

# FT-ICR Study of Chemical Reaction of Silicon Clusters<sup>\*</sup>

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## Abstract

Chemical reaction of small silicon cluster ions  $\text{Si}_n^+$  ( $11 \leq n \leq 20$ ) with ethylene was studied with a newly implemented Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. Silicon clusters were generated by a pulsed laser-vaporization supersonic-expansion cluster beam source directly connected to FT-ICR spectrometer. Injected and size selected silicon clusters were thermalized to the room temperature by collisions with argon gas. The exposure time of ethylene gas before the mass detection was varied in order to study the reaction kinetics. The reaction rate of chemisorption of first ethylene molecule was generally in good agreement with the ion drift tube experiments. Effect of a hydrogen atom hidden in isotope distribution of mass spectra was clearly determined. Furthermore, the saturated reaction products were summarized.  $\text{Si}_n(\text{C}_2\text{H}_4)_m^+$  when  $n + m = 19$  were observed to be remarkably stable. Furthermore, it was found that a hydrogen atom terminated the reaction as an ethylene molecule.

**Key Words:** Silicon Cluster, Chemical Reaction, Ethylene, FT-ICR, Mass Spectroscopy

## Nomenclature

$I$	=	abundance of cluster ions
$I_0$	=	initial abundance of cluster ions
$k$	=	reaction rate constant
$m$	=	number of ethylene molecules
$n$	=	number of atoms in a silicon cluster
$p$	=	fraction of more reactive isomer
$t$	=	reaction time

## 1 Introduction

The understandings of silicon surface reaction are crucial for the thin-film technology such as the CVD deposition process using silane ( $\text{SiH}_4$ ) as the starting material. Since most of chemical reagent is not attacking the perfect (111)-(7×7) surface during the deposition process, the adequate modeling of chemical reaction for atomically irregular surface is demanded. Here, silicon clusters are best material to compare the theoretical modeling with experimental results. Furthermore, silicon clusters formed in the gas phase before deposition in CVD process are suggested to have essential

effect on the quality of the thin film product.

On the other hand, silicon clusters have been extensively studied in order to understand how the properties of a bulk material change as atomic dimensions are approached. It is well known that such efforts for carbon clusters lead to the discovery of fullerene and nanotube [1]. Geometrical and electronic structures of very small silicon clusters with less than 8 atoms have been well understood by recent progress in theoretical [2,3] and experimental studies [4,5]. Difficulty in *ab initio* calculations increased exponentially for larger clusters with increase in complexity of electronic structure and geometrical configurations that need to be considered. Hence, most of *ab initio* or density functional calculations have been tried for the geometric configurations based on physical insight [2]. Simulated annealing technique [3] or genetic algorithm [6] with Car-Parrinello molecular dynamics with LDA approximation, tight-binding molecular dynamics or classical molecular dynamics have been tried, as well. Experimentally, the practical preparation of size-selected clusters larger than 8 atoms has been possible with the laser-vaporization cluster beam source. Smalley and co-workers have probed chemical reaction with ammo-

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nia [7,8], ethylene [9,10], and trimethylamine [11] with the Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. On the other hand, Jarrold [12] and co-workers have extensively studied chemical reaction with ethylene [13,14], O<sub>2</sub> [15], water [16], and ammonia [17,18] using the ion drift tube apparatus. They also measured the mobility of clusters and distinguished some geometric isomers [19-23]. There has been a serious controversy between results of these 2 groups. From FT-ICR reaction experiments with ammonia and ethylene, Si<sub>33</sub>, Si<sub>39</sub>, and Si<sub>45</sub> were demonstrated to be unreactive. However, ion drift tube experiments showed completely no specialty in these cluster sizes. In spite of many efforts to explain this controversy such as laser annealing [10] and collision induced annealing experiments [12], it is still unclear.

In this paper, we have implemented a new FT-ICR spectrometer with direct injection cluster beam source similar to Smalley's group. Since most of experiments with FT-ICR concentrated on silicon clusters larger than 30, here, measurements of smaller size range Si<sub>n</sub><sup>+</sup> (11 ≤ n ≤ 20) to ethylene were performed for the direct comparison with ion drift tube experiments. Furthermore, new experimental information such as saturated products after long enough reaction time is discussed.

## 2 Experimental Apparatus and Procedure

The experimental apparatus implemented are similar to Smalley's group [9-11, 24] and the detailed characteristics are described in elsewhere [25-27]. Fig. 1 and Fig. 2 show the cluster beams source and direct injection FT-ICR apparatus, respectively. The silicon cluster beam was generated outside of magnetic field by the laser-vaporization cluster beam source shown in Fig. 1.

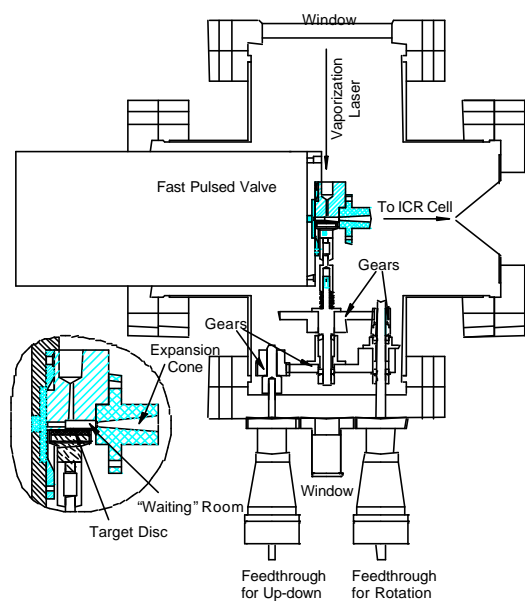


Fig. 1 Laser-vaporization cluster beam source

A pulsed gas valve, the sample motion mechanism and a skimmer were installed in a 6-inch 6-way UHV cross. A solid sample disk was vaporized by the focused beam of Nd: YAG laser (2nd Harmonics) while timed pulsed gas was injected to the nozzle. In the atmosphere of helium gas, vaporized atoms condensed to clusters, and then, were carried and cooled by the supersonic expansion of helium gas. The cluster beam was directly injected to the magnetic field through a skimmer with the opening diameter of 2 mm and a deceleration tube [24].

The FT-ICR is the unique mass spectroscopy based on the ion-cyclotron motion of clusters in a strong magnetic field. In principle, extremely high mass-resolution at high mass-range such as resolution of 1 amu at 10,000 amu range can be obtained. Furthermore, since the ions can be trapped in the vacuum for a few minutes, it is possible to perform the chemical reaction experiments. The ICR cell, 42 mm I.D. 150 mm long cylinder was placed in a stainless tube (SUS316) of 84 mm I.D. which penetrated the homogeneous 5.87 Tesla superconducting magnet commercially available for NMR. Two turbo-pumps (300 ℓ/s) fore-pumped by a smaller turbo-pump of 50 ℓ/s were placed at the floor in order to avoid the effect of strong magnetic field. The typical background pressure was 3 × 10<sup>-10</sup> Torr.

The typical experimental procedure was as follows:

- Cluster beam was injected in 10 Hz for 10 s to the ICR cell. Size range of cluster ions was roughly selected by the deceleration voltage [24] as shown in Fig. 3.
- The kinetic energy of clusters was thermalized with room temperature argon gas. This procedure was skipped for present study.
- Unwanted clusters were over-excited and excluded from ICR cell by SWIFT (Stored Waveform Inverse Fourier Transform) excitation [8, 28].
- Remaining clusters were thermalized with room temperature argon gas at 10<sup>-5</sup> Torr for 10 s.
- Ethylene gas with typically 10<sup>-5</sup> Torr was injected to the cell by 10 Hz pulsed valve for predetermined

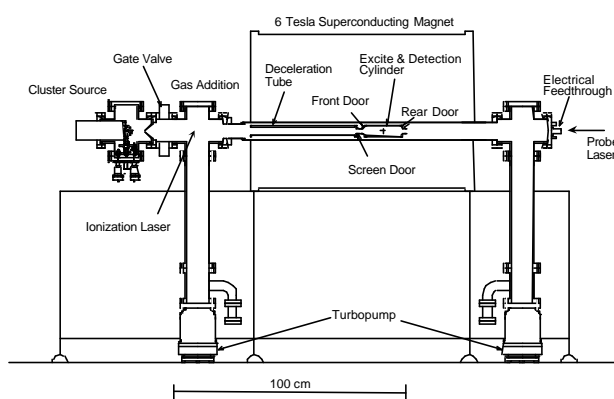


Fig. 2 FT-ICR apparatus with direct injection cluster beam source

reaction time period.

- After pumping out for about 8 to 10 s, cluster ions were excited to detect the mass distribution.

### 3 Experimental Results

#### 3.1 Generated Silicon Clusters and Contamination

Fig. 3 shows typical silicon cluster ion mass spectrum. It should be noticed that clusters entering the ICR cell was restricted to the mass range by the pulsed-voltage deceleration technique. No special size distribution such as well known in carbon clusters [1] was observed. There were only a little bit contamination signals in between pure silicon clusters. More detailed view is shown in Fig. 4. Apparent contaminants for “clean” condition (expanded view of Fig. 3) were hydrogen, carbon and oxygen atoms. The small amount of carbon contamination was due to the carbon cluster experiments performed previously. A spectrum measured with “dirty” cluster source condition is compared with the calculated isotope distribution based on the natural abundance of silicon isotopes with fitted percentage of contaminants in Table 1. It seems that water molecules sticking in helium carrier gas line and sample surface caused all contamination except for carbon. The relative variation of peak height seen in Fig. 3 can also roughly explained by the reactivity with water measured by ion drift tube (18, 20 is reactive and 19 is unreactive). It seems that water molecules were dissociatively chemisorbed on silicon clusters. Here, the worst contaminants were H and H<sub>2</sub>, because they could not be distinguished in most of ion mass detectors in practical experimental conditions. Even with FT-ICR experiments, careful and painful examinations were necessary.

#### 3.2 Chemical Reaction Kinetics

Fig. 5(a) shows the FT-ICR mass spectrum of the injected and trapped clusters. In order to observe the chemisorption reaction product on a clean baseline, all clusters except for Si<sub>17</sub><sup>+</sup> were excited away from the

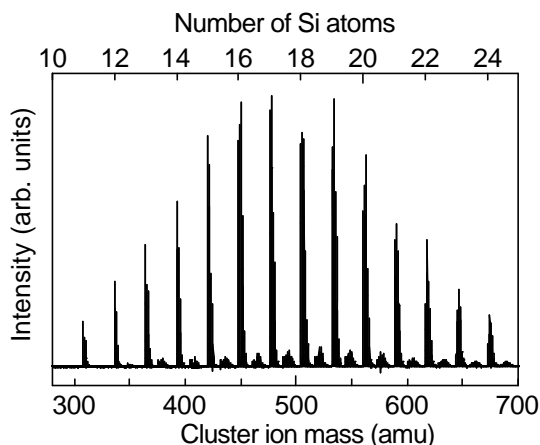


Fig. 3 Silicon cluster mass spectrum as injected.

ICR cell by the selective RF excitation called “SWIFT” technique [8,28]. It was especially crucial for reaction of ethylene that has the same mass as silicon atom. Clusters were well thermalized to the room temperature by exposures to argon at a pressure of at  $1 \times 10^{-5}$  Torr for 10 seconds (about 2000 collisions) after SWIFT. Fig. 5(b) shows the mass spectrum measured after this mass selection. Fig. 5(c) shows the results of exposure of Si<sub>17</sub><sup>+</sup> to ethylene at  $1 \times 10^{-5}$  Torr for 0.2 seconds. Successive chemisorption of ethylene molecules were observed. Even though most of Si<sub>17</sub><sup>+</sup> chemisorbed one or two ethylene already at 0.2 s, some Si<sub>17</sub><sup>+</sup> still remained un-reacted for 5 s. The existence of small amount of less reactive isomer will be discussed.

For the chemisorption of first ethylene molecule, reaction kinetics was explored for Si<sub>n</sub><sup>+</sup> ( $11 \leq n \leq 20$ ) by changing the reaction time. The pseudo-first-order kinetics of the reaction is expressed as

$$\ln(I/I_0) = -k[C_2H_4]t, \tag{1}$$

assuming that number density of Si cluster is much smaller than that of ethylene,  $[Si_n^+] \ll [C_2H_4]$ . Here,  $I_0$  and  $I$  are initial and final abundance of Si<sub>n</sub><sup>+</sup> in a reaction for time  $t$ , respectively. Here,  $I_0$  was summation of parent and all product signals. An example of the log-normal plot of  $\ln(I/I_0)$  versus time for Si<sub>17</sub> is

Table 1 Estimated percentage of contaminants

	H	H <sub>2</sub>	C	O	H <sub>2</sub> O	H <sub>2</sub> O <sub>2</sub>	2(H <sub>2</sub> O)
Si <sub>16</sub>	12	0	8	7	15	5	3
Si <sub>17</sub>	16	0	10	7	15	5	3
Si <sub>18</sub>	12	15	8	10	15	4	2
Si <sub>19</sub>	25	15	7	8	5	3	1

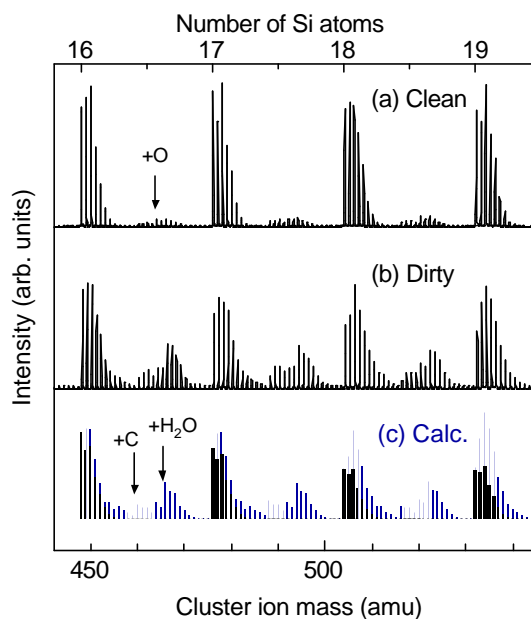
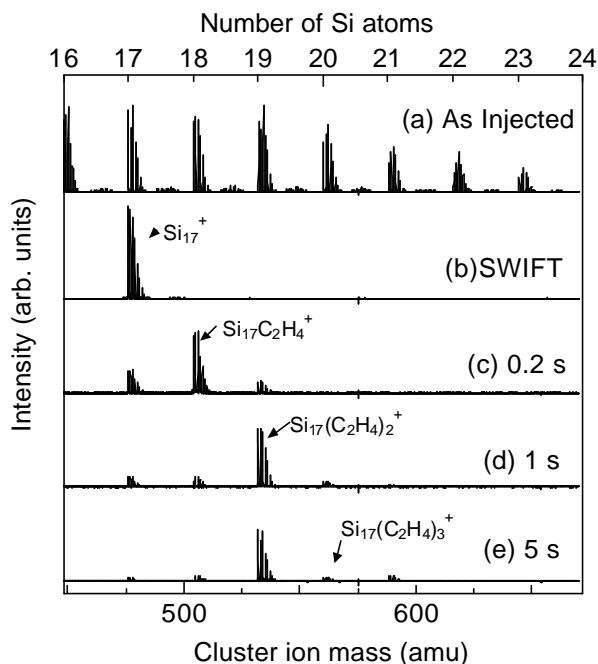


Fig. 4 Contamination with H<sub>2</sub>O, C, O, and H. A slightly thicker line in (c) represents pure silicon isotopes.


 Fig. 5 FT-ICR spectra of reaction of  $\text{Si}_{17}^+$  with ethylene.

plotted in Fig. 6. Except for  $\text{Si}_{14}^+$ , all clusters investigated did not follow this pseudo-first-order kinetics. As demonstrated by Jarrold *et al.* [14], this trend strongly suggests the existence of structural isomers. Then, assuming that there are two isomers with different reaction rate,  $k_1$  and  $k_2$ , the kinetics of reaction can be rewritten as

$$I/I_0 = p \cdot \exp(-k_1 \cdot t) + (1-p) \cdot \exp(-k_2 \cdot t) \quad (2)$$

where  $p$  denotes the fraction of isomer with rate constant  $k_1$ . In Fig. 6, the solid line represents a fitted curve with equation (2). From these fittings, the reaction rate  $k_1$ ,  $k_2$  and the fraction  $p$  were estimated. The size dependence of average reaction rate  $k = pk_1 + (1-p)k_2$  is plotted in Fig. 7 in comparison with ion drift tube experiments [13,14]. The over-all trend in dependence of the rate constant  $k$  on cluster size was in good agreement to Jarrold's ion drift tube experiments. It seems that the remarkable discrepancies of experimental results between ion drift tube experiments by Jarrold *et al.* and FT-ICR experiments of Smalley's group was not realized in this size range. In general, present experimental results showed less abundance of less-reactive isomers compared to Jarrold's experiments. Apparently,  $\text{Si}_n^+$  ( $n = 11, 18, 19$ ) did not show the first-order-kinetics in contrast to Jarrold's. However, the effect of contamination by hydrogen atom was revealed for these clusters. Actually the less reactive part of these clusters was all hydrogen contaminated clusters not structural isomers as shown in Fig. 8. Since contamination with only 1 or 2 hydrogen atoms is usually not discriminated by practical mass spectroscopy for cluster beams, it is a crucial warning. Small

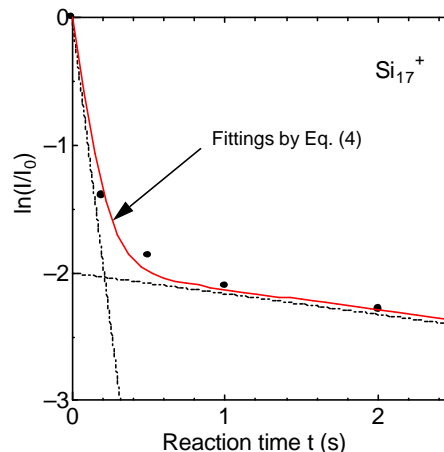
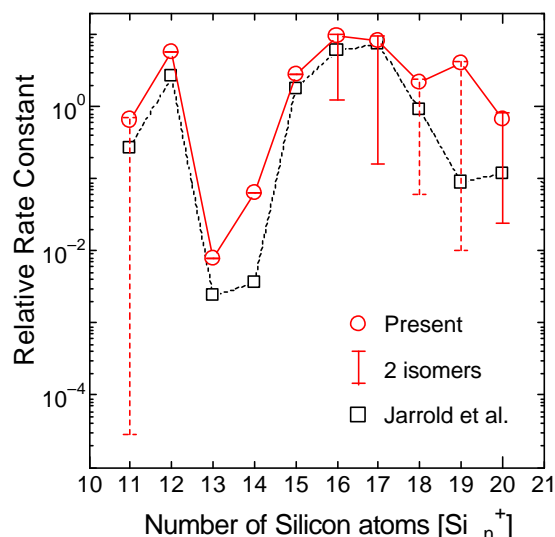

 Fig. 6 Example of Reaction kinetics for  $\text{Si}_{17}^+$ .


Fig. 7 Rate constant of first ethylene chemisorption.

cluster beams, it is a crucial warning. Small difference of reactivity observed for  $\text{Si}_{19}$  might be also due to the hydrogen contamination, since the contamination was severe only for  $\text{Si}_{19}$  experiments.

### 3.3 Saturated Reaction Products

As shown in Fig. 5(d) and 5(e), the product distribution became almost the same after some time of reaction process. These saturated product distributions were summarized for all cluster size in Fig. 8. Usually the saturation of reaction is regarded as the equilibrium of forward and backward reactions for certain pressure and temperature. This possibility was not likely from pressure-dependence experiments [14] except for  $\text{Si}_{14}$ . More direct experimental prove is shown in Fig. 9. Here, after finishing the saturated condition by 15 s reaction in Fig. 9(c) (compare with Fig. 8(e)), only  $\text{Si}_{15}(\text{C}_2\text{H}_4)_4$  was further selected by second SWIFT technique (Fig. 9(d)). As shown in Fig. 9(e) further exposure to ethylene for 10 s resulted no further reaction or dissociation toward equilibrium. The same result was obtained for

$\text{Si}_{15}(\text{C}_2\text{H}_4)$ . This means that final saturated products such as  $\text{Si}_{15}(\text{C}_2\text{H}_4)$  and  $\text{Si}_{15}(\text{C}_2\text{H}_4)_4$  were distinctive unreactive clusters either from different isomers of  $\text{Si}_{15}$  or isomerization [28] due to the chemisorption of ethylene molecules.

A remarkable special stability of  $\text{Si}_n(\text{C}_2\text{H}_4)_m^+$  when  $n + m = 19$  is clearly shown in Fig. 8. This means that  $\text{Si}_n$  easily accepts up to  $m$  ethylene but hates to accept more than  $m$ . Some less prominent stable structure is observed for  $n + m = 16, 17, 21$ . Here,  $\text{Si}_{19}$  and  $\text{Si}_{21}$  were reported to be less reactive magic numbers toward ammonia [8] and water [16], respectively. However, interestingly enough  $\text{Si}_{19}$  itself was not less reactive at all as shown in Fig. 7 in our experiment.

It is still not clear how ethylene molecule chemisorbed in silicon clusters. Jarrold *et al.* [13] suggested strong  $\pi$  bonding through measured binding energy of first ethylene chemisorption to  $\text{Si}_4$  through  $\text{Si}_{10}$ : varying between 0.8 eV to 2.0 eV. On the other hand, a recent theoretical work suggested a di- $\sigma$  bonding for  $\text{Si}_5$  [28]. Anyway, the clear structure observed in the saturated condition should help to further determine the geometrical structure of silicon clusters.

Finally, the effect of hydrogen contamination turned out to be very important information of reaction mechanism. Clusters marked in circle in Fig. 8 had almost 100 % hydrogen atom, i.e.,  $\text{Si}_{11}\text{H}^+$ ,  $\text{Si}_{14}\text{H}(\text{C}_2\text{H}_4)_2^+$ , ... This means that those clusters with hydrogen were selectively left over the reaction process and that a hydrogen blocked the chemisorption of ethylene molecule. It is also clearly shown that  $\text{Si}_n\text{H}(\text{C}_2\text{H}_4)_m^+$  for  $n + m = 16$  are stable. It can be regarded that a hydrogen atom can work as well as ethylene to saturate the reaction. The effect of a hydrogen atom for  $\text{Si}_{11}^+$  was more dramatic.  $\text{Si}_{11}\text{H}^+$  did not react at all where most of  $\text{Si}_{11}^+$  accepted 5 ethylene molecules.

#### 4 Conclusions

FT-ICR apparatus with direct injection cluster beam source was implemented for the chemical reaction experiments of silicon clusters, and chemical reaction of small silicon cluster ions  $\text{Si}_n^+$  ( $11 \leq n \leq 20$ ) with ethylene was measured with FT-ICR. The overall size dependence of reaction rate coincided with ion drift tube experiments. Furthermore, the saturated reaction products were presented for the future theoretical studies of medium sized silicon clusters.  $\text{Si}_n(\text{C}_2\text{H}_4)_m^+$  where  $n + m = 19$  were observed to be remarkably stable. Furthermore, it was found that a hydrogen atom terminated the reaction as an ethylene molecule.

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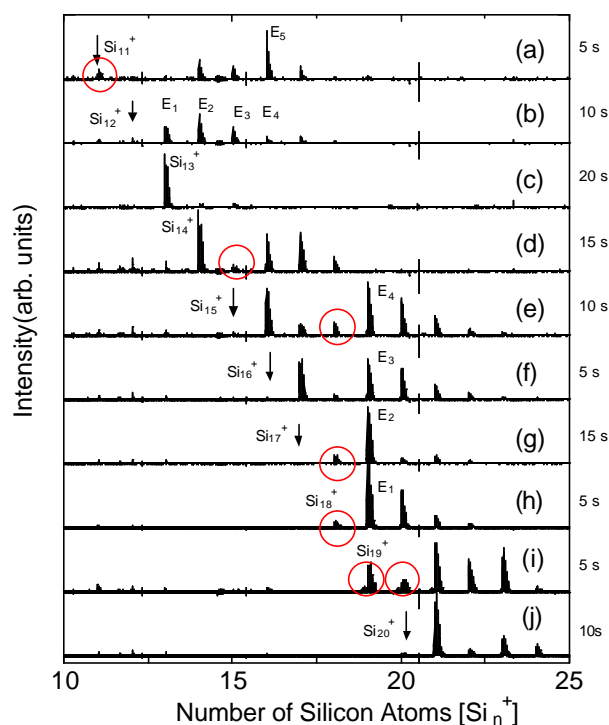


Fig. 8 Saturated reaction products.

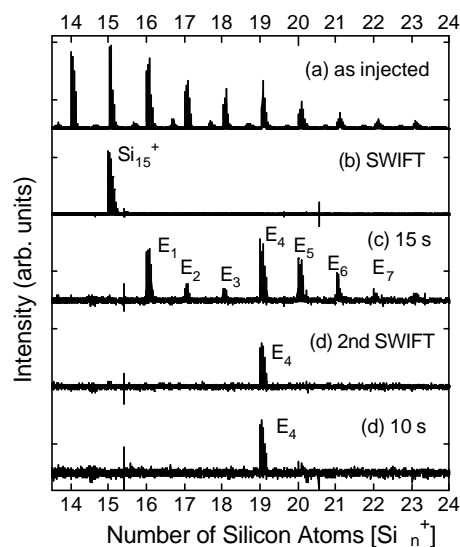


Fig. 9 Further reaction of selected once reacted product.

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#### References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, "C<sub>60</sub>: Buckminsterfullerene," *Nature*, 318-14 (1985), 162-163.
- [2] K. Raghavachari and C. M. Rohlfing, "Bonding and Stabilities of Small Silicon Clusters: A Theoretical Study of Si<sub>7</sub>-Si<sub>10</sub>," *J. Chem. Phys.*, 89-4 (1988), 2219-2234.

- [3] M. Ramakrishna and A. Bahel, "Combined Tight-Binding and Density Functional Molecular Dynamics Investigation of Si<sub>12</sub> Cluster Structure," *J. Chem. Phys.*, 104 (1996), 9833-9840.
- [4] E. C. Honea, A. Ogura, D. R. Peale, C. Felix, C. A. Murray, K. Raghavachari, W. O. Sprenger, M. F. Jarrold, and W. L. Brown, "Structures and Coalescence Behavior of Size-Selected Silicon Nano-Clusters Studied by Surface-Plasmon-Polariton Enhanced Raman Spectroscopy," *J. Chem. Phys.*, 110-24 (1999), 12161-12172.
- [5] S. Li, R. J. Van Zee, W. Weltner, Jr, and K. Raghavachari, "Si<sub>3</sub> - Si<sub>7</sub>. Experimental and theoretical Infrared Spectra," *Chem. Phys. Lett.*, 243 (1995), 275-280.
- [6] K-M. Ho, A. A. Shvartsburg, B. Pan, Z-Y. Lu, C-Z. Wang, J. G. Wacker, J. L. Fye, and M. F. Jarrold, "Structure of Medium-Sized Silicon Clusters," *Nature*, 392-9 (1998), 582-585.
- [7] J. L. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley, "FT-ICR Probes of Silicon Cluster Chemistry: The Special Behaviors of Si<sub>39</sub><sup>+</sup>," *J. Chem. Phys.*, 87-4 (1987), 2397-2399.
- [8] J. M. Alford, R. T. Laaksonen, and R. E. Smalley, "Ammonia Chemisorption Studies on Silicon Cluster Ions," *J. Chem. Phys.*, 94-4 (1991), 2618-2630.
- [9] L. R. Anderson, S. Maruyama and R. E. Smalley, "Ethylene Chemisorption on Levitated Silicon Cluster Ions: Evidence for the Importance of Annealing," *Chem. Phys. Lett.*, 176-3,4 (1991), 348-354.
- [10] S. Maruyama, L. R. Anderson and R. E. Smalley, "Laser Annealing of Silicon Clusters," *J. Chem. Phys.*, 93-7 (1990), 5349-5351.
- [11] S. Maruyama, L. R. Anderson and R. E. Smalley, "Laser Annealing of Semiconductor Clusters: Trimethylamine Reactions with Positive and Negative Clusters," *Mat. Res. Soc. Symp. Proc.*, 206 (1991), 63-70.
- [12] M. F. Jarrold, "Silicon Cluster Ions," *Cluster Ions*, Ed. C. Y. Ng, T. Bear and I. Powis, John Wiley & Sons (1993), 165-215.
- [13] M. F. Jarrold, J. E. Bower, and K. Creegan, "Chemistry of Semiconductor clusters: A Study of the Reactions of Size Selected Si<sub>n</sub><sup>+</sup> (n = 3-24) with C<sub>2</sub>H<sub>4</sub> Using Selected Ion Drift Tube Techniques," *J. Chem. Phys.*, 90-1 (1989), 3615-3628.
- [14] K. M. Creegan and M. F. Jarrold, "Chemistry of Semiconductor Clusters: Reactions of Si<sub>n</sub><sup>+</sup> (n = 11-50) with C<sub>2</sub>H<sub>4</sub> Show Evidence for Numerous Structural Isomers," *J. Am. Chem. Soc.*, 112 (1990), 3768-3773.
- [15] M. F. Jarrold, U. Ray, and K. M. Creegan, "Chemistry of Semiconductor Clusters: Large Silicon Clusters Are Much Less Reactive Towards Oxygen than the Bulk," *J. Chem. Phys.*, 93-1 (1990), 224-229.
- [16] U. Ray and M. F. Jarrold, "Reactions of Silicon Cluster Ions, Si<sub>n</sub><sup>+</sup> (n = 10-65), with Water," *J. Chem. Phys.*, 94-4 (1991), 2631-2639.
- [17] U. Ray and M. F. Jarrold, "Interaction of Silicon Cluster Ions with Ammonia: The kinetics," *J. Chem. Phys.*, 93-8 (1990), 5709-5718.
- [18] M. F. Jarrold, Y. Ijira, and U. Ray, "Interaction of Silicon Cluster Ions with Ammonia: Annealing, Equilibria, High Temperature Kinetics, and Saturation Studies," *J. Chem. Phys.*, 94-5 (1991), 3607-3618.
- [19] M. F. Jarrold and V. A. Constant, "Silicon Cluster Ions: Evidence for a Structural Transition," *Phys. Rev. Lett.*, 67-21 (1991), 2994-2997.
- [20] M. F. Jarrold and J. E. Bower, "Mobilities of Silicon Cluster Ions: The Reactivity of Silicon Sausages and Spheres," *J. Chem. Phys.*, 96-12 (1992), 9180-9190.
- [21] M. F. Jarrold and E. C. Honea, "Dissociation of Large Silicon Clusters: The Approach to Bulk Behavior," *J. Phys. Chem.*, 95 (1991), 9181-9185.
- [22] K-M. Ho, A. A. Shvartsburg, B. Pan, Z-Y. Lu, C-Z. Wang, J. G. Wacker, J. L. Fye, and M. F. Jarrold, "Structure of Medium-Sized Silicon Clusters," *Nature*, 392-9 (1998), 582-585
- [23] R. R. Hudgins, M. Imai, M. F. Jarrold, and P. Dugourd, "High-Resolution Ion Mobility Measurements for Silicon Cluster Anions and Cations," *J. Chem. Phys.*, 111-17 (1999), 7865-7870.
- [24] S. Maruyama, L. R. Anderson and R. E. Smalley, "Direct Injection Supersonic Cluster Beam Source for FT-ICR Studies of Clusters," *Rev. Sci. Instrum.*, 61-12 (1990), 3686-3693.
- [25] S. Maruyama, T. Yoshida, and M. Kohno, "FT-ICR Studies of Laser Desorbed Carbon Clusters," *Trans. JSME*, B65-639 (1999), 3791-3798.
- [26] S. Maruyama, T. Yoshida, M. Kohno and M. Inoue, "FT-ICR Studies of Laser Desorbed Carbon Clusters," *5th ASME/JSME Thermal Eng. Conf.*, San Diego, AJTE99-6513 (1999).
- [27] S. Maruyama, H. Kinbara, H. Hayashi, and D. Kimura, "Photo-Ionized TOF Mass Spectrometry of Atomic Clusters," *Micro. Thermophys. Eng.*, 1-1 (1997), 39-46.
- [28] A. G. Marshall and F. R. Verdun, *Fourier Transforms in NMR, Optical, and Mass Spectrometry*, Elsevier, Amsterdam (1990).
- [29] M. Qiu, M. Jiang, Y-J. Zhao, and P-L. Cao, "Reconstruction of Small Si Cluster after Ethylene Adsorption: A Full Potential Linear Muffin Tin Orbital Molecular Dynamics Study," *J. Chem. Phys.*, 110-22 (1999), 10738-10745.