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Direct observation of Si-related and Ge-related ring clusters on Si(1 1 1)-(7 × 7) surface

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Abstract

In a scanning tunnelling microscope (STM) study of Si(1 1 1)-(7 × 7) surfaces, we observed the Si-related ring cluster and one new type of Ge-related ring cluster. For both clusters there is an electron transfer between them and the nearby Si centre atoms and their local density of states near the Fermi level is obviously reduced. Moreover, by differences in their electron transfer, the Si-related ring cluster and Ge-related ring cluster can be easily distinguished from each other.
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Keywords: Scanning tunnelling microscopy; Si(1 1 1)-(7 × 7); Ring clusters

1. Introduction

Si and Ge clusters with enhanced stability in free space have been extensively studied by experimental techniques and theoretical methods [1,2]. Recently, the clusters on substrates also caught much attention because of their fundamental interest and potential applications. Constructing the clusters on a substrate is important for the realization of the emerging nanotechnology because it may be one method or concept for improving the size or structural uniformity of nanostructures and the precision of the spatial arrangement.

The ring clusters on Si(1 1 1) surface, which are induced by transition metals, have been reported for the Ni/Si(1 1 1) and the Co/Si(1 1 1) system [3–4]. Each SRC consists of a single-transition metal atom surrounded by six Si adatoms, of which three are bridge-bonded with the transition metal atom, and the other three Si atoms are the "cap atoms", each having a single dangling bond [4–6]. Here, we name this type of cluster as a Si-related ring cluster (SRC). The electronic properties and energetic stability of the SRC have also been explored [5]. Moreover, the experiments show that the SRC is very stable even at high temperature [6].

In this paper, using an ultra-high vacuum scanning tunnelling microscope we observed some new electronic characteristics of the SRC on the Si(1 1 1)-(7 × 7) surface, such as the electron transfer phenomenon. Moreover, we identified one new cluster on the Si(1 1 1)-(7 × 7) surface, a Ge-related ring cluster (GRC), which is very similar to the SRC. The GRCs usually occur in

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the growth of Ge on Si(1 1 1)-(7 × 7) surfaces [7]. However, they have been actually ignored in the previous studies. In the following text, we focus on examining similarities in and differences between the GRC and the SRC electronic structure.

2. Experiments

The experiments were performed in an Omicron UHV–STM with a base pressure below 1×10^{-10} mbar. The samples used in the experiments were cut from lightly p-doped mirror-polished Si wafers ($\rho \sim 1-2\,\Omega$ cm, thickness ~0.51–0.54 mm). The Si sample was degassed overnight at 800 K, flashed to 1500 K for 20 s, and cooled down at fast rates (> 2 K/s). Some SRCs can then be observed in narrow disordered regions at lower step edges and at or near (7 × 7) domain boundaries. In the experiments with GRCs, a clean Si(1 1 1)-(7 × 7) surface was first obtained, and then a submonolayer of Ge was deposited on the Si surface at room temperature using DC heating of a small piece of Ge, and finally, the samples were annealed at 1200 K. After the treating process of the Si sample had been repeated several times, only the GRCs could be observed on the Si(1 1 1)-(7 × 7) surface.

3. Results and discussion

3.1. Si-related ring clusters

Fig. 1 is an STM image showing a high density of SRCs imbedded in a large domain, which is similar to Fig. 2 in Ref. [6]. Parikh et al. have made a systematic study to determine the range of transition metals that can result in the SRC structure [6]. Infinitesimal transition metal contamination could form SRCs on the Si surface by high-temperature annealing. In the process of Si sample treatment, a transition metal like nickel could diffuse from the forceps and the sample holders used to hold the Si wafers. We thus believe that it is transition-metal contamination that causes the SRCs, and this result acts as a warning to engineers involved in the production of nanoelectronic devices.

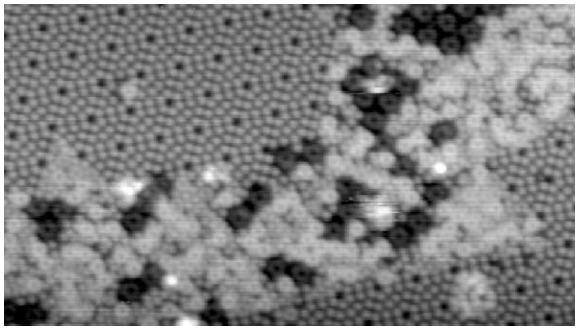

Fig. 1. STM image of SRCs on a domain boundary. Most of the SRCs are distributed at the domain boundary. The sample bias and tunnelling current are + 1.4 V and 0.3 nA, respectively.

In this experiment, we found that the brightness of the SRCs changed under different conditions. This indicates that the SRCs have peculiar electronic behaviour because the local density of states is associated with the STM image. Figs. 2a–c show a sequence of STM images of the same small domain boundary under different sample biases. On the one hand, the brightness of some SRCs is related to their sites. For instance, in Fig. 2a the SRCs indicated by the wide arrows are dimmer than those indicated by the narrow arrows. On the other hand, the brightness of SRCs at different bias is changeable. For example, the SRCs indicated by the wide arrows in Fig. 2a could not be observed at low positive bias (see Fig. 2b).

Because the analysis of SRC's interior structure on the domain boundaries is quite difficult, we focus on the electronic characteristics of the SRC on the Si(1 1 1)-(7 × 7) surface. One such example is shown in the circled region of Fig. 2. At the bias of + 1.2 V (Fig. 2a), the SRC have three lobes, which are mainly due to the cap atoms [5–6]. As the bias is decreased to + 0.6 V, the site of the SRC gets darkened as shown in Fig. 2b. Moreover, at negative bias, the SRC becomes bright (see Fig. 2c), again. As is well known, STM images at different sample biases reflect the information of density of states in different energy levels. Experimentally, we find the site of the SRC is dark at the range of sample biases from + 1.0 V to 0.0 V, which means that the density of states of the SRC

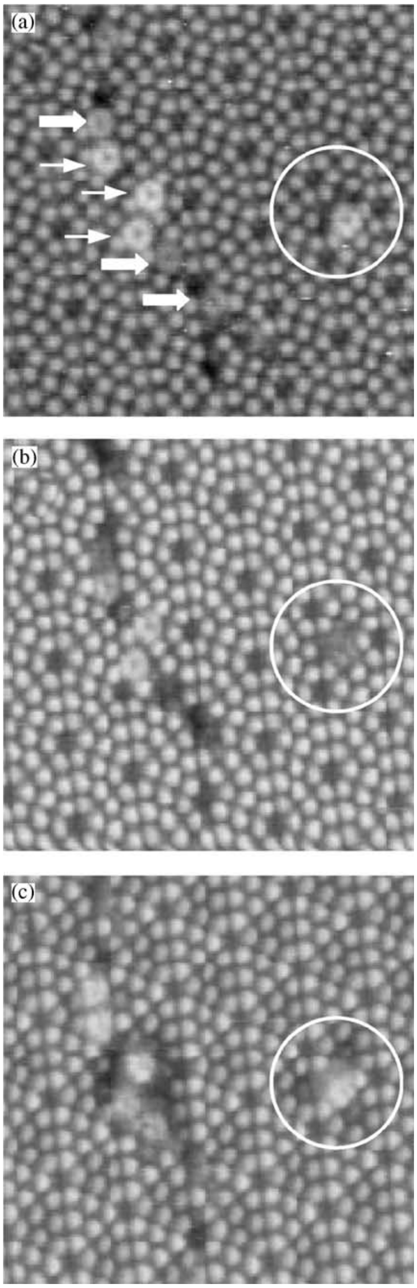

Fig. 2. A sequence of STM images under different biases showing the SRCs located in and near a small domain boundary. The sample tunnelling current is 0.5 nA, and the bias is (a) +1.2 V, (b) +0.6 V and (c) −0.5 V, respectively. The SRCs indicated by wide arrows are dimmer than those indicated by thin arrows. The SRC on the Si(1 1 1)-(7 × 7) surface is inside the circle frame.

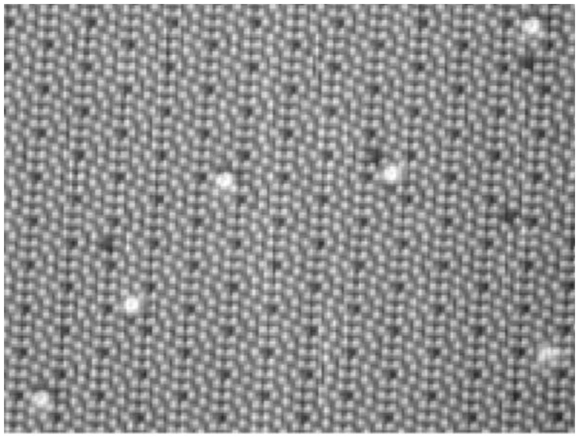

Fig. 3. The STM image shows some GRCs on the Si(1 1 1)-(7 × 7) surface. The sample bias and tunnelling current are +1.5 V and 0.4 nA, respectively.

is drastically reduced between 0 eV and +1.0 eV with respect to the Fermi level. Thus it can be seen that the SRC displays semiconductor behaviour, i.e., there exists a band gap near and above the Fermi level, which is in agreement with the experimental and theoretical results of the ring clusters in the Co/Si(1 1 1) system [5].

Furthermore, electron transfer is another characteristic of the SRCs, which was first reported. It can be seen from Fig. 2c that in the domain boundary some Si adatoms around some SRCs cannot be observed at negative sample bias due to the electrons of the Si adatoms transferring to the SRCs. As for the SRC on the Si(1 1 1)-(7 × 7) surface, the three Si centre adatoms near the SRC are not visible under negative bias voltage (see the circle frame in Fig. 2c). The reason for these phenomena is that the electrons of the invisible Si centre adatoms were transferred to the SRC across the dimer rows between them. The electron transfer indicates the electronegativity disparity between the SRC and the corresponding Si centre adatoms, and also provide a guide for further understanding of the SRCs on the Si(1 1 1)-(7 × 7) surface.

3.2. Ge-related ring clusters

A submonolayer of Ge was deposited onto the Si(1 1 1)-(7 × 7) surface at room temperature and

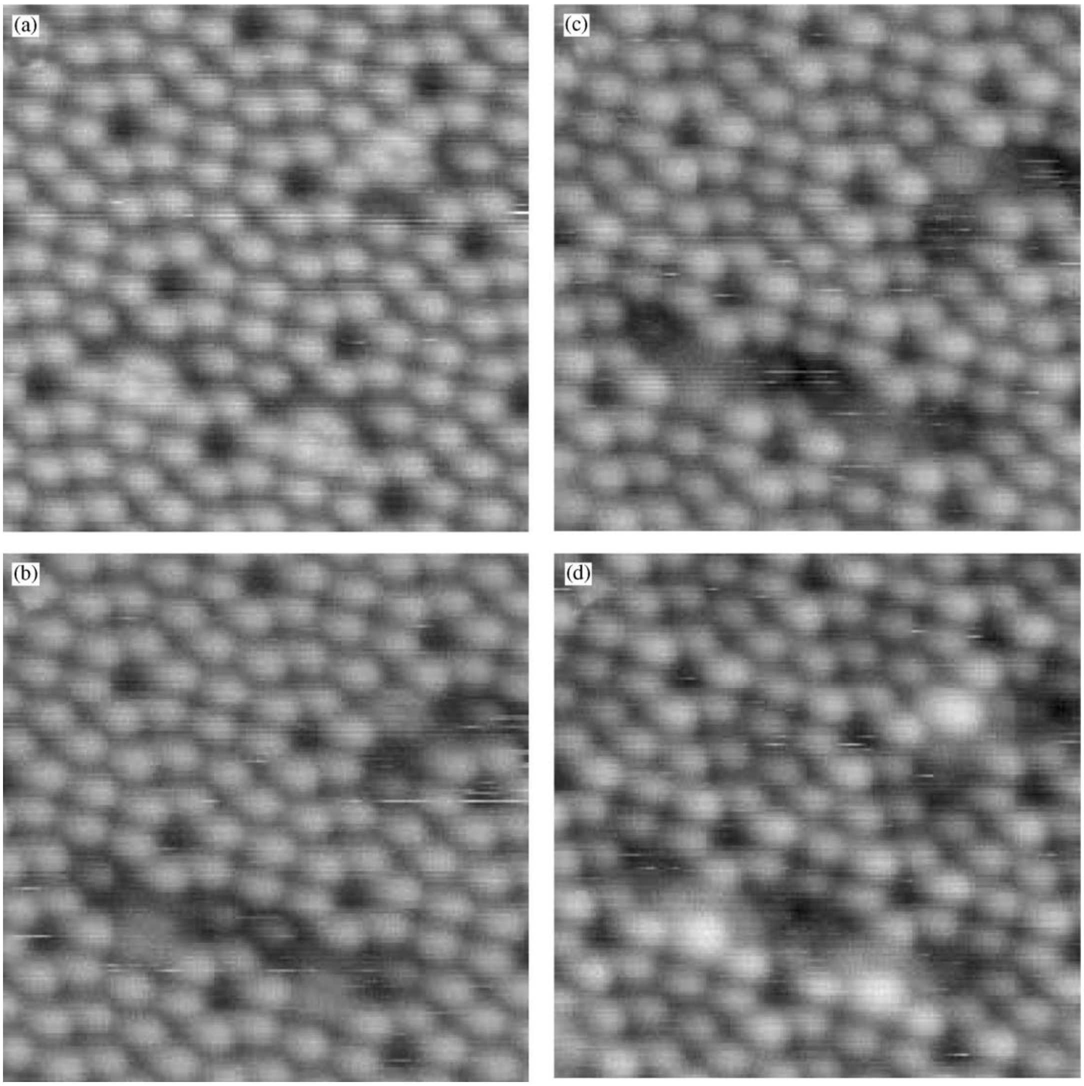

Fig. 4. A sequence of STM images under different bias voltages showing the GRCs on the Si(1 1 1)-(7 × 7) reconstruction. The tunnelling current is 0.85 nA, the sample bias is (a) +0.6 V, (b) +0.3 V, (c) −0.3 V and (d) −0.6 V, respectively.

then annealed at high temperature (1200 K). After this process was repeated several times, some ring clusters similar to those on SRC can often be observed on the Si(1 1 1)-(7 × 7) surface (Fig. 3). We believe that this type of cluster is related to the deposited Ge atoms and transitional metal contamination, so we called it a Ge-related ring cluster (GRC).

Fig. 4a–d show a sequence of STM images for GRCs in the same region under different sample biases. It can be noticed that the STM patterns of the GRCs strongly depend on the bias, too. Fig. 4a shows that the STM pattern of each GRC also presents three lobes at positive bias and their sites are the same as those of the SRC on a perfect Si(1 1 1)-(7 × 7) surface. At a decreased positive bias voltage of 0.3 V, the brightness for both the GRC and the two Si centre adatoms which exist in two half units near the GRC (Fig. 4b) are much weakened. Moreover, under a negative bias of

$-0.3\,V$, the GRCs contract to the shape of dots while the above two corresponding Si centre atoms in the two half units near the GRC become invisible due to drastical electron transfer (Fig. 4c). By increasing negative bias to $-0.6\,V$, the brightness of these GRC dots becomes enhanced and the two Si centre atoms remain invisible (Fig. 4d).

Since the STM image of GRC becomes dim under both low positive and low negative bias voltages, the local density of states for the GRC on Si(1 1 1)-(7 × 7) is small near the Fermi level because the type of GRC becomes dim which is similar to the case of SRC on Si(1 1 1)-(7 × 7) to some extent. A somewhat surprising point, however, is that the two centre Si adatoms near the GRCs also become obscure under low positive bias. Electron transfer may be one possible explanation: the Fermi level of the GRCs is appreciably higher than that of the Si centre adatoms. Thus the electrons from the GRC will transfer to the adjacent Si centre adatoms, and the electrons that tunnel from the tip to the Si centre atom will be reduced, making the Si centre adatoms appear faint in the STM image. Under negative bias, the difference between GRCs and SRCs in terms of electron transfer is also obvious: the electron transfer occurs between GRC and only two nearby centre adatoms, while there are three adjacent centre adatoms involved in the electron transfer in the case of SRC. This may be due to the difference in the chemical bonding ability between two types of ring clusters and the Si atoms in a Si(1 1 1)-(7 × 7) reconstruction. Further study is needed to describe in more detail how electron transfer is realized between the ring clusters and corresponding centre adatoms.

4. Conclusions

The SRC on Si(1 1 1)-(7 × 7) surface displays semiconductor behaviour and electron transfer occurs between the SRC and three nearby Si centre adatoms. In the process of depositing Ge on a Si(1 1 1)-(7 × 7) surface, a new type of ring cluster, i.e., GRC, was identified. The local density of states of the GRC on Si(1 1 1)-(7 × 7) is reduced near the Fermi level. Futhermore, under both negative and low positive bias, we observed the electron transfer phenomenon taking place between the GRC and its nearby two Si centre adatoms which is the most distinct characteristic when compared with the SRC on the Si(1 1 1)-(7 × 7) surface.

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