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Description	

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Low-flux elucidation of initial growth of Ge clusters deposited on Si(111)-7×7 observed by scanning tunneling microscopy

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Deposition of Ge on Si(111)-7×7 under very low Ge flux is examined using ultrahigh vacuum scanning tunneling microscopy; Ge atoms are deposited at 150 °C under a flux of ~0.005 or 0.05 ML/min. Initially Ge atoms are substituted for Si atoms on corner adatom sites of faulted half unit cells. At a Ge coverage of 0.08 ML under the lower flux, hollow-centered hexagonal Ge clusters with six protrusions are formed preferentially on faulted half unit cells, which are uniform and separated from other clusters. At the higher flux various types of clusters grow, frequently neighboring with others. This indicates that the low flux is needed to elucidate the stable type of Ge clusters grown on Si(111)-7×7.

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Growth of self-organized Ge nanostructures on Si surfaces has been extensively studied because of their unique properties and potential applications to optoelectronics and nanotechnology.[1–10] While Ge nanostructures have been widely studied on Si(001) surfaces,[1–3] there has been growing interest for Ge nanostructures on a Si(111)-7×7 reconstructed surface with dimer rows, adatoms, and stacking fault (DAS) explained by the DAS model.[11] Many reports of Ge growth on Si(111)-7×7 surfaces presented thermodynamic fluctuations on morphology of nanostructures grown at different temperatures and fluxes;[6–10,12–19] the morphology delicately changes with growth conditions.

Previously we reported formation of ordered hexagonal nanostructures on a Si(111)-7×7 surface covered with a 0.45 ML Ge overlayer deposited at room temperature (RT).[12] Creation of the hexagonal nanostructure can be categorized into self-organization, implying that the regular array of unit cells of the 7×7 with a periodicity of 2.69 nm has the potential to be used as a template for fabrication of nanostructures with the same periodicity. On the other hand, at 100 °C a Ge atom was initially substituted for a Si adatom, and with increasing Ge deposition various types of clusters were formed on half unit cells (HUCs) of the 7×7 reconstruction as a result of complex and diverse bonding configurations.[13–17,19] The diverse Ge nanostructures indicate that formation of self-organized nanostructures crucially depends on coverage, temperature, flux, quality of substrate, and so on, which are key factors to produce well-ordered and uniform nanostructures.[6–10,12–19] To elucidate the growth conditions and mechanism, systematic study is strongly recommended.

In this Brief Report, we examine initial growth of Ge deposition on Si(111)-7×7 at a substrate temperature of 150 °C under a low Ge flux of ~0.005 or 0.05 ML/min using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The growth condition changes the growth mode; the low flux leads to formation of uniform Ge clusters with a hollow-centered hexagonal shape. From observation of the well-controlled Ge growth, the initial growth dynamics and stable structure of Ge clusters on Si(111)-7×7 are discussed.

A homemade UHV STM with a base pressure better than 1×10^{-11} Torr was used in this Brief Report.[12,15] The STM chamber was equipped with a field emission microscope for tip evaluation and a resistive heating type of Ge source. Cuts ($12\times2\times0.5$ mm^3) from an *n*-type Sb-doped Si(111) wafer with a resistivity of ~0.02 Ω cm were used as substrate. An atomically cleaned Si(111)-7×7 surface was prepared according to a standard procedure.[12,15] Submonolayer amounts of Ge from 0.008 to 0.12 ML were deposited at a substrate temperature of 150 °C under a controlled Ge flux of ~0.005 or 0.05 ML/min, where 1 ML was referred to as 7.82×10^{14} atom/cm^2 required to form one complete Si layer. The Si substrate was placed about 20 cm away from the Ge source to control a uniform Ge flux precisely. The deposition rate was monitored using a quartz-crystal oscillator, and the Ge coverage was evaluated from a value of deposition duration multiplied by a reading of the rate, which was previously calibrated by counting the fraction of surface covered with Ge in STM images. While Ge was being deposited, the vacuum was kept $\sim1.5\times10^{-10}$ Torr, which recovered to 1×10^{-11} Torr quickly after deposition. STM images were obtained at RT using chemically etched [111]-oriented single crystal W tips.[20]

Typical filled state STM images of Ge covered Si(111)-7×7 surfaces deposited at 150 °C under a low flux of ~0.005 ML/min are shown in Fig. 1. At a Ge coverage of 0.008 ML, in Fig. 1(a), remarkably brighter atoms were seen at corner adatom sites preferentially on faulted half unit cells (FHUCs), similar to those observed for deposition at 100 °C.[13,15,16] The brighter ones were attributed to a Ge atom substituted for a Si atom at an adatom site since the number of bright spots increased with increasing Ge deposition. The brighter spot at a corner adatom was depicted about 0.2 Å higher than a normal Si corner adatom, seen in a line profile in Fig. 1(b), much less than a Si-Ge bond length of 2.4 Å. This means that a Ge atom is substituted for a Si atom at the adatom site, that is, does not adsorb directly over

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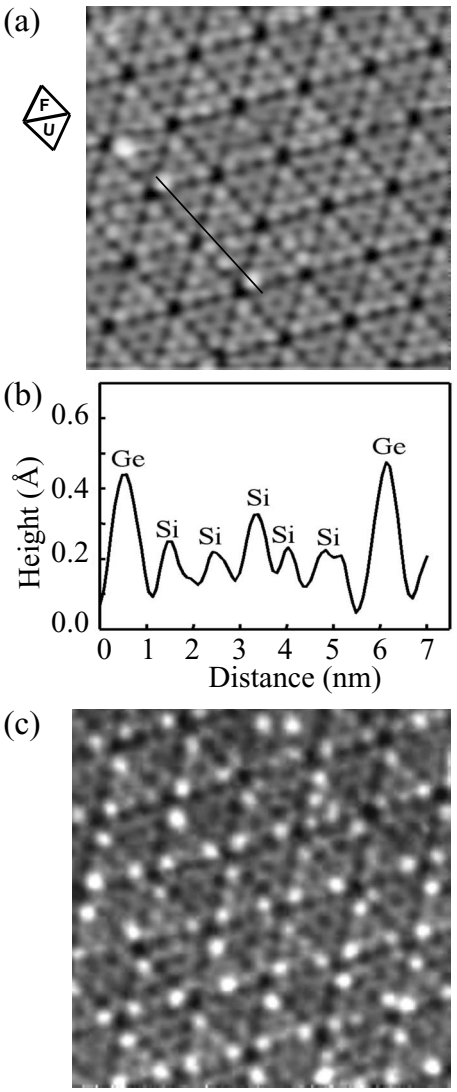

FIG. 1. STM images at RT with submonolayer Ge deposition on Si(111)-7×7 at 150 °C under a low flux of ~0.005 ML/min. (a) Filled state image of ~0.008 ML Ge; sample bias voltage (V_s) =−2.0 V, tunneling current (I_t)=0.04 nA, and scan area: 15 ×15 nm^2. (b) Line profile along a line in (a). (c) At 0.05 ML Ge, exhibiting a triangular pattern on each FHUC; V_s=−1.8 V and I_t =0.04 nA.

a Si adatom. Some brighter adatoms were also found on unfaulted half unit cells (UFHUCs), probably corresponding to Ge atom substituted for Si adatom. The knocked-out Si atoms presumably diffused to a high coordination B_2 site on the surface;[13,15,16] they possibly caused faint changes in atomic contrast irregularly in unit cells of 7×7 reconstruction, as seen in Fig. 1.

Increasing the Ge coverage to 0.05 ML, we observed that Si adatoms at three corner adatom sites on a FHUC were regularly replaced by Ge atoms, resulting in a triangle brighter feature over a FHUC, in Fig. 1(c). Brighter features possibly due to substitution of Ge atoms were sometimes observed on UFHUCs, mostly occupying center adatom sites and rarely corner adatom sites. From analysis of many images we estimated that the ratio of Ge adatom occupying

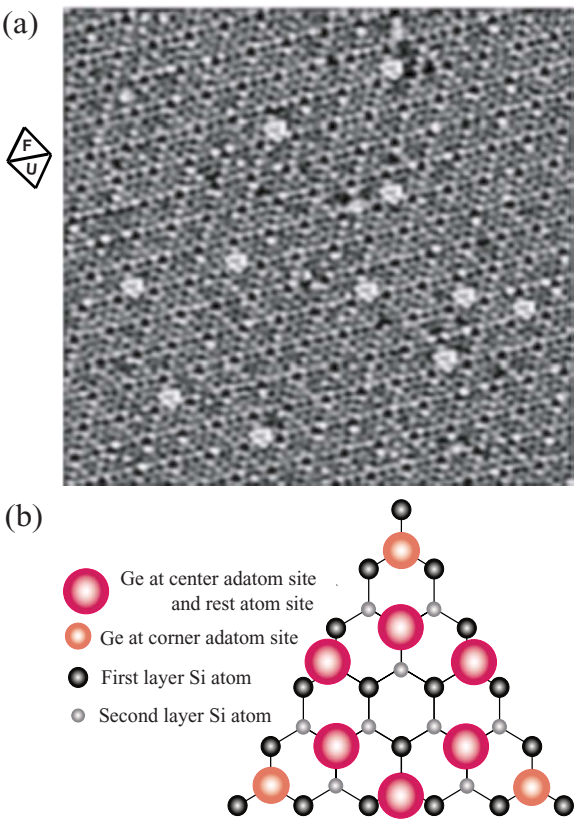

FIG. 2. (Color online) (a) STM image of 0.08 ML Ge on Si(111)-7×7 at 150 °C under a low flux of ~0.005 ML/min, exhibiting hollow-centered Ge clusters; V_s=−2.0 V, I_t=0.05 nA, and scan area: 40×40 nm^2. (b) Model of a hollow-centered Ge cluster over a half unit cell of Si(111)-7×7.

FHUCs with respect to UFHUCs was 20:1, in agreement that Ge atoms are preferentially adsorbed on FHUCs.[10,12–18] Preferential adsorption of Ge atoms over corner sites on FHUCs and over center adatom sites on UFHUCs probably results from competition of activation energy with respect to adsorption energy for Ge atoms to diffuse over these sites. The similar results were reported by Wang *et al.*[13] for 100 °C (Ref. 15) and Ma *et al.*[19] for 150 °C; exclusive adsorption on corner adatom sites indicates that the sites on FHUCs are the most favorable for Ge atoms at these elevated temperatures.[13,15,16,19,21] Up to the coverage of 0.05 ML deposited under the low flux, our observed results agreed with those reported.[13,15] The separation between two protrusions corresponding to two Ge atoms occupying corner adatom sites on each FHUC was measured 1.2–1.5 nm, less than the distance for Si adatoms; Ge adatoms seem shifted slightly toward the center of FHUC, which may bear high stress as explained using density-functional theory (DFT) calculations,[22,23] or the spatial distribution of electronic states seems slightly distorted.

At a higher coverage of 0.08 ML deposited under the low flux of ~0.005 ML/min, we observed Ge hexagonal clusters with a unique and uniform shape exclusively on FHUCs, as shown in Fig. 2(a), exhibiting a hollow-centered and seemingly equilateral triangle with a side of ~1.2 nm, composed of six bright spots. Three corner adatoms surrounding

the cluster exhibited faint brighter contrast but 0.02–0.03 Å lower than the six bright spots of the triangle, probably corresponding to Ge atoms substituted for Si corner adatoms. The hollow-centered clusters were intact after annealing at 200 °C for 5–10 min. To our knowledge, this type of cluster was not reported; the cluster features were slightly different than those previously grown at 100 °C,[13,15] and the adsorption sites did not match with those theoretically proposed by Wang *et al.*[13] and Zhao *et al.*[16] By comparing positions of the protrusions with the DAS model, three inner protrusions were located over rest atom sites and the other three protrusions slightly stuck out of the FHUC. The stuck-out protrusions were almost over the dimer row, possibly attributed to a change in electronic states when three Si center adatoms are replaced by Ge atoms or a quasistable Ge adsorption site may exist over a dimer. Assuming that the protrusions correspond to Ge atoms, a simple model is proposed, as shown in Fig. 2(b). Statistical counting analysis showed that about 94% of the clusters occupied FHUC and 6% occupied UFHUC. Assuming that the Arrhenius relation $N_f/N_u = \exp(\Delta E/k_B T)$ holds, where N_f and N_u are the population occupying the FHUC and the UFHUC, respectively, k_B is the Boltzmann constant, and ΔE is the difference in adsorption energy between UFHUC and FHUC; ΔE was calculated to be ~0.1 eV. This implies that uniform creation of the unique Ge clusters at 150 °C under a low flux leads to more regular cluster arrays with distinct occupation difference between FHUC and UFHUC than those we reported.[12,15]

Growths of similar hollow clusters on Si(111)-7×7 were reported for various metals:[24–26] Li *et al.*[24] proposed that multivalent transition metals occupy the high coordination sites on HUCs, resulting in the hollow cluster formation, while Zhang *et al.*[26] reported that Ag hollow clusters were apparent features caused by a Ag atom hopping traced with a low-temperature STM. In addition, Hwang *et al.*[27] observed hollow Si clusters on Si(111)-7×7, attributed to hopping of Si adatoms on HUCs. We, however, did not observed the indication of Ge atom hopping. On one hand, Yang *et al.*[28] reported that hollow Ge clusters were attributed to the contamination of transition metals, such as Ni, from use of their forceps during sample preparation. In this Brief Report, we did not use metallic tools and parts except Ta holders. In addition, it is noted that the increase in Ge deposition amount led to the increase in the number of Ge clusters; the possibility of foreign atoms, except Ge, affecting the formation of cluster can be denied.

At 0.08 ML deposited at 150 °C under a higher flux of 0.05 ML/min, nonuniform hollow clusters with faded contrast and other clusters were found, as well as isolated Ge bright adatoms, as shown in Fig. 3(a). Some clusters had brighter spots, which seemed to be over the hollow of cluster composed of Ge atoms. At some places a pair or three clusters grown on adjacent FHUCs and UFHUCs were seen, separated by dimer rows. This implies that a Ge cluster on a FHUC triggers cluster growth on neighboring HUCs owing to induced stress, leading to cooperative assembly of Ge clusters. At a higher coverage of 0.12 ML, in Fig. 3(b), the number of connected clusters grown on adjacent halves increased, possibly resulted from cooperative motion of many Ge atoms among HUCs under the higher flux. It is noted that

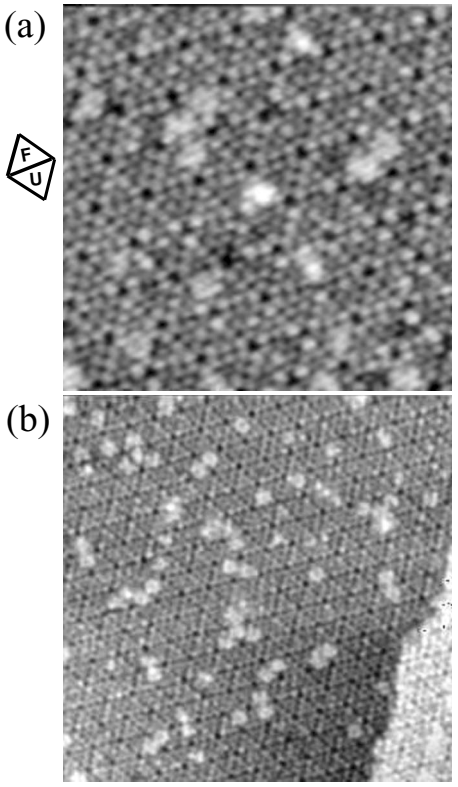

FIG. 3. STM images of submonolayer Ge on Si(111)-7×7 at 150 °C under a high flux of 0.05 ML/min. (a) At 0.08 ML of Ge; V_s=−2.0 V, I_t=0.05 nA, and 20×20 nm^2. (b) At 0.12 ML; V_s =−1.8 V, I_t=0.04 nA, and 40×40 nm^2.

some hollow clusters were still seen as isolated, separated by dimer rows; the clusters with a hollow center seem to be stable.

The rate of incoming atoms, their diffusion, and settling time onto preferential adsorption sites play key roles for formation of an overlayer. In addition, cooperative motion should also contribute to the formation of self-organized Ge nanostructures. Since at a low flux there is enough time for individual Ge atoms to diffuse onto more stable sites without any collision with other deposited atoms, we guess that the hollow-centered hexagonal cluster with six protrusions on a FHUC is really stable for growth at 150 °C. Consequently, the clusters exhibited almost the same shape and were located only on FHUCs, as shown in Fig. 2(a), although the reason why the clusters were created there is still unclear.

Here we mention a scenario for the growth of clusters with references as follows. At the very beginning of cluster formation corner adatom sites act as a trap for Ge atoms at 100–150 °C,[13,15,16,19] and the sites on FHUCs are more stable,[12,16,19] as in Fig. 1. After most Si atoms at corner adatom sites are replaced by Ge atoms, a Ge atom landing on a HUC can escape the shallow diffusion potential wells within HUC (Refs. 26 and 27) at 150 °C. Since the diffusion length of the Ge atom is estimated to be longer than several times of a unit length of 7×7, the initial cluster formation is dominated by pure collision of two or more than two Ge atoms on a HUC as a result of long travel of Ge atoms. Consequently, the HUC, within which the Ge atoms collide and are bound,

is strained and presumed to act as a new trapping center for next coming Ge atoms, leading to the formation of a hollow-centered hexagonal cluster, as shown in Fig. 2. In conclusion, for this case of low flux, since individual Ge atoms have enough time to overcome a diffusion barrier so that they slowly incorporate into the hollow-centered hexagonal cluster matured to be stable, the complicated kinematic paths of diffusing Ge atoms can be ignored on discussion of the formation mechanism. When Ge flux is high, as the first stage the hollow-centered clusters or their nuclei are partially formed, similarly to the case of low flux. Under the high flux, however, some next coming Ge atoms have a chance to meet each other on the HUCs adjacent to the cluster or the nucleus and stay for a while since the adjacent HUCs are slightly strained due to the preceding growth of the hollow-centered cluster. The meeting Ge atoms constrain each other, that is, they are trapped. Further coming Ge atoms are also trapped there, and as a result, clusters neighboring the preceding clusters are formed, as seen in Fig. 3. Accordingly the clusters exhibit diverse features linking but freezing to the matured hollow-centered hexagonal cluster.

In summary, using UHV-STM we observed Ge cluster growth on Si(111)-7×7 with submonolayer coverages at 150 °C under controlled low Ge flux. Initially deposited Ge atoms were substituted for Si, preferentially on corner adatom sites of faulted half unit cells. At a coverage of 0.08 ML under a low flux of ~0.005 ML/min, uniform hollow-centered hexagonal Ge clusters composed of six protrusions were found, which were isolated from other clusters, preferentially on faulted half unit cells. On the other hand, under a higher flux of 0.05 ML/min nonuniform hollow clusters frequently grew with clusters on adjacent half unit cells. This indicates that elaboration of growth control, in particular, flux, is demanded to elucidate the stable type of clusters when the kinematic pathway is complicated and the difference in formation energy among various types of clusters is small. The low flux growth can lead to fabrication of well-controlled regular arrays of a uniform self-organized Ge nanocluster on a half unit cell of 7×7.

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