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Self-assembled growth of ordered Ge nanoclusters on the Si(1 1 1)-(7 × 7) surface

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Abstract

The self-assembled growth of submonolayer Ge on the Si(1 1 1)-(7 × 7) surface grown by solid phase epitaxy has been studied using scanning tunneling microscopy. Ordered Ge nanoclusters on the surface are formed by the deposition of the submonolayer of Ge at room temperature and subsequent annealing. It is proposed that adsorbate Ge atoms are trapped in the attractive potential wells on the faulted half of the (7 × 7) unit cell. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The growth of Ge on Si substrate has received much attention in the past decades, through both fundamental studies and technological applications. One of the major advantages of Ge is its compatibility with conventional Si integrated-circuit technology, potentially allowing the incorporation of devices utilizing spontaneously formed Ge islands into Si integrated-circuit technology. Electronic and atomic structures of Ge and Si adsorption on the Si(1 1 1)-(7 × 7) surface have been extensively studied [1–6]. Understanding the dependence of the island size and uniformity on the deposition conditions is of importance. Sys-

tematic variation of the deposition parameters can lead to better understanding of the formation mechanisms, controlling island formation and obtaining uniform islands of desired size. Sato et al. [4] have studied the initial stage of the Si adsorption process on Si(1 1 1) substrate. It was suggested that the mode of Si adsorption process depended on the sample temperature and different self-organization took place depending on the way in which the adsorption atoms diffuse. Owing to their interesting properties in quantum physics and potential application, self-assembled semiconductor quantum structures such as SiGe [7–9], InAs [10], and metal [11–14] quantum dots and wires have grown by different techniques. However, the controlled growth of ordered Ge nanostructures at the Si(1 1 1)-(7 × 7) surface remains a difficult challenge. If the size and position of Ge islands can be precisely controlled, new

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physical properties such as quantum size effect can be expected.

In this letter, we report on the possibility of controlling Ge nanocluster position and size on the Si(1 1 1)-(7×7) surface, and describe the formation of an ordered array of two-dimensional Ge nanoclusters on this surface. The process is mediated by the intrinsic attractive potential wells that existed on the faulted halves of the Si(1 1 1)-(7×7) unit cells [15], which can effectively trap diffusing Ge adsorbate atoms to create a regular arrangement of islands of well-defined size. By depositing 0.15 monolayer (1 ML = 7.8×10^{14} atoms/cm²) of Ge on the Si(1 1 1)-(7×7) surface and then annealing the sample at different temperatures, the self-assembled growth process can be investigated.

2. Experimental

The experiment was conducted in an Omicron ultrahigh vacuum scanning tunneling microscopy (UHV-STM) to get atomic resolution images. The base pressure of the chamber was maintained at 5×10^{-11} Torr. The sample used in our experiment was cut from a lightly P-doped mirror-polished Si(1 1 1) wafer with a resistivity of 1–2 Ω cm and a size of $12 \times 2 \times 0.5$ mm³. The sample was out-gassed at 600 °C for 12 h, followed by flashing up to 1200 °C for 1 min with direct current heating. Then, the temperature of the sample was cooled down to room temperature at a rate of less than 1 °C/s by decreasing the heating current slowly. After repeating the last two steps, a large area (7×7) reconstruction can be obtained. During the sample preparation process, the pressure in the preparation chamber was better than 4.0×10^{-10} Torr. The STM was operated at room temperature using an electrochemically etched tungsten tip. The surface morphologies presented here were in situ investigated in real space using STM, and obtained in the constant current mode at sample bias voltages between –2.0 and +2.0 V and tunneling currents between 0.1 and 0.5 nA.

Ge deposition was carried out in the UHV-STM preparation chamber. A small piece of Ge with purity of 99.9999% was used as the deposition

source, held by Ta electrodes. Ge was sublimed at about 800 °C by DC heating and the deposition rate was estimated to be about 0.005 ML/min. Submonolayer Ge was deposited on the Si surface at room temperature and then annealing the sample at different temperatures.

3. Results and discussion

The self-assembled growth process of Ge on the Si(1 1 1)-(7×7) surface is investigated by depositing submonolayer of Ge on the Si(1 1 1) surface and then annealing the sample subsequently. Fig. 1 shows STM images of 0.15 monolayer Ge on the Si(1 1 1)-(7×7) surface grown by solid phase epitaxy at substrate kept at room temperature (a) and then annealed at 150 °C (b), 200 °C (c) and 250 °C (d) respectively. The surface of the as-deposited sample is almost continuously covered with amorphous-like Ge clusters, shows very rough, granular features, which are equally distributed on the faulted and unfaulted halves of the Si(1 1 1)-(7×7) unit cell. The STM image shows that holes arranged in a (7×7) periodicity still exists. The holes are originate from the corner holes of the Si(1 1 1)-(7×7) reconstruction. After annealing the as-deposited sample at 150 °C for 10 min, the surface becomes much smoother and is covered with adatoms. Fig. 1b shows the STM images recorded with negative sample bias. The larger Ge clusters begin to decompose into smaller ones, which are also equally distributed on the faulted and unfaulted halves of the Si(1 1 1)-(7×7) surface, and the interface (7×7) reconstruction keeps intact.

Annealing the sample at higher temperature, the Ge clusters begin aggregating through surface diffusion. Fig. 1c shows STM image of the sample after annealing at 200 °C for 10 min. The images are recorded at the sample bias and tunneling current were –1.5 V and 0.42 nA. We can observed the ordered packed Ge clusters over the surface, and the nanoclusters are almost the same in size from the STM image illustrated in Fig. 1c and the line profiles (not shown). It can be found that the site of the formed Ge clusters is on the faulted half of the Si(1 1 1)-(7×7) unit cell.

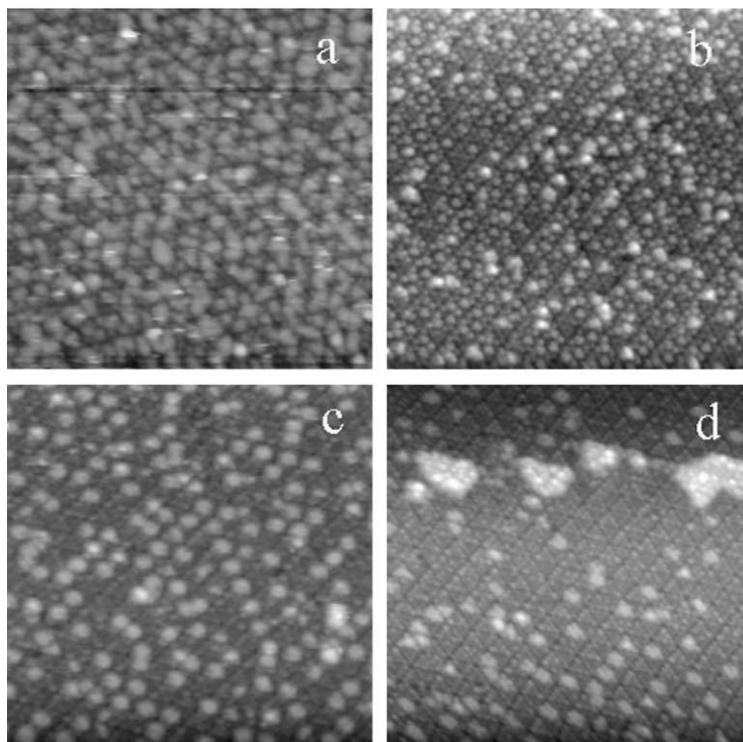


Fig. 1. STM images of 0.15 monolayer Ge deposited on Si(111)-(7 × 7) substrate kept at room temperature, (a) as-deposited; and subsequent annealing at (b) 150 °C, (c) 200 °C, (d) 250 °C. The scanning area was 40 × 40 nm, and the sample bias and tunneling current were −1.5 V and 0.4 nA.

On annealing the sample at 250 °C, the Ge clusters begin to grow into larger islands through surface diffusion. Fig. 1d shows the surface image of the sample after annealing at 250 °C for 10 min. This result indicates that the 250 °C annealed Ge layer aggregate to form new reconstruction and that the Si(111)-(7 × 7) interface reconstruction is still intact. With increasing annealing temperature of the as-deposited sample, the surface diffusion coefficient D increased considerably, and adsorbate atoms diffusion set in, resulting in the formation of larger clusters by coalescence. The size of these clusters depends exponentially on the annealing temperature.

The preferential adsorption of adsorbate atoms on the faulted halves of Si(111)-(7 × 7) unit cells at lower coverages has been reported for a variety of metals, such as Pb, Sn, Ag, Pd, and alkali metals. Vitali et al. [14] have observed the formation of ordered superstructures for thallium on the

Si(111)-(7 × 7) surface. On the other hand, the bonding of adatoms on the Si(111)-(7 × 7) surface and identification of stable binding sites as well as the determination of surface diffusion pathways are important problems of interest for the detailed understanding of the initial stages of Ge adsorption on Si substrate. Cho and Kaxiras [16] studied the adsorption and diffusion of adsorbate atoms on the reconstructed Si(111)-(7 × 7) surfaces by density function theory (DFT) total energy calculations, and introduced the so-called *basins of attraction*, which contain stable adsorbate positions as high-coordination sites rather than surface dangling bond sites.

Cho and Kaxiras (CK) performed calculations for six different positions of the adsorbate atoms, as shown in Fig. 2a as 1–6, which refer to these positions as T₁, H₃⁻, B₂⁻, T₄⁻, B₂['] and H₃[']-type. Notice that the positions 2, 3 and 4 (H₃⁻, B₂⁻ and T₄-type) are repeated symmetrically around the

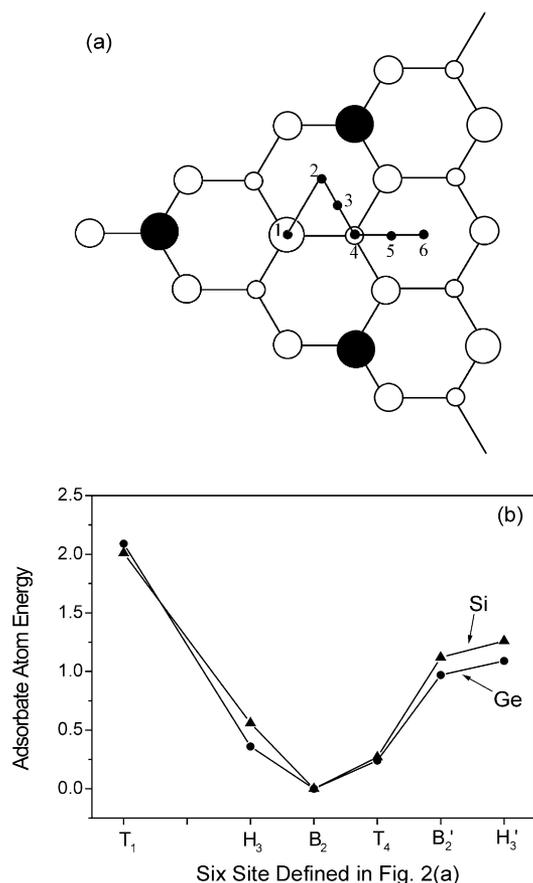


Fig. 2. Schematic drawings of a portion of the Si(111)-(7 × 7) reconstruction containing three Si adatoms and one rest-atom (a). The numbers 1–6 indicates the sites where adsorbate atoms are placed. (b) Plots of the adsorbate atom energies along the six sites defined in (a), as adapted from Ref. [16] for Si and Ge on Si(111). The energies are relative to the lowest energy sites for each adsorbate atom.

central T₁ position, forming a closed path of which the segment shown in Fig. 2a is one-sixth (as the “2–3–4 closed path”). In this path, a moving atom would stay within one basin defined by the central rest-atom and the three surrounding Si adatoms. Paths along the position 5 and 6 would bring the moving atom into adjacent basin. The energies of the six positions for Ge adsorbate atoms is illustrated in Fig. 2b. The T₁ site is the high-energy site, and the lowest-energy sites are the B₂-type sites for Si and Ge. All the lowest-energy sites are within the basin formed by the three Si adatoms around

the rest-atom and are high-coordination sites. Moreover, the DFT calculations of CK yield much high energies for adsorbate atoms (Si and Ge et al.) attached to dangling bond T₁ sites above intrinsic Si adatoms or rest-atoms, the possibility that adsorbate atoms will attach to dangling-bond sites (either the rest-atom or the adatom) on the Si surface has therefore been disregarded.

CK introduce so-called basin of attraction, which contain the stable adsorption sites for all the adsorbate atoms as high-coordination surface sites rather than the surface dangling bond sites. The important aspect of the CK model for the present discussion is that Ge adsorbate atoms become trapped in basin of attraction around rest-atom sites, which provide stable adsorbate atom position in terms of high-coordination sites; these are the T₄-, B₂-, and H₃-type positions, which surround a center T₁ position on top of the test atom. The basins display threefold symmetry and contain thus three equivalent high-coordination sites each. The diffusion barriers between the T₄-, B₂-, and H₃-type positions are low thus allowing for fast adsorbate atom diffusion in a closed path within the basin of attraction, but due to higher barriers surrounding the basin, diffusion across basins is slower. Attractive potential wells exist on the faulted halves of the Si(111)-(7 × 7) unit cells, consisting of three CK basins of attractions each, which act as effective traps of Ge adsorbate atoms. The adsorbate atoms are mobile within the potential wells, but diffusion out of the wells is restricted by the boundaries of the Si(111)-(7 × 7) unit cells.

Interestingly, for coverage beyond that for the formation of ordered nanoclusters, the nature of the trapping potential is radically changed. This is illustrated in Fig. 3 by the comparison of the images at (a) 0.15 ML to that of (b) 0.2 ML, where the unfaulted halves of the (7 × 7) unit cells are also populated. There are lots of pyramid-like clusters on the faulted half unit, and a few dome-like clusters on the unfaulted half. Three pyramid- and three dome-like clusters can compose a circular ring. This structure can be due to the energy difference between adsorption on the faulted and unfaulted unit cell halves. However, the dimer walls of the (7 × 7) unit cells remain clear of Ge

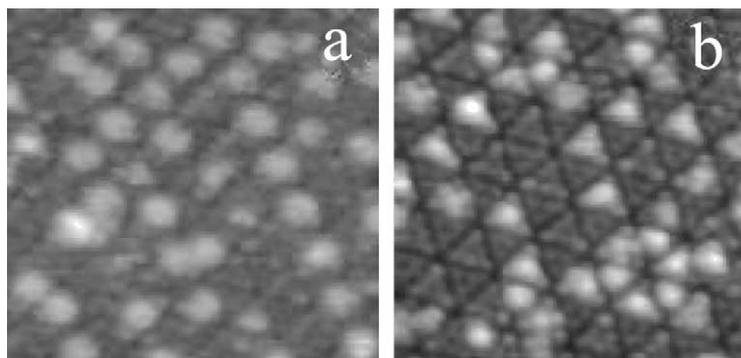


Fig. 3. STM images for different Ge coverages on the Si(111)-(7 × 7) deposited at room temperature and then annealed at 200 °C for 10 min. Coverage are: (a) 0.15 ML and (b) 0.2 ML. The scanning area was 18 × 18 nm, the sample bias and tunneling current were −1.5 V and 0.42 nA.

adatoms, which indicate that the repulsive potential of the dimer rows is retained.

4. Conclusions

In summary, we have observed the growth process of self-assembled Ge nanoclusters on the Si(111)-(7 × 7) surface using scanning tunneling microscopy. This observation has been phenomenologically described by a model, which relies on adsorbate atom trapping in attractive potential wells on the faulted halves of the (7 × 7) unit cells. The adsorbate atoms are selectively confined in each faulted half of unit cell by three basin of attraction, which contain high-coordination sites for adsorbate atom bonding as conceptualized by Cho and Kaxiras [16]. The detailed potential balance on the Si(111)-(7 × 7) surface appears to be particularly favorable for the trapping of Ge adsorbate atoms into ordered array of nanoclusters at low adsorbate coverages.

Acknowledgements

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