Initial adsorption of Ge on Si(1 1 1)-(7 × 7) surface at room temperature

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Abstract

The initial stage of Ge adsorption on Si(1 1 1)-(7 × 7) surface has been investigated by ultrahigh-vacuum scanning tunneling microscopy at room temperature. We demonstrate that there is a critical nucleus for the adsorbed Ge clusters on Si(1 1 1)-(7 × 7) surface. Such clusters can behave like quantum dots, which display two states at +1.5 and −1.5 eV with respect to the Fermi level. The formation mechanism of the clusters is discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ge growth on Si substrates is of great interest in photo-electronic and low-dimensional devices. To realize an epitaxial interface between Ge and Si, the growth temperature has to be high enough. Otherwise, the Ge deposited on the surface may appear amorphous at low temperature. Efforts have been paid to the epitaxial growth, while less work has been done on deposition of Ge on Si at low temperatures and therefore the adsorption process has been not well understood. As well known, the Si(1 1 1)-(7 × 7) surface reconstructs with the dimer-adatom-stacking fault (DAS) structure [1], which is very stable and significantly influences epitaxial growth [2–6]. Especially, at low

temperatures the Si(1 1 1)-(7 × 7) surface can act as a template, limiting diffusion and adsorption of Ge adatoms [4,5,7]. Köhler et al. have explained that due to the dangling bonds of the adatoms and rest atoms Ge atoms can be adsorbed preferentially in the triangular half-cells of the (7 × 7) surface, leaving dimer walls and corner holes uncovered. This is the same as Si adsorption on the Si(1 1 1)-(7 × 7) surface [4]. The observed clusters, built up with the adsorbed atoms, seem to be irregular in shape. And it is therefore difficult to say whether or not the clusters could exist in some specific structures. Moreover, in the theoretical studies of the initial stage of Ge on Si(1 1 1)-(7 × 7) reconstruction, the results Minot and coworkers [8–11] obtained by the crystalline extension of the extended Hückel theory are inconsistent with those Cho and Kaxiras [12,13] obtained by density functional theory total-energy calculation in many aspects.

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In this paper, we demonstrate that at room temperature the irregular Ge clusters on the Si(1 1 1)-(7 × 7) surface actually originate from the Ge critical nuclei in the middle of the triangular half-cells. These critical nuclei have same shape and may be of certain structure. Besides, all the clusters behave like quantum dots and display two states at ±1.5 eV with respect to the Fermi level.

2. Experimental

The experiments were performed using an ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) system (Omicron, Germany) with a base pressure below 1×10^{-10} Torr. N-doped Si substrates ($\rho \sim 1$–2 Ω cm, thickness ~ 0.51–0.54 mm) were degassed for 12 h at 900 K, and then flashed to 1500 K for 20 s by direct current (DC) heating. Finally, atomically flat Si(1 1 1)-(7 × 7) surfaces were obtained. A small piece of Ge was selected as the deposition source, which was sublimed at about 1100 K by DC heating. The deposition rate was about 0.005 ML/min. Once sub-monolayer Ge was deposited on the Si surfaces kept at room temperature, the samples were immediately imaged by STM at room temperature.

3. Results and discussion

3.1. Critical nucleation of Ge on Si(1 1 1)-(7 × 7) surfaces

Fig. 1a shows a typical STM image of the Si(1 1 1)-(7 × 7) surface covered with 0.15 ML Ge at room temperature. The surface morphology is actually the same as that observed by Köhler et al. The irregular Ge clusters are arranged in the (7 × 7) half-cells. And the uncovered part of the (7 × 7) surface, such as the corner holes and dimer rows, seems to indicate that the DAS (7 × 7) reconstruction remains intact. However, by decreasing amount of Ge deposited, we find that the Ge clusters tend to become smaller in size but more regular and similar in shape. As shown in Fig. 1b, the surface is covered with 0.08 ML Ge. Some bright dots, such as denoted by arrows,
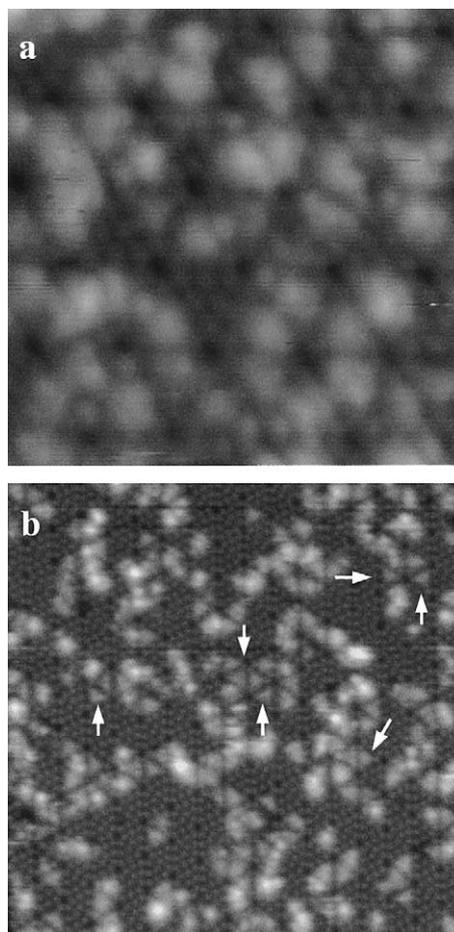

Fig. 1. (a) STM images of ∼0.15 ML Ge on Si(1 1 1)-(7 × 7) surface at room temperature. The scanning area is 130 × 130 Å². The sample bias and tunneling current are +1.5 V and 0.5 nA, respectively; (b) STM images of ∼0.08 ML Ge on Si(1 1 1)-(7 × 7) surface at room temperature. The scanning area is 350 × 350 Å². The sample bias and tunneling current are +1.4 V and 0.6 nA, respectively.

appear almost no different from one another. In our experiments it is found that those dots are the smallest ones so far. So they might be Ge critical nuclei at the initial adsorption stage.

The critical nuclei are in fact located at the center positions of (7 × 7) half-cells, which can be seen in a high-resolution STM image. As shown in Fig. 2a and b, except for an irregular cluster denoted by B, the three Ge dots appear without any difference and triangular shape. Further observa-
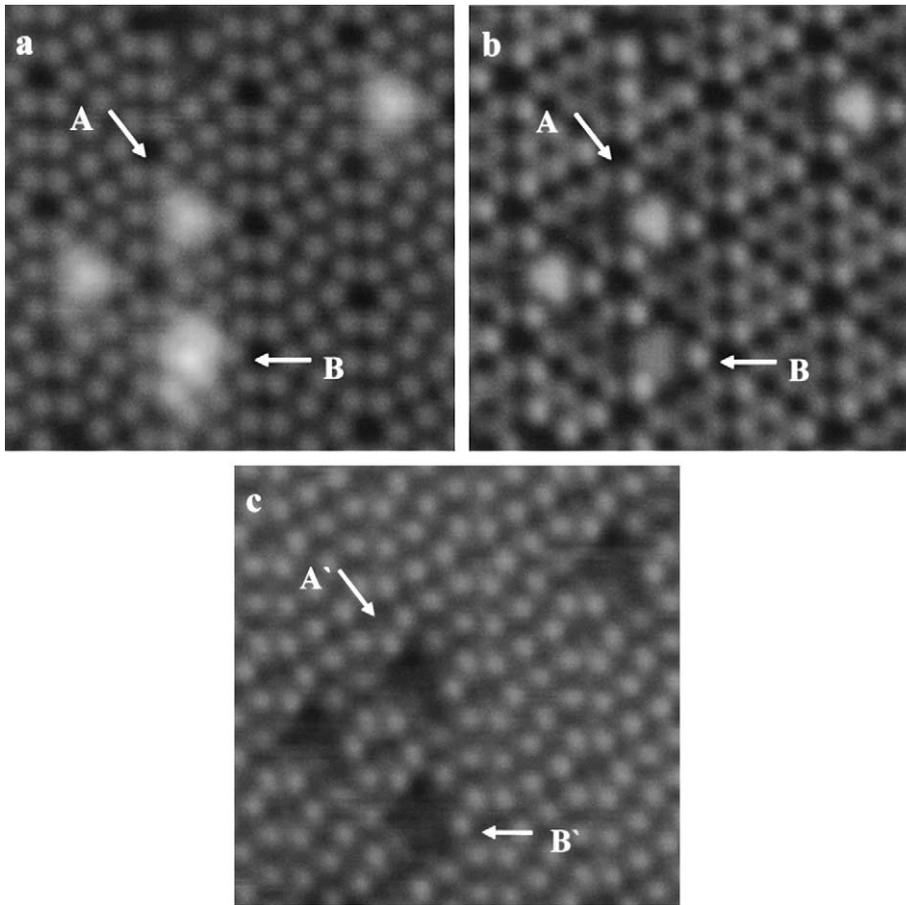
Fig. 2. STM images of ∼0.01 ML Ge on Si(1 1 1)-(7 × 7) surface at room temperature. The scanning area is 80×80 Å^2. The sample bias and tunneling current are (a) +1.5 V and 0.5 nA, (b) −1.5 V and 0.5 nA, and (c) +0.7 V and 0.5 nA, respectively. The critical nucleus is indicated by A in (a) and (b), respectively; the dark areas indicated by A′ in (c) is due to three center adatom, which is related with the critical nucleus, being not visual.

tion shows that around the dot indicated by A, three corner adatoms of the (7 × 7) are clearly seen in both the empty and filled state STM images, and the other three center adatoms seem to be covered by the Ge dot. Moreover, the dot appears lower and flatter in the filled state STM image than that in the empty state STM image, as if the three adatoms covered by the dot would emerge. So it is reasonable to conclude that a certain number of Ge atoms are just adsorbed in the middle of the three center adatoms. Thus, the shape and brightness of the Ge dot in the empty state image indicate that the maximum state density is at the center of the adsorption area.

One should note a half-cell of the (7 × 7) DAS structure, as shown in Fig. 3. The adsorption area mentioned above is surrounded by the dangling bonds of the adatoms and rest atoms while there is no dangling bond in it, as shown in the region enclosed by the dashed lines. Actually, from STM image the adsorption area is encircled by the dangling bonds of the three center adatoms, as shown in the region enclosed by the wave lines. So, it looks like that Ge atoms are trapped in area bounded by three center adatoms. The side length of the bright dot is ∼7.6 Å, whereas the bond lengths of Si–Ge and Ge–Ge are 2.36 and 2.4 Å, respectively. So the dots should contain more than
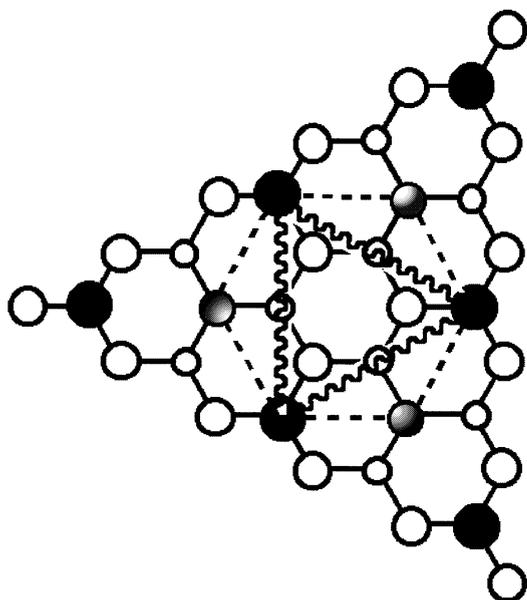
Fig. 3. The schematic illustration of the adsorption site for the critical nucleus. The region surrounded by the dashed lines and the wave lines indicates the adsorption area.

six Ge atoms if the cluster is constructed with the chemical bonds between the Ge atoms and the Si atoms on the substrate. In order to understand further the critical nuclei, average atom number of one Ge cluster as a function of the Ge coverage is estimated as follows: ∼6 in 0.15 ML coverage, ∼4 in 0.08 ML coverage, ∼3 in 0.01 ML coverage. So one critical nucleus maybe only consists of three Ge atoms. And thus the possibility of bond is very small. The Ge atoms may be physically adsorbed with Si atoms on the substrate. Moreover, the smallest Ge dots, i.e. the critical nuclei, look very similar to STM image of single Pb atoms on Si(1 1 1)-(7 × 7) surfaces [14]. The latter is caused by the fast diffusion of single Pb atoms between the various adsorption sites offered by triangular cells by the silicon substrate. The high-resolution STM image of the critical nucleus does not show a well-resolved spot, either. So it may be the result of a dynamic effect caused by some mobility of the Ge atoms within the region encircled by the three center adatoms. It should be pointed out that the critical nucleus need to be further investigated in theory. However, it has clearly shown that the nucleation mechanism of Ge is completely differ-ent from that of Si, in which three kinds of Si-adsorbed structures have been observed at the initial stage of Si deposition [15–17]. Moreover, this kind of critical nucleus model indicates that the adsorption state of the Ge clusters on the Si(1 1 1)-(7 × 7) surface may be metastable or thermodynamically under quasi equilibrium con-dition. Experimentally, we indeed observed that the adsorbed Ge clusters disappeared after the as-deposited samples were annealed at about 500 K for 2 min.

3.2. Electronic behaviors of the Ge clusters

In the experiment, we found that the brightness of the adsorbed clusters drastically changed with the bias voltage, which indicates that the Ge clusters have some peculiar electronic behaviors. For instance, Fig. 2c is an empty-state STM image acquired at a low sample bias by scanning the same surface region shown in Fig. 2a and b. It can be seen that the corresponding positions of the bright dots become dark. Moreover, except for the dark area marked by B' in Fig. 2c, the dark area (marked by A' in Fig. 2c) corresponding to the dot indicated by A is due to three center adatoms being not visual. This observation further dem-onstrates that the critical nucleus is only related to three center adatoms rather than corner adatoms. The same phenomenon is also observed in low negative voltage in our STM experiments.

Moreover, the phenomenon always occurs in the range of Ge coverage from 0.01 to 0.15 ML. Fig. 4a–f show a series of STM images of the same region at various sample biases after 0.10 ML Ge was deposited onto the Si(1 1 1)-(7 × 7) surface. As shown in Fig. 4a and d, at the sample bias of +1.5 and −1.5 V, the bright dots induced by Ge cluster can be obviously observed on the Si(1 1 1)-(7 × 7) surface. As the bias voltage is at near +0.8 and −0.7 V (see Fig. 4b and e), most of the bright dots disappear. With continuously decreasing to +0.4 and −0.4 V (see Fig. 4c and f), the areas covered by bright dots in Fig. 4a have almost become dark.

The local density of states, which can embody the electronic characteristics of the adsorbed clusters, is associated with the STM image at various sample biases. Under low sample biases,
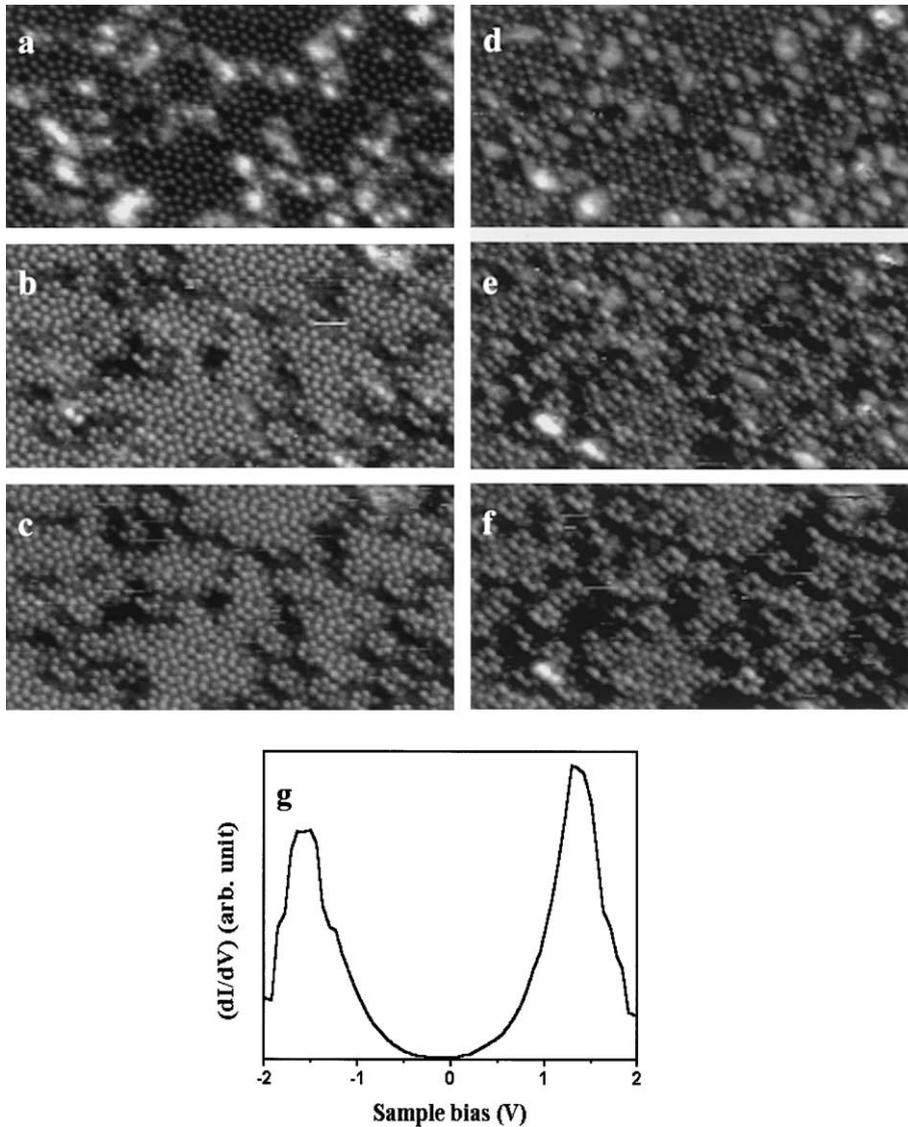
Fig. 4. STM images of ~0.10 ML Ge on Si(1 1 1)-(7 × 7) surface at room temperature. The scanning area is 130 × 260 Å². The tunneling current is 0.4 nA and the sample bias is (a) +1.5 V, (b) +0.8 V, (c) +0.4 V, (d) −1.5 V, (e) −0.7 V, and (f) −0.4 V. The STS spectrum from the critical nuclei is shown in (g).

STM images correspond to density of states near Fermi level. Compared with uncovered (7 × 7) unit cells the positions of Ge clusters become dark at low sample biases. This means that the density of states of the Ge clusters near Fermi level is drastically reduced. It should be noted that the adatom positions of clean Si(1 1 1)-(7 × 7) surface are characterized by metallic-like surface states, which make the STM scan (7 × 7) images at small sample bias. So the clusters display semiconductor behavior.

The remarkable character is further supported by an analysis of the scanning tunneling spectroscopy (STS) of adsorption sites. Fig. 4g displays

the STS of the critical nuclei, which is the average value after measurements for several times in order to ensure the reliability. In the STS the two peaks at ±1.5 V indicate the high density of states at ±1.5 eV with respect to the Fermi level, while the gap of electron states near the Fermi level is clearly seen. This is a typical semiconductor spectrum. Because the tunneling current measured by STM is caused by resonance tunneling through the electronic states of the cluster, the peaks at +1.5 and −1.5 V show that the critical nuclei have two discrete energy levels near Fermi level. The STS of the big Ge clusters has similar character. Thus it can be seen that the electronic characters of the Ge clusters are similar to those of the artificial atoms or quantum dots, i.e., when the electrons are confined to the artificial atoms or quantum dots, the electrons can only exist in certain discrete energies. However, detailed theoretical calculations of electron states for the Ge clusters adsorbed on Si(1 1 1)-(7 × 7) surfaces will be needed to clarify the origin of the observed gap.

4. Conclusion

The critical nuclei of Ge on Si(1 1 1)-(7 × 7) surfaces preferentially adsorb in area encircled by three center adatoms at room temperature. Moreover, the clusters display two states at +1.5 and −1.5 eV with respect to the Fermi level. Almost all of the clusters have the electronic behaviors of quantum dots. So the adsorbed Ge clusters on Si(1 1 1)-(7 × 7) surfaces probably have scientific interest and potential application.

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