# Growth mechanisms in Ge/Si(111) heteroepitaxy with and without Bi as a surfactant

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We compare the initial stages of growth of Ge on Si(111) with Bi as a surfactant and without surfactant. At the beginning of growth, three-dimensional islands with a strain relieving dislocation network at their base are formed in both growth systems. These islands can be regarded as seeds of a flat relaxed Ge layer on Si(111). However, such Ge layer forms at later stages of growth only in the growth with Bi surfactant, while the growing Ge layer without surfactant remains rough. What makes the difference and the success of Bi surfactant mediated epitaxy is the lateral growth and coalescence of the seed islands that cover the entire surface within first 15 bilayers of Ge deposition. This happens due to a kinetic limitation of the incorporation of Ge into the growing layer in the presence of surfactant.

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In heteroepitaxy of Ge on Si, a tendency of the system to grow in a Stranski-Krastanov growth mode[1,2] can be suppressed by the presence of a third species on the surface, so-called surfactant. In this surfactant mediated epitaxy (SME), a flat relaxed Ge layer grows on Si in a layer-by-layer mode.[3,4] Moreover, on (111) oriented Si substrates, an effective mechanism for canceling out the strain relieving stacking faults in the bulk of the Ge layer is provided. The strain in the Ge layer is relaxed by a dislocation network confined to the Ge/Si interface in this case.[4–9]

The layer-by-layer growth in SME of Ge/Si(111) is observed for a Ge coverage larger than $\approx 10$ bilayers (BL). At the beginning of growth, a complex transition behavior is observed. Well studied is the action of Sb as surfactant in Ge/Si(111) heteroepitaxy: After growth of a 2 BL thick Ge wetting layer (WL), small undislocated three-dimensional (3D) islands nucleate. Dislocations at the Ge/Si interface are introduced later during coalescence of 3D islands at Ge coverage of $\approx 5$ BL. This relieves the strain in the Ge layer and the growth of Ge approaches the layer-by-layer mode.[6,7]

Recently, Bi as a surfactant in Ge/Si(111) heteroepitaxy has drawn a considerable attention due to its extremely low incorporation in the Ge layer,[10] possibility to remove the Bi after surfactant mediated growth[11] and the ability to greatly suppress Ge-Si intermixing that allowed fabrication of self-organized Ge/Si nanostructures on the Si(111) surface.[12]

Here we present a scanning tunneling microscope (STM) study of the initial stages of growth of Ge on Si(111) by Bi surfactant mediated epitaxy (Bi SME). We compare the growth morphology observed in Bi SME to the growth morphology obtained in the epitaxy without surfactant. In both cases, growth starts with creation of the wetting layer and nucleation of 3D islands with a strain relieving dislocation network at their base. These islands can be regarded as seeds of a flat relaxed Ge layer on Si(111). However, the transition to layer-by-layer growth and subsequent growth of the flat relaxed Ge layer is observed only in Bi SME. This suggests that it is not the nucleation of the strain relieving dislocation network that determines the success of Bi SME of Ge/Si(111). A key mechanism is the spreading of the dislocation network over the surface via lateral growth of the 3D islands. This process is fast and complete in the case of Bi SME due to the growth morphology that is determined by kinetic limitations of Ge incorporation into the growing layer. In the epitaxy without surfactant, seed islands grow mainly in height as the system minimizes its free energy.

Experiments were performed in an ultrahigh vacuum chamber with a base pressure $<5\times10^{-11}$ torr. Si(111) substrates doped to $1\times10^{19}$ cm$^{-3}$ Sb were resistively heated by passing dc current. Standard flashing procedure yields clean Si(111)$7\times7$ surface.[11] For Bi SME, this surface was kept at 500 °C and terminated by Bi evaporated at a rate 1 BL/min (1 BL$=1.56\times10^{15}$ atoms/cm$^2$) from a Knudsen cell. Ge was subsequently deposited at a rate 0.5 BL/min from a graphite crucible heated by electron bombardment. The surface was kept at 500 °C and Bi was codeposited at a rate 1 BL/min. For epitaxy without surfactant, Ge was deposited on a clean Si(111)$7\times7$ surface at 400 °C and 0.5 BL/min. The lower temperature for the epitaxy without surfactant was selected in order to obtain a comparable density of 3D islands in both experiments. After the preparation, samples were quenched to room temperature and observed in situ by STM.

The growth morphology in the initial stages of growth of Ge on Si(111) is qualitatively the same in Bi SME (Fig. 1) and in the epitaxy without surfactant (Fig. 2). In both cases a Ge wetting layer is formed that covers the whole surface. On top of the wetting layer 3D islands nucleate. The strain in the islands is relaxed by a dislocation network at their base. A detailed consideration, however, reveals different mechanisms determining the growth of the Ge layer in the two cases.

In Bi SME, the wetting layer has a thickness of 2 BL. Growth of 3D islands on top of the wetting layer proceeds in a ''modified layer-by-layer mode'': It starts with nucleation of 1 BL high islands on WL terraces [Fig. 1(a)] and 1 BL high decoration of the step edges [Fig. 1(b)]. On top of the 1 BL high islands and the step edge decoration, subsequent bilayers of Ge grow rapidly and 3D islands with height up to 5 BL are formed. These islands are flat mesa structures formed by stacked Ge bilayers [Figs. 3(a) and 3(b)]. The bilayers at island edges can be distinguished in STM. Therefore, edges of 3D islands are no facets. Rather, they are a staircase of 1 BL high steps.

 

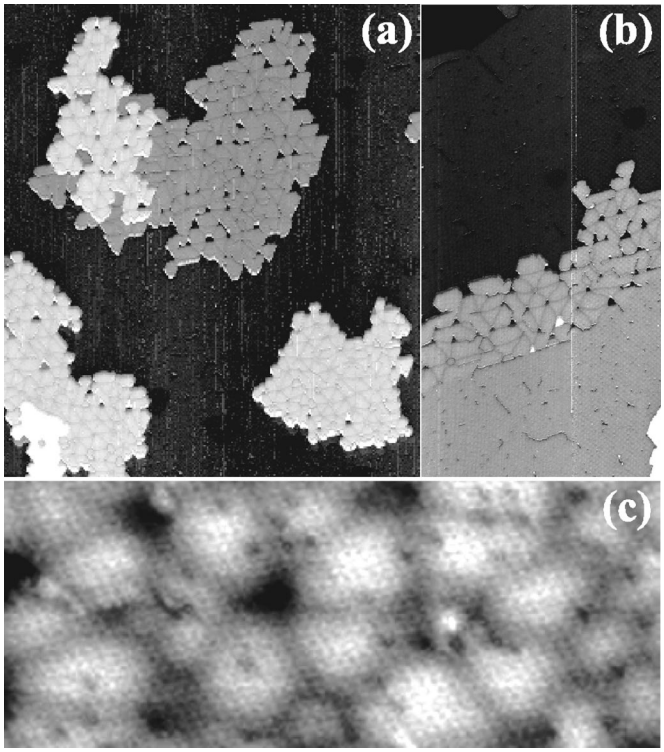


FIG. 1. (a) Island growth on the completed wetting layer in Bi SME of Ge on Si(111). (b) Step edge decoration on the same sample. (c) $\sqrt{3}\times\sqrt{3}$ structure with $\approx 1$ Å high undulations on top of islands and step edge decoration indicates the presence of an underlying dislocation network. Ge coverage is 2.2 BL, image width is 290 nm, 170 nm, 60 nm in (a), (b), (c), respectively.

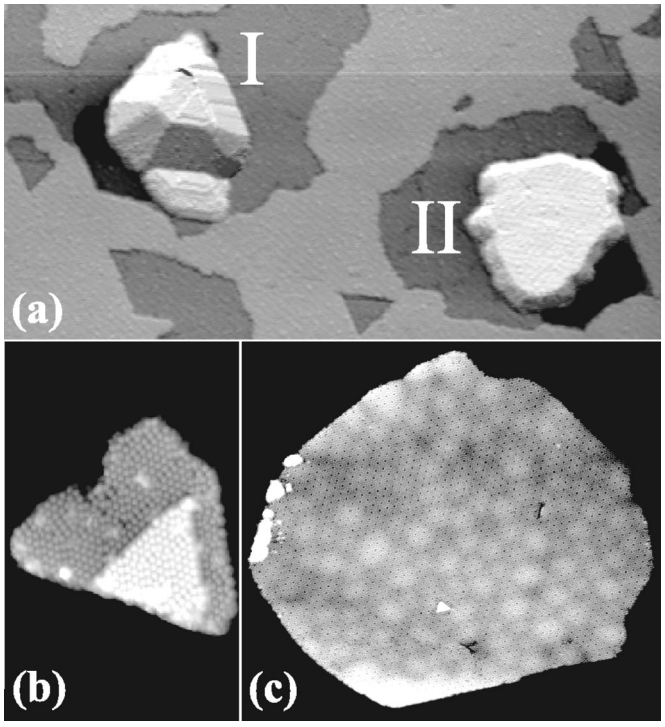


FIG. 2. (a) Two types of islands formed on the completed wetting layer in epitaxy of Ge on Si(111) without surfactant. (b) Tall islands (I in a) show $2\times n$ reconstruction. (c) Flat islands (II in a) show $7\times 7$ reconstruction and $\approx 1$ Å high undulations indicating the presence of an underlying dislocation network. Ge coverage is 3 BL, image width is 230 nm, 25 nm, 160 nm in (a), (b), (c), respectively.

Growth of 3D islands in the modified layer-by-layer mode indicates that in Bi SME, 1 BL high step edges are very effective traps for Ge atoms. This happens when the detachment of the Ge atoms from the step edges and kinks of the growing Ge layer is strongly suppressed. In such a case, the growing strained system loses the possibility to minimize its free energy. Thus, the observed morphology of Ge layer in Bi SME (Fig. 1) is *kinetically determined*. This has been confirmed in an experiment when the sample with Ge coverage 2.2 BL prepared by Bi SME at 500 °C (Fig. 1) was annealed under continuing Bi flux at increased temperature of 560 °C for 80 min. Obtained morphology differed substantially from that of Fig. 1. Ge accumulated in islands with height 10–40 BL and well developed facets. As observed in the STM, the $\sqrt{3}\times\sqrt{3}$ structure on the sample was not disturbed after annealing showing that the used Bi flux was sufficient to compensate for the Bi desorption at elevated temperature.[13]

Kinetic limitations have been mentioned as the cause of the layer-by-layer growth also in the previous studies of surfactant mediated epitaxy, As SME of Ge/Si(001) (Ref. 3) and Sb SME of Ge/Si(111).[7,14] As a cause of the kinetic limitations, smaller effective diffusion rate of Ge adatoms was mentioned based on observation of higher island density in the growth with surfactant.[15] In our study, density of observed islands is approximately the same in Bi SME and in the growth without surfactant. This points to another kinetic limitation identified in SME, in particular, to a slow exchange/deexchange process by which the Ge atoms diffusing on top of a surfactant layer incorporate into the growing Ge layer below the surfactant and vice versa.[16,17]

Top facets of the 3D islands show a $\sqrt{3}\times\sqrt{3}$ structure with $\approx 1$ Å high undulations indicating the presence of a strain relieving dislocation network in the Ge/Si interface underlying the islands [Fig. 1(c)].[6] The undulations can be observed already on top of the initial 1 BL high islands, i.e., at places, where Ge in the third bilayer started to accumulate [Figs. 1(a) and 1(b)]. The undulation network extends to the edges of 1 BL high islands which are aligned with the dislocation lines of the network. This shows that the lateral growth of the third Ge bilayer and the formation of the dislocation network take place simultaneously. Thus, in spite of the kinetic limitations in Bi SME, the strain relieving dislocation network is created at the base of all 3D islands at the moment when they are formed on the WL. This process is unique to Bi SME of Ge/Si(111) and contrary to, e.g., Sb SME of Ge/Si(111). There the strain relieving dislocation network at Si/Ge interface forms only after coalescence of 3D islands, much later than in Bi SME.[6–8]

In the growth without surfactant, the wetting layer has a thickness of 3 BL. 3D Ge islands are formed on the completed WL without any intermediate stage observable in our experiment [Fig. 2(a)]. Islands are truncated pyramids with well developed facets. Faceting shows that the system effec-

tively minimizes its surface free energy during growth. This signalizes fast reevaporation of Ge atoms trapped in surface structures back to gas of diffusing adatoms. Under such conditions, the strained growth system minimizes the total free energy by forming 3D islands, a process called strain relieving surface roughening.[18] In and around the islands the strain energy is decreased by elastic strain relief, overweighing the increase of the surface free energy due to the increased surface area. Formation of strain relieving 3D islands is a fast, many particle process as observed in real time STM observations.[19] The appearance of these islands and the morphology in Ge/Si(111) epitaxy is *thermodynamically driven.*

Two types of islands are observed: tall [I in Fig. 2(a)] and flat [II in Fig. 2(a)]. Tall islands have been described in detail in previous studies.[2,20,21] They have a height of $\approx 40$ BL, and represent $\approx 60\%$ of the island population. The height of these islands allows them to relax elastically by outward relaxation in the upper layers achieving the Ge lattice constant at the topmost layer as indicated by the presence of Ge $2\times n$ reconstructions, Fig. 2(b).[2,20–22] In this work, we present a detailed observation of the second type of islands. The flat islands have a height of $\approx 15$ BL and represent $\approx 40\%$ of the island population. Similarly to Bi SME, a network of $\approx 1$ Å high undulations on top of the flat islands indicates a strain relief via formation of dislocation network at the base of these islands [Fig. 2(c)]. The topmost layer of the flat islands is not relaxed completely, as indicated by the presence of Ge(111)$7\times 7$ reconstruction.[22] Introduction of dislocations in the flat islands is a competing strain relief mechanism to the surface roughening.[18] This mechanism is rather effective under the growth conditions employed in this work, despite the fact that in a highly strained Ge/Si(111) system the nucleation of 3D islands represents the dominating strain relieving mechanism.[18] In the flat islands, strain energy is relieved to great extent by the dislocation network. Therefore, their minimal energy shape [II in Fig. 2(a)] has a smaller height than that of the tall islands [I in Fig. 2(a)].

An unexpected observation is that *both* in Bi SME and epitaxy without surfactant, 3D islands with the strain relieving dislocation network at the island base appear [Figs. 1(a), 1(b), and 2(c)]. These islands can be considered as seeds of a flat relaxed Ge layer with abrupt Ge/Si interface. Such Ge layers are one of the goals in the Ge/Si(111) epitaxy. They have been prepared so far only in surfactant mediated epitaxy.[4,10] Observation of seeds of the flat relaxed Ge layer in both Bi SME and in the epitaxy without surfactant shows that it is not the nucleation of the strain relieving dislocations at Ge/Si interface that determines the success of surfactant mediated epitaxy.

As we demonstrated above, the early stages of Bi SME of Ge/Si(111) and normal epitaxy of Ge/Si(111) are determined by different growth mechanisms. The growth is kinetically determined in the former case, while it is thermodynamically driven in the latter. The different growth mechanisms cause the different evolution of the morphology in later stages of growth, particularly the different evolution of the 3D islands with the strain relieving dislocation network at their base we consider as seed islands of a flat relaxed Ge layer.

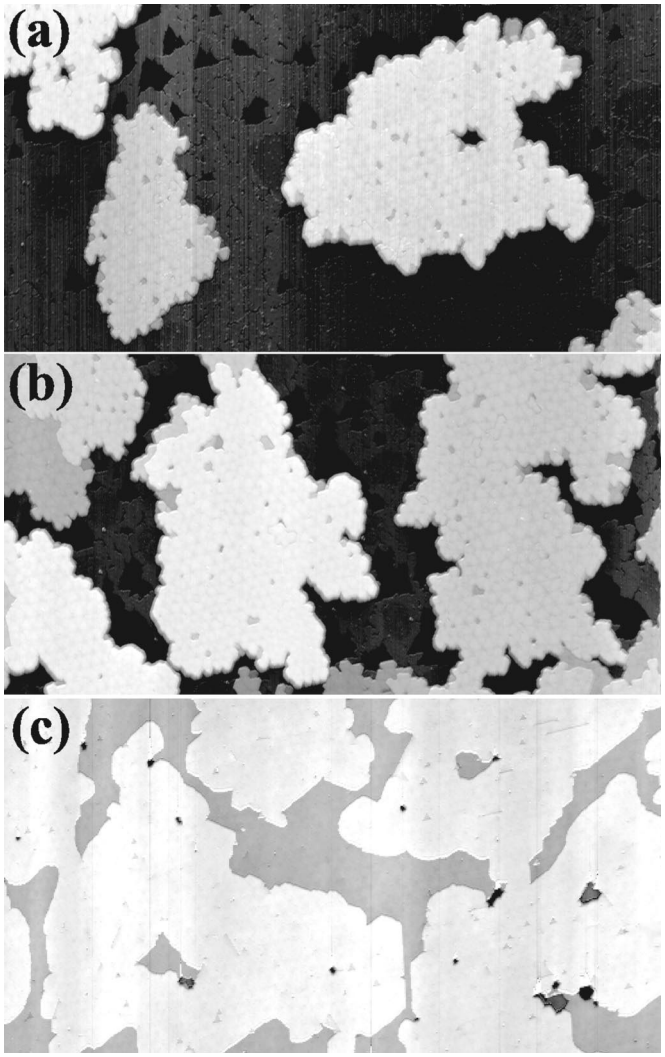


FIG. 3. (a) and (b) In Bi SME of Ge on Si(111), 3D islands with an underlying dislocation network grow preferentially in the lateral direction. Ge coverage is 2.5 BL in (a), 3.5 BL in (b). The dislocation network extends over the whole area of the islands. Growing islands spread the dislocation network over the surface. (c) At a Ge coverage of 15 BL the islands have coalesced, the dislocation network covers the whole Ge/Si interface and relaxed Ge layer grows in a layer-by-layer mode. Image width is 270 nm in (a), (b), (c), respectively.

For Bi SME, the evolution of the morphology of the seed islands upon further deposition of Ge is displayed in Fig. 3. Kinetic limitations due to the presence of the Bi surfactant cause that the Ge atoms are quickly incorporated at 1 BL high step edges. This causes a fast propagation of the edges of the seed islands that are a staircase of 1 BL high steps in the lateral direction. Seed islands double their area between 2.5 BL of deposited Ge [Fig. 3(a)] and 3.5 BL of deposited Ge [Fig. 3(b)]. Due to the easy nucleation of the dislocation network in the Ge/Si interface at places, where the Ge layer thickness exceeds 2 BL [Figs. 1(a) and (b)] the strain relieving dislocation network is spread over the surface as the seed islands grow laterally. After the seed islands coalesce, the rest of the WL between islands are covered by Ge and the strain relieving dislocation network spreads to the whole

Ge/Si interface. Quick incorporation of the Ge atoms into 1 BL high step edges facilitates filling of the pits between coalesced islands with Ge. Ge layer becomes homogeneous and the growth of Ge proceeds in a layer-by-layer mode at coverage larger than $\approx 15$ BL [Fig. 3(c)], yielding a flat relaxed Ge layer.

In normal Ge/Si(111) epitaxy, seed islands are the 3D islands identified in Fig. 2(c). Their shape is determined by the tendency of the strained growth system to minimize its free energy. This tendency causes that the seed islands grow initially preferentially in height. The growth in height may be slower than the growth of the tall islands[20,21] [Fig. 2(b)] due to the presence of the strain relieving dislocation network, however, the tendency to grow in height remains. An additional effect slowing down the lateral growth of the seed islands in normal Ge/Si(111) epitaxy is their higher height to width ratio compared to the seed islands in Bi SME. For the same advance of the island edge, more material has to be incorporated. The incorporation of material into the sides of the seed islands may be also slowed down by a kinetic limitation to incorporation of material into the facetted strained islands.[23,24] Growth of the seed islands in normal Ge/Si(111) epitaxy thus proceeds in the Stranski-Krastanov mode where the coalescence occurs at a high coverage and results in rough dislocated Ge layers.

To conclude, we studied the initial stages of growth of Ge on Si(111) with a Bi surfactant and without surfactant. In both cases, flat 3D islands with strain relieving dislocations at their base are formed in the initial stages of growth. These islands can be considered as seeds of a flat relaxed Ge layer with dislocations confined to Ge/Si interface. However, such Ge layer evolves from the seed islands only in the Bi surfactant mediated epitaxy. We attribute this to kinetic limitations of incorporation of Ge into the growing layer in the presence of the surfactant.

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