Direct Observation of Reaction-Limited Aggregation on Semiconductor Surfaces

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We report a discovery that the nucleation and growth of two-dimensional (2D) Ge islands at a Pb layer covered Si(111) surface are reaction limited. Using scanning tunneling microscopy, a compact-to-fractal island shape transition is observed as the deposition flux is lowered, the temperature is raised, or at a low Ge coverage. This behavior is completely opposite to what was predicted from those theories based on diffusion-limited aggregation and previous experimental observations. Energy barriers are found to exist for the nucleation and growth of Ge islands, indicating that their growth behavior is exchange-reaction rate limited.

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Knowledge of atomic processes on surfaces is important for the production of good quality thin films. The study of nucleation and growth at early stages of deposition provides crucial information in this regard. Diffusion and reaction are two major microscopic processes that govern the nucleation and growth behavior. Depending on which one is the rate-limiting process, diffusion-limited and reaction-limited regimes can be defined in epitaxial growth. The traditional atomistic theory of nucleation [1] has been shown to describe well the aggregation of metal atoms on metal surfaces. It is also widely applied to many other systems to extract physical parameters such as surface mobility of adatoms. This theory assumes that incoming atoms attach to island edges without encountering an energy barrier, i.e., the reaction is so fast that it is not a rate-limiting factor. Thus, the traditional nucleation theory is basically in the diffusion-limited regime. On the other hand, one would wonder whether there are systems that are in the reaction-limited regime and what kind of growth behavior and growth morphology such systems would have. In this new regime, there is an energy barrier, significantly higher than the diffusion barrier, for nucleation and growth to occur.

Here we report the discovery of a system in surfactant-mediated epitaxy (SME) [2], where the nucleation and growth processes are reaction limited. Interestingly, a compact-to-fractal island shape transition occurs when the temperature is increased or when the deposition flux is decreased. On many metal-on-metal systems, fractal islands are formed at low temperatures, and a transition to compact islands occurs at high temperatures [3–5]. Traditionally, fractal island growth has been understood by the diffusion-limited aggregation (DLA) model [6]. In this model, a deposited adatom diffuses on the surface and sticks to an island edge irreversibly at the first point it hits. In real systems, however, every adatom reaching an island can still relax to a lower energy site by diffusion along the island edge if the temperature is high enough [3–5]. When the edge diffusion becomes faster than the rate a new adatom arrives at the island, a morphological transition from fratal-to-compact island growth occurs. Thus, the traditional nucleation theory predicts the occurrence of a compact-to-fractal island shape transition as the growth temperature is reduced, or as the deposition flux is increased [7].

The system we study is nucleation and growth of Ge islands at Pb covered Si(111) surfaces. We recently found that, when mediated by a monolayer of surfactant Pb, smooth Ge films can be grown on Si(111) at room temperature [8]. This is a typical example of SME [2]. Our experiments are performed in an ultrahigh-vacuum chamber. Before deposition of Ge, we prepare the 1×1 Pb/Si(111) phase [8], which is an unreconstructed Si substrate with each first-layer Si atom terminated by a Pb atom [9]. The Pb coverage is one monolayer ($1\ \mathrm{ML} = 7.84 \times 10^{14}\ \mathrm{cm}^{-2}$). We find that Ge atoms do not attach to the step edges of the Si substrate; thus the substrate steps have only minor effects on nucleation and growth of Ge islands. In this work, unless the substrate temperature is specified, deposition and scanning tunneling microscopy (STM) imaging are done at room temperature (RT). STM images are obtained at least 30 min after the deposition. We note that the 2D Ge islands shown here are also covered by a monolayer of Pb having a height of a bilayer (equal to 2 ML), which is the physical layer for growth on Si(111).

In a previous STM study of this system at RT [10], we found that there is a threshold coverage, $\Theta_c \sim 0.14$ ML, for the nucleation of 2D Ge islands to start. Above it, the number density increases rapidly, but the average size actually decreases rapidly at first, and then increases slowly again. Here we report a perplexing behavior of island shape transition that resulted from a change in the coverage, the deposition flux, and the temperature. At very low deposition fluxes (<0.003 ML/s), the islands formed are always fractal-like, though the detailed shape depends on the coverage. Figure 1(a) is a large, branched, fractal-like island formed at a coverage right above Θ_c

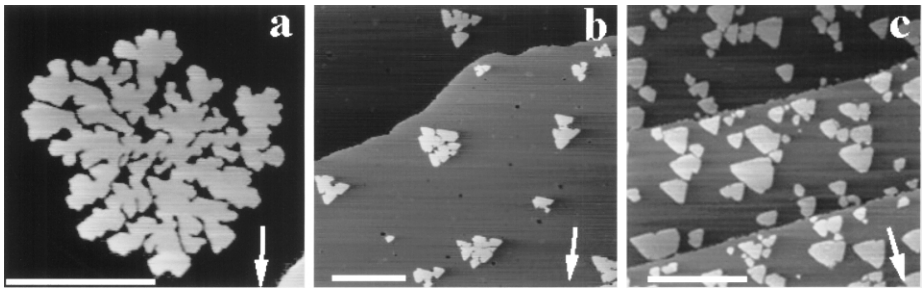

FIG. 1. Topographs showing nucleation of 2D Ge islands at the Pb covered Si(111) surface at a coverage right above Θ_c with the flux of 0.0012 ML/s (a), $1.5\Theta_c$ with the same flux (b), and at a coverage $\sim 4.5\Theta_c$ with the flux of 0.0067 ML/s (c). The bar indicates the length of 1000 Å and the arrow specifies the $[2\bar{1}\bar{1}]$ direction, which both will be adopted in the rest of the figures.

with a deposition flux of 0.0012 ML/s. The very low island density ($\sim 2\ \mu\mathrm{m}^{-2}$) indicates a long diffusion length of Ge atoms on these Pb covered Si(111) surfaces. The island shape here is quite different from those observed in metal-on-metal systems [3–5], where the branches are more uniform. The island seen in Fig. 1(a) shows very narrow inner branches, but the outer ones tend to be wide and appear to be faceted along the substrate $\langle 01\bar{1}\rangle$ directions. For a coverage $\sim 1.5\Theta_c$ with the same flux, the number density is much higher at 49 $\mu\mathrm{m}^{-2}$, and they now appear to be composed of smaller triangles [Fig. 1(b)].

What is most interesting is that a fractal-to-compact island shape transition occurs when the coverage exceeds $1.2\Theta_c$ at a higher deposition flux of 0.0067 ML/s. An example is shown in Fig. 1(c), which is prepared with deposition $\sim 4.5\Theta_c$. Now many triangular islands with edges faceted along $\langle 01\bar{1}\rangle$ appear. However, when the coverage is right above Θ_c, we observe large fractal-like islands of low number density even for this high deposition flux [see also Fig. 3(b)].

The effect of temperature on the island shape is even more interesting. In many systems, when the temperature is increased, the island shape transforms from fractal to compact. But for this system, when the deposition temperature is increased to 80 °C at a similar coverage and flux like those in Fig. 1(c), large fractal-like islands are formed [Figs. 2(a) and 2(b)]. The outer part of the islands is composed of triangular elements with edges faceted along $\langle 01\bar{1}\rangle$. The detailed island shape also depends on the coverage, as those shown in Figs. 2(c) and 2(d). The general trend is that islands become less compact as the coverage is reduced, with a lower deposition flux, or with a higher deposition temperature. Obviously, DLA, even with the modified concept of edge diffusion, cannot explain the shape transition we have observed here. In our system, the surface is passivated by a layer of Pb atoms. In order for Ge atoms to grow on the substrate silicon surface, Ge atoms have to exchange with Pb atoms to reach the substrate. The nucleation and growth of Ge islands should be exchange-reaction rate limited if the exchange barriers [11] are significantly higher than the diffusion barriers.

Evidence of exchange barriers is presented in the following. We find that no nucleation occurs even two days after deposition if the Ge coverage is less than Θ_c. On a sample which has been deposited with $0.95\Theta_c$ of Ge at RT, amazingly 2D Ge islands appear (with the number density $\sim 2\ \mu\mathrm{m}^{-2}$) after this sample is annealed to ~80 °C for 10 min [Fig. 3(a)], indicating that nucleation of Ge islands requires overcoming an energy barrier by thermal activation. This behavior is opposite to the traditional-held concept that nucleation can be induced by undercooling. At RT when the Ge coverage is lower than Θ_c, nucleation of Ge islands is inhibited by the Pb layer. Ge adatoms are very likely to collide with each other to form atom clusters. These Ge adatoms and clusters are probably highly mobile on top of the Pb layer, as none of them can be seen in our high-resolution STM images [10]. The concentration of large clusters is very low but increases with the Ge coverage. The above

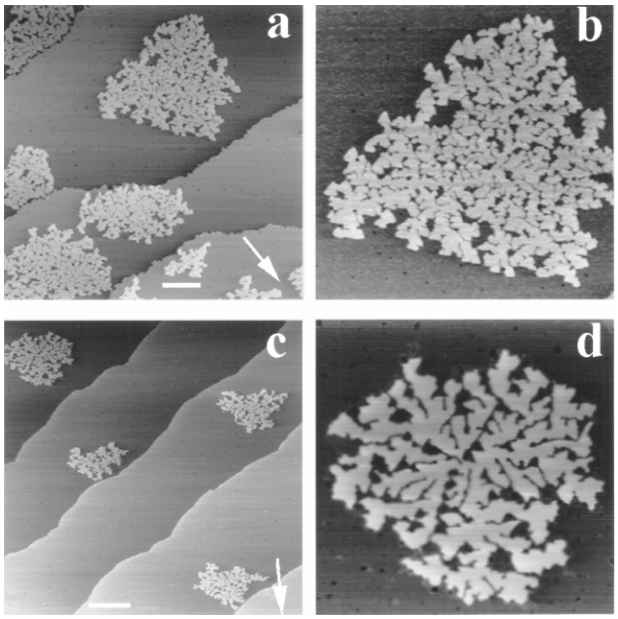

FIG. 2. Surface morphology at the flux of 0.0067 ML/s with the deposition temperature of ~80 °C. (a) shows the image after deposition of $\sim 4.5\Theta_c$, and (b) is a close-up of the island on the upper right-hand side. (c) shows the image after deposition of $\sim 1.3\Theta_c$, and (d) is a close-up of the island on the upper left-hand side.

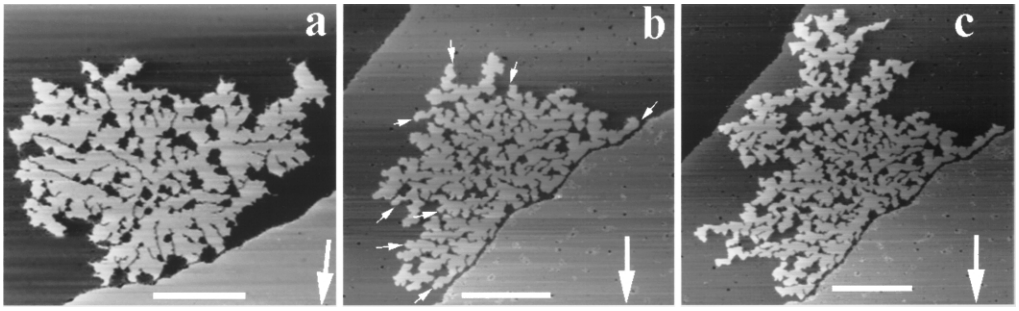

FIG. 3. (a) Nucleation of a 2D island occurs after annealing. Notice that the island edges are no longer faceted. (b) shows a large fractal-like island seen after deposition right above Θ_c with the flux of 0.0067 ML/s. Small arrows indicate the tips where growth of new branches takes place after annealing to 80 °C (c).

observation suggests that only clusters larger than a critical size can overcome the exchange barrier in order to nucleate as a stable island, and that this critical size decreases with increasing temperature. This implies that the exchange barrier at flat terraces decreases with an increasing cluster size.

Besides the nucleation, we also observe further growth from existing 2D islands after annealing. Figure 3(b) shows a large fractal-like island that appears after deposition right above Θ_c with the flux of 0.0067 ML/s. This island does not change shape with time at RT, but further growth is seen after annealing to ~80 °C for 5 min [Fig. 3(c)]. Notice that most of the edges of the original island remain intact, and growth occurs only from the tip of several branches. There is no doubt that a concentration of Ge atoms is moving on the Pb covered surface without attaching to the Ge island in Fig. 3(b). This is consistent with the previous study [10] which estimates this concentration to be ~0.09 ML. These Ge atoms may also form clusters, but their incorporation at island edges is inhibited at RT by the high exchange barriers. That growth occurs again when the sample is annealed implies the existence of a cluster-size-dependent exchange barrier similar to that in the nucleation process. Clearly, the nucleation and growth process in our system is exchange-reaction limited.

More direct evidence of energy barriers for Ge incorporation at island edges is shown below. A sample prepared with deposition right above Θ_c at the flux of 0.003 ML/s exhibits large fractal-like islands of the density ~3 μm^{-2} [Fig. 4(a)]. Three hours after the first deposition, another $0.42\Theta_c$ of Ge is deposited onto this sample with the same flux; we observe a few small fractal-like 2D islands in addition to some large islands [Fig. 4(b)]. The island size exhibits a distinctly bimodal distribution. The large islands are of the same density as those seen after the first deposition but with a slightly larger average size. We have done similar experiments but with more Ge deposited at the second stage. A higher number density of islands is seen besides those large islands. An example is seen in Fig. 4(c), which shows the surface morphology after the second deposition of $0.63\Theta_c$. Interestingly, these extra islands are small and compact. Notice that the trend for the extra islands is very similar to that for continuous deposition [10]. The strong tendency in the second deposition for Ge adatoms to nucleate instead of attaching to existing island edges indicates the existence of high energy barriers at island edges.

The current study of the shape transition and our previous study of the island density for Ge growth at Pb/Si(111) [10] provides the first experimental exploration in the reaction-limited regime on epitaxy. This new regime clearly exhibits a nucleation and growth behavior very different from predictions based on the traditional nucleation theory. A summary of our observations is presented in Table I. These observations demonstrate the need to consider the reaction process [11] in developing a more comprehensive nucleation theory. Reaction may

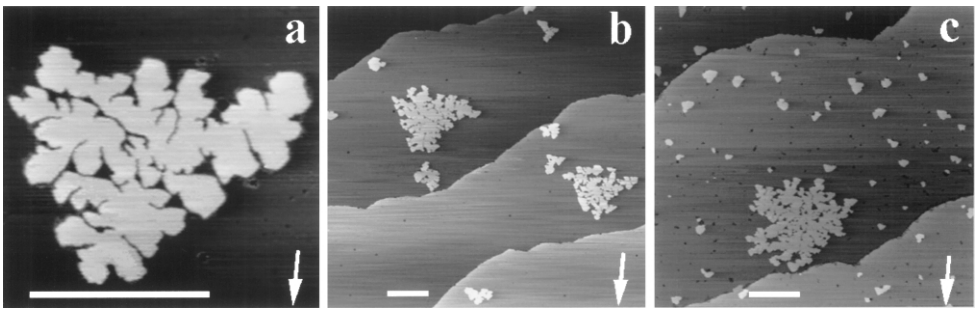

FIG. 4. Morphology of two-stage deposition with first deposition right above Θ_c at the flux of 0.003 ML/s. (a) shows an image after the first deposition. (b) and (c) show images taken after the second depositions of $0.42\Theta_c$ and $0.63\Theta_c$, respectively.

TABLE I. Nucleation and growth behavior for 2D Ge islands at Pb/Si(111) surfaces.

Below Θ_c	No nucleation occurs.
Right above Θ_c	Large, low number density of fractal-like islands appear.
$\Theta_c < \Theta < 1.5\Theta_c$ at RT	1. The island density increases rapidly, but the average island size decreases with the increasing coverage. 2. The island shape becomes more compact as the coverage increases.
$\Theta > 1.5\Theta_c$ at RT	1. The island density reaches the maximum and levels off, while the average island size increases with the increasing coverage. 2. The maximum island density scales with the deposition flux F, $N_{\max} \propto F^{1.76}$. 3. The island shape becomes more compact as the deposition flux increases.
At elevated substrate temperatures	1. The increase of the island density above the threshold coverage is not as rapid as that for RT deposition. 2. The maximum island density decreases; the average island size increases as the substrate temperature increases. 3. The islands become fractal-like as the substrate temperature increases. 4. The threshold coverage for nucleation to occur decreases as the substrate temperature increases.

play an important role in surfactant-mediated epitaxy and chemical vapor deposition, as the surface in both cases is covered by a third species of material. Even for growth on semiconductor surfaces without a third material, reaction may not be neglected either [12] for the atoms on the terrace and at island edges often reconstruct. Nucleation and growth would thus require overcoming an energy barrier in order to break the bonds. Reaction may also be important in many other aggregation processes. For example, both DLA and reaction-limited aggregation have been reported in many colloidal systems [13,14].

As to the mechanism for our observed island shape transition, Liu *et al.* [15] have recently carried out kinetic Monte Carlo simulations based on the assumptions of a small diffusion barrier on top of the surfactant layer, a rate-limiting exchange barrier for nucleation, and a second highest barrier for the aided exchange of atoms to get incorporated at island edges. They also assume a shielding effect for the 2D island growth. Then they find a fractal-to-compact island shape transition induced by either decreasing the growth temperature or increasing the deposition flux. This would give a good explanation for the novel island shape transition we have observed and presented here.

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