PHYSICAL REVIEW B VOLUME 46, NUMBER 23 15 DECEMBER 1992-I

Scanning-tunneling-microscopy study of Ge/GaAs(110). I. Initial nucleation and growth

Y.-N. Yang, Y. S. Luo, and J. H. Weaver

Department of Materials Science and Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455

(Received 16 June 1992)

Scanning tunneling microscopy (STM) has been used to study the initial nucleation and growth of Ge on GaAs(110) at 420 °C. Multilayer islands of crystalline Ge with heights of four or more layers were formed upon deposition of 0.2 and 0.4 monolayer. We show that the energetics are responsible for the absence of thinner islands and that the energetics account for the Ge island shape. Analysis of the spatial distribution of the islands on the surface demonstrates that there is a depletion zone around each island, the size of which is a measure of the kinetics available during growth. Depletion zones are directly evident in STM images when surface steps are present because they act as preferred nucleation sites. At the same time, island formation at these same steps is not energetically favored, as demonstrated by the movement of Ge islands away from the steps when the surface is annealed at 550 °C.

INTRODUCTION

The initial nucleation and the growth modes are of crucial importance for thin films or overlayers because they determine the properties that are related to "structure." These properties include interfacial roughness and the density of dislocations and other defects. As a consequence, they will affect the electronic properties of a junction.[1,2] A fundamental understanding of the initial stage of growth is essential to our ability to engineer new materials.

The deposition of atoms onto a substrate results in a two-dimensional (2D) lattice gas. The subsequent condensation of this gas to form islands involves both kinetics and energetics. Adatoms diffuse on the surface until they meet and form clusters. Once such nucleation centers are established, they are likely to grow to larger islands, inhibiting nucleation in their immediate neighborhood[3] by acting as sinks for the diffusing atoms. The competition between this growth and the nucleation of new clusters depends on the temperature and the deposition rate. Such kinetic factors establish a correlation between the size and spatial distribution of the clusters. Thermodynamics is also important because the overlayer atoms will rearrange to form crystallites to minimize the system free energy. Thus cluster shape is controlled by the energetics during growth.

While this growth picture is generally accepted, direct experimental confirmation is rather sparse. Several recent studies have concentrated on surface diffusion, providing important insight into growth kinetics.[4-6] In contrast, the role of energetics has received relatively little experimental attention. Moreover, theoretical studies of growth have often neglected the energetics while taking into account only the kinetics.[7-9] This state of affairs motivated us to undertake a detailed experimental study of the role of energetics in overlayer growth and its interaction with the available kinetics.

In this paper, we report a scanning-tunneling-microscopy study of Ge growth on GaAs(110) at elevated temperature. The nearly perfect Ge-GaAs lattice match makes this a good system for study because Ge can be grown without significant strain (lattice mismatch ~0.1% at 300 K) (Refs. 10 and 11) and the energetics of the system can be easily modeled. Our experiments at low coverages [< 1 monolayer (ML)] show that Ge forms islands with flat tops at 420 °C and the island density is dictated by nucleation events. By analyzing the shape of the islands, we demonstrate that island formation is driven by the thermodynamics of the system. In contrast, the growth kinetics determine island sizes, an effect demonstrated by the formation of depletion zones around the islands and near steps. An interesting interplay between kinetics and energetics is observed near steps. In particular, Ge islands nucleate at step edges during growth but move away from the steps upon annealing. Hence steps can play quite different roles in the nucleation and energy minimization processes. We will show that the results can be explained via a simple model that focuses on the energetics of the overlay.

EXPERIMENT

The experiments were performed in an ultrahigh-vacuum chamber equipped with a commercial scanning tunneling microscope (STM) (Ref. 12) and low-energy electron diffraction (LEED) optics. The system operating pressure was $\sim 5\times10^{-11}$ Torr. Clean GaAs(110) surfaces were obtained by cleaving $2\times3\times8$ mm^3 posts that were Zn doped at 3×10^{18} cm^{-3}. Heating was achieved by radiation from a tungsten filament behind the sample holder. The temperature of the sample was monitored with an infrared pryometer. Ge, evaporated from W baskets, was condensed on hot GaAs substrates. One monolayer is defined as the surface atom density of GaAs(110), 8.86×10^{14} cm^{-2}, corresponding to 2.01 Å for Ge. Ge depositions were determined by timed exposures to the source after a stable evaporation rate had been established. The deposition rates were determined with a water-cooled quartz-crystal thickness monitor. The heater was shut off immediately following deposition, and the sample was cooled quickly to room temperature for STM imaging. The images were acquired in the constant current mode with a typical tunneling current of 0.2 nA. The STM images reproduced here are oriented so that the [1$\bar{1}$0] direction of the (110) surface runs from the upper-left to the lower-right corner.

ISLAND FORMATION ON FLAT TERRACES

Figures 1(a) and 1(b) show 1400×1400 Å^2 STM images taken following depositions of 0.2 and 0.4 ML of Ge on freshly cleaved GaAs(110) at 420 °C. The deposition rate was ~1 ML/min. The bright protrusions in the images correspond to Ge clusters. From the images, it is clear that Ge growth in this low coverage region proceeds through nucleation because the cluster density increases with the amount of material deposited. The Ge clusters are stable, as demonstrated by the fact that annealing at the growth temperature, 420 °C, for 4 h produced no observable change in the cluster density. When annealed at 500 °C for 30 min, however, the clusters were larger and their density was greatly reduced, as shown in Fig. 1(c).

Figure 1(d) shows a closeup of a typical Ge cluster grown by the deposition of 0.2 ML at 420 °C with no further annealing. These clusters have flat tops. The cluster shown in Fig. 1(d) exhibits two ordered rows along [1$\bar{1}$0]. The row separation of 5.6 Å coincides with the unreconstructed unit cell of Ge. The island height is ~10 Å or 5 ML and its diameter is ~45 Å. The island shape and surface ordering demonstrate the crystalline character of the cluster.[13] Dual images that probed filled and empty states (±1.67 V) revealed the same appearance, ensuring that the STM results approximated the surface morphology. Quantitative measurements of island heights and sizes from dual images gave identical results, within experimental uncertainty.

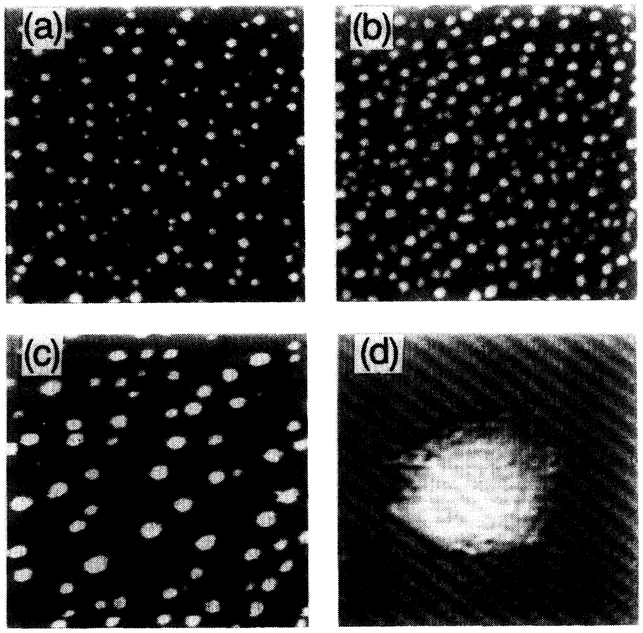


FIG. 1. (a) and (b) 1400×1400 Å^2 images showing the surface morphology after deposition of 0.2 and 0.4 ML of Ge at 420 °C. The [1$\bar{1}$0] runs from the upper-left to lower-right corner in all of the images presented here. (c) 1400×1400 Å^2 scan showing the morphology of regrowth for 0.4 ML Ge after annealing at 500 °C for 30 min. (d) A closeup of a typical Ge island at 0.2 ML showing the shape and the flat top with surface order. The image size is 80×80 Å.

Thermodynamics: Island height-to-radius distribution

The importance of thermodynamics is widely recognized as far as its influence on growth modes is concerned. Island growth (Volmer-Weber) results when $\sigma_s < \sigma_0 + \sigma_i$ where σ_s and σ_0 are the surface free energies for the substrate and the overlayer and σ_i is the interfacial free energy. The energetics of the system are also important in determining the shape of the islands. This can be seen by considering a cylindrical island of constant volume $V = \pi R^2 H$ on a surface with area A, as depicted in the inset of Fig. 2. The free energy of the system can be written

$$\begin{aligned} E &= \pi R^2 \sigma_0 + 2\pi R H \sigma_2 + \pi R^2 \sigma_i + (A - \pi R^2)\sigma_s \\ &= \pi R^2 \sigma_1 + 2\pi R H \sigma_2 + A\sigma_s \,, \end{aligned} \tag{1}$$

where σ_2 is the surface free energy for the side of the cylinder and $\sigma_1 = \sigma_0 + \sigma_i - \sigma_s$. While this is an oversimplified model, the way that the energetics control the growth mode and island shape can be easily demonstrated utilizing Eq. (1). In $\sigma_1 < 0$, the first term is negative and the system free energy E decreases with increasing R (decreasing H for constant volume). Hence lateral growth is favored and the system will grow in the layer-by-layer mode (Frank–van der Merwe). For island growth, $\sigma_1 > 0$ and the minimization of E under the constraint of constant cylindrical volume gives $H/R = \sigma_1/\sigma_2$. For a more general island shape, such as

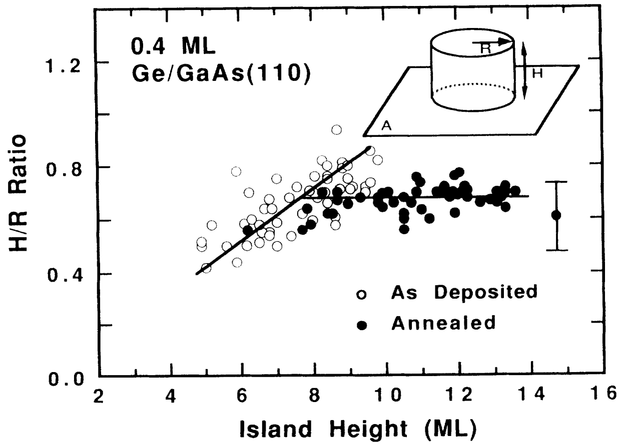


FIG. 2. Measured height-to-radius distributions for 0.4 ML Ge deposited at 420 °C and after annealing at 500 °C for 30 min. The ratio is independent of island height for the annealed surface but it increases with increasing height for the as-deposited surface. The inset serves to define the island height and radius.

a truncated cone, energy minimization results in $H/R=\sigma_1\sin\theta/(\sigma_2-\sigma_0\cos\theta)$ where σ_2 is the surface free energy for the side of the cone and θ is the angle between the base and the side. Therefore the ratio between the island height and its lateral dimension should be a constant, if the energy is indeed minimized during island growth.

Figure 2 summarizes the measured H/R ratios as a function of Ge island height for 0.4 ML deposition at 420 °C and after annealing at 500 °C. For the annealed surface, the ratios approached a constant with an average value of 0.68 ± 0.04, independent of island size. This demonstrates that island formation and island shapes are indeed controlled by thermodynamics when the system is allowed to approach equilibrium. For the as-deposited surface, the ratio H/R increases as the height increases so that the energy minimization is not fully realized. While this is not a surprise, what is interesting is that the values of H/R are centered around 0.68, the value for the equilibrium surface. This indicates that the energetics of the system still play an important role in shaping the islands even though the energy of the system is not minimized during growth. This argument becomes more convincing if we take into account the fact that island sizes before and after annealing are very different, as shown in Figs. 2(b) and 2(c). In fact, as we will show below, the energetics of the system are, in part, to blame for the observed large variations in H/R for as-deposited Ge islands.

Thermodynamics: Island height distribution

To further examine the surface morphology, we measured the island height distribution for depositions of 0.2 and 0.4 ML at 420 °C and for 0.4 ML annealed at 500 °C. For 0.2 ML, the distribution shown in Fig. 3(a) is very narrow and it reaches a maximum at an island height of 5 ML. For 0.4 ML, the distribution width increases and the peak shifts to 7–8 ML, Fig. 3(b). This increase reflects the fact that the islands are larger. Islands with heights of 3 ML or less are not present for 0.2 or 0.4 ML deposition. After annealing at 500 °C, the island size becomes much larger, and this is reflected in the height distribution of Fig. 3(c) for 0.4 ML. The distribution shape after annealing is very similar to that before annealing, but the peak has increased to 12 ML.

The analysis of the island height-to-radius distribution shows that the driving force for island formation is the system energetics, even though the free energy is not fully minimized. Inspection of Fig. 3 reveals that the width of the height distribution increases with increasing Ge deposition and that small height islands are not observed. The question, then, is whether these effects are due simply to kinetics or whether energetics are partially responsible.

From Eq. (1), it is clear that there is an energy minimum as a function of island height H that gives the equilibrium configuration if $\sigma_1>0$. However, the rate at which the system approaches that configuration and the morphological deviations from it during growth depend on the magnitude of the force that drives the system toward equilibrium. Figure 4 makes it possible to examine such an energetic behavior by plotting the system energy E calculated from Eq. (1) as a function of island height for two fixed volumes that give minimum energies at $H_{\min}=5$ and 7 ML. While it is not realistic to expect quantitative agreement between the simple model and the experimental results, the two island volumes were chosen

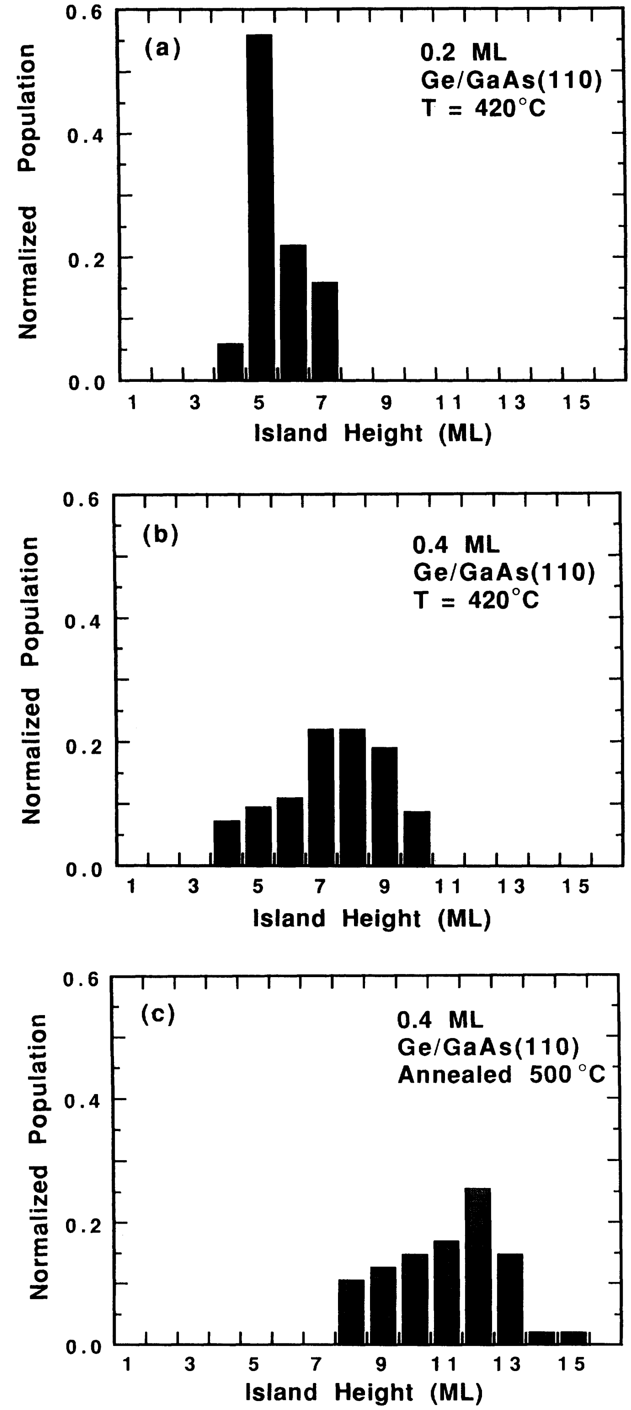


FIG. 3. (a)–(c) Measured island height distributions for 0.2 and 0.4 ML deposition of Ge at 420 °C and 0.4 ML of Ge annealed at 500 °C for 30 min. The width of the distribution increases with Ge deposition and islands that have heights less than or equal to 3 ML are absent.

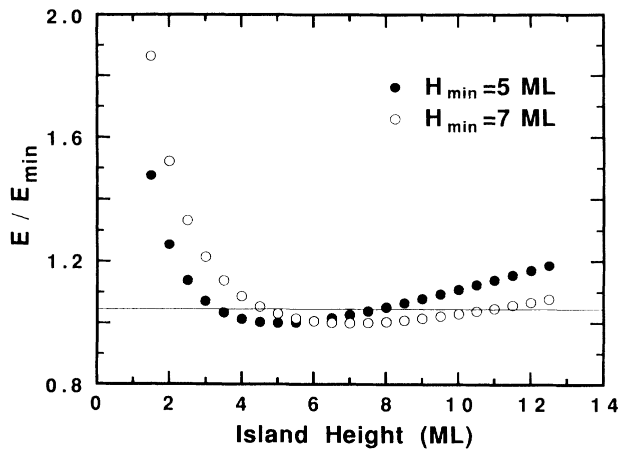


FIG. 4. Calculated energy versus island height for the cylindrical island model for two island volumes. The energy increases very sharply with decreasing island height while the energy change in the vicinity of the minimum is very small. The horizontal line represents the energy that is 4% higher than the minimum energy.

to give $H_{\min}$ values that correspond to the most probable heights observed for 0.2 and 0.4 ML Ge deposition, as shown in Figs. 3(a) and 3(b). The ratio σ_1/σ_2 is assumed to be 0.68. A striking characteristic of the energy versus island height plot of Fig. 4 is that the system free energy for a given volume increases sharply with decreasing height. This represents a large driving force that increases the height of the vertically impaired islands. Our simple model then reveals the energetic reason for the observed absence of such islands.

When the island heights approach their equilibrium value, the picture is much different because the change of E is very small in the vicinity of the minimum (Fig. 4). Hence the driving force toward energy minimum is small and the evolution toward equilibrium is expected to be slow. As expected, equilibrium is not obtained for 0.4 ML deposition of Ge at 420 °C, as reflected by the large variation in H/R in Fig. 2. Annealing at 500 °C for 30 min provides sufficient kinetics that the system is able to reach the equilibrium configuration, as shown by the height-independent distribution of H/R in Fig. 2.

The solid horizontal line in Fig. 4 represents an energy that is 4% higher than the minimum value. The intersections of this line with the curve for $H_{\min}=5$ ML occur at 3.5 and 7.5 ML while the intersections with the curve for $H_{\min}=7$ ML give 4.5 and 10.5 ML. Hence the range of height for small islands is less than for larger islands for the same energy deviation from the minimum. Accordingly, morphological deviations from the equilibrium configuration have decreasing effect on the change of system energy as the volume of this island increases. This thermodynamic property of islands is consistent with the observation that the height distribution for 0.2 ML is much narrower than for 0.4 ML where the islands are larger. In reality, of course, not all islands at a given coverage have the same size and this can further contribute to variations in island height.

Kinetics: Nearest-neighbor distance distribution

The above has shown that thermodynamics is largely responsible for the observations related to the island shape, if the size of the island is given. The island size distribution, however, is determined by kinetics during growth. The absence of islands with heights smaller than 4 ML (Fig. 3) demonstrates that Ge islands smaller than a certain volume are not present on GaAs(110) at 420 °C.

During growth, an adatom impinging on the surface will diffuse until it is incorporated into an existing island or it combines with other adatoms to form a cluster. Which process accounts for the monomer disappearance depends on the growth temperature, the deposition rate, and, most importantly, the local environment where the atom lands. In general, there is a zone around each island known as the depletion zone within which it is more likely for an adatom to find the island than to find other adatoms and nucleate a new cluster. This implies that small clusters will be few in number and, conversely, the absence of small clusters suggests that a depletion zone should be evident in the surface morphology. While such zones are not obvious in Fig. 1, their existence can be demonstrated through simple modeling and measurements of the distance distribution of nearest-neighbor islands.

For randomly distributed clusters of density n, the probability of having no clusters within a circle of radius r is $\exp(-n\pi r^2)$ and the probability of having a cluster outside the circle within a distance of dr is $n2\pi r dr$. Therefore the combined probability, termed the distance distribution of nearest neighbors for randomly nucleated clusters, is[7,14–16]

$$W_{\text{random}}(r,\Delta r)=2\pi r n \exp(-\pi n r^2)dr \ . \tag{2}$$

From the STM images, we can measure the distribution

$$W_{\text{measured}}(r,\Delta r)=n(r,\Delta r)/N \ , \tag{3}$$

where $n(r,\Delta r)$ is the number of clusters with nearest-neighbor distance between r and $r+\Delta r$ and N is the total number of clusters counted. Figures 5(a) and 5(b) compare the measured distributions to the random distribution for Ge depositions of 0.2 and 0.4 ML (420 °C), showing that the measured distributions are shifted to larger distances, as expected if there is a depletion zone around each cluster.

From Fig. 5, it is evident that the measured distributions are narrower than the random distributions and that the widths decrease with increasing coverage. These effects are easy to understand in terms of cluster-cluster interactions. For a random distribution, the nucleation of a given cluster is independent of all others. For Ge cluster growth on GaAs(110), the depletion zone implies that cluster nucleation is strongly influenced by the proximity of existing clusters. Effectively, there is a repulsive interaction among the clusters and the clusters tend to have equal separation. The observed narrowness of the measured distributions reflects this tendency. As the

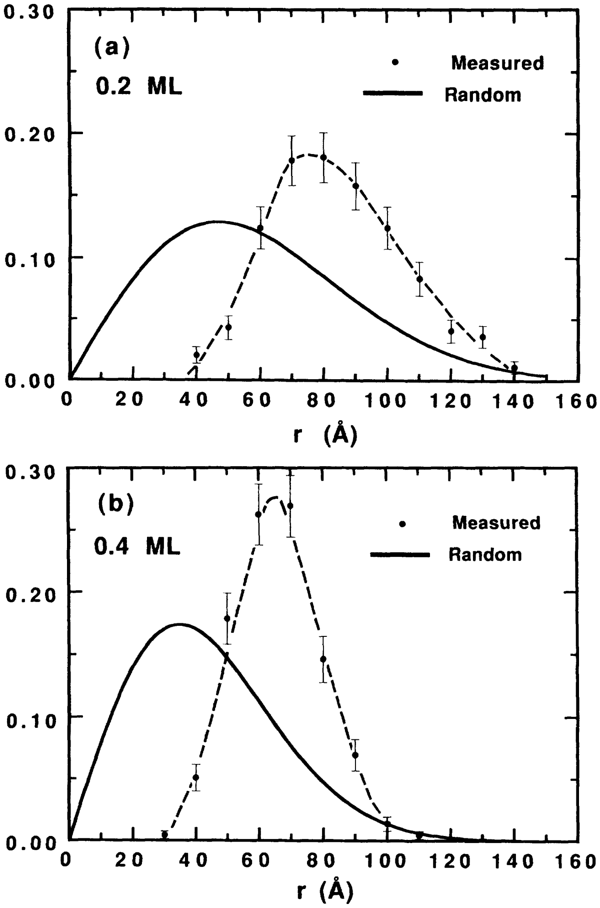


FIG. 5. (a) and (b) Comparisons of measured nearest-neighbor distance distributions and the distributions predicted from a random nucleation model for 0.2 and 0.4 ML depositions.

overlayer deposition increases, the cluster density increases and the interactions among the clusters become stronger. This change in strength is responsible for the sharpening of measured distribution as the coverage increases.

In principle, a kinetic theory could be developed so that the depletion zone width could be deduced by fitting to measured distributions. Such a fitting has been performed for Au clusters on NaCl.[17] However, this fitting is complicated and the value of the zone size cannot be determined unambiguously. In fact, depending on whether small clusters were assumed to be mobile, in addition to monomers, the zone sizes between 225 and 450 Å were obtained. Therefore we feel that until better theory is developed such an estimate is not very meaningful.

ISLAND FORMATION NEAR STEPS

Through comparison of measured nearest-neighbor distance distributions with the random distributions, we have demonstrated the existence of depletion zones around stable clusters. Surface steps can also act as nucleation centers and depletion zones in this case can be readily seen from STM images.[18–20] The mosaic image of Fig. 6(a) shows Ge island nucleation near steps following 0.2 ML deposition at 420 °C. The left side of the image shows two steps separated by ~600 Å that are decorated with Ge islands. The macroscopic step direction is at 62° with respect to [1$\bar{1}$0] which runs from the upper left to lower right of a given image. The surface steps downward from left to right in the image. As a result of preferred nucleation, there are depletion zones on either side of a given step. The right side of Fig. 6(a) shows another pair of steps separated by ~200 Å. In this case, there are no Ge islands on the terrace between the steps, establishing a lower bound on the size of the depletion zone of ~100 Å.

To better estimate the size of the depletion zone, we measured the cluster density as a function of distance away from the bottom and the top of the steps. The interval width of 70 Å was chosen to ensure reasonable counts of clusters while being small enough to reflect changes in cluster density as a function of distance. The results are shown in Fig. 6(b) where the error bars correspond to the square root of the number of clusters. As shown, the cluster density increases with distance from the step and saturates at 400 Å. If we define the size of

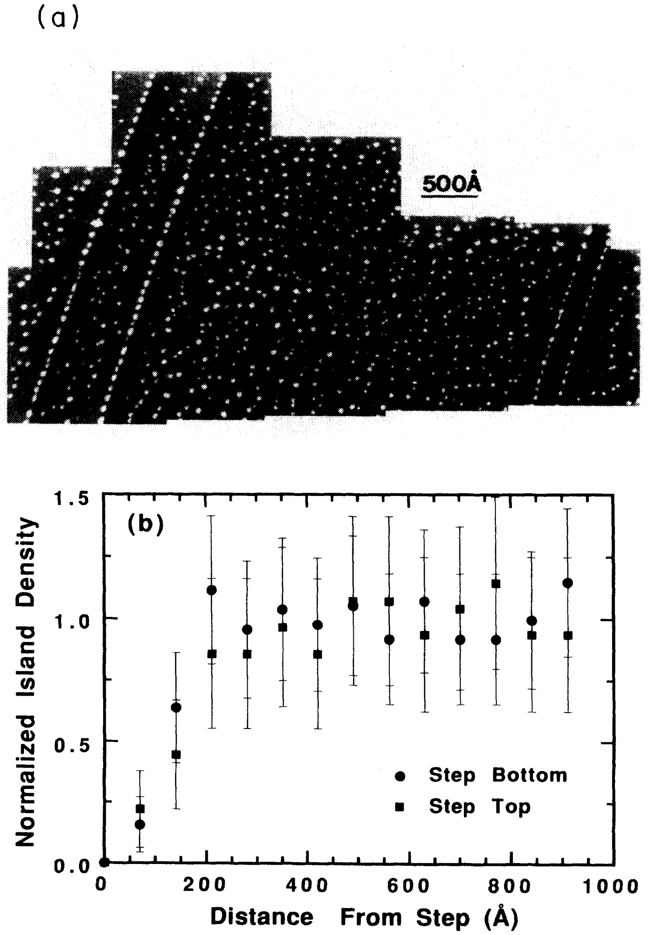


FIG. 6. (a) Ge cluster nucleation showing decoration at steps for 0.2 ML of Ge deposited at 420 °C. (b) Measured cluster densities as a function of distance away from the step edge on both the top and the bottom of the steps.

the depletion zone as the distance at which the density is then half of the saturation density, we obtain 150 Å.

Figures 7(a)–7(d) show a sequence of STM images near a step with different magnification. Common features have been labeled for easy identification. The step edge resembles a sawtooth, as shown in Figs. 7(c) and 7(d), with step edges along [001] and roughly along $[1\bar{1}0]$, as depicted in Fig. 7(e). From Figs. 7(a)–7(d), the Ge clusters nucleate preferentially at the [001] step edges and most of the volume of a given cluster is found on top of the step. Preferential nucleation at [001] edges can be understood in terms of the number of dangling bonds at step edges. At $[1\bar{1}0]$ step edges, there is one dangling bond per atom. This is the same as any atom on a GaAs(110) terrace so that such edges offer little advantage for cluster nucleation. In contrast, one extra dangling bond per atom is introduced upon creation of a step along [001] (total two dangling bonds per atom). Hence [001] edges present sites that have much stronger bonding than $[1\bar{1}0]$ edges or the terraces.

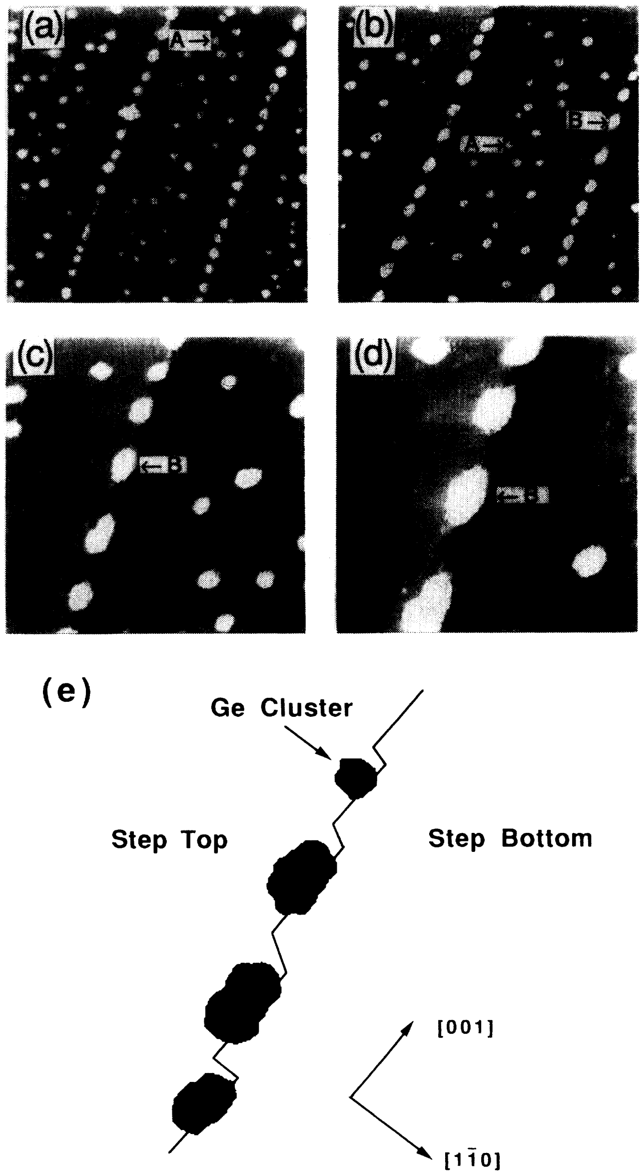


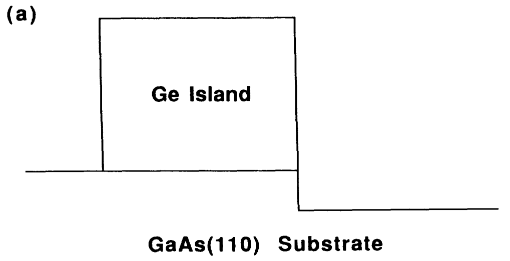
FIG. 7. (a), (b), (c), and (d): A sequence of STM images of a step region on GaAs(110) following 0.2 ML of Ge deposition at 420 °C showing the details of the island morphology at the step edges. The image sizes are 1400×1400, 1100×1100, 560×560, and 350×350 Å^2 for (a), (b), (c), and (d), respectively. (e) A sketch of Ge island formation at the step edge showing a sawtooth step edge and preferential nucleation at [001] edge with large percentage of the island volume on the step tops.

In Fig. 7(d), where the substrate atomic structure is clearly resolved, there are small dark and bright features on the surface in addition to large Ge clusters. Similar features have also been observed in our STM studies of the annealing effect on clean GaAs(110). Therefore we associate these features with defects on GaAs(110). It is evident that these defects do not affect the nucleation of Ge clusters.

Preferred growth on the tops of steps

The observation that most of the Ge cluster volume appeared on top of the step was surprising because nucleation starts from the bottom of the step. One possible cause of growth on the step top is that the kinetics, such as diffusion and accommodation at a step, are different on the two sides of a step. If this were the case, then the depletion zones on the top and bottom of a step should be different. From Fig. 6(a), it is not obvious that this is the case. While examination of the density versus distance plot of Fig. 6(b) shows that the density from the top of the step increases with distance a little slower, the difference is well within the error bars of the measurement. Even if the difference is real, it is too small to account for the cluster morphology where $\sim 80\%$ of a given cluster volume is found on top of the step.

A more satisfactory explanation for preferred growth on the step top lies in the energetics. In particular, we postulate that it is energetically more favorable for a cluster with a flat top to be on the top of the step than on the bottom. To show this, we consider two cluster configurations at a step edge, as sketched in Figs. 8(a) and 8(b). Figure 8(a) depicts growth on the step top while Fig. 8(b) depicts growth on the step bottom (or growth on both sides). The main difference is whether the step edge is exposed. If we neglect the interfacial free energy[21] but count the surface free energy, then one configuration has a term associated with the GaAs step edge *A* while the other has a term from a Ge face *B* having the same orientation as the step edge [see Fig. 8(b)]. Thermodynamically, it is a matter of whether substrate step edge *A* or Ge face *B* has the lower free energy. We notice that the plane through a [001] step edge that is perpendicular to the (110) surface is another GaAs(110) plane. The fact that Ge forms clusters on GaAs(110) terraces demonstrates that the surface free energy of GaAs(110) is lower than Ge(110). Since [001] step edge atoms have the same crystallographic structure as any of the linear atomic chains in the (110) plane, it is reasonable to expect that face *B* of Ge would have a higher energy than the GaAs [001] step edge. In such a case, it is thermodynamically preferable to have the substrate step edge exposed and the top of the step is favored for Ge island growth. Note



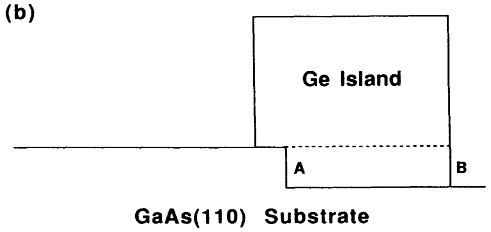


FIG. 8. (a) and (b) Sketches of island formation at a step edge corresponding to an island on the step top and an island on the step bottom.

that this is valid independent of step orientation so long as the step edge has a lower free energy.

Within the framework of our simple model, there is no thermodynamic difference between an island on top of the step and an island grown far from the step. However, the bottom of a step represents an energetically unfavored location for growth. Therefore a question arises as to why Ge clusters grow at steps if the steps offer no advantage in terms of energetics. The answer is related to the kinetics of growth. In particular, the extra dangling bonds at step edges make them preferred sites for nucleation and, once nucleated, these clusters trap incoming atoms. This kinetic effect is clearly demonstrated by the depletion zones near step edges (Fig. 6). Thus cluster decoration of step edges is a result of nucleation kinetics. Thermodynamics serves to shape the islands, as for Ge islands on terraces. The drive toward the equilibrium configuration depicted in Fig. 8(a) and the rearrangement of atoms within an island yield the observed step edge morphology where most of the Ge volume is found on the step tops. To reach this configuration, a substantial number of Ge atoms must be transported through self-diffusion from the step bottom to the step top (Ge diffusion on Ge). While this might seem to be a difficult kinetic process, the very formation of multilayer Ge islands ensures that it can occur.

Cluster movement from step edges

The above discussion demonstrates that Ge clustering at step edges is due to nucleation kinetics. Once formed, the clusters cannot move away at the growth temperature even though the steps are the energetically most unfavorable sites. According to our simple model, however, if the system is driven toward equilibrium by annealing, then one should see fewer Ge clusters at step edges. Figure 9 shows a STM mosaic obtained after the deposition of 0.8 ML of Ge at 350 °C with annealing at 550 °C for 50 min. The terrace on the right is lower than the one on the left. The surface morphology following deposition was similar to that of Fig. 7(a), with steps decorated by Ge clusters. After annealing to 550 °C, there were no Ge clusters at the step bottom and there was only one cluster at the edge of the step on the top. It is clear from the image that the morphology at the step is not a statistical coincidence as any straight line parallel to the step on the terraces passes through at least one Ge cluster; only a line coincident with the step itself passes through regions without a cluster.

The surface morphology shown in Fig. 9 can be understood in the context of the model presented above. If there were no steps, then the clusters would be distributed in a random fashion. Since the bottom of a step represents a thermodynamically unfavored location for cluster growth, there should be no clusters at the bottom of the step. On the upper terrace (left of the step in the image), there is no thermodynamic preference of Ge clusters at the step or far away from it. Therefore the spatial distribution of clusters should remain random and, statistically, there should be some clusters at the step edge. Indeed, we find one Ge cluster on the top of the step edge. This Ge cluster is completely on top of the step, indicating that its presence does not involve any renucleation at the bottom of the step.

Our thermodynamic model provides a basis for the observed deficiency of Ge clusters at step edges following annealing. However, the transformation from a morphology where a large number of Ge clusters are found at step edges (Fig. 7) to a morphology where there are almost none (Fig. 9) cannot be explained by thermodynamics alone. Since there is no energetic difference between clusters at the top of the step and far from the step, there is no thermodynamic driving force that would move them away from the step. Thus it is important to examine the kinetics responsible for the regrowth of the Ge clusters when the system is annealed.

The effect of annealing to 550 °C is to transform small

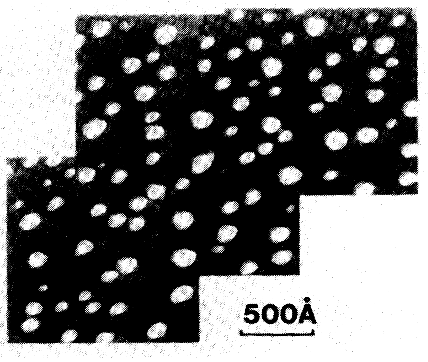


FIG. 9. Mosaic STM image of 0.8 ML Ge annealed at 550 °C for 50 min showing Ge island deficit at the step edge, reflecting the unfavored thermodynamics for the formation of Ge islands at the step edge. See text for detailed discussion.

clusters into larger clusters. There are two possible processes that might account for this. First, the small clusters could become unstable at high temperature, increasing the local 2D vapor pressure.[20] This pressure is higher in the vicinity of small clusters so that large clusters grow at the expense of small ones. In this coarsening process, a large number of monomers would be generated. Since the step acts as a preferred nucleation site, some clusters would nucleate and the regrowth would leave some clusters at the step edge. This is not consistent with the experimental observation that no clusters appear at the bottom of the step. The second possibility is that the small clusters, as a whole, would become mobile at higher temperature.[22] In this case, there is no reason for the clusters to stay at the step edge and the higher initial density of small clusters at the step relative to the terrace would provide a driving force for diffusion. In this picture, the large clusters cannot be stabilized at the bottom of the step edge due to unfavorable energetics. On the upper terrace, small clusters will be immobilized when they form large stable clusters and whether or not there is a cluster at the step edge is simply a matter of statistical probability. The observed Ge cluster morphology at the step edge then suggests that small Ge clusters are mobile at ~550 °C.

SUMMARY

Perhaps the most important aspect of this study has been its ability to distinguish the effects of both energetics and kinetics during the early stages of a growth process. Through analysis of the surface morphology at low coverage, we have shown that Ge island formation is driven by thermodynamics, even though the minimum energy configuration is not obtained at the growth temperature. While the island shape is largely controlled by the energetics, the island size and density are determined by the kinetics during growth. On flat terraces, postgrowth annealing allows the islands to approach the equilibrium configuration. However, a dramatic difference between energetically favored configurations and growth structures is found for Ge island formation in the presence of atomic steps. In this case, steps present favorable nucleation sites due to local bonding configurations and they are decorated with Ge islands. Upon annealing to 550 °C, however, the islands are driven away from the step edge by the unfavorable energetics for the island formation at step edges.

ACKNOWLEDGMENTS

This work was supported by the Office of Naval Research and the National Science Foundation.

---

[1] A. G. Milnes and D. L. Feucht, *Heterojunctions and Metal-Semiconductor Junctions* (Academic, New York, 1972).

[2] W. Mönch and H. Gant, Phys. Rev. Lett. **48**, 512 (1982); R. S. Bauer and J. C. McMenamin, J. Vac. Sci. Technol. **15**, 1444 (1978).

[3] J. A. Venables, Philos. Mag. **27**, 697 (1973).

[4] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).

[5] G. W. Jones, J. M. Marcano, J. K. Nørskov, and J. A. Venables, Phys. Rev. Lett. **65**, 3317 (1990).

[6] R. Kunkel, B. Poelsema, L. K. Verheij, and G. Comsa, Phys. Rev. Lett. **65**, 733 (1990).

[7] B. Lewis and J. C. Anderson, in *Nucleation and Growth of Thin Films* (Academic, New York, 1978).

[8] D. E. Wolf and J. Villain, Europhys. Lett. **13**, 389 (1990).

[9] Z.-W. Lai and S. Das Sarma, Phys. Rev. Lett. **66**, 2348 (1991).

[10] P. Chen, D. Bolmont, and C. A. Sebenne, J. Phys. C **15**, 6101 (1982).

[11] W. Mönch and H. Gant, J. Vac. Sci. Technol. **17**, 1094 (1980).

[12] Park Scientific Instruments STM-SU 2, Mountain View, CA.

[13] In this paper, we will use the words cluster and island interchangeably.

[14] J. C. Zanghi, J. J. Métois, and R. Kern, Philos. Mag. **31**, 743 (1975); B. A. Joyce, R. R. Bradley, B. E. Watts, and G. R. Booker, *ibid.* **19**, 403 (1969).

[15] H. Schmeisser and M. Harsdorff, Philos. Mag. **27**, 739 (1973).

[16] R. D. Evans, *The Atomic Nucleus* (McGraw-Hill, New York, 1955).

[17] H. Schmeisser, Thin Solid Films **22**, 83 (1974).

[18] B. F. Usher and J. L. Robins, J. Cryst. Growth **24**, 285 (1974).

[19] V. Halpern, Phys. Lett. **32A**, 2 (1970).

[20] M. G. Lagally, Y.-W. Mo, R. Kariotis, B. S. Swartzentruber, and M. B. Webb, in *Kinetics of Ordering and Growth at Surfaces,* Vol. 239 of *NATO Advanced Study Institute, Series B: Physics,* edited by M. G. Lagally (Plenum, New York, 1990).

[21] Our conclusion does not depend on this assumption. Similar arguments taking interfacial free energy into account can be constructed using the model presented in the text.

[22] Mobile small clusters have been observed for Au/MgO(111). See J. J. Métois, K. Heinemann, and H. Poppa, Philos. Mag. **35**, 1413 (1977).

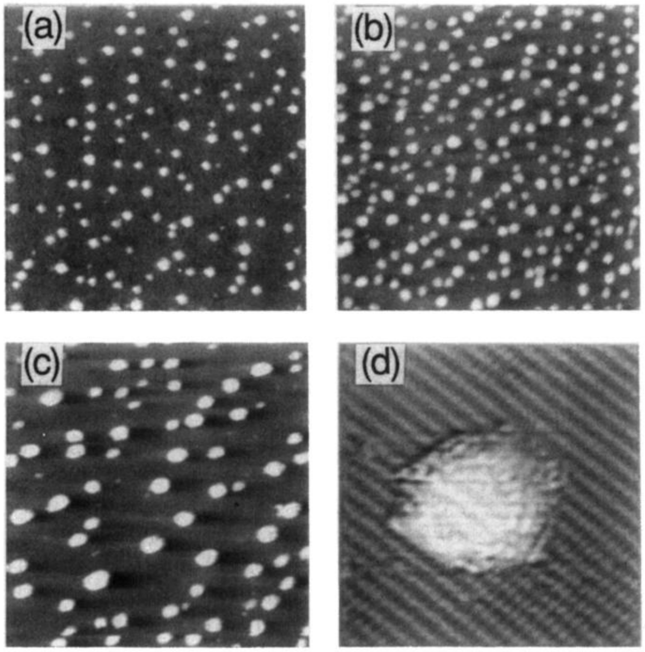


FIG. 1. (a) and (b) 1400×1400 Å^2 images showing the surface morphology after deposition of 0.2 and 0.4 ML of Ge at 420 °C. The $[1\bar{1}0]$ runs from the upper-left to lower-right corner in all of the images presented here. (c) 1400×1400 Å^2 scan showing the morphology of regrowth for 0.4 ML Ge after annealing at 500 °C for 30 min. (d) A closeup of a typical Ge island at 0.2 ML showing the shape and the flat top with surface order. The image size is 80×80 Å.

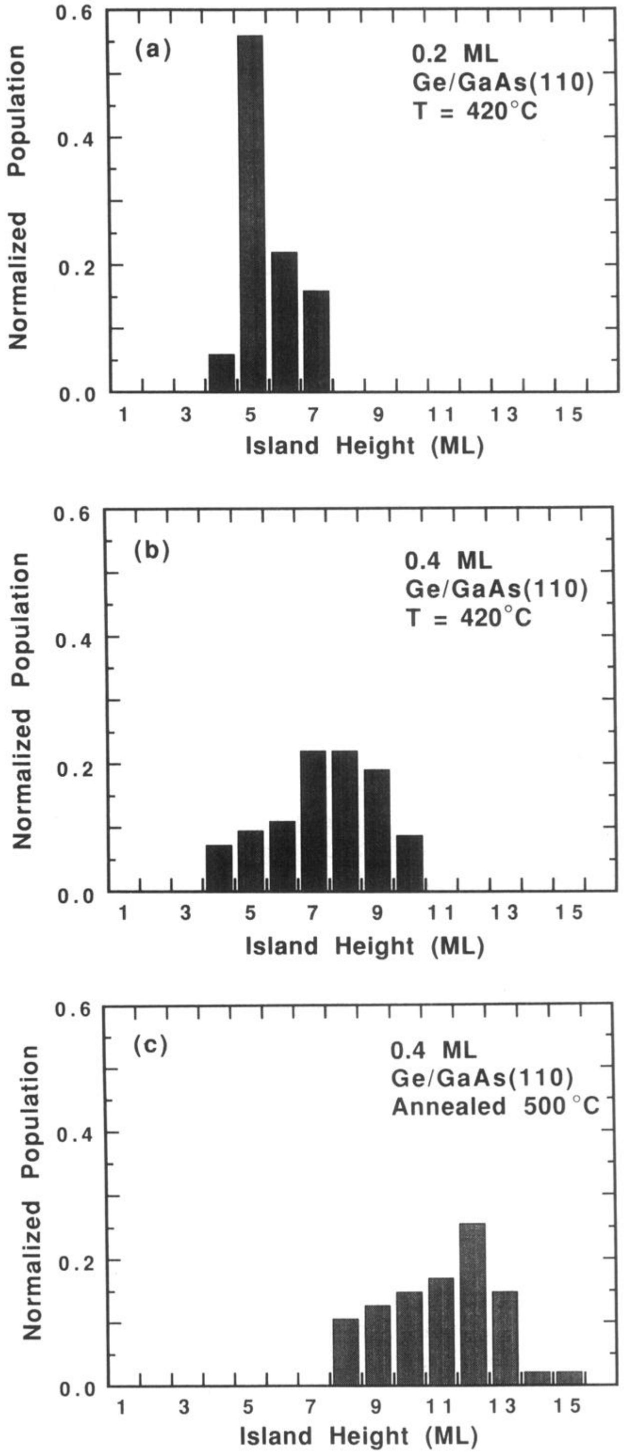


FIG. 3. (a)–(c) Measured island height distributions for 0.2 and 0.4 ML deposition of Ge at 420 °C and 0.4 ML of Ge annealed at 500 °C for 30 min. The width of the distribution increases with Ge deposition and islands that have heights less than or equal to 3 ML are absent.

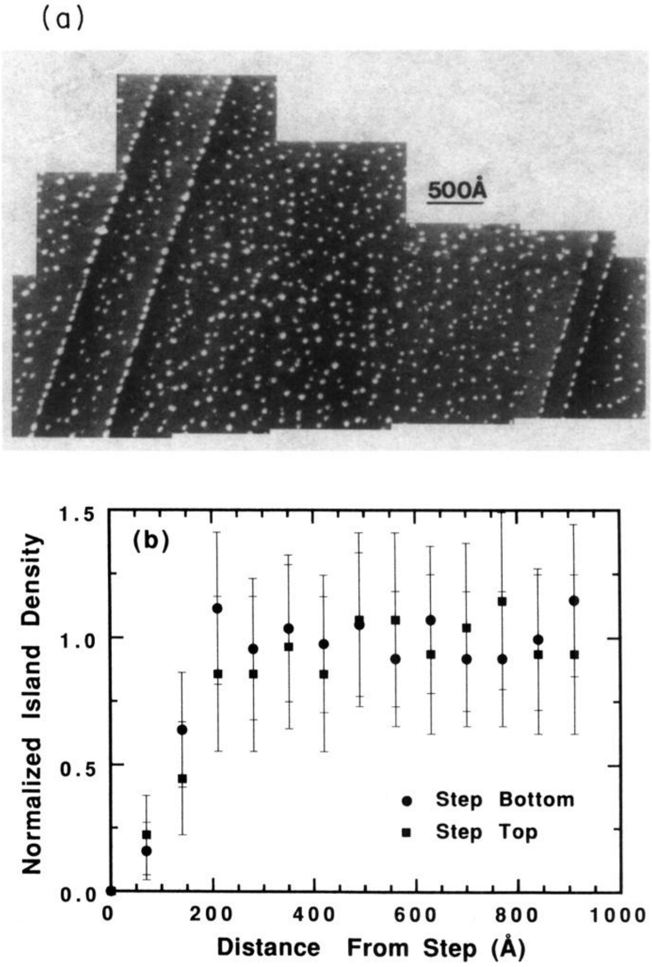


FIG. 6. (a) Ge cluster nucleation showing decoration at steps for 0.2 ML of Ge deposited at 420 °C. (b) Measured cluster densities as a function of distance away from the step edge on both the top and the bottom of the steps.

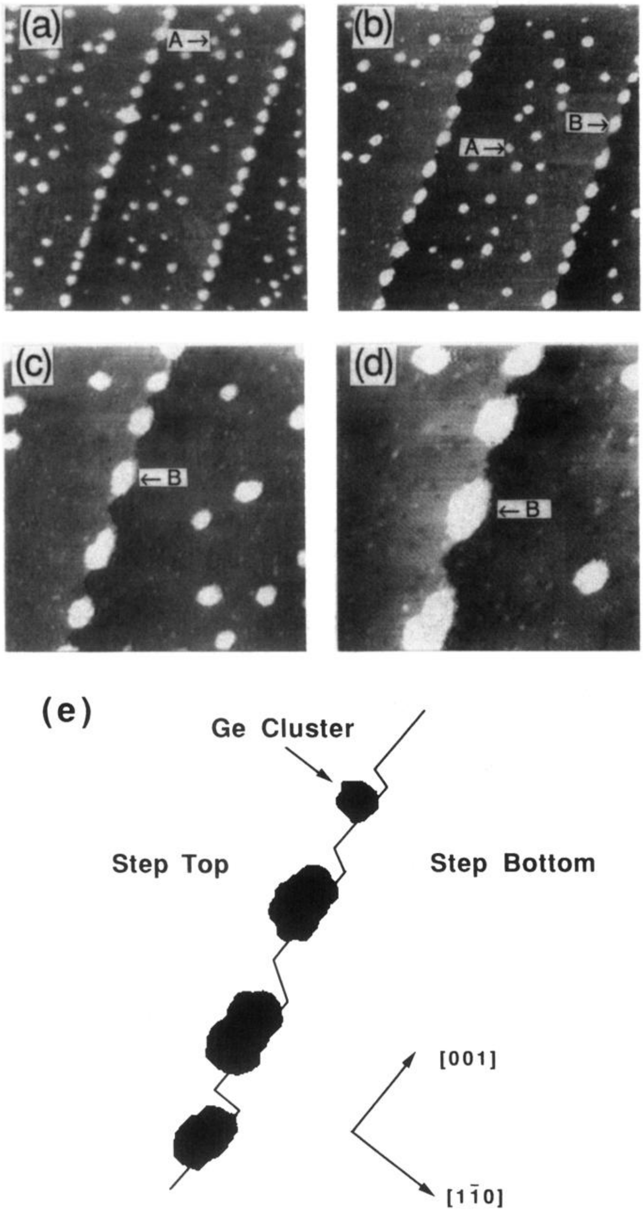


FIG. 7. (a), (b), (c), and (d): A sequence of STM images of a step region on GaAs(110) following 0.2 ML of Ge deposition at 420 °C showing the details of the island morphology at the step edges. The image sizes are 1400×1400, 1100×1100, 560×560, and 350×350 Å^2 for (a), (b), (c), and (d), respectively. (e) A sketch of Ge island formation at the step edge showing a sawtooth step edge and preferential nucleation at [001] edge with large percentage of the island volume on the step tops.

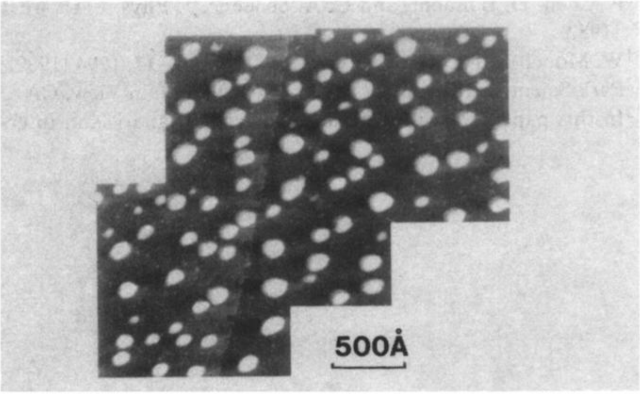


FIG. 9. Mosaic STM image of 0.8 ML Ge annealed at 550 °C for 50 min showing Ge island deficit at the step edge, reflecting the unfavored thermodynamics for the formation of Ge islands at the step edge. See text for detailed discussion.