Transition from Metallic to Covalent Structures in Silicon Clusters

James R. Chelikowsky
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

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The structural properties of silicon clusters are examined to determine at what size clusters with covalentlike open structures become energetically more stable than those with metalliclike close-packed structures. By calculation of the total energy of diamond and face-centered cubic fragments as a function of the number of atoms, an estimate of the "critical" cluster size is made. The estimate is that for clusters of less than about 50 atoms, metallic structures are favored over covalent structures, with the inequality reversed for more than 50 atoms. This result agrees well with recent observations on the relative stability of $\mathrm{Si}_n{}^+$.

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Suppose we imagine building up an infinite crystal by adding one atom at a time. Small crystalline fragments could have a different, ground-state structure, or bonding configuration, from that of the bulk crystal of the same material. For example, in the case of a material like silicon, the most stable structures of small fragments or clusters of less than ten atoms are clearly of a metallic nature, at least from theoretical studies.[1-6] However, the bulk crystal of silicon is clearly covalent. Thus, it would seem that at some point with increasing cluster size a "first-order" transition must occur from clusters with a metalliclike structure to those of a covalentlike structure. Of course, there is no reason to believe that this transition need be abrupt; however, it is clear that some sort of crossover behavior should occur and that this transition is of fundamental interest in the understanding of the progression from atomic to solid-state physics.

Crude estimates have been made for the cluster size at which this structural transition occurs, and they are quite disparate. One estimate[1] based upon pseudopotential-local-density techniques for small clusters, i.e., ten atoms or less, has yielded an estimate of over 4000 atoms as the critical cluster size. Another estimate[5] has been obtained from empirical valence force-field calculations[5-13] and yields a cluster size closer to 200-300 atoms. The two estimates may differ because of the rather different approximations involved. In the pseudopotential case, the estimate is based on a rather severe extrapolation from ten atoms to thousands of atoms; however, the validity of the calculation for accurate structural energies for small clusters is not questioned. The classical valence force-field approach treats much larger clusters, but the accuracy of this approach is not so great as the pseudopotential method.

Here I intend to make a comparison by considering a method which allows us to treat much larger clusters at small cost in accuracy.[14] This approach combines a sum of eigenvalues from a single-particle Schrödinger equation with a classical valence force field.[1,14,15] The general form of this expression is given as

$$E(\{\mathbf{R}_i\}) = \textstyle\sum_i E_i + E_{2B} + E_{3B} + U\sum_i (q_0 - q_i)^2, \qquad (1)$$

where

$$E_{2B} = \sum_{i<j} e_{2B}(R_{ij}),$$

$$e_{2B}(R_{ij}) = A_0 \exp[-2\beta(R_{ij} - R_0)] \times \{1 - 2\exp[-\beta(R_0 - R_{ij})]\} - \textstyle\sum_i E_i,$$

and

$$E_{3B} = B_0 \sum_{i<j<k} \cos(\theta_{ijk} - \theta_0), \quad 0° \le \theta_{ijk} \le 180°.$$

The first term in Eq. (1) is a sum over the eigenvalues obtained from semiempirical pseudopotentials and a Gaussian basis as outlined elsewhere.[14,16] The second term, E_{2B}, is a two-body interaction. This term contains the parameters A_0, β, and R_0 which are fitted to the silicon dimer with Eq. (1), i.e., $e_{2B}(R) + \sum_i E_i$ where R is the interatomic distance. By construction, the experimental values of the binding energy, bond length, and vibrational frequency for the silicon dimer will be exactly reproduced (see Ref. 1). The three-body term, E_{3B}, is similar to one used elsewhere.[5] θ_{ijk} is the angle formed by vectors from atom i to the nearest-neighbor atoms j and k (I cut this term off for distances greater than 10% of the crystalline bond length). B_0 and θ_0 are determined from the trimer and larger clusters; effectively these parameters are fitted to reproduce more rigorous calculations[1-4] for small n. This term is not allowed to grow without bound as the cluster size increases. E_{3B} is saturated so that each term is less than some maximum value, i.e., $B_0 \cos(\theta_{ijk} - \theta_0) < E_{\text{bond}}$ where the bond energy is taken to be $E_{\text{bond}} = -2.5$ eV. Finally, with respect to Eq. (1), we have a term which accounts for the lack of a self-consistent solution. U is adjusted so that the silicon trimer dissociates properly in terms of the total energies known for the mononer and the dimer. q_0 is taken as 4 to suppress ionic configurations. The values for the various parameters in Eq. (1) are summarized in Table I.

This procedure can be compared with several classical models and more sophisticated quantum mechanical results.[1-4] This form contains quantum mechanical effects via the first term in Eq. (1), yet it is far easier to evaluate than a full self-consistent-field solution of the electronic structure problem. The number of basis functions which we use is minimal. Typically, eight Gaussians which have the form $\{1,x,y,z\}\exp(-\beta r^2)$ with two sets of β's, i.e., two s- and six p-symmetry Gaussians with $\beta=0.25$ and 1.0, are used[16] so that for the largest cluster considered here, the matrix size was on the order of 400×400. The chief deficiency of this method compared with a fully self-consistent solution is its failure to account for charge transfer properly and the need to parametrize significant interactions. Compared with other tight-binding models or linear combination of atomiclike orbitals (LCAO) methods, it has the advantage of not employing bond counting terms,[1] nor do we have to scale matrix elements as we calculate directly the required matrix elements.[1,15] With respect to valence force-field descriptions, we have the advantage of including some quantum effects, e.g., hybridization and coordination effects, which are difficult to include with classical valence force fields. Most notably those classical approaches which fail to account for incomplete coordination have been unreliable for the structural energies of clusters and interstitial defects.[5,7]

In determining the structural properties of Si_n, I adjusted the parameters in Table I to fit the pseudopotential-local-density calculation of Tomanek and Schlüter.[1] A comparison is given in Fig. 1. Over all the agreement is quite good; however, notable disagreements occur at $n=2$ and to a lesser extent at $n=8$. My dimer is fitted to experiment; the pseudopotential calculation is not. Another point to emphasize is the excellent agreement of my semiempirical calculation of the energy of the $n=6$ and 10 structures both for the lowest-energy structures (which are metalliclike) and for the diamond-structure fragments corresponding to a sixfold ring and an open cage structure.[1] As I intend to compare the diamond fragments with metallic structures, it is important to verify that I obtain structural energies in regimes which we know to be correct.

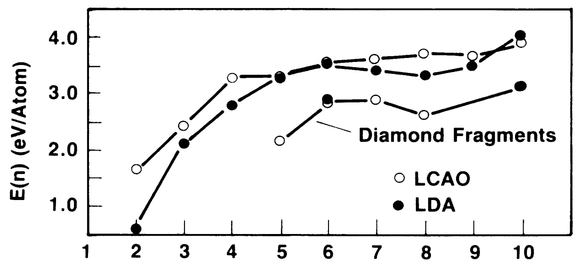

FIG. 1. Binding energy in electronvolts of silicon clusters as a function of cluster size. The curve labeled "diamond fragments" are for clusters which correspond to fragments of the diamond crystal. Results from two calculations are indicated. Open circles are from the present work (LCAO) and filled circles are from Ref. 1 (LDA).

TABLE I. Parameters for evaluation of the total energy via Eq. (1); also see Ref. 14.

A_0	3.26 eV
β	0.579 a.u.$^{-1}$
R_0	4.25 a.u.
B_0	0.725 eV
θ_0	90°
U	0.9 eV

My estimate of the structural differences between the diamond and close-packed structures is performed for $n \rightarrow \infty$ by consideration of fcc fragments and diamond fragments and by calculation of the structural energy for large clusters, i.e., large being on the order of $\simeq 40$ atoms. I then fit a functional behavior of the form

$$E(n)/n = E_b(1 - a/n^{1/3} - b/n^{2/3}), \tag{2}$$

where $E_b = E(n)/n$ in the limit $n \rightarrow \infty$, i.e., the binding energy for the solid state. $E_b(\mathrm{dia})$ and $E_b(\mathrm{fcc})$ are fixed by experiment[17] and theory,[18] respectively. I fixed the parameters (a,b) for both the diamond and fcc fragments by fitting to the structural energies as a function of n. (a,b) may be interpreted as decreasing the binding energy of the solid by the creation of surface and edge atoms. Initially for small n, the bulk binding energy is expected to be dramatically reduced and by different amounts for the two types of structures. Metallic structures with their greater coordination are able to support more readily the presence of surfaces, whereas open structures such as the diamond structure are not. My extrapolation of $E(n)/n$ is very similar to the work of

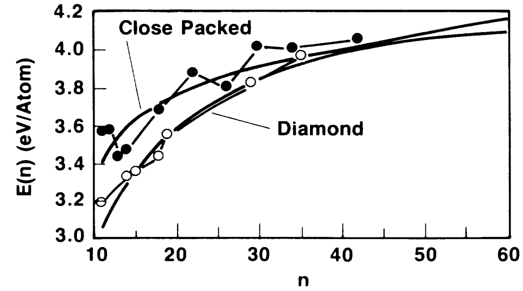

FIG. 2. Binding energy of large silicon clusters as a function of size. The open circles correspond to fragments of a diamond crystal; the filled circles correspond to fragments of an fcc crystal. The solid curves are after Eq. (2); see text.

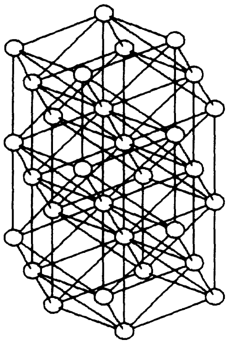

FIG. 3. Crystal fragment of the fcc lattice consisting of 30 Si atoms.

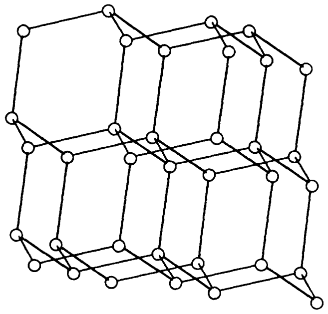

FIG. 4. Crystal fragment of a diamond lattice consisting of 35 Si atoms.

Tomanek and Schlüter.[1] However, they have not included a term corresponding to "edge" atoms in their limiting case. The omission of this term and the implicit assumption of a large n leads to an estimate of the critical value of n_c, i.e., $E_{\text{dia}}(n_c) = E_{\text{fcc}}(n_c)$, of $n_c \approx 4000$ atoms, a value which seems intuitively too large. Second, the procedure they use for determining the parameters a(dia) and a(fcc) is to consider only the structures at $n = 10$ for the diamond and fcc fragments and to assume that no bulklike contributions exist for the total energy.

I present the structural energy as a function of n for diamond and fcc fragments in Fig. 2. The structures I used for the diamond fragments come from the work of Saito, Ohnishi, and Sugano.[6] They assumed perfect sp^3 bonding and determined the optimal structure for diamond fragments via a valence force-field calculation. While I do not feel that this procedure is accurate in terms of comparing different types of structural configurations, I feel that for the restricted set of diamondlike structures it is reliable. Saito, Ohnishi, and Sugano[6] do not give structures for $n > 20$ so here I have simply taken diamond fragments formed by taking nearest-neighboring shells; e.g., if we include fifth-nearest neighbors to a Si atom in the diamond lattice, this would generate a cluster of 29 atoms. For the close-packed structures, I have taken an fcc fragment of ten atoms and considered symmetric structures built up from this core. In Figs. 3 and 4 are displayed typical fragments for fcc and diamond structures which I considered.

From Fig. 2, the crossover point at which diamond and fcc silicon fragments are comparable in energy is about 40–50 atoms. Clearly, this is only an estimate. I have not fully optimized the structure in the fcc or diamond fragments. However, I emphasize several points here. First, the diamond fragments are expected to have greater relaxation, or reconstruction energies, than the fcc clusters. This effect would tend to push the crossover point to lower values of n. Second, in Eq. (2) I fixed E_b from a knowledge of the bulk Si energies. However, if E_b is allowed to be determined by an extrapolation from the cluster energies for $n < 40$, reasonable values are obtained for E_b, i.e., within $\pm 10\%$ of the known values. Third, by consideration of regular polyhedra, the "edge" sites of the cluster all have similar symmetry. This mitigates variations with increasing cluster size in my extrapolation. Finally, even if I have not achieved a highly accurate energy for the fcc and diamond fragments, I do not believe that my estimate would be off by more than a few tenths of an electronvolt, which would bracket the crossover point between 20 and 100 atoms. Thus, I find a much lower transition point than what I believe are less reliable estimates.

One can also compare to the recent experimental work of Smalley and co-workers[19] which lends support to my estimate. Smalley and co-workers find for clusters of Si_n^+ undergoing reaction with NH_3 that dramatic oscillations in reactivity occur with n. They observe that for clusters above $n = 47$ the oscillations subsided and a slow monotonic increase in activity occurs. Phillips[20] has suggested that the periodicity can be explained by a cylindrical morphology for $n \leq 47$. I have not examined charged clusters, but for neutral clusters I find that cylindrical structures can be competitive with metallic structures, at least for $n \leq 24$, supporting Phillip's model. Moreover, the lack of oscillations for $n \geq 47$ is certainly suggestive of a morphology change occurring near $n = 50$, which is consistent with this work.

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