Laser annealing of silicon clusters

S. Maruyama,[a] L. R. Anderson, and R. E. Smalley
Rice Quantum Institute and Departments of Chemistry and Physics, Rice University, Houston, Texas 77251

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Three years ago in an earlier communication from this laboratory[1] evidence was presented that certain clusters of silicon were special. In particular the positively charged clusters of silicon with 21, 25, 33, 39, and 45 atoms were found to be relatively unreactive toward chemisorption of ammonia, while clusters with only one atom more or less reacted rapidly. This striking observation led to the suggestion that silicon clusters in this size range may adopt special geometrical forms, and a considerable amount of activity has since resulted amongst theorists in considering just what these special forms may be.[2–8] This is a matter of substantial importance since structure is a critical aspect of chemistry. If small clusters of such elements as silicon are to be useful as a model of the surface chemistry of the bulk, it will be necessary to find a reliable way to anneal them to a well-defined structure. We report here evidence that such annealing is possible through the use of laser excitation of the clusters levitated in the magnetic field of a Fourier transform ion cycltron resonance (FT-ICR) spectrometer.

Figure 1 gives an example of the critical data for this experiment. The top panel displays the FT-ICR mass spectrum of silicon clusters in the 36–53 atom size range as injected from a laser vaporization supersonic cluster beam source. This source and the associated cluster FT-ICR apparatus were of a greatly simplified design in comparison with earlier ICR experiments with silicon clusters from this group.[1,9,10] Extensive discussion of this new apparatus can be found elsewhere.[11,12] The principle difference from earlier designs was that the entire supersonic cluster beam was directly injected into the ICR trap. By adjusting the amplitude and timing of a deceleration pulse during the injection, the desired mass range was trapped in the analyzer cell. For the top panel of Fig. 1, the injection process was repeated for 100 successive cluster beam pulses at a rate of 10 Hz in order to adequately fill the ICR trap. The trapped clusters were then thermalized for 3 seconds by collisions with argon at 2×10^{-5} Torr (roughly 2000 collisions) followed by an additional 10 second waiting period while the system was pumped down to less than 10^{-7} Torr prior to exciting the ICR transient.

To prepare the cluster sample for reaction studies it was necessary to sweep all but every third cluster from the cell so that the chemisorption reaction products could be observed on a clean baseline. The second panel of Fig. 1(b) shows the silicon cluster distribution in the ICR trap after selective RF excitation was used to sweep these selected clusters out of the trap—a technique often referred to by the acronym "SWIFT," which involves the calculation of the inverse Fourier transform of the desired RF excitation and the use of a fast digital to analog converter to place this computed wave form on the excitation plates of the ICR cell.[9–12] In this case the SWIFT excitation was followed by a second 2000 collision thermalization period with argon to insure the clusters were at the 300 K temperature of the ICR trap walls. Note that the SWIFT excitation was chosen such that different isotopic widths were left for each cluster size remaining in the ICR trap. This provides a convenient means of sorting out reaction products of the various clusters when they fall in the same mass range.

The third panel of Fig. 1(c) shows the result of exposure of these selected clusters to ethylene at 1×10^{-5} Torr for 20 seconds—sufficient time for the typical silicon cluster ion to undergo roughly 5000 collisions. Note that the isotopic width does serve as a nice tracer of the parentage of each reaction product. As we have described in another publication,[12] ethylene chemisorption on these silicon clusters is somewhat selective. As seen here in panel (c) Si_{39}^+, Si_{45}^+, and Si_{48}^+ appear a bit less reactive than the other clusters, but it is clear that considerable reaction has occurred even for these "special" clusters. We have shown[12] that much of this reactivity appears to be due to the presence of geometrical isomers which are much more reactive than the dominant isomer of these special clusters, and to a great extent these reactive isomers may be "titrated" away.

However, the bottom panel of Fig. 1(d) now demonstrates a more significant point: these reactive isomers of the special clusters 39, 45, and 48 also turn out to be less stable energetically, and they can be annealed into the unreactive form by laser excitation. The panel shows the result of reaction with ethylene just as in panel (c), except now the cluster had been irradiated with 30 pulses of light from a XeCl excimer laser (photon energy 4.0 eV) at a fluence of 1 mJ cm^{-2} per pulse, and then allowed to cool with an additional 3 second, 2000 collision thermalization period with argon. Note that the reactivity of the clusters with 39, 45, and 48 atoms has been sharply reduced by this laser treatment, while the clusters with 36, 42, and 51 silicon atoms appear to be even more reactive. In fact, careful examination of the isotopic widths of the reaction products near Si_{39}^+ and Si_{45}^+ reveals that the majority of these reaction products are actually the result of multiple chemisorptions on smaller clusters. The annealed forms of the 39 and 45 atom clusters appear to be quite unreactive.

Figure 2 further illustrates this point. In this case all injected ions except 39 and 42 were swept from the cell. The top panel shows the reaction with ethylene after 5000 collisions. Again it is evident that, as injected, both clusters have a considerable fractional population of various reactive structural forms. However, the lower panel reveals that

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[a] RQI Visiting Fellow, Permanent address: Department of Mechanical Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

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there is in fact a tremendous difference in the annealed forms of these two clusters. The annealed Si_{42}^+ remains highly reactive, while the annealed Si_{39}^+ displays no evidence of any reaction at all.

A particularly significant aspect to the top and bottom panels of Figure 2 is that they have the same vertical scale factor. The markedly higher apparent intensity of the unreacted Si_{39}^+ signal in the bottom panel therefore is real: the reactive forms initially present for this cluster size have been efficiently converted into the unreactive form by the laser treatment. It is therefore certain that the dominant effect of the laser treatment is, in fact, annealing.

Figure 3 presents similar results for these clusters with ammonia as a reactant. Again the initial cluster distribution in the ICR trap was selectively ejected, leaving clusters 36, 39, 42, 45, 48, and 51 in the trap with the isotopic distribution as shown in Fig. 1, panel (b). The top panel of Fig. 3 shows the result of exposure of these cluster ions to 1000 collisions with ammonia. Note that our current nozzle conditions produce clusters which initially display only a slight variation in apparent reactivity toward ammonia. Yet the bottom panel shows again clear evidence of laser-induced annealing: Si_{39}^+ and Si_{45}^+ have been rendered far less reactive than any of the other clusters in this region.

Experiments such as these have been carried out over a range of XeCl excimer laser fluences from 0.03 to 1.6 mJ cm^{-2} per pulse, and over a broad range of laser pulse rates (2.5–50 Hz). In all cases the effect on the apparent cluster reactivities was found to be linear in the total fluence, suggesting the process requires absorption of a single 4.0 eV photon per cluster. Assuming the clusters had an internal temperature of 300 K to begin with, and further assuming that radiationless transitions and randomization of the initial laser excitation was fast, the annealing temperature for

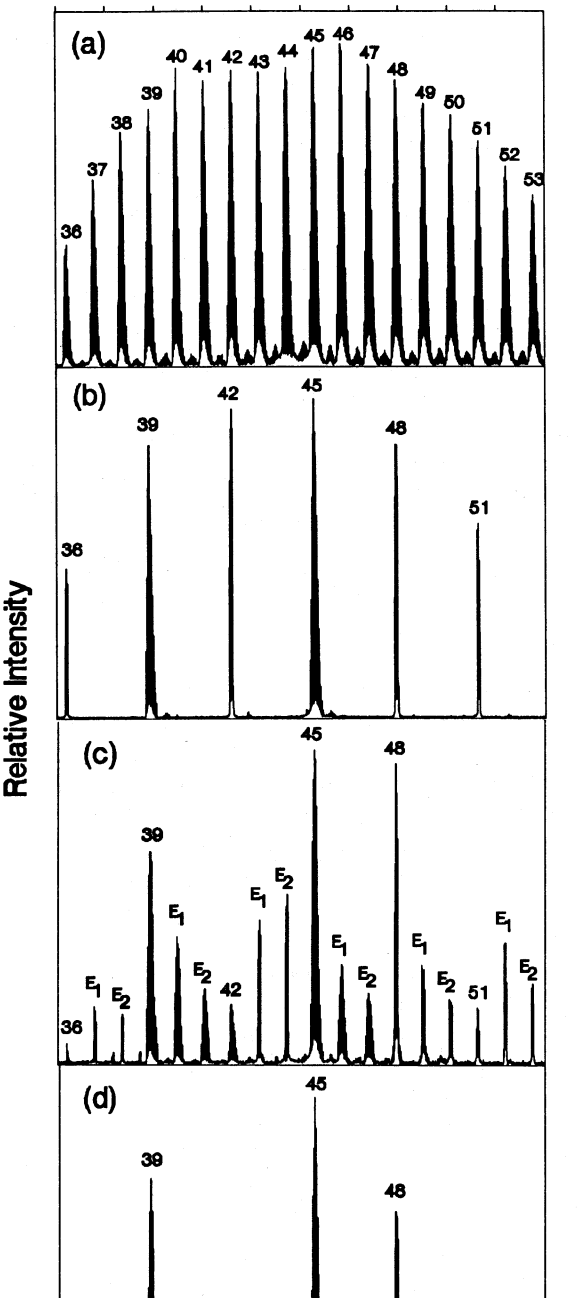

FIG. 1. Laser annealing study of gas phase silicon cluster ions via FT-ICR: Panel (a) shows the original Si_n^+ cluster ion distribution as injected from the laser vaporization supersonic beam source; panel (b) shows this distribution after selective "SWIFT" ejection of some clusters to prepare a clean baseline; panel (c) shows the result of exposure of these clusters to roughly 5000 collisions with ethylene [the $Si_x(C_2H_4)_y^+$ chemisorption products are marked with the symbol E_y.] Panel (d) is the same reaction experiment as Panel (c) except that the clusters were annealed prior to reaction by irradiation with 30 pulses of XeCl excimer laser at 10 Hz at a fluence of 1 mJ cm^{-2} pulse^{-1} followed by a 3 second, 2000 collision thermalization period with argon.

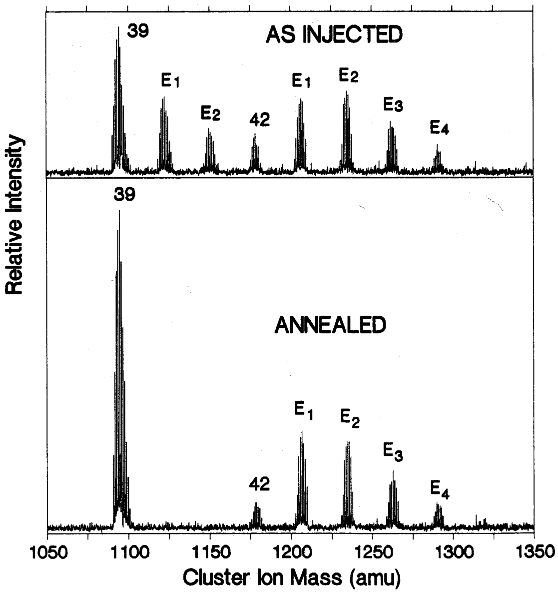

FIG. 2. Ethylene chemisorption study of Si_{39}^+ compared to Si_{42}^+. All other silicon clusters having been selectively ejected from the ICR trap. Top panel: the as-injected clusters after 5000 collisions with ethylene; Bottom panel: the same cluster reaction study performed after annealing with 30 pulses of XeCl excimer laser at 1 mJ cm^{-2}.

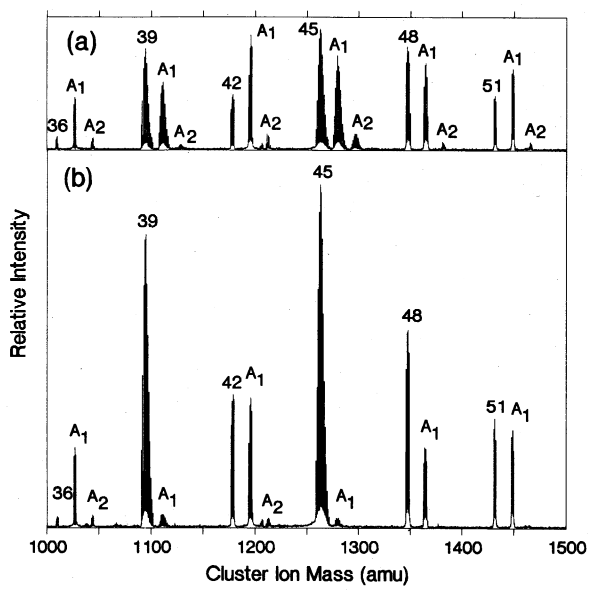

FIG. 3. Ammonia chemisorption experiment similar to Fig. 1. Top panel: the as-injected silicon clusters after 1000 collisions with ammonia; Bottom panel: reaction results on laser annealed clusters. The $Si_x(NH_3)_y^+$ chemisorption products are marked with the symbol A_y.

clusters in this size range appears to have been less than about 600 K. Although at the highest fluences some loss of clusters due to photofragmentation was observed, this fragmentation only slightly favored clusters 39 and 45, (which therefore do appear to be slightly more stable energetically). However, experiments performed at the rather moderate fluence and repetition rate as the data recorded in Figs. 1–3, indicated less than 5% loss due to fragmentation for any cluster.

These dramatic changes in reactivity persist even when the reaction cycle is initiated directly after the excimer laser annealing pulses, without an intervening thermalization process through collisions with argon. The clusters must therefore be able to anneal while cooling radiatively and perhaps also through the first few collisions with the reactant gas over the roughly 1–2 second interval necessary for this reactant gas pressure to build to a steady value.

Such laser annealing experiments provide additional evidence that the non size-selective reactivity behavior of silicon clusters towards ammonia and ethylene reported by Jarrold and co-workers[13–15] is due to inadequate annealing of the clusters produced by their continuous jet source. We have argued that the amount of poorly annealed clusters produced in a source should be sensitive to the temperature conditions in the growth region of the source, and to the relative importance of growth by single atom addition compared to growth by aggregation.[12] It is clear in comparison with earlier work from our laboratory that even with pulsed sources the relative amount of poorly annealed clusters in this 30–60 atom size range can vary substantially as a function of minor variations in the source conditions. Some sort of downstream annealing procedure may always be necessary with these supersonic cluster beam sources if reproducible results are to be obtained with silicon clusters.

To our knowledge this is the first reported example of a successful annealing experiment on gas phase clusters of any kind. This technique offers great promise for the future study of single, well-defined cluster "crystals" of silicon, and gives strong support to the notion that gas phase metal and semiconductor clusters in general may be annealed into single well formed structures.

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[1] J. L. Elkind, J. M. Alford, F. D. Weiss, R. T. Laaksonen, and R. E. Smalley, J. Chem. Phys. **87**, 2397 (1987).

[2] J. C. Phillips, J. Chem. Phys. **88**, 2090 (1988).

[3] D. A. Jelski, Z. C. Wu, and T. F. George, Chem. Phys. Lett. **150**, 447 (1988).

[4] J. R. Chelikowsky and J. C. Phillips, Phys. Rev. B **39**, 5735 (1990).

[5] E. Kaxiras, Chem. Phys. Lett. **163**, 323 (1989).

[6] E. Kaxiras, Phys. Rev. Lett. **64**, 551 (1990).

[7] C. H. Patterson and R. P. Messmer, Phys. Rev. B (in press).

[8] C. H. Patterson and R. P. Messmer, Phys. Rev. Lett. (submitted).

[9] J. M. Alford and R. E. Smalley, Mat. Res. Soc. Symp. Proc. **131**, 3 (1989).

[10] J. M. Alford, R. T. Laaksonen, and R. E. Smalley, J. Chem. Phys. (submitted).

[11] S. Maruyama, L. R. Anderson, and R. E. Smalley, Rev. Sci. Instrum. (in press).

[12] L. R. Anderson, S. Maruyama, and R. E. Smalley, Chem. Phys. Lett. (submitted).

[13] M. F. Jarrold, J. E. Bower, and K. M. Creegan, J. Chem. Phys. **90**, 3615 (1989).

[14] M. F. Jarrold, U. Ray, and K. M. Creegan, J. Chem. Phys. **93**, 224 (1990).

[15] U. Ray and M. F. Jarrold, J. Chem. Phys. (in press).