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Scanning-tunneling-microscopy study of surface morphology at the initial growth stage of Si on a 7×7 superlattice surface of Si(111)

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Scanning-tunneling-microscopy (STM) images were taken from the surface of a Si layer grown at a rate of 0.6 nm/min on a Si(111)-7×7 substrate held at 250 °C in order to study the surface morphology change in terms of the thin-film-growth process. Each STM image was obtained from the Si layer whose growth was terminated at an arbitrary value of the specular reflected high-energy electron-beam intensity (I). At the initial growth stage on the native Si(111)-7×7 substrate, the amplitude of I does not oscillate regularly, and three-dimensional (3D) islands nucleate and grow layer by layer. When a second bilayer has a mean thickness between $1\frac{3}{4}$ and $2\frac{1}{4}$ bilayers, the layer growth starts with the nucleation and growth of 2D islands, and is followed by regular oscillation in I. The transition from a 3D to a 2D growth mode can be deduced from the difference in the nucleation and growth processes of islands on the native Si(111)-7×7 substrate and the growing Si layer; this is because the latter surface is composed of small domains with metastable 2×1, 2×2, 5×5, 7×7, and 9×9 superlattices.

Molecular-beam epitaxial growth of Si has been studied and monitored by many investigators with observations of reflection high-energy electron diffraction[1–4] (RHEED) and low-energy electron diffraction (LEED).[5] From their studies we note that the amplitude and period in RHEED and LEED intensity oscillations become irregular during the growth of the initial few layers of Si on a 7×7 superlattice surface of Si(111), whereas the oscillation becomes regular on a Si(001)-2×1 substrate.[1] We suppose that the difference between the growths on Si(111) and (001) is related to the rearrangement of the stable 7×7 structure on the Si(111) substrate during growth, which is based on the view that atoms in the stable stacking-fault layer in the dimer–adatom–stacking fault (DAS) structure[6] of the Si(111)-7×7 should be rearranged to obtain the 1×1 phase, which has a staggered configuration satisfying the epitaxial relation along the [111] direction.

Much work on the growth process of Si layers on Si(111) substrates was performed at substrate temperatures (T_s) above 350 °C. At $T_s \leqslant 300\,°\mathrm{C}$ the film growth, which is initially epitaxial, becomes amorphous when the thickness of the Si layer exceeds a certain value d_c.[7,8] The value of d_c becomes larger when the growth is performed at higher T_s and lower incident flux.[9,10] This has been called low-temperature epitaxial (LTE) growth by Eaglesham, Gossmann, and Cerullo.[9] We consider that the change from epitaxial to amorphous growth under the LTE growth condition is related to two mutual processes: the surface diffusion process of arriving atoms and the structural rearrangement process of atoms in a condensed phase during the layer growth.[8,10] To the best of our knowledge, the latter process has not been elucidated yet because the relaxation time for the rearrangement would be less than of the order of milliseconds. We suppose that inadequate structural rearrangement leads to the formation of various surface structures on the Si film. In particular, under the LTE growth condition, if structural rearrangement of atoms does not progress sufficiently, metastable surface structures will be formed. From this viewpoint, we studied the growth process and the surface structure of Si film grown on Si(111)-7×7 under the LTE growth condition.[7,8,10,11] By examining the formation mechanism of the various surface structures, the epitaxial growth mechanism on an atomic scale will be clarified.

All experiments were carried out in an ultrahigh-vacuum (UHV; U-STM, ULVAC JAPAN Co. Ltd.) system that contains scanning-tunneling-microscopy (STM) and RHEED systems and an electron evaporation source. The base pressure of the UHV system was routinely maintained at less than 1×10^{-8} Pa. We prepared atomically clean surfaces of the Si(111) wafers by heating them up to about 1150 °C for 2–3 h and flushing at approximately 1180 °C for 1 min with a direct current flow at background pressure below 1×10^{-8} Pa. We carried out the growth of Si films on Si(111)-7×7 substrates with the temperature held at 250 °C at a pressure below 3×10^{-7} Pa. The film growth was monitored while observing RHEED oscillation, and the rate (R) was monitored with a quartz oscillator and kept at 0.6 nm/min, which corresponds to 2 bilayer/min (BL/min) along the [111] direction of the Si crystal. We estimated R from the deposition time (t_d) and thickness (d), the latter of which was determined with a multiple-beam Fizeau-type interferometer for Si films at $10<d<60$ nm.

We determined the RHEED intensity change of the (0,0) spot (I) during the film growth, using a television camera connected to an interface and a microcomputer. The primary electrons with kinetic energy of 10 keV were incident at a glancing angle of 1° on the incident plane in the $[11\bar{2}]$ direction. Figure 1 shows the RHEED intensity oscillation, which becomes regular with period T, after the layer growth of $1\frac{3}{4}$ BL thick. T corresponds to the deposition time that is required for the growth of one layer with the thickness of a bilayer (0.31 nm). In the initial growth state below $1\frac{3}{4}T$, the RHEED oscillation becomes irregular: (1) the first maximum appears at $\frac{1}{4}T$ [stage (B)] and the first minimum at $\frac{3}{4}T$ [stage

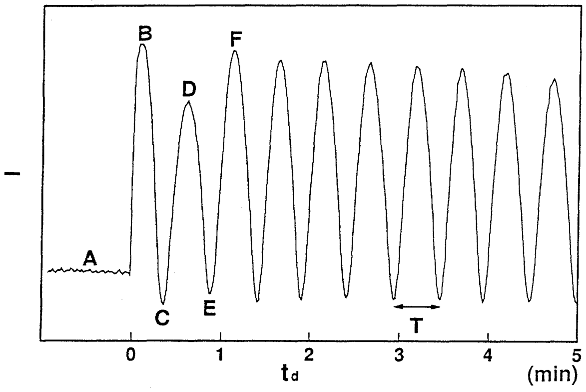

FIG. 1. Change in RHEED intensity (I) during the growth of Si layers as a function of deposition time (t_d).

(C)]; (2) the first minimum and the second maximum at stage (D) become smaller than the corresponding values in the regular oscillation that is seen at an arbitrary stage beyond stage (F). We also observed that RHEED patterns that consist of the fractional-order spots corresponding to the 7×7 structure disappeared after stage (B), and the pattern that consists of diffuse rods appeared at positions $(\frac{1}{2},0)$ and $(0,\frac{1}{2})$. From these results, we conclude that a distorted or localized 2×2 structure is formed as reported in the previous works based on LEED observation.[7,8] Later we will show that the diffuse rods at positions $(\frac{1}{2},0)$ and $(0,\frac{1}{2})$ in the RHEED pattern correspond to the formation of small domains with 2×2, 5×5, 7×7, and 9×9 structures because the adatoms show the localized 2×2 structure in the half unit of 5×5, 7×7, and 9×9 structures.

We observed the STM images at room temperature at a constant tunneling current of 1 nA and sample voltage of +1.5 V relative to a W tip. Figures 2(a)–2(f) show STM images (100×100 nm^2) from each growing film whose growth was terminated at each stage of (A)–(F) in Fig. 1. We will first describe the features of each image, and then consider the relation between the film-growth process and the irregular oscillation in RHEED.

In stage (B) at $t_d=\frac{1}{4}T$ we see bright areas, which correspond to the first-layer two-dimensional (2D) islands with height of 1 BL and width of about 6 nm, accounting for about 20% of the substrate surface. An enlarged image (20×20 nm^2) of stage (B) is given in Fig. 3, in which we also see other islands (gray areas) with height of $\frac{1}{2}$ BL relative to the substrate level. The height is determined from a height profile along the t-t' line as plotted in the lower part of Fig. 3. The latter islands were not observed in the further growth stages (C)–(F).

In stage (C) at $t_d=\frac{3}{4}T$, the first-layer 2D islands (gray areas) developed with the total area accounting for about 60% of the substrate surface (dark areas). The second-layer 2D islands (bright areas) with a height of 1 BL nucleate and grow on the first Si layer.

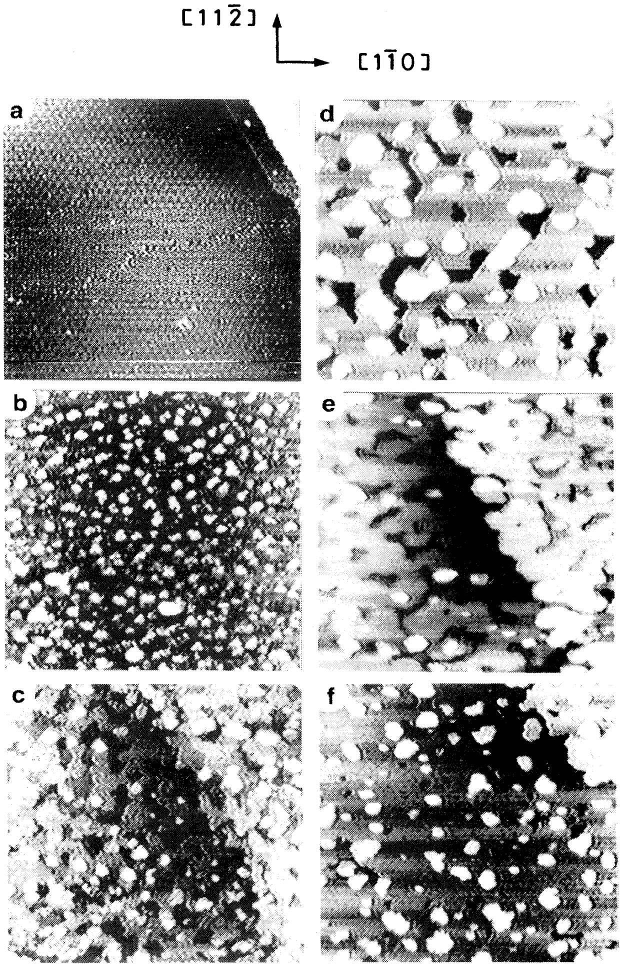

FIG. 2. STM images (100×100 nm^2) of (a) Si(111) substrate, (b) after deposition of $\frac{1}{4}$ BL at 250 °C, (c) $\frac{3}{4}$ BL, (d) $1\frac{1}{4}$ BL, (e) $1\frac{3}{4}$ BL, and (f) $2\frac{1}{4}$ BL, where (a)–(f) correspond to stages (A)–(F) in RHEED oscillation in Fig. 1, respectively.

The substrate surface was not covered completely with the first Si layer even in stage (D) at $t_d=1\frac{1}{4}T$. We note that the contour of the first layer shows straight lines. This feature is also seen in stage (C) [see Fig. 2(c)]. Figure 4(a) shows an enlarged STM image (20×20 nm^2) of stage (C), where the contour of the first Si layer (gray areas) showing straight lines forms steps along the $\langle 110\rangle$ directions that align with the dimer row in the DAS structure on the substrate. In stage (D), we also see that the third-layer 2D island grows on the second-layer 2D island as indicated by an arrowhead in Fig. 4(b) (40×40 nm^2).

In stage (E) at $t_d=1\frac{3}{4}T$, the substrate surface was completely covered with the first Si layer (dark areas), and the second Si layer (gray areas) with coverage of about 80% was observed to grow on the first one. We note that the contour of the second Si layer is curved, similar to a shape, resulting from the coalescence of round 2D islands, which forms a sharp contrast with the growth of the first 2D island on the substrate, as shown in Figs. 2(c) and 2(d). From this result it is clear that the lateral growth of the second bilayer on the first one is different from that of the first one on the 7×7 structure of the substrate. In addition to the difference in the lateral growth, we also note that the density of the third-layer 2D islands (bright areas) on the second Si layer is very low, as shown in Fig. 2(e). As shown in Fig. 4(b), these islands

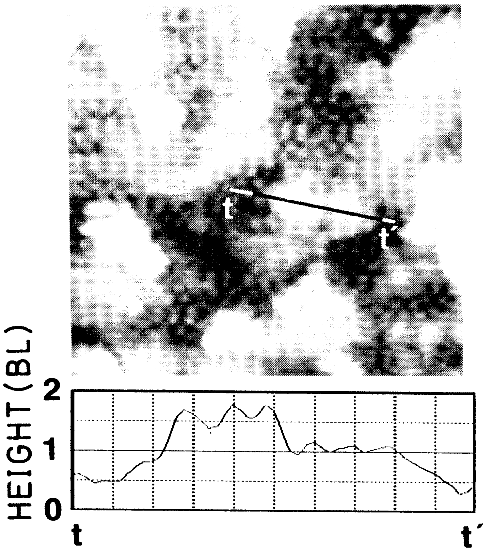

FIG. 3. Enlarged STM image (20×20 nm^2) of stage (B). The height profile was taken along the t-t' line across adjacent islands: one island with a height of 1 BL (bright area) and another with a height of $\frac{1}{2}$ BL (gray area) relative to the substrate level at t and t' were observed.

start to nucleate at stage (D), and no additional islands nucleate during the growth between stages (D) and (E).

In stage (F) at $t_d = 2\frac{1}{4}T$, the first Si layer was almost covered with the second one (gray area) and very small islands started to nucleate on it. Since the small third-layer 2D islands did not nucleate at stage (E), we assume that the small ones nucleate after the second Si layer covers the first Si layer completely, while the large ones start to nucleate at stage (D). Figure 5 shows enlarged STM images for the second Si layer in stage (F), which is composed of domains of 2×2, 5×5, 7×7, and 9×9 structures that are smaller than those obtained during growth at 520 °C, as reported by Köhler, Demuth, and Hamers.[12] We note that a domain with the 2×1 structure, which is known as the surface structure on vacuum-cleaved Si(111) (Ref. 13) and on Si islands grown on Si(111)-7×7 at $T_s = 500$ °C,[14] is also observed, as shown in the upper left-hand corner of Fig. 5(a).

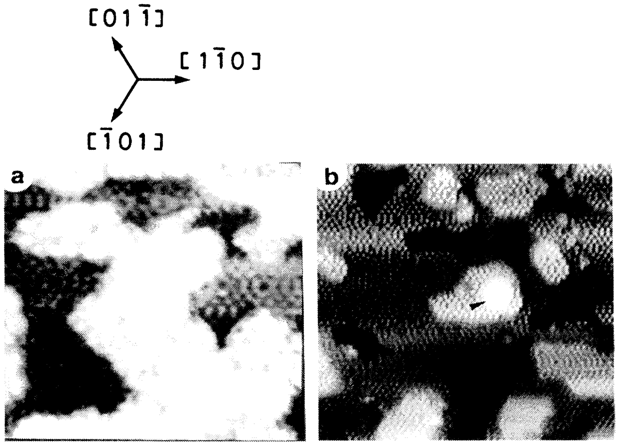

FIG. 4. Enlarged STM images (a) of stage (C) (20×20 nm^2) and (b) of state (D) (40×40 nm^2). The step edge of the first Si layer forms along the ⟨1$\bar{1}$0⟩ direction as indicated in the upper part of (a). The third-layer 2D island nucleates on the second-layer 2D island as indicated by the arrowhead in (b).

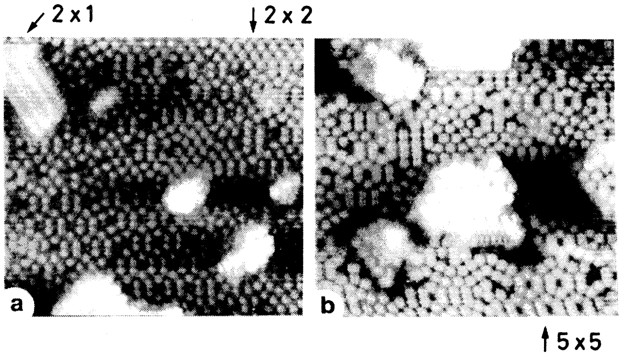

FIG. 5. Enlarged STM images (20×20 nm^2) at stage (F). The 2×2, 5×5, and 2×1 structures are indicated by arrows.

From these results we assumed that the irregular oscillation in RHEED intensity during the deposition of the first few BL of Si on Si(111)-7×7 is related to the nucleation and growth of multilayer (3D) islands composed of the first-, second-, and third-layer 2D islands, before the surface of the Si(111)-7×7 substrate is completely covered with the first Si layer. When the Si(111)-7×7 substrate is completely covered with the first Si layer at stage (D), the third-layer 2D islands stop growing and the second Si layer grows laterally. In other words, under the present growth condition, the 3D islands, which grow by the 2D layer-by-layer mode, nucleate and grow before the Si(111)-7×7 substrate is completely covered with the first Si layer. Such a growth mode change from the formation of 3D to 2D islands has also been pointed out from the analysis of the LEED intensity profile of the Si film grown at higher temperature (517 °C) by Altsinger *et al.*,[5] in comparison with our results that have been obtained from the Si film grown at 250 °C.

The growth of the 3D islands at the initial stage is probably caused by prevention of the lateral growth of the first Si layer required for rearranging the stable 7×7 DAS structure of the substrate surface. This view is supported by the STM image in Fig. 4(a), in which the progress of the lateral growth seems to be prevented along the dimer row in the DAS structure of the substrate. We assume that the rearrangement of atoms due to breaking of bonds in the dimer row and the faulted layer is caused by the crystallization of some disordered phase formed on the adjacent faulted and unfaulted halves,[15] which correspond to the additional first-layer islands with a height of $\frac{1}{2}$ BL as shown in Fig. 3. On the other hand, the lateral growth of 2D islands formed on the as-grown Si layer could progress without such a process as the rearrangement of atoms in the faulted half, because the as-grown surface is composed of small domains of metastable 2×2, 5×5, and 9×9 structures with distorted boundaries, as shown in Fig. 5.

We suppose that the difference in the surface structure of the Si layer on the native Si(111)-7×7 substrate and the as-grown Si layer results from that of the surface diffusion length (X_D) of adsorbed Si atoms and the size of critical nuclei (i^*). We note, by comparing the STM image in Fig. 3(b) with that in Fig. 3(f), that the island density becomes markedly low when the native substrate surface is completely covered with the first and second Si layers. The marked change in the island density is probably due to the increasing of X_D and i^* for the growing Si layer. We also obtained preliminary results for the Si film grown on Si(111)-7×7 at $T_s = 380\,^\circ\mathrm{C}$, which are summarized as follows. (1) The regular intensity oscillation starts at $t_d = 3$ BL,[3–5] while t_d is 2 BL at $T_s = 250\,^\circ\mathrm{C}$. (2) The surface of the first Si layer is almost entirely composed of the 7×7 superlattice. (3) The contour of each island becomes sharper than that at $T_s = 250\,^\circ\mathrm{C}$. (4) Metastable 2×2, 5×5, and 9×9 structures are formed on the surface of the second Si layer. These can also be interpreted from the change in the values of X_D and i^* with increasing T_s. In order to evaluate X_D and i^*, further observations on the growth sequence on the order of $\frac{1}{10}T$ are required.

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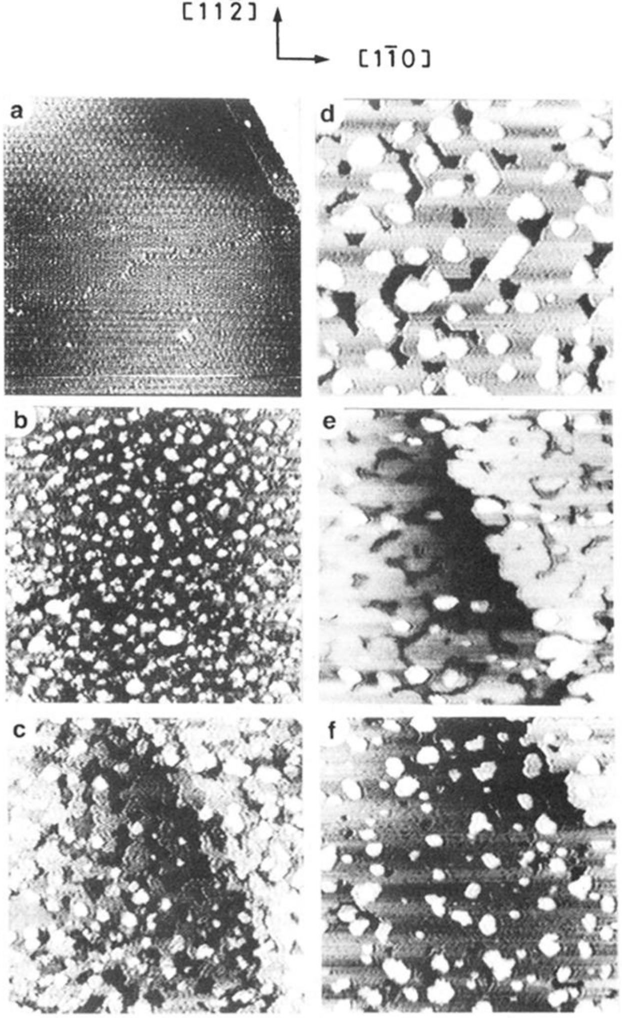

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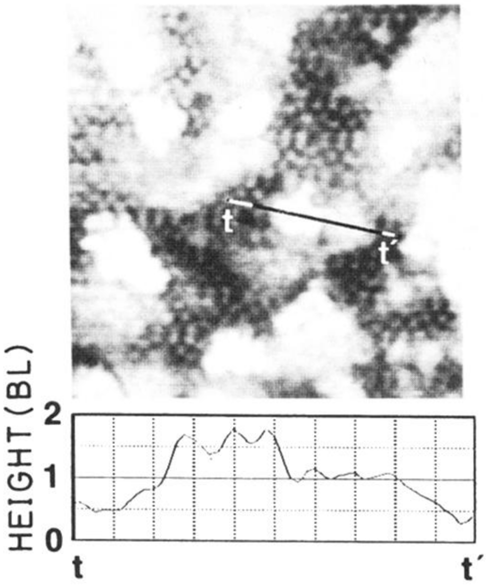

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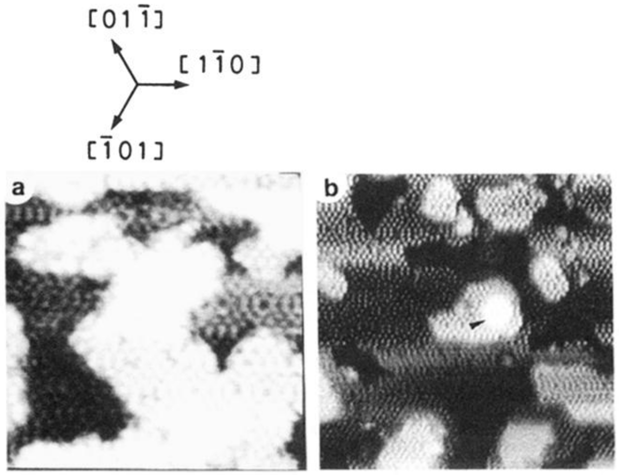

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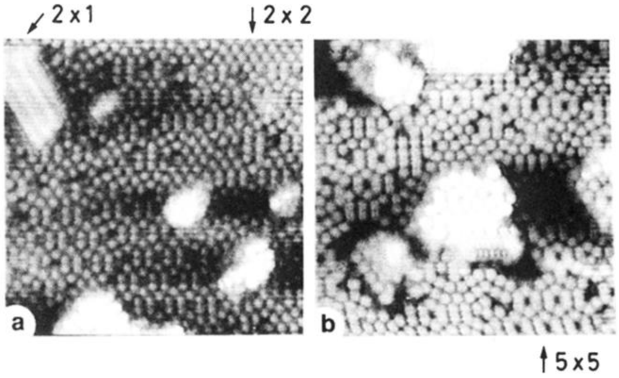

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