Thermal Adatoms on Si(001)

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Thermal adatoms (present on the surface at elevated temperature, in equilibrium with the step edges) are of key importance in dynamic phenomena such as step capillary wave motions, epitaxial growth, surface phase transitions, and the decay of nonequilibrium structures by surface diffusion. Here we present the first direct measurements of the thermal adatom concentration on Si(001) at elevated temperatures, from which we determine an adatom formation energy of 0.35 ± 0.05 eV. Comparison with first-principles theory shows that the adatoms occur as dimers. These observations have direct implications for our understanding of surface diffusion and epitaxial growth. [S0031-9007(98)06726-X]

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A surface in thermodynamic equilibrium contains a two-dimensional gas of adatoms in equilibrium with the atomic step edges, much like a condensed substance in equilibrium with its three-dimensional vapor. This two-dimensional adatom gas is of crucial importance for a variety of surface dynamic phenomena. On Si(001), capillary waves of atomic steps are caused by exchange of adatoms between the atomic steps and the terraces between them [1]. Ostwald ripening of two-dimensional islands is mediated by the adatom gas between the islands [2]. The annealing of nonequilibrium corrugations on the surface (formed by lithography and etching [3], or by nonequilibrium *in situ* processes such as electromigration [4], etching [5], or growth [6]) relies on surface diffusion, i.e., the motion of thermal adatoms in response to a gradient in the surface chemical potential. During homoepitaxial growth the incoming adatoms force the surface out of thermodynamic equilibrium. Depending on the relative concentrations of “external” and “thermal” adatoms, the processes of nucleation and growth may be profoundly different [7]. A large (small) adatom supersaturation will give rise to dense (sparse) nucleation and a small (large) critical nucleus size. Thus, the growth mode will depend sensitively on the thermal adatom concentration. Finally, phase transitions frequently rely on the motion of adatoms on the surface, in particular, when the atomic density is not conserved across the phase transition [8]. For instance, the Si(111)-(7 × 7) structure has an atomic density 4.1% higher than the bulk-terminated 1 × 1 surface. Such density differences occur not only in phase transformations on atomically clean surfaces but also when different atomic species are adsorbed and give rise to new structural phases [9].

While the importance of thermal adatoms in a wide range of surface dynamic phenomena is obvious, the formation of thermal adatoms and their concentration at elevated temperatures have not been widely studied. If they are sufficiently plentiful they are also very mobile and not observable with an atomic resolution probe such as the scanning tunneling microscope (STM). Single adatoms and addimers on Si(001) have been observed with STM only near room temperature [10,11]. Furthermore, these studies observed adatoms and addimers deposited from the vapor phase, so that their density was far in excess of the equilibrium concentration. While valuable insight has been gained concerning the diffusion paths and energies under these conditions, much remains unknown about the *equilibrium* surface and the formation energies.

An important observation was made recently by Johnson *et al.* in their studies of GaAs surfaces [12]. When a surface is quenched from high temperature the adatom gas becomes supersaturated during the rapid cooldown, resulting in nucleation and growth of two-dimensional islands, as well as diffusion and attachment to the atomic steps on the surfaces. In our lab we made similar observations on Si(001). However, a quantitative analysis of these data has been lacking. In the case of GaAs the complications arise from the fact that this is a two-component system where the surrounding pressure of As during the experiments is of great importance. In the case of Si(001) (and presumably also in the GaAs case) the loss of adatoms from the terraces to nearby step edges during the quench is both unavoidable and difficult to quantify. Thus, while one may use microscopic methods to determine the density of adatoms quenched into two-dimensional islands and thus measure the adatom concentration at the temperature from which the sample is quenched, experimental problems have prevented a quantitative measurement of temperature dependent adatom concentrations and of the adatom formation energy.

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In this paper we present experimental results on the concentration of thermal adatoms in the range of 750–1050 °C, obtained using carefully controlled surface morphologies to avoid the experimental problems discussed above. Briefly, very large step-free regions were prepared on Si(001), either by selection of a suitable starting morphology on the surface which was then further expanded by careful annealing during *in situ* observation, or by deliberate lithography, etching, and vacuum processing [13] to arrive at such large terraces. In this work we have used step-free terraces ranging from 3 to 10 μm in lateral extent. There are no systematic or significant differences in the results obtained over this range of terrace sizes, indicating that loss of adatoms to the surrounding atomic steps is insignificant in the sample areas analyzed (near the center of the terraces).

In situ observations were made using low energy electron microscopy (LEEM), using the $(\frac{1}{2}, 0)$ diffracted beam due to the 2×1 dimer reconstruction [14]. The reconstruction rotates by 90° when crossing an atomic step, so that only every other terrace diffracts into the $(\frac{1}{2}, 0)$ beam, with the intervening terraces diffracting into the $(0, \frac{1}{2})$ beam. As a consequence, alternating terraces are imaged in an alternating dark-bright contrast. Atomic-layer-high two-dimensional islands are imaged bright on a dark background, or vice versa, at an imaging electron energy of 3.5 eV. The step-free terraces were imaged with LEEM at high temperature, in real time. To determine the thermal adatom concentration at a given temperature T, the surface was held and imaged at this temperature, to ensure sample cleanliness and the absence of atomic steps or other undesired features such as Si-carbide particles. Under these conditions the area of interest has a uniform contrast as illustrated in Fig. 1(a). While the area contains numerous thermal adatoms, these are not visible in the image because they are smaller than the microscope resolution (~100 Å). Next, the sample is rapidly quenched by turning off the electron beam current heating the sample from behind. As the temperature drops the adatom gas becomes supersaturated, and nucleation and growth of two-dimensional islands can be observed in real time. Figure 1(b) shows the same sample area as shown in Fig. 1(a), after quenching. Numerous two-dimensional (white) islands can be seen on the (dark) underlying terrace. Near the step edge along the outer perimeter of the area an island-free denuded zone can be seen, resulting from diffusion and attachment of adatoms to the nearby step during the quench. However, most of the area is not affected by the far-away steps and the island concentration is uniform. To determine the adatom concentration at the original temperature T, we measure the fractional area near the center of the terrace covered by the two-dimensional islands. This is easily done with a particle analysis routine in the image analysis software. This experiment is repeated at different temperatures, and for different terrace sizes. At the lower end of the temperature range that we investigated care must be taken to determine the two-dimensional island area after the quench accurately. The adatom concentration is lower, as is the temperature from which we quench—and thus the diffusion coefficient is smaller also. This results in a higher nucleation density, and smaller island sizes. To obtain a reasonably accurate measurement the sample was reheated to ~600 °C after the quench, allowing the islands to coarsen (and some of the adatoms to return to the adatom gas). It has been shown previously that the loss in island area can be kept negligible [2]. After coarsening the temperature is reduced, allowing the excess thermal adatoms to reattach to the two-dimensional islands. Finally, the area is determined without electron beam heating applied to the sample. Overall, we estimate the uncertainty in the coverage determination to be 0.5% of a monolayer.

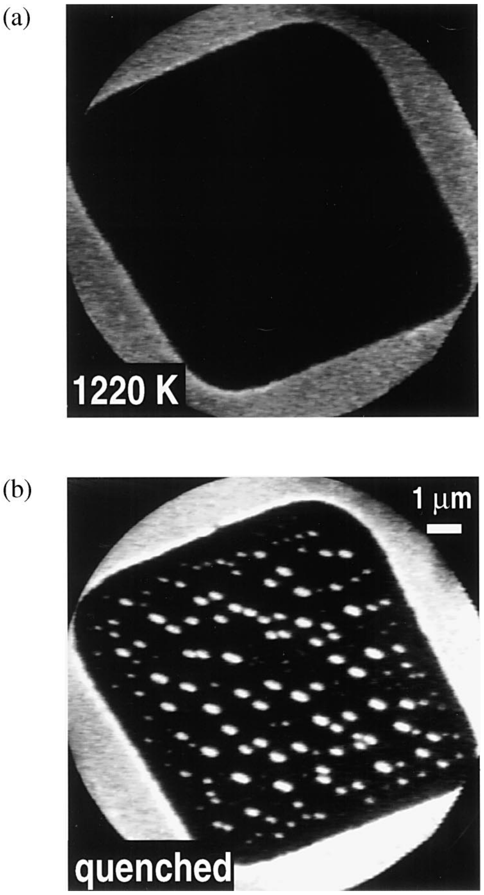

FIG. 1. Dark-field $(\frac{1}{2}, 0)$ LEEM images of a large atomically flat terrace on Si(001) imaged at 1220 K (a) and after quenching (b).

Figure 2 shows the results of these experiments: adatom density as a function of temperature. The numbers are quite remarkable: at 900 °C the adatom concentration is about 0.03 (3% of a monolayer); for 650 °C we extrapolate a coverage of about 0.01. These coverages are very high, indicating a low formation energy. To obtain the formation energy we compare our

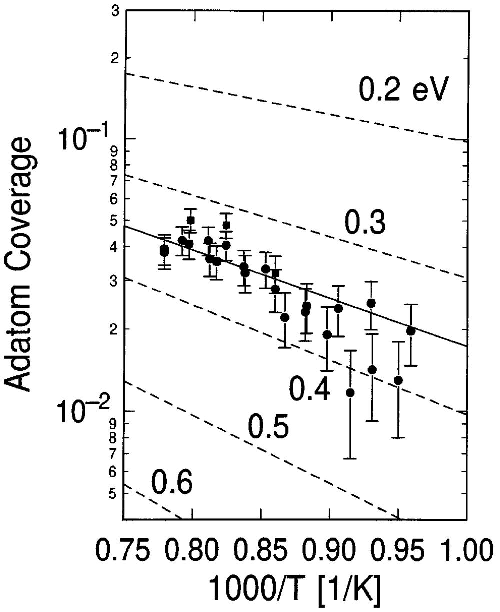

FIG. 2. Adatom concentration versus $1/T$ measured from quenching experiments as shown in Fig. 1(a). Lines are calculated adatom concentrations for the formation energies shown. The best-fit formation energy (0.35 ± 0.05 eV) agrees well with the calculated formation energy of an addimer, rather than an adatom.

data with a simple theoretical prediction. In a single component system the thermal adatom density c_0 is given by $c_0 = n_0 \exp(-E_{\mathrm{af}}/kT)$, where n_0 is the density of atomic sites on the Si(001) surface, E_{af} is the adatom formation energy, and k is Boltzmann's constant. The dashed lines in Fig. 2 (where we plot c_0/n_0) are predictions for different adatom formation energies, ranging from 0.2 to 0.6 eV. We obtain an adatom formation energy of 0.35 ± 0.05 eV (solid line). This formation energy appears to be surprisingly low for an adatom, with its relatively low coordination number. Binding energies of adatoms and addimers on Si(001) were calculated by Brocks *et al.* using a first-principles, local density pseudopotential method [15]. While the binding of a single adatom is not very strong (i.e., its formation energy is high), the formation energy of a dimer was found to be small: 0.3–0.4 eV, comparable to the number we find experimentally. The reason for this small formation energy is that the addition of a dimer does not lead to an increase in the number of dangling bonds, and this addimer looks much like a dimer embedded in a flat surface. Therefore we conclude that the atomic-scale species formed thermally at elevated temperatures are not adatoms but addimers, and that the dominant diffusing species are dimers.

The calculations by Brocks *et al.* also show that there are two possible adsorption geometries for the addimer (rotated by 90°), with a relative energy difference of 0.06 eV as measured by Swartzentruber [11]. These experiments can measure the energy *difference* between the two adsorption geometries but not the addimer formation energy itself. The 0.35 eV formation energy measured here averages over these two geometries.

Experimentally we observe *only* the formation of two-dimensional islands during the quench, not two-dimensional holes which would be indicative of vacancies (the two can be distinguished easily as their elliptical equilibrium shapes are rotated by 90°). It is possible that some addimers are annihilated by reaction with vacancies, but the complete absence of holes in these experiments indicates that the concentration of vacancies is much smaller than the addimer concentration. Conservatively, one may view the addimer formation energy of 0.35 eV as an upper bound. Annihilation of some of the adatoms with vacancies would lead to an underestimate of the addimer concentration, i.e., an overestimate of the formation energy.

Next we discuss the implications of these measurements for two different phenomena: surface diffusion and homoepitaxial growth. The activation barrier for surface diffusion has been measured to be 2.4 eV [16]. Assuming that the surface diffusion coefficient is of the form $D_s = D_{\mathrm{ad}} c_0$, where D_{ad} is the thermally activated diffusion coefficient of a single dimer [$D_{\mathrm{ad}} = \nu \exp(E_d/kT)$], we obtain an activation barrier for dimer diffusion of $2.4-0.35 = 2.05$ eV. Diffusion of single dimers on Si(001) has been studied experimentally near room temperature by Swartzentruber *et al.* They find an activation energy of about 1 eV, i.e., half the value arrived at here. Near room temperature diffusion is also strongly anisotropic [10,11]. However, the width of the denuded zone near the boundary of the flat region in Fig. 1(b) shows no significant anisotropy. While it is difficult to provide a unique explanation for this discrepancy, we suggest that the diffusion pathways may be different at room temperature and at the higher temperatures studied here. At lower temperatures dimers are thought to hop *over* the surface from one adsorption site to the next. Indeed, Brocks *et al.* calculate an upper value of the activation energy for such a process of 1.5 eV. However, for self-diffusion on metal surfaces Feibelman has shown that another diffusion process, involving site exchange between the adsorbed atom and a substrate atom is more favorable [17]. Such site exchanges between adsorbed dimers and "substrate" dimers occur readily on Si(001) at elevated temperatures. For instance, adsorbed Ge atoms incorporate into the terraces at temperatures exceeding ~500 °C, giving rise to an alloyed outer layer, reducing the effect of the Ge misfit strain [18]. Similarly, when either Si or Ge is adsorbed on a surface terminated with an Sb or As monolayer ("surfactant mediated growth") the arriving Si or Ge atoms rapidly exchange sites with the Sb or As atoms, which "float" on top of the growing film [19]. Again, this efficient site exchange mechanism is operative at temperatures exceeding 500 °C. While diffusion *over* the surface is the dominant process at lower temperatures, we suggest that *exchange* diffusion may be important at higher temperatures, with a higher activation energy (near 2 eV). Alternatively, atomic steps may play a significant role in macroscopic surface diffusion measurements, in which case the diffusion coefficient is no longer of the simple form $D_s = D_{\mathrm{ad}} c_0$.

The addimer concentration itself is an interesting quantity in the context of epitaxial growth. At room temperature we extrapolate an equilibrium coverage of 10^{-6} monolayers, i.e., much smaller than typical defect concentrations seen on Si(001). Thus, exposing the surface to a Si molecular beam will supersaturate the two-dimensional adatom concentration by several orders of magnitude, giving rise to dense nucleation, and a small critical nucleus size. However, at 650 °C the equilibrium concentration is about 0.01 monolayer. This relatively large number, combined with much increased diffusion, leads to low supersaturation during homoepitaxial growth. The 2D supersaturation in nucleation and growth experiments at 650 °C was recently determined to be as small at 2% or less [7]. In this case growth proceeds in near-equilibrium conditions, leading to sparse nucleation (only on the largest terraces), and a very large critical nucleus size (hundreds of dimers). Similarly, strong coarsening effects have been seen during the growth of Ge quantum dots on Si(001), again indicating growth in near-equilibrium conditions [20]. While the notion of crystal growth near thermodynamic equilibrium may seem counterintuitive, such conditions may in fact be required for the growth of electronic-grade, low-defect-density material, and crystal growers may have gravitated towards such growth conditions [12], common perceptions of high supersaturation and far-out-of-equilibrium growth notwithstanding.

In conclusion, we have presented the first quantitative measurements of thermal addimer concentrations and of the addimer formation energy on Si(001). The low formation energy has important implications for a wide range of surface dynamic phenomena, such as surface diffusion (where we suggest that an exchange process may be important at temperatures exceeding 500 °C), and for the technologically important process of homoepitaxial growth in near-equilibrium conditions.

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