The structural and morphological evolution of low dimensional Fe-Ge structures (i.e. 0D/1D) during the reactive deposition of Fe on Ge(001) has been comprehensively studied by using a ultra-high vacuum in-situ transmission electron microscope. The reactive deposition of Fe on Ge(001) lead to the formation of hexagonal Fe13Ge8 islands on the cubic Ge surface at all temperatures studied. It has been observed that the epitaxial relationship between the hex-Fe13Ge8 islands and underlying substrates keeps the same at all growth temperatures. However, the morphology of these islands shows remarkably different geometry with different deposition temperatures. It was observed that all islands could grow into Ge(001) substrate through endotaxial growth. At kinetically constrained regime, islands morphology evolved from small compact shape to wire-like one, mainly attributed to anisotropic ledge diffusion and corner barrier. However, at high temperature, NWs disappeared while dome-like islands formed with much larger size than those grown at low temperatures. By comparing the total energy of the islands formed below and above 510 °C, these islands formed at higher temperature have a lower total surface/interface energy per unit volume. The shape transition, i.e. from NW to domes observed in high temperature regime is therefore driven by minimization of total surface and interface energies of the growing islands, more akin to the growth in the equilibrium regime. On the basis of the observations on Fe growth on Ge(001), it has been demonstrated that self-assembly nanowire can be formed not only due to strain induced instability as predicted by conventional models, but also by the ‘endotaxy’ growth. It also illustrates that nanowires can be formed through kinetic constraints in terms of anisotropy in ledge diffusion and corner barriers. More significantly, this study shows that not all the compact islands or nanowires are necessary thermodynamically equilibrium structures. In this Fe13Ge8/Ge material system, large compact islands formed at high temperatures are equilibrium structures instead of the nanowire formation. In addition, this work suggests that temperature can provide an avenue to selectively control dimensionality (i.e. 0D and 1D) and configuration (i.e. facets evolution) of growing islands at both thermodynamically limited and kinetically constrained growth regimes.

**Keywords:** Endotaxy; Equilibrium; Kinetic; Interface; Transmission electron microscopy

### 1. Introduction

Low-dimensional nanostructures, such as quantum dots, nanorods, nanotubes, and nanowires (NWs), are essential building blocks for bottom-up approaches in nanotechnology device fabrications [1,2]. Self-assembly growth has been approved as an efficient way to fabricate the uniformly ordered nanostructures in the bottom-up process. A fundamental issue for self-assembly growth is the understanding of the physical mechanisms dominating the morphology and size distribution of nanostructures [3,4]. Therefore, in order to fabricate well-controlled nanostructural materials, e.g., with uniform morphology and/or narrow size distribution, it is desirable to obtain detailed knowledge of the fundamental growth processes. The morphological evolution of low dimensional structures in self-assembly system is determined by the complex interplay between materials surface energy, interface energy, and strain energy [5]. Taking the widely observed heteroepitaxial growth for example, it involves the growth of dissimilar materials with different lattice parameters on top of another. The crystal structure of deposited layer can have either similar (e.g. cubic on cubic) or different (e.g. hexagonal on cubic) crystallographic systems. It is well established that the driving force for heteroepitaxial structure formation is the anisotropic strain arising from lattice mismatch in the heteroepitaxial growth process [6,7].

In this study, we investigate Fe-Ge nanostructure formation over a temperature range from 350 °C to 675 °C. Systematic observations of the nanostructure morphology transition as a function of deposition temperature are performed accordingly. In-situ ultra-high vacuum transmission electron microscopy (UHV-TEM) can provide a unique view into nanostructure formation, and was utilized to explore the kinetics of the reaction and growth mechanism of Fe-Ge nanostructures during epitaxial growth. Previous studies have reported that most theoretical and experimental reports of NW formation in other systems were performed at high temperatures (i.e., ~ 800 °C) and assumed that growth occurred due to equilibrium conditions driven by thermodynamics considerations [8,9]. Therefore, it is also necessary to explore whether NWs can be formed at high deposition temperatures, as well as, whether the NWs in this material system are in the kinetically constrained or equilibrium state. This can provide us fundamental understanding of the growth mechanism for heteroepitaxial system.
2. Experimental

The Fe-Ge material system has been investigated by examining the shape evolution of Fe-Ge islands during each individual deposition process, using the same deposition flux at different deposition temperatures on different samples. Experiments were performed in an in-situ JEOL2100 UHV-TEM operated at 200 kV using a JEOL double-tilt heating specimen holder. After the specimen is thermally cleaned in the TEM chamber by out-gassing and flashing to obtain atomic cleaned surface, it is ready for the reactive deposition at ultra-high vacuum (10^{-9} Torr) condition. Constant deposition flux has been used throughout all samples even though the deposition temperatures are different. Ex-situ cross-sectional TEM observations were also carried out accordingly. The experimental set up and procedures have been discussed in details elsewhere [10,11].

3. Results and discussion

3.1 In-situ TEM observation of island growth on Ge(001)

Figure 1 is the time sequence of TEM bright-field (BF) images of Fe-Ge island growth at 450 °C on Ge(001) substrate. Fig. 1a is a clean Ge(001) substrate before deposition. When the electron beam evaporator shutter was opened, spatially random islands begin to nucleate on the Ge(001) surface with initial elongated or rectangular shape (Fig. 1b). As reactive deposition going on, nucleated islands increase their sizes rapidly by increasing in both length and width while their length increase much faster than width, which leading to the formation of rectangular islands, as shown in Figs. 1c and d. It was also noticed that all the rectangular islands were elongated along two orthogonal azimuths equally, with no preference nucleating along either orthogonal azimuth.

Figure 2 is a diffraction pattern of Ge substrate before deposition, (b) Ge substrate together with grown islands on top, (c) and (d) are corresponding simulated diffraction patterns of Ge and Fe_{13}Ge_{8} respectively. From the diffraction patterns shown in Fig. 2, it can be noticed that all the newly appeared diffraction spots, rather than those coming from Ge substrate, should be originating from the grown islands as observed in Fig. 1. Those newly appeared diffraction spots are also highly symmetric to Ge substrate diffraction spots, indicating all islands are epitaxially grown on substrate. Through the diffraction analysis combined with simulated diffraction patterns (Figs. 2d and c), it can be concluded that the phase of islands grown on Ge substrate is Fe_{13}Ge_{8}. Also, the epitaxial orientation between grown islands and underlying substrate can be determined, which is Fe_{13}Ge_{8}[1102] //Ge[001] and Fe_{13}Ge_{8}(11-20) //Ge(110) [10].
3.2 Endotaxial growth

Figure 3a is a typical BF TEM cross-sectional view of Fe$_{13}$Ge$_8$ islands grown on Ge(001) substrate. It can be noted that all the islands are not sitting on top of substrate surface, while all islands has grown into the substrate. This can be clearly seen in Fig. 3b, which was observed along the length azimuth of the island. Moreover, Fig. 3c shows another typical example of an island grown into substrate, which was observed along the width azimuth. According to the high resolution TEM observation shown in Fig. 3d, we can get the phase information from the fast Fourier transform diffractograms of the lattice images. By analyzing the diffractograms, identification of both Fe$_{13}$Ge$_8$ and Ge, as well as the related orientation and interfaces can be determined. Based on the combination of high resolution cross-sectional TEM observations and diffractogram analysis, Fe$_{13}$Ge$_8$ islands grew into the Ge substrate, inclined along the Ge{111} planes as shown in Figs. 3d and e. The interfacial plane can be identified as Fe$_{13}$Ge$_8$(4-401) //Ge(-111) in Fig. 3d. Moreover, similar ‘grow-in’ phenomenon also occurred at other islands grown on Ge(001) substrate, another typical example is shown in Fig. 3e.

As we know, in most heteroepitaxial system, crystals are different, not only in atomic spacing but also in crystal structure, resulting in complex interface structures. Consequently, the final stable structure will be a complex interplay between the surface, strain, and different interfacial energies. In the case of the hex-Fe$_{13}$Ge$_8$ and cubic Ge system, the expectation is that interfacial planes would consist of a combination of coherent and low energy semi-coherent interfaces, due to reduction in rotational symmetry. A plot of stereographic projections (Fig. 4a) enabled identification of these interfacial planes, like showing in Fig. 4a, which is an overlay of two stereographic pole projections, with Ge (green circle) and Fe$_{13}$Ge$_8$ (red circle), aligned to the experimental defined epitaxial relationship. Those poles in which Ge and Fe$_{13}$Ge$_8$ coincide are parallel planes in which interfaces are likely to form. From the stereographic projection, there are four such possible parallel planes (denoted as dashed circle), which exist around both Ge[001] and Fe$_{13}$Ge$_8$ [-1102] zone axis. This demonstrates that parallel planes of Fe$_{13}$Ge$_8$ hexagonal crystalline structures (a=0.7976 nm, c=0.4993 nm) were exactly registered on Ge cubic (a=0.5658 nm) with the previously defined epitaxial relationship. These parallel planes thereby become possible interface planes that form between Fe$_{13}$Ge$_8$ islands and the Ge substrate. However, this is not the only criteria for interface formation. The most favorable interface planes must also be those planes with the most coherent interface in order to minimize interfacial energy. In order to identify the exact interfacial planes, further analysis of the interface atomic structure of both Fe$_{13}$Ge$_8$ and Ge crystals was performed.

Fig. 3 (a) Cross-sectional overview of islands grown on Ge substrate. Typical examples of the cross-section view of islands grown on Ge substrate observed along (b) length azimuth, and (c) width azimuth. (d) and (e) are high resolution cross-sectional TEM observations of islands grown on Ge substrate, with corresponding diffraction analyses. These TEM images clearly demonstrate that all islands have grown into Ge substrate.

Fig. 4 (a) Stereographic projection of Fe$_{13}$Ge$_8$ and Ge with defined epitaxial relation. (b) is the simulated atomic structures of the only well-matched planes between Fe$_{13}$Ge$_8$ and Ge.
According to computer simulated atomic structures for all types of parallel planes obtained from stereographic projection analysis, it was found that there was only one pair of parallel planes can be well matched between Fe$_{13}$Ge$_8$ and Ge lattice places, which was shown in Fig. 4b. This interface is energetically more favorable than other types of interfaces bounded around grown islands. It thereby be understood that the minimization of interfacial energy to lower the total energy of heteroepitaxy system, promotes the driving force for continual island growth. This causes preferential Fe$_{13}$Ge$_8$ island growth along the inclined Ge\{111\} plane to attain a low-energy coherent interface with the substrate, leading to the endotaxy island growth observed in this study. More details about the endotaxy island growth have been discussed elsewhere [12].

3.3 Kinetically constrained island growth

As above mentioned, the hex-Fe$_{13}$Ge$_8$ island formation occurs via endotaxy growth. It is interesting to further understand the mechanism that whether the process is in the equilibrium or kinetically limited growth regime. Particularly, we probe the growth dynamics and island shape transition as a function of deposition time and vary the growth temperatures. To probe and follow the Fe$_{13}$Ge$_8$ island growth pathway, the in-situ UHV-TEM has been used to monitor the formation and evolution of endotaxial Fe$_{13}$Ge$_8$ island growth on Ge(001) substrate during reactive deposition of Fe on Ge at elevated temperature ranging from 350 to 510°C, similar to the study shown in Fig. 1. Fig. 5 demonstrates two typical examples of Fe$_{13}$Ge$_8$ islands grown at different temperatures (350 and 510 °C respectively). At low temperature (Figs. 5a-d), the island retained its initial formed compact shape, with a mean aspect ratio ~ 1-1.5. An increase in deposition temperature to 510 °C (on a different sample, Figs. 5e-h), leads to the formation of nanowire. The insets in Figs. 5e and h are the corresponding diffraction pattern of the grown island, indicating the island has the same phase and epitaxial relation during growth process. More details about Fe$_{13}$Ge$_8$ islands grown at deposition temperatures ranging from 350 to 510°C have been discussed in the previous report [10].

Fig. 5  Real time observation of islands grown on Ge(001) substrate by in-situ UHV-TEM at different deposition temperatures (a) 350 °C and (b) 510 °C, respectively.

Fig. 6  Plots of islands growth rates as a function of deposition temperature, all data were extrapolated from in-situ TEM images.
From the Arrhenius plot analysis, the growth rate as the function of temperature as shown in Fig. 6, we can get the activation energy barrier along the island length and width. As we know, for these nucleated islands to grow, adatoms prefer to diffuse along ledges with lower surface/interface free energy. Since the two orthogonal azimuths of these Fe$_{13}$Ge$_8$ islands are bound with different facet/interface planes, therefore, at high temperature, the channeling of adatoms diffusion along the ledge with lower surface/interface energies will result in a greater probability of adatoms crossing over the corner barriers and incorporated at the width. This will also lead to lower migration rates to coherent facets/interfaces, which bound the length while the higher migration of semicoherent facets/interfaces bound the width, and therefore, generates nanowires. Interestingly, the formation of the preferred facet/interface planes which bound the length, appear to be a thermally activated process, limited by both ledge-diffusion and corner barriers as previously reported [13]. Hence at low temperature, formation of compact islands with small aspect ratio occurs as growth of the preferred facet/interface and is kinetically constrained.

3.4 Shape transition from kinetically constrained to equilibrium regime

The shape transition discussed in the previous section (occurred at 350 to 510 °C) appears to be dominated by kinetic process, associated with migration and attachment/detachment of adatoms. These activated processes are strongly affected by growth temperature. The use of higher temperatures may drive the growth process towards the equilibrium regime leading to a further change in the growth morphology. We also note that in the literature, most theoretical and experimental reports of NW formation mainly occurred at high temperatures and assumed at equilibrium condition which was driven by thermodynamics considerations [8,14]. The island morphology transition as a function of deposition temperature, while keeping the same deposition flux and time was investigated thereafter.

Figure 7 represents the typical morphology evolution of Fe$_{13}$Ge$_8$ islands grown at different temperatures ranging from 430 to 675°C. Fig. 7a is a TEM image of islands grown at 430 °C, which clearly shows that all grown islands are predominately small and square in shape at orthogonal directions to the substrate. At 510°C, NWs are formed (Fig. 7b). However, as the deposition temperature was further increased to 675°C, NWs could be seldom observed, which was unexpected from the trend of island shape evolution that occurred between deposition temperatures from 350 to 510 °C as discussed in the previous session. At 675 °C, all islands have compact shape (Fig. 7c). Nevertheless, these square islands have a much larger size than those formed at lower temperatures (i.e. 350 or 430 °C).

Figure 8 shows the TEM results about the aspect ratio (height above substrate versus height below substrate) as a function of deposition temperatures. Insets are typical cross-sectional TEM images of Fe$_{13}$Ge$_8$ islands with different configurations.
On the basis of the quantitative study shown in Fig. 8, islands observed in this study can be divided into two types. For the type of islands grown below 510 °C, they all have distinct shallow facets bound at each side and have a truncated pyramid-like shape (the left inset in Fig. 8, denoted as type-I). For islands formed above 510 °C, all the surrounding shallow facets disappear and are substituted by steeper facets, leading to multifaceted dome-like islands (the right inset in Fig. 8, denoted as type-II). According to cross-sectional TEM observations, all islands have grown into substrate via endotaxial growth. It should be emphasized that island morphology evolution at different temperatures in the endotaxial growth can be explained not only by the height above the substrate, but also by the height below the substrate. Therefore, it is essential to characterize the height evolution by comparing island height both above and below the substrate. Cross-sectional TEM results of the corresponding epitaxial/endotaxial ratio (height above substrate versus height below substrate) of Fe$_{13}$Ge$_8$ islands grown at different temperatures were represented in Fig. 8. It clearly illustrates that island height aspect ratios change significantly at temperatures below and above 510 °C. From Fig. 8, all type-I islands have an average height ratio ~ 0.5, which is independent of the island’s basal shape (e.g., square, rectangle or wire). However, the average height ratio of type-II islands greatly increases to ~2 above 510 °C. It was believed that the faceting process could provide the possibility to stabilize the island configuration and reach its equilibrium state [15-17]. At high temperatures, adatoms can obtain sufficient energy to overcome surface and interface diffusion barriers/corner barriers, hence can rapidly diffuse on the facets to find the most stable sites, subsequently forming low surface/interface energy facets/planes. In this case, island growth usually terminates at lower surface/interface energy planes [18-20]. In addition, in order to be epitaxially registered on the isotropic Ge(001) surface, islands prefer to adopt a square shape which can reflect the symmetry of the underlying substrate and thus to reduce the length/width aspect ratio to reach the equilibrium state. Consequently, this growth process can lead to the formation of type-II islands. This scenario has been generally demonstrated in Fig. 9. Moreover, all islands grown above 510 °C maintain their square shape during the whole annealing process, which indicates that type-II islands exist in their equilibrium state. This island shape transition at different deposition temperatures provides a dramatic illustration of the importance of surface and interface energies in controlling the island growth habit and formation, especially for the endotaxial growth process.

4. Summary

To summarize, Fe$_{13}$Ge$_8$ islands formation on single crystal Ge(001) substrates at elevated temperatures have been comprehensively studied. At low temperatures (~350 °C) small square islands form in general. As the deposition temperature increased, islands grew with elongated shapes (~430 °C). The island length versus width aspect ratio increased as a function of the deposition temperature, leading to NWs formation at high temperatures (~510°C). Nevertheless, larger square-like islands formed at higher temperatures (above 510°C) in preference to the NWs. All the islands have the same phase and share the same epitaxial relationship to the underlying Ge(001) substrate. It suggests that this type of temperature dependent island shape transition is not due to a phase transformation. We propose that island morphology evolution below 510°C is mainly due to kinetic constraints in terms of anisotropic ledge diffusion and corner barriers. Whereas at temperatures above 510 °C, facets/interfaces bounded around islands begin to change. Below 510 °C, all the islands have a similar cross-sectional shape and is defined as type-I. They appear as truncated pyramids with shallow facets at each side and a flat facet at the top. Type-II islands generally appear above 510 °C, and have much steeper facets at the bottom with larger heights above the substrate, forming dome-like shape with a square base. It was illustrated that minimizing the total surface and interface energies to reach their equilibrium state may be the driving force that leads to the shape transition from type-I to type-II. Moreover, this study demonstrates that the NWs formed in the hex-Fe$_{13}$Ge$_8$/Ge system are not structures in thermodynamic equilibrium. This work provides a comprehensive understanding of low dimensional structure formation and shape transition from kinetically constrained to equilibrium regimes.
Fig. 9 Two types of endotaxial islands grown at kinetically constrained and equilibrium regimes.

References