

Chemical Reactivity and Electronic Structure of Silicon Microclusters

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4.1 Introduction

Small semiconductor clusters are of great interest both to fundamental science and for applications. At present, however, both the basic properties and the kinetics behind the cluster formation are largely unknown. In supersonic beams where Si clusters can be grown, the random-like kinetics of Si atoms is suitable for growing both small and large clusters with various structures. However, experiments on these clusters show clear patterns, like periodicity in the reactivity and a photofragmentation pattern which indicate underlying structure. This obviously reflects the patterns in the conformation of the clusters with growing size.

We discuss in this chapter properties of small and medium-sized Si clusters from a theoretical perspective. The topics we include are the structure, reactivity and photofragmentation of Si clusters. The point of view will be the tight-binding (TB) model, which allows one to treat relatively large clusters compared to *ab initio* methods. The TB model has been shown to be good for the treatment of electronic structure of bulk silicon, silicon surfaces^[1] and small silicon clusters.^[2] It is a simple and transparent method, which does not involve need for computations of the complexity required in *ab initio* methods.

Our primary reason for focusing on the TB model is twofold: First is the calibration of the TB method, with an eye toward establishing the limits of applicability to medium-sized clusters. Second is the elucidation of the structure of large silicon clusters, for which more sophisticated techniques are impractical. As our goals require comparison with both experiment and other calculations, we have chosen Si₁₀ as a model system since much data on the species already exists.^[1-8] The treatment of larger Si clusters in this model is straightforward,^[9, 10] but the results are considerably more speculative given the absence of experimental data. Nevertheless, we will touch base with some important experimental parameters, and we believe that the theoretical results presented here are plausible.

As an example, consider the following. A dramatic variation in the reactivity of silicon clusters with ammonia and methanol as a function of cluster size is observed.^[3] A periodicity in reactivity in units of six atoms is also observed, with Si₃₆⁺ and Si₄₂⁺ being most reactive, while Si₃₉⁺ is less reactive by two orders of magnitude. Clearly, this variation cannot be attributed to cluster stability. Starting with a model proposed by Phillips,^[11] we have tested the notion

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that clusters in this size range are arranged in stacked, six-membered rings, with the left-over atoms forming a cap.^[9]

4.2 The Tight-Binding Model

The cohesion energy E_{coh} of a cluster is a sum of the band structure energy of electrons and an interatomic repulsion energy,²

$$E_{\text{coh}} = -(E_{BS} + E_R). \quad (4.1)$$

The band structure energy is defined as

$$E_{BS} = \sum_{\alpha} n_{\alpha} \varepsilon_{\alpha} - \sum_{\beta} n_{\beta}^0 \varepsilon_{\beta}^0 + U \sum_{\mu} (q_{\mu} - q_{\mu}^0)^2, \quad (4.2)$$

where the first two terms denote the sums over one-electron energies of the cluster, ε_{α} , and those of the isolated atoms, ε_{β}^0 , respectively. The third term is an intra-atomic Coulomb energy due to charge transfer among the atomic sites μ . Each term contains a charge difference at a site, between the cluster charge distribution and that of the isolated atom.

The electronic levels of the cluster are obtained from diagonalizing the TB (nearest-neighbor) Hamiltonian. Assuming for the moment bulk Si, with a basis set per atom of four atomic levels (s, p_x, p_y, p_z), the diagonal elements of the s - and p -levels are -5.25 eV and 1.20 eV, respectively. The off-diagonal elements are assumed to vary as $1/r^2$; at the equilibrium bond length of the bulk material, namely 2.35 Å, their values are $V_{ss\sigma} = -1.938$ eV, $V_{sp\sigma} = 1.745$ eV, $V_{pp\sigma} = 3.050$ eV and $V_{pp\pi} = -1.075$ eV.^[1] (The notation refers to the orbitals, i.e. s or p , on a nearest-neighbor pair, and the bond type formed, i.e. σ or π .) The net charge transfer required for the third term of Eq. (4.2) is calculated using a Mulliken population analysis, and $U \approx 1$ eV.^[2] The repulsion energy, E_R , consists of the sum of pairwise repulsive potentials, whose magnitudes depend on the interatomic distances, together with a term which depends on the total number of bonds in the cluster.

The one-electron levels turn out to be very sensitive to the geometry: very minute changes in the conformation cause large changes in the energy levels. For this reason, the minimization of the total energy through geometry optimization is crucial in the study of clusters. Therefore, we first use Hellmann-Feynman forces to bring the system close to equilibrium, and then a multivariate minimization technique to optimize the structure without symmetry restrictions.

4.3 Structure of Si₁₀ Clusters

First let us consider three isomers of Si₁₀: a *tetracapped triangular prism* (TTP), a *bicapped tetragonal antiprism* (BTA) and a *tetracapped octahedron* (TO). These have all been suggested in the literature^[4,6,7,8] to be the lowest-energy conformations of Si₁₀. TB calculations indicate two additional stable but distorted BTA-related structures, which we refer to as DBTA-I and DBTA-II. These are illustrated in Fig. 4.1. The DBTA-I structure differs from the

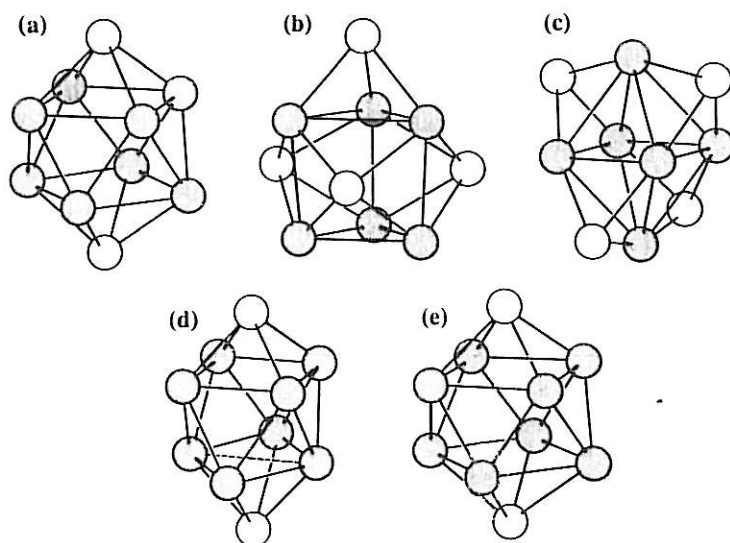


Figure 4.1: Structures for the (a) BTA, (b) TTP, (c) TO, (d) DBTA-I and (e) DBTA-II clusters. The unshaded atoms are the caps.

BTA in that it is stretched in one dimension and squeezed in another. Hence there is an additional bond (or a partial bond) with a bond length of about $3.30 \text{ \AA}$. This reduces the symmetry of the species from D_{4d} to C_2 . DBTA-II contains no additional bonds, but involves a stretching and twisting of the original BTA form, also resulting in C_2 symmetry. The BTA-related structures are so-called Jahn-Teller distortions (which lower the total energy) of more symmetrical species, and are stable in that there is a local energy minimum for each conformation. The activation energy between them is very low.

Chelikowski *et al.*^[7] report the BTA structure as being the most stable, whereas Bal-lone *et al.*^[6] cite TTP as the energy minimum. On the other hand, *ab initio* calculations of Raghavachari^[4] result in either TO or TTP as being the most stable structure. Raghavachari and Roling^[4] have investigated BTA in two different electronic configurations, but without the inclusion of the effects of distortion. Within the accuracy of our TB calculations, the BTA and TTP forms appear to be degenerate, though neither matches the experimental photoelectron spectroscopy data. The TB calculations also indicate no band gap for BTA, but for TTP the HOMO-LUMO transition is 2.6 eV . The latter value is consistent with that obtained from the more elaborate calculations reported for the same structure in Ref. 6. However, the experimental value observed by Cheshnovsky *et al.*^[5] is 1.2 eV . A possible resolution is in the DBTA-I structure. As is shown in Table 4.1, the TB band gap of DBTA-I is 1.4 eV , which closely matches the experimental result.

It is interesting to note that, with the exception of DBTA-I, all stable structures contain 24 bonds, or have an average coordination number of 4.8. This is to be compared with the bulk value of four. The adamantane-like structure is a 10-atom fragment of the bulk solid. It is

Table 4.1: The cohesion energies, HOMO–LUMO transition energies, and LUMO energies of the various Si₁₀ structures shown in Fig. 4.1. The LUMO one-electron energy, which is a rough indication of the electron affinity, is given relative to the “HOMO” level of the bulk.

Species	Cohesion Energy (eV/atom)	HOMO–LUMO gap (eV)	LUMO level (eV)
DBTA-I	−3.98	1.4	+0.18
DBTA-II	−3.92	0.6	−0.50
BTA	−3.90	0.0	
TTP	−3.91	2.6	+1.21
TO	−3.61	2.9	+2.00

relatively open, rather than close-packed. As a result, it has an average coordination number of 2.4, only half that of the other structures. TB calculations agree with the results of Ref. 2 in finding the adamantane form of the 10-atom cluster to be unstable. Geometric optimization rapidly leads to the formation of additional bonds.

Experimental work^[12] on Si₁₀ clusters indicate a reactivity that is not unique. Two distinct rate constants are measured, one at least an order of magnitude larger than the other. The above TB results explain the reactivity as follows. An estimate of the electron affinity of each isomer is listed in Table 4.1 as the energy of the LUMO level. This is an indication of the propensity of the isomer to accept an additional electron, i.e., the lower the LUMO level, the greater the electron affinity. Similarly, a small HOMO–LUMO gap indicates a greater reactivity, since this implies that valence electrons have a greater freedom to rearrange in bond formation. It can be seen from the table that the BTA-related structures have a greater electron affinity and a smaller band gap, implying that they are relatively reactive. Conversely, TTP and TO have a low electron affinity, indicating low reactivity. Taken together with the energetics, the dual reactivity results of Ref. 12 can thus be explained by concluding that two stable isomers of Si₁₀ exist, namely, DBTA-I and TTP, with the more common (the DBTA-I structure at ~ 85% abundance) being approximately an order of magnitude more reactive than the other.

4.4 Reactivity of Si₃₀–Si₄₅ Clusters

A periodic reactivity pattern of silicon clusters has been reported.^[5] The reactions appear to be chemisorption, though it is unclear whether they are dissociative or not. We start our analysis by noting that the cluster stability does not necessarily have much to do with the reactivity. The former is thermodynamic whereas the latter is kinetic. The reasons for the variation in reactivity are mainly expected to be due to the electronic structure: charge distribution within the cluster, existence of open shells (partly occupied HOMO) and dangling bonds. The electronic structure, of course, is then expected to have a strong interplay with the conformation.

We now present some possible models to account for the correlation between the charge distribution and the observed periodic reactivity pattern. These are connected to hypotheses

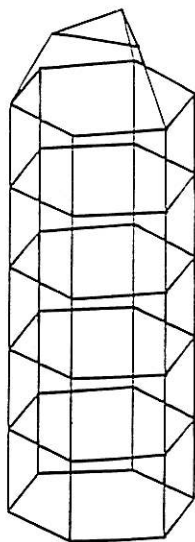


Figure 4.2: A model of Si_{39}^+ composed of stacked six-membered rings.

about the structure of various sized Si clusters. Beginning with Phillips' hypothesis that silicon clusters are arranged in stacked, six-membered rings, we have calculated the most stable geometries and their charge distributions by minimizing the energy of Eq. (4.1). The clusters we discuss here are all singly-charged cations, ranging in size from $n = 25$ to $n = 45$.

We find that all clusters can assume a cylindrical shape—i.e., there is a local energy minimum near these geometries. There may, of course, be many other stable (and possibly even more stable) configurations. Thus, evidence for the actual existence of the cylindrical shape stems from the reactivity pattern, and not necessarily from the cluster stability. The cohesion energy per atom for all clusters from $n = 25\text{--}45$ is found to be between 3.1 and 3.5 eV, i.e., differing by only a few tenths of an electron volt. Since a TB calculation is relatively primitive, we do not believe these differences to be significant. This is consistent with the experimental observation that all clusters appear in equal abundance.

The most apparent aspect about the geometry is the flatness of the rings. This, along with the fact that the intra-planar distances are frequently smaller than the distance *between* planes, suggests that the rings are slightly conjugated. This hypothesis is borne out by a calculation of the bond orders. The bond order between ring atoms ranges around 1.10, whereas the bond order between planes is closer to 0.90.

As illustrated by Fig. 4.2 for Si_{39}^+ (other clusters look very similar), the atoms in the "body" of the cluster are tetrahedrally coordinated, as in bulk Si, though the shape is altered due to strain. The atoms at the end tend to be triply coordinated, though the existence of the cap complicates that generalization. In any case, it is obvious that there are a large number of dangling bonds in the cluster. Interestingly, in our calculations we find no significant variation in the number of dangling bonds as a function of cluster size. (Si_{36}^+ was found to have the

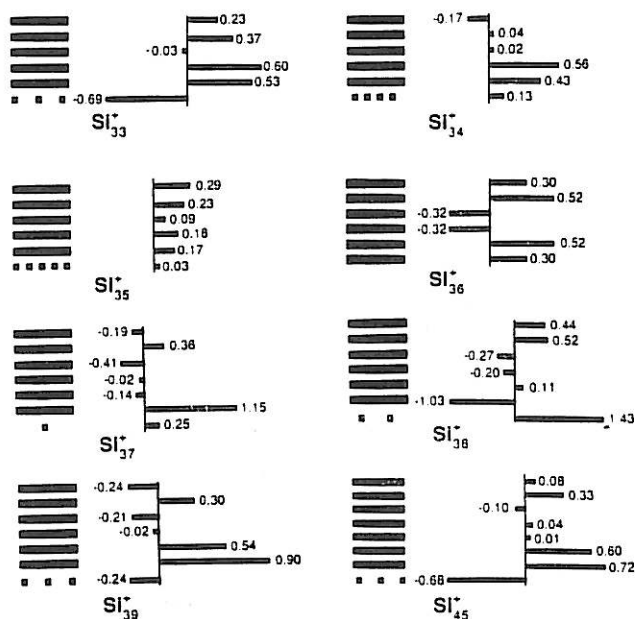


Figure 4.3: Total electronic charge per layer for different silicon clusters. The diagrams on the left of each figure represent a schema of the cluster geometry, with the solid bars denoting a six-membered ring. The individual atoms of the cap are shown explicitly. The bar graphs on the right show the total charge per layer, i.e. the sum of the charges of each atom constituting a single layer.

fewest dangling bonds, as one would expect, due to the higher degree of symmetry—i.e., no cap.) Thus, the experimental result that all species react rapidly with free radicals such as NO is clearly accommodated by this model, as one would suppose that free radicals would react with dangling bonds.

Of considerable significance is the charge distribution within the cluster. Despite all clusters being singly-charged cations, we can see from Fig. 4.3 that there is a significant variation in charge density within the clusters. For Si_{36}^+ , the molecule is symmetric and the positive charge is concentrated at each end. The center of the cluster is negatively charged, consistent with the notion that the rings are slightly conjugated and thus able to support an additional number of electrons.

Recently, we have carefully investigated the structure of Si_{45} cluster,^[13] which was experimentally found unreactive like Si_{39}^+ . It turns out that for this cluster a highly symmetric tetrahedral conformation exists, as illustrated in Fig. 4.4. This Si_{45} isomer is very stable, which implies large abundance. Moreover, its closed-shell electronic structure together with a high coordination number (more than four, resulting from 96 bonds) reduces the number of dangling bonds and leads to a large HOMO–LUMO gap. This explains the inertness in chemical

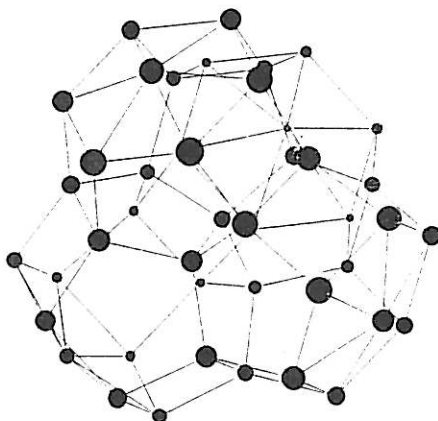


Figure 4.4: The tetrahedral model of Si_{45} from Ref. 13.

reactions very nicely. Finally, this conformation still accommodates the periodic reactivity pattern since it is possible to remove a “six-atom ring” from the tetrahedral Si_{45} resulting in a Si_{39} with the same “inert” features in the electronic structure.

A suggested conformation for Si_{39}^+ was shown in Fig. 4.2. As mentioned above, an additional structure may be derived by removing one of the six-membered rings from Si_{45} (Fig. 4.4), leaving the cluster with approximate triangular pyramidal geometry. We note that it is impossible to make a tetrahedral cluster from 39 atoms, and therefore any lack of reactivity observed in Si_{39}^+ must be due to some other pattern. The sequential removal of six-membered rings seems to be a logical guess, though the periodic reactivity pattern itself has been disputed recently.^[14]

4.5 Photofragmentation of Large Silicon Clusters

When Si_{60}^+ is fragmented with an ArF laser,^[15] almost all daughter fragments are in the 6–11 atom range. A small amount fragments by losing one atom, yielding an Si_{59}^+ cluster. The laser intensity dependence indicates that this may be a two-photon process. Of the smaller fragments, Si_{10}^+ is the most common. Because any charge will tend to form on the larger daughter, the absence of any larger charged clusters probably indicates that they are not formed at all, rather than being neutral and hence undetected. The experimenters report that other clusters also fragment into 10-atom pieces, where most notably Si_{10}^+ is almost exclusively the daughter fragment.

The obvious extension of our structural hypothesis outlined in the previous section is to suppose that Si_{60} consists of naphthalene-like planes, as illustrated in Fig. 4.5. Note that most atoms are tetra-coordinated, though those on the top and bottom have only three nearest neighbors, while those in the middle have five. The charge density within the planes reflects this: i.e., less coordinated atoms are more positively charged, whereas atoms in the middle

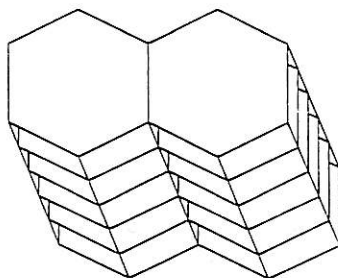


Figure 4.5: Proposed structure for the Si_{60} cluster, consisting of six stacked, 10-atom naphthalene-like rings.

of the cluster are more negative. The cohesion energy of the Si_{60} cluster is 3.6 eV/atom. This compares with a bulk cohesion energy of 4.6 eV/atom, and that of Si_{10} of about 3.9 eV/atom.^[2, 4, 8]

For clusters of intermediate size, the close-packed structure is not possible. Surface effects prevent the stability of the bulk lattice. So the cohesion energy is lower than either the 10-atom cluster or the bulk. For comparison, a similar analysis of Si_{60} , treating it as a bulk fragment arranged as spherically as possible to minimize surface energy, leads to a cohesion energy of only 3.2 eV/atom.

To compare with experimental fragmentation data, we have calculated the bond orders, which describe the strength of the bonds. In Fig. 4.6, the strongest bonds in a given plane are those marked $\circ$. This strength is due to the conjugated nature of the rings and the fact that the atoms in this group are no more than tetra-coordinated. The next-strongest bonds in the plane are those marked $\times$. These involve atoms with higher coordination numbers, requiring the sharing of electrons over additional bonds. (The average value of the (1–6) bond taken alone is 0.137 eV.) Finally, the weakest bonds occur between the planes, though not all are weak. Fragmentation of the cluster into 10-atom pieces is supported by this result.

In Fig. 4.6b we illustrate the average bond strength connecting each of the layers. The bond strength parallels the charge density distribution. The atoms at each end contribute electrons to their neighbors, and hence the bonds between the extreme planes and those just inside are strong. Similarly, the electron density is small in the center of the molecule, and so the bond between planes 3 and 4 is also strong. The weakest bonds are found between planes 2, 3 and 4, 5. Thus any fragmentation of the molecule is likely along these lines, which would result in three, 20-atom fragments.

We believe that the above accounts well for the photofragmentation data. Unfortunately, it fails to account for most other data. For example, the photofragmentation effect appears universal across the entire spectrum of silicon clusters, starting at 20 atoms. For any model to describe this, it must either be independent of the geometry of the parent cluster or suppose some consistent geometry. We are increasingly drawn toward the former premise. It seems improbable that clusters of such a wide size range would have similar geometries and yet be dramatically different in other respects. We therefore come reluctantly to the conclusion that

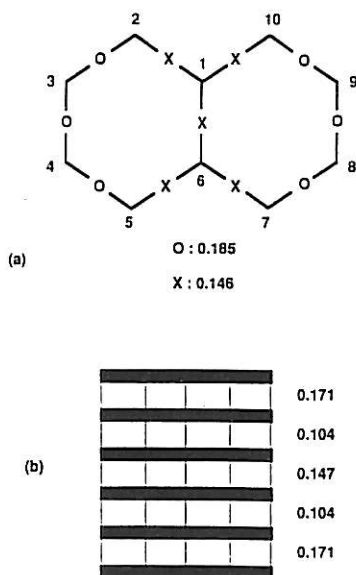


Figure 4.6: Average relative bond strength (bond order) for different categories of bonds within the proposed Si_{60} cluster: (a) within a plane; (b) between the planes. Each number is an average over 10 bonds.

the photofragmentation data yields little or no information about the structure of the parent ion.

Instead, in our opinion the photofragmentation data can be better explained by fragmentation kinetics and properties of daughter clusters. Very small clusters (three or four atoms) are too small to have large coordination numbers, and therefore are very reactive. Thus it may be that large clusters are broken apart into small pieces, but that these rapidly react with each other to form the highly-coordinated Si_{10} species. It is not therefore, that Si_{10} is exceptionally stable or that 10-atom fragments are hidden in every cluster, but rather that it is relatively unreactive.

4.6 Summary

TB calculations indicate that a distorted form of the bicapped tetragonal antiprism (DBTA) is the most stable structure for the Si_{10}^+ cluster. In addition, the HOMO–LUMO “band gap” and electron affinity data agree with experiment. We view this as a justification of the use of the TB model (optimized for the electronic structure of the bulk solid and for the bond length of the dimer), for medium-sized clusters. This is consistent with previous work, most notably with Ref.7, in which BTA is proposed as the stable configuration for Si_{10}^+ .

Reactivity is a property of the electronic structure, and thereby indirectly affects the con-

formation of the cluster. In this spirit we have presented some models for reactivity. Ultimately we prefer a model emphasizing the role of dangling bonds and the HOMO-LUMO gap over the role of the charge distribution.

The interesting photofragmentation data, which show that the daughter clusters are mainly 10-atom fragments, were explained by a new and alternative view. Because the relative abundance of 10-atom clusters is large, and independent of the parent clusters, we conclude that the fragmentation kinetics together with the inertness of the daughters, rather than the properties of the parents, may be the essential factor in the observed photofragmentation pattern. In other words, variously formed small pieces may rapidly react to form the unreactive Si_{10} clusters.

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