Growth and Transport of Hydrogenated Si Clusters

Noriyuki Uchida[1,*], Miyoko O. Watanabe[2] and Toshihiko Kanayama[1,†]

[1]*JRCAT-NAIR* and [2]*JRCAT-ATP*

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

Fax:81-298-54-2576, e-mail: uchida@jrcat.or.jp

We have studied growth and transport of hydrogenated Si cluster ions, $Si_nH_x^+$ grown in an External Quadrupole and Static attraction Ion Trap (EQSIT) for deposition on solid surfaces. The mass distribution of the grown $Si_nH_x^+$ ions was measured for $n = 1 - 10$, showing always several distinct peaks at Si_3H^+, $Si_6H_x^+$ ($x = 1, 7, 13$), and $Si_8H_x^+$ ($x = 7, 19$). These clusters experimentally obtained corresponded to the theoretically calculated stable structures. The clusters were transported as an ion beam from the EQSIT to a solid substrate without the cluster structures being changed, and deposited on Si(111) at a deposition energy of 18 eV.

Key words: Hydrogenated Si clusters, Ion trap, Cluster ion beam

1. Introduction

It is expected that structure-controlled nanostructures are formed when the clusters with specified structures are arranged on solid surfaces. Although much effort has been made to study cluster deposition on solid surfaces, it was difficult to obtain well-defined clusters with a sufficient quantity for deposition on solid surfaces. We have developed an ion trap, External Quadrupole and Static attraction Ion Trap (EQSIT)[1,2] for growth of well-defined clusters. It was demonstrated that hydrogenated Si cluster ions, $Si_nH_x^+(n = 1 - 10)$ were grown from silane gas in the EQSIT. The stable structures of some of these clusters have been investigated, being compared with the *ab-initio* calculation results[3]. We have also developed an ultrahigh vacuum system for growth of $Si_nH_x^+$ clusters and their deposition on solid surfaces[4].

In this work, we study which kinds of $Si_nH_x^+(n = 1 - 10)$ are grown and transported on solid surfaces using this system.

2. Experimental

The cluster deposition system is shown in Fig.1. This system consists of three vacuum chambers; a growth chamber equipped with an EQSIT, a mass-selection chamber containing a quadrupole mass filter and a deposition chamber which installs an electrostatic quadrupole deflector. The EQSIT

*Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 133-8656, Japan

†Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan
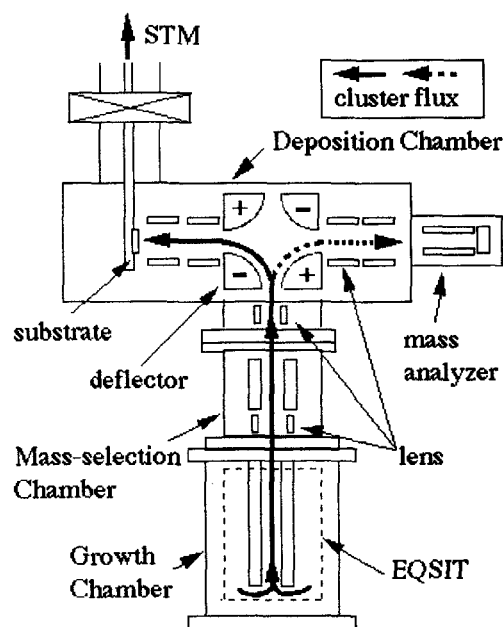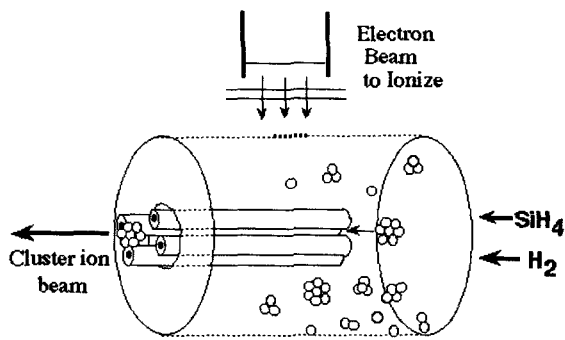
Figure 1: The developed system for cluster growth, transport and deposition of clusters.

in the growth chamber consists of a cage 17 cm in diameter and 20 cm in length and a set of linear quadrupoles 1 cm in diameter and 15 cm in length, as shown in Fig.2. To the quadrupole, ac voltage of opposite phases are connected with a dc bias voltage to generate a trapping potential. The stable trapping position r, that is a distance from the axis of the quadrupole, for a cluster ion with a mass m is given by

$$r \sim \left(\frac{q\,V_{ac}^2}{4\pi^2 m f^2\,V_{dc}}\right)^{\frac{1}{6}} \quad (1)$$

where q is the ion charge, f is the ac frequency ,

Figure 2: The EQSIT for growth of $Si_nH_x^+$ cluster ions. Cations generated by electron irradiation are confined in the EQSIT and allowed to react with SiH_y radicals.

V_{ac} is the amplitude of the ac voltage, and V_{dc} is the dc bias voltage. The grown cluster ions with small mass values are distributed near the cage and clusters with big mass values are distributed near the quadrupole. These cluster distributions are controlled with tuning of the frequency and amplitude of the ac voltage. The $Si_nH_x^+$ clusters were grown from silane gas (2.0×10^{-5} Pa) in the presence of H_2 gas ($\sim 10^{-2}$ Pa) with continuous electron irradiation of ~ 100 eV and ~ 20 mA in the EQSIT. A dc bias voltage of -3 V and ac voltage between 50 and 190 V with varying frequencies between 500 and 920 kHz were applied to the quadrupole of the EQSIT.

The clusters can pass through the inside field of the quadrupole if the inequality

$$m > \frac{1.1q\ V_{ac}}{\pi^2 f^2 R_0^2} \tag{2}$$

is fulfilled, where $R_0(=0.5$ cm) is the internal radius of the quadrupole, i.e., the clusters with bigger mass values than a threshold value are automatically driven into the internal region. According to this principle the $Si_nH_x^+$ ions grown to a pre-determined mass are automatically extracted from the EQSIT as an ion beam, and injected to the deposition chamber through a mass filter, which was used as a simple beam guide in this study. The cluster ions are deflected by $\pm 90°$ at a higher energy of 200 eV to get rid of neutral species. The deflection angle is controlled with the voltage applied to the quadrupole deflector. The ion beam deflected to the solid substrate is for cluster deposition. The mass distribution of the ion beam deflected to the opposite direction is measured by a quadrupole mass spectrometer. The

mass distribution measured in this way should be identical with that at the substrate position.

3. Results and Discussion

The mass distribution of the deflected $Si_nH_x^+$ ions was measured for $n = 1 - 10$, as shown in Fig.3. The mass spectra were measured within a mass accuracy of 1.0 amu. For this purpose, the clusters were extracted by tuning the EQSIT parameters for each value of n. The mass spectra always showed several distinct peaks at Si_3H^+, $Si_6H_x^+$ ($x = 1,7$ and 13), and $Si_8H_x^+$ ($x = 7$ and 19), indicating that these clusters were stable enough to be transported to a solid substrate.

These clusters obtained experimentally were compared with the theoretically calculated ones[3,5,6,7]. The stable structures of Si_nH_x and $Si_nH_x^+$ clusters were examined theoretically by using a density-functional total-energy minimization method[3]. The results indicated that the structures of $Si_nH_x^+$ cations corresponded to neutral clusters of Si_nH_{x-1} when x is odd number. This view is simply understandable because clusters are in general stable when the total number of valence electrons is even. This is consistent with the result in Fig.3, where all the obtained cluster ions have even electrons. Therefore, the experimentally obtained $Si_nH_x^+$ cations are thought to correspond to neutral Si_nH_{x-1}. The detailed comparison between the experimental results and the calculated ones were performed for $n = 6$[8], and showed that the stable structures of $Si_6H_x^+(x = 1, 7$ and 13) cations shown in Fig.4 are the same as those of neutral Si_6H_{x-1} clusters except that an additional H atom joins in[3]. The other cluster cations, Si_3H^+ and $Si_8H_{19}^+$ also correspond to the calculated stable structures of neutral Si_3 and Si_8H_{18} clusters shown in Fig.5. However, the $Si_8H_7^+$ cations does not have a neutral; the stable structure of Si_8H_6 has never been calculated. The stable neutral cluster consisting of atoms similar to those of $Si_8H_7^+$ is Si_8H_8, which has a cubic structure as shown in Fig.5. Addition of a H atom to the Si_8H_8 structure might be energetically more deficient than losing a H atom from this structure, when ionized.

We have examined the dependence of the quantity of transported $Si_6H_{13}^+$ ions, which has a stable ring structure with sp^3 bonding and a large amount of the clusters are obtained, on the growth parameters of the EQSIT. The quantity of the transported $Si_6H_{13}^+$ ions was measured by the mass
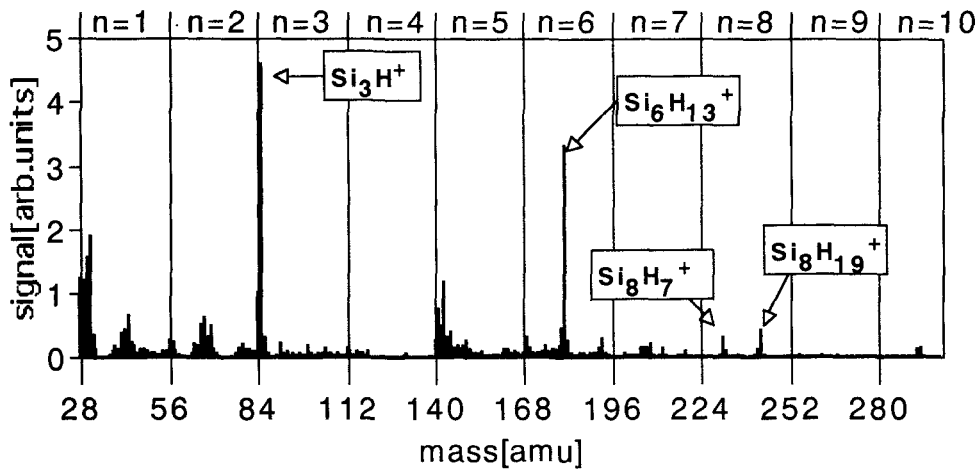
Figure 3: Mass spectrum of the deflected $Si_nH_x^+$ ions measured at a position corresponding to the substrate position for $x = 1 - 10$.

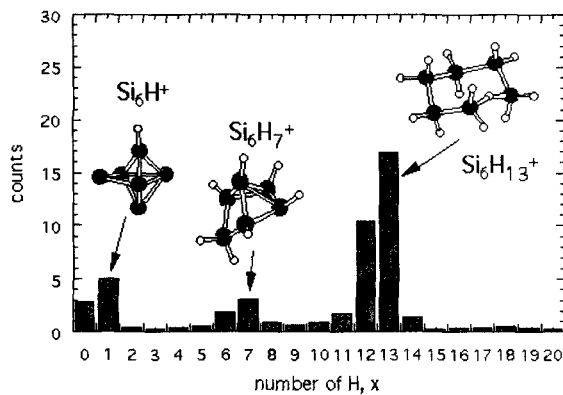Figure 4: Mass spectrum of $Si_6H_x^+$ ($x = 0$-20) and calculated stable structure of $Si_6H_x^+$ ($x = 1,7$ and 13).

spectrometer, together with $m = 169$ and $m = 194$, which formed peaks near to $Si_6H_{13}^+$ ($m = 181$) in the spectra. Figure 6 shows the quantity of the transported clusters against the ac frequency f applied to the quadrupole. The measured quantity increased rapidly when f exceeded a threshold value. The threshold value was higher for the clusters with a smaller mass, being consistent with the principle of the EQSIT. The gradual decrease with f in the frequency region higher than the threshold is due to reduction in the trap capacity.

The $Si_6H_{13}^+$ ions were actually deposited on a Si(111) substrate at a deposition energy of 18 eV. Figure 7 shows the obtained ion beam current as a function of time lasting for 5 hours. The

current was 11 pA when the deposition started, and gradually increased to a saturation current, 36 pA. This change in the $Si_6H_{13}^+$ ion beam current shows that the cluster growth rate in the EQSIT increased with time. The rate mainly depends on the quantity of the reactants for the cluster growth. The initial density of these reactants is low because a large amount of these reactants are adsorbed on the growth chamber wall in the early stage of the cluster deposition. The total cluster quantity deposited on the substrate was 3.15×10^{12} clusters. The cluster density distribution was measured with STM, which was described elsewhere[9], and the results showed that the cluster ion beam was focused in 2mm in diameter on the substrate surface. The density was estimated to be about 1.0×10^{14} clusters/cm^2. This density is high enough for various surface analyses.

4. Summary

The $Si_nH_x^+$ ions were grown from silane gas in the presence of H_2 gas with continuous electron irradiation in the EQSIT and were transported to a solid substrate. The mass spectrum of $Si_nH_x^+$ ($n = 1 - 10$) was measured at a position corresponding to the substrate position by a quadrupole mass spectrometer. The mass spectra always showed several distinct peaks at Si_3H^+, $Si_6H_x^+$ ($x = 1,7$ and 13), and $Si_8H_x^+$ ($x = 7$ and 19). The stable structures were examined for these clusters. The $Si_6H_{13}^+$ clusters were selected and deposited on Si(111) with deposition energy of 18 eV. The deposition current was obtained to be more than 30 pA.
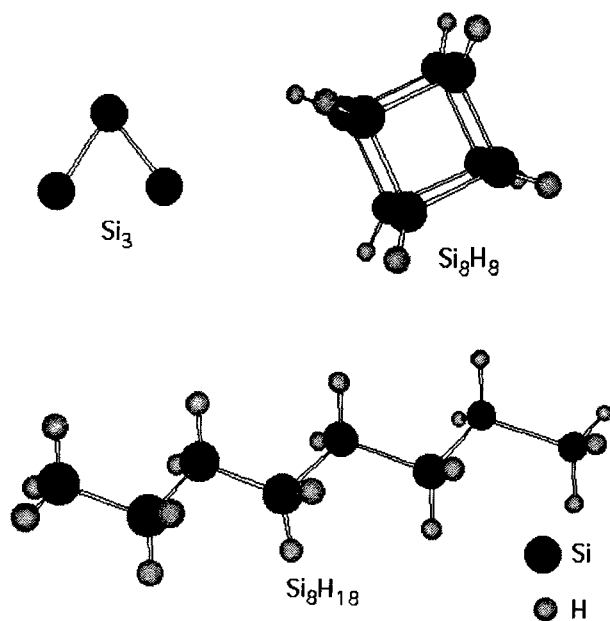
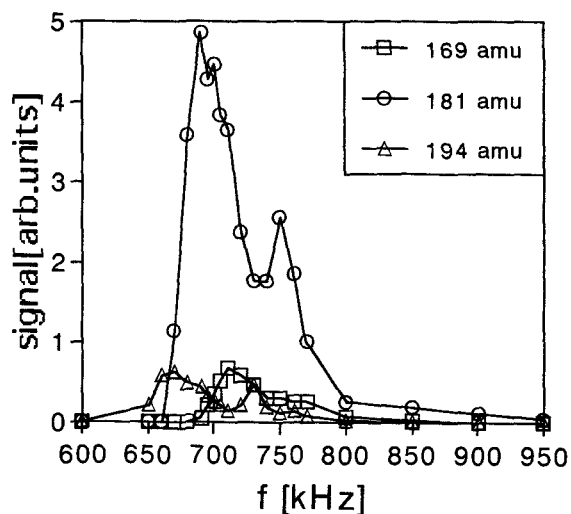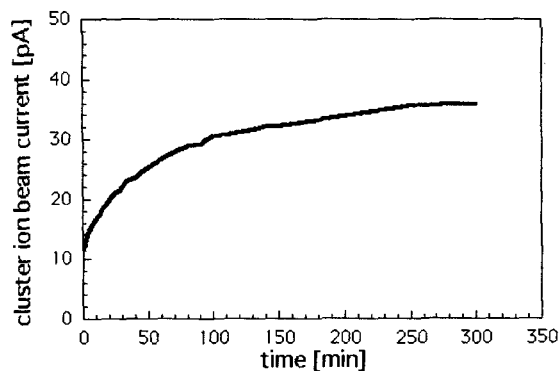Figure 5: Calculated stable structure of Si_3, Si_8H_8 and Si_8H_{18}.

Figure 7: Beam current of $Si_6H_{13}^+$ cluster ions at 18 eV measured at the substrate as a function of deposition time.

Acknowledgments

References

1) T. Kanayama, Jpn. J. Appl. Phys. **33** 1792 (1994).

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

3) T. Miyazaki, T. Uda, I. Štich, and K. Terakura, Chem. Phys. Lett. **284** 12 (1998).

4) M. O. Watanabe, N. Uchida, and T. Kanayama, to be published in Eur. J. Phys. D.

5) O. F. Sankey, D. J. Niklewski, D. A. Drabold, and J. D. Dow, Phys. Rev. B. **41** 12750 (1990).

6) G. Onida and W. Andreoni, Chem. Phys. Lett. **243** 183 (1995).

7) N. Oyama, T. Takano, E. Ohta, K. Takeda, and K. Shiraishi, Trans. MRS-J. **20** 438 (1996).

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

9) M. O. Watanabe, T. Miyazaki, and T. Kanayama, Phys. Rev. Lett. **81** 5362 (1998).

Figure 6: The quantity of cluster ions (m =169, 181 and 194 amu) as a function of the ac frequency. V_{ac} =383 V.