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Trace of interface reconstruction in Ge solid-phase epitaxy on Si(111)

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We describe the mechanism of solid-phase epitaxy (SPE) of Ge on a Si(111)-7×7 surface using reflection high-energy electron diffraction and scanning tunneling microscopy. Amorphouslike Ge layers crystallize in the registry of the 7×7 reconstruction preserved at the Ge/Si interface. The preferred basic unit of epitaxy is a triangular domain corresponding to four half-units of the 7×7 reconstruction. Faultedly stacked (twinned) domains cover almost half of the surface at the initial stage of SPE because Ge grows epitaxially on both the unfaulted and faulted halves of the 7×7 reconstruction. These twinned Ge layers are transformed into normally stacked Ge layers above 400 °C.

To understand epitaxial growth in atomistic terms has been a long-standing goal in material science. This understanding will provide a wider range of possibilities for synthesizing artificial structures. Recent progress in microscopic techniques has made it possible to investigate epitaxial growth on an atomic scale.[1] In particular, scanning tunneling microscopy (STM) has provided a wealth of varied information about the growth mechanism.[2] Because STM has little sensitivity to the subsurface atomic structure, much more investigation has been done in molecular-beam epitaxy than in solid-phase epitaxy (SPE).[3] However, because STM is a very powerful tool for investigating local, disordered atomic structures, STM should also give fruitful information about SPE.[3]

It has been reported that the 7×7 periodicity on a clean, reconstructed Si(111) surface is preserved at the amorphous Si/Si(111) (Ref. 4) [*a*-Si/Si(111)] and *a*-Ge/Si(111) interfaces[5] formed by room-temperature (RT) deposition. Recently, we, along with our co-workers, have reported that relaxed Ge islands grown by SPE are arranged in a mesh pattern because the crystallization of Ge layers is initiated at steps and out-of-phase boundaries of the 7×7 reconstruction, where 7×7 periodicity is broken.[6] These results show that the 7×7 reconstruction is conspicuously stable against overlayer growth. However, the interface 7×7 reconstruction is destroyed during SPE. The buried reconstruction should therefore greatly influence the epitaxial growth of the amorphous material. In order to clarify the SPE growth mechanism, it is important to investigate how the interface 7×7 reconstruction is destroyed. This investigation would also explain the stability of the 7×7 reconstruction against overlayer growth.

In this paper, we investigate Ge SPE growth on a Si(111) surface on an atomic level using STM. The growth mechanism is clarified based on comparisons between STM and reflection high-energy electron diffraction (RHEED) results. The geometry of the 7×7 reconstruction is described by a dimer, adatom, and stacking-fault (DAS) model.[7] In the DAS model, unfaulted and faulted triangular regions covered with adatoms are connected by dimers. We demonstrate that the 7×7 reconstruction on the substrate acts as a seed of Ge epitaxial growth and Ge layers grow epitaxially on both the unfaulted and faulted halves (henceforth UH and FH) of the 7×7 unit cell. Faultedly stacked (twinned) Ge layers therefore cover almost half of the surface in the initial stages of SPE. These twinned layers are transformed into normally stacked layers at higher temperatures because the underlying stacking fault is energetically unfavorable.

We used a commercial STM (JEOL JSTM4500VT) to investigate Ge SPE growth on Si(111). A Si(111) sample (B-doped, $\rho = 1-10\ \Omega$ cm) was chemically cleaned by repeated oxidation in H_2O_2:H_2SO_4 (1:4) and oxide removal in a HF solution. The sample was introduced through a load lock into a UHV chamber with a base pressure of 2×10^{-10} Torr. It was outgassed at about 500 °C for 3–10 h, cleaned by flashing at 1250 °C, and thereafter cooled to RT. Ge was deposited using a W filament, and the Ge thickness was derived from the deposition time and the Ge deposition rate determined from the RHEED oscillation. The sample was annealed by passing electric currents through it. The sample temperature below 600 °C was estimated by extrapolating the relation[8] between the sample current and the above-600 °C temperature measured with an infrared pyrometer. The uncertainty of the temperature is probably less than ±50 °C. STM images were taken at RT after the surface was annealed at various temperatures for 1 min.

Following is a brief summary of the RHEED observations during Ge SPE. Even after depositing 10-Å-thick Ge films at RT, the RHEED pattern exhibits 7×7 spots. This is due to the fact that the 7×7 reconstruction on the original surface is preserved at the Ge/Si interface.[4] The 7×7 diffraction spots on the lines running through integral order spots are stronger than the others. This structure is called δ-7×7.[9] Adatom arrangement is lost by Ge deposition at RT, but dimer and stacking-fault features remain.[9] When the sample is annealed above 200 °C, diffuse integral order streaks appear in the RHEED pattern. This indicates that the Ge layers begin to crystallize at about 200 °C. Ge grows on the Si(111) surface in the Stranski-Krastanov mode. When the Ge layers are thicker than 4 monolayers (ML) (6.5 Å) (1 ML = 7.8×10^{14} atoms/cm^2), three-dimensional relaxed islands are formed after annealing.[10,11] During SPE, the

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intensities of the 7×7 spots get stronger than those diffracted from the as-deposited sample, within a certain temperature range. Even after annealing at 400 °C, RHEED patterns of the 7-Å-Ge layers clearly show 7×7 spots as well as transmission diffraction spots created in relaxed Ge islands. Annealing above 500 °C causes the 7×7 reconstruction to be transformed into a 5×5 reconstruction.

Figure 1 shows STM images of 4-ML Ge layers as deposited and annealed at 300–640 °C. Their Fourier transforms (FT) are shown as insets. STM studies on the SPE process of Ge layers thinner than 4 ML will be described elsewhere.[12] The STM image of the as-deposited sample [Fig. 1(a)] shows very rough, granular features, with variations in height of about 6 Å. On the 300 °C-annealed sample [Fig. 1(b)], there are small islands 3–6 Å high. Except for the islands, however, the surface is much smoother than that of the as-deposited sample. Furthermore, local periodic structures can be seen. These results indicate that Ge layers crystallize locally. This STM result agrees with the diffuse integral order streaks in the RHEED patterns of the sample.

Although the 300 °C-annealed Ge layers are rather continuous, there are many holes in the 380 °C-annealed Ge layers [Fig. 1(c)]. When a 7×7 mesh is overlaid, the holes are shown to be arranged in a 7×7 periodicity. This indicates that the Ge layers grow in the registry of the underlying 7×7 reconstruction. The holes are probably attributed to the corner holes in the 7×7 reconstruction. They are regularly spaced about $14a$ ($2\times 7a$) apart, a being an atomic spacing on a Si(111) surface; 3.84 Å. We can therefore observe hexagonal hole arrangements in some places. Additionally, Fig. 1(c) shows that the surface is mainly divided into two types of small triangular domains whose boundaries are imaged at a positive sample bias as trenches, in the middle of which bright spots are arranged. One of these domains has peaks directed toward $\langle 11\bar{2}\rangle$ (A domain) and the other

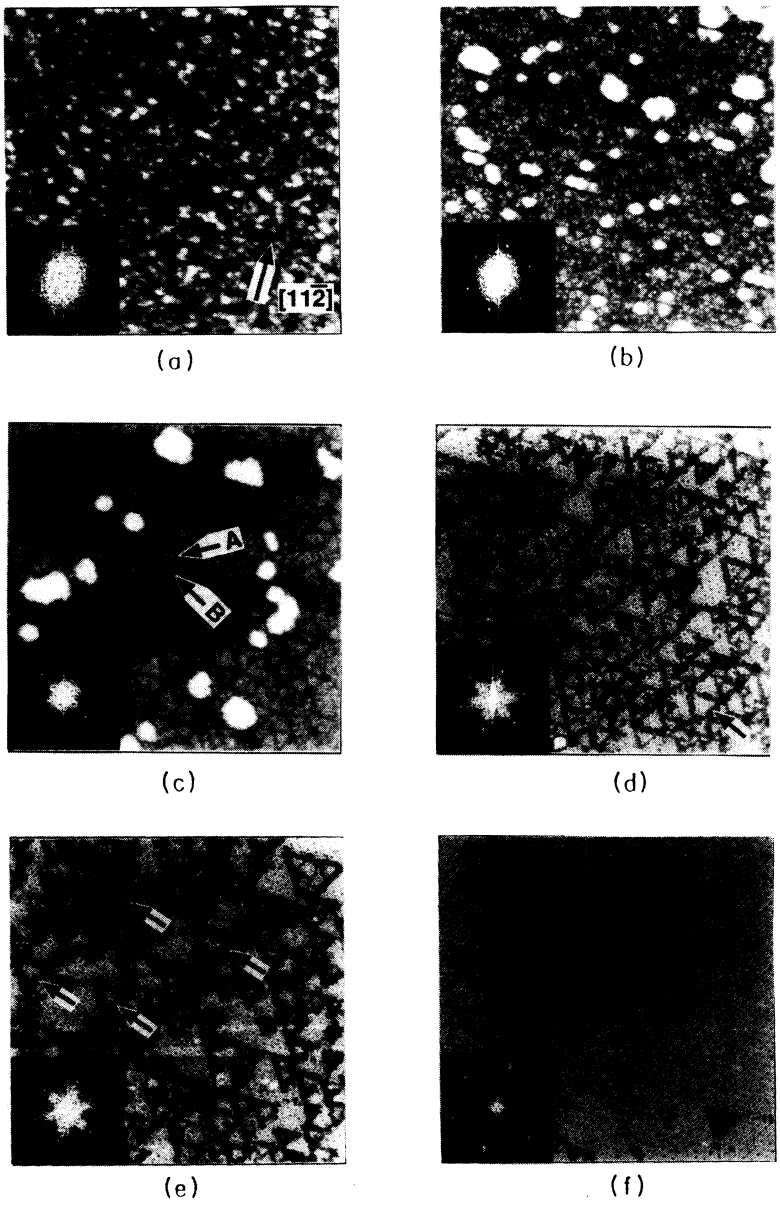


FIG. 1. STM images of 4-ML Ge/Si(111) during SPE. (a) is as deposited; (b)–(f) are after annealing at 300 °C, 380 °C, 480 °C, 540 °C, and 640 °C, respectively. The scanning area is 810×810 Å^2. The sample bias and tunneling current are +2 V and 0.2 nA. Insets show their Fourier transforms.

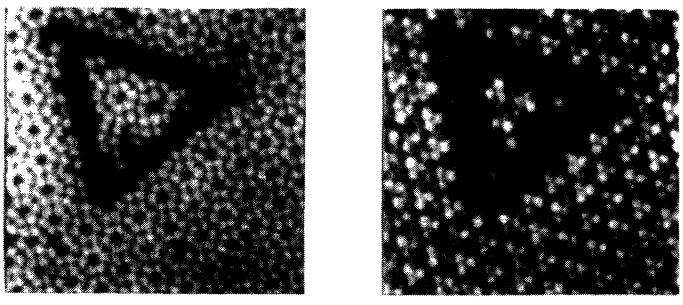
has peaks directed toward $\langle \bar{1}\,\bar{1}2 \rangle$ (B domain). Examples of the A and B domains are marked in Fig. 1(c). The triangular domains are often determined by three holes. Therefore, their sides are typically $14a$ long. In the higher resolution images of the triangular domains, we can observe arrangements of adatomlike protrusions, indicating that the A and B domains are preferred basic units of Ge epitaxial growth on Si(111).

Figure 1(d) shows an STM image of the sample further annealed at about 480 °C. This surface is also divided into A and B domains; but the shape of the A domain is now a composite of triangles since A domains grow by the transformation of B domains into A domains. DAS-like $(2n+1)\times(2n+1)$ reconstructions are clearly visible in the A domains, and 5×5 reconstruction is predominant. On the other hand, the B domain is still in a triangular shape because A domains are rarely transformed into B domains. Furthermore, small islands observed on the 300 °C- and 380 °C-annealed samples disappear on the 480 °C-annealed sample. This is due to the fact that the small islands agglomerate into larger ones or are absorbed into pseudomorphic Ge layers with the destruction of the interface 7×7 reconstruction. When the sample is annealed at higher temperatures, the A domains grow wider and wider, as shown in Fig. 1(e). Eventually, only a few small triangular B domains are left among or within the large 5×5-reconstructed A domains. A typical STM image of this is shown in Fig. 1(f).

Figure 2 shows high-magnification STM images of a B domain left behind in an A domain on the 640 °C-annealed sample. Figures 2(a) and 2(b) are empty- and filled-state images of the same region. In the STM images, we can see 5×5 reconstruction in the B domain. The filled-state image shows that the higher, brighter half of the 5×5 reconstruction in the B domain has reversed orientation compared with that of the 5×5 reconstruction in the A domain. In the filled-state image of the DAS reconstruction, the FH is higher than the UH. Crystallographic orientation is therefore reversed in the B domain. This indicates that the B domain itself is faultedly stacked (twinned) and that there is a stacking fault at the Ge/Si interface. This is because Ge layers can grow epitaxially on the FH of the interface 7×7 reconstruction. Such reversed DAS reconstructions in the B domains are observed even on the 480 °C-annealed sample. For example, reversed DAS reconstructions were confirmed in the B domains marked by arrows in Figs. 1(d) and 1(e) at a negative sample bias. Thus, we can conclude that Ge layers grow epitaxially on both the UH and FH at the initial stage of SPE. Figure 2(b) also shows that a triangle determined by FH of the 5×5 reconstruction in the B domain has a reversed orientation from that determined by the B domain itself. This indicates that the basic unit of the B domain, a triangle $14a$ long, is formed on three FH's and one UH. We observed twinned Ge domains on molecular-beam-epitaxy-grown Ge/Si(111) surfaces, as well.[13] Stacking faults might easily be introduced at the Ge/Si interface by the lattice mismatch between Si and Ge.

We will now describe the mechanism of Ge SPE growth on Si(111) using RHEED and STM results. After 4-ML Ge is deposited at RT, the RHEED pattern still includes 7×7 spots, but the STM image is very rough and granular, and its FT shown in Fig. 1(a) includes very faint 7×7 peaks. The FT of the STM images shows the periodicity of the outermost surface. On the other hand, RHEED patterns include the periodicity of the surface as well as the substrate because electron beams penetrate into the sample. Amorphouslike Ge layers are therefore formed with the 7×7 reconstruction preserved at the interface. When the sample is annealed above 200 °C, diffuse integral order streaks appear in the RHEED pattern with the 7×7 spots unchanged. The STM images of the 300 °C-annealed sample showed that the surface gets smoother. These indicate that Ge layers crystallize locally with the 7×7 reconstruction intact. The crystallization of Ge starts at a lower temperature than the destruction of the 7×7 reconstruction does.

RHEED intensities of 7×7 spots from the 380 °C-annealed sample were stronger than those from the as-deposited sample. This intensity increase is also apparent in the STM images. The interface 7×7 reconstruction is not completely destroyed as confirmed by the existence of strong 7×7 RHEED spots on the lines running through the integral order spots. Additionally, as shown in Fig. 1(c), holes are arranged in a 7×7 periodicity on the 380 °C-sample. This indicates that Ge layers themselves also have a 7×7 periodicity. We therefore investigate the periodicity included in the Ge layers using the FT insets in Fig. 1. Although almost no 7×7 periodicity is seen in the FT in Fig. 1(a), those in Figs. 1(b)–1(e) clearly exhibit 7×7 peaks. These peak intensities are the strongest in Fig. 1(c) and get weaker as the annealing temperature is further increased. In the FT in Fig. 1(e), diffuse 5×5 peaks are identified while the FT in Fig. 1(f) shows only 5×5 periodicity. The Ge layers of the 380 °C-annealed



(a) (b)

FIG. 2. STM images of 4-ML Ge/Si(111) grown by SPE at 640 °C. (a) and (b) are taken at the sample biases of +2 and −2 V, respectively. The tunneling current is 0.2 nA. The scanning area is 170×170 Å^2.

sample contribute to the 7×7 spot intensity the most. Moreover, an incident electron beam is easier to transmit through the epitaxially grown Ge layers than the amorphouslike layers. Diffraction spots from the residual interface 7×7 reconstruction are thereby intensified. This also contributes to the increase in 7×7 spot intensity.

Ge grows epitaxially on both the UH and FH in the DAS reconstruction. This result is consistent with the x-ray diffraction and transmission electron microscopy results, which show that partially occupied layers grown epitaxially on both the UH and FH extend into the amorphous region at the *a*-Si/Si interface.[14,15] Furthermore, we have shown that there is a preferred basic unit of Ge epitaxial growth, a triangle whose sides are 14*a* long. The *B* domain is basically formed by a triangle consisting of three FH's and one UH. There is a problem, however, with the interface structure. At the interface beneath the *B* domain, we must determine if the three FH's and one UH connected via dimers still remain or if a stacking fault is formed through dimer breaking and transition from normal to faulted stacking. This problem is closely related to how the interface 7×7 reconstruction is destroyed. We cannot precisely answer this question using only RHEED and STM results. However, if a UH (FH) remains beneath the triangular *B* (*A*) domain, there must be corner holes between the peaks. Nevertheless, holes in the Ge layers are always at the peaks in the *A* and *B* domains. We can see no special features in the trenches between the peaks. This probably indicates that there is no UH (FH) beneath the *B* (*A*) domain. When the *B* (*A*) domain is formed, the UH (FH) of the 7×7 reconstruction is transformed into a FH (UH), and a uniform stacking fault forms at the Ge/Si interface beneath the *B* domain. However, dimers are probably preserved at the boundaries between *A* and *B* domains because normal and faulted stackings are connected there. As shown previously, islands on the 300 °C- and 380 °C-samples disappeared after annealing at 480 °C. This temperature range coincides with the temperature at which the interface 7×7 reconstruction is actively destroyed. This suggests that the Ge islands are not agglomerated into larger islands, but instead absorbed into the pseudomorphic layers. When the sample is annealed at higher temperatures, the unfaulted domains get wider through the transformation from faultedly stacked (twinned) domains (*B* domain) into normally stacked domains (*A* domain) because the stacking fault at the Ge/Si interface is energetically unfavorable.

Next, we must ask "Why is the basic unit of epitaxy a triangle corresponding to four half-units of the 7×7 reconstruction?" If the 7×7 reconstruction is stable at the SPE temperature, amorphouslike Ge layers should crystallize equally on the UH and FH. Therefore, Ge layers may be crystallized in each half-unit of the 7×7 reconstruction; however, the smaller the size, the more atoms there are at the boundaries. Therefore, smaller units are energetically unfavorable. On the other hand, as the unit of epitaxy enlarges, the ratio between the number of UH's and FH's included in the unit approaches unity. When the ratio is close to unity, it is difficult to determine whether the Ge layers are normally or faultedly stacked. These competing factors probably determine the basic unit of epitaxy.

In conclusion, we have described the mechanism of solid-phase epitaxy of Ge on a Si(111) surface. The mechanism is unique in three ways: (1) Ge layers crystallize before the 7×7 reconstruction at the interface is destroyed; (2) Ge layers grow epitaxially on both the unfaulted and faulted halves of the 7×7 reconstruction; and (3) Ge layers easily crystallize in units of triangles with sides each 14*a* long. Such an interesting mechanism is due greatly to the stability of the 7×7 reconstruction.

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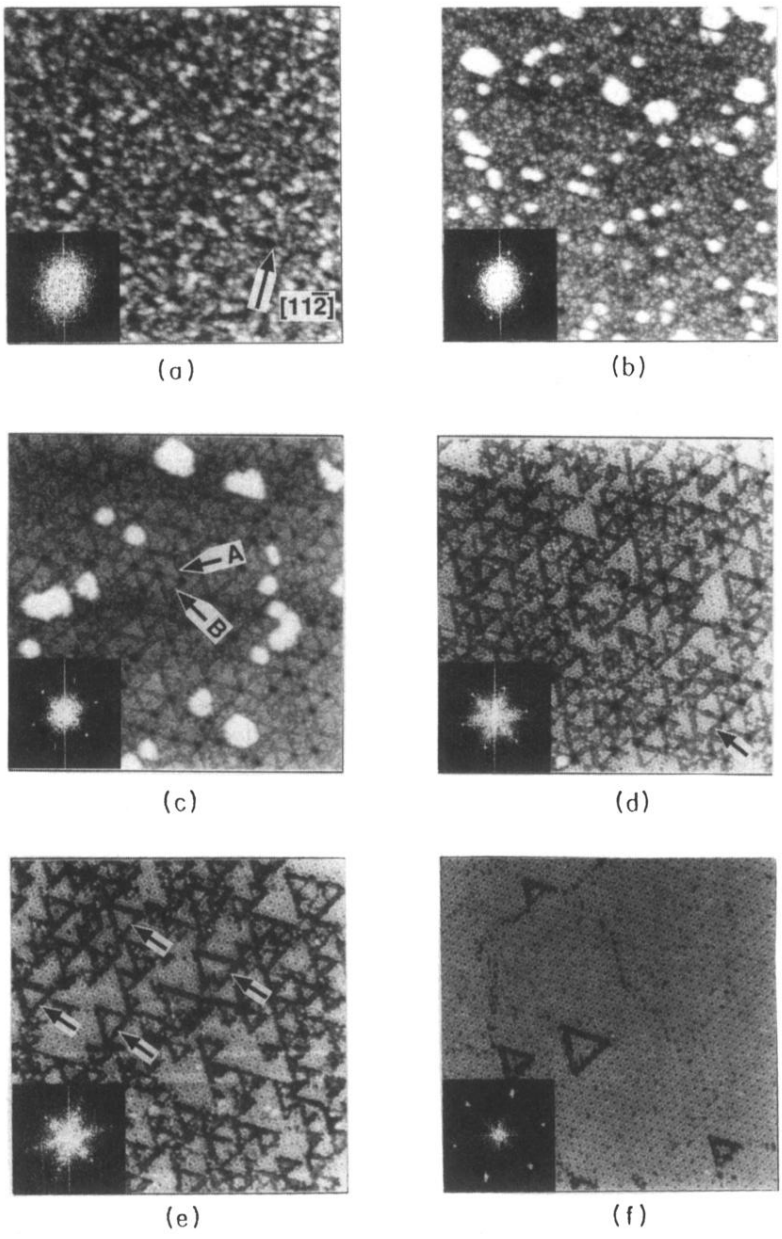

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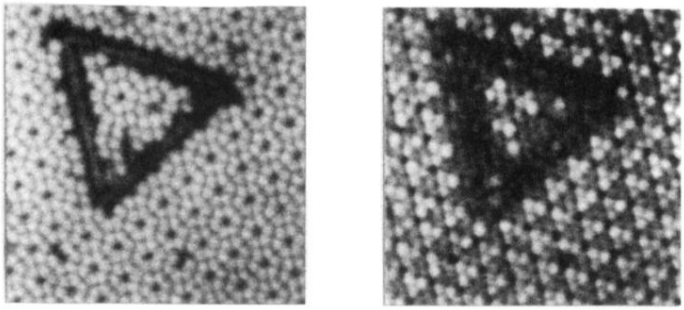

(a) (b)

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