Instability of two-dimensional layers in the Stranski-Krastanov growth mode of Ge on Si(111)

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The surface morphology of Ge on Si(111) was studied using scanning reflection electron microscopy and energy dispersive x-ray spectroscopy. We found that in the Stranski-Krastanov growth mode, the nucleation of three-dimensional (3D) Ge islands at coverages above 2.3 bilayers (BL's) initiates disintegration of about 1 BL of a surface component of 2D Ge layers between the islands. Such a succession of structural transformation mainly determines the island size at coverages close to the 2D-3D transition. In the absence of islands, the 2D Ge layer at coverage between 1.5 and 2.3 BL remains thermally stable up to 500 °C. Annealing at higher temperatures causes the transformation of the unstable surface component of the 2D layer into large (up to 3 μm in lateral dimension) flat islands. The surface morphology transforms through the generation of a supersaturated adlayer around the islands, which is similar to Ostwald ripening. [S0163-1829(98)03747-3]

I. INTRODUCTION

The growth of highly strained semiconductor layers often occurs under the Stranski-Krastanov (SK) growth mode in which two-dimensional (2D) growth is followed by formation of 3D islands.[1–6] The 3D islanding in the early stages of heteroepitaxy provides the dislocation-free lattice strain relaxation.[3,7,8] This transition from 2D to 3D growth was recently offered as a unique mechanism for fabricating self-assembled quantum dots.[8–10] For Ge on Si, the SK growth mode leads to the formation of rather large 3D islands with lateral sizes between 30 and 100 nm on Si(111) Refs. 5 and 11 or 3D islands with broadly distributed sizes between 30 and 600 nm on Si(100).[4,12] However, the effects of quantum carrier confinement in electronic devices can be achieves when an island size is about 20 nm or less.[13,14] The dependence of surface morphology on the growth temperature has been observed for the 3D island formation.[4,7,15,16] This dependence indicates the complicated competition between the growth kinetics and the thermodynamics of equilibrium surface morphology. Understanding the surface instability in the formation of self-organized islands is therefore crucially important for reducing the island size.

A pseudomorphic 2D Ge layer on a Si(111)7×7 surface forms at coverages of up to two bilayers (BL's) and has a 5×5 reconstruction. The transition from 2D to 3D growth proceeds when Ge coverage exceeds 2 BL.[2,5,11] The 3D islands are shaped like a frustum of a tetrahedron with (113) facets on the side walls.[5] In this work we show that the 3D Ge-island nucleation leads to the self-induced growth of the islands. This process is supported by the disintegration of the surface component of 2D layers between the islands. This feature mainly determines size of 3D islands at coverages near the transition from 2D to 3D growth. Such a succession of structural transformations in which a surface component of a 2D layer is intermediate and disintegrates after 3D island nucleation seems to be a general feature of the SK growth mode of Ge on Si surfaces. In epitaxy of Ge on Si(100), the equilibrium layer has thickness of 3 ML.[1,17] However, *in situ* observations with reflection high-energy electron diffraction (RHEED) have shown the existence of 2D growth up to 6 ML.[18] A comparison of the data known for Ge on Si(100) Refs. 4 and 19 and obtained here for Ge on Si(111) indicates that the intermediate 2D Ge layer on Si(100) is much less stable than that on Si(111). The better stability provides an opportunity for the stimulated formation of 3D islands.[20]

II. EXPERIMENT

The experiments were carried out in an ultrahigh-vacuum (UHV) chamber with a base pressure of about 1×10^{-8} Pa. The chamber was equipped with an UHV field-emission scanning-electron-microscope gun, a microprobe reflection high-energy electron diffraction detector, a secondary-electron detector, and an energy-dispersive x-ray (EDX) spectrometer. Scanning reflection electron microscope (SREM) images were formed using the (444) specular spot intensity in the RHEED pattern. The SREM images were taken from the sample at room temperature. The kinetic energy and diameter of the incident electron beam were 30 keV and about 2 nm, respectively. Details of the apparatus have been described elsewhere.[21] The 12×1.5×0.4-mm sample was cut from an *n*-type Si(111) wafer with a miscut angle $<1'$ and a resistivity of 5–10 Ω cm. Clean Si surfaces were prepared by flash direct-current heating at 1200 °C. A Knudsen cell with a PBN crucible was used to deposit Ge. The Ge-growth rate was calibrated from the period of the RHEED intensity oscillation during pseudomorphic Ge-layer growth on the Si(111) surfaces. In this calibration, 3D islands appear on the Si(111) surfaces at $T=480$ °C when the Ge deposit reaches coverage between 2.3 and 2.4 BL at a rate of 0.004 BL/s. To estimate the thickness of the Ge on local areas of the surface, the ratios of EDX signals of Ge to Si were obtained. The Ge thickness was calculated on the assumption that this ratio for big areas of the surface corresponds to the average Ge thickness calculated from the deposition rate.

III. EXPERIMENTAL RESULTS

The 3D Ge islands appear on the 2D Ge layer on Si(111) as small dark structures on the light background in the

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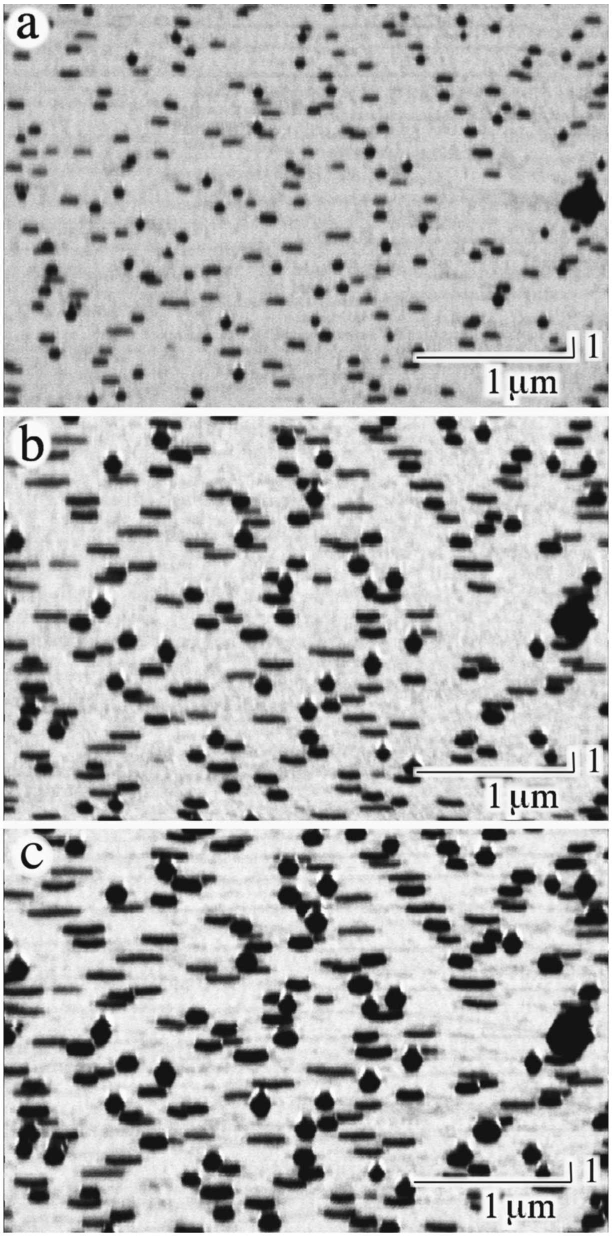

FIG. 1. SREM images of the same surface area with 3D islands appeared on Si(111) after (a) depositing approximately 2.4 BL of Ge at $T=480$ °C, and (b) subsequent annealing for 10 min and (c) for 25 min at the same temperature. A big island at the right side of the images is a SiC island used as a marker.

SREM images. Figure 1(a) shows the SREM image of the surface covered with 3D Ge islands when sample heating was turned off in a few seconds after finishing of about 2.4-BL Ge deposition at a rate of 0.004 BL/s at 480 °C. Curve (*a*) in Fig. 2 shows that 3D Ge islands appear when Ge coverage exceeds 2 BL. This is in agreement with the well-known data for Ge on Si(111).[2,5,11] Figure 1(b) shows that postdeposition annealing for 10 min at 480 °C results in growth of the islands while the number density of islands has not changed. The lateral dimension of islands increased more than two times. The additional annealing caused the further insignificant growth of the islands as shown in Fig. 1(c). The growth of islands during postdeposition annealing can only occur due to Ge diffusion from areas surrounding the islands.

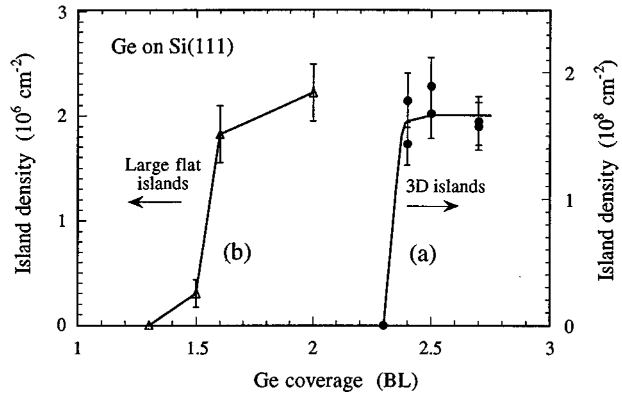

FIG. 2. Number density of Ge islands as a function of coverage. (a) The 3D islands were formed after Ge deposition at $T=480$ °C, and (b) the large flat islands appeared after Ge deposition at $T\approx480$ °C and postdeposition annealing at $T\approx700$ °C. The error bar reflects the difference in island density on different areas of the surface.

This indicates that the thickness of the 2D Ge layer between the islands decreases during annealing. This also indicates instability of the 2D layer. The island growth as a result of post deposition annealing was observed in this work at temperatures down to 380 °C.

The thermal stability of the 2D layer depended on its thickness. At coverages between 1.5 and 2 BL, the 2D Ge layers were thermally stable at temperatures up to 550 °C, and the formation of a few of large flat islands was observed after annealing at higher temperatures [curve (*b*) in Fig. 2]. The temperatures at which this transformation proceeded, decreased as the Ge coverage increased. Figure 3(a) shows the islands on the surface covered with 2.2 BL of Ge after annealing for 15 min at 510 °C. Since thicker areas of a 2D layer have darker contrast in SREM images, the bright areas around the islands in Fig. 3(a) indicates the decrease of the Ge thickness because of Ge diffusion to the islands. Further annealing at higher temperature caused the growth of the flat islands up to 3 μm in lateral dimension and the formation of stripes along the atomic steps, as seen in Fig. 3(b). The brighter stripes of the thinner 2D Ge layer were located on the upper side of the atomic steps. The 2D layer at coverages up to 2.3 BL remains stable against the formation of the large flat islands under annealing for times longer than 10 min at temperatures below 500 °C. A 5×5 reconstruction was observed with RHEED on the 2D Ge layers in each case. This reconstruction is typical for 2D Ge layers on Si(111) when the Ge coverage exceeds 1 BL.[5] The surfaces with either the 3D islands or the large flat islands were thermally stable and did not transform one into the other under annealing up to 700 °C.

The decrease of the Ge thickness between the islands under postdeposition annealing was measured with EDX. The turning-off of sample heating in a few seconds after a finishing of about 2.4-BL Ge deposition at a rate of 0.004 BL/s results in the formation of an approximated 2.2-BL 2D Ge layer between the 3D islands as shown by curves $(a)-(c)$ in Fig. 4 at time $t=0$. The decrease of the thickness because of annealing was faster at higher annealing temperatures. A value of about 1.4 BL characterizes the thickness of the equilibrium 2D Ge layer between the islands as seen in Fig. 4.

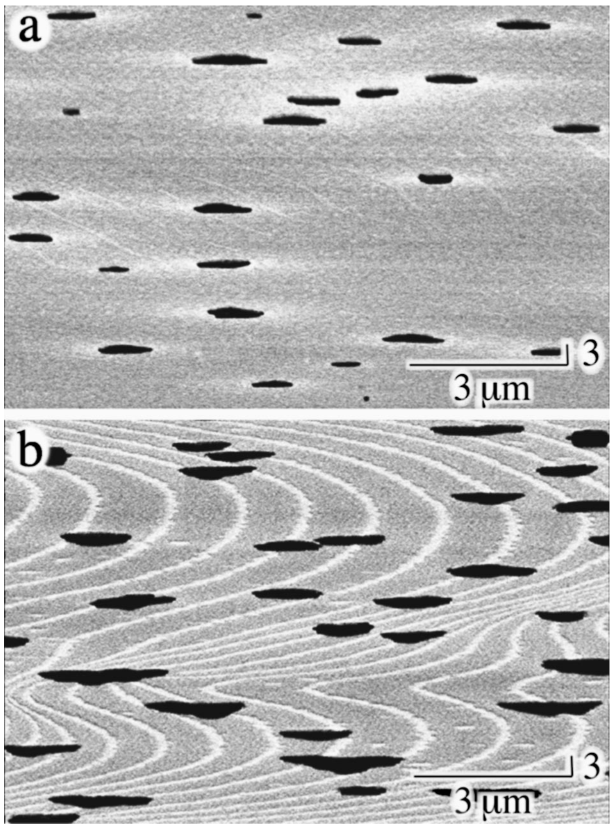

FIG. 3. SREM images of large flat Ge islands appeared (a) after depositing approximately 2.2 BL of Ge at $T=510\ °C$ and subsequent annealing for 15 min at the same temperature, and (b) after additional annealing for 10 min at $T\approx 650\ °C$.

The evolution of the Ge thickness under high-temperature annealing in the case of the formation of the large flat islands is shown by curve (*d*) in Fig. 4. After deposition of about 1.9 BL of Ge at 480 °C, no islands were observed on the surface. This corresponds to the average Ge thickness shown in curve

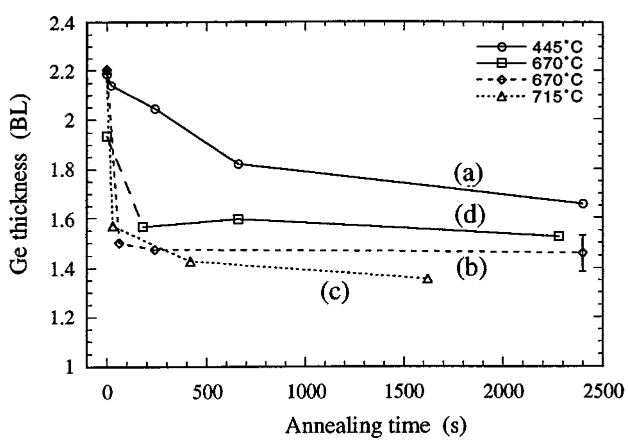

FIG. 4. Thickness of Ge measured with EDX between islands as a function of postdeposition annealing time at various temperatures. Curves (*a*), (*b*), and (*c*) were obtained for surfaces covered with 3D Ge islands. The islands were formed under the Ge flux after depositing approximately 2.4 BL at temperatures: (*a*) 445 °C, and (*b*) and (*c*) 480 °C. Curve (*d*) was obtained for large flat islands appeared after depositing approximately 1.9 BL of Ge at $T=480\ °C$ (time $t=0$) and subsequent annealing for 3 min at $T=670\ °C$.

(*d*) in Fig. 4 at $t=0$. After annealing for 3 min at 670 °C, the large flat islands were formed, and the thickness between 1.5 and 1.6 BL between the islands remained constant in subsequent annealing. A small difference in the Ge thickness between the 3D islands and the large flat islands is seen in Fig. 4. The 2D Ge layer between the islands has areas of different thickness as shown in Fig. 3(b). Since dark fields in SREM images correspond to areas of thicker Ge coverage, it might be suggested that the amount of such areas is smaller between the 3D islands than that between the large flat islands. It might be also suggested that the thickness of the equilibrium 2D Ge layer is slightly smaller between the 3D islands of higher number density.

The results show that the stable surface morphology contains the 3D Ge islands and the 2D Ge layer that is approximately 1.4 BL thick between the islands. Therefore, about 1 BL of the surface component of the 2D Ge layer disintegrates after 3D island nucleation under the deposition flux at coverages between 2.3 and 2.4 BL. Note that the transition from 2D to 3D growth for Ge on Si(111) has been characterized as ''abrupt''.[5,11] This is also seen in Fig. 2 [curve (*a*)]. Our data show that the enhanced growth of 3D islands, which is not proportional to a deposition flux, takes place because Ge atoms appear from disintegration of the surface component of 2D layers. This self-induced island growth initiated by the island nucleation gives the impression of ''abrupt'' island formation.

IV. DISCUSSION

The surface morphology determined by growth kinetics under the Ge flux transforms to the equilibrium shape in subsequent annealing. This transformation occurs through the generation of adatoms. The disintegration of the surface component of 2D layers after nucleation of the 3D islands is similar to Ostwald ripening, in which the difference in adatom density between areas around small and large 3D islands leads to the growth of large islands, while the small islands decrease in size and disappear.[22] The intermediate formation of the unstable 2D layer before nucleation of the 3D Ge islands probably arises from the existence of the large critical 3D Ge islands, i.e., the islands that have a high probability of growing after the attachment of one more Ge adatom. By measuring the flux dependence of the density of the 3D Ge islands, we determined the size of the critical islands to be about nine atoms for Ge on Si(111).[23] The formation of such large critical islands requires a high density of adatoms. This might create a high kinetic barrier for new phase nucleation. The 3D islands nucleated under the Ge flux are coherently strained when not grown much beyond 100 nm.[3,24] In the absence of Ge flux, the adatom density thermally generated by the unstable 2D layer is insufficient to nucleate the 3D Ge islands, and Ge coverage up to 2.3 BL remains as a 2D layer at temperatures below 500 °C. At higher temperatures, under the lattice strain between Ge and Si, the misfit dislocations become easy to form.[25] The formation of dislocations is accompanied by growth of the flat islands which are characterized by a low aspect ratio, i.e., height divided by base length.[11,25,26] This process does not require a high density of adatoms.

Our results show that the most stable formation of Ge on

Si(111) is the 2D layer up to 1.4 BL thick. This layer is stabilized by a 5×5 reconstruction. At larger coverage, the amount of Ge over 1.4 BL is unstable and is expended in growth of islands after their nucleation. At temperatures below 500 °C, the density and size of the coherent 3D islands nucleated at coverages above 2.3 BL strongly depend on the substrate temperature and Ge deposition rate.[23] As a result, the stable surface morphology is determined by the growth kinetics. At $T>500$ °C, the formation of flat dislocated islands relates to the generation of dislocations on the interface between the Ge and the Si. The resulting surface morphology is independent of external growth conditions.

In epitaxy of strained and nonstrained layers, growth of islands, occurring right after nucleation, proceeds by incorporating adatoms from the supersaturated adlayer usually created by the deposition flux.[21] This growth is rapid and therefore makes impossible the controllable fabrication of very small islands of a size not much greater than the critical nucleus, even if the deposition flux is interrupted. Disintegration of the unstable surface component of the 2D layer in the SK growth mode supports the further uncontrollable growth of 3D islands in the absence of deposition flux during subsequent annealing for stable surface morphology. We have recently shown that a stable structure of very small 3D islands can be formed when the oxidized silicon surface containing open Si(111) surface windows is used as a substrate for Ge deposition.[27] In this case the opposite sequence, between formation of a 2D layer and 3D islands on Si(111), takes place during annealing for thermal decomposition of the oxidized layer covered with Ge. In the early period of the annealing, the conditions for nucleation of 3D islands appeared in the Si(111) windows due to Ge diffusion to the windows from surrounding oxidized areas. Then, after complete decomposition of the rest of oxidized layer, the 2D Ge layer was formed on areas between the islands. The 3D islands decreased in size and were able to be completely dissolved into the 2D layer in the following period of annealing if the deposited Ge coverage was less than 1.5 BL.[27] As a result, 3D Ge islands of less than 20 nm in lateral dimension were formed on Si(111) surfaces when the Ge coverage was only slightly thicker than the equilibrium 2D Ge layer between the islands.

Germanium on Si(100) has been considered as a system in which the intermediate formation of unstable 2D Ge layers precedes the appearance of 3D islands.[21,28] Indeed, the thickness of the equilibrium 2D Ge layer on Si(100) is known to be 3 ML,[1,17] whereas the 2D growth up to 6 ML has been observed *in situ* with RHEED in the wide temperature range between 350 and 600 °C.[18] However, the data obtained using scanning transmission electron microscopy have only indicated that the intermediate 2D layer has not grown much beyond 3 ML, even when the growth was carried out at temperatures as low as 375 °C.[19] Instead of unstable 2D layers, the intermediate phase of the ''hut'' clusters, which precedes the formation of the equilibrium ''macroscopic'' clusters, has been found.[4] The existence of this intermediate phase has been considered to be a result of the competition between kinetics and thermodynamics; that is, the hut clusters form easily and hence preferentially form before the energetically preferable but slowly growing macroscopic clusters.[4] The easy formation of the hut clusters explains why the unstable 2D layer has not been observed after Ge deposition on Si(100) in many studies.[1–4,17,24,25] In the epitaxy of Ge on Si(113) Ref. 15 and probably on Si(015),[16] the thickness of the 2D Ge layers at which 3D islands appeared under the deposition flux, decreased when the growth temperature increased. Such a dependence is similar to that previously shown by Marée *et al.*[2] in a phase diagram of Ge on Si(111) and was related here to the existence of unstable 2D layers. Because the thickness of equilibrium 2D layers between 3D islands is expected to be independent of temperature, this dependence indicates the intermediate formation of unstable 2D layers at low deposition temperatures in the cases of Ge on Si(113) and Si(015).

V. CONCLUSIONS

In contrast to the intermediate phase of the hut clusters in the epitaxy of Ge on Si(100),[4] we found the intermediate formation of 2D layers in the case of Ge on Si(111). Approximately 1 BL of the 2D Ge layer disintegrates after 3D Ge island nucleation under the deposition flux at coverages above 2.3 BL. This process supports the growth of the islands, even if the deposition flux is interrupted. The stable surface morphology contains the 3D islands and approximately 1.4 BL of the 2D Ge layer between the islands. At coverages between 1.5 and 2.3 BL, the 2D Ge layer remains thermally stable at temperatures below 500 °C in the absence of 3D islands. Annealing this layer at higher temperatures results in the appearance of large flat islands and an inhomogeneous 2D layer that is approximately 1.5 BL thick between the islands. Formation of intermediate phases seems to be an integral feature of the SK growth mode of Ge on Si. This feature arises from the competition between the kinetics of island nucleation and the formation of stable surface morphology.

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