Strain relaxation by alloying effects in Ge islands grown on Si(001)

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Transmission electron microscopy is used to study the morphology and the composition profile of ''pure'' Ge islands grown at high temperature on Si(001) by molecular beam epitaxy. An alloying process, involving mass transport from the substrate to the islands during the island growth, was identified. It was found that, as a result of Si mass transport to the Ge islands, the island/substrate interface moves towards the substrate, and trenches form on the substrate surface around the islands. Reduction of the misfit strain at the island/substrate interface is the driving force for this process. [S0163-1829(99)00748-1]

Semiconductor quantum dots (QD's) are attracting increasing interest because of their significant optoelectronic properties.[1] Although QD's can be produced in many ways, the method of coherent island formation is of great importance for materials with large lattice mismatch (such as Ge(Si)/Si[2,3] and $In_xGa_{1-x}As/GaAs$[4] because of the possible combination of the QD growth and semiconductor integration techniques. Of crucial importance in determining the optoelectronic properties of the QD's are the structural parameters of the QD's including the shape, size and composition.[5] Uniformity in and control over these parameters are a prerequisite for many applications. To achieve this goal, a complete understanding of the mechanism of the QD growth is necessary. Although many investigations have concentrated on the shape and size[6,7] and evolution[8,9,10] during the QD growth, relatively less attention has been paid to the composition.[11,12,13]

In the classical Stranski-Krastanow[14] (S-K) mode of coherent island formation, one material with a different lattice parameter and low interfacial energy is initially deposited on a substrate surface, layer by layer, forming a ''wetting layer''. When the wetting layer reaches a critical thickness [usually three to five monolayers for pure Ge on Si(001),[3,15] island growth starts to partially release the mismatch strain energy between the epitaxial layer and the substrate. However, in the case of InAs/GaAs, recent investigations suggest that, for higher temperature growths, there is significant mass transport from both the wetting layer and the substrate to the islands.[16] Furthermore, the wetting layer in InAs/GaAs systems has been reported to be an (In,Ga)As alloy with temperature dependent composition.[17] The composition of the alloy wetting layer will certainly affect any subsequent island growth procedure. These points suggest that the classical S-K growth mechanism needs to be modified to explain the details of island growth. In this paper, we demonstrate evidence for mass transport from the Si substrate to the Ge islands during high temperature molecular beam epitaxy (MBE) growth of ''pure'' Ge islands on the Si(001) substrate. The mass transport changes the composition of the islands, moves the Ge/Si interface below the original substrate surface, and forms a trench around each island. It is proposed that the driving force for this mechanism is a reduction in the strain energy. As a consequence, a modified S-K mode is suggested for the island growth at high temperature.

P-type Si(001) wafers with resistivity of 1 Ω cm were used as substrates. Ge islands were grown on the Si substrates by solid source MBE at a growth temperature of 700 °C and a growth rate of 0.02 nm/s. Prior to Ge deposition, a 30-nm-thick Si buffer layer was grown on the substrates. Two different thicknesses of Ge were then deposited: Sample *A* (0.8 nm) and sample *B* (1.4 nm).

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. Cross-section TEM specimens were prepared using Ar^+ ion-beam thinning in a Gatan PIPS with an accelerating energy of 3 keV. TEM investigations were carried out using a Philips CM12 operating at 120 keV, a Philips EM430 operating at 300 keV, and a Philips CM120 BioTEM equipped with energy filtered imaging operating at 117 keV.

Figures 1(a) and 1(b) show two typical [001] zone-axis bright-field diffraction contrast images taken from samples *A* and *B*, respectively. It was found that most of the islands in sample *A* are uniform in size with a base width of approximately 95 nm. However, islands in sample *B* have a range of sizes, with the smallest being of a similar size to those in sample *A*. The reason for the size nonuniformity in strained island growth has been discussed elsewhere.[9,10,18] It was also found that small islands in both samples have a square shaped base with rounded corners, as has been observed by atomic force microscopy (AFM).[19]

Cross-section TEM studies showed that, viewed along ⟨110⟩, islands in both samples have a similar height to base-diameter aspect ratio (about 1:5), irrespective of the size of the islands. Figures 2(a) and 2(b) are typical bright-field

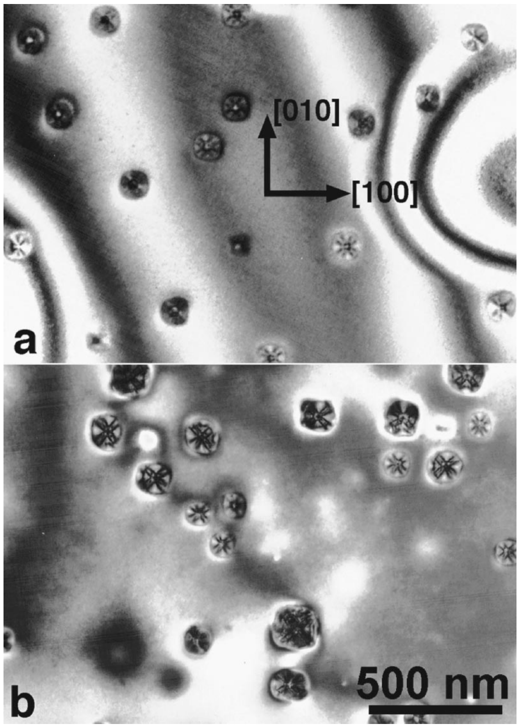

FIG. 1. Plan-view [001] on-zone bright-field images of (a) sample *A* and (b) sample *B*.

cross-sectional TEM images of the islands in samples *A* and *B*, respectively, taken from areas thinner than the dimension of the basal diameters of the islands. Trenches are seen around the islands, and it was found that, for all the islands in this study (including those which are partially relaxed), the trenches has a similar dimension and cross-section profile, with a depth of approximately 7 nm (i.e., the cross-section profile and size of the trench is approximately independent of the island's size in both samples). Figure 2(c) is an enlarged image of a part of Fig. 2(a). It is seen that the island/substrate interface is about 7 nm below the flat wetting layer surface, and at the same depth as the bottom of the trench. The island/substrate interface is slightly curved. Figure 2(c) has been taken with the specimen oriented to give bright contrast at the wetting layer interface. This interface is marked by an arrow and is seen to lie uniformly across the entire interface. It is important to note that the layer follows the surface of the trench. Figure 2(d) is an enlarged image of a part of Fig. 2(b), showing trench features similar to those in Fig. 2(c) at an area surrounding the edge of the relaxed island.

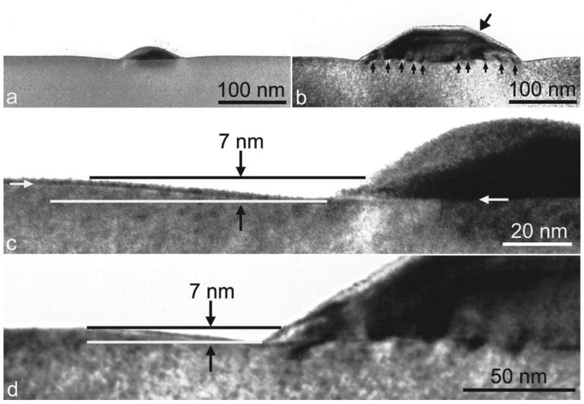

FIG. 2. Cross-section bright-field images: (a) a coherent island in sample *A*; (b) a relaxed island in sample *B* where misfit dislocations at the island/substrate interface and a stacking fault are arrowed: (c) an enlarged image of a part of (a) showing a clear wetting layer. White arrows at the left and right sides of the image mark the wetting layer/substrate interface and the island/substrate interface, respectively. A white line below the wetting layer represents the depth level of the island/substrate interface. A trench with a depth of about 7 nm at the edge of the island is clearly seen; (d) an enlarged image of a part of (b) where a trench with approximately the same features as the trench in (c) is clearly seen.

Extensive TEM investigations on the cross-section specimens show that the islands in sample *A* and the smaller islands in sample *B* are coherent, while the larger islands in *B* are relaxed by the formation of misfit dislocations and stacking faults [see arrows in Fig. 2(b)]. Bright-field images taken along $\langle 110 \rangle$ suggest that the wetting layer is thicker than the normal wetting layer of pure Ge (3–5 monolayers). If this is the case, it suggests that alloying might occur in the wetting layer, in agreement with Auger electron spectroscopic measurements.[20] High-resolution experiments are being conducted to investigate this point. In fact, substantial intermixing of Ge and Si at the initial stage of Ge/Si(001) epitaxial growth at 500 °C has been reported, which supports our conclusion of alloying in the wetting layer.[21]

It is of interest to investigate where the Si that previously existed in the trench areas has gone. A possible process is that the Si has been transported into the islands. To test this hypothesis, cross-sectional TEM specimens were prepared by ion-beam thinning. To reduce the possibility of Si being sputtered onto the islands from the substrate during the cross-section specimen preparation, a copper support material was glued face-to-face to the sample surface (touching the islands), and the Ar^+ ion beam bombarded the specimen from the copper side. These specimens were studied using an energy filtering TEM,[22] which gives images mapping Si and Ge separately. Images were formed with the energy loss window centered at the Si K edge of 1839 eV and at the Ge L_3 edge of 1217 eV, and with a window width of 50 eV. Examples are shown in Fig. 3. Figure 3(a) is an image using electrons with zero energy loss showing a complete image of an island on the substrate surface covered by an epoxy resin. Figure 3(b) is a Si map; it clearly shows the presence of Si in the island. Figure 3(c) is a Ge map that shows the Ge island together with the thin Ge wetting layer. Note that the wetting layer appears across the entire substrate surface. Because of the strength of the Si signal from the island, and its absence from the surrounding material (epoxy), we conclude that there is Si within the dot.

If the total amount of the Si lost beneath and surrounding the island is assumed to transport to the island, the amount of Si in the island can be evaluated. As mentioned earlier, the depth of the island/substrate interface and the cross-section profiles of the trenches are approximately the same (i.e., have the same dimension and shape) for all the islands studied here regardless of the island sizes. Hence, we can compare the mass ratios within the islands at different growth stages. If we assume that the shape of the island is independent of size, then the mean Si composition within an island de-

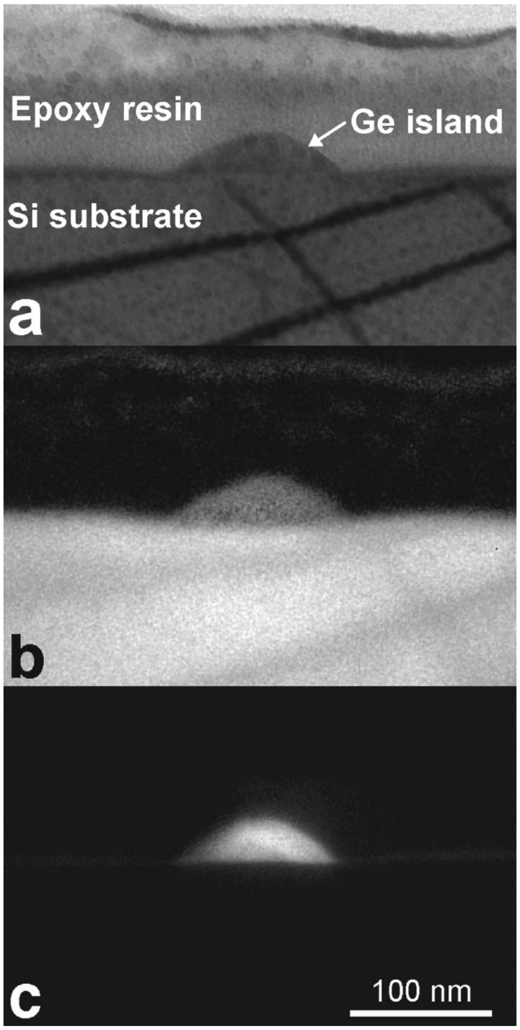

FIG. 3. Cross-section energy-filtered images: (a) a zero-loss image showing the complete morphology of the TEM specimen; (b) an energy-loss (1839 eV) image that represents a Si map. Si is clearly seen within the island; and (c) an energy-loss (1217 eV) image that represents a Ge map. A wetting layer is seen uniformly throughout the entire substrate surface.

creases with increase in size of the island. This is because the volume of the island scales as d^3 and the volume of the consumed Si substrate scales as d^2, where d represents the base diameter of the island.

By considering only the removed Si under the islands, a simple geometrical analysis gives the composition of the island in Fig. 2(a) to be 60% Si, and 30% Si for Fig. 2(b). The figure is even higher when the Si missing from the trenches around the island is included. This result is in excellent agreement with the work of Kamins *et al.*[23] who showed not only alloying between Ge and Si, at 650 °C, but also (by macroscopic x-ray diffraction) a composition of $Si_{0.5}Ge_{0.5}$.

Taking the above experimental observations into account, a modified S-K mode for high temperature growth of Ge islands on Si is proposed, as shown diagrammatically in Fig. 4. In classical S-K growth, layer-by-layer growth takes place at the initial stage of Ge deposition, as shown in Fig. 4(a). However, the layer by layer growth at high temperature is accompanied by an alloying process, resulting from Si transport to the wetting layer.[21] Following the layer-by-layer

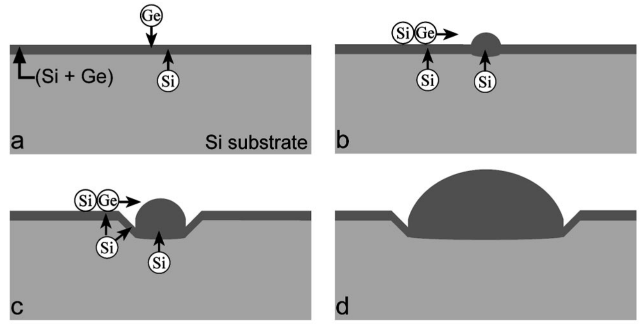

FIG. 4. Schematic diagrams of a modified S-K growth mode at different growth stages.

growth, surface migration of both Ge and Si results in island growth [Fig. 4(b)]. The formation of the small coherent island only partially releases the misfit strain. With the growth of the island, misfit strain builds up. The strain energy can be reduced in four ways: (i) by increasing the height to base diameter aspect ratios of the islands;[7,24,25] (ii) by the introduction of misfit dislocations at the interface. This requires high strain and occurs only for the larger islands; (iii) by lowering the misfit between the island and the substrate which could result from the alloying of Si into the Ge island; and (iv) by reorienting the interface to accomplish partial detachment of the island, thereby lowering the strain energy.

It is evident from Figs. 2(c) and 2(d), that Si from trenches and from under the island has gone somewhere, and it is reasonable to assume that it has gone into alloying within the island (see earlier). This will achieve strain energy reduction by mechanisms (iii) and (iv). This transfer of Si into the island can be either through transport from the wetting layer, or directly by bulk diffusion from the bottom of island/substrate interface, or both [as in Fig. 4(c)]. The relative importance of surface and bulk migration will depend upon the activation energies, but it is clear that some bulk migration is essential, even if only to provide Si to transport through the wetting layer. The lower mobility[26] of Si than Ge implies that while Ge can be transported from a longer distance, most of the Si consumed comes from areas surrounding the islands. This results in a trench around the island, as illustrated in Fig. 4(c). The subsequent island expansion necessarily starts from the bottom of the trenches and the lateral Si migration process continues as the island grows, as shown in Fig. 4(d). Bulk diffusion can also explain the slightly curved island/substrate interface in Fig. 2(a), in which the middle of the interface is slightly deeper than the edge of the interface, since the middle area has been formed longer.

It is noted that trenches surrounding Ge islands grown on Si substrates have been reported previously. Using AFM, Kamins *et al.*[27] found trenches surrounding Ge islands in a sample grown on Si(001) by chemical vapor deposition at a growth temperature of 600 °C. Although the trenches were approximately 1 nm beneath the surface, which is deeper than the expected thickness of the wetting layer, it is much shallower than the trench depths reported here. This difference can be explained by the dependence of the migration coefficient of Si on the growth temperature. This argument is further supported by the fact that Ge islands had no trench when the growth temperature was only 500 °C.[2] On the other hand, Floro *et al.*[28] reported observation of trenches around islands in the $Ge_{0.2}Si_{0.8}$/Si (001) sample grown by MBE at 755 °C. However, the island/substrate interface in their sample is located at the original Si substrate surface. This implies that in their system, the trenches might be formed only after the island growth, and can be explained by the fact that, in the case of small lattice mismatch (only about 0.8% in $Ge_{0.2}Si_{0.8}$/Si system), the driving force for mass transportation will be smaller. Furthermore, the trenches are formed by consuming the wetting layer in the $Ge_{0.2}Si_{0.8}$ system, resulting in an uneven wetting layer thickness, which is different from our observation in the Ge/Si system. The appearance of the trenches modifies the substrate surface, and hence reduces the local volume of material experiencing a stress concentration.[28]

Daruka *et al.*[29] have investigated theoretically the equilibrium growth modes (''phases'') of strained heteroepitaxial systems as a function of the coverage of deposited material and lattice mismatch for different surface energies. They have predicted seven possible phases in terms of the growth mode. However, their theory incorporated only the growth of the wetting layer, dislocation-free island formation, and ripening. Our scenario of the mass transport and alloying during the strained heteroepitaxial growth implies the existence of an extra phase due to alloying effects.

In conclusion, mass transport of Si from the Si substrate to Ge islands, and consequently alloying in the islands, has been found in the Ge/Si system grown by MBE at the temperature of 700 °C. This finding suggests a modified S-K growth mode. Reduction of the misfit strain between the substrate and the islands is believed to be the driving force for the process. Besides three-dimensional island growth and the formation of misfit dislocations at the interface, alloying is another way to release the misfit strain. However, since the mass transport is kinetically limited by the element migration coefficient, alloying can only be observed at sufficiently high growth temperatures.

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