Kinetic Pathway in Stranski-Krastanov Growth of Ge on Si(001)

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The transition from 2D to 3D growth of Ge on Si(001) has been investigated with scanning tunneling microscopy. A metastable 3D cluster phase with well-defined structure and shape is found. The clusters have a {105} facet structure. Results suggest that these clusters define the kinetic path for formation of "macroscopic" Ge islands.

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The growth of Ge on Si has been a subject of intense study for several years, driven by the desire to create Si-Ge heterojunction superlattices, which would form the basis of optoelectronic devices.[1-4] Because of the ~4% lattice mismatch between Ge and Si, Ge grown on Si(001) grows in a layer-by-layer mode for only several layers, after which 3D islands form.[5-9] In order to improve the likelihood of 2D layer formation, the use of surfactants has been suggested and some success achieved.[10] This system is an example of Stranski-Krastanov (SK) growth, one of three basic growth modes postulated on the basis of interface thermodynamics. If the lattice constants are not too different and the surface energy of material "*A*" is larger than that of "*B*," *B* will wet *A*, forming a layer that is strained, until the effects of the *A* interface are no longer felt (typically one to three layers). After these several layers, the free energy of the new *B* surface is sufficiently lower so that there no longer is an energy benefit in further wetting of strained *B* by new *B*, compared to the formation of *B* clusters. These then form from newly arriving flux.

This simple picture of growth rests on the assumption of thermodynamic equilibrium: the free energy of a "macroscopic" 3D cluster competing with that of an epitaxial film. Details of the kinetics of SK growth, including diffusional processes, the transition from 2D to 3D, and the existence of possible intermediate phases, are in general not known. In this Letter, we report a scanning tunneling microscopy (STM) study of the transition from 2D growth to 3D growth for Ge on Si(001). We establish the existence of an intermediate phase between 2D layers and macroscopic 3D clusters. This intermediate phase consists of small clusters with a precise facet crystallography and a specific alignment with respect to the substrate. We demonstrate that this intermediate phase must be part of the kinetic pathway for the formation of the final macroscopic 3D clusters on the 2D layers. Understanding the crystallography of this intermediate phase may allow a determination of the atomic forces that play a role in Ge-on-Si growth.

The experiments are carried out in a UHV chamber operating in the 10^{-11}-Torr range with a STM, a LEED system, and deposition sources. Substrates are nominally flat Si(001) wafers, with an actual vicinal angle, determined by STM, of ~0.04°. The substrates are cleaned by heating briefly to ~1525 K, which leaves them with a very low defect density and regularly spaced steps. Ge is evaporated from a wafer at a system pressure of $<3\times10^{-10}$ Torr, for several substrate temperatures. The substrate is quenched to room temperature immediately after deposition or annealing and transferred to the STM. The deposition rate is determined by counting atoms on STM images of the surface after a submonolayer of Ge is deposited at ~475 K, a temperature at which diffusion is sufficiently slow so that only a negligible amount of Ge is lost to substrate steps.[11] There is no evidence, using STM, of contamination more than 12 h after initial substrate cleaning.

To investigate 2D growth we deposited Ge from 0.1 to 3 monolayers (ML) at a variety of temperatures. Submonolayer doses of Ge form 2D islands either at steps or freely on Si terraces, similar to homoepitaxy of Si.[12,13] Multiple layers, grown at typical temperatures (e.g., 3 ML at 775 K), have a rough growth front often involving two to three layers in a 200-Å×200-Å area. This roughness is reduced after annealing at higher temperatures (e.g., 875 K) for a few minutes. The layers maintain their 2D nature, confirming that 2D growth is not a result of kinetic limitations but actually corresponds to the equilibrium structure.

Deposition beyond 3 ML leads to Ge cluster formation. However, in addition to the macroscopic widely separated clusters that have been observed,[5-9] we find a large concentration of generally much smaller clusters with well-defined shapes, crystal structure, and orientations differing from those of the macroscopic clusters. Figure 1 shows two STM images of these special clusters. A scanning electron micrograph (SEM) over a much larger area is also shown in Fig. 1. Only the macroscopic clusters are visible in SEM. Their bases are square with sides parallel to ⟨110⟩ directions. STM scans on these macroscopic clusters indicate that they have very complicated facet structures, with mostly {113} planes, confirming earlier work.[8] They are terminated on top with perfect Ge(001) surface.

The major new feature of our observations is the small clusters. In both these and the macroscopic clusters, the crystal structure is a "continuation" of that of the Si

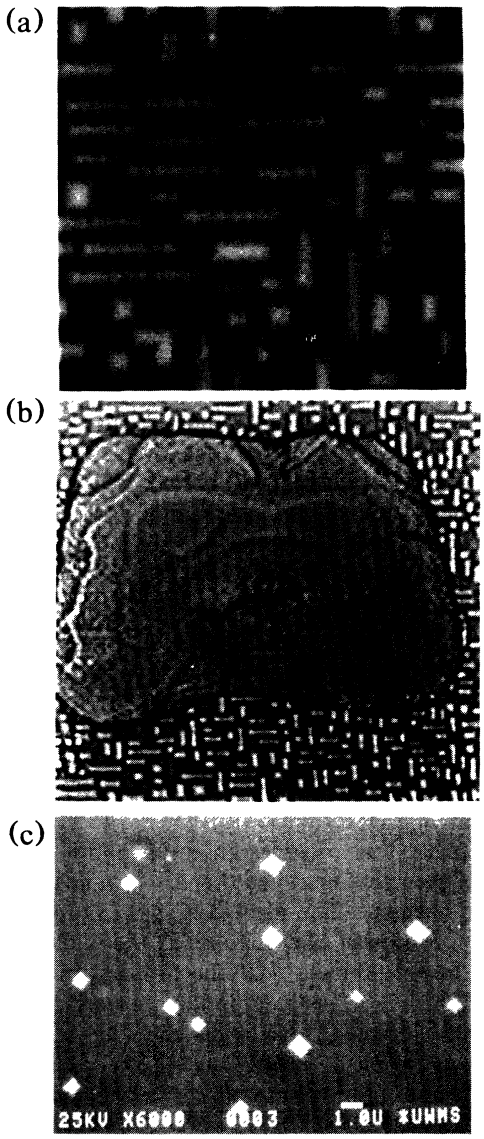

FIG. 1. STM and SEM images of two types of Ge clusters on Si(001). (a) STM image, 2500×2500 Å. "Hut" clusters have rectangular or square bases, in two orthogonal orientations, corresponding to ⟨100⟩ directions in the substrate. Clusters are $\lesssim$1000 Å long and 20–40 Å high. (b) STM image 8000×8000 Å, showing a "macroscopic" cluster surrounded by many of the hut clusters shown in (a). The macroscopic cluster is ~250 Å high. Because of this height and a STM tip effect, it appears irregular in shape. The image is shown in a curvature mode, to remove the large height difference. (c) SEM image showing large clusters. The square sides are parallel to ⟨110⟩ directions. The hut clusters are not visible in SEM.

substrate (i.e., bond orientations are the same), but the shapes of the clusters are quite different. The small clusters have predominantly a prism shape (with canted ends), in some cases a four-sided pyramid, with the same atomic structure on all four facets as shown in Fig. 2. They appear as small huts, and to distinguish them

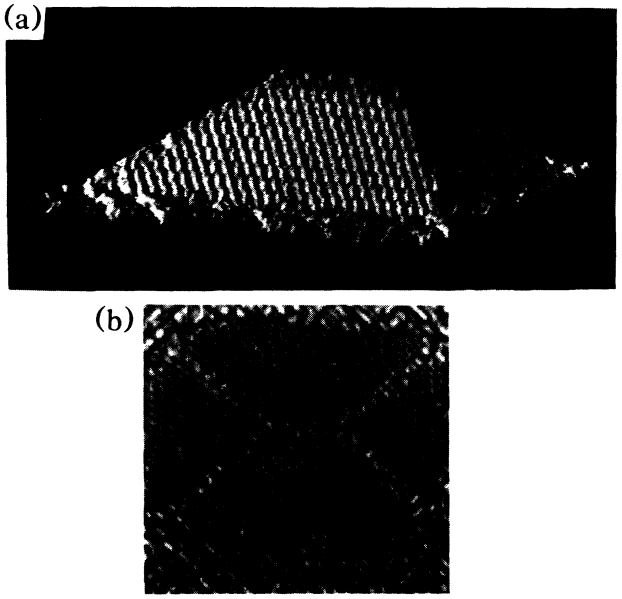

FIG. 2. STM images of single "hut" cluster. (a) Perspective plot. Scan area is 400 Å×400 Å. The height of the hut is 28 Å. (b) Curvature-mode grey-scale plot. The crystal structure on all four facets as well as the dimer rows in the 2D Ge layer around the cluster are visible. The 2D layer dimer rows are 45° to the axis of the cluster.

clearly from the macroscopic clusters, we shall refer to them as "hut" clusters. They grow on the strained 2D Ge layers, which appear not to be modified. Their principal axes are strictly along two orthogonal ⟨100⟩ directions. By carefully measuring the relevant length and angle parameters, all four of their faces are determined to be {105} planes. We propose the following model for the structure, as shown in Fig. 3. The {105} plane is simply a vicinal (001) surface tilted up 11.3° (the angle measured by STM is 11° ± 1°) with the projection of the surface normal lying along ⟨100⟩, i.e., at 45° to either of the substrate dimer row directions. Each facet plane thus consists of (001) terraces each one face-centered-square unit mesh wide separated by single-atomic-height steps along ⟨010⟩. To reduce dangling bonds, surface atoms desire to dimerize. However, every other atom at upper edges does not have another atom with which to pair. These atoms are absent, making the periodicity parallel to the hut ridge $2a$, where a is the side length of a face-centered square, 5.66 Å for bulk Ge. The periodicity up the face of a facet is $2.5a$, because it takes two steps for the dimer orientation to rotate back and at each step there is an additional $1/4a$ shift. The unit mesh is therefore rectangular, $2a \times 2.5a$. Although it appears that the huts have the Ge lattice constant, our distance measurements are not sufficiently certain that we can make this claim unequivocally.

There are two interesting features of these hut clusters. One is the perfection of the facet planes. We never observe a partly completed layer on a facet. This obser-

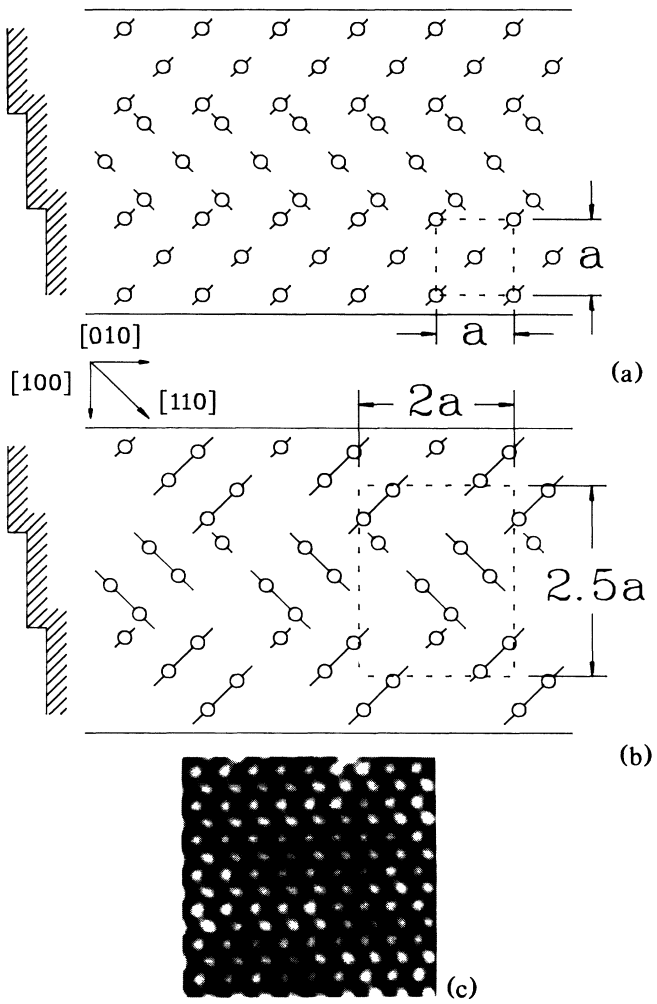

FIG. 3. Model of cluster facets. (a) Unreconstructed (105) plane projected onto (001) plane; (b) reconstructed (105) plane projected onto (001) plane. In both only top-layer atoms are shown to avoid confusion. Side views of the associated (001) terraces and steps are shown at the left. (c) An STM scan on one of the facets, 100×100 Å. Each bright spot in the image corresponds to a pair of dimers. The unit mesh with the displaced center can easily be observed. The top of the cluster corresponds to the top of all three panels.

vation, as well as a second one, namely, that the number density of huts increases rapidly while their size grows only slowly as the Ge dose is increased, is in accord with well-known concepts about the stability of low-free-energy surfaces. For such surfaces a nucleation process is required for each new layer but once this occurs, the layer completes very rapidly. Because of the layer nucleation barrier, the growth of an existing island is not overwhelmingly favored over formation of new islands around it. The second feature of the hut clusters is their generally elongated base shape and their base orientations. Because all four facets are the same, they must have the same surface free energy and sticking coefficient for arriving atoms. The prism axes are at 45° to the dimer row directions, and therefore the Si substrate does not provide any preference in terms of surface stress[14] or anisotropic diffusion.[15] What then can cause elongated shapes and specific base orientations? We suggest that ⟨100⟩ steps (running at 45° to the dimer row directions), formed in the Ge layers during growth, act as nucleation sites. There are two orthogonal sets of these steps, corresponding to the principal axes of the clusters we observe. STM measurements on samples miscut toward ⟨100⟩ by 2.5° support this idea of the role of ⟨100⟩ steps. Small clusters now predominantly form with their principal axis aligned along these steps. Because the step density is now also greater, the number density of small clusters is much larger and their size is reduced. Recent work[16] claims that a partial relaxation without dislocations exists between macroscopic Ge clusters and the Si substrate. We cannot unequivocally determine whether a discrepancy exists between this work and our results. The hut clusters, which are not shown in Ref. 16, appear to have a considerable relaxation although we cannot, as already mentioned, give a definitive value. We speculate that the influence of steps may be able to produce 3D Ge structures with greater lattice relaxation than might be possible on a flat terrace.

What is the role of hut clusters in the transition from 2D to 3D structure? We believe that they are an intermediate step in the formation of the large clusters, a metastable phase that provides an easier and faster way to accommodate arriving atoms than direct nucleation of macroscopic clusters. The idea of a system progressing through a succession of phases to reach the final equilibrium phase is well known.[17] If the direct formation of the equilibrium phase has a large kinetic barrier, a system may find it easier to reach this state through intermediate phases, each of which has a lower barrier for formation. These intermediate phases will be metastable relative to the final phase. Several observations support the idea that the hut clusters are an intermediate phase that is metastable. The hut clusters form preferentially at lower growth temperatures, $T < 800$ K; growth at 850 K results in only macroscopic clusters. Upon annealing at 850 K for 10 min, almost all hut clusters formed at lower growth temperatures vanish and more macroscopic clusters form. These observations indicate that the huts are metastable. Additionally, the concentrations of the hut and macroscopic clusters are drastically different, being, for example, $\sim 7\times 10^{10}$ and $\sim 4\times 10^{7}$ cm^{-2}, respectively, for the conditions shown in Fig. 1. Hence, it appears that the huts are much easier to nucleate on the 2D Ge layers than the macroscopic clusters, indicating that the formation barrier is lower for the hut clusters.

Using the idea of succession of phases, we can imagine the following scenario. The macroscopic clusters are the final equilibrium state; they are widely separated with no apparent heterogeneous nucleation site. Their structure is quite different from that of the huts. The hut clusters form more easily and hence preferentially form first and

at higher concentrations. We believe that they are nucleated at ⟨100⟩ steps that develop in the growth of the 2D Ge layers. Growth at steps may also be a direct mechanism for strain relief. We can only speculate on the process of formation of the macroscopic clusters from the hut clusters, but it seems clear that the kinetic path to their formation is through the existence of the latter. Hut nucleation slows as the concentration of huts gets large and available sites for their nucleation decreases. We suggest that the consequent increase in supersaturation of adatoms causes the homogeneous nucleation of the macroscopic clusters. Their subsequent growth is then mediated by the huts: Continued incoming flux must find its way by diffusion to the macroscopic clusters, at least in part by adsorption or desorption from the huts. The huts therefore provide an easy way for 3D structures to appear at the surface initially, and consequently they delay the onset of formation of the macroscopic clusters.

In summary, we have used STM to study the SK growth of Ge on Si(001). We have discovered a metastable 3D phase consisting of small (hut) clusters that have a specific facet crystallography and alignment of their principal axes with respect to the substrate. The clusters consist of prims or four-sided pyramids with four equivalent {105} facets. We believe that they are heterogeneously nucleated at ⟨100⟩ steps and that this provides an easy way for the initial formation of clusters. We speculate that they are an intermediate phase in the formation of the macroscopic clusters that have been observed,[5-9] i.e., that the succession of phases for Ge on Si(001) is Si, 2D Ge (~three layers), hut clusters, and, finally, macroscopic clusters. A theoretical study of the formation and structure of this intermediate phase may shed light both on the energetics of the 2D Ge surface and on the kinetics of the SK transformation.

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Note added.— D. Eaglesham, using TEM, has recently also observed what appear to be our hut clusters.

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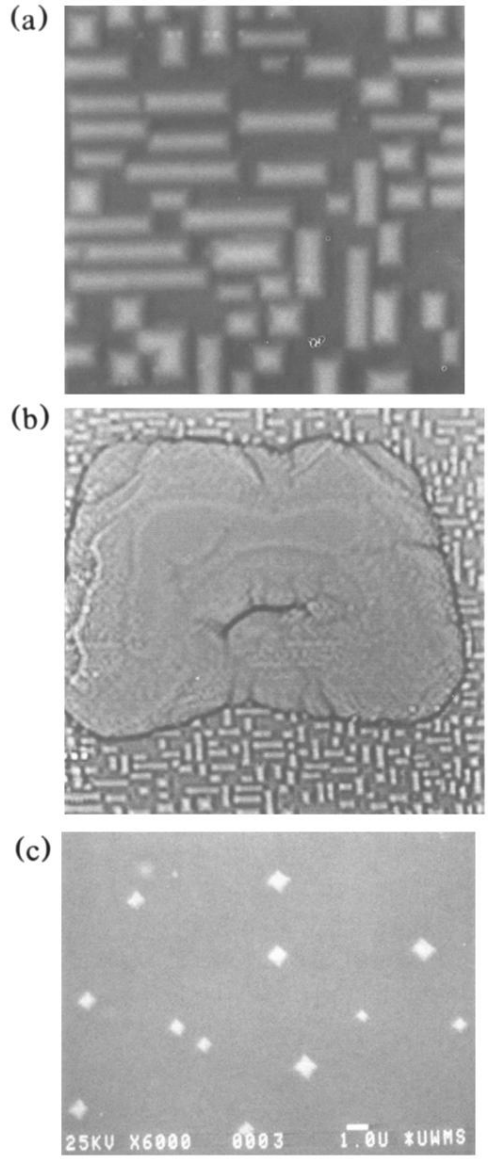

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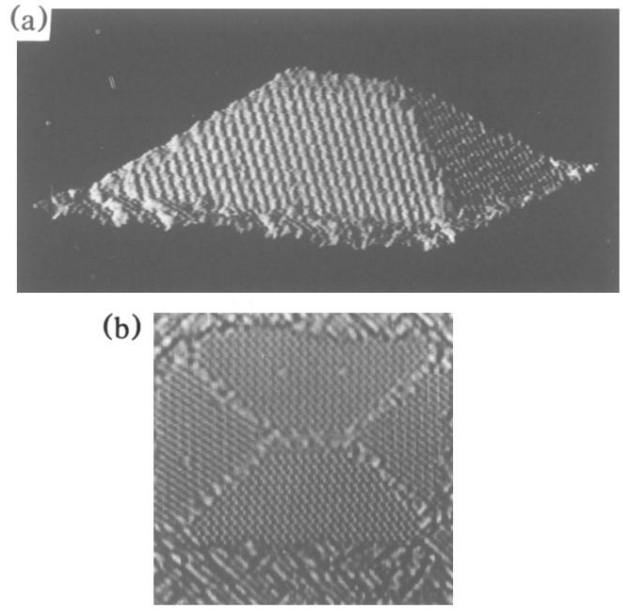

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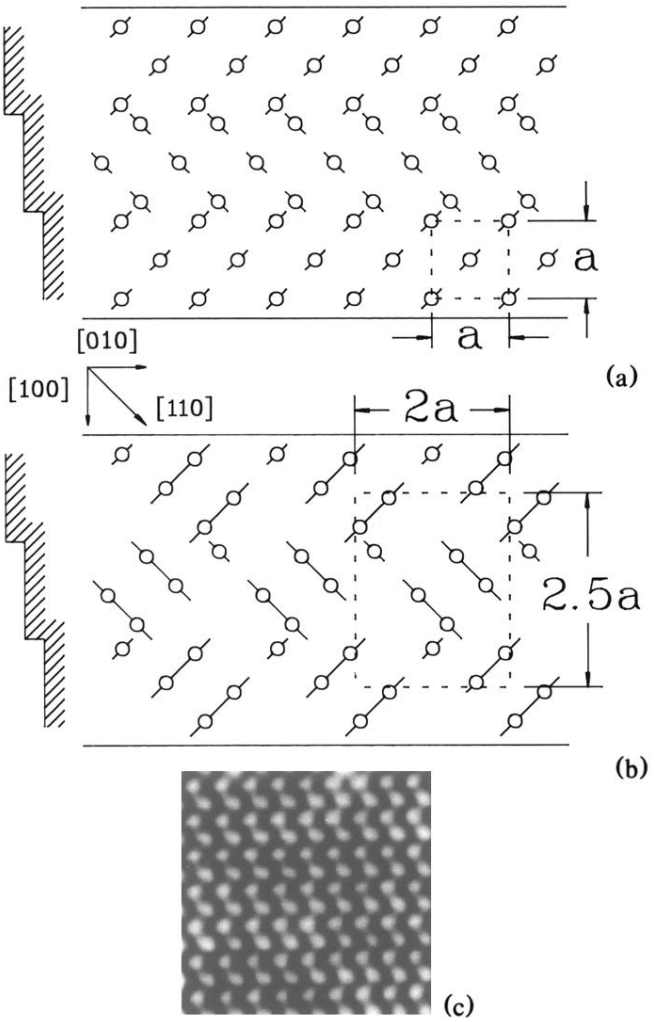

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