Eur. Phys. J. D **9**, 571–573 (1999)

THE EUROPEAN PHYSICAL JOURNAL D

EDP Sciences

Hydrogenated silicon clusters for deposition on solid surfaces

M.O. Watanabe[1], N. Uchida[2], and T. Kanayama[2,a]

[1] Joint Research Center for Atom Technology (JRCAT) – Angstrom Technology Partnership, 1-1-4 Higashi, Tsukuba 305-0046, Japan
[2] JRCAT – National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba 305-8562, Japan

Received: 1 September 1998 / Received in final form: 20 October 1998

Abstract. We have investigated formation characteristics of stable hydrogenated Si cluster ions, $Si_nH_x^+$, for deposition on solid substrates. The $Si_nH_x^+$ clusters were grown from silane gas in an ion trap developed for cluster growth, and transported to the solid substrate through an electrostatic quadrupole deflector. Several kinds of the clusters ($n = 4 - 10$) were grown and transported to the solid substrate. Among them, $Si_6H_{13}^+$ had the largest population under the optimized conditions. When the $Si_6H_{13}^+$ cluster ion beam was focused to less than 3 mm in diameter on the solid substrate with a deposition energy of 3 eV/Si atom, the beam current obtained was more than 30 pA, which is in the range useful for observation of cluster adsorption structures on solid surfaces.

PACS. 36.40.Qv Stability and fragmentation of clusters – 36.40.Wa Charged clusters – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

1 Introduction

Atomic semiconductor clusters have been a subject of intense basic and applied research because of interest in the fundamental characteristics with the cluster size and their structures [1]. Silicon atomic clusters are the most important, since Si is the most useful material in microelectronics. Owing to the continuous push to smaller features in semiconductor devices, it is clearly desirable to know how the properties of Si crystals change as the sizes approach atomic scales. From this point of view, it is especially important to deposit well-defined clusters on solid surfaces and investigate the resulting structures and properties. The deposited clusters can also be used as nanodevices in suitable technological applications.

Silicon atomic clusters are known to have entirely different structures from the bulk-like sp^3 bonding: so-called compact structures [2–4]. This arises from the fact that the bulk-like structure inherently results in the presence of many dangling bonds, making it inadequate to use Si clusters to investigate how the properties vary with the size. The addition of hydrogen atoms has restored the sp^3 nature [5], allowing one to examine genuine dependence on the cluster size, if hydrogenated Si clusters with identified structures can be prepared.

We have developed an ultrahigh vacuum (UHV) system for growth of hydrogenated Si clusters and their deposition on solid surfaces [6, 7]. This allows us to deposit well-defined hydrogenated Si clusters on Si surfaces. In this paper, we investigate which kinds of hydrogenated Si clusters can be grown and transported on solid surfaces using this system. We also show that a flux of the clusters sufficient for deposition can be obtained by optimization of the growth conditions.

2 Experimental details

The developed system for cluster growth and deposition is shown in Fig. 1. It consists of three chambers; a cluster growth chamber equipped with a quadrupole ion trap for selective cluster growth in a low-pressure gas phase [8], a mass selection chamber containing a quadrupole mass filter, and a cluster deposition chamber, which installs an electrostatic quadrupole deflector [9].

Only a basic outline of the cluster growth technique is given here, since the details have already been reported elsewhere [5–8, 10]. The role of the ion trap is to accept ions with a wide range of mass values, allowing confined ions to react with gaseous species to grow to cluster ions under controlled conditions. Hydrogenated Si cluster cations, $Si_nH_x^+$, were grown from silane (SiH_4) gas in the ion trap in the presence of H_2 gas [6]. A dc bias voltage of -3 V and ac voltages between 50 and 190 V with frequencies between 500 and 920 kHz were applied to the quadrupole of the ion trap. The SiH_4 pressure was fixed to be at 10^{-5} Pa and the H_2 pressure was regulated at 10^{-2} Pa. These are the optimized pressures to generate $Si_6H_x^+$ clusters efficiently [6, 7]. with electrons of 200 eV.

[a] *Permanent address*: Electrotechnical Laboratory, Tsukuba 305-8586, Japan

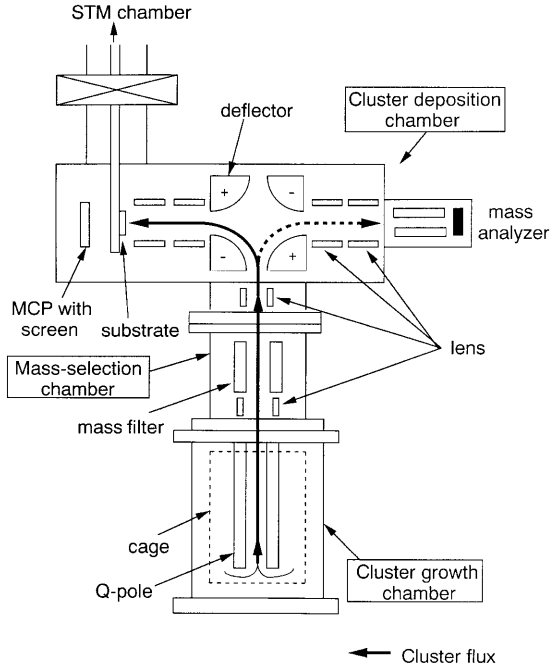

Fig. 1. A schematic diagram of the growth and deposition system of cluster ions.

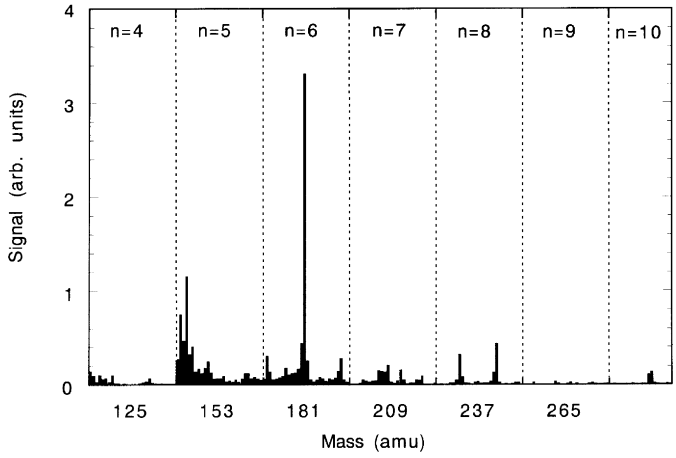

Fig. 2. Mass spectrum of $Si_nH_x^+$ $(n = 4-10)$ measured by a mass spectrometer installed after the quadrupole deflector (see Fig. 1). Each section of the spectrum for different values of n was measured by tuning of the trap parameters for respective values of n.

The SiH_y^+ ions generated were confined in the ion trap and were allowed to grow to $Si_nH_x^+$ clusters.

The $Si_nH_x^+$ ions grown to a predetermined mass were automatically extracted from the ion trap through the inside of the quadrupole [10, 11] and injected as an ion beam into the mass-selection chamber, where the ions could be further mass-selected by a mass filter. The mass-selected cluster ions were focused and injected into the deposition chamber. Then they were deflected by $\pm 90°$ at a higher kinetic energy, 200 eV, to get rid of neutral species effusing from the ion trap. The deflection angle was controlled with the voltages applied to the quadrupole deflector. The ion beam, deflected by 90°, was decelerated to a final deposition energy between 0.1 and 50 eV/atom and focused on the substrate surface. The ion beam deflected by $-90°$, in the opposite direction, was similarly decelerated, and the mass distribution was measured by a quadrupole mass spectrometer, as shown by a dotted curve in Fig. 1. The measured mass distribution should be identical with that at the substrate position. The substrate samples, on which the clusters had been deposited, were transferred in UHV to the Scanning Tunneling Microscopy (STM) chamber connected to the deposition chamber. The background pressure in the growth chamber and the deposition chamber was about 1.0×10^{-7} Pa and 1.0×10^{-8} Pa, respectively.

3 Results and discussion

The mass distribution of the deflected $Si_nH_x^+$ ion beam was measured for $n = 1-10$. For this purpose, the clusters with mass m were extracted from the ion trap by the tuning of the ac frequency ω, and their amplitude, V_{ac}, as $\omega^2/V_{ac} \propto m$ [10, 11]. The typical mass spectrum for the clusters ($n \geqq 14$) is shown in Fig. 2. Although the $Si_nH_x^+$ spectrum showed many peaks, several distinct and reproducible peaks were observed at $Si_5H_3^+$, Si_6H^+, $Si_6H_7^+$, $Si_6H_{13}^+$, $Si_8H_7^+$, and $Si_8H_{19}^+$. Among them, the highest peak for $n \geqq 4$ was always at $n = 6$ and $x = 13$ under the growth conditions adopted here, as clearly seen in Fig. 2. This result is similar to that for $Si_nH_x^+$ clusters growing in the ion trap [5], indicating that the clusters were transported to the solid substrate without their structures being changed. The formation energy and the stable structure of $Si_6H_n^+$ ions were theoretically calculated [12, 13]. The results showed that the $Si_6H_{13}^+$ has the largest formation energy among $Si_6H_x^+$ clusters, predicting that the $Si_6H_{13}^+$ is the most stable. Thus, good agreement between the experimental and calculated results was obtained. The calculation also showed that $Si_6H_{13}^+$ has a bulk-like ring structure with sp^3 bonding, in which an additional H atom occupies a center position between two Si atoms.

We shall confine ourselves to the $Si_6H_{13}^+$ clusters for deposition. The mass spectrum of the beam ejected from the trap was measured under a condition in which the ion trap parameters were tuned for $Si_6H_{13}^+$ clusters, and no further mass selection was performed in the mass filter. The result is shown around $Si_6H_{13}^+$ in Fig. 3, where it is clear that the $Si_6H_{13}^+$ clusters ($m = 181$) are dominant. The signal at $m = 180$ is a tail of the signal at $m = 181$, owing to the resolution of the quadrupole mass spectrometer. The signals of the mass spectrum outside the indicated region ($m < 168$, $m > 195$) were at noise level. The fraction of $Si_6H_{13}^+$ in the total ion beam at the solid substrate was estimated to be 0.90, which is high enough for deposition purposes, although the ion beam was not mass-selected.

The $Si_6H_{13}^+$ clusters obtained under the same conditions as in Fig. 3 were deposited on Si(111) substrates with a deposition energy of 18 eV. The deposition energy of 18 eV

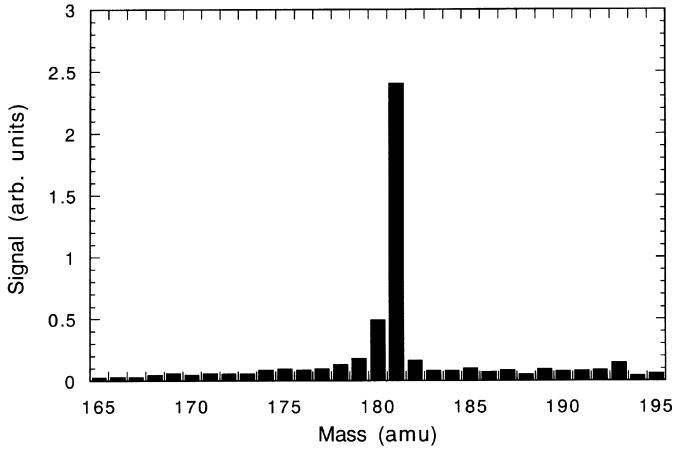

Fig. 3. Mass spectrum of $Si_6H_x^+$ clusters. The data were obtained under the conditions where the trap parameters were tuned for $Si_6H_{13}^+$ ions.

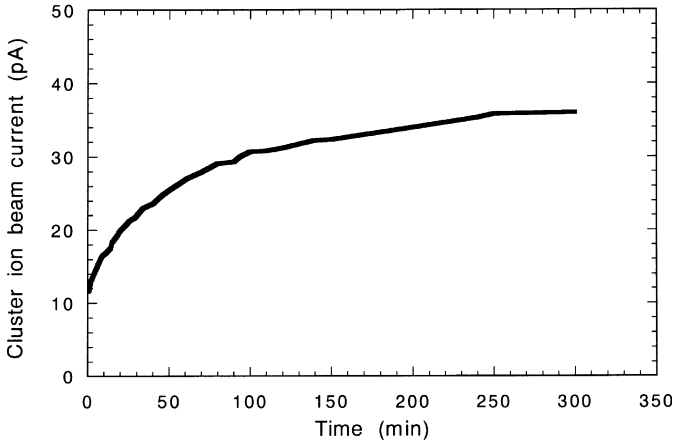

Fig. 4. Time dependence of $Si_6H_{13}^+$ ion beam current measured at the substrate position.

is expected to result in nondestructive landing of the clusters on the surface. The effect of deposition energy was examined for metal clusters [14], and it is accepted that the deposition is nondestructive with the energy of 1 eV/atom or less. The deposition energy of 18 eV corresponding to 3 eV/Si atom for $Si_6H_{13}^+$ was selected, since the $Si_6H_{13}^+$ cluster consists of stable sp^3 bonding and is expected to be more stable than metal clusters.

Figure 4 shows the obtained ion beam current, as a function of time, lasting for five hours. The current was 11 pA when the deposition started, and gradually increased to saturation current around 36 pA. The total amount deposited on the substrate was 3.5×10^{12} clusters, if the sticking coefficient was 1.0. The beam shape was observed by the multichannel plate with a phosphorescent screen, which was set behind the sample substrate, showing that the beam spot was an ellipse with 3 mm and 5 mm diameters. Accordingly, the deposited area on the sample surface was estimated to be 0.12 cm^2 or less, because the beam was focused on the sample surface. Thus, the cluster density deposited with the run shown in Fig. 4 was estimated to be higher than 3.0×10^{13} clusters/cm^2. This corresponds to a density higher than 1.9 clusters/(7×7) unit cell of Si(111) surfaces [15], which is sufficient for STM observation.

4 Summary

We have examined characteristics of $Si_nH_x^+$ cluster ion beams obtained from the ion trap for deposition on solid surfaces. The clusters were grown from SiH_4 gas in a low-pressure gas phase in the ion trap and were transported to a solid substrate after 90° adjustment by a deflector. The mass spectrum of $Si_nH_x^+$ $(n = 4-10)$ was measured by a mass spectrometer at a position corresponding to the sample substrate, and several peaks were observed. The highest peak was always for $Si_6H_{13}^+$, with a ring structure consisting of the bulk-like sp^3 bonding. The $Si_6H_{13}^+$ clusters were selected and deposited on Si(111) with a deposition energy of 18 eV, and the deposition current was more than 30 pA.

We thank T. Miyazaki for fruitful discussions. This work, partly supported by NEDO, was performed in the JRCAT under the joint research agreement between the National Institute for Advanced Interdisciplinary Research (NAIR) and the Angstrom Technology Partnership (ATP).

References

1. A.P. Alivisatos: Science **271**, 933 (1996)
2. K. Raghavachari, V. Logovinsky: Phys. Rev. Lett. **55**, 2853 (1985)
3. E.C. Honea, A. Ogura, C.A. Murray, K. Raghavachari, W.O. Sprenger, M.F. Jarrold, W.L. Brown: Nature **366**, 42 (1993)
4. M.F. Jarrold: Science **252**, 1085 (1991)
5. H. Murakami, T. Kanayama: Appl. Phys. Lett. **67**, 2341 (1995)
6. M.O. Watanabe, N. Kawashima, T. Kanayama: J. Phys. D **31**, L21 (1998)
7. M.O. Watanabe, T. Kanayama: Appl. Phys. A **66**, S1039 (1998)
8. T. Kanayama: Jpn. J. Appl. Phys. **33**, L1792 (1994)
9. H.D. Zeman: Rev. Sci. Instrum. **48**, 1079 (1977)
10. T. Kanayama, H. Murakami: J. Vac. Sci. Technol. **15**, 2882 (1997)
11. M.O. Watanabe, H. Murakami, T. Miyazaki, T. Kanayama: Appl. Phys. Lett. **71**, 1207 (1997)
12. T. Miyazaki, I. Stich, T. Uda, K. Terakura: Chem. Phys. Lett. **284**, 12 (1998)
13. T. Miyazaki, T. Uda, I. Stich, K. Terakura: Chem. Phys. Lett. **261**, 346 (1996)
14. K. Bromann, C. Felix, H. Brune, W. Harbich, R. Monot, J. Buttet, K. Kern: Science **274**, 956 (1996)
15. K. Takayanagi, Y. Tanishiro, M. Takahashi, S. Takahashi: J. Vac. Sci. Technol. A **3**, 1502 (1985)