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STM study of initial stage of Ge epitaxy on Si(001)

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A scanning tunneling microscope (STM) was employed to study the superstructures and the formation process of islands at the initial stage of epitaxial growth of Ge layers on the Si(001) surface. Amount of Ge deposition was varied from one half of a monolayer (ML) to 4 ML. At a low Ge coverage the Ge layers were developed at step edges and on terraces forming two-dimensional (2D) islands and exhibited c(4 × 2) and p(2 × 2) structures on the Si substrate at 300°C. At a higher coverage of about 2 ML, a new superstructure with a periodicity of about 7 times of the unit cell was observed and the new cells were found to be the cores of the 3D islands. The number of islands increased and the islands grew with Ge coverage. Most Ge islands disappeared by annealing at 500°C and the 2D superstructure appeared again. Formation and growth mechanisms of the 3D Ge islands and the relaxation of the stress due to Si–Ge lattice mismatch will be discussed in analyzing the observed STM images.

1. Introduction

Heteroepitaxial growth on a Si surface is an essential subject for the development of electronic and opto-electronic devices. The Si–Ge heterojunctions are utilized in various new devices such as strained layer superlattice devices [1] and heterojunction bipolar transistors [2]. Furthermore, the Ge layer serves as a buffer for growing of GaAs layer on Si substrate [3]. Since the characteristics of these devices strongly depend on the structure of the Ge layer, the clarification of the layer structure is an essential requirement for improving the devices. However, the structure of the grown layer has not been fully understood at present because the lattice distortion due to 4.2% Si–Ge lattice mismatch complicates the growth mechanism.

The Si–Ge junctions have been investigated by various methods. Distortion at an atomically abrupt boundary of the Si and Ge layers was observed by Raman spectroscopy [4]. The studies by low-energy electron diffraction (LEED) [5], Auger electron spectroscopy (AES) [5], reflection high-energy electron diffraction (RHEED) [6,7] and X-ray diffraction [8] reported the layer-by-layer pseudomorphic growth on the heated Si(001) surfaces up to the critical thickness (a few monolayers) and the formation of dislocations and islands for thicker layers to relax the lattice distortion. However, diffraction patterns reflect statistically dominant ordered structures and hardly provide the information on disordered structures.

On the contrary, scanning tunneling microscopy (STM) [9] could be one of the most suitable techniques for the direct observation of surface structure because of its high atomic resolution. Accordingly, Mo et al. [10] and the authors [11] conducted the study of the Ge/Si(001) system with STM and reported the formation of microscopic islands or "hut clusters". However, no detailed report on the surface structure with a submonolayer deposition and the structure at the initial stage of the formation of microscopic islands is available. In this paper the newly found superstructure is discussed correlating the core formation of the islands, and the relaxation mechanism of the distortion of the Ge lattice on the Si substrate is examined.

2. Experiment

An ultrahigh vacuum STM [12] with a base pressure of 1×10^{-10} Torr was used. The n-type specimen of the Si(001) surface with a resistivity of 0.01 Ω cm was chemically polished in atmosphere by the Shiraki method [13] and then introduced into a vacuum chamber through a vacuum lock. The specimen was resistively heated at 600–730°C for several hours and then repeatedly flashed at 1200–1250°C. The cleaned and outgassed specimen was transferred to the STM unit in the chamber and surface cleanliness was confirmed by scanning over a wide area and observing the (2×1) reconstructed structure. Then the specimen was flashed again at 1200°C at the heat stage and germanium was deposited on the Si surface cooled at 300°C. Finally STM observation was conducted at room temperature. The Ge evaporator was a fine Ge rod wound by a W filament and thoroughly outgassed before Si cleaning. The amount of Ge deposition was controlled by a quartz thickness monitor and the vacuum while deposition was maintained below 5×10^{-9} Torr.

3. Results and discussion

3.1. Initial stage of epitaxial growth

Fig. 1 shows the STM image of the Si(001) surface covered by a Ge layer of 0.5 ML. Diagonal lines are dimer rows of Si and Ge. Since the chemical properties of the Si and Ge are very

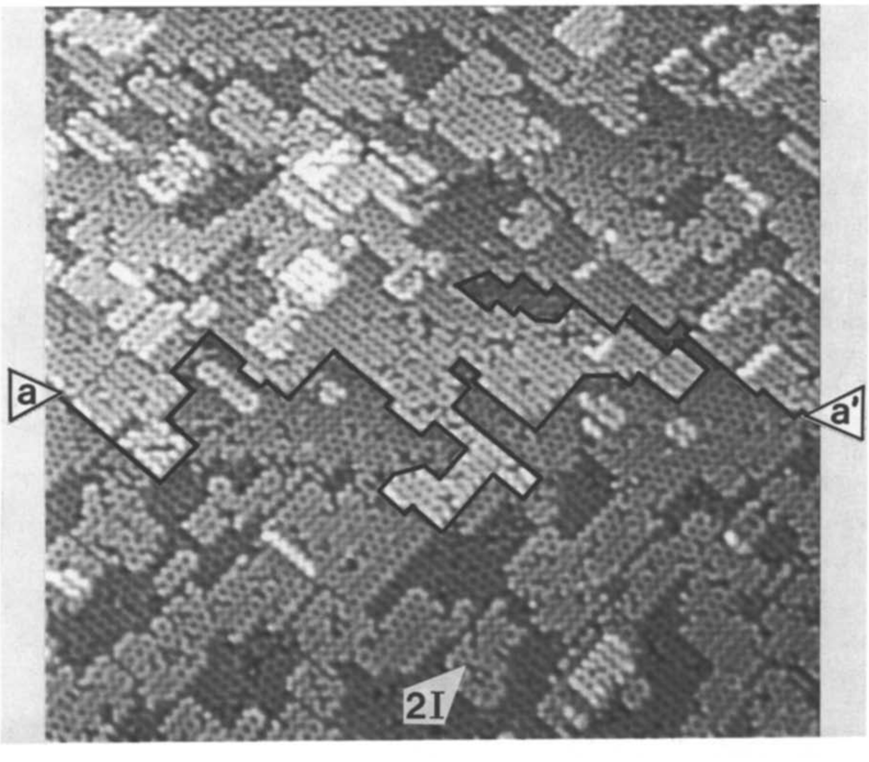

Fig. 1. STM image of Ge-covered Si surface. Arrow "2I" points a 2D island. The kinked solid line between a and a′ shows the complicated terrace edge due to lateral growth of Ge dimer rows from the step edge. Ge coverage 0.5 ML, sample bias voltage $V_s = -2.0$ V, tunneling current $I = 0.5$ nA. Scanned area 480×480 Å.

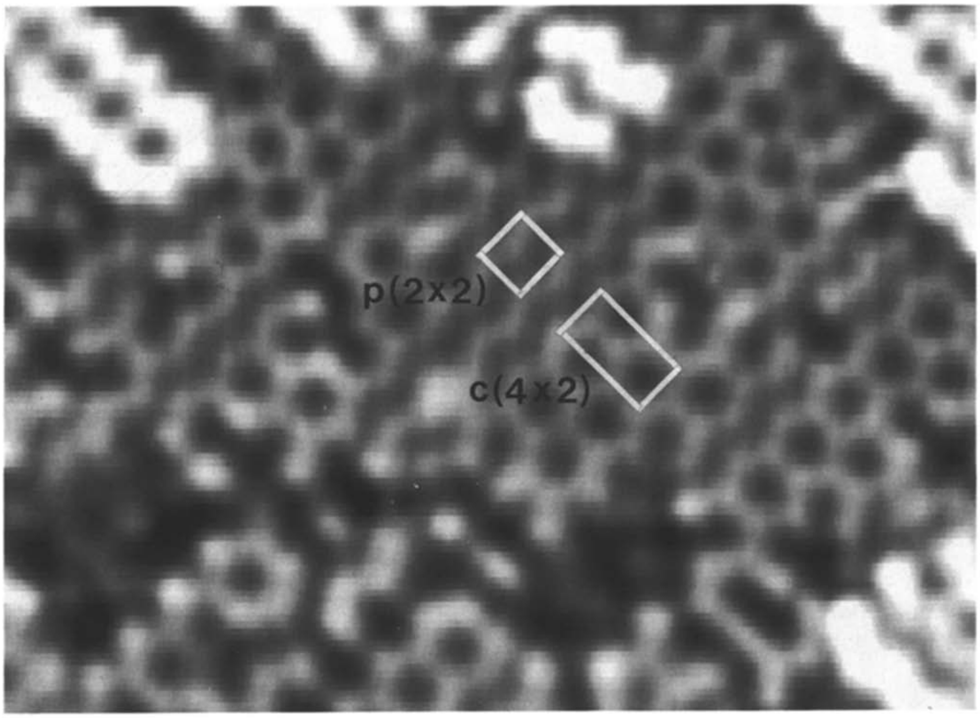

Fig. 2. Enlarged STM image of fig. 1. Two closed boxes indicate the unit cells of the c(4×2) and p(2×2) structures. Scanned area: 120×90 Å.

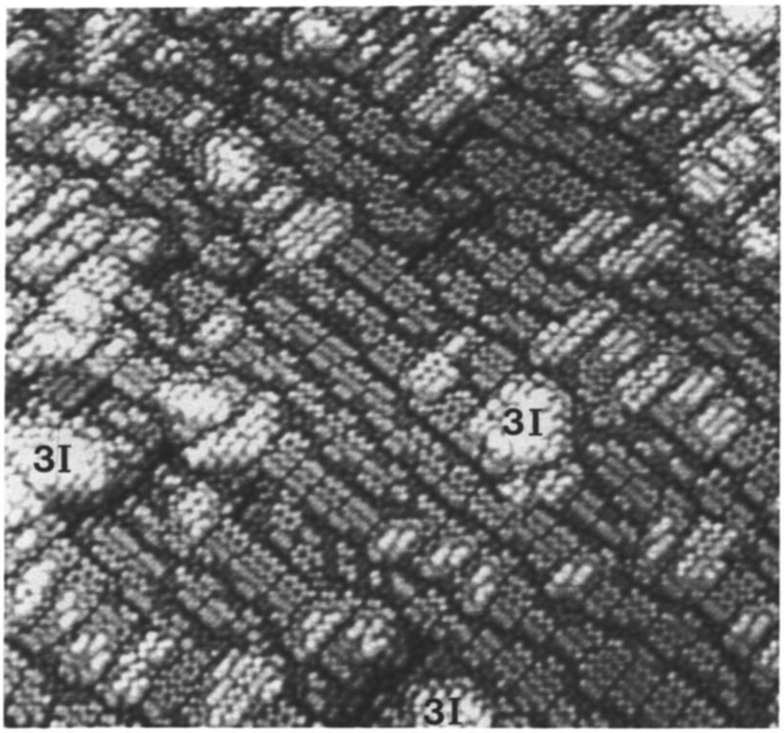

Fig. 3. STM image of Ge overlayer. The entire surface is covered by the patches consisting of a few short dimer rows which form the superstructure with a long seven-fold periodicity on average. The islands denoted by "3I" are small 3D islands. Ge coverage 3 ML, $V_s = -2.0$ V, $I = 0.2$ nA. Scanned area 480×480 Å.

close, it has been apprehended that Ge layers are hardly discriminated from the Si substrate. However, careful inspection of the STM image discriminates most of the deposited Ge layers at step edges and on terraces because the step edges of a clean Si surface are fairly straight and smooth and two-dimensional (2D) Si islands are not seen on the terraces [14]. For example, the 2D islands as indicated by arrow "2I" in fig. 1 are Ge layers and the rugged irregular terrace edges suggest the development of Ge layers from the step edges of Si substrate. The terrace edge indicated by a zig-zag black line between arrows a and a′ is quite complicated due to the lateral growth of Ge dimer rows from the step edge. Consequently, fig. 1 indicates that the Ge layers grow pseudomorphically by two mechanisms at the stage of 0.5 ML deposition; the formation of the 2D islands and the lateral growth from the step edges.

It is observed that the dimers on the clean Si(001) surface and the homo-epitaxially grown Si layer are normally symmetric. However, most Si and Ge dimers shown in fig. 1 are asymmetric and exhibit zig-zag dimer rows. The asymmetric dimers also show $c(4 \times 2)$ and $p(2 \times 2)$ surface structures [15] (fig. 2). The buckling induced by the deposition of foreign atoms was noticed for alkali metals on the Si(001) surface [16]. Figs. 1 and 2 clearly show that even an element with the same crystal structure such as Ge induces the buckling. Since a theoretical study [17] concluded that the energy difference between the symmetric and asymmetric dimers is small, the buckling could be easily induced and stabilized by a difference in electronic binding properties and bond lengths between Si and Ge. Furthermore, there is the possibility of intermixing of Si and Ge during the growth of Ge layers and the formation of dimers of buckling Si and Ge atoms due to charge transfer between the Si and Ge atoms.

At deposition of more than 2 ML a new superstructure appears. Small patches formed by a few short dimer rows cover the entire Si surface with Ge deposition of 3 ML (fig. 3). The patches are

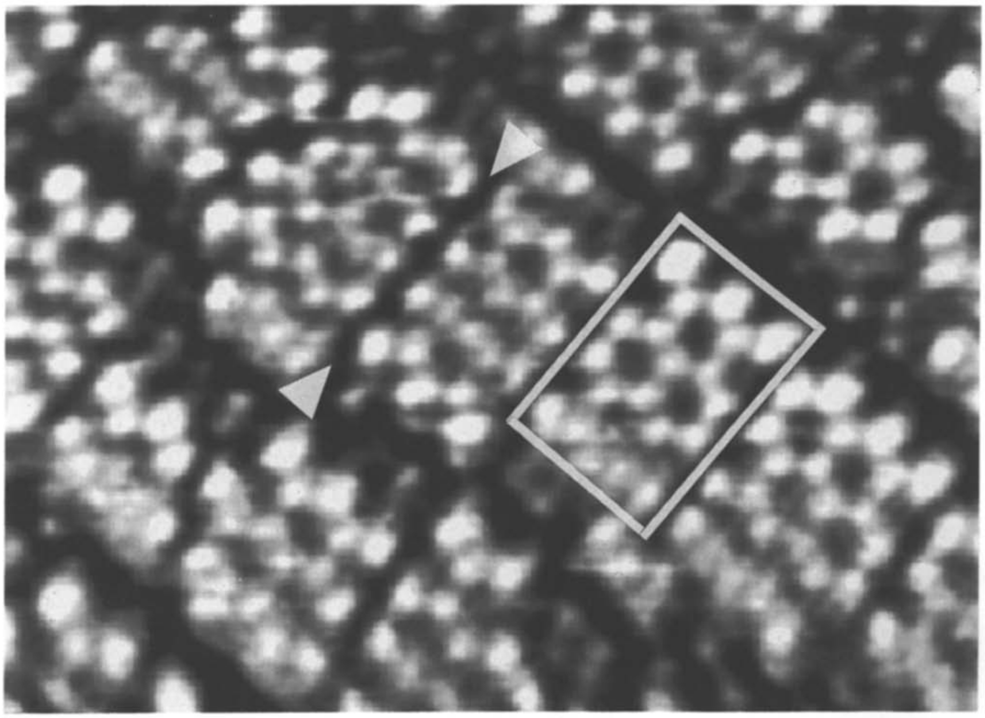

Fig. 4. Enlarged STM image of patch structure. A box closed by a white line indicates a patch of 5-dimer long 4-dimer rows. Arrows point a missing dimer-type defect. $V_s = -2.0$ V, $I = 0.2$ nA. Scanned area 110×90 Å.

fairly regularly arranged in the parallel and normal directions of the dimer rows constructing a superstructure with a long-range periodicity. An enlarged image of the patched surface (fig. 4) shows that short dimer rows consist of 5–6 dimers and the patches are partitioned by the missing dimer-type defects. Thus the periodicity of the patched structure is 6–7 times of the lattice constant in the dimer row direction. On the contrary, the number of dimer rows in the patches randomly varies from two to more than five. Accordingly, the periodicity in the normal direction of the dimer rows is hardly obtainable.

In order to find the periodicity, 2D Fourier transformation was conducted for an STM image of a wide area (fig. 3). In the Fourier spectrum of fig. 5 the spots at $\frac{1}{2}0$ and $0\frac{1}{2}$ correspond to the periodicity of 2 times the lattice constant of the dimer structure. The bright cross near the center corresponds to long-range periodicities and the diffused spots pointed by arrows located at the positions dividing the spots at $\frac{1}{2}0$ and $0\frac{1}{2}$ by about 3.5. Thus the superstructure of fig. 3 has a periodicity of about 7 times the lattice constant, on average, in the parallel and normal directions of the dimer rows. The structure of the patches is rather disordered and most boundaries between the patches are out of phase. Therefore, such a superstructure may not be recognized by diffraction methods and is not reported up to date. Accordingly the direct observation of the superstructure demonstrates the excellent capability of the STM for investigating the localized changes in atomic arrangement.

Small 3D Ge islands denoted "3I" in fig. 3 were grown on the 2D Ge layers. The 3D islands are localized stackings of a few atomic layers and grow to the "hut clusters" observed by Mo et al. [10] for heavier deposition as shown later. Thus the small islands are the embryos of the hut clusters and the image indicates that the larger islands grow through the stage of superstructure

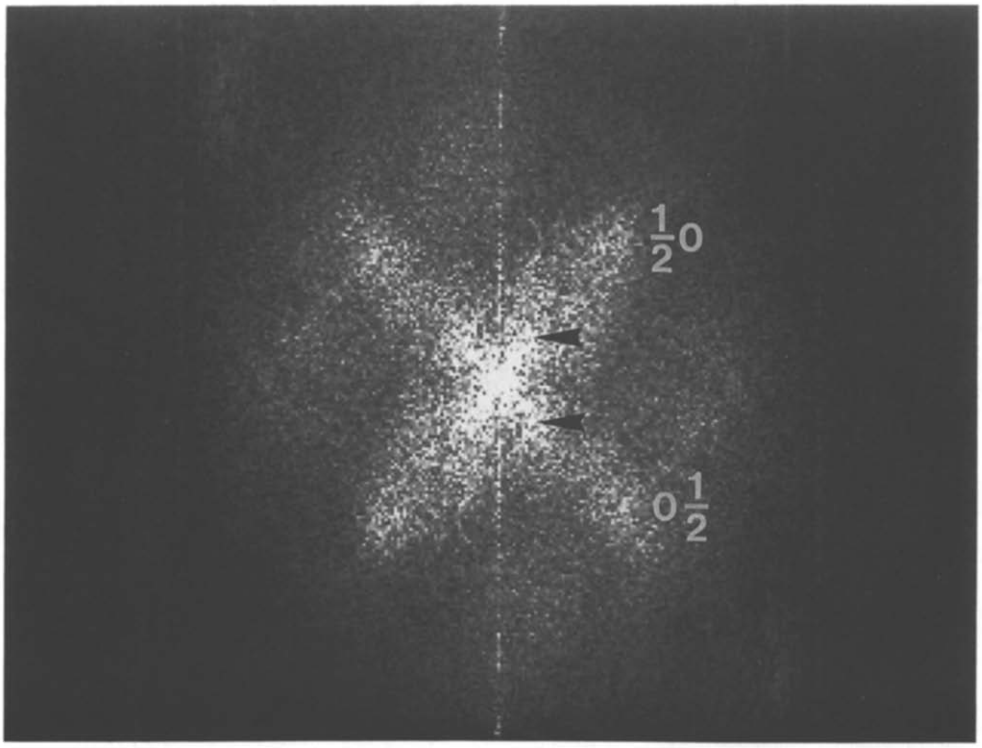

Fig. 5. 2D Fourier spectrum of fig. 2. The spots denoted by $\frac{1}{2}0$ and $0\frac{1}{2}$ correspond to the periodicity of the 2×1 structure and the arrows point to diffused spots corresponding to the superstructure with seven-fold periodicity.

with missing dimer-type defects. Fig. 6 supports this growth process showing the dimer rows of the second Ge layer on a relatively large underneath Ge path. The growth of dimer rows is impeded by a defect of the first layer. Then the monatomically stacked third layer covers the defect, building a small island.

The Ge islands grow to the hut clusters by deposition of 4 ML (fig. 7). Basically these islands have the same structure with four {015} facets denoted "F" and the (001) terrace denoted "T" on top [10,11]. The 2D patch structure is still seen between the islands implying that the growth mode is of Stranski–Krastanov type at a substrate temperature of 300°C.

3.2. Annealing effect

Annealing may induce two effects on the Ge-deposited Si(001) surface. One is the rearrangement of the surface structure from the structure constructed under non-equilibrium state to that of the equilibrium state, and the other is the interdiffusion of Si and Ge across the interface. Iyer et al. [7] observed Si–Ge interdiffusion above 350°C by Raman spectroscopy. In the present study, the Si surface covered by Ge 4 ML was annealed at 500°C for 5 min. The number of the 3D Ge islands decreased and the size of the islands increased by annealing. Then a flat and smooth area with a well ordered patch structure similar to that of fig. 3 appeared (fig. 8). The cause of the structure variation could be attributed to Ge diffusion forming large islands and to Si–Ge interdiffusion which forms an alloy.

3.3. Relaxation of lattice strain

Observation of 2D patch structures after deposition of ~ 2 ML on the Si(001) surface at 300°C and annealing the Si surface with a 4 ML overlayer at 500°C, suggests that the growth of the

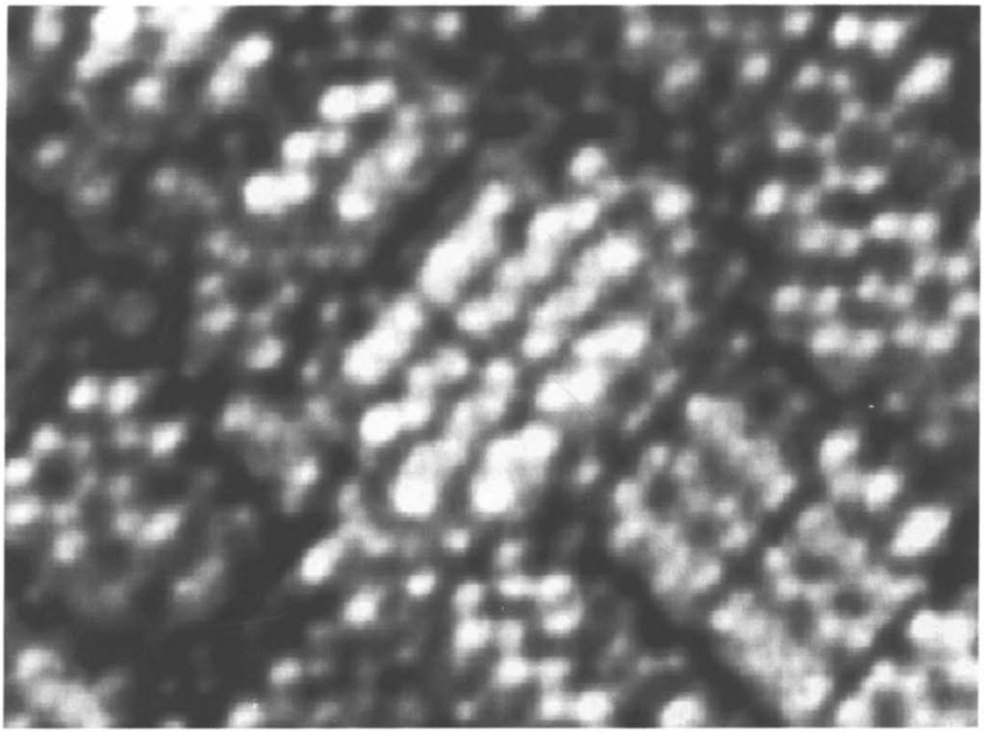

Fig. 6. Enlarged STM image of fig. 3. The growth of the second Ge overlayer on the 2D Ge island is impeded by the missing dimer-type defect of the underneath layer. Scanned area 140×90 Å.

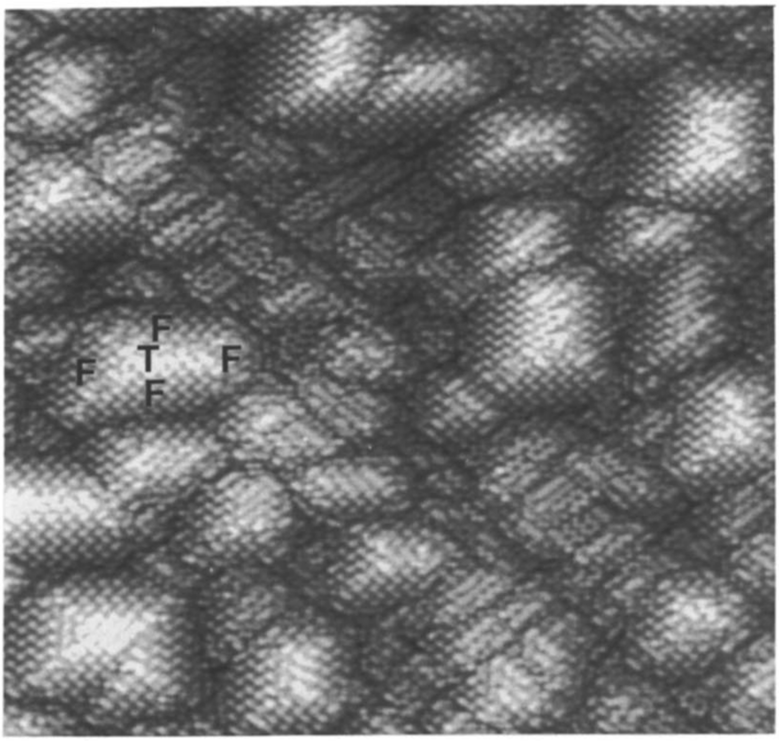

Fig. 7. STM image of Si surface covered by a Ge overlayer of 4 ML. "F" and "T" denote the {015} facets and small (001) terrace on top of the island. $V_s = -2.0$ V, $I = 0.5$ nA. Scanned area 480 × 480 Å.

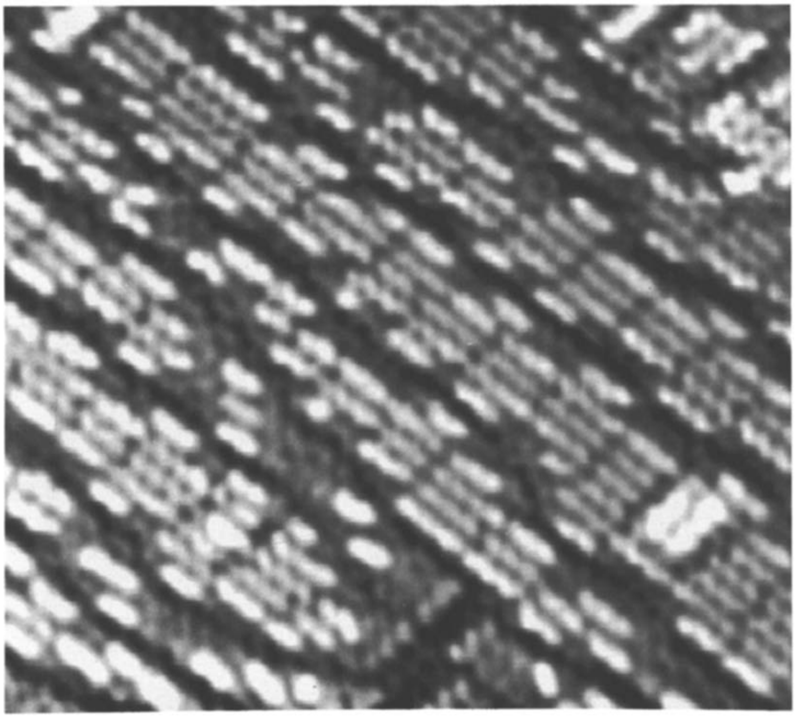

Fig. 8. STM image of annealed Ge deposited surface. Ge coverage is 4 ML. Most Ge islands shown in fig. 7 disappeared by annealing at 500°C for 5 min, after which a 2D patch structure with missing dimer-type defects is seen. $V_s = -2.0$ V, $I = 0.2$ nA. Scanned area 200 × 200 Å.

overlayer is more dominantly controlled by relaxation of the lattice strain than the kinetics limitation at the initial stage of the layer growth. Since the length of Ge bonds is longer than that of Si bonds, a large strain would be generated at the Ge–Si interface by the formation of a long dimer row. Thus the structure with periodical missing dimer-type defects would be the appropriate arrangement for the partial relaxation of the strain. The partial lattice relaxation in the Ge layer that developed on the Si surface was observed by the study with RHEED [18] and was found to be consistent with the present study. Furthermore, no patch structure is observed by Si deposition on the Si(001) surface. This fact supports the above mentioned partial relaxation mechanism.

4. Conclusion

The superstructure, which appeared at the initial stage of the growth of Ge layers on Si(001), and the growth process of 3D Ge islands were observed by STM. The Ge deposition of 0.5 ML on the substrate at 300°C resulted in the formation of 2D islands and in lateral growth from the terrace edges. The deposition also induced the buckling of dimers, and $c(4 \times 2)$ and $p(2 \times 2)$ structures of the Si substrate were observed. At an increased Ge deposition of ~ 2 ML, patches of new superstructure with a periodicity close to 7 times of the unit cell and embryos of the 3D islands on the patches were observed. By a larger deposition the 3D Ge islands grew and their number increased. However, most of the 3D islands disappeared by annealing at 500°C and the 2D patch structure appeared again. Consequently, based on the observed results, a new growth mechanism was proposed: at the initial stage of overlayer growth the construction of the superstructure with missing dimer-type defects to relax the lattice strain is more dominant than the kinetics limitation during the growth.

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