Strain relaxation in self-assembled Ge(Si)/Si quantum dots

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Interfacial morphology, composition profile and defect formation in the self-assembled Ge(Si)/Si(001) quantum dot system were investigated using transmission electron microscopy. The experimental results on the coherent quantum dots suggest different growth mechanisms for the samples grown under different growth conditions. For the low temperature (575°C) growth, kinetics dominate the growth process, resulting in quantum dots with Ge enriched in the middle of the dots, while in the case of the high temperature (700°C) growth, Ge segregation to the top of the dots was found with a trench surrounding each quantum dot. A high-resolution transmission electron microscopy investigation of relaxed dots leads to the discovery of a new misfit dislocation generation mechanism.
1. Introduction

The growth process of the strain-driven Stranski-Krastanov (S-K) growth\(^1\) of quantum dots has been intensively investigated experimentally and theoretically by many research groups due to the potential in electronic and opto-electronic applications of the quantum dots. A general conclusion has been reached: following the layer-by-layer growth, coherent dots start to form with a small aspect ratio of height-to-base diameter. As the growth continues, the aspect ratio increases to more effectively release the built-up strain, and the contact angle between the dot side-wall and the substrate increases also.\(^2,3\) Although most of the investigations have focused on the shapes and sizes of S-K grown dots and on how they help to release strain, less attention has been given to the composition of the dots, a parameter which is very important in determining the system strain energy and the opto/electronic properties of the dots. Furthermore, with further growth, quantum dots collapse by the introduction of misfit dislocations. Since these misfit dislocations damage the opto-electronic properties of devices based on the quantum dot structures, understanding the nature of these defects and their generation mechanisms is important in order to develop means of avoiding them during the growth of device quality material. In this paper, we present the results of investigations of the strain relaxation processes in molecular beam epitaxy (MBE) grown Ge(Si)/Si(001) quantum dots which occur by composition segregation in coherent dots and by the introduction of misfit dislocations.

2. Experimental

Three samples were investigated. For sample A, a nominal thickness of 1.6 nm pure Ge was deposited on (001) Si wafers by gas-source MBE at a growth temperature of 575\(^\circ\)C and a growth rate of 0.4 nm/min. For sample B and C, Ge, with nominal thicknesses of 0.8 and 1.4 nm respectively, was grown on (001) Si wafers by solid-source MBE, at a growth temperature of 700\(^\circ\)C and a growth rate of 1.2 nm/min.

Plan-view transmission electron microscopy (TEM) specimens were prepared using chemical etching with a solution of HF and HNO\(_3\) in the ratio of 1:9. \(<\text{110}>\) cross-section TEM specimens...
were prepared by mechanical thinning followed by ion-beam thinning with a Gatan precision ion polishing system with an accelerating energy of 3 keV.

TEM investigations were carried out using a Philips CM12 operating at 120 kV (for cross-section diffraction contrast imaging), a Philips EM430 operating at 300 kV (for plan-view diffraction contrast imaging), a Philips CM120 equipped with Gatan image filter (GIF) system operating at 117 kV (for energy filtered imaging), a JEOL 3000F operating at 300 kV (for phase contrast imaging) and a VG 601HB STEM equipped with an Oxford x-ray energy dispersive spectroscopy (EDS) system operating at 100 kV (for x-ray microanalysis).

In our investigations, we used the three-window technique of energy filtering transmission electron microscopy (EFTEM) to carry out elemental (Si and Ge) mapping. Si and Ge maps were obtained using the Si L\textsubscript{2,3} edge (at 99.2 eV in the electron energy loss spectrum) and the Ge L\textsubscript{2,3} edge (at 1217 eV), respectively. During the experiment, strong diffraction conditions were avoided to minimize the uncertainty of background removal caused by strong diffraction.

Image simulations for explaining [001] zone-axis plan-view diffraction contrast images were performed using multi-beam dynamical electron scattering theory with the strain fields of model quantum dots calculated using the finite element analysis software STRAND6 (for details of image simulation procedure, see Ref. [10]).

3. Results and discussion

3.1 Coherent quantum dots

Figure 1(a) shows a bright-field diffraction contrast image taken from a thin cross-section TEM specimen of sample A. In this study, EFTEM was used to investigate the elemental distribution of the quantum dots (details, see Ref. [11]). Figures 1(b) and 1(c) are EFTEM images of the dot shown in Fig. 1(a), showing a Ge map and a Si map, respectively. The local relative atomic ratio of Ge and Si can be directly related by dividing Ge map by Si map, as shown in Fig. 1(d) (the accurate ratio can be obtained by multiplication of a K-factor, the ratio of partial ionization cross sections of the two elements). To present the intensity distribution of Fig. 1(d)
more clearly, a pseudo-color (spectrum) image is shown in Fig. 1(e), with the highest Ge/Si presented in red and the lowest in purple. It is seen that Ge is concentrated in the middle of the quantum dot. Figure 2 shows the intensity profiles across the quantum dot and across the wetting layer [marked with “1” and “2” in both Figs. 1(d) and 2, respectively]. The Ge/Si ratio profile of the same quantum dot was also measured by x-ray microanalysis using the ratio of the Ge-K peak to the Si-K peak. The result, in Fig. 2, shows a similar relative composition distribution profile to the results obtained from EFTEM [Fig. 1(e)].

Three points can be seen from Figs. 1(e) and 2: (i) the Ge is concentrated in the middle of the quantum dots; (ii) there is a wetting layer of approximately 3 nm thickness; and (iii) Ge has diffused into the substrate (the level of the wetting layer/substrate interface is marked as a black line), resulting in a lowered dot/substrate interface.

We now study sample B. Figure 3 shows a plan-view [001] zone-axis bright-field diffraction contrast image of the Ge(Si) coherent dots. The image background of white-and-black stripes is due to the substrate thickness variation of the TEM specimen (the thickness fringes), with the thinnest area located at the left bottom corner. The dots are relatively uniform in size with the base diameter measured along <110> of about 100 nm. Four different forms of contrast are seen, marked a, b, c and d. The same contrast appears periodically with the period of the thickness fringes. For example, contrast c appears in white fringes while contrast d appears at the middle of black fringes. This implies that the dot diffraction contrast is a function of the specimen thickness.

To extract structural information of the quantum dots from the diffraction contrast image shown in Fig. 3, extensive image simulations have been carried out (for details see Ref. [12]), for models with and without Ge and Si segregation within the dot. It was found that Ge/Si segregation takes place in this system. Because of this, several segregation models have been tested. It has been found the best fit between simulated and experimental images is obtained with the composition distribution shown in Fig. 4. This model is Ge-rich at the top of the quantum dot. Simulated
images for this model and their corresponding experimental images for a range of substrate thicknesses are shown in Figs. 5 (a) ~ (d) and in Fig. 5 (aE) ~ (dE), respectively.

The experimental images marked a, b, c, and d in Fig. 5 are enlarged in Fig. 5 (aE) ~ (dE) (the first row), respectively. Features of these images are: (i) the image aE is blurred and the coupled bars are thicker at the middle (the thicker area at one of the coupled bars is marked by two white arrows); (ii) although both bE and dE show a distinct double-cross with diverging coupled bars, the centres of the images are different: bE has a circular ring while dE has four black spots (one of the black spots is marked with a white arrow); (iii) while most of the quantum dot in cE has dark contrast, there are four brighter spots arranged with four fold symmetry at the centre of the image. Simulations were carried out with varying substrate thicknesses over steps of 2.5 nm, noting from the results above that the images repeat periodically with thickness. Figures 5 (aS) ~ (dS) (the second row), show the images which best fits aE to dE. It can be seen that all of the image features (i) to (iii) discussed above are found in the simulated images. Remarkably good agreement is observed between the experimental and the simulated images, showing how well the experimental and simulated images agree. This level of agreement was not found for other quantum dot models tested. It is clear that images in each column of Fig. 5 have the same image features. The excellent match of the experimental and simulated images shows that the image simulation method is a powerful tool for understanding the diffraction contrast of the quantum dots. But more importantly for this paper, it shows that the model of a quantum dot with segregation produces images which agree with experiment over a wide range of sample thickness.

Figure 6 is a typical bright-field diffraction contrast images taken from a thin cross-section TEM specimen of the sample B. Two points which are not seen in sample A can be noticed: (i) a trench surrounding the edge of the quantum dot and (ii) the dot/substrate interface has been lowered to be around the level of the bottom of the trench. Extensive TEM studies have confirmed that trenches exist in all quantum dots in this sample and the interface is lowered, regardless of the quantum dot size.14
Comparing the results of two samples (A and B), three similarities have been observed: (i) alloying takes place in the quantum dots, (ii) Ge segregation was found, and (iii) Ge has diffused into the Si substrate. In contrast, two significant differences have also been identified: (i) the form of Ge segregation was different (i.e. the highest concentration of Ge was in the middle of quantum dots in sample A while the highest concentration of Ge was at the top of the quantum dots in sample B) and (ii) there is trench around the quantum dot in sample B, but not in sample A.

This comparison allows us to develop pictures of the growth mechanisms of Ge quantum dots on (001) Si at different growth conditions. Schematic diagrams of the two growth models are shown in Fig. 7.

At the initial stage of Ge deposition, layer-by-layer growth takes place with an accompanying strain-driven intermixing between the deposited material and the substrate material, resulting in the wetting layer being a GeSi alloy. The degree of the alloying is higher in the high temperature growth. When the built-in strain cannot sustain this growth mode, dot growth follows. Tersoff suggested that, at the stage of dot nucleation, segregation of the larger-misfit component (in this case, Ge) to the dots occurs, which reduces nucleation barrier and therefore improves the dot nucleation rate, leading to Ge enrichment in the quantum dot in the early stages of the dot growth [see step III in Fig. 7].

With further growth, the growth mechanism depends upon the growth conditions. It is generally believed that surface diffusion dominates the dot growth. In the case of low temperature growth, the mechanism is dominated by the diffusion of Ge from the wetting layer to the quantum dots. However, the strain energy in the quantum dots can be relieved by inter-diffusion of Ge and Si through the dot/substrate interface, and by diffusion of Si to the quantum dots from the wetting layer. Towards the end of the growth (particularly when the incident flux is switched off), a Ge depleted wetting layer is expected. Therefore, the residual growth of the quantum dot would result in reduced Ge in the outmost layers of the quantum dots, as is evident in the sample A (see Fig. 1(d)].
However, in the case of high temperature growth, thermodynamics dominate the growth. Following the nucleation of the quantum dot [as illustrated in step III in Fig. 7(b)], the inter-diffusion between the Ge-rich quantum dot and the Si substrate occurs rapidly, because the increased diffusion rate at the high temperature allows diffusion across the quantum dot/substrate interface to relieve the high quantum dot strain more effectively [as illustrated in step IV in Fig. 7(b)]. With further growth, misfit strain builds up. The inter-diffusion continues strongly during this stage together with the Ge and Si surface diffusion. Since Ge diffuses faster than Si and since the Si diffusion can result in a high strain in the wetting layer (although it can reduce the strain energy in the dot), the most of diffused Si would come from the edge of the quantum dots, leading to the trench formation.14'17'18 This process leads to two consequences: (i) a lowered dot/substrate interface to the level near the bottom of the trench; and (ii) a composition gradient along the growth direction, Ge-rich at the top of the quantum dots [as illustrated in step V in Fig. 10(b)]. After the trench is formed, the further growth is dominated by the diffusion of Ge from the wetting layer and inter-diffusion between the Si and Ge across the interface (particularly at the corner of the quantum dots, where highest strain exists). During this stage of the growth process, the compositional profile across the quantum dots remains stationery until the end of growth, leading to Ge enrichment towards the top of the quantum dots [as illustrated in step VI in Fig. 10(b)]. [To further relieve the misfit strain, the system can also (i) increase the aspect ratio of quantum dot height to base diameter19 and (ii) reorient the interface (i. e. the corner of the dot) to accomplish partial detachment of the dot, thereby lowering the strain energy, but we do not explore these processes here.]

3.2 Relaxed quantum dots

A large size distribution of quantum dots is observed in sample C, containing coherent and relaxed quantum dots. <110> cross section TEM specimens were investigated to determine the nature of misfit dislocations and consequently to determine their generation mechanism.
Figure 8 is a typical $<110>$ cross-section bright-field TEM image of a relaxed quantum dot, showing several perfect misfit dislocations near the dot/substrate interface, as well as a stacking fault as marked. Extensive cross-section TEM studies suggest that stacking faults are common in this system. As a stacking fault which terminates within the crystal must do so at a partial dislocation, a knowledge of the nature of these partial dislocations will give information about the generation mechanism of the stacking faults. High-resolution electron microscopy (HREM) was used for this purpose. Figure 9(a) shows the positions of two partial dislocations in a quantum dot, one (marked P1) near the dot/substrate interface and another (marked P2) close to the dot surface. In both cases, the other end of the associated stacking fault extends to the dot surface. Figures 9(b) and 9(c) are enlarged images, showing the core structure of the partials P1 and P2. By drawing a Burgers circuit,\textsuperscript{20} their Burgers vectors were determined to be $30^\circ$ in nature. This configuration suggests that the $30^\circ$ partial misfit dislocations may be generated from the surface of the quantum dot through a half-loop (for details, see Ref. [21]). We believe that this misfit dislocation generation mechanism is enhanced in the high temperature (700$^\circ$C) growth, in which a significantly high nucleation rate of these loops is expected. Furthermore to this model, with a further nucleation of a $90^\circ$ partial dislocation at the stacking fault surface as suggested by Chen et al\textsuperscript{22} followed by the glide towards to the dot/substrate interface and combine with the $30^\circ$ partial misfit dislocation, $60^\circ$ perfect dislocation can be formed. This means that some of the $60^\circ$ perfect misfit dislocations observed could be formed in such a mechanism.

4 Conclusion

For the Ge(Si) coherent quantum dots grown on (001) Si substrates, we have demonstrated that the different growth conditions lead to different morphologies and compositional profiles in the quantum dots due to different growth mechanisms. In the case of growth with a low temperature (575$^\circ$C), Ge segregation in the middle of the dots was found, while in the case of growth with a higher temperature (700$^\circ$C), Ge segregation on the top of the dots was observed with a trench
surrounding the quantum dots. Growth models for the two growth conditions have been suggested and illustrated (see Fig. 7).

Studies of the relaxed quantum dots in the sample grown at high temperatures suggests that 30° partial misfit dislocations may be generated from the surface of the quantum dots.

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Figures caption:

Figure 1.  (a) a bright-field cross section TEM image of sample A; (b) Ge energy loss elemental map; (c) Si energy loss elemental map; (d) Ge map/Si map; (e) a pseudo-color image showing the intensity (brightness) distribution of (d) a dark line is drawn passing through the wetting layer/substrate interface.

Figure 2  Relative Ge/Si profiles. The solid lines correspond to the profile measured from Fig. 1(d) (EFTEM technique) and the dotted line represents the profile measured using the EDX technique.

Figure 3  A [001] on-zone bright-field diffraction contrast image taken from a plan-view TEM specimen of sample B, showing coherent Ge(Si)/Si(001) quantum dots having a similar size distribution. The arrows indicate <110> directions.

Figure 4  A schematic diagram showing the Ge segregation model, for which the simulated images match the experimental images.

Figure 5  Comparison of experimental and simulated images using 300 kV electrons. The first row shows enlarged experimental images of Fig. 3. The second row shows simulated images with the substrate thickness shown at the top of each image.

Figure 6  <110> cross-section bright-field image showing a coherent quantum dot in sample B. A trench surrounds the dot edge and the dot/substrate interface is lowered.

Figure 7  Schematic diagrams showing the growth mechanisms of (a) low temperature growth and (b) high temperature growth.

Figure 8  A bright-field <110> cross-sectional TEM image showing perfect dislocations and a stacking fault in a relaxed quantum dot.

Figure 9  HREM images showing partials dislocations: (a) two partials with one (P1) close to the dot/substrate interface and the other (P2) near the dot surface; enlarged HREM images [P1 in (b) and P2 in (c)] showing both partials have 30° character.
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Figures caption:

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Figure 3

Figure 4

Figure 5
Figure 6

Figure 7