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Formation of Ge nanoclusters on Si(1 1 1)-7×7 surface at high temperature

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Abstract

We report on Ge nanocluster formation on Si(1 1 1)-7×7 surface at elevated substrate temperatures during deposition. The shape and size of the Ge clusters are more uniform than those obtained at room temperature due to an increase in the average mobility of the additional atoms. The Ge clusters have a preferential adsorption site in the faulted halves. Some clusters in the faulted and the unfaulted halves exhibit two different features, which indicate the different adsorption energy and chemical activity of the two half-cells. We also observe some clusters forming in a characteristic star shape at a particular positive bias voltage. The formation mechanism and possible structures are discussed.

Keywords: Germanium; Clusters; Silicon; Scanning tunneling microscopy

1. Introduction

SiGe heterojunction structures have attracted much attention in the past decades due to their applications in micro and optoelectronic devices and their compatibility with Si processing [1,2]. The surface structure of the Si substrate is confirmed to have a great and direct influence on the nucleation and growth of the Ge epitaxial layers [3–5]. The growth dynamics of Ge on Si(1 1 1)-7×7 surface exhibits classic Stranski–Krastanov mode behavior, in which coherently strained epitaxial layers grow layer by layer to a critical thickness followed by three-dimensional island formation. Meanwhile, the adsorption process during the initial growth stage of Ge on the Si(1 1 1)-7×7 surface has been far from well understood. Kohler et al. [6] report that Ge atoms are adsorbed preferentially in the triangular half-cells of the (7×7) surface and form irregular Ge clusters in size and shape, and Suzuki and Shigeta [7] present the formation of uniform Ge islands on Si(1 1 1)-7×7 substrate with very low coverage at the temperature of 300–360 °C, showing that the lateral growth of a Ge island is a rearrangement process of a stacking-fault layer.

The initial adsorption process of Ge on Si(1 1 1)-7×7 surface at room temperature has already been investigated in our previous studies [8–11]. In this letter, we report new progress on Ge cluster formation on Si(1 1 1)-7×7 surface at

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higher temperatures using scanning tunneling microscopy (STM). Ge clusters with more uniform sizes have been achieved. We will also report on one type of cluster appearing in a star shape at a particular positive STM bias voltage, and their formation mechanism and possible structures are discussed.

2. Experimental

The experiments were performed in an Omicron ultrahigh vacuum (UHV) system (base pressure $\sim 5\times10^{-11}$ mbar) equipped with scanning tunneling microscope (STM), low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The samples used in the experiments were antimony-doped n-type Si(1 1 1) wafers (resistance $\rho \sim 0.03\ \Omega$ cm, thickness $\sim$0.5 mm). Clean Si(1 1 1)-7×7 surface was obtained by flashing to 1200 °C while keeping the vacuum better than 1×10^{-9} mbar after degassing at 600 °C for 12 h by direct current heating. The deposition source was a small piece of Ge held by Ta electrodes. Ge was sublimated at about 900 °C by a direct current through the two electrodes. During the evaporation, the substrate was kept at various temperatures (room temperature, 100 and 300 °C, respectively), and the pressure in the chamber was better than 1×10^{-10} mbar. The deposition rate of Ge onto the Si(1 1 1) substrates was about 0.01 ML/min (1 ML $= 7.83\times10^{14}$ atom/cm^2), which was calibrated with Auger electron spectroscopy. Ge coverage used is between 0.10–0.40 ML. Each sample was cooled down to room temperature, and then observed by the UHV-STM. Chemically etched tungsten tips were used for STM measurement.

3. Results and discussion

Fig. 1 shows the STM images of the Si(1 1 1)-7×7 surface, on which 0.10 and 0.30 monolayer (ML) of Ge was deposited at room temperature. The irregular Ge clusters are almost located in the triangular half-cells of the Si(1 1 1)-7×7 surface, where the area with the greatest dangling bond density adsorbs Ge atoms preferentially. The images also show equal probabilities of Ge clusters occupying the faulted and the unfaulted halves. It is estimated that at room temperature Ge atoms do not have enough mobility to span the dimer wall after arriving on the surface [6]. With increasing Ge coverage, there is no change in the size of the Ge clusters and only their density increases. After the Ge clusters grow to saturate all dangling bonds in the triangular halves, the

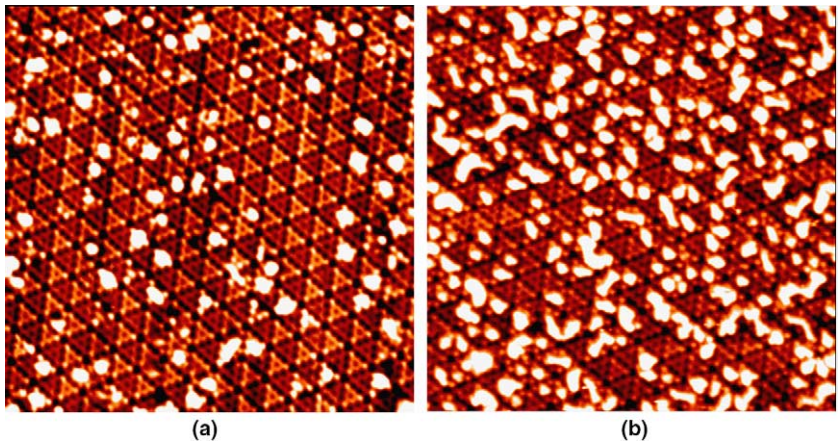

Fig. 1. The topographic STM images of the Si(1 1 1)-7×7 surface on which (a) 0.10 ML and (b) 0.30 ML Ge were deposited at room temperature. Scanning area: 40×40 nm^2. $U_{bias} = -1.5$ V, $I_t = 0.20$ nA. The irregular Ge clusters are almost all located in the triangular half-cells of the Si(1 1 1)-7×7 surface.

adsorption of the dangling bonds and Ge clusters for additional atoms will become very weak, and the mobility of the additional Ge atoms will increase correspondingly. So the additional Ge atoms can move preferentially to the smaller cluster and the growth of Ge clusters is suppressed. However, it is also found that some clusters continue to accumulate atoms and coalesce together to form a large cluster irrespective of the boundaries of the triangles. The size fluctuation of Ge clusters still indicates the lower mobility of Ge atoms at room temperature.

The STM images of 0.10 and 0.20 ML Ge deposited on the Si(1 1 1)-7×7 surface with the substrate temperature increasing to 100 °C are shown in Fig. 2a and b, respectively. The size distribution of Ge clusters is much different from that at room temperature, and more uniform size and shape can be achieved. All Ge clusters are formed within the boundaries of the triangular half-cells with sizes of about 1.6 ± 0.4 nm. The characteristics of the size distribution is similar to the result in our previous study [10] using diffusion-controlled aggregation, in which Ge clusters with nearly uniform sizes can also be obtained by depositing Ge on the Si(1 1 1)-7×7 surface at room temperature and then annealing the sample at a higher temperature. It is well known that the deposition of atoms onto a substrate is a non-equilibrium process, the adsorbed atoms migrate on the surface, and when meeting each other they can form critical nuclei, which subsequently can grow to clusters by attachment of further adatoms. The surface diffusion coefficient D of an additional atom is related to the site-to-site hopping rate k_s, $D = a^2 k_s$, where a is the effective hopping distance between sites, and $k_s \propto \exp(-V_s/kT)$, where V_s is the potential-energy barrier from site to site, T is the substrate temperature, and k is the Boltzmann constant. At room temperature most Ge atoms stay at the triangle half where they land due to the small diffusion length. So the deposition yields a broad distribution of cluster sizes. If we increase the substrate temperature during the deposition process, the average mobility of the additional atoms will be enhanced greatly. Then Ge atoms can migrate more easily to form nuclei and clusters in the triangles of (7×7) surface that are prone to adsorb Ge atoms.

Another obvious feature in the images is that the number of Ge clusters distributed in the faulted half unit cells is about three times that in the unfaulted halves, which is similar to the adsorption behavior reported for a variety of metals [12–14]. As the two halves in the (7×7) cell taking on different reaction activities, the preference of Ge

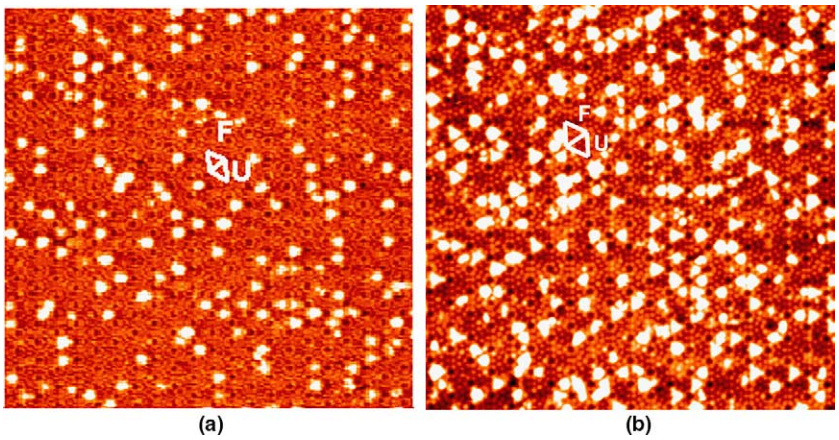

Fig. 2. STM images of (a) 0.10 ML and (b) 0.20 ML Ge deposited on a Si(1 1 1)-7×7 surface with the substrate temperature increasing to 100 °C. Scanning sizes: 50×50 nm^2, $U_{bias} = 2.0$ V, $I_t = 0.20$ nA. Ge clusters with more uniform sizes can be seen, showing the preferential adsorption in the faulted half unit cell of Si(1 1 1)-7×7 structure. There are two different forms of Ge clusters (exhibiting triangular and round shape, respectively) on the faulted halves and the unfaulted halves.

cluster adsorbed in the faulted half means it has a lower total energy than that in the unfaulted half. The adsorption energy difference between the two halves can be estimated by the Boltzmann formula $N_F/N_U = \exp(-\Delta E/kT)$, where N_F and N_U are occupation numbers on the faulted half unit cell and the unfaulted one at temperature T, respectively, where ΔE is the energy difference, and k is the Boltzmann constant [14].

In addition, many clusters on the faulted halves and the unfaulted halves exhibit two different structures, with triangular and round shapes, respectively, which is more prominent in STM image at 0.20 ML Ge coverage. We suggest that it might be due to the different adsorption energy and chemical activity of these two halves. Ge atoms have a more favorable total energy to adsorb on the faulted halves, on which the clusters can comprise a greater number of Ge atoms at higher coverage. Nevertheless, the dimer walls and corner holes can also be clearly observed, indicating potential barriers along the boundaries of the Si(1 1 1)-(7×7) unit cells still exist in effect.

It is of interest that some clusters can appear in a characteristic star-like shape at bias voltages between +1.5 and +2.0 V in our STM image, as shown in Fig. 3a and c. While at a higher positive voltage, the horns of "star" will fade out and the

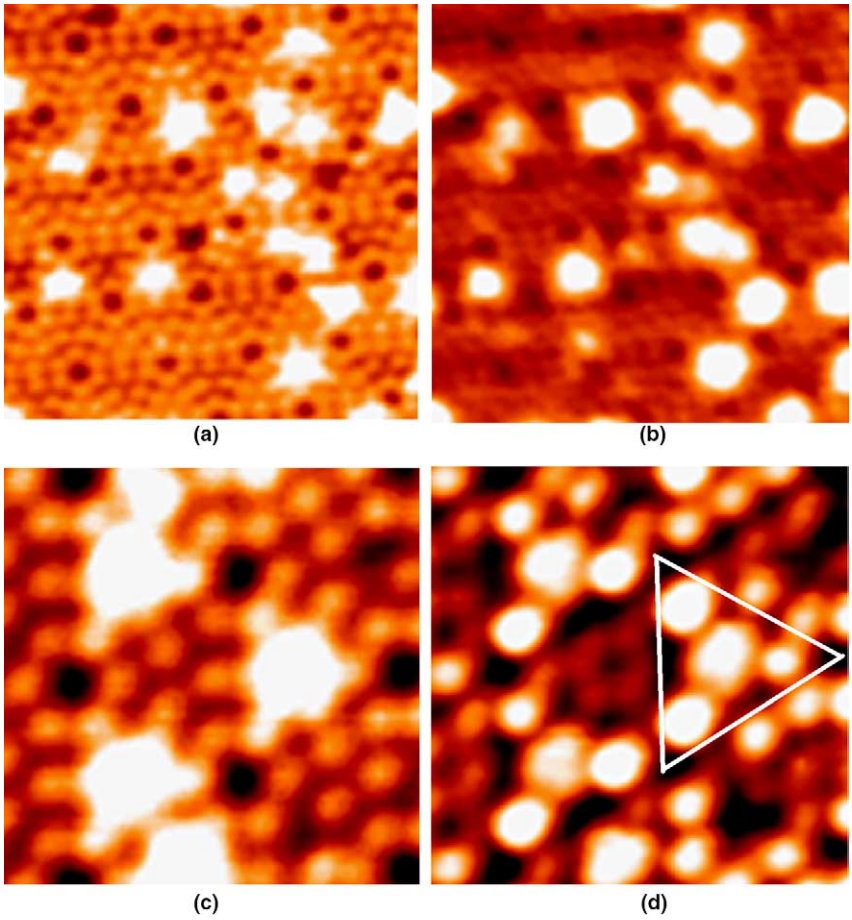

Fig. 3. STM images of "star"-shaped clusters at various bias voltage, (a) and (c) $U_{bias} = +2.0$ V, some clusters appear in characteristic star shape; (b) $U_{bias} = +3.0$ V, the "star"-shaped clusters in the same area with (a) transform its appearance to the rounded shape; (d) $U_{bias} = -1.5$ V. In (c) a cluster is located in the center of the triangle of (7×7) unit cell, and some bright satellite dots are distributed at the nearest adatoms sites around the central cluster. The tunneling currents in all images are 0.20 nA.

cluster can transform its appearance to the round shape (see Fig. 3b). To understand the structures of the star-like clusters, we investigate their characteristics in the filled-state STM image, which seems very different from that in the empty-state image. Fig. 3d shows the STM image ($U_{bias} = -1.5$ V) of the star-like clusters in Fig. 3c. The appearance of one cluster in the triangular half of the (7×7) unit cell is marked with a white triangle. There is a central cluster located in the center of the triangle. Some bright dots look like satellites distributed at the nearest adatoms sites around the central cluster.

Because the observed structures of the clusters are not directly related to the internal configuration, but to their electronic structures, various bias voltage STM images can reflect the difference of local density of states (LDOS) at various energy levels. We consider that the central cluster has a great influence on the electronic structures of the nearest adatoms, including the three corner adatoms in the triangle and three center adatoms in the neighboring triangles (as illustrated in Fig. 4). So the cluster can appear in different forms when the bias voltage changes. From STM images it follows that only a few clusters exhibit the normal hexagram form, while most of clusters have irregular star shapes. One explanation is that the central clusters with different structures will have different effects on various nearest adatoms. However, the strong voltage dependence of STM images cannot make it possible to definitively establish detailed electronic structure and configuration of Ge clusters without the aid of theoretical calculation and simulation. Our further theoretical ab initio calculations are in progress. Moreover, it is worth noting that all clusters capable of giving rise to the star shape have smaller sizes to make three corner adatoms in the triangle visible in filled-state images.

Further increase of the substrate temperature causes coarsening of clusters and intermixing between Ge and Si atoms simultaneously, which is believed to be due to the mobility of Ge atoms. Therefore, the uniformity of Ge clusters in size and shape shows no obvious change in our experiments. When the substrate temperature is increased to about 300 °C or even higher temperature, the growth of epitaxial Ge wetting layers will begin. As shown in Fig. 5, the typical surface morphology of Ge triangular epitaxial islands at submonolayer

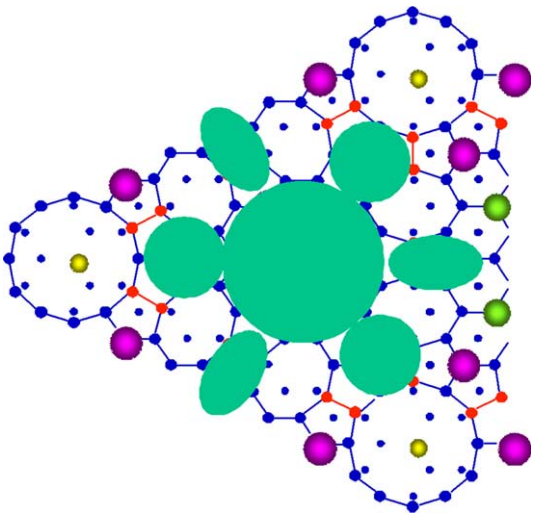

Fig. 4. Top view of a possible structural model proposed for the "star"-shaped clusters. A cluster is located in the center of the triangle. The strong voltage dependence of the appearance results from a great effect of the central cluster on electronic structures of the nearest adatoms.

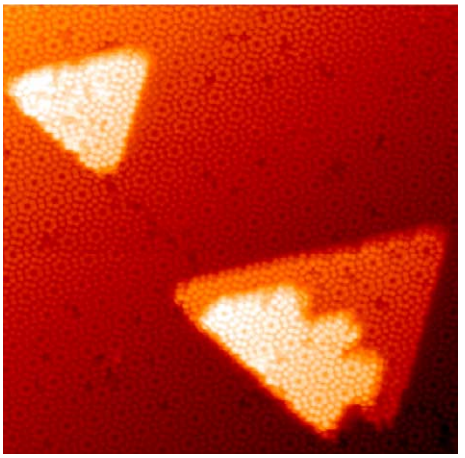

Fig. 5. STM images of 0.20 ML Ge deposited on the Si(1 1 1) 7×7 surface with the substrate temperature increasing to 300 °C. Scanning sizes: 45×45 nm^2, $U_{bias} = 2.0$ V, $I_t = 0.10$ nA. Two-dimensional Ge triangular epitaxial islands with the same orientation and reconstruction on the Si(1 1 1)-7×7 substrate are formed.

coverage, with the same reconstruction and orientation as the Si(1 1 1)-7×7 substrate. As reported many times in the literature [15,16], Ge–Si intermixing and alloying can exist at high temperature, and play an important role in epitaxial growth of Ge islands.

4. Conclusions

At room temperature, irregular Ge clusters adsorbed in the triangular halves of the Si(1 1 1)-7×7 surface. With an increase of the substrate temperature during the deposition process, the average mobility of the additional atoms can be enhanced greatly, and the Ge clusters have more uniform sizes and preferentially adsorb in the faulted halves. Moreover, some star-like clusters are observed in our empty-state STM images. They can appear in different forms at various bias voltages. The Ge cluster in the triangle is found to have a great influence on electronic structures of the nearest adatoms.

Acknowledgements

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