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Formation and local electronic structure of Ge clusters on Si(111)-7×7 surfaces*

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We report the formation and local electronic structure of Ge clusters on the Si(111)-7×7 surface studied by using variable temperature scanning tunnelling microscopy (VT-STM) and low-temperature scanning tunnelling spectroscopy (STS). Atom-resolved STM images reveal that the Ge atoms are prone to forming clusters with 1.0 nm in diameter for coverage up to 0.12 ML. Such Ge clusters preferentially nucleate at the centre of the faulted-half unit cells, leading to the 'dark sites' of Si centre adatoms from the surrounding three unfaulted-half unit cells in filled-state images. Bias-dependent STM images show the charge transfer from the neighbouring Si adatoms to Ge clusters. Low-temperature STS of the Ge clusters reveals that there is a band gap on the Ge cluster and the large voltage threshold is about 0.9 V.

Keywords: scanning tunnelling microscopy, Si(111)-7×7 surface, Ge cluster
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The growth of self-organized Ge clusters on Si surfaces is an important subject for the design and engineering of quantum devices.[1−3] In the regime between 0.1 and 0.5 ML, different types of Ge clusters on the Si(111)-7×7 surface at room temperature (RT) have been extensively studied in the past.[4−15] Köhler *et al* used scanning tunnelling microscopy (STM) to investigate submonolayer Ge coverages and found that the individual Ge clusters at first have random shapes, and finally form a nearly ordered array on the substrate.[4] On the other hand, at elevated temperatures (300 C° − 360 °C), Suzuki and Shigeta revealed that the round shape with a diameter of 3.8 nm is energetically the most favourable for the Ge clusters.[5] Furthermore, Yan *et al* suggested that Ge clusters have the critical nucleus at very low coverage. According to scanning tunnelling spectroscopy (STS) at RT, such clusters display semiconductor behaviour with a band gap between ±1.5 V.[6] Most recently, ordered hexagonal Ge nanostructures grown at RT were obtained on the Si(111)-7×7 surface at a Ge coverage of 0.5 ML by Ansari *et al*.[7] However, no further studies on the single Ge cluster formation and its intrinsic electronic structure at variable temperatures have been performed yet since it was found. Some basic questions still exist about the single Ge cluster. For instance, what induces the Ge atoms to form clusters? The Ge cluster is obtained at RT, and then does it still exist at low temperatures and what is its intrinsic electronic structure? It is necessary to do more experiments to clarify its formation and local electronic structure. Thereafter, detailed studies of Ge clusters on the Si(111)-7×7 surface enable us to control the further growth of Ge clusters and the subsequent fabrication of Ge/Si based nanodevices.

In this letter, we report the formation of Ge cluster and its electronic structure studied by variable temperature (VT)-STM and low-temperature STS. As the coverage increases, Ge atoms begin to form shapely clusters with typical diameters of 1.0 nm on the faulted-half unit cells (FHUCs) preferentially. These initial clusters on the FHUCs have a strong influence on the adjacent unfaulted-half unit cells (UHUCs), where three neighbouring centre adatoms become 'dark sites' (DS) in the filled-state STM images. The bias-dependent STM images show the real-space charge redistribution from the nearby DS to Ge clusters. The *in situ* low-temperature STM/STS measurements elucidate that Ge clusters hold a band gap with larger threshold value of $V_{\rm th} = +0.9$ V, and the corner adatoms around the clusters are Si atoms.

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cron variable-temperature STM apparatus with a base pressure below 8.0×10^{-9}Pa. The substrates were cut from a commercial arsenic-doped n-type Si(111) wafers (misorientation $< 0.5°$) with a resistivity of $0.001 - 0.005\Omega$·cm and a thickness of 0.381 mm, and cleaned using acetone, pure ethanol and ultra pure water in an ultrasonic bath successively before inserted into the UHV system. After degassed in UHV for several hours at ∼600 °C, a well-defined Si(111)-7×7 reconstructed surface was obtained by flashing to 1200 °C with the pressure better than 1×10^{-8} Pa. Germanium (99.9999% purity) was resistively evaporated onto the as-prepared Si(111)-7×7 surface kept at 150 °C by irradiation. A typical deposition rate of ∼0.01 ML/min was routinely achieved. Here, one monolayer is defined as the atomic density of the unreconstructed Si(111) (1ML=7.84×10^{14} atoms/cm^2). The electrochemically etched tungsten tip with a diameter 0.13 mm was used for STM scanning.

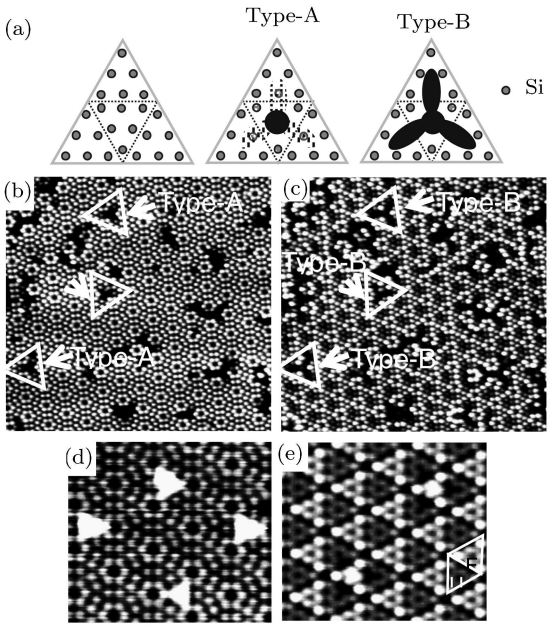


Fig.1. (a) The schematic modes of Type-A and Type-B patterns shown in (b) and (c), respectively. (b) Empty-state STM image of about 0.12 ML Ge coverage on Si(111)-7×7. Sample bias: +1.0 V; tunnelling current: 0.02 nA. (c) Filled-state STM image of the same area. Sample bias: −1.0 V; tunnelling current: 0.02 nA. Both scanning areas are 40nm×40 nm. (d) Empty-state STM image of Ge clusters at a higher sample bias. Sample bias: +2.5 V; tunnelling current: 0.02 nA. (e) Filled-state STM image at a higher sample bias. Sample bias: −2.5 V; tunnelling current: 0.02 nA. Both scanning areas are 11nm×12 nm.

Figures 1(b) and 1(c) show the empty-state (sample bias: $V_s = +1.5$ V, tunnelling current: $I_t = 0.02$ nA) and filled-state ($V_s = -1.0$ V, $I_t = 0.02$ nA) STM images respectively for the same region on Si(111)-7×7 surface with a Ge coverage of 0.12 ML deposited at 150 °C. The DS with different sizes and shapes are distributed disorderly, and the separate three-blade airscrew-like structures and those forming dendritic structures coexist in both filled-state and empty-state STM images. This indicates that the Ge atoms seem to form a three-blade airscrew-like structure on the Si(111)-7×7 surface at RT, denoted by Type-A in Fig.1(b) and Type-B in Fig.1(c). In the three prominent Type-A structures, shown in Fig.1(b), the three Si centre adatoms are totally dark in one half unit cell (HUC), and the adjacent Si centre adatoms in the surrounding three HUCs become dim. While the three adjacent Si centre adatoms corresponding to the same area shown in Fig.1(c) [three Type-B structures] also become DS. The schematic modes corresponding to Type-A and Type-B patterns are shown in Fig.1(a). In contrast, at higher bias voltages, all the Ge clusters appear actually in the STM images and occupy the centre of the HUCs, as shown in Figs.1(d) and 1(e), respectively. Each one has a size of 1.0 nm in diameter. Moreover, the Ge clusters show a distinct preference for FHUCs. Such inclination is consistent with the previous reports.[16,17]

Since these Ge clusters look different at different bias voltage, then, the formation of this kind of Ge clusters may be clarified finally if the bias-dependent STM images taken by focusing on the same single Ge cluster are obtained. Figures 2(a)–2(f) show a series of high resolution filled-state and empty-state STM images for the same single Ge cluster. In Figs.2(a) and 2(d), the Ge cluster turns into DS in the centre region of the FHUC. At the same time, the individual Ge cluster has a strong effect on its three neighbouring UHUCs, in each of which the Si centre adatom, i.e. the nearest neighbour of the cluster, is invisible in the filled-state STM images (Figs.2(a)–2(c)). However, these Si adatoms are certainly located at their original places in the 7×7 reconstruction, as shown in the empty-state STM images (Figs.2(d)–2(f)). Since an observed 'darkening' of the reacted site in STM image can be attributed to the saturation of the dangling bonds or a reduction in the local density of states (LDOS),[18] then, a possible explanation for our results is that the charge transfer from the vicinal Si centre adatoms to Ge cluster itself occurs, due to the larger electronegativity of Ge than that of Si. As the filled-stated image reflects a spatial distribution

of occupied surface electronic states, we can infer that the vicinal Si centre adatoms transfer charges to the nearby Ge cluster and subsequently stabilize the Ge cluster formation, driven by a saturation of dangling bonds and a reduction in the LDOS.

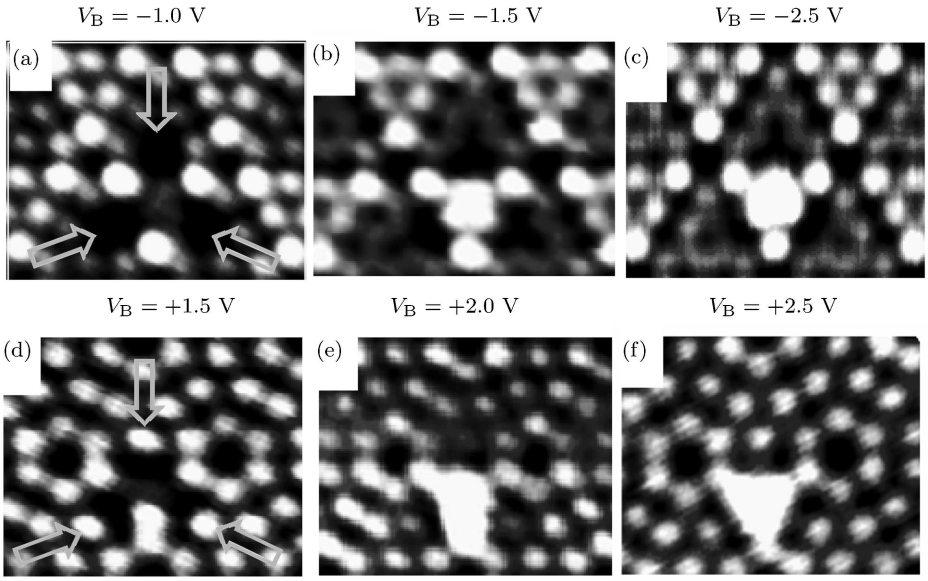


Fig.2. (a)–(c) Filled-state STM image of a single characteristic Ge cluster on Si(111)-7×7 surface at RT. Sample bias: −1.0; −1.5; −2.5 V, respectively; tunnelling current: 0.02 nA. (d)–(f) Empty-state STM image of the same Ge cluster. Sample bias: +1.5; +2.0; +2.5 V, respectively; tunnelling current: 0.02 nA. All scanning areas are 5nm×6nm.

From the above STM images at RT, it is noted that the individual atom could not be resolved in the Ge cluster. A possible explanation comes from the dynamic effect caused by the possible high mobility of the Ge adatoms within the cluster, as reported earlier for Ag, Cu, Au[19] and alkali metals. To verify this guess, the empty-state STM image of Ge clusters on the Si(111)-7×7 surface was measured at 27 K, as shown in Fig.3(b). Compared with the RT image shown in Fig.3(a), the Ge clusters display the same shape and size, and still occupy the centre of the HUC. No single Ge atom can be resolved, either. This denies the dynamic effect guess and confirms the stability of Ge clusters at RT.

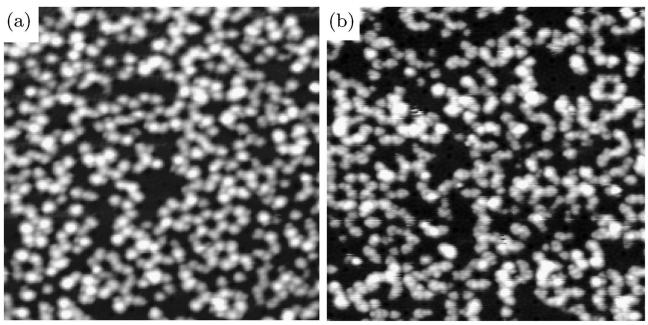


Fig.3. (a) Empty-state STM image of about 0.4 ML Ge coverage on Si(111)-7×7 at RT. (b) Empty-state STM image of about 0.4 ML Ge coverage at 27 K. Both sample bias: +2.5 V; tunnelling current: 0.02 nA. The scanning areas are 50nm×50 nm.

To obtain the intrinsic electronic structure of the Ge cluster, *in situ* low-temperature STS measurements of two clusters have been performed systematically by fixing the STM tip above the top of the two clusters and their nearby adatoms, successively. Their different electronic properties were probed by the differential conductance ($\mathrm{d}I/\mathrm{d}V$) spectroscopy at 27 K, which are presented in Figs.4(a) and 4(b), respectively. The insets show the corresponding filled-state STM images of the two Ge clusters on the Si(111)-

7×7 surface, with stars denoting the tip fixing positions during STS measurements. The $\mathrm{d}I/\mathrm{d}V$ signal, which is detected with a lock-in amplifier, gives a measure of the LDOS. Compared with the metallic Si substrate, larger threshold value $V_{\mathrm{th}} = +0.9$ V is observed on Ge clusters above Fermi level, as shown in Fig.4(a). This means that Ge clusters hold a band gap even at 27 K. On the other hand, the STS of the surrounding two adatoms [Fig.4(b)] show maxima at $V = 0.7$ V, which is similar to that of the Si adatoms on the pure Si(111)-7×7 surface. This proves that the corner adatoms around Ge clusters are Si atoms. These STS measurements demonstrate that Ge clusters and their nearby adatoms have different electronic properties. It is speculated that the electron transfer from the nearby Si adatoms to the Ge clusters opens the band gap above the metallic substrate.

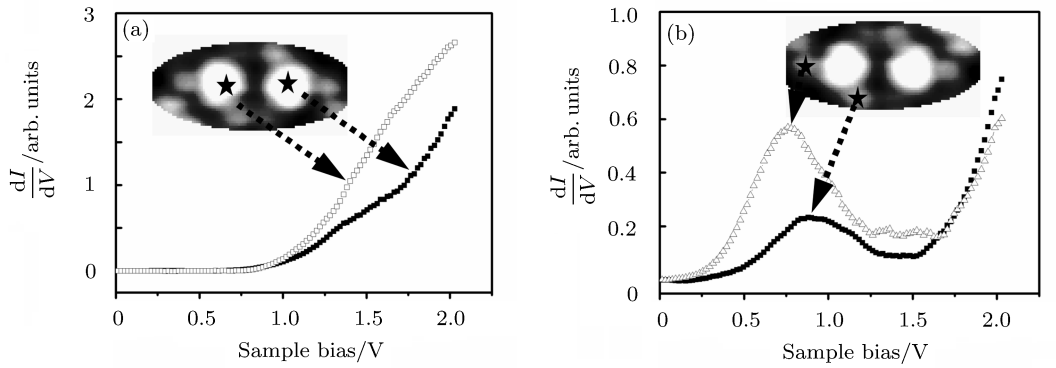


Fig.4. (a) $\mathrm{d}I/\mathrm{d}V$ spectra of the two Ge clusters at 27 K. (b) $\mathrm{d}I/\mathrm{d}V$ spectra of the corner adatoms around Ge clusters at 27 K. The inset filled-state STM images show these two Ge clusters on Si(111)-7×7 at 27 K. Sample bias: −2.6 V; tunnelling current: 0.03 nA.

In conclusion, by combining bias-dependent STM images at RT and *in situ* low temperature STS spectra, we have shown the formation and electronic structure of Ge clusters on Si(111)-7×7. These single Ge clusters have the same shape and uniform size with 1.0 nm in diameter, and are just adsorbed in the centre of FHUC preferentially. Meanwhile, these Ge clusters are very stable at temperatures from RT to 27 K. The charge transfer from the surrounding Si centre adatoms to Ge clusters cause the neighbouring Si adatoms in the surrounding HUCs to be dark in filled-state STM images. In addition, the low-temperature STS measurement shows that the Ge clusters hold band gaps, and the corner adatoms around them are Si atoms. Our results are helpful for understanding and controlling the formation of Ge nanostructure on the Si(111)-7×7 surface and the applications in the Ge/Si-based nanodevices.

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