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Anomalous Si Incorporation into MBE-Grown Ge on Si(111)

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Ge islands are grown by MBE on Si(111) surfaces with an SPE-grown buffer layer, which was expected to prevent intermixing between the epitaxial Ge layer and the Si substrate. Anomalous Si incorporation into the Ge islands is observed using the TEM Moiré pattern and SAM techniques. This phenomenon cannot be explained by the bulk diffusion mechanism. The TEM Moiré pattern technique is shown to be effective for studying the early stage of Ge growth on Si.

1. Introduction

The early stages of growth of Ge on Si have been extensively studied by RHEED[1)], LEED and AES[2)], TEM[3-6)], RBS[7,8)] and STM.[9)] It is well known that the Ge/Si heteroepitaxial system belongs to the Stranski-Krastanov (SK) growth mode[2,4,6-8)]: 3D cluster growth after the formation of a 2D uniform layer. However, the mechanisms of 3D cluster or island growth and Ge/Si lattice relaxation are still not clear.

This paper reports a new phenomenon of surface-enhanced intermixing between Ge and Si observed in Ge/Si(111) heteroepitaxial systems. The result is of interest from the viewpoint of suggesting a limitation on the perfection of Si-Ge superlattices, in which sharp interfaces between the individual Si and Ge layers are usually assumed. Using transmission electron microscopy (TEM) and scanning Auger electron microscopy (SAM), we found that the composition of the 3D islands was Ge alloyed with Si, indicating that anomalous intermixing between Ge and Si occurred on the surface. Moreover, the results showed that the intermixing was enhanced in the periphery of the islands.

2. Experimental

The samples were prepared as follows:

1. Surface cleaning: The surface was cleaned by the procedure reported by Ishizaka and Shiraki.[10)] After cleaning, the sharp 7×7 RHEED pattern was observed and no trace of contamination could be detected by AES.
2. a-Ge deposition: Amorphous Ge (3 ML) was deposited on the substrate at room temperature using a PBN Knudsen cell.
3. Solid phase epitaxy (SPE): The specimen temperature was raised to about 600°C and maintained for 10 min. The amorphous Ge layer was crystallized epitaxially in solid phase. A clear 5×5 RHEED pattern was observed. Thin Ge layers grown by SPE were reported to be pseudomorphic, with no interfacial mixing of Si into the Ge layer.[5,7,8)] Here, the thin Ge layer is referred to as a 'buffer layer'. The buffer layer was introduced for suppressing the Si incorporation into Ge islands.
4. MBE: An additional 10 ML of Ge was deposited at 600°C. A diffuse 7×7 pattern superimposed onto a 5×5 pattern was observed in RHEED pattern.
Finally, amorphous Ge was deposited on the sample at room temperature as a cap layer to protect the surface morphology.

After the sample preparation *in vacuo*, the samples were removed and analyzed by TEM and SAM.

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3. Results and Discussion

Figure 1 shows planar TEM images observed at various magnifications. When the 2D Ge buffer layer was formed by SPE, the islands were laterally larger than those without the buffer layer (not shown here).

The Moiré patterns can be seen clearly. The TEM Moiré pattern technique, which was originally used to study dislocations in metals such as Pd/Au,[11] can be used to investigate the early stages of Ge growth on Si, because of the high lattice perfection of the Si substrate. The Moiré pattern for the Ge/Si(111) was formed by combining doubly diffracted beams (002), (220) and (202) with the 00 beam. Spacing of the Moiré fringe D is given by $D=d_{Si}d_{Ge}/|d_{Si}-d_{Ge}|$, where d_{Si} and d_{Ge} are (220) lattice spacings of Si and Ge layers in Ge/Si(111) system. The ideal D-value in the completely relaxed Ge/Si(111) system is calculated to be 4.8 nm from bulk lattice constans. The spacings observed here were, however, wider than the ideal values.

The epilayer composition can be estimated from the Moiré fringe spacing.

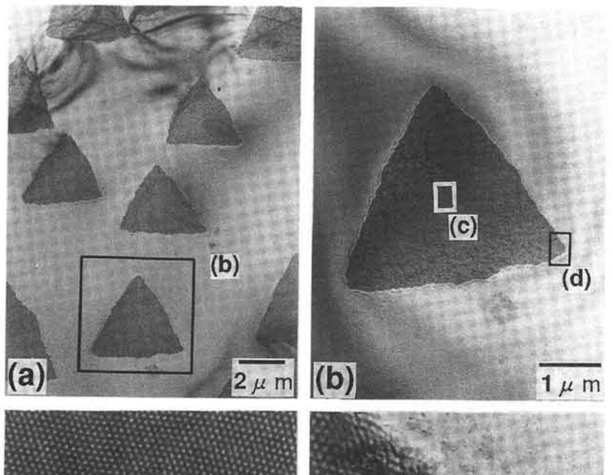

Fig. 1. Planar TEM images observed from the Ge/Si sample at low (a), medium (b) and high (c),(d) magnification. (c) and (d) were at the central and outer regions of the island in Fig. (b). Moiré fringes are clearly observed in the images at high magnification. The mark M points to typical misfit dislocations.

Figure 2 shows the relationship between D, the spacing of the parallel Moiré patterns for g=(220), and the value of x in the $Si_{1-x}Ge_x$. Lattice constants for $Si_{1-x}Ge_x$ are based on the data obtained by E. R. Johnson.[12] According to Fig. 2, a wider spacing indicates that the island is Si-Ge alloy rather than pure Ge. In the outer regions of the island (Fig. 1(d)), the Moiré fringe spacing was much wider than in the central regions (Fig. 1(c)). D varied from 4.93-5.61 nm in the center to 6.55-7.79 nm at the outer area, which, as shown in Fig. 2, correspond to the $Si_{1-x}Ge_x$ alloy x-values of 0.89-0.98 and 0.61-0.73, respectively. (A TEM lattice image of a Si(111) substrate was used as a standard to calibrate the magnification.) This result indicates that the alloying of Ge with Si is more pronounced in the outer region of the island, and that intermixing occurs during MBE to distribute the incorporated Si atoms in the Ge islands unevenly along the Ge/Si interface.

The x-value of the $Si_{1-x}Ge_x$ island was cross-checked by SAM. SAM images and space-resolved Auger spectra were obtained using an electron beam a 300-400 nm in diameter. The depth profile of the SAM images was obtained by sputtering at RT. Figure 3 shows a SAM image of the surface after sputtering for 15min. Figure 4 shows compositional depth profiles at the points marked 1 (on an island) and 2 (on the substrate) in Fig. 3. Figure 4(b) indicates that the a-Ge cap layer was almost completely removed after sputtering for 19 min. The unclear plateau observed between

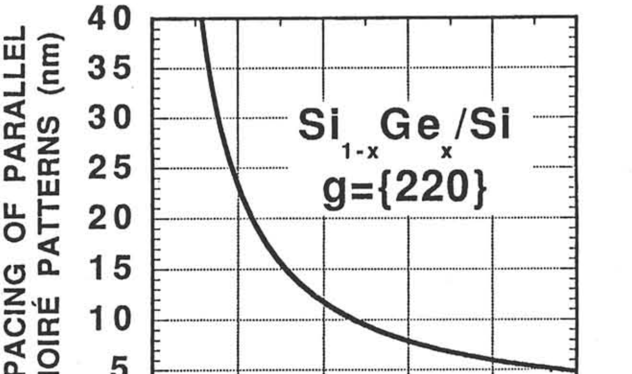

Fig. 2. Dependence of parallel Moiré pattern spacing on the composition of the $Si_{1-x}Ge_x$ layer on Si(111). Diffraction vector g={220}.

16 and 20 minutes of sputtering in Fig. 4(a) may correspond to sputter-etching of the island. Consequently, the x-value of 0.6±0.1 in the $Si_{1-x}Ge_x$ alloy observed on the island area after 19-20 minutes of sputtering (Fig. 4(a)) could be considered

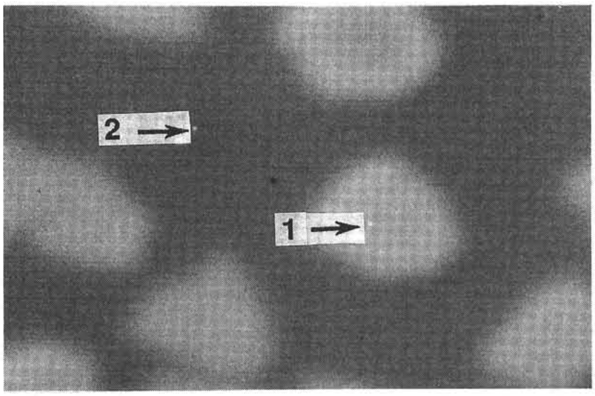

Fig. 3. A SAM image of the surface: white triangular regions correspond to "Ge" islands and the black area to the Si substrate.

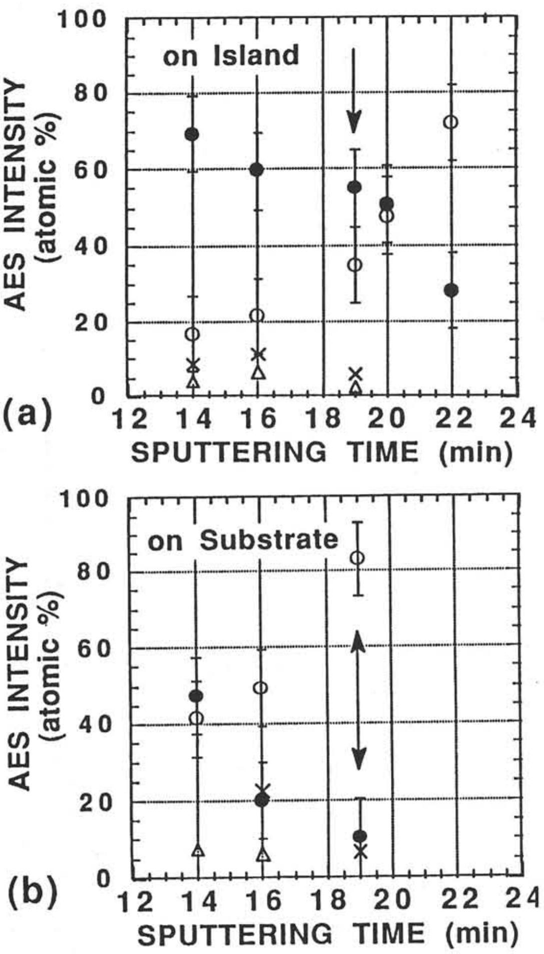

Fig. 4. Compositional depth profiles at (a) point 1 (on island) and (b) point 2 (on substrate) in Fig. 4. Open and closed circles, crosses and triangles denote Si, Ge, C and Fe, respectively. The a-Ge caplayer was removed after sputtering for 19min, as shown by arrows in (a) and (b).

to be that of the island. The x obtained here was consistent with the value obtained from the Moiré fringes. Therefore, the SAM result supports the occurrence of intermixing that was concluded from the Moiré analysis.

McVay and DuCharme[13] reported that the activation energy of the diffusion of Ge into Si was very high (about 4.7 eV) and was similar to the value for Si self-diffusion. This seems reasonable because both Ge and Si are group-IV elements and have the same number of valence electrons; therefore one would expect the relative charge of Ge atoms dissolved in Si to be zero. If we could assume the same mechanism for Si diffusion into Ge, we might use the Ge self-diffusion constant as the diffusion constant of Si into Ge. Then Si diffusion into Ge would be negligible at the growth temperature and time of this experiment. Therefore, the intermixing observed here cannot be explained by a bulk diffusion mechanism and is an anomalous phenomenon.

4. Summary

Ge islands grown by MBE on Si(111) with an SPE-grown buffer layer were investigated by TEM Moiré pattern and SAM techniques. We observed anomalous Si incorporation into the Ge islands, which cannot be explained by a bulk diffusion mechanism. The Moiré pattern technique was shown to be effective for studying the early stages of Ge growth on Si.

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