Universality in shape evolution of Si$_{1-x}$Ge$_x$ structures on high-index silicon surfaces

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Abstract – The shape evolution of MBE grown Si$_{1-x}$Ge$_x$ islands on ultraclean reconstructed high-index Si(5512), Si(557) and Si(553) surfaces has been studied experimentally and explained using a phenomenological kinetic Monte Carlo (kMC) simulation. We show that a self-assembled growth at optimum thickness leads to interesting shape transformations, namely spherical islands to rectangular rods up to a critical size beyond which the symmetry of the structures is broken, resulting in a shape transition to elongated trapezoidal structures. We observe a universality in the growth dynamics in terms of aspect ratio and size exponent, for all three high-index surfaces, irrespective of the actual dimensions of Ge-Si structures. The shape evolution has been simulated using kMC by introducing a deviation parameter ($\epsilon$) in the surface barrier term ($E_D$) to take the effect of anisotropic diffusion as one of the plausible mechanisms.

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Introduction. – The implementation of Ge and Si$_{1-x}$Ge$_x$ nanostructures into Si-based devices is of great potential for future high-speed devices, due to advantages like enhanced carrier mobility and smaller bandgap [1–3]. Growth of Ge islands on clean Si substrates (particularly on low-index–oriented) has been extensively studied as a model system to understand hetero-epitaxy and Stranski-Krastanov (SK) growth mechanism [4,5]. But, the study of Ge growth on high-index surfaces, such as Si(5 5 12), Si(5 5 7) and Si(5 5 3), is an area where very limited research work has been carried out [6–8]. Previous study by Kim et al. [7] reported on relatively thinner Ge growth on Si(5 5 12) and did not observe any shape transformation of the Si-Ge structures. For the Ge on Si system, strain relief and diffusion play a role in determining the morphology and composition of Ge or Si-Ge structures [4,5,9]. In the present work, we have observed the variation in the size of the Si$_{1-x}$Ge$_x$ structures depending on the substrate orientation while having the similar aspect ratios and size exponent values for all three substrate orientations. The variation in the size of the islands has been explained by considering the experimentally observed composition of the structures and strain associated in them. The universal nature of shape evolution and exponent values are simulated with 2D kMC simulations. With the interesting reconstructions on high-index surfaces and anisotropic diffusion dominating during the direct current heating conditions, the present work stimulates the self-assembly growth related work in the area of nanoscience and nanotechnology.

A high-index (vicinal) surface is misoriented from the low-index plane by a small angle $\theta$ (vicinal angle or miscut angle), relative to low-index surfaces, e.g., [001] or [111]. The anisotropic surface reconstruction inherent to high-index silicon surfaces makes them potentially significant substrates for electronic device fabrication. Reconstructed high-index silicon surfaces consisting of alternating terraces and atomic steps can be used as templates to form aligned one-dimensional (1D) nanostructures [10–12]. Atomic steps on the high-index silicon surfaces are responsible for many surface dynamic processes like surface migration and step diffusion. It is possible to use the high-index substrates for the growth of self-organized nanostructures [6]. Among the high-index silicon surfaces, Si(5 5 12) is oriented 30.5° away from (001) towards (111) with one-dimensional periodicity over a large unit cell width [10,13]. Si(5 5 7) with vicinal angle of 9.45° from (111) towards (112) [14] and Si(5 5 3), tilted at $-12.27^\circ$ from the (111) plane towards the (001) plane [15], are

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important high-index Si surfaces. In all the above vicinal surfaces, the step edges are along ⟨1¯10⟩ direction.

It is known that strained epitaxial layers tend initially to grow as dislocation-free islands and as they increase in size, may undergo a shape transition [9,16]. Below a critical size, islands can have a compact symmetric shape. But at larger sizes, they adopt a long shape, which allows better elastic relaxation of the island’s stress [9,16,17]. Tersoff and Tromp proposed a model to explain the growth kinetics involving a shape transition at a critical size by finding an expression for energy of dislocation-free strained islands [16]. Also, Heyn reported the kinetic Monte Carlo (kMC) methods to study the influence of the anisotropy of surface diffusion and of the binding energies [18]. Kinetic Monte Carlo methods have been used to study the formation of nanoisland structures in a number of works [19,20]; however, shape transition phenomena have hardly been studied.

Experimental details. – The experiments discussed in the following were performed in ultra-high vacuum (UHV), at a base pressure of \( \sim 2.5 \times 10^{-10} \) mbar in a custom built molecular beam epitaxy (MBE) system [21]. Samples of Si(5 5 12), Si(5 5 7) and Si(5 5 3) were prepared from the commercially available high-index surfaces (boron doped wafers, of resistivity of 10–15 Ω cm). Substrates were degassed at 600 °C for about 12 hours followed by repeated flashing (with direct current heating) for 30 s at a temperature of 1250 °C to remove the native oxide layer to obtain a clean and well-reconstructed surface. The reconstruction has been confirmed with in situ reflection high energy electron diffraction. The temperature was monitored with an infra-red pyrometer calibrated with a thermocouple attached to the sample holder. Ge was deposited to various thicknesses of 3 to 10 monolayer (ML) at substrate temperature 600 °C (with direct current heating (DH)). The samples were then post annealed at a temperature of 600 °C for 15 minutes by DH method. Also a set of samples were prepared with radiative heating (RH) (where heating is achieved through a filament underneath). The post growth characterization of the samples was carried out ex situ by field emission gun based scanning electron microscopy (FEGSEM) with 20 kV electrons. We have used the P08 beam line at Petra III for carrying out high-resolution X-ray diffraction (HRXRD) measurements for compositional analysis.

Results and discussion. – Figures 1(a) and (b) depict the FEGSEM image for 3 ML and 5 ML thick Ge film deposited on the Si(5 5 12) substrate. As shown in fig. 1(a), the island structures are found to be rectangular in shape for a 3 ML and 5 ML Ge deposition. For the 8 ML and 10 ML deposition cases, we observe aligned trapezoidal structures (figs. 1(c), (d)). The composition of these nanostructures has been characterized by the synchrotron-based high-resolution X-ray diffraction (HRXRD). The HRXRD showed presence of graded Si\(_{1-x}\)Ge\(_x\) system for the Si(5 5 12) and is also confirmed by RBS measurements. RBS measurements show no prominent graded Si\(_{1-x}\)Ge\(_x\) structures for the case of Si(5 5 3) and Si(5 5 7) substrate orientations (data not shown). In fig. 2, the HRXRD data show corresponding compositions of Si\(_{0.25}\)Ge\(_{0.75}\), Si\(_{0.5}\)Ge\(_{0.5}\), Si\(_{0.75}\)Ge\(_{0.25}\) as seen from the three peaks. It should be noted that this three-layer system has been formed in one-step growth process on high-index planes. Under the similar conditions, such graded Si-Ge alloy was not formed for low-index plane systems, such as Si(100) and Si(111). The formation of graded Si-Ge alloy is a necessary condition for forming large (micrometer size) island structures. As we do not observe the graded Si-Ge alloy structures in case of Si(5 5 7) and Si(5 5 3), the island structures are an order of magnitude smaller compared to
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Si$_{(5\,5\,12)}$, though they have similar shapes. This shows the importance of strain, as for the Si-Ge systems, the lattice mismatch is reduced by formation of an alloy, resulting in larger structures.

In fig. 3, Ge growth of overlayer 3 ML to 10 ML on Si$_{(5\,5\,7)}$ has been shown where spherical nanoslabs and rectangular nano rods are formed for 3 ML and 5 ML thicknesses (figs. 3(a), (b)) and trapezoidal structures in the case of 8 ML and 10 ML Ge growth (figs. 3(c), (d)). We have maintained the same growth condition for Si$_{(5\,5\,3)}$ substrate and seen that the growth kinetics and shape transformation follow in a similar way resulting from rectangular nanorod to nanotrapezoid, as shown in fig. 4.

We have measured the length and aspect ratio (length/width) of all the Ge-Si structures which has been shown in a tabular form in table 1 and table 2. In the case of Ge/Si$_{(5\,5\,12)}$ system, the size of the aligned structures are of micrometer size. But for the Si$_{(5\,5\,7)}$ and Si$_{(5\,5\,3)}$ systems, the size of the aligned structures are of nanometer size, though the shape evolution and also the aspect ratios are similar to that of Si$_{(5\,5\,12)}$. From table 1, it is clearly seen that with increasing thickness, the size and aspect ratio of the Si-Ge alloy structures increase accordingly. The aspect ratios of the Si-Ge elongated structures on Si$_{(5\,5\,12)}$, Si$_{(5\,5\,7)}$ and Si$_{(5\,5\,3)}$ increase in a similar fashion as a function of increasing Ge growth coverages, which has been shown in table 2. We found from our experiments that the mean length of islands $\langle l \rangle \sim t^\alpha$, where $t$ is the time of deposition. The length exponent from the experimental data is found to be about 0.75 ± 0.02 for the case of the direct heating and 0.5 ± 0.01 for the radiative heating case in all the three systems (table 3). In fig. 5, the log-log plot for size (length) vs. deposition time shows almost same slope ($\alpha$) irrespective of the size of the Si-Ge structures on the three substrates.

Theoretical modeling. — The kMC were performed on a $L \times L$ square lattice with $L =$ 100, 200, 300 and 400. We would like to emphasize that this model is a general model which describes the shape transition on a two-dimensional square lattice where the dynamics is constrained by the underlying symmetries of the high-index surfaces. As we have described earlier, the step edges on the Si surfaces are directed along the (110) direction. The larger side of the trapezoidal structures is aligned along the same direction (i.e., (110)). In view of this, a coordinate system has been chosen such that the $x$-axis is directed along perpendicular to the step edges. In this coordinate system, the trapezoids have a reflection symmetry about the lines parallel to the $x$-axis and passing through the center of the trapezoids. We define horizontal bond as a pair of nearest-neighbor atoms having the same $y$-coordinates and vertical bond having the same $x$-coordinates, respectively. The hopping rate of an adatom is given by

$$w = v_0 e^{-(E_D+n_1E_1+n_2E_2+n_3E_3)/k_B T},$$

(1)
where \( k_B \) is the Boltzmann constant, \( T \) is the temperature and \( \nu_0 = 2k_BT/h \) is the vibrational frequency in the direction of the hopping. A typical value for our case is \( \nu_0 = 3.6 \times 10^{13} \text{ s}^{-1} \). The quantities \( E_1, E_2 \) and \( E_3 \) denote the binding energies for the horizontal bond, vertical bond and the next-nearest–neighbor interaction, respectively; \( n_1, n_2 \) and \( n_3 \) are the number of horizontal bonds, vertical bonds and next-nearest neighbors, respectively. \( E_D \) is a surface barrier term. For \( E_D \) and \( E_i \), (i = 1, 2, 3) constant, we obtained spherically symmetric island structures in the kMC simulation, since the binding energies are same for all bonds and surface barrier term is independent of the direction. To obtain asymmetrical structures, we need to break the hopping symmetry. In our model, we introduce anisotropy through binding energies of different types of bonds and the dependence of the surface barrier on the direction of hopping. For the isotropic cases, however, the hopping rate depends only on the nearest- and next-nearest-neighbor interactions but does not depend on the specific arrangement of the neighboring atoms. In our experiment, the shape transformation has been observed when Ge is grown under the DH condition \([8]\). To simulate the experimentally observed shape variations, the surface barrier term is modified, so that it allows an asymmetric hopping of an adatom along the direction perpendicular to the step edge (i.e., \( \pm x \) direction). The values of \( E_D \) along the step edges are same in both \( \pm y \)-directions. When \( E_1 = E_2 \) and \( E_D \) does not depend on the direction of hopping, spherical islands are formed. Symmetric elongated structures are formed for \( E_2 > E_1 \) and \( E_D \) uniform in all the directions of hopping. Trapezoidal islands can only be obtained when an asymmetric hopping term is present. The values of \( E_D \) are defined as follows: a) \( E_D = E_0(1 + \epsilon) \) for hopping along the positive \( x \)-direction; b) \( E_D = E_0(1 - \epsilon) \) for hopping along the negative \( x \)-direction; and c) \( E_D = E_0 \) for hopping along the \( y \)-axis where \( \epsilon \) depends only on the magnitude of the current (but for the simulations, this is a parameter only). Also, \( 0 < \epsilon < 1 \), so that, the probabilities are strictly less than unity. Note that, when \( \epsilon = 0 \), it reduces to the RH case and \( \epsilon > 0 \) leads to the DH case. When \( E_2 > E_1 \), anisotropic island forms as in the case of ref. \([18]\) and isotropic islands form for \( E_2 = E_1 \) as in ref. \([22]\). Therefore, in our kMC simulations, a nonzero value of \( \epsilon \) should correspond to the MBE growth done under DC heating. The mean shape of islands for this case is found to be trapezoidal.

We follow the kMC algorithm as given in ref. \([22]\). We set the total coverage as \( \theta \) and the total number of Monte Carlo steps as \( N_{MC} \). Particles are deposited at a constant flux \( \theta/N_{MC} \). Here \( \theta \) may not be exactly correspond to the experimental coverages, since here, we are modelling the island growth by a 2D kMC simulation. However, we are successfully able to show that with an increase in coverage \( \theta \) there is a shape transformation. We define a dimensionless scale parameter, \( \phi = E_0/K_BT \), where \( E_0 \) is the surface energy barrier of the system when \( \epsilon = 0 \). This sets the time step for the simulation. An atom with empty adjacent site is called active. An active atom is chosen at random and a single diffusion event is allowed to occur with a probability consistent with equation 1. If an atom is already there on the site to which it chooses to hop, then hopping fails. Time is incremented irrespective of whether the hopping is successful or not. The following parameters were used for our kMC simulations: \( \phi = 1.0, E_0 = 1.0, E_2 = 6.0, E_3 = 0.5, \theta = 1.0, \epsilon = 0.8 \) and coverage is 2.5%. It is important to note that the relative strength of the energy values is crucial in determining the shape of the structures.

The above set of energy parameters is one such example. The absolute values of binding energies and diffusion barrier are not important here since energy scales with temperature. In kMC simulations, the island structures with the desired properties are found only in a specific range of energy values. Although we cannot fix the exact values of these energy parameters, we can estimate the order of magnitude. Experimentally we have found that the mean island size varies linearly as function of temperature. From our kMC simulations, we obtained the mean island size as a function of energy (see fig. 6). We note that for \( 1.5 < E < 3.0 \), the mean island size shows a linear dependence on \( E \). Therefore for \( E_3 \) and \( E_D \) fixed at the above values, we need to specify values of \( E_{1,2} \) in this window. However, if we take other values of \( E_3 \) and \( E_D \), then this window may shift or shrink. For the DH case (i.e., \( I \neq 0 \)) the value of \( \epsilon \) has to be specified. Nonzero values of \( \epsilon \) give asymmetric hopping which, in turn, lead to the formation of elongated trapezoidal island for \( E_2 > E_1 \). Since \( 0 < \epsilon < 1 \), we choose \( \epsilon = 0.8 \) which shows elongated trapezoidal structures as seen in the
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Fig. 6: (Colour on-line) Mean island size vs. energy in kMC simulations.

Fig. 7: (Colour on-line) Snapshot of kMC island growth: (a) spherically shaped islands at $\epsilon = 0$, $E_1 = E_2$; (b) $\epsilon = 0.8$, $E_1 < E_2$ rod-like structures at coverage 0.29; and (c) $\epsilon = 0.8$, $E_1 < E_2$ showing shape transition by forming trapezoidal island structures at coverage $\theta$.

Critical area of shape transitions. – The above-mentioned high-index surfaces have one-dimensional symmetry. In this case, the island growth up to a critical size has a one-dimensional wire or quasi-one-dimensional rod shape. Beyond the critical size, the island grows in trapezoidal shape. At this point, let us try to make a quantitative idea of shape transition. To do so, we have measured the individual length, width and area of the Si-Ge structures for all thicknesses from 3 ML to 10 ML. We calculated the area of individual structures. Here, one obvious question, one can ask is that, what is the optimal area of an island to attain rectangular rod shape? To find the answer, we have plotted $L_1, L_2$ vs. area plots (fig. 8). Figure 8(a) shows the shape transition plot for Ge/Si(5 5 12) system. Here we notice that, the Si-Ge island grows in rectangular form ($L_1 = L_2$) up to a critical size following the one-dimensional symmetry of the substrate. For the largest rectangular rod, the area is $L_1 \times L_2 = 6.48 \mu m^2$ (measured). Beyond this critical area, the island grows in trapezoidal shape ($L_1 > L_2$). The plot clearly shows a bifurcation at the point of optimal area. When $\frac{L_1}{L_2} = 1$, the curve is linear and while $\frac{L_1}{L_2} > 1$, the curve bifurcates to show the discontinuity. Figures 8(b) and (c) show the similar plots for the Ge/Si(5 5 7) and Ge/Si(5 5 3) systems, where the critical areas for the shape transformations are 10845.6 nm$^2$ and 9456.8 nm$^2$, respectively. The plots are in reasonable agreement with the gross features of the Tersoff and Tromp theory [16].
Conclusion. – In summary, we report the shape evolution of MBE grown Si$_{1-x}$Ge$_x$ islands on reconstructed high-index Si(5 5 12), Si(5 5 7) and Si(5 5 3) surfaces. We show that a self-assembled growth at optimum thickness leads to interesting shape transformations, namely, spherical islands to rectangular nanostructures and then to elongated trapezoidal structures. We have experimentally observed a universality in the growth dynamics of the islands for all three high-index surfaces. Our kMC simulations show that such variations can be understood by introducing a deviation parameter $\epsilon$ in the surface barrier term $E_D$. The experimentally observed shape variations are in good agreement with kMC simulations. This suggests the role of the stochastic process involved in the shape transitions of nanoscale structures.

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