

# Growth of $\text{Si}_8\text{H}_x^+$ Cluster Ions and Deposition on Si Surfaces

Noriyuki Uchida<sup>1,\*</sup>, Leonid Bolotov<sup>2</sup> and Toshihiko Kanayama<sup>1,†</sup>

<sup>1</sup>JRCAT-NAIR and <sup>2</sup>JRCAT-ATP

1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, JAPAN

Fax:81-298-61-2576, e-mail: uchida@jrcat.or.jp

We have studied growth of hydrogenated Si cluster ions,  $\text{Si}_8\text{H}_x^+$  in an EQSIT (External Quadrupole and Static attraction Ion Trap) and their deposition on Si surfaces. The  $\text{Si}_8\text{H}_x^+$  clusters were grown from silane gas in the presence of  $\text{H}_2$  gas with continuous electron irradiation in the EQSIT. The mass distribution of the grown  $\text{Si}_8\text{H}_x^+$  ions always showed distinct peaks at  $\text{Si}_8\text{H}^+$ ,  $\text{Si}_8\text{H}_7^+$ ,  $\text{Si}_8\text{H}_{19}^+$ . We extracted the  $\text{Si}_8\text{H}_{19}^+$  clusters, which have an  $sp^3$  bonding network, from the EQSIT and deposited them on Si(111)-(7×7) surfaces with different kinetic energies of the clusters at 6 and 12 eV. The surface structures with the clusters were observed by Scanning Tunneling Microscopy (STM).

Key words: Hydrogenated Si clusters, Ion trap, Cluster ion beam deposition, Scanning Tunneling Microscopy

## 1. Introduction

It is widely accepted that cluster deposition on solid surfaces is one of useful nanostructure-fabrication processes. In particular, deposition of structure-controlled semiconductor clusters is expected to be used for nanostructure fabrication with atomic accuracy. It also enables necessary control over properties of nanostructures, because the fundamental characteristics of semiconductor clusters are widely tunable owing to the sensitivity to the cluster size and structures.

We have developed an ion trap, External Quadrupole and Static attraction Ion Trap (EQSIT) for growth of well-defined clusters<sup>1)</sup> and set up an ultrahigh vacuum system for cluster deposition using this ion trap<sup>2)</sup>. It was demonstrated that hydrogenated Si cluster ions,  $\text{Si}_n\text{H}_x^+$  ( $n = 1 - 10$ ) were grown from silane gas in the EQSIT<sup>3)</sup>. The stable structures of some of these clusters were investigated, being compared with the *ab-initio* calculation results<sup>3,4)</sup>.

We previously studied the deposition of the  $\text{Si}_6\text{H}_{13}^+$  cluster ions, which have a ring structure with  $sp^3$  bonding, on the Si(111)-(7×7) surfaces<sup>5)</sup> using STM. It was found that the cluster ions preferentially adsorbed at the lower terrace of the steps which have kink sites resulting in local hexagonal-type ordering. This indicated that the clusters have

soft-landed and diffused on the Si(111)-(7×7) surfaces.

In this paper, we have compared deposition of  $\text{Si}_8\text{H}_x^+$  cluster ions with that of  $\text{Si}_6\text{H}_{13}^+$  on Si(111)-(7×7) surfaces, controlling the kinetic energy of the cluster ions down to 2 eV. To observe how the cluster behavior depends on the cluster size.

## 2. Experimental

The cluster deposition system used in this work was reported previously<sup>2)</sup>. This system consists of three vacuum chambers; a growth chamber equipped with the EQSIT, a mass-selection chamber containing a quadrupole mass filter and a deposition chamber which installs an electrostatic quadrupole deflector. The EQSIT, which consists of a cage electrode and a set of linear quadrupoles, can trap cluster ions with a wide mass range, making itself useful for cluster growth. The  $\text{Si}_n\text{H}_x^+$  clusters were grown from silane gas ( $2.0 \times 10^{-5}$  Pa) in the presence of  $\text{H}_2$  gas ( $\sim 10^{-2}$  Pa) with continuous electron irradiation of  $\sim 100$  eV and  $\sim 25$  mA in the EQSIT. The ions grown to a pre-determined mass were automatically extracted from the EQSIT as an ion beam, and injected into the deposition chamber through the mass-selection chamber. The mass filter was used not as a mass separator but as a simple beam guide in this study. The ion beam was then deflected by  $90^\circ$  and deposited to the solid substrate. The mass distribution of the ion beam deflected to the opposite direction was measured by a quadrupole mass spectrometer. The mass distribution measured in

\*Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

†Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

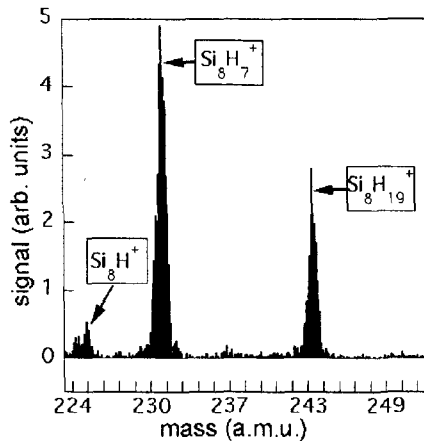


Figure 1: Mass distribution in  $\text{Si}_8\text{H}_x^+$  ion beam.

this way should be identical with that at the substrate position. The kinetic energy distribution of the ion beam was measured at the substrate position by a retarding-field energy analyzer. The results indicated that the deposition system delivers a cluster-ion beam with a kinetic energy distribution of 2 eV at FWHM. This enabled us to control the deposition impact energy  $E_d$ , *i.e.* the kinetic energy at which the clusters collide with the surface, down to 2 eV.

The cluster ions were deposited at room temperature on  $\text{Si}(111)-(7 \times 7)$  substrates, whose surfaces were prepared by heating the substrates at more than  $1200^\circ\text{C}$  for 1 minute while keeping the pressure better than  $2.0 \times 10^{-7}$  Pa. The substrates were transferred in ultrahigh vacuum (UHV) to an STM chamber (background pressure was  $5.0 \times 10^{-9}$  Pa) after the deposition. For STM observation of the deposited surfaces, the  $\text{W}(111)$  tips etched electrochemically were used after preparation with field ion microscopy.

### 3. Results and Discussion

The mass distribution of  $\text{Si}_8\text{H}_x^+$  ion beam is shown in Fig.1. The mass spectra always showed distinct peaks at  $\text{Si}_8\text{H}^+$  (225 amu),  $\text{Si}_8\text{H}_7^+$  (231 amu), and  $\text{Si}_8\text{H}_{19}^+$  (243 amu), indicating that these clusters were able to be transported to the substrates.

Now we consider the possible structures of  $\text{Si}_8\text{H}_x^+$  ( $x=1, 7, \text{ and } 19$ ) cluster ions. The stable structures of  $\text{Si}_n\text{H}_x^+$  and  $\text{Si}_n\text{H}_y$  clusters

were calculated by using a density-functional total-energy minimization method<sup>6</sup>. In particular, the structures of  $\text{Si}_6\text{H}_x^+$  were compared with  $\text{Si}_6\text{H}_y$  structures<sup>6</sup>. The results indicated that the structures of  $\text{Si}_6\text{H}_{x+1}^+$  cations correspond to stable neutral  $\text{Si}_6\text{H}_x$  clusters when  $x$  is even number. This is simply understandable because clusters are in general stable when the total number of valence electrons is even. Thus, a singly charged cluster cation is stable when it has one more H atom than the neutral counter part<sup>6</sup>.

It has been suggested that the cation-neutral cluster correspondence is not limited to the  $n=6$  case but is applicable to  $n \geq 7$ <sup>3,6</sup>. We considered that  $\text{Si}_8\text{H}_x^+$  structures correspond to the structures of the neutral  $\text{Si}_8$ ,  $\text{Si}_8\text{H}_8$ , and  $\text{Si}_8\text{H}_{18}$  clusters, by adding or removing one H atom, as shown in Fig.2. The structure of  $\text{Si}_8\text{H}^+$  corresponds to  $\text{Si}_8$  which has the compact structure<sup>7</sup>. The  $\text{Si}_8\text{H}_8$  structure has a cubic Si bonding network with full termination of the dangling bonds by H atoms, which is called an octasilacubane<sup>8,9</sup>. The  $\text{Si}_8\text{H}_{18}$  structure has a linear chain consisting of  $sp^3$  bonding network of Si atoms and the dangling bonds of the Si atoms are saturated with H atoms, namely polysilane. If an H atom be added to Si clusters already saturated with H atoms, it is inserted into the Si-Si bonding center because these clusters has no dangling bonds. The H atom insertion was observed in crystalline silicon and explained from a theoretical point of view<sup>10</sup>. Thus the structure of  $\text{Si}_8\text{H}_{19}^+$  corresponds to the  $\text{Si}_8\text{H}_{18}$  structure, adding one H atom to the Si-Si bonding center. In contrast, the structure of  $\text{Si}_8\text{H}_7^+$  is derived from the  $\text{Si}_8\text{H}_8$ , by removing one H atom. One possible reason for this is that the insertion to the Si-Si bond among the  $\text{Si}_8\text{H}_8$  structure which does not have  $sp^3$  bonding is energetically unfavorable.

The  $\text{Si}_8\text{H}_{18}$  may have several structural isomers. We consider that the structures of isomers are classified into linear-chain and branching types as shown in Fig.3, according to our calculations, similarly the  $\text{Si}_8\text{H}_{19}^+$  clusters also include the isomers corresponding the  $\text{Si}_8\text{H}_{18}$  isomers.

Next let us consider deposition of the hydrogenated Si clusters on  $\text{Si}(111)-(7 \times 7)$  surfaces. We selected  $\text{Si}_8\text{H}_{19}^+$  cluster ions for deposition because they have a stable  $sp^3$  bonding network. After optimization of growth and transport conditions for  $\text{Si}_8\text{H}_{19}^+$  ion beam deposition, the mass spectra of the ion beam (Fig.4) indicated that about 90% of

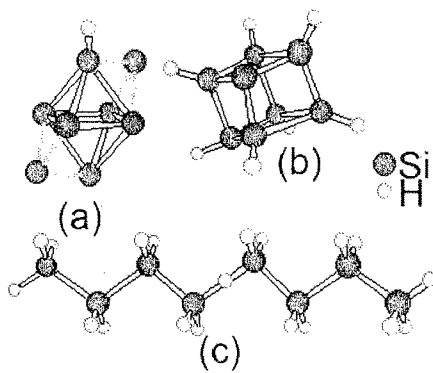


Figure 2: Possible structures of  $\text{Si}_8\text{H}_x^+$  ( $x=1, 7, \text{ and } 19$ ) cluster ions. (a)  $\text{Si}_8\text{H}^+$ , (b)  $\text{Si}_8\text{H}_7^+$ , (c)  $\text{Si}_8\text{H}_{19}^+$ .

the total ion beam consisted of  $\text{Si}_8\text{H}_{19}^+$  ions. Using this ion beam, we deposited  $\text{Si}_8\text{H}_{19}^+$  with  $E_d = 6$  and  $12 \pm 1$  eV on substrates at room temperature.

When the  $\text{Si}_8\text{H}_{19}^+$  ions reach the Si(111)-(7×7) surfaces, they are neutralized because the surface is metallic. According to the calculation, the Si-H-Si complex among the  $\text{Si}_8\text{H}_{19}^+$  structure has a non-bonding character and becomes unstable when neutralized<sup>10</sup>. Therefore, we considered that the  $\text{Si}_8\text{H}_{19}$  neutral cluster was converted into stable  $\text{Si}_8\text{H}_{18}$  by losing a H atom from the Si-H-Si complex or separated into stable small clusters.

In Figs.5, (a) and (b) show STM images of the Si(111)-(7×7) surfaces following the deposition of  $\text{Si}_8\text{H}_{19}^+$  ions with  $E_d = 6$  and 12 eV, respectively. These samples were obtained with the deposition of  $2.4 \times 10^{11}$  cluster ions. This amount of supplied clusters was estimated by the ion beam current absorbed into the substrate. These images were observed with a constant current of 0.2 nA and a sample bias voltage of -1.5 V (Fig.5 (a)) and -1.6 V (Fig.5 (b)) probing of filled states of the deposited surfaces.

After the  $\text{Si}_8\text{H}_{19}^+$  deposition at  $E_d = 6$  and 12 eV, these clusters appeared as several type bright dots and were found preferentially on the faulted half of the Si(111)-(7×7) unit cell. When deposited at  $E_d = 6$  eV, we observed circular and elliptic dots which are due to adsorption of the  $\text{Si}_8\text{H}_{18}$  clusters, indicating the existence of the structural isomers as shown in Fig.5 (a). At  $E_d = 12$  eV, We observed several size dots and dark holes of the Si(111)-(7×7) surfaces as shown in Fig.5 (b). The larger size dots are the  $\text{Si}_8\text{H}_{18}$  clusters because the sizes of the dots

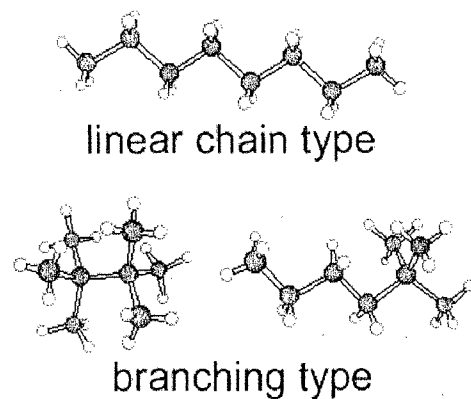


Figure 3: Structural isomers of the  $\text{Si}_8\text{H}_{18}$  clusters.

are similar to the  $\text{Si}_8\text{H}_{18}$  in Fig.5 (a). The small dots and holes were not seen in Fig.5 (a). We consider that the smaller dots consist of fragmented  $\text{Si}_8\text{H}_{19}^+$  clusters, resulting from separation of Si-H-Si complex, and the holes are due to surface defects caused by attack of the cluster ions. In the  $\text{Si}_6\text{H}_{13}^+$  case, when deposited at  $E_d \leq 18$  eV, the clusters adsorbed at the Si(111)-(7×7) surfaces without the fragmentation of the clusters.<sup>11</sup> The difference in the cluster behavior of the  $\text{Si}_6\text{H}_{13}^+$  and  $\text{Si}_8\text{H}_{19}^+$  on the surfaces is due to the structure difference. The  $\text{Si}_6\text{H}_{13}^+$  have a ring structure with  $sp^3$  bonding and the  $\text{Si}_8\text{H}_{19}^+$  have a chain structures consisting  $sp^3$  bonding. We consider that the ring structure is more durable for deposition than the chain structures.

#### 4. Conclusion

The  $\text{Si}_8\text{H}^+$ ,  $\text{Si}_8\text{H}_7^+$ , and  $\text{Si}_8\text{H}_{19}^+$  clusters were grown stably in the EQSIT. We discussed that the  $\text{Si}_8\text{H}_x^+$  structures correspond to the neutral cluster structures with adding or removing an H atom. The  $\text{Si}_8\text{H}_{19}^+$  ions were deposited on the Si(111)-(7×7) surfaces with  $E_d = 6$  and  $12 \pm 1$  eV. From the STM observations of the surfaces, the  $\text{Si}_8\text{H}_{19}^+$  cluster ions were adsorbed preferentially on the faulted half of the Si(111)-(7×7) unit cell, and different structures were observed depending on the impact energy, which suggests fragmentation and presence of isomers.

#### Acknowledgments

This work, partly supported by NEDO, was performed at JRCAT under the joint research agree-

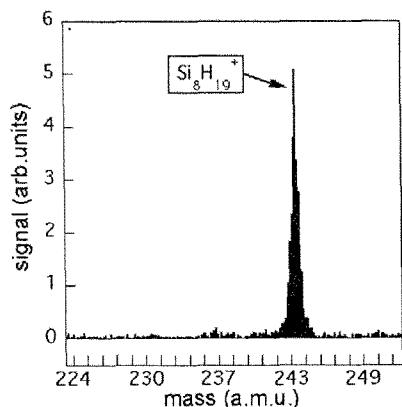
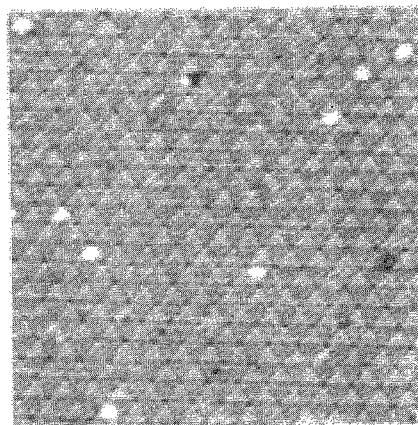


Figure 4: Mass distribution of the  $\text{Si}_8\text{H}_{19}^+$  ion beam used for the deposition.

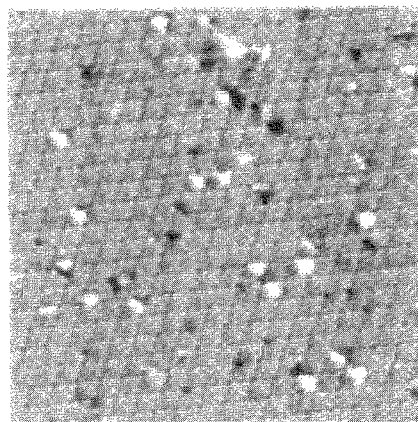
ment between the National Institute for Advanced Interdisciplinary Research (NAIR) and Angstrom Technology Partnership (ATP). The authors wish to thank Prof. K. Kimura of University of Tokyo for his encouragement and discussions.

#### References

- 1) T. Kanayama, Jpn. J. Appl. Phys. **33** 1792 (1994).
- 2) M. O. Watanabe, N. Uchida, and T. Kanayama, Eur. J. Phys. D. **9** 1-3 (1999).
- 3) N. Uchida, M. O. Watanabe, and T. Kanayama, Trans. MRS-J. **24**[1] 113-116 (1999).
- 4) M. O. Watanabe, H. Murakami, T. Miyazaki, and T. Kanayama, Appl. Phys. Lett. **71** 1207 (1997).
- 5) M. O. Watanabe, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **81** 5362 (1998).
- 6) T. Miyazaki, T. Uda, I. Štich, and K. Terakura, Chem. Phys. Lett. **284** 12 (1998).
- 7) A. A. Shvartsbrung *et al.*, Phys. Rev. Lett. **83** 2167 (1999)
- 8) N. Oyama, T. Takano, E. Ohta, K. Takeda, and K. Shiraiishi, Trans. MRS-J. **20** 438 (1996).
- 9) G. Onida and W. Andreoni, Chem. Phys. Lett. **243** 183 (1995).
- 10) Chris G. Van de Walle, Physica B. **170** 21-32 (1991)
- 11) M. O. Watanabe, N. Uchida, and T. Kanayama, to be published in Phys. Rev B.



(a)



(b)

Figure 5: STM images of the Si(111)-(7×7) surfaces deposited with  $\text{Si}_8\text{H}_{19}^+$ ; (a)  $E_d = 6$  eV and (b)  $E_d = 12$  eV. The images were taken with the sample bias of -1.5 V (a) and -1.6 V (b).

(Received December 17, 1999; Accepted March 29, 2000)