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Sequential reactions of silicon clusters with SiD_4: constrained heterogeneous nucleation of deuterated silicon particles

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The sequential clustering reactions of gas phase silicon cluster ions are ideally suited for studying heterogeneous nucleation of silicon particles. Stepwise reactions of silicon cluster ions with silane have been observed which lead to growth of larger deuterated silicon clusters. Extensive information is obtained about their exothermic gas phase reaction rates and product distributions as a function of cluster size and degree of hydrogenation. What is found is that each size of silicon cluster exhibits a unique pattern of growth. Furthermore, nearly all of the silicon clusters encounter chemical constraints to rapid nucleation. These constraints are a consequence of specific electronic and structural requirements in the chemical reactions. The nature of these requirements are deduced using experimental results in concert with ab initio electronic structure theoretical calculations of the energetics and structures of various species.

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I. Introduction

Deleterious effects of gas phase particles as components of atmospheric pollution, dust contaminants of electronic devices, etc. have stimulated an increasing need to know how they are formed. Both experimental and theoretical studies of particle nucleation have highlighted the first stages of growth as critical factors in the rate of particle formation [1]. Here, the critical nucleus size is formed which can then undergo rapid spontaneous growth, limited only by factors such as diffusion and availability of monomers. Processes by which these critical nuclei form are poorly understood. The examples which have been the most studied involve the simple aggregation of monomeric species such as rare gases or stable molecules [2]. Formation of nuclei in this type of process is endoergic and proceeds relatively slowly. The rapid nucleation observed in most naturally occurring systems, however, requires that the condensation nucleus be formed efficiently and exothermically. One way that this can be accomplished in the gas phase is by a sequence of exothermic chemical reactions. Yet, such a sequence has never been clearly delineated.

The sequential clustering reactions of gas phase ions are particularly salient to the questions of silicon particle nucleation. Ions are currently believed to control the chemistry and kinetics of prenucleation of these aggregates under plasma conditions used for depositing silicon films in device fabrication [3]. We have undertaken a study of the sequential clustering reactions of positively charged silicon clusters with SiD_4. In these reactions, growth of larger silicon clusters is found to occur primarily by stepwise addition of $-SiD_2$ accompanied by loss of D_2. A silicon cluster species is sought which undergoes unlimited incremental growth since such a species could ultimately form the critical nucleus required for rapid growth of large deuterated silicon particles. What is found instead is that all of the bare silicon cluster ions encounter chemical constraints to rapid nucleation and growth. These constraints appear to arise because the chemical reactions of $Si_xD_y^+$ with SiD_4 have specific electronic and structural requirements. The nature of these requirements are deduced using experimental results in concert with ab initio electronic structure theoretical calculations of the energetics and structures of various species.

II. Experimental method

Si_{1-7}^+ and Si_{1-6}^- clusters are created by laser evaporation of a bulk silicon target located outside the low pressure ($\sim 10^{-9}$ Torr) side of a differentially pumped dual ion cell of a modified Nicolet FT/MS-1000 Fourier transform mass spectrometer (FTMS). A single cluster size is selected from the resulting ion population using double resonance techniques and reacted with $1-10 \times 10^{-7}$ Torr 99.7 atom% deuterium-enriched SiD_4 for times ranging from 0.1–10 s. The progress of the reaction is interrogated by recording the mass spectrum of the ions in the cell at regular time intervals. Mass spectra are obtained with mass resolutions of at least 10,000 which allows for separation of mass doublets. Accurate mass determination within 20 ppm allows for straightforward assignment of reactant and product ion stoichiometries. Standard double resonance techniques are also used to confirm reaction pathways.

III. Results

Ground state Si_{1-3}^+ and Si_5^+ react exothermically with SiD_4 in a sequential fashion to form larger hydrogenated silicon cluster ions. Si_4^+, Si_6^+ and Si_7^+ do not react with SiD_4 on the time scale of these experiments. No reactions are observed for the negatively charged silicon cluster ions, Si_{1-7}^-.

The clustering sequence and associated rates for each step of the sequence can be deduced from the time dependences of the evolving cluster ion populations. For example, the ion intensities as a function of time for Si_3^+ and its sequential reaction products with SiD_4 are shown in Fig. 1. Analysis of the exponential behavior of each ion intensity yields pseudo-first-order rate constants for each step of these reactions as well as those for the other starting cluster ions, Table 1. All of the products and rates are obtained under conditions which ensure that they pertain to the exothermic reactions of ground state species which are in thermal equilibrium with the cell wall temperature at 300K.

IV. Discussion

The sequential clustering reactions of Si_{1-7}^+ with SiD_4 are severely chemically constrained. In all but one case, each reaction gives remarkably similar products,

$$Si_n^+ + SiD_4 \rightarrow Si_{n+1}^+ + 2D_2 \qquad (1)$$

$$\rightarrow Si_{n+1}D_2^+ + D_2 \qquad (2)$$

Yet, all of the clustering sequences rapidly reach terminating structures, with the possible exception of Si_3^+. Once a terminating structure is reached, further growth is limited to slow bimolecular attachment of SiD_4 to the cluster ion. The underlying reasons for the constraints to infinite growth can be found in an examination of the structures and bonding of the various $Si_xD_y^+$ clusters involved in these reactions. Some of the possible cluster structures have been calculated by Raghavachari using ab initio electronic structure theory [4–5]. Overall, terminating cluster structures are found to be saturated in deuterium or

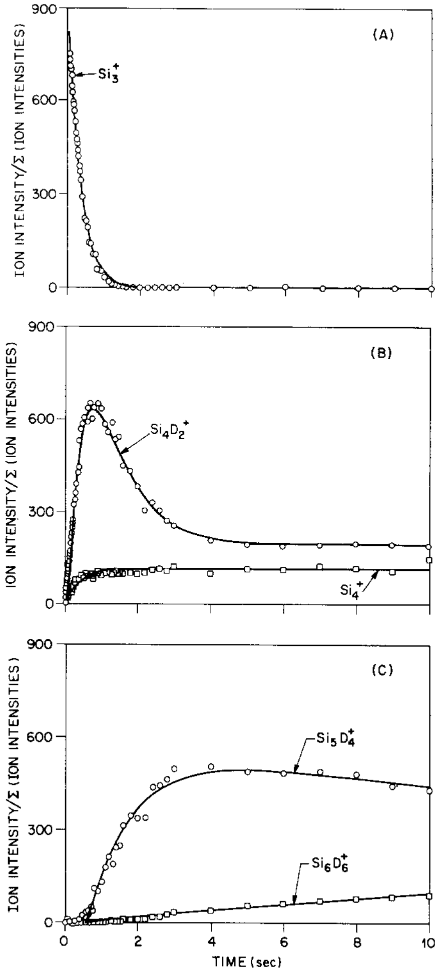


Fig. 1A–C. Time dependences of the evolving ion populations in the sequential clustering reactions of Si_3^+ with 1.7×10^{-7} Torr SiD_4. **A** The decay of the initial Si_3^+ ion population. **B** The rise and decay of the primary reaction products, $Si_4D_2^+$ and Si_4^+. Note that a portion of the $Si_4D_2^+$ plus the entire Si_4^+ populations do not react on this timescale. **C** The rise and decay of the secondary ion product, $Si_5D_4^+$ plus the rise of the tertiary $Si_6D_6^+$ product

Table 1. Sequential clustering reactions of Si_{2-7}^+ and $^{29}Si^+$ with SiD_4[a]

Reaction[b]		Product fraction (%)	Rate constant (× 10^{10}) (cm^3 $molecule^{-1}$ s^{-1})	Reaction probability[c]
$*Si^+ + SiD_4$	$\rightarrow *Si_2D_2^+ + D_2$	85 ± 4	8.1 ± 0.4[d]	0.82 ± 0.04
	$Si^+ + *SiD_4$	15 ± 4		
$*Si_2D_2^+ + SiD_4$	$\rightarrow *Si_3D_4^+ + D_2$	88 ± 5	0.36 ± 0.04[d]	0.036 ± 0.004
	$Si_2D_2^+ + *SiD_4$	12 ± 5		
$*Si_3D_4^+ + SiD_4$	$\rightarrow *Si_4D_6^+ + D_2$	87 ± 5	2.0 ± 0.3[d]	0.20 ± 0.03
	$Si_3D_4^+ + *SiD_4$	13 ± 5		
$Si_4D_6^+ + SiD_4$	$\rightarrow Si_5D_{10}^+$	100	0.0010 ± 0.0003	0.00010 ± 0.00003
$Si_2^+ + SiD_4$	$\rightarrow Si_3D_2^+ + D_2$	100	2.5 ± 0.4	0.25 ± 0.04
$Si_3D_2^+ + SiD_4$	$\rightarrow Si_4D_6^+$	100	0.010 ± 0.003	0.0010 ± 0.0003
$Si_3^+ + SiD_4$	$\rightarrow Si_4^+ + 2D_2$	14 ± 2	4.8 ± 0.7	0.48 ± 0.07
	$Si_4D_2^+ + D_2$	86 ± 2		
$Si_4D_2^+ + SiD_4$	$\rightarrow Si_5D_4^+ + D_2$	70 ± 3	1.8 ± 0.3	0.18 ± 0.03
	N.R.	30 ± 3	$\leqslant 0.001$	$\leqslant 0.0001$
$Si_5D_4^+ + SiD_4$	$\rightarrow Si_6D_6^+ + D_2$	100	0.036 ± 0.009	0.0036 ± 0.0009
$Si_4^+ + SiD_4$	$\rightarrow$ N.R.	100	$\leqslant 0.006$	$\leqslant 0.0006$
$Si_5^+ + SiD_4$	$\rightarrow Si_6D_2^+ + D_2$	58 ± 5	0.8 ± 0.1	0.08 ± 0.01
	$Si_6D_3^+ + D$	41 ± 5		
$Si_6D_2^+ + SiD_4$	$\rightarrow$ N.R.	100	$\leqslant 0.01$	$\leqslant 0.001$
$Si_6D_3^+ + SiD_4$	$\rightarrow$ N.R.	100	$\leqslant 0.01$	$\leqslant 0.001$
$Si_6^+ + SiD_4$	$\rightarrow$ N.R.	100	$\leqslant 0.001$	$\leqslant 0.0001$
$Si_7^+ + SiD_4$	$\rightarrow$ N.R.	100	$\leqslant 0.005$	$\leqslant 0.0005$

[a] "N.R." indicates that no reaction products have been observed for a particular reacting ion. Previously determined rates for Si^+ reacting with SiD_4 can be found in Ref. 7

[b] Reactions here are all exothermic with ground state ions at 300 K. Neutral species are inferred from thermodynamics. Silicon-29 isotope labelling of Si^+ and its sequentially formed cluster ions is designated with an asterisk. For example, $*Si_3D_4^+ \equiv {}^{29}Si^{28}Si_2D_4^+$. No isotope labelling is included for Si_{2-7}^+ and their sequentially formed clusters since isotope exchange with SiD_4 is not observed for these clusters

[c] The probability of reaction is calculated as the ratio of the measured reaction rate to the Langevin ion-molecule collision rate

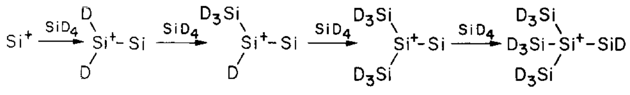
[d] Rate constant includes the isotope exchange process

have other electronic constraints preventing further interaction with SiD_4. In some cases, there is sufficient theoretical and experimental information to quantitatively test the proposed silicon cluster structures using statistical phase space theory [6–7].

A. Clustering sequences of the reactive clusters, $Si_{1-3,5}^+$

1). $Si^+ + SiD_4$. Si^+ is observed to undergo three sequential additions of $-SiD_2$ to form $Si_4D_6^+$ [7]. The clustering reactions then stop and further growth of $Si_4D_6^+$ only occurs slowly by bimolecular attachment of SiD_4 to form $Si_5D_{10}^+$. If isotopically labelled Si^+ is used, e.g. $^{29}Si^+$, another process is seen at each step of the clustering sequence where part of the isotopically labelled silicon is exchanged with $^{28}SiD_4$, Table 1. At each step, the exchange of label occurs on the same timescale with the formation of the $Si_{n+1}D_{2n}^+$ product. These observations indicate that the microscopic pathways of all of the clustering reactions of Si^+ and its progeny have two significant energetic barriers. This allows for a branching between product formation in a forward process and isotopic exchange in a reverse process.

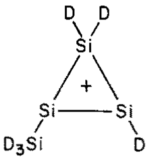
The mechanism and energetics for all of the reaction pathways have been derived by Raghavachari using ab initio electronic structure theory [4]. These calculations find that the two energetic barriers correspond to two important transition states in the reaction: a Si-D bond insertion transition state (TS1) and a D_2 elimination transition state (TS2). The structures of the growing hydrogenated silicon cluster ions are shown below.

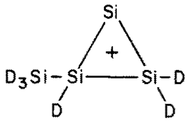


The reaction terminates with the highly branched $Si_5D_{10}^+$ structure. This structure is nearly saturated with deuterium which raises the energy of TS2, thus blocking loss of D_2. Using statistical phase space theory (PST) in conjunction with the experimentally derived forward and reverse reaction rates, we are able to test the accuracy of the calculated energetics of TS1, TS2, as well as the binding energy (CBE) of $Si_5D_{10}^+$ [6–7]. The results of these calculations are given in Table 2 [7]. Good quantitative agreement is found between the PST and ab initio results which confirms the validity of the calculated microscopic reaction pathways.

2). $Si_2^+ + SiD_4$. The first clustering reaction of Si_2^+ with SiD_4 occurs readily. By analogy to the reactions of Si^+, $Si_2D_2^+$, etc., the initial step of the Si_2^+ reaction with SiD_4 probably involves a Si-D insertion to form either $(D)(SiD_3)Si_2^+$ or $(SiD_3)Si_2D^+$. Both of these complexes have been investigated and are calculated to be energetically well below the starting reactants, $Si_2^+ + SiD_4$, at -1.4 and -0.87 eV, respectively [4, 8]. Elimination of D_2 follows, forming the $Si_3D_2^+$ product. The most energetically favored form for $Si_3D_2^+$ is the cyclic $^2A_1$ structure where the deuteriums reside on different silicon atoms [5]. If this is the final product, then the overall reaction is calculated to be exothermic by 0.78 eV. An alternative cyclic structure with the deuteriums on the same center is not favorable; its formation is calculated to be 0.52 eV endothermic. The linear $^2B_1$ product, $(D_2Si)Si_2^+$, is also estimated to be slightly endothermic, by ~ 0.1 eV. Further investigation of this structure, especially bending along the Si–Si–Si bond, is probably warranted since in Si_3 the bent form has been found to be more stable than the linear form by 0.4 eV [9].

The available theoretical data is insufficient to determine whether the $Si_3D_2^+$ product is cyclic or not. However, the next clustering step of the reaction to form $Si_4D_4^+$ does not occur and only the collisionally stabilized adduct, $Si_4D_6^+$ is seen. It is difficult to conceive of an energetic or structural reason why loss of D_2 would be blocked in any linear form of $Si_3D_2^+$, suggesting that the $Si_3D_2^+$ product has the stable cyclic form. To be consistent with this explanation, formation of the $Si_4D_6^+$ adduct would have to leave the $Si_3D_2^+$ cyclic form intact. From the experimental formation rate of the $Si_4D_6^+$ complex, we have performed a phase space calculation of its binding energy, showing that it lies between 1.2 and 1.4 eV below the reactants. This binding energy is consistent with either form of $Si_4D_6^+$ shown below. Additional theoretical calculations will prove invaluable for ascertaining why elimination of D_2 is endothermic from these structures.





3). $Si_3^+ + SiD_4$. Si_3^+ exhibits the most extensive clustering with SiD_4 of all of the Si_{2-7}^+ clusters. On the timescale of our experiments, three additions of $-SiD_2$ occur. Nonetheless, the Si_3^+ clustering sequence does not follow a single course. The first reaction of Si_3^+ forms three products, two of which do not continue to react with SiD_4. Two of these products have the same stoichiometry, $Si_4D_2^+$, but are chemically distinct in further reactivity with SiD_4. This is a

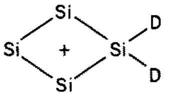
Table 2. Comparison of PST and *ab initio* calculations of transition state (TS1-2) or intermediate complex binding (CBE) energies for each sequential clustering reaction of $^{29}Si^+$ with SiD_4 [4, 7]

	Energy (eV)					
	PST calculations			*ab initio* calculations		
Reaction	TS1	TS2	CBE ($Si_5D_{10}^+$)	TS1	TS2	CBE ($Si_5D_{10}^+$)
$^*Si^+ + SiD_4 \rightarrow \begin{cases} ^*Si_2D_2^+ + D_2 \\ Si^+ + {}^*SiD_4 \end{cases}$	-0.34 ± 0.05	-0.29 ± 0.04	—	-0.46	-0.01	—
$^*Si_2D_2^+ + SiD_4 \rightarrow \begin{cases} ^*Si_3D_4^+ + D_2 \\ Si_2D_2^+ + {}^*SiD_4 \end{cases}$	-0.16 ± 0.02	-0.14 ± 0.02	—	-0.21	-0.05	—
$^*Si_3D_4^+ + SiD_4 \rightarrow \begin{cases} ^*Si_4D_6^+ + D_2 \\ Si_3D_4^+ + {}^*SiD_4 \end{cases}$	-0.27 ± 0.02	-0.19 ± 0.02	—	-0.21	-0.06	—
$Si_4D_6^+ + SiD_4 \rightarrow Si_5D_{10}^+$	—	—	-0.80 ± 0.02	—	—	-0.98

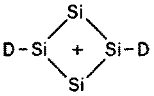
clear example that pathways leading to multiple non-interconverting isomers are energetically and kinetically accessed starting with a given initial reactant Si_x^+ ion.

The first clustering reaction of Si_3^+ with SiD_4 forms both Si_4^+ and $Si_4D_2^+$. From the ab initio electronic structure determinations of the fragmentation energies for $Si_n^+ \rightarrow Si_{n-1}^+ + Si$, the formation of the lowest energy D_{2h} rhombus structure of Si_4^+ is calculated to be exothermic by 1.0 eV [8, 10]. Based on ab initio calculations of the relative energetics of alternative Si_4^+ structures, formation of any other geometric isomer of Si_4^+ would be endothermic by 0.1–2.4 eV. Additional confirmation that Si_4^+ formed from Si_3^+ has the lowest energy rhombus structure is that it is not observed to react further with SiD_4. This is exactly the same as for the Si_4^+ population which is formed initially from evaporation of the silicon target.

The other ionic product formed in the reaction of Si_3^+ with SiD_4 is $Si_4D_2^+$. As can be seen in its subsequent reaction with SiD_4, this product consists of two chemically distinct species (Table 1). As discussed below, Si_4^+ also does not react with SiD_4 because of its unusually stable rhombus structure. This immediately suggests that the nonreactive $Si_4D_2^+$ is structurally similar to D_{2h} Si_4^+ in such a way that the electronic configuration responsible for the stability of the Si_4^+ rhombus is not disrupted. Ab initio calculations find that structure (*I*) above is the only possibility which satisfies this criterion [5]. Theoretical investigations of other possible $Si_4D_2^+$ forms indicate that structure (*II*) is energetically well below other cyclic and non-cyclic forms [5]. In (*II*), however, the electronic configuration which results in the rhomboid shape in Si_4^+ has been sacrificed in order to bind the two deuterium atoms. The resulting structure (*II*) is nearly a D_{4h} square which is high enough in energy to react further with SiD_4. *A distinguishing feature of structures* (*I*) *and* (*II*) *is that, experimentally, they are found to be non-interconverting even via a single deuterium migration.* This is the first evidence that deuterium migration may be constrained in some of these highly unsaturated species.



(I)



(II)

The reactive portion of the $Si_4D_2^+$ population interacts further with SiD_4 exclusively by sequential addition of $-SiD_2$ to form $Si_5D_4^+$ and then $Si_6D_6^+$. Currently, there is insufficient experimental and theoretical information to ascertain the structures of $Si_5D_4^+$ and $Si_6D_6^+$. One possibility is that they are silyl ($-SiD_3$) substituted versions of structure (*II*). No $Si_7D_x^+$ products are observed during our experimental time scale, indicating that further growth must proceed at less than 1% of the collision rate.

3). $Si_5^+ + SiD_4$. Si_5^+ is only observed to undergo one clustering step with SiD_4, forming $Si_6D_2^+$ and $Si_6D_3^+$. Further clustering of $Si_6D_{2,3}^+$ does not occur within our experimental time limits (Table 1).

The reaction of Si_5^+ has a small rate of only about one-tenth of the Langevin rate. Nonetheless, the overall reaction energetics are sufficiently favorable that one of the products, $Si_6D_3^+$, results from the loss of a deuterium *atom*. This is the only reaction that is observed for the Si_n^+ clusters with SiD_4 where a radical product is formed. Based on the relative energetics of possible structures for $Si_6D_3^+$, loss of a deuterium atom can probably occur only if the addition of SiD_3 to Si_5^+ is accompanied by rearrangement and ring closure to form a deuterated Si_6^+ cluster similar to the bare Si_6^+ cluster itself. Formation of any functionalized Si_5^+ clusters, such as $(Si_5)(SiD_3)^+$, is estimated to be endothermic by 1.1–1.2 eV [5, 8, 11]. However, Si_6^+ is sufficiently stable relative to the Si_5^+ structure that the addition of a silicon atom to Si_5^+ to form the most stable edged capped trigonal bipyramid C_{2v} form of Si_6^+ is exothermic by 5.5 eV. This energy is comparable to that for addition of a silicon atom to Si_3^+. In the case of Si_3^+, the exothermicity appears to allow for elimination of *two* molecules of D_2 to form the stable D_{2h} rhombus structure. In contrast, for Si_6^+, three deuteriums remain on the cluster and loss of a deuterium atom occurs. This provides additional evidence that substantial ring closure and rearrangement can occur for some of these highly unsaturated silicon clusters as more silicon atoms are added to the framework.

B. The non-reacting clusters with SiD_4: Si_4^+, Si_6^+, and Si_7^+

Three clusters, Si_4^+, Si_6^+, and Si_7^+, are inert with respect to reaction with SiD_4. In addition, none of these clusters are observed to form collisionally stabilized bimolecular adducts with SiD_4. The nonreactivity of Si_6^+ and Si_7^+ is not unusual. To date, they have not been observed to react with any organic or organosilicon reagent, including CH_3SiH_3, CH_3C_2H, $(CH_2)_2C$, and C_2H_2, with the exception of CH_3OH [12]. The failure of Si_4^+ to react with SiD_4 as an isolated cluster size, however, is unprecedented for silicon cluster ions.

The non-reactivity of Si_4^+, Si_6^+ and Si_7^+ may well be related to their unusual stability. Photofragmentation and collisional fragmentation studies as well as ab initio electronic structure calculations have shown that these cluster sizes are energetically more stable than other small silicon cluster sizes [8, 10, 13, 14]. Furthermore, the calculated energies for the addition of a silicon atom to these clusters to form the ground state structure of the next larger cluster, $Si_n^+ + Si \rightarrow Si_{n+1}^+$, are the lowest of all of the silicon clusters containing between two and ten atoms [8, 10, 14]. As discussed above, addition of $-SiD_2$ to a bare Si_n^+ cluster appears to make a cluster which has a structure closely related to the lowest energy isomer of the Si_{n+1}^+ cluster. Thus, the energies calculated for the addition of a silicon atom can be used to provide a first approximation for the thermochemistry of the reaction involving addition of $-SiD_2$. Although the actual values should not be taken too seriously, this approximation shows that the addition of $-SiD_2$ to either Si_4^+ or Si_7^+ would be significantly less exothermic as compared to the other clusters, including Si_6^+. This suggests that the reaction of Si_4^+ and Si_7^+ with SiD_4 may well be endothermic or be so close to thermoneutral that any transition state energies would be endothermic. *The estimated reaction thermodynamics do not explain why* Si_6^+ *is unreactive.*

The most plausible reason for the inertness of Si_6^+ is that its dangling electrons have the wrong electronic character to insert into the Si-D bond of SiD_4. The net result is that the energy of the first transition state involving Si-D insertion rises well above the available reaction energy. Previously, we have postulated that a divalent (silylene) silicon center having a localized lone pair of non-bonding electrons is the chemically active site on the cluster for Si-D bond insertion [12]. This suggestion originates from the well-established solution phase organosilicon chemistry of divalent silicon centers [15]. Recently, extensive ab initio electronic structure calculations have been performed on the Si-D insertion transition states involved in the sequential clustering reactions of Si^+ with SiD_4. These calculations clearly indicate the essential role played by the silylene lone pair in both the attachment of the incoming D of SiD_4 and in the formation of the Si-D insertion transition state. The smaller silicon clusters, Si_{2-5}^+ contain divalent silicon centers. These divalent silicon centers are replaced by trivalent and higher valency centers in silicon clusters with six or more atoms. In this light, the non-reactiveness of Si_6^+ and Si_7^+ may well reflect not the overall reaction thermochemistry but rather the chemistry available to their valence electrons. Similarly, larger silicon clusters are predicted to be unreactive towards SiD_4.

V. Implications for prenucleation of hydrogenated silicon particles in silane plasmas and vapors

Chemical vapor deposition of epitaxial, polycrystalline and amorphous silicon films is widely used in the fabrication of VLSI circuits, solar cells and other silicon devices. Silane is the source gas of choice for deposition of polycrystalline and amorphous silicon films; it is also used to deposit epitaxial films when low deposition temperatures are required to minimize diffusion, autodoping, etc [6]. All of these silane processes share a serious problem: gas phase nucleation of silicon particles which ultimately contribute to poor film quality and device failure [16].

Despite numerous investigations, the formation mechanisms of these particles has yet to be proven [17]. Several chemical models have been developed to explain the formation of these particles [3]. At the heart of the models lies chemical condensation reactions of the form,

$$Si_xH_y^{(+)} + SiH_4 \rightarrow Si_{x+1}H_z^{(+)} + mH_2 + nH$$
$$y = 2m + n + z - 4 \qquad (3)$$

where the superscript "(+)" signifies that the species may be either neutral or positively charged. These models have become increasingly sophisticated in their treatments of the important chemical and physical conditions in high temperature vapors and plasma reactors. Nonetheless, they are severely limited by the lack of hard chemical data concerning the reaction rates and energetics for the quintessential condensation reactions embodied by (3). In the absence of this information, all of these models have been forced to make simplifying assumptions about the condensation reactions. One assumption is that a single reaction rate can be used to describe all of the condensation reactions embodied by (3), except for the association reaction rate ($n+m=0$) which involves three body collisions. As a corollary to this working hypothesis, cluster growth is characterized by the number of silicon atoms regardless of the number of hydrogens. Another assumption is that the structures of the evolving silane species do not significantly affect their chemistry. For example, it has been invoked that these may consist of linear silane polymer chains with an unsaturated "growing" end. Finally, it is assumed that the condensation reactions are limitless and that termination can only occur by another chemical or physical route, such as deposition on a surface.

The results of our studies of the sequential clustering reactions of silicon clusters cations with silane clearly indicate that simplifying assumptions about the chemistry of embryonic hydrogenated silicon particles should be postponed. We find that the rates and products of their reactions varies with the cluster size and number of deuteriums. Table 1 lists reaction rates that span three orders of magnitude for condensation reactions of the type in (3). Furthermore, higher $Si_xD_y^+$ species appear to have highly diverse structures involving branched chains, rings and more highly compact forms. These geometric structures have a profound influence on the electronic structures —and therefore the chemistry of these higher $Si_xD_y^+$ ions. Finally, all of the clustering sequences that we have monitored appear to be highly constrained. Most of them terminate and further cluster growth can only occur by inefficient bimolecular association reactions. In cases where the sequence termination is not directly observed, all but one of the clustering sequences proceeds to a reaction with a probability of less than 0.1% of the ion-molecule collision rate. All of these observations point to the need for further study of the individual reactions which lead to spontaneous growth of hydrogenated silicon particles. Key information on the prenucleation steps may eventually lead to rational design of intervention measures to prevent or control the occurrence of these particles.

VI. Conclusions

Bare silicon cluster ions undergo exothermic sequential clustering reactions with SiD_4. The overall reaction in all of the sequences is the addition of SiD_2 accompanied by loss of D_2. None of the clustering sequences exhibit unconstrained growth of increasingly larger $Si_xD_y^+$ species. Of the cluster ions studied, $Si_{2-7}^{+/-}$, only $Si_{2-3,5}^{+}$ react with SiD_4 in their ground state. No reactions are found for the negative silicon cluster ions.

Electronic structure theoretical calculations of the energetics of various possible forms are used to deduce the structures of the products ions in these clustering reactions. Overall, it appears that the structures of the growing $Si_xD_y^+$ ions are closely related to the lowest energy structures that have been found for the bare clusters when the degree of hydrogen saturation is low. This suggests that considerable rearrangement of the silicon framework in these clusters is possible during the reaction. Nonetheless, non-converting geometric isomers are also found which indicates that not all structural rearrangements are energetically accessible. The unreactiveness of the largest clusters appears to arise from the lack of the appropriate divalent silicon center which is necessary for the Si-D insertion transition state early along the reaction pathway. The nonavailability of the divalent silicon centers occurs because these larger silicon clusters have increased intramolecular silicon-silicon binding resulting in higher valencies.

The early bottlenecks found in the sequential clustering reactions of Si_x^+ with SiD_4 indicate that ground state, bare silicon cluster ions are not the important precursors in the formation of hydrogenated silicon dust in silane plasmas. Furthermore, the chemical constraints that are found for these clusters are undoubtedly ubiquitous in the reactivity of unsaturated $Si_xD_y^+$ species. A more complete understanding of the prenucleation of particulates awaits additional information about the structures and chemistry of these types of unusual species.

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