(001), comparing room-temperature (RT) adsorption with adsorption at 500°C.<sup>13</sup> At 1-ML coverage RT and 500°C adsorption gave identical results, indicating that Ge is present at the surface only, without incorporation in subsurface sites. At 2- and 3-ML coverage, RT adsorption gives rise to much narrower Ge depth distributions than adsorption at 500°C, indicating that Ge diffuses into the subsurface region at higher temperatures, but only when the coverage exceeds 1 ML.

Finally, the change in surface stress during Ge adsorption was measured *in situ*, during Ge growth at  $\sim 500^\circ\text{C}$  using optical deflection.<sup>5</sup> While the stress versus coverage curve is linear at coverages above 2 ML, the initial rate of stress increase is slow and nonlinear. Again, if Ge-terminated regions would form, coexisting with Si-terminated regions, the surface stress would increase more or less linearly. The nonlinearity was explained by assuming the formation of isolated Ge dimer rows on the Si surface at low coverage, coalescing at higher coverage. This picture is not consistent with recent LEEM and STM results. A better explanation is provided by dispersive incorporation of Ge in the terraces at low coverages, proceeding to complete Ge termination at 1 ML. Since the strain is shared between Si and Ge at submonolayer coverage, the strain energy (quadratic in strain) is lowered substantially (by about a factor 2 at half-monolayer coverage), and increases nonlinearly with coverage up to a monolayer. The stress increases nonlinearly with coverage as a result of the reduction of  $n$  in the ( $2 \times n$ ) structure with increasing Ge coverage.

The results reviewed above provide a coherent picture of submonolayer Ge adsorption on Si(001). The Ge atoms displace Si from the terraces, allowing for more effective reduction of the Si-Ge misfit strain. The expelled Si atoms diffuse and adhere to the step edges, giving the appearance of simple step-flow growth. Since Ge adsorption is dispersive, no Ge-related contrast is seen in LEEM. Because the Ge dangling-bond energy is lower than the Si dangling-bond energy, the surface is fully Ge-terminated at 1 ML. This picture is remarkably similar to what was presented in the introduction for As adsorption, and indeed the phenomena are virtually identical. Below 1 ML lowering of surface stress drives displacive and dispersive adsorption of As or Ge on the terraces. At 1 ML the energetics are dominated by chemical effects, driving complete termination with Ge or As. Schematically, the situation can be represented with the help of Fig. 1, which plots the surface energy as a function of coverage. The clean surface ( $\theta=0$ ) has a higher energy than the fully covered surfaces ( $\theta=1$ ). In the simplest case adsorption would proceed by formation of regions where locally  $\theta=1$ , coexisting with other regions

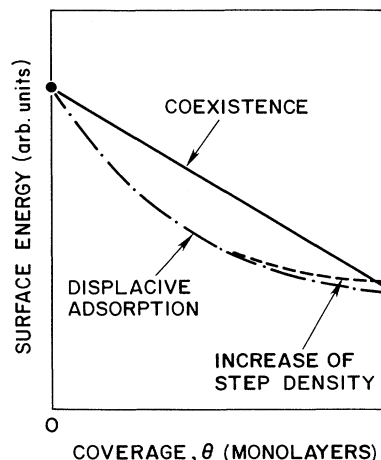


FIG. 1. Schematic diagram of surface energy as a function of (Ge or As) coverage, between 0 and 1 ML. If regions of  $\theta=1$  coexist with regions of  $\theta=0$  below 1 ML, then the solid line is followed. Displacive adsorption, driven by reduction of surface stress, allows lowering of the surface energy at intermediate coverages (dash-dotted line). Kinetic limitations may cause islanding on the terraces in the later stages of adsorption, leading to increased step density at the expense of step energy (dashed line).

where  $\theta=0$ . Simple step flow would be an example of this scenario. In this case the average surface energy would depend linearly on  $\theta$  (solid line in Fig. 1). However, at coverages below 1 ML the surface can do better by displacive adsorption, which puts lower surface energy dimers in the surface (thus obtaining chemical energy benefits), alternating them with Si dimers to lower the elastic surface strain energy. Thus, this displacive adsorption process allows the surface to follow a path of lower energy towards full coverage (dash-dotted line in Fig. 1). In the As-adsorption case we have seen that the surface may have higher step density at 1 ML than the clean surface, due to kinetic limitations leading to 2D island formation.<sup>7</sup> The effect of this is to increase the surface energy over the ideal value at 1-ML coverage, as indicated by the dotted line in Fig. 1.

We have shown that reduction of surface stress gives rise to displacive adsorption of both As and Ge on Si(001) at submonolayer coverages. The physics in both cases is almost identical, with kinetic limitations near 1 ML playing a more important role for As. While the role of surface stress in initial states of interface formation and displacive adsorption has not been widely studied, we believe that the results presented here may have wide significance, including formation of epitaxial interfaces on compound semiconductors and metals.

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