Enhanced epitaxial growth on substrates modified by ion sputtering: Ge on GaAs(110)

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The growth morphology of Ge on GaAs(110) has been modified by using ion sputtering at elevated temperatures to create GaAs vacancy islands prior to Ge deposition. Scanning tunneling microscopy studies of growth on such surfaces show that the Ge nucleation density is increased significantly and that this leads to island coalescence and uniform film formation at lower coverages than observed on unsputtered substrates. The driving force for this change in morphology is the reduction in energy achieved by saturation of dangling bonds at vacancy island steps. Vacancy islands with lateral sizes less than 100 Å are most effective for such a growth.

I. INTRODUCTION

Ge/GaAs heterostructures have considerable potential for device applications.[1] Although it is recognized that the quality and performance of such devices will be enhanced if the Ge layers can be grown as uniform thin films, the fact is that Ge nucleates as multilayer islands when deposited on GaAs(110),[2] producing nonuniform films. Several methods have been used to suppress island formation, most notably the incorporation of a surfactant in the growth front.[3] Unfortunately, this method also introduces impurities into the growing film. An alternative way to enhance planarity would be to increase the density of nucleation sites, but this possibility has not been investigated as thoroughly as surfactant-mediated epitaxy.

One such method of modifying the nucleation density is to bombard the surface with energetic ions at elevated temperature. Recent homoepitaxy studies have shown that ion sputtering prior to deposition can lead to a modification in growth morphology.[4] On such surfaces, vacancy islands are produced from vacancies created by ion impacts. For GaAs(110), Wang *et al.*[5,6] have demonstrated that the morphology and step density associated with vacancy islands could be controlled by varying the sputtering temperature and fluence. In principle, an increased GaAs step density should lead to an increased nucleation density, an effect that would result in the coalescence of the film at an earlier stage.

With this in mind, we investigated Ge growth on ion-sputtered GaAs(110) to determine the evolution of the overlayer. Using scanning tunneling microscopy (STM), we found that Ge nucleates preferentially at steps associated with vacancy islands, significantly increasing the density of Ge islands. This makes it possible for the Ge film to cover the substrate at a smaller thickness than for an unsputtered substrate. Such growth can be understood in terms of a step energy model that takes into account the vacancy island size because the change in growth morphology reflects the energy gained by saturation of dangling bonds at steps. We show that small vacancy islands were filled and were stable after annealing to 420 °C. For larger vacancy islands, which are more elongated, Ge located preferentially along the higher curvature [001] steps and there was only partial vacancy island filling for the same Ge deposition. The differences are related to the contrasting curvature (kink density) of small and large vacancy islands.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed in an ultrahigh vacuum chamber equipped with both STM and low-energy electron-diffraction capabilities (base pressure 8×10^{-11} Torr). Clean, well-ordered GaAs(110) surfaces were prepared by cleaving *p*-type single crystals (Zn doped at $\sim2\times10^{18}$ cm^{-3}). The cleaved surfaces were bombarded with 2-keV Xe^{+} ions generated from a differentially pumped ion gun. The chamber pressure during sputtering was maintained at $\sim5\times10^{-9}$ Torr. Ge was evaporated from a Ta boat at about 1 ML/min, while maintaining the chamber pressure below 5×10^{-9} Torr. 1 ML was defined by the surface atom density of GaAs(110), 8.84×10^{14} cm^{-2}. This corresponds to 2 Å for Ge. Deposition rates were measured by a water-cooled quartz-crystal oscillator. Total amounts were determined by timed exposures. The substrate temperature was raised by radiation from a hot filament. It was monitored with an optical pyrometer and a thermocouple (absolute accuracy ±20 °C). STM images were taken in the constant current mode at room temperature, normally with a negative sample bias of 2–5 V and a tunneling current of 0.05–0.5 nA.

III. RESULTS AND DISCUSSION

A. Nucleation on an ion-sputtered surface

In an extensive study, Yang, Luo, and Weaver[2] investigated the growth of Ge on cleaved GaAs(110). They showed that multilayer islands were formed at a deposition temperature of 420 °C. After deposition of 0.4 ML of Ge, these islands had heights that ranged between 4 and 10 ML, with a most probable height of 8 ML. The islands were crystalline with nearly circular base shape and flat, ordered tops. Analysis showed that the nucleation density was 7.4×10^{11} cm^{-2} and that the islands had a height-to-radius ratio of 0.4–0.84. The islands exhibited static coalescence after 4-ML deposition with heights in the range 6–12 ML. Increased deposition to 7 ML produced a film that covered 85% of the surface, containing holes that extended to the substrate. After 10 ML

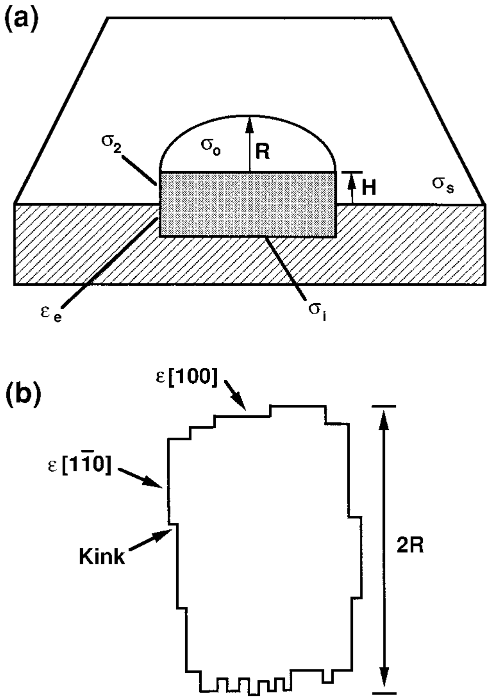

FIG. 1. (a) Cross-sectional schematic showing the terms used in the step energy model. (b) Diagram showing the measurement of island size.

had been deposited, the substrate was completely covered. Yang, Luo, and Weaver[2] observed preferential Ge nucleation at cleavage steps.

Previous STM studies of GaAs(110) have shown that vacancies created by the impact of individual ions can form vacancy islands, the size of which depends on the temperature and ion fluence.[7] Most islands formed in this way are 1 ML deep, although a few are 2 ML deep. Vacancy islands are bounded by irregular $[1\bar{1}0]$ and $[001]$ steps and, while their size increases with temperature, their density decreases accordingly. Since steps represent favorable sites for Ge nucleation, it was thought that sputtering could be used to control the island density. The investigation of this phenomenon as a function of island size represents the thrust of this paper.

When considering growth at vacancy island steps, we can define surface free energies for the substrate (σ_s), for the Ge island top (σ_0) and side (σ_2), and for an interface (σ_i) between the island and the substrate, as shown in Fig. 1; we assume the cylindrical islands have constant volume. Strain effects can be ignored since the lattice mismatch between Ge and GaAs is small at the temperatures used in this study. At the perimeter of the vacancy island, the effective energy ($\varepsilon_{\text{step}}$) per unit step length is reduced by Ge bonding to a value ε_e. This is idealized, of course, because steps have energies that depend on their orientation and they have kinks. The surface free energy for a system having a surface area A with a cylindrical island of radius R and height H bounded by a circular vacancy island having the same radius will be

$$E = A\sigma_s + \pi R^2\sigma_1 + 2\pi RH\sigma_2 - 2\pi R\varepsilon_e, \tag{1}$$

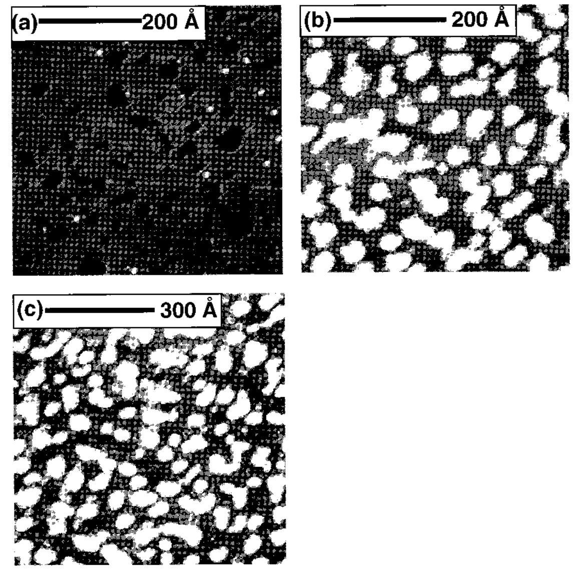

FIG. 2. (a) GaAs(110) after 45-μA sec Xe^+ bombardment at 350 °C to remove 0.25 ML. (b) Deposition of 0.5 ML of Ge at 350 °C onto the surface shown in (a). (c) Morphology after the surface in (b) was annealed at 420 °C for 15 min. All images are taken with a negative sample bias. $[1\bar{1}0]$ runs from upper right to lower left.

where $\sigma_1 = \sigma_0 + \sigma_i - \sigma_s$. A term $2\pi R\varepsilon_{\text{step}}$ is omitted since it is established by ion sputtering and vacancy island formation and does not change during Ge island growth. Energy minimization with respect to R under conditions of constant island volume $V = \pi R^2 H$ and fixed vacancy island step profiles gives

$$H/R = [\sigma_1 - (\varepsilon_e/R)]/\sigma_2. \tag{2}$$

The quantity H/R is an indication of whether vertical growth is preferred to lateral growth. For vacancy islands of small R, when the step term $2\pi R\varepsilon_e$ is important, Eq. (2) suggests that the islands will be shorter and their coverage of the surface will be greater for the same amount of material deposited. Furthermore, we can define an effective interface energy term $\sigma_i^* = \sigma_i - \varepsilon_e/R$. For two-dimensional (2D) growth, the condition $\sigma_s > \sigma_0 + \sigma_i^*$ must be satisfied. Effectively, bonding at step edges reduces the interface energy by ε_e/R per unit area. If this reduction is large then it could facilitate 2D growth in small vacancy islands, suggesting that a complete filling might be possible. However, as R increases the term ε_e/R becomes negligible and growth will revert to 3D islanding, as observed on a flat surface,[2] with $H/R = \sigma_1/\sigma_2$. This means that the step energy gain will not be sufficient to allow filling of large vacancy islands and one should expect a number of Ge islands to decorate the steps. Thus the size of a vacancy island should have a marked effect on the epitaxy of the Ge film.

B. Nucleation at small vacancy islands

Figure 2(a) represents GaAs(110) sputtered by 2-keV Xe^+ at 350 °C with 0.25 ML removed. These conditions were chosen to produce vacancy islands that were small

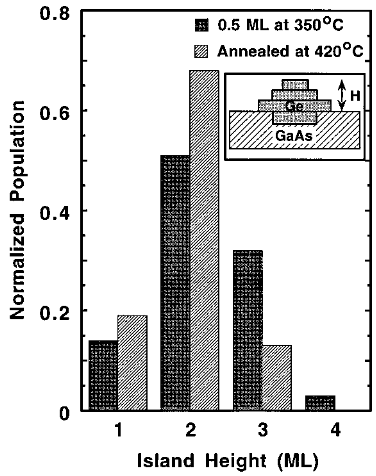

FIG. 3. Measured island height distributions for 0.5-ML deposition of Ge on ion-sputtered GaAs(110) at 350 °C before and after annealing at 420 °C for 15 min. The inset shows how the island heights were measured.

(<100 Å wide) and a single layer deep (density 2.5×10^{12} cm^{-2}). Onto this surface, 0.5 ML of Ge was deposited at 350 °C, producing the morphology shown in Fig. 2(b). The absence of vacancy islands indicates that they were completely filled by Ge. Moreover, the Ge island density was 3.1×10^{12} cm^{-2}, four times higher than for deposition on a pristine GaAs(110) terrace, and the growth features resembled the vacancy islands. This surface was then annealed at 420 °C for 10 min and, as shown in Fig. 2(c), the effect was to reduce the density of islands to 2.3×10^{12} cm^{-2}, a value close to the starting vacancy island density. The change in Ge island density induced by annealing indicates that some clusters had formed on the terraces and that these clusters were less stable than those associated with vacancy islands.

The step energy model predicts a reduction in H/R for growth on an ion-sputtered surface compared to an ideal terrace. Figure 3 shows the island height distribution following 0.5-ML deposition on the sputtered surface. The island heights were measured from the original GaAs terrace to the top of the island profile, as depicted in the inset of Fig. 3. For deposition at 350 °C, more than 80% of the islands reached 2 or 3 ML in height, though line profiles showed that they were irregular and had stepped character. Annealing at 420 °C eliminated the 4-ML islands, sharply reduced the number of 3-ML islands, and increased the population of 2-ML islands as the line profiles became more regular. In contrast, the deposition of 0.4 ML of Ge on a flat surface at 420 °C produced islands with heights of 4–10 ML, where the most probable island height was 7 ML. No islands smaller than 4 ML were observed.[2]

The smaller island heights for the sputtered surface for the same nominal Ge coverage reflect the increased nucleation density. Analysis of the island profiles grown at 350 °C shows that their tops are stepped. This irregular top surface arises because of restricted diffusion on the growing island, especially at 350 °C, and new layers form before underlying layers are complete. Annealing to 420 °C promotes interlayer transport that flattens the islands, reducing the number of

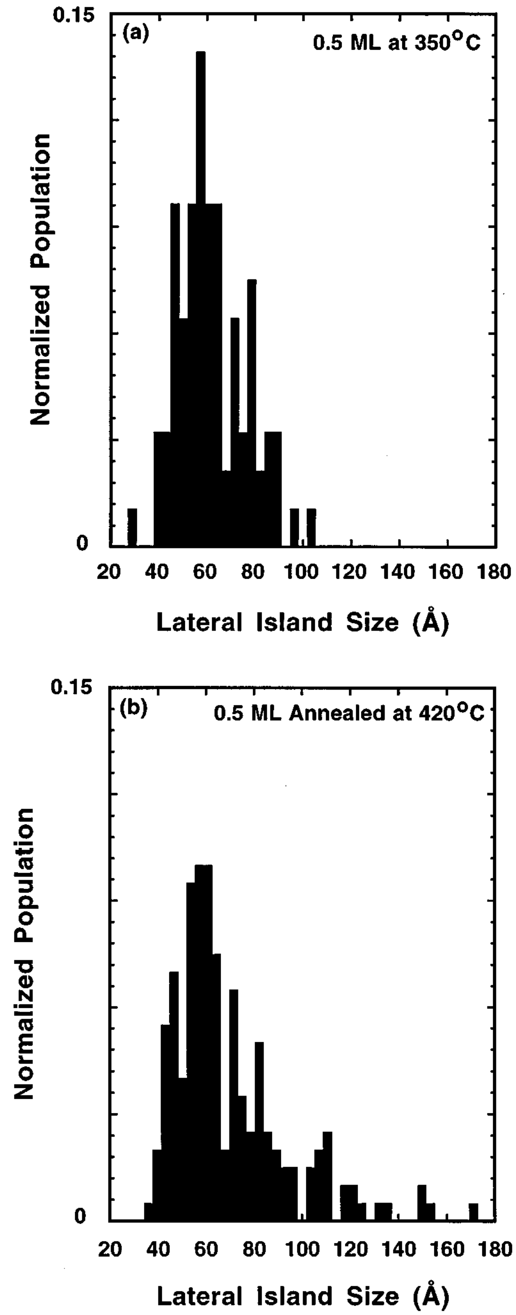

FIG. 4. Measured island sizes for the surfaces analyzed in Fig. 3.

dangling bonds at the edges of the stepped layers. The majority of islands shown in Fig. 2(c) are flat.

Figure 4 shows the size distribution of the Ge island, where the size was defined by measuring the largest lateral dimension of each island. At 350 °C, the lateral sizes are concentrated between 40 and 90 Å, but annealing broadens the distribution. This broadening is due to the transfer of atoms from islands that had nucleated on the terrace to the edge of an island stabilized at a vacancy island, since these islands are thermodynamically more stable.

Analysis of the height and lateral size of each island makes it possible to determine the H/R ratio. This ratio falls between 0.03 and 0.34, with a mean value of 0.17, following growth at 350 °C. Essentially the same values are obtained

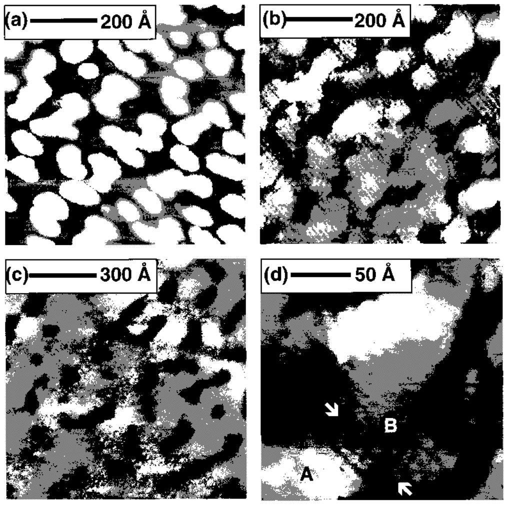

FIG. 5. (a) Island coalescence after Ge deposition of 2.5 ML at 350 °C. (b) Network structure observed after deposition of 4 ML. The Ge islands exhibit 3× periodicity along [001]. (c) Film morphology after the surface in (b) was annealed at 450 °C for 15 min. (d) Island coalescence between islands A and B at sites of high kink density, as indicated by the arrow. $[1\bar{1}0]$ runs from upper left to lower right in all images.

after annealing to 420 °C (0.04–0.32, mean 0.15). These values are considerably lower than those for growth under the same deposition conditions on unsputtered GaAs(110) (range 0.4–0.84), consistent with our model. Since the island radii R are comparable to those on an unsputtered surface,[2] the reduction in H/R is mainly a result of a decrease in H. The lowest H/R values were derived from islands having lateral sizes greater than 100 Å. Since the vacancy islands exhibit a range of sizes, from Eq. (2) we would expect a range in H/R. This is observed experimentally.

C. Coalescence of growth structures from small vacancy islands

Figures 5(a) and 5(b) show the morphology after the amount of Ge deposited was increased to 2.5 and 4 ML, respectively. The islands of Fig. 5(a) are $\leqslant 6$ ML above the GaAs terrace. Island coalescence is evident in Fig. 5(a) and ordered tops indicate that the structures retain crystallinity. The network evident in Fig. 5(b) is derived from islands with heights of 4–6 ML. The island tops reveal rows with 3× periodicity along [001], consistent with the observation of a 3×1 low-energy electron-diffraction pattern,[8] and all islands are oriented parallel to the $[1\bar{1}0]$ direction of the substrate. Figure 5(c) shows the change in this structure after annealing at 450 °C for 15 min. At this stage, the Ge film is more uniform, covers 85% of the surface, and has a height variation of only 1 ML. Holes are also observed, and scanning profiles show that the majority extended to the substrate with a steep wall profile and flat bottoms. The holes had lengths varying from 30 to 200 Å.

Growth of the Ge film can be visualized as follows. First, the vacancy islands are filled. Thereafter, the Ge structures act as sinks, but the H/R value indicates a preference for lateral growth over vertical growth. The result is a large number of Ge islands of limited height. Ultimately, the islands establish contact, facilitated by Ge diffusion and formation of a neck. An example of a neck is shown in Fig. 5(d) along the line indicated by arrows; region A is one layer higher than region B. Such necks are regions of high kink density and they have high energies. Accordingly, the system is driven to reduce the kink density and lateral growth dominates over vertical growth. This explains the constant island heights for depositions between 2.5 and 4 ML (island coalescence was apparent by 2.5 ML and further deposition increased island size in preference to island height). The fact that holes are observed is indicative of the weak Ge-substrate interaction, so that bonding to a Ge island edge is preferential to bonding to GaAs and filling the base of the holes. In contrast, growth on an unsputtered surface results in island coalescence after 4 ML (compared to 2.5 ML) and a topology with Ge covering 85% of the surface was not found until after 7-ML deposition (compared to 4 ML). Moreover, the film was less uniform because there were many islands having heights $\geqslant 10$ ML prior to the onset of coalescence. Only after depositions >10 ML was the film height variation as low as those observed here at 4 ML. Therefore, we have reached the same end point, a uniform film, at a *lower* Ge coverage.

D. Nucleation at large vacancy islands

From our model, the tendency to fill vacancy islands should be reduced for larger vacancy islands. To test this, we formed larger vacancy islands, sputtering GaAs(110) at higher temperatures to produce islands that were elongated, with straight $[1\bar{1}0]$ steps and irregular steps roughly aligned along [001]. Figure 6(a) shows an image obtained after sputtering at 420 °C, with the removal of 0.23 ML of the substrate (vacancy island density 1.8×10^{12} cm^{-2}). Many of the vacancy islands had lateral sizes exceeding 100 Å. Subsequently, 0.5 ML of Ge was deposited at 420 °C to produce the morphology shown in Fig. 6(b). Analysis shows that the Ge island density was 2.0×10^{12} cm^{-2}, still higher than for growth on the unsputtered surface. The small vacancy islands were completely filled, but the larger ones had Ge features only near steps, resulting in partial filling. This is evident at the island marked VI in Fig. 6(b). Annealing at 460 °C for 15 min reduced the island density to 1.5×10^{12} cm^{-2} because the Ge structures moved along the $[1\bar{1}0]$ steps to form larger, more compact islands at [001] steps. This can be seen in Fig. 6(c), where the large vacancy islands in the center and bottom are decorated by Ge islands at [001] steps. The result is that more $[1\bar{1}0]$ steps are exposed. For the same Ge coverage, greater areas of large vacancy islands remain exposed, even though the amount of Ge deposited exceeded the area of the island.

From Fig. 7 the population of 4-ML-high islands increased after annealing, and analysis of the images shows that the majority of the 4-ML islands were located at [001] steps. Such an increase in island height, which is also observed on unsputtered surfaces, contrasts with the reduction in island height discussed above for surfaces with small vacancy islands. For the surfaces shown in Fig. 6(c), H/R ranged between 0.06 and 0.38 (mean 0.21). From the step energy model, accommodation at steps reduces the interface

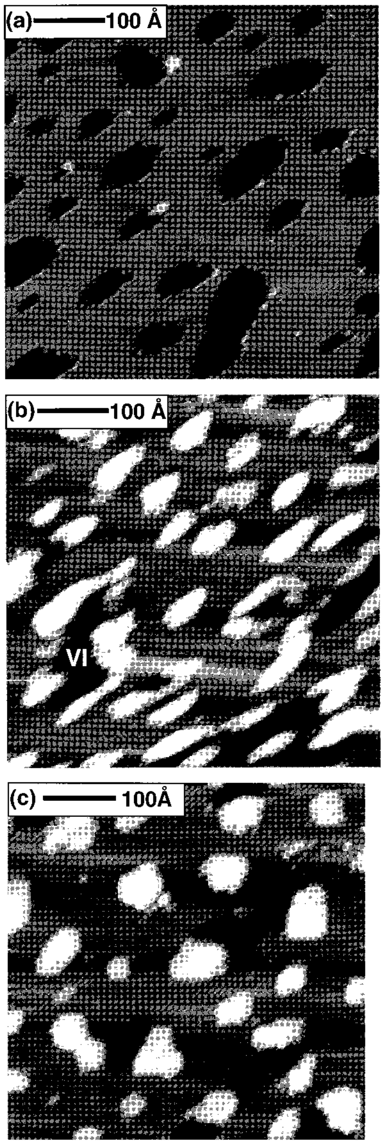

FIG. 6. (a) GaAs(110) after 0.23 ML removal by Xe^+ bombardment at 420 °C, showing large vacancy islands (lateral size >100 Å). (b) Same surface after 0.5 ML of Ge was deposited at 420 °C. The image shows the formation of Ge features around the perimeter of large vacancy islands, for instance, marked VI, resulting in incomplete filling of large vacancy islands. The elongation of the islands is due to thermal drift. (c) Surface in (b) annealed at 460 °C for 15 min, showing movement of Ge islands along straight $[1\bar{1}0]$ steps to higher curvature [001] steps. $[1\bar{1}0]$ runs from upper right to lower left in all images.

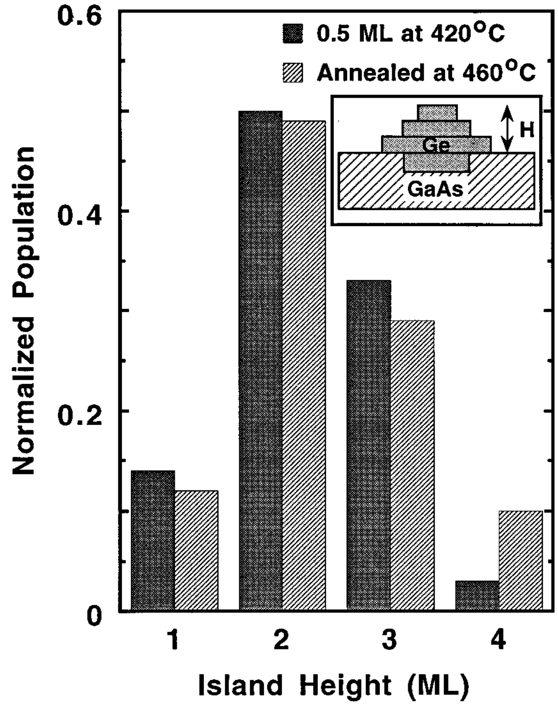

FIG. 7. Measured island height distributions after 0.5-ML deposition of Ge onto GaAs(110) containing large vacancy islands. The inset shows how the island heights were measured.

energy by $\sigma_i^* = \sigma_i - \varepsilon_e R$. However, as R increases, σ_i^* approaches σ_i and growth tends toward that observed on the unsputtered surface, i.e., 3D islanding. This is reflected by the increased mean value of H/R. The upper limit of H/R approaches the lower limit found on unsputtered surfaces, indicating a tendency toward the unsputtered growth morphology as the influence of the steps diminishes.

The redistribution of Ge islands at the steps of large (but not the small) vacancy islands reflects the differences of their contrasting shapes. Small vacancy islands show a high degree of curvature, forming closed-loop step edges. These high curvature regions have high kink densities and a high density of dangling bonds. Such regions pin the Ge islands, and migration away from them is not likely. Larger vacancy islands exhibit straight $[1\bar{1}0]$ steps bounded by step edges of high curvature, roughly aligned along [001]. Deposition at 420 °C produces Ge islands at both [001] and $[1\bar{1}0]$ steps, as seen in Fig. 5(b), but annealing at 460 °C allows some of these islands to migrate from straight $[1\bar{1}0]$ steps toward high curvature [001] edges. This is consistent with our step energy model since the term ε_e/R describes the curvature associated with a vacancy island and, ultimately, the kink density.

Although the Ge islands may redistribute at large vacancy islands after annealing, they remain in contact with the steps. This is in contrast to what has been reported on unsputtered GaAs since the Ge islands moved away from the cleavage steps toward flat terraces.[2] This observation highlights the difference in character between straight cleavage steps and the closed step edges of vacancy islands, which can be related to their contrasting shapes. We also note that the strain field is known to change with step configuration[9] and could possibly be different at the closed-loop steps of vacancy islands.

IV. CONCLUSION

We have demonstrated the potential of ion sputtering as a technique to modify growth via an increase in the overlayer nucleation density. The result is a thin uniform film at a lower coverage than for growth on unsputtered substrates.

The thermodynamic driving force for this change in morphology is the reduction in the dangling-bond density at steps. Indeed, an important feature of this method is its ability to control the substrate surface energy. This paper represents an initial investigation into the feasibility of surface modification and its impact in epitaxy. We note that vacancy islands can also be obtained by dry halogen etching, and this method has the advantage of causing no damage to the bulk material. With this in mind, we plan to investigate systems where the substrate will be modified by halogen etching.

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