Deposition of Hydrogenated Si Clusters on Si(111)-(7 × 7) Surfaces

M. O. Watanabe
Joint Research Center for Atom Technology (JRCAT)–Angstrom Technology Partnership, 1-1-4 Higashi, Tsukuba 305-0046, Japan

T. Miyazaki* and T. Kanayama†
JRCAT–National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba 305-8562, Japan

(Received 28 August 1998)

We have studied surface structures arising from the deposition of stable hydrogenated Si cluster ions, $Si_6H_{13}{}^+$ on Si(111)-(7 × 7), using scanning tunneling microscopy. The $Si_6H_{13}{}^+$ clusters, which have a ring structure with sp^3 bonding, have been deposited on Si(111) with a deposition energy of 18 eV at room temperature. The clusters preferentially adsorbed at the lower terrace of the steps. Few clusters were observed on the flat surfaces, showing that the cluster is mobile on the surface due to its weak interaction with Si(111). Hexagonal-type ordering with the $(\sqrt{7} \times \sqrt{7})R \pm 19.1°$ configuration consisting of Si_6H_{12}, which was converted from $Si_6H_{13}{}^+$ after landing, was observed partially. [S0031-9007(98)07949-6]

PACS numbers: 68.35.Bs, 36.40.–c, 61.16.Ch, 61.46.+w

If clusters composed of a specified set of atoms can be deposited on top of well-defined surfaces, it will allow us to build up new materials. This in turn will realize peculiar properties of materials by taking advantage of the fact that clusters exhibit variable characteristics depending on size and structure together with conditions of assembly. From this viewpoint, semiconductor clusters are particularly attractive in that their properties are especially sensitive to their size and structure [1–4]. While much effort has been made in recent years to study cluster deposition on solid surfaces [1,4–9], the deposition of well-defined semiconductor clusters has not been achieved.

Since silicon is the most widely used semiconductor material in microelectronics, an enormous effort has been devoted to the study of atomic Si clusters [7,9–11]. Pure Si clusters are known to have entirely different structures from the bulklike sp^3 bonding, i.e., the compact structures [9–11]. This arises from the fact that the bulklike structure inherently results in the presence of many dangling bonds. The addition of hydrogen atoms has been reported to restore the sp^3 nature [12], giving stabler structures of Si clusters. Accordingly, deposition of hydrogenated Si clusters on clean Si surfaces is one of the best systems in exploiting size dependence of properties. A new growth technique using an ion trap has enabled us to prepare well-defined hydrogenated Si cluster ions, $Si_nH_x{}^+$ in a low-pressure gas phase [13], and to deposit them on Si surfaces in ultrahigh vacuum (UHV).

In this Letter, using scanning tunneling microscopy (STM), we show that nondestructure deposition of stable $Si_6H_{13}{}^+$ clusters on Si(111) surfaces results in a partial ordering of the clusters near the step edges.

We used the cluster ion growth technique and the deposition instruments described previously [12–16]. Hydrogenated Si cluster cations $Si_nH_x{}^+$ were grown from silane (SiH_4) gas with H_2 ambient gas [17] in an ion trap consisting of a linear quadrupole surrounded by a cage electrode. A dc bias voltage of −3 V and ac voltages of 190 V with frequencies around 700 kHz were applied to the quadrupole. The SiH_4 pressure was fixed to be at 2×10^{-5} Pa and the H_2 gas pressure was regulated at 10^{-2} Pa. These conditions were optimized to efficiently generate $Si_6H_{13}{}^+$ clusters [15,17]. The background pressure in the ion trap was 1×10^{-7} Pa. The ionization of SiH_4 was carried out in the cage by electron irradiation of 150 eV. The $SiH_y{}^+$ ions generated were confined in the cage of the ion trap and were grown to $Si_nH_x{}^+$ cluster cations through the reactions with SiH_4 molecules or radicals. We measured the mass spectra of $Si_nH_x{}^+$ clusters grown in the ion trap for $n = 1–10$. The highest peak in the spectra was always at $Si_6H_{13}{}^+$, indicating that this cluster is the stablest [14]. This is consistent with the theoretically calculated results [18]. The calculation was based on the local-density approximation using the density-functional theory, and predicted that the $Si_6H_{13}{}^+$ is composed of a six-membered ring of SiH_2 units with an additional H atom occupying a bond center position between two Si atoms. The role of the additional H atom is to restore the even number of valence electrons, making this cluster particularly stable in a singly charged state.

The cluster cations grown to a specified mass number were automatically ejected from the ion trap through the inside of the trap quadrupole. No further mass selection was performed for the ejected ion beam. The clusters were deflected by 90° from the straight pass at a kinetic energy of 200 eV, slowed down to a final deposition energy of 18 eV and were focused on a substrate surface. The background pressure around the substrate position was less than 1.0×10^{-8} Pa. We deposited $Si_6H_{13}{}^+$ cluster ions, because these are the stablest and the largest amount of the clusters was obtained. The mass spectra of $Si_6H_x{}^+$ measured at a substrate position shown in Fig. 1 indicated that about 90% of the total ion beam

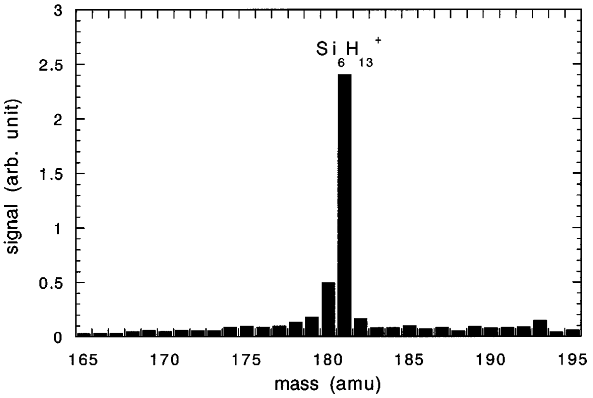

FIG. 1. Mass spectrum of the $Si_nH_x^+$ cluster ion beam measured at the substrate position. The growth parameters were tuned to produce $Si_6H_{13}^+$ ions.

consisted of $Si_6H_{13}^+$ ions. In Fig. 1, the signal at $m = 180$ is a tail of the signal at $m = 181$ due to the resolution of the quadrupole mass spectrometer used for the measurement.

Vicinal Si(111) substrates were cut into 3 mm × 8 mm pieces from an n-type Si wafer with resistivity of 5–8 Ω cm whose surface was tilted from (111) by 1.7° toward the $[\bar{1}\bar{1}2]$ direction. The Si surfaces were cleaned by heating at 1200 °C for 1 min while keeping the pressure below 1×10^{-7} Pa. The $Si_6H_{13}^+$ ions were deposited on clean Si(111)-(7 × 7) surfaces at room temperature. The ion beam current was about 7 pA and was stable during deposition for more than several hours. After the deposition, the samples were transferred in UHV better than 1.0×10^{-8} Pa to an STM (Omicron, UHV-STM). The background pressure was 5.0×10^{-9} Pa in the STM chamber. The [111] oriented W tips [19] were electrochemically etched, and were prepared with field ion microscopy at room temperature for cleaning, modification, and characterization of the tip apexes. We confirmed that contamination at the tip apexes were removed and one atom or three atoms were arranged on top.

Figure 2 shows typical STM images of Si(111)-(7 × 7) surfaces following the deposition of $Si_6H_{13}^+$ cluster ions. The images in Figs. 2(a) and 2(b) were obtained for samples with the cluster deposition of 8.7×10^{11} ions and 9×10^{10} ions, respectively. These images were acquired with a constant current of 0.1 nA and a bias voltage of −1.5 V applied to the sample to observe the filled electronic states. The Si(111)-(7 × 7) structure was safely preserved, indicating that the samples were kept in a clean vacuum during the deposition. Apart from the (7 × 7) structures, circular dots larger than the adatom image were visible at lower terraces of the step edges. The minimum distance between the dots was 10.3 Å, while the adatom-adatom distance of the (7 × 7) surfaces was 7.7 Å. These structures were never observed without the cluster deposition, and the observed density of the dots corresponded to the deposited cluster amount. Therefore, these are identified to be due to the deposited clusters. Figures 3(a) and 3(b) show STM images obtained from the same area for filled states obtained at a sample bias voltage of −1.5 V and for empty states obtained at 1.5 V, respectively. In the empty state images, the clusters could not be recognized, but the substrate (7 × 7) structure was faintly seen in the region where the cluster structures were observed with the negative voltage, verifying that the observed dots are certainly due to the deposited clusters. This implies that the band gap of the deposited clusters is larger than 1.5 eV, being consistent with the calculation which predicted an energy gap of about 5 eV for the Si_6H_{12} cluster [18], which is the form of the clusters after adsorption, as described below.

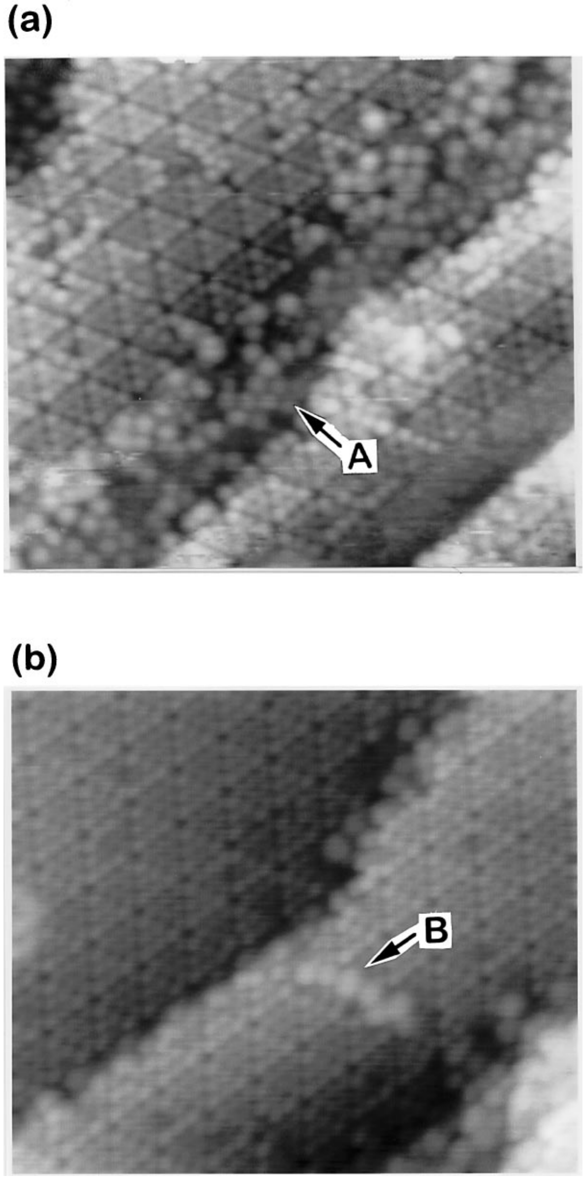

FIG. 2. STM images of the Si(111)-(7 × 7) surfaces with cluster deposition of (a) 8.7×10^{11} ions and (b) 9×10^{10} ions. In (a) a local ordering with hexagonal symmetry is seen in the region marked A. In (b) a one-dimensional cluster array is seen, marked as B.

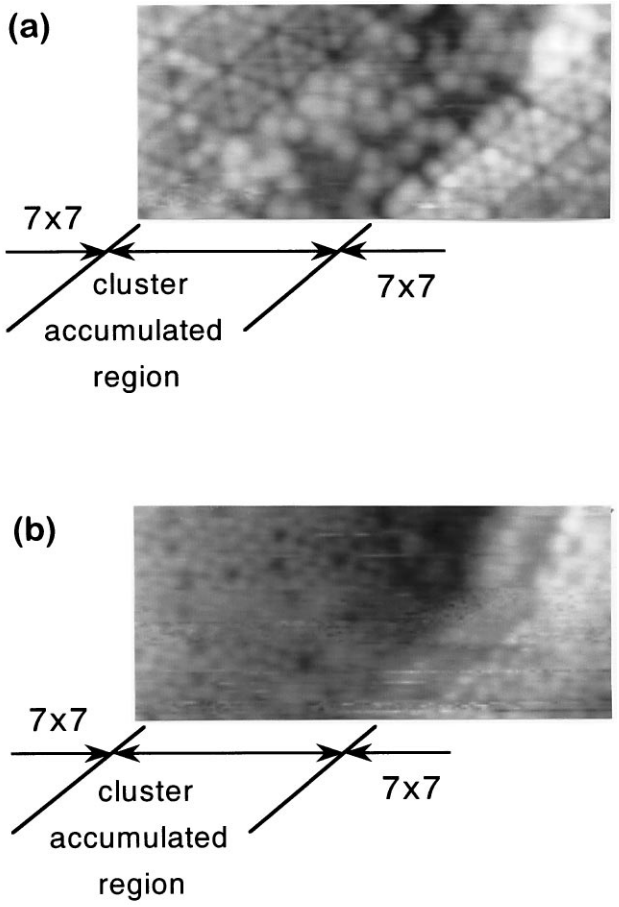

FIG. 3. STM images acquired from the same region of the cluster deposited Si(111)-(7 × 7) surface. The image (a) represents a filled state image with a sample bias of −1.5 V, and the image (b) represents an empty state image with a bias of 1.5 V.

The deposited clusters were mainly observed at the lower terrace of the step edges. Fewer clusters were observed on the flat surfaces, indicating that the cluster has fairly high mobility on the surface even at room temperature due to its weak interaction with the perfect Si(111)-(7 × 7) structure. Moreover, the clusters were not observed along the straight steps, e.g., the one at bottom right in Fig. 2(a), but were adsorbed near the kink site. This indicates that not the straight but the irregular part of the step works as a nucleation site for cluster aggregation. Interestingly, a linear array of the clusters was sometimes observed at the domain boundary of (7 × 7) phases of the substrate, as shown in Fig. 2(b), indicating that the domain boundary also acts as a nucleation site.

The cluster density distribution was also measured in the STM images along one axis of the sample surface. The results showed that the cluster ion beam was focused in 2 mm in diameter on the Si(111) substrate. The sticking coefficient of the clusters was estimated to be 0.90 ± 0.05.

There remains a question as to the composition and charge state of the deposited clusters. After impinging on the substrate, the $Si_6H_{13}{}^+$ ions may possibly be neutralized because the (7 × 7) surface is known to be metallic. This view is confirmed by the fact that the clusters assemble closely on the surface as seen in Fig. 2. It is also evidence of the neutralization that the (7 × 7) structure is still visible just near the deposited clusters in Fig. 2 and even through the adsorbed clusters in Fig. 3(b). When neutralized, Si_6H_{13} becomes less stable and is converted into stable Si_6H_{12} by losing a H atom. Thus we infer that the clusters stay on the surface in the form of neutral Si_6H_{12}. The theoretical calculation, however, tells us that this process of H release is energetically deficient by 0.58 eV, but the incident energy of the cluster ions, 18 eV, enables the occurrence of this process. Another route for H release is the transfer of the H atom to the substrate surface, which may be energetically favorable, but no significant amount of H adsorption was observed in our STM images, ruling out this process as a possibility. Probably, the structural hindrance makes the H transfer to the surface difficult. In contrast, there is no structural barrier for H desorption into free vacuum, suggesting that this process is actually at work for the composition change in the clusters. According to the calculation, Si_6H_{12} has a ring structure consisting of SiH_2 units where each Si atom has the bulklike sp^3 bonding [20], as shown in Fig. 4. The size of Si_6H_{12} was calculated as 7.32 Å in diameter and 3.84 Å in height.

The array of the deposited clusters on the surface was investigated. Although some types of local ordering were partially observed, the most typical ordering was a hexagonal lattice, as marked as *A* in Fig. 2(a). The nearest neighbor distance in the ordered region was 10.3 ± 0.4 Å. If the Si_6H_{12} clusters simply assemble by the van der Waals interaction irrespective of the Si(111)

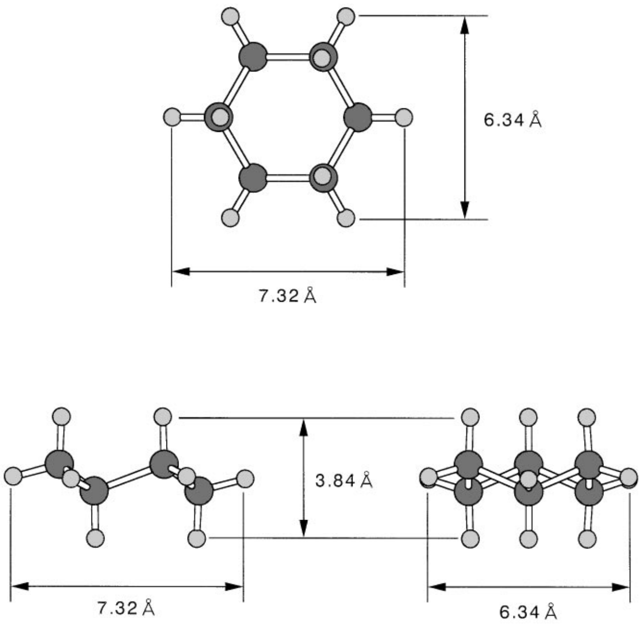

FIG. 4. Calculated stable structure of Si_6H_{12}, which is considered to be the adsorbate converted from $Si_6H_{13}{}^+$.

surface, the intercluster distance is expected to be the sum of the cluster diameter and the van der Waals diameter of H atom, 9.7 Å, or less. However, the measured distance was larger than the expected value, suggesting that the Si(111) surface is exerting a somewhat significant effect on the cluster array. The role of the substrate surface was even further exhibited by the fact that the cluster lattice aligned ±19° from the $[\bar{1}\,\bar{1}2]$ steps. This shows that the lattice structure is a $(\sqrt{7} \times \sqrt{7})R \pm 19.1^\circ$ superstructure, whose period is 10.2 Å and consistent with the measured values of 10.3 ± 0.4 Å. The $(\sqrt{7} \times \sqrt{7})R \pm 19.1^\circ$ superstructure was reported to be observed with the adsorption of metals, Ag, Al, Co, Pt, and Ni, on Si(111) [21–23]. However, it is unlikely that the deposition caused contamination with these metals. Furthermore, these metals are also reported to show different types of superstructures together with $(\sqrt{7} \times \sqrt{7})R \pm 19.1^\circ$. Thus the observed $(\sqrt{7} \times \sqrt{7})R \pm 19.1^\circ$ structure is attributed to the Si_6H_{12} clusters. This superstructure is commensurate with the (7×7) structure; a (7×7) unit cell contains seven clusters, indicating that the clusters were arranged on the (7×7) structure. This is consistent with the fact that the (7×7) structure was observed with the positive sample voltage in the region covered with the clusters.

The above results show that the clusters soft-landed on the surface without fragmentation and substrate damage with the deposition energy of 18 eV, i.e., 3 eV per Si atom for ${Si_6H_{13}}^+$. The effect of deposition energy has been examined for Ag clusters on Pt(111) [8], which showed that energy of 1.0 eV per atom resulted in a soft-landing while 2.9 eV per atom caused fragmentation. The threshold energy was lower than the cohesive energy of Ag, 2.95 eV per atom. The ${Si_6H_{13}}^+$ clusters consisting of stable sp^3 bonding are expected to be stabler than metal clusters, since the cohesive energy of Si, 4.63 eV per atom is higher than that of Ag. In addition, the present cluster-substrate combination is very efficient in momentum transfer because of the following reasons. First, the deposited clusters consist of the same atoms as the substrate. Second, the incident velocity, 4.4×10^3 m/s is less than the longitudinal sound velocity of Si substrates in the [111] direction, 9.4×10^3 m/s. These are considered to be the reasons why the relatively large deposition energy did not cause the cluster fragmentation.

In summary, we have examined the deposition of the stable hydrogenated Si cluster ions, ${Si_6H_{13}}^+$ on Si(111)-(7×7) surfaces with a kinetic energy of 3 eV per Si atom. The clusters deposited were thought to be converted to neutral Si_6H_{12}, and preferentially adsorbed at the lower terrace of the steps with a sticking coefficient of 0.90 ± 0.05. Local hexagonal-type ordering with the $(\sqrt{7} \times \sqrt{7})R \pm 19.1^\circ$ configuration was observed, indicating that well-defined hydrogenated Si clusters have been deposited on the surface nondestructively. These results will open the possibility of examining how different characteristics from the bulk material are derived from an ordered assembly of well-defined clusters made up of Si atoms stabilized by H atoms.

This work, partly supported by NEDO, was performed at JRCAT under the joint research agreement between the National Institute for Advanced Interdisciplinary Research (NAIR) and the Angstrom Technology Partnership (ATP).

---

*Present address: Electrotechnical Laboratory, Tsukuba 305-8586, Japan.

†Permanent address: Electrotechnical Laboratory, Tsukuba 305-8586, Japan.

[1] A. P. Alivisatos, Science **271**, 933 (1996).

[2] V. L. Colvin, A. P. Alivisatos, and J. G. Tobin, Phys. Rev. Lett. **66**, 2786 (1991).

[3] A. N. Goldstein, C. M. Echer, and A. P. Alivisatos, Science **256**, 1425 (1992).

[4] J. Shi, S. Gider, K. Babcock, and D. D. Awschalom, Science **271**, 937 (1996).

[5] E. Ganz, K. Sattler, and J. Clarke, Phys. Rev. Lett. **60**, 1856 (1988).

[6] J. Xhie, U. Mueller, N. Venkateswaran, and G. Raina, Phys. Rev. B **43**, 8917 (1991).

[7] Y. Kuk, M. F. Jarrold, P. J. Silverman, J. E. Bower, and W. L. Brown, Phys. Rev. B **39**, 11 168 (1989).

[8] K. Bromann, C. Felix, H. Brune, W. Harbich, R. Monot, J. Buttet, and K. Kern, Science **274**, 956 (1996).

[9] E. C. Honea, A. Ogura, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, Nature (London) **366**, 42 (1993).

[10] M. F. Jarrold, Science **252**, 1085 (1991).

[11] K. Raghavachari and V. Logovinsky, Phys. Rev. Lett. **55**, 2853 (1985).

[12] H. Murakami and T. Kanayama, Appl. Phys. Lett. **67**, 2341 (1995).

[13] T. Kanayama, Jpn. J. Appl. Phys. **33**, L1792 (1994).

[14] M. O. Watanabe, H. Murakami, T. Miyazaki, and T. Kanayama, Appl. Phys. Lett. **71**, 1207 (1997).

[15] M. O. Watanabe and T. Kanayama, Appl. Phys. A **66**, S1039 (1998).

[16] T. Kanayama and H. Murakami, J. Vac. Sci. Technol. B **15**, 2882 (1997).

[17] M. O. Watanabe, N. Kawashima, and T. Kanayama, J. Phys. D **31**, L63 (1998).

[18] T. Miyazaki, T. Uda, I. Stich, and K. Terakura, Chem. Phys. Lett. **284**, 12 (1998).

[19] H.-W. Fink, IBM J. Res. Dev. **30**, 460 (1986).

[20] T. Miyazaki, T. Uda, I. Stich, and K. Terakura, Chem. Phys. Lett. **261**, 346 (1996).

[21] V. G. Lifshits, A. A. Saranin, and A. V. Zotov, in *Surface Phases on Silicon* (John Wiley and Sons, Chichester, 1994).

[22] R. J. Hamers, Phys. Rev. B **40**, 1657 (1989).

[23] T. Yao, S. Shinabe, and M. Yoshimura, Appl. Surf. Sci. **104/105**, 213 (1996).