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Annealing of Silicon Clusters

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Abstract: Cluster growth often occurs by sequential addition of atoms, a process which may not result in the lowest energy geometric structure. In this paper we describe experimental methods that have been developed to anneal the clusters, estimate activation energies for annealing, and estimate the relative stabilities of the isomers. The effects of annealing were investigated using the chemical reactivity of the clusters as a probe. Annealing does not appear to dramatically alter the structure of silicon cluster ions containing up to 50 atoms, but changes the relative abundances of the structural isomers that are present. For some clusters the more reactive isomer is the more thermodynamically stable and its relative abundance increases as these clusters are annealed. This indicates that the chemical reactivity of the silicon clusters is not related to their thermodynamic stability. For the larger clusters studied ($n > 25$) the estimated activation energies for interconversion between the different structural isomers are between 1.0 and 1.5 eV and do not vary systematically with cluster size. It was not possible to anneal most of the clusters to a single structure, suggesting that there are only small differences between the stabilities of the isomers. The stability differences, estimated from the experimental results, are typically ~0.2 eV.

Introduction

Recent studies of the chemical reactions of silicon clusters, Si_n^+ ($n = 10$–50), have shown that at least two structural isomers exist for virtually all cluster sizes.[1] The observation of multiple structural isomers raises several important issues. Cluster growth generally occurs by addition of atoms, and it is possible that this sequential growth sequence does not result in the lowest energy structure. For example, amorphous silicon results from deposition of silicon atoms onto a room temperature substrate. Second, if the clusters are in their lowest energy forms, are there several low-energy geometries? Is it possible to anneal the clusters to a single structural isomer, or is the energy difference between the isomers so small that several different isomers coexist at room temperature?

In order to anneal the clusters it is necessary to heat them up and then cool them down. The clusters may be heated using a laser (as in some recent experiments reported by Smalley and co-workers[2] or by high-energy collisions (as in the work described here). Regardless of the method used to heat the clusters, particular care must be taken to ensure that the clusters are thermalized after the annealing cycle so that any changes in their reactivity can be attributed, unambiguously, to structural changes. We have recently investigated the effects of collisional annealing on the reactivity of silicon clusters with ammonia; annealing the clusters did not influence their reactivity with this reagent.[3] The reactions with ammonia occur at close to the collision rate at room temperature and result in molecular adsorption of ammonia (under our experimental conditions), so these reactions are not expected to be particularly sensitive to cluster structure. In our previous studies of the reactions of silicon cluster ions with oxygen,[4] water,[5] ammonia,[3,6] and ethylene[1,7] we found the reactions with ethylene to be particularly sensitive to the presence of structural isomers. Thus ethylene should be a good reagent to probe whether annealing changes the structure of the clusters.

In the work described in this paper, cluster annealing is accomplished by injecting the cluster ions at high energy into a drift tube where they are rapidly excited by multiple collisions with a buffer gas. After the clusters' kinetic energy is thermalized, they undergo further collisions with the buffer gas which thermalizes their internal energy. Figure 1 illustrates the time dependence of the excitation and subsequent cooling of the clusters. These results were obtained from a simple simulation where we assumed that, on each collision, a constant fraction of the center of mass collision energy is converted into internal energy and that the cooling rate is proportional to the temperature of the cluster. The results, which are not intended to be quantitative, demonstrate the transient heating that occurs when the clusters are injected into the drift tube at high kinetic energies. As suggested by Figure 1, the amount of energy deposited in the cluster can be varied by changing the injection energy. Thus it is possible to estimate the size of the activation energy for annealing. The relative stabilities of the isomers can be estimated from their relative abundances after annealing.

Experimental Methods

A schematic diagram of the experimental apparatus is shown in Figure 2. Silicon cluster ions are generated by pulsed laser vaporization of a silicon rod in a continuous flow of helium buffer gas. The cluster ions are derived from the laser vaporization plasma and undergo $>10^5$ collisions with the buffer gas, so they are expected to be at room temperature when they leave the source. After exiting the source the cluster ions are focussed into a quadrupole mass spectrometer where a particular cluster size is selected. The size-selected clusters are then focussed into an ion beam and injected at various energies into a drift tube. Two different drift tube configurations, shown schematically in Figure 2, were employed in this work. The first (labeled A) is similar to that used in our previous work.[1,3–7] The second (labeled B) is a double drift tube assembly where the buffer gas is admitted into the first stage and the reagent is admitted into the second. The objective of this configuration is to allow the clusters to undergo many thermalizing collisions with the buffer gas in the first section before they pass into the second section and undergo chemical reactions with the reagent diluted in the buffer gas. In order for this configuration to perform as desired, the reagent must be prevented from entering the first section by the buffer gas flow from the first section to the second section, and in addition there must be complete mixing of the reagent gas and buffer gas in the second section. According to the experimental tests we have performed it appears that both these criteria have been satisfied. From experiments in which the reaction times in the two sections were varied (by adjusting the drift voltages), the reagent pressure in the first section was determined to be <1% of the reagent pressure in the second section. Rate constants measured using the two-stage configuration are in good quantitative agreement with those obtained using the single-stage configuration, which indicates that complete mixing of the reagent and buffer gas occurs in the second section.

At the end of the drift tube a small fraction of the product ions and unreacted cluster ions exit through a small aperture and are subsequently mass analyzed by a second quadrupole mass spectrometer. The ions were then detected by an off-axis collision dynode and dual microchannel plates. The reagent gas pressure was directly measured using a capacitance manometer and calibrated to account for the transport of the reagent gas out of the drift tube by the buffer gas flow.[7] For the single stage drift tube, all measurements were performed with neon buffer gas at a pressure of 0.80 Torr. For the two-stage drift tube, the neon buffer gas pressure in the second (reaction) stage was also 0.80 Torr, while the neon pressure in the first stage, though not directly measured, was es-

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(2) Maruyama, S.; Anderson, L. R.; Smalley, R. E. *J. Chem. Phys.* **1990,** *93,* 5349.
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(5) Ray, U.; Jarrold, M. F. *J. Chem. Phys.* **1991,** *94,* 2631.
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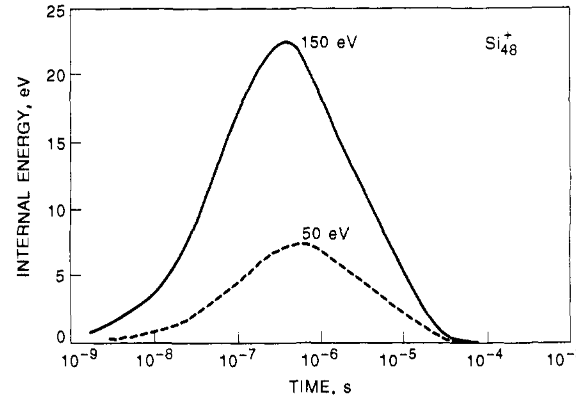

Figure 1. Plot of the internal energy against time for Si_{48}^+ injected into the drift tube at 50 and 150 eV. The results are from a simple simulation described in the text and are not intended to be quantitative.

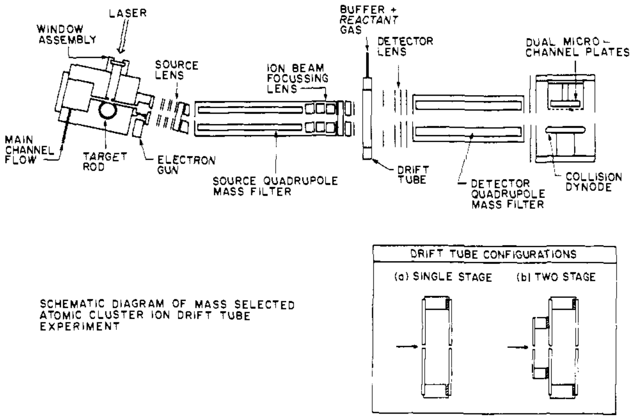

Figure 2. Schematic diagram of the experimental apparatus. The insert shows the two different drift tube configurations used in this work.

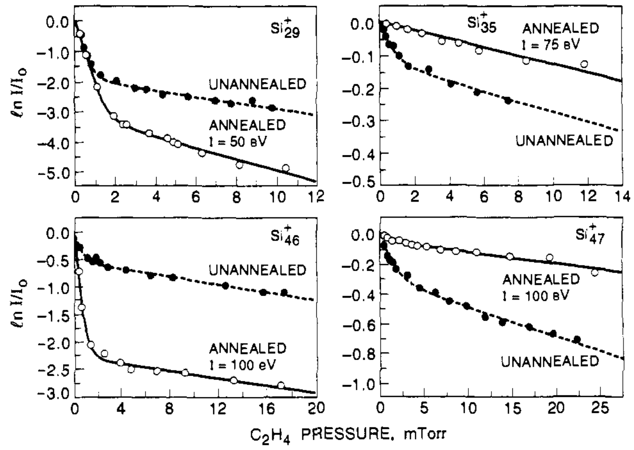

Figure 3. Kinetic data for the reactions of unannealed and annealed silicon cluster ions with C_2H_4. The figure shows a plot of ln (I/I_0) against C_2H_4 pressure in the drift tube for clusters with 29, 35, 46, and 47 atoms. The measurements were performed using a drift field of 1.0 V/cm and a Ne buffer gas pressure of 0.8 Torr. The points are the experimental results and the lines are the result of a simulation to determine the rate constants for the reactive and inert components and the relative abundances of the two components.

timated to be ~2.5 Torr (from the drift velocity, which scales with pressure,[8] and from calculated conductances). The time the clusters spend in the drift tube was determined by allowing a 40-μs pulse of cluster ions to enter the drift tube and measuring the arrival time distribution at the detector using a multichannel analyzer. For the two-stage drift tube these measurements were performed as a function of the drift field in the first section. The drift times in the first and second sections can then be determined from a plot of the total drift time against 1/(drift field in the first section).

Results

Evidence for Isomers. Under the conditions employed chemical reactions in the drift tube are expected to follow pseudo-first-order kinetics with

$$\ln \frac{I}{I_0} = k_r[C_2H_4]t_r \qquad (1)$$

where k_r is the rate constant, $[C_2H_4]$ is the C_2H_4 number density, t_r is the reaction time, and I_0 and I are the initial and final Si_n^+ intensities, respectively. Figure 3 shows kinetic data recorded for the reactions of Si_{29}^+, Si_{35}^+, Si_{46}^+, and Si_{47}^+ with C_2H_4. The only products observed arise from simple adsorption of C_2H_4 onto the clusters to give a range of $Si_n(C_2H_4)_m^+$ species. The figure shows plots of ln (I/I_0) against reagent pressure. According to eq 1, this plot should result in a straight line with a slope proportional to the rate constant for the reaction. The experimental results clearly do not lie on a straight line. There appear to be two components present (different structural isomers[1]) which react at different rates. The lines drawn through the experimental data are the results of simulations assuming that there are two different components present in each case. This two-component model provides an excellent fit to the experimental data for all the clusters studied; however, this is not proof that only two structural isomers are present for each cluster.

Effects of Annealing. Kinetic data are presented in Figure 3 for both annealed and unannealed clusters. The results for the unannealed clusters were obtained with the single-stage drift tube configuration using a low injection energy (5 eV). The results for the annealed clusters were obtained with the two-stage drift tube configuration using injection energies which ranged from 50 (for Si_{29}^+) to 100 eV (for Si_{47}^+). As the clusters are injected into the drift tube at these high injection energies they undergo many collisions with the neon buffer gas and are excited. As discussed in more detail below, we estimate that with an injection energy of 100 eV, ~15 eV is deposited as internal energy into the clusters. After their kinetic energy is thermalized, the clusters undergo a further ~10^4 collisions with the buffer gas before entering the second (reaction) section of the two-stage drift tube. Thus the annealed clusters should have cooled down before they are exposed to the reagent. It is apparent from the results shown in Figure 3 that annealing the clusters does not appear to significantly affect the reaction rates of the two components present (the slopes of the lines are nearly identical in most cases). This indicates that the clusters have cooled down after they were annealed. While the reaction rates have not changed significantly, the relative abundances of the isomers has clearly been influenced by annealing. Table I shows a summary of the results for other clusters which we have investigated in detail. The table gives rate constants for the more reactive and less reactive components along with the relative abundances of the more reactive component for both annealed and unannealed clusters. These values were obtained from a least-squares fit of a two-component model to the experimental data. The results for the unannealed clusters presented in Table I are in reasonable quantitative agreement with our previous measurements made using slightly different experimental conditions.[1]

For Si_{29}^+ and Si_{46}^+ (shown in Figure 3) the relative abundance of the more reactive component increases with annealing. These clusters are converted almost entirely into the more reactive form while for Si_{35}^+ and Si_{47}^+ (also shown in Figure 3) the relative abundance of the more reactive component decreases as these clusters are annealed. Si_{35}^+ is converted entirely into the less reactive isomer. As can be seen from Table I, Si_{33}^+ is also converted entirely into the less reactive isomer when it is annealed. However, with the exception of these two cluster sizes, both isomers remain after annealing. For Si_{29}^+ and Si_{46}^+, and several other clusters in Table I (Si_{17}^+ and Si_{44}^+), the more stable isomer (the one which dominates for the annealed clusters) is the more reactive. Clearly there is no relationship between thermodynamic

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[8] McDaniel, E. W.; Mason, E. A. *The Mobility and Diffusion of Ions in Gases*; Wiley: New York, 1973.

Table I. Kinetic Data for the Reactions of Unannealed and Annealed Silicon Clusters with C_2H_4[a]

cluster	unannealed			annealed		
size	k_r, cm^3 s^{-1}	k_i, cm^3 s^{-1}	F_r	k_r, cm^3 s^{-1}	k_i, cm^3 s^{-1}	F_r
17	1.7×10^{-10}	2.9×10^{-12}	0.86	1.5×10^{-10}	4.4×10^{-12}	0.84
19	5.7×10^{-12}		1.00	5.5×10^{-12}		1.00
26	1.8×10^{-10}	1.4×10^{-13}	0.24	1.4×10^{-10}	1.2×10^{-13}	0.20
29	6.1×10^{-11}	1.9×10^{-12}	0.85	5.5×10^{-11}	3.9×10^{-12}	0.96
33	5.2×10^{-11}	3.1×10^{-13}	0.10		3.0×10^{-13}	0.00
35	2.6×10^{-11}	2.7×10^{-13}	0.11		2.8×10^{-13}	0.00
38	2.3×10^{-11}	1.4×10^{-13}	0.14	8.7×10^{-12}	6.0×10^{-14}	0.06
39	1.3×10^{-11}	4.9×10^{-13}	0.43	1.5×10^{-11}	4.0×10^{-13}	0.27
44	3.6×10^{-11}	8.7×10^{-13}	0.55	4.8×10^{-11}	1.3×10^{-12}	0.84
45	1.3×10^{-11}	3.4×10^{-13}	0.32	7.3×10^{-12}	1.9×10^{-13}	0.24
46	3.0×10^{-11}	5.1×10^{-13}	0.41	4.5×10^{-11}	5.4×10^{-13}	0.90
47	1.1×10^{-11}	2.9×10^{-13}	0.26	1.4×10^{-11}	1.3×10^{-13}	0.05
48	1.8×10^{-11}	5.9×10^{-13}	0.35	1.0×10^{-11}	2.5×10^{-13}	0.47

[a] The table shows rate constants for the reactive (k_r) and inert (k_i) components along with the relative abundance of the more reactive component (F_r) for the clusters studied in detail.

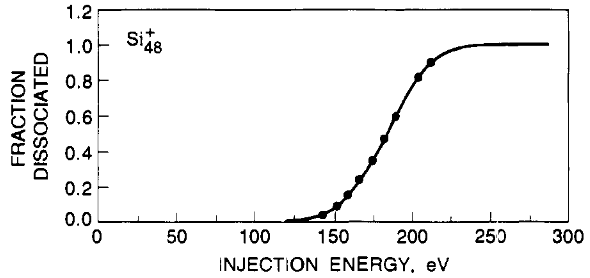

Figure 4. Results for the dissociation of Si_{48}^+. The figure shows a plot of the fraction of Si_{48}^+ clusters which dissociate against injection energy. There is a sharp threshold at around 180 eV. These results were measured using the single-stage drift tube configuration with 0.8 Torr of neon. The points are the experimental data and the lines are the results of simulations described in the text.

stability and chemical reactivity for isomers of these clusters.

Estimate of the Internal Energy Distribution. In order to determine the amount of energy required to anneal the clusters it is necessary to estimate the fraction of the injection energy that is converted into internal energy as the clusters enter the drift tube. One way to relate the internal energy to the injection energy is to determine thresholds for dissociation of the clusters. Some typical results are shown in Figure 4 for Si_{48}^+. The figure shows a plot of the fraction of Si_{48}^+ clusters which dissociate against injection energy. A relatively sharp threshold for dissociation of this cluster occurs for injection energies of ~180 eV.

Since the clusters contain many internal degrees of freedom, it is necessary to account for the statistical nature of the dissociation or annealing process. The fraction of clusters which dissociate or isomerize within a particular time can be obtained from

$$f(t) = \int_0^\infty \frac{dE_v\, \rho_v(E_v) e^{-E_v/k_BT}}{Q_v} (1 - e^{-k(E_i+E_v)t}) \qquad (2)$$

where E_v is the vibrational energy initially in the clusters (which are assumed to be at room temperature), E_i is the extra internal energy added as the clusters are injected into the drift tube, Q_v is the vibrational partition function, $\rho_v(E_v)$ is the vibrational density of states, and $k(E_i + E_v)$ is the rate constant for dissociation or isomerization. Since little is known about the vibrational frequencies or the nature of the transition states, $\rho_v(E_v)$ and Q_v were evaluated using a classical density of states and the Debye frequency,[9] and $k(E_i + E_v)$ was determined from quantum RRK (Rice–Ramsperger–Kassel) theory.[10]

In a recent paper we described an analysis of the dissociation thresholds, like that shown in Figure 4, for silicon clusters containing up to 70 atoms.[11] In that work we deduced that the fraction of the clusters injection energy that is converted into internal energy as the clusters enter the drift tube, F_{ie}, could be estimated from

$$F_{ie} \approx C\frac{(n-1)(1-c)}{2n} \qquad (3)$$

where n is the number of atoms in the cluster

$$c = \frac{m_{Si} - m_B}{m_{Si} + m_B} \qquad (4)$$

and m_B is the mass of the buffer gas. Equation 3 is essentially the value of F_{ie} predicted by an impulsive collision model (similar to that recently described by Uggerud and Derrick[12]) and C is an empirical correction factor deduced from our previous studies of the dissociation of the silicon clusters.[11] The line in Figure 4 is the result of a simulation using the models described above and incorporating a distribution of internal energies (in the excited clusters) characterized by a normal distribution function. The internal energy distribution is narrow (the threshold in Figure 4 is sharp) because of the averaging that occurs in the multicollision excitation process.[11]

Activation Energies for Annealing. If the reagent pressure in the drift tube is fixed and the injection energy varied it may be possible to identify a threshold associated with interconversion between the different structural isomers similar to the dissociation threshold described above for Si_{48}^+. The results of some of these experiments are shown in Figure 5 where the quantity ln (I/I_0) is plotted against injection energy for Si_{29}^+ and Si_{47}^+. For Si_{29}^+ the reactivity changes dramatically as the injection energy is increased from 20 to 40 eV and then remains relatively constant up to an injection energy of 90 eV. At an injection energy of 90 eV, the Si_{29}^+ clusters are sufficiently excited as they enter the drift tube that ~70% dissociate. As can be seen from Figure 5, Si_{29}^+ gets more reactive as the injection energy is increased. This is expected from the results shown in Figure 3 where it appears that the relative abundance of the more reactive component increases as this cluster is annealed. A sharp injection energy threshold is also observed for the annealing of Si_{47}^+ (see Figure 5). But in contrast to Si_{29}^+, the reactivity decreases as Si_{47}^+ annealed. As can be seen from Figure 3, for Si_{47}^+ the relative abundance of the more reactive component decreases as this cluster is annealed. Similar sharp thresholds were observed for nearly all the clusters that were studied in detail.

It is apparent from the results shown in Figures 4 and 5 that the injection energies required for cluster annealing are substantially smaller than those required for dissociation. This indicates that the activation energies for annealing are a small fraction of the clusters' dissociation energies. The solid line in

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(10) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: London, 1972. Forst, W. *Theory of Unimolecular Reactions*; Academic: New York, 1973.

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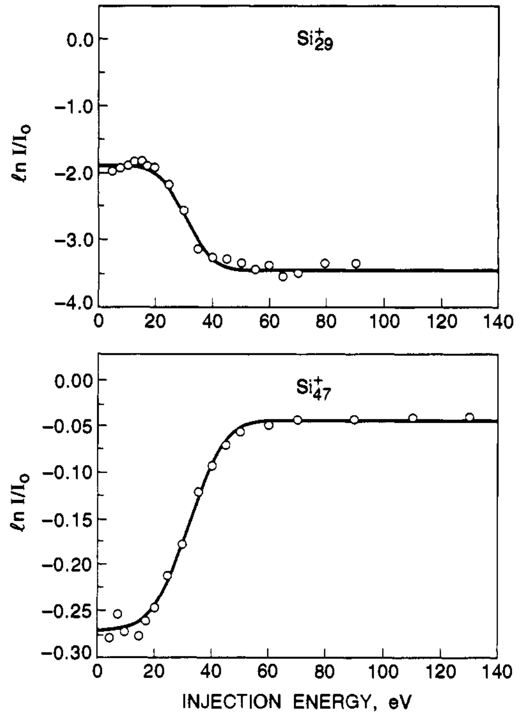

Figure 5. Plots of ln (I/I_0) against injection energy for Si_{29}^+ and Si_{47}^+. The points are the experimental data and the lines are the result of a simulation described in the text. The measurements were performed using the single-stage drift tube configuration with a drift field of 1.0 V/cm and a Ne buffer gas pressure of 0.8 Torr. The C_2H_4 pressures were 2.1 mTorr for Si_{29}^+ and 2.0 mTorr for Si_{47}^+.

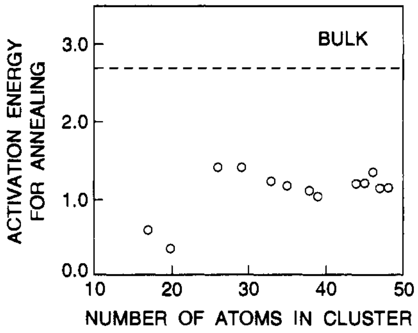

Figure 6. Plot of the activation energies for interconversion between the different structural isomers against cluster size. The dashed line shows the activation energy for annealing of bulk amorphous silicon (for solid-state epitaxy).[21]

Figure 5 shows the results of simulations to obtain a more quantitative estimate of the activation energy associated with annealing. These simulations are similar to those mentioned above (and described in detail elsewhere[11]) for the dissociation of Si_{48}^+. The activation energies estimated in this way are given in Table II and plotted in Figure 6. The activation energy for Si_{20}^+ was deduced from our previous observation[1] that this cluster isomerizes on a millisecond time scale at room temperature. The activation energies for the larger clusters ($n > 25$) are between 1.0 and 1.5 eV and do not show a systematic variation with cluster size. The estimated uncertainty associated with the activation energies is ±0.25 eV. It is reasonable to assume that the activation energies determined above are for going from the less stable isomer to the more stable. Thus as the clusters are annealed the dominant component (after annealing) increases for nearly all of the clusters studied in detail (see Table I). This is not always the case because it is possible that the cluster growth sequence could favor the lower energy structure by more than expected on the basis of its thermodynamic stability.

Relative Stabilities of the Isomers. The observation that in many cases we were not able to anneal the clusters to a single structural isomer provides a clue that the difference between the stabilities of the isomers is extremely small. An estimate of this stability difference can be obtained in the following way. If a given cluster is excited to just below its dissociation threshold, it will be isomerizing rapidly between several structures. An equilibrium will be established with

$$k_A[A] = k_B[B] \qquad (5)$$

where we have assumed that there are only two isomers, A and B. As the cluster is cooled by collisions with the buffer gas, the isomerization rates, k_A and k_B, will decrease. Eventually the isomerization rates will drop below the cooling rate (which is essentially the collision rate with the buffer gas) at which point the isomer populations will be "frozen in" as the cluster cools to room temperature. At the internal energy where the isomerization rates approximately equal the collision rate (~10^7 s^{-1})

$$\frac{[A]}{[B]} = \frac{k_B}{k_A} = \frac{\Gamma/\rho_B}{\Gamma/\rho_A} = \frac{\rho_A}{\rho_B} \qquad (6)$$

where Γ is the sum of states at the transition state for isomerization. Since we have no knowledge of the vibrational frequencies of the isomers, the vibrational densities of states were evaluated classically using the Debye frequency.[9] Estimates of the stability differences between the isomers are shown in Table II. For clusters where the dominant component (after annealing) decreases as the clusters are annealed, the stability difference is shown as a negative value. The stability differences are very small, typically ~0.2 eV, and do not appear to show a systematic variation with cluster size. For clusters for which only one isomer was observed after annealing, only a lower limit on the relative stabilities of the isomers can be derived. In the estimates of the relative stabilities of the isomers performed above we assumed that the vibrational frequencies of the isomers were the same because the frequencies are not known. We need to estimate the uncertainty introduced by this assumption. Using the results of Raghavachari and Rohlfing's[13] theoretical calculations of the vibrational frequencies of the two Si_{10} isomers and taking into account that the average frequency change is likely to be smaller for the larger clusters studied here, we estimate that the uncertainty associated with the relative stabilities of the isomers is ±0.15 eV.

Table II. Activation Energies for Annealing (E_{act}^{anneal}) and the Differences between the Stabilities of the Isomers (ΔE^{isomer}) for the Clusters Studied in Detail

cluster size	E_{act}^{anneal}, eV	ΔE^{isomer}, eV	cluster size	E_{act}^{anneal}, eV	ΔE^{isomer}, eV
17	0.60	-0.08	38	1.10	0.20
19		>0.40	39	1.03	0.07
20	0.37	0.05	44	1.20	0.13
26	1.40	-0.13	45	1.20	0.09
29	1.40	0.30	46	1.35	0.19
33	1.23	>0.37	47	1.13	0.21
35	1.18	>0.35	48	1.15	-0.01

Discussion

What Are the Isomers? As noted in the Introduction, we have investigated the reactions of silicon cluster ions with a number of different reagents. The reactions with C_2H_4 appear to be particularly sensitive to the presence of structural isomers. While nonlinear kinetic behavior was observed for some clusters with some of the other reagents studied, it was not as prevalent or as obvious as with C_2H_4. This observation implies that the reactions with C_2H_4 occur most readily at special types of site on the cluster. On bulk silicon surfaces C_2H_4 is believed to bind in a di-σ-bonded configuration.[14] It is not difficult to imagine that this bonding

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[13] Raghavachari, K.; Rohlfing, C. M. *J. Chem. Phys.* **1988**, *89*, 2219.

[14] Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *J. Chem. Phys.* **1988**, *87*, 7332. Yoshinobu, J.; Tsuda, H.; Onchi, M.; Nishijima, M. *Solid State Commun.* **1986**, *60*, 801. Piancastelli, M. N.; Kelly, M. K.; Kilday, D. G.; Margaritondo, G.; Frankel, D. J.; Lapeyre, G. J. *Phys. Rev. B* **1987**, *35*, 1461. Clemen, L.; Wallace, R. M.; Taylor, P. A.; Dresser, M. J.; Choyke, W. J.; Weinberg, W. H.; Yates, J. T. Adsorption and Thermal Behavior of Ethylene on Si(100)-(2×1), *J. Chem. Phys.*, submitted for publication.

configuration places rather severe constraints on the electronic and geometric structure of the binding site.

Our results have been interpreted in terms of two isomers. The experimental data are consistent with this assumption, but it would be naive to assume that only two isomers exist for each cluster. It is plausible that the reactions with C_2H_4 pick out those clusters which contain a special type of site. Clusters with that site react rapidly, clusters without one of these sites react much more slowly. There could be several different forms of the clusters which have at least one of these sites (and react at similar rates), and several different forms that do not and are considerably less reactive.

It is apparent from the results shown in Table I that the absolute rate constants measured for the annealed and unannealed clusters are essentially the same. In a few cases the rate constants differ by around a factor of 2. Differences of this magnitude in the rate constants are on the borderline of what we consider significant because similar variations were found between the rate constant measurements reported here for the unannealed clusters and our previous measurements performed under slightly different conditions. If several different reactive and unreactive forms of the clusters exist, the small variations in the rate constants observed upon annealing could arise from changes in the relative abundances of these several different forms.

The Importance of Annealing. Laser vaporization sources tend to result in diffusion-limited cluster growth[15-17] where the high-pressure buffer gas ensures that every time an atom encounters a cluster it sticks and does not re-evaporate. Because there is a large excess of buffer gas the growing clusters are effectively cooled between successive addition of atoms. In contrast, in oven sources the clusters tend to grow more under equilibrium conditions and the clusters' relative abundances tend to reflect their stabilities. Thus "magic numbers" which are often observed from oven sources are usually diminished or totally absent in cluster distributions from laser vaporization sources (unless they are enhanced by the ionization process). As noted in the Introduction, if silicon (and many other materials) is grown one atom at a time by deposition on a room temperature substrate, an amorphous material results. Thus, diffusion-limited cluster growth may ultimately result in amorphous clusters. From the results presented in Table I it appears that annealing the clusters does not result in a dramatic change in cluster structure (at least within the specificity provided by the reactions with C_2H_4), instead a redistribution among several low-energy isomers occurs. This implies that clusters in the size range examined here are at least partially annealed in the source by the energy released when an atom binds to the growing cluster. Isomerization rates calculated using the activation energies reported in this work are consistent with this conclusion. As the cluster size increases the effective temperature increase caused by binding an atom to the cluster decreases. So clusters considerably larger than the sizes examined here, say several hundred atoms, may be amorphous when they exit the source.

The Relationship between Thermodynamic Stability and Reactivity. For some clusters the more reactive isomer is the more thermodynamically stable. This result indicates that there is no relationship between thermodynamic stability of the isomers and their chemical reactivity. Generally, if something is stable we expect it to be unreactive. But this does not mean that there is always a direct linear correlation between stability and reactivity. For example, at room temperature, the (2 × 1) reconstruction of the Si(111) surface is slightly less stable than the (7 × 7) reconstruction,[18] yet the (2 × 1) surface is considerably less reactive toward oxygen than the (7 × 7) surface.[19] According to our results the differences between the stabilities of the isomers is extremely small, a few tenths of an electronvolt, so there is no reason to expect that the lower energy isomer must be the least reactive. The extreme sensitivity to cluster structure observed for these reactions with C_2H_4 indicates that structure, not stability, is the factor which controls the clusters' reactivity.

Activation Energies and Isomer Relative Stabilities. In the preceding discussion it was pointed out that several reactive and several unreactive forms of the clusters may exist. If this is the case then the measured activation energies for annealing and isomer relative stabilities are average values. These values can be compared to the analogous quantities for amorphous silicon. Amorphous silicon is ~0.1 eV/atom less stable than the crystalline form.[20] The activation energy for solid-state epitaxy in amorphous silicon films is 2.7 eV for Si(100).[21] An activation energy of 4.0 eV has been measured for crystallization by random nucleation and growth in amorphous silicon films.[21] All these quantities are considerably larger than those found for the clusters. The difference between the clusters and the bulk may be simply a result of physical size. Because the clusters are not part of an extended piece of bulk material they can readily adopt a number of low-energy structures separated by relatively small activation energies. A good example is provided by a 13-atom cluster for which interconversion between cubic close packed, hexagonal close packed, and icosahedral structures is a relatively trivial operation. A similar procedure for the bulk material would require a massive reorganization.

The observation of such small differences in the stabilities of the isomers and the small activation energies for interconversion between the different forms suggest that determining the geometric structures of these clusters will be a formidable task. In particular, the theorist performing calculations of these species must now assume that there may be several low-energy forms of these clusters which lie within a few tenths of an electronvolt of the ground state. The results reported here were obtained for silicon clusters. Silicon is a material which has strongly directional covalent bonding so the activation energies and stability differences are expected to be smaller for materials, such as metals, which have more diffuse bonding. Thus these results suggest that many metal clusters in the size range examined here will not have well-defined structures at room temperature. They will be rapidly isomerizing between a number of low-energy forms. This may account for why isomers of metal clusters have only been observed in a few cases,[22] though there have been many studies of their chemical properties.

Comparison with the Results of Smalley and Co-workers. In a recent series of papers Smalley and co-workers have argued that clusters with 33, 39, and 45 atoms are particularly unreactive.[2,23-26] They first observed the low reactivity of these clusters in their studies of the reactions with ammonia[23] and subsequently reported similar behavior with C_2H_4.[25] In our studies of the reactions with ammonia we found that all the clusters reacted at close to the collision rate at room temperature.[6] We subsequently showed that the products observed in these reactions with ammonia (at room temperature) arise mainly from molecular adsorption, under our experimental conditions.[3] It appears that formation of this mo-

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Table III. Relative Abundances of the More Reactive Isomer

cluster size	measured $k_c = 10^7\ \mathrm{s}^{-1}$	calculated $k_c = 10^2\ \mathrm{s}^{-1}$	calculated eqbm at 300 K
17	0.84	0.95	0.95
19	1.00	1.00	1.00
20	0.16	0.16	0.16
26	0.20	0.10	0.01
29	0.96	0.99	1.00
33	0.00	0.00	0.00
35	0.00	0.00	0.00
38	0.06	0.01	0.00
39	0.27	0.17	0.07
44	0.84	0.94	0.99
45	0.24	0.13	0.03
46	0.90	0.97	1.00
47	0.05	0.01	0.00
48	0.47	0.45	0.42

lecularly adsorbed product is not favored in the lower pressure FT-ICR experiments, and the product observed in those experiments presumably arises mainly from a much slower dissociative chemisorption process.

As can be seen from Table I, Si_{39}^{+} and Si_{45}^{+} anneal to the less reactive form. This is in agreement with the results previously reported by Smalley and co-workers. So it appears that the results obtained by the two groups are qualitatively the same. Smalley and co-workers have reported that it is possible to anneal Si_{39}^{+} and Si_{45}^{+} essentially completely to the unreactive isomer.[2] On the other hand incomplete annealing is observed in our experiments. This difference probably reflects the different time scales of the experiments. As discussed above the isomer distribution observed in our experiments reflects their relative abundances when the isomerization rate equals the cooling rate ($10^7\ \mathrm{s}^{-1}$). At this point the isomer populations are "frozen-in" as the clusters are cooled to room temperature. In the FT-ICR experiments the clusters are believed to be cooled mainly by infrared radiative emission. For medium-sized molecular ions infrared radiative emission rates are typically 1–10 s^{-1}.[27] For the clusters to be effectively cooled by this mechanism the rate must be $>10^2\ \mathrm{s}^{-1}$. In Table III we have shown the measured isomer relative abundances along with calculated relative abundances assuming a cooling rate of $10^2\ \mathrm{s}^{-1}$, and assuming equilibrium at room temperature. These results suggest that even under equilibrium conditions at room temperature a significant amount of both isomers will coexist for a number of the clusters. However, it is also clear that as the cooling rate decreases the relative abundances of the more stable isomers increase, and this could go a long way toward accounting for the slightly different isomer populations observed by the two groups.

While our observations about the annealing of the clusters are in agreement with those of Smalley and co-workers, our conclusions concerning Si_{33}^{+}, Si_{39}^{+}, and Si_{45}^{+} differ. From the results presented in Table I it does not appear that these clusters are much less reactive than their neighbors. While we were able to anneal Si_{33}^{+} essentially completely into an unreactive form, the same is true for Si_{35}^{+}. The annealed forms of these clusters appear to react with almost identical rates. For both Si_{38}^{+} and Si_{39}^{+} we find that the less reactive form dominates when these clusters are annealed, but the less reactive form of Si_{39}^{+} appears to be significantly more reactive than the less reactive form of Si_{38}^{+}. A comparison of the reactivity of Si_{44}^{+}, Si_{45}^{+}, and Si_{46}^{+} is interesting because for Si_{44}^{+} and Si_{46}^{+} the lower energy isomer is the more reactive but for Si_{45}^{+} the lower energy isomer is the less reactive one. Thus just comparing these three clusters it appears that Si_{45}^{+} is particularly unreactive. On the other hand Si_{47}^{+} is just as unreactive as Si_{45}^{+}, as is the dominant form of Si_{48}^{+} (though for this cluster a substantial amount of the more reactive form will coexist even under equilibrium conditions at room temperature). In their study of the reactions of silicon cluster ions with $\mathrm{C_2H_4}$, Smalley and co-workers appear to have only investigated the reactivity of six clusters (n = 36, 39, 42, 45, 48, and 51). Our results are consistent with their observations, but when comparison is made to a broader distribution of cluster sizes Si_{33}^{+}, Si_{39}^{+}, and Si_{45}^{+} do not appear to be particularly unreactive toward $\mathrm{C_2H_4}$.

Conclusions

New experimental methods have been developed to investigate the annealing of atomic clusters and they have been used to examine the annealing of silicon cluster ions. The effects of annealing were investigated by using the chemical reactivity of the silicon cluster ions with $\mathrm{C_2H_4}$ as a probe. Previous studies have shown that $\mathrm{C_2H_4}$ is a reagent that is particularly sensitive to the presence of structural isomers. Annealing does not dramatically alter the structure of clusters containing up to 50 atoms (at least within the specificity provided by the reactions with $\mathrm{C_2H_4}$), but it changes the relative abundances of the isomers that are present. For some clusters the more reactive isomer is the more stable. The relative abundance of this isomer increases as the clusters are annealed and it dominates for the annealed clusters. This indicates that the chemical reactivity of these isomers is not related to their thermodynamic stability. A direct correlation between chemical reactivity and stability is not expected, particularly for these reactions where structure appears to play such a critical role. Activation energies for interconversion between the different structural isomers have been estimated. For the larger clusters studied ($n > 25$), the activation energies are 1.0–1.5 eV and do not vary systematically with cluster size. It was not possible to anneal most of the clusters to a single structure. The isomer populations are "frozen-in" when the isomerization rate drops below the cooling rate. If slower cooling rates were employed the isomer populations would more closely approach their equilibrium values at room temperature. However, even at room temperature it appears that both isomers will coexist for a number of the clusters studied. The difference between the stabilities of the isomers was estimated from the experimental results. The energy differences are extremely small, typically around 0.2 eV. Both the stability differences and the activation energies for annealing are considerably smaller than for bulk amorphous/crystalline silicon. Given the strongly directional covalent bonding in silicon, the activation energies for isomerization are likely to be considerably smaller for metals which have more diffuse bonding. Thus, many metal clusters in the size range examined here may have fluxional structures at room temperature.

Registry No. Si_{17}^{+}, 122781-59-3; $\mathrm{Si}_{1}39^{+}$, 122781-61-7; Si_{20}^{+}, 122781-62-8; Si_{26}^{+}, 129735-61-1; $\mathrm{Si}_{2}\infty 9^{+}$, 129735-64-4; Si_{33}^{+}, 129735-67-7; Si_{35}^{+}, 129735-69-9; Si_{38}^{+}, 129735-72-4; Si_{39}^{+}, 129735-73-5; Si_{44}^{+}, 129735-78-0; Si_{45}^{+}, 129735-79-1; Si_{46}^{+}, 129735-80-4; Si_{47}^{+}, 129735-81-5; Si_{48}^{+}, 129735-82-6; $\mathrm{C_2H_4}$, 74-85-1.

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