Empirical-potential studies on the structural properties of small silicon clusters

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An empirical potential for silicon has been developed. Molecular-dynamics methods and simulated annealing techniques have been used to study the structural properties of small silicon clusters with this potential. A detailed comparison has been made between our results and those obtained from other theoretical methods. It is found that our results are close to those obtained using *ab initio* techniques. A significant improvement over other empirical potentials has been made.

Atomic clusters constitute a state of matter intermediate between the atom and the solid. These finite systems exhibit properties observed in atomic or molecular physics on the one hand, and in condensed-matter physics on the other hand. The extensive understanding of structures and properties of small clusters can help to explain phenomena such as crystal growth, catalysis, surface reconstruction, etc.

There have been a few attempts to study theoretically the equilibrium structures of small silicon clusters. Raghavachari and Logovinsky[1] have optimized small silicon clusters within the given symmetry constraints with several basis sets at the Hartree-Fock level of theory. The molecular-orbital method[2] and the combined density-functional–tight-binding method[3] have also been used to investigate small silicon clusters. These kinds of methods can only be used to search for the lowest-energy state by exploration of a severely limited number of atomic configurations. In fact, the molecular-dynamics method is a more efficient way to search for the ground state and is also suitable for the study of the thermal behavior of clusters since it exploits the techniques of statistical mechanics to explore fractions of atomic configuration space. A few authors have tried to calculate structural properties of Si_n by the molecular-dynamics methods in conjunction with the use of empirical potentials.[4] Unfortunately, the results are in disagreement with the results of the configuration-interaction (CI) calculations.[1] This clearly suggests that the empirical potential fitted from the bulk-silicon phase is not suitable for silicon clusters.

It is believed that the *ab initio* molecular dynamics with local-density approximation (LDA) with (Ref. 5) can be a good candidate to study the structural properties of clusters. Unfortunately, because the *ab initio* molecular-dynamics relaxes ions and electrons simultaneously, the calculation is very intensive. With today's computers, it is difficult to apply this method, with reasonable accuracy, to study the properties of clusters consisting of a few tens of atoms. An empirical-potential model, which describes the interaction between atoms in the cluster, has the advantage that the dynamical behavior of very large clusters can be studied. In other words, numerical experiments can be conducted on simulated collisions between clusters and their fragmentation at different temperatures. Thus, development of an empirical potential for studying clusters is very useful and necessary.

A few analytical model potentials for silicon have been proposed in the last decade. Pearson *et al.*[6] developed a potential with a long-range two-body and a nonseparable three-body term. Stillinger and Weber[7] have developed a potential with two- and three-body terms which are short ranged. Tersoff[8] has also proposed a potential with two-body terms only. Use of these kinds of model potentials has resulted in the reproduction of some bulk and surface properties of crystal,[9] but it turns out that they are less successful in the study of the structural properties of small silicon clusters. Andreoni and Pastore[10] have calculated the properties of some silicon clusters by using model potentials proposed by Tersoff and Chelikowsky and Phillips[8,11] and compared them with results from *ab initio* molecular-dynamics calculations (LDA) in which the forces on atoms are calculated simultaneously from the ground state of the electrons. They found that agreement between the LDA and empirical-potential calculations is quite poor, and they concluded that the model potentials obtained by considering the bulk phases do not reproduce good results for small clusters. So, for the purpose of studying small clusters by using empirical potentials, it is necessary to take into account not only the data from bulk phases, but also some data from clusters. In this paper, based on the Stillinger-Weber (SW) potential, we form a model potential for silicon by fitting data from small clusters and perfect crystalline phases, and then apply this new potential to study small silicon clusters. We find that our results on structural properties of silicon clusters are in good agreement with *ab initio* calculations.

In the SW model potential[7] for silicon, the two-body term has the following form:

$$V_2(r_{ij})=A(Br_{ij}^{p}-r_{ij}^{-q})\exp[(r_{ij}-a)^{-1}] ,$$

and the three-body term is taken to be

$$V_3(r_i,r_j,r_k)=h(r_{ji},r_{ki})+h(r_{kj},r_{ij})+h(r_{ik},r_{jk})$$

with

$$h(r_{ji},r_{ki})=\lambda\exp\{\gamma[(r_{ji}-a)^{-1}+(r_{ki}-a)^{-1}]\}\times(\cos\theta_{jik}+\tfrac{1}{3})^2 ,$$

where $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$, and θ_{jik} as the angle subtended by r_{ji} and r_{ki} with the vertex at the ith site. A, B, p, q, a, λ, and γ are parameters determined by fitting to the bulk-phase data. The three-body term always increases the total energy, which becomes zero only when the angle is the perfect tetrahedron angle θ_t ($\cos\theta_t=-\frac{1}{3}$). This model potential is short ranged, and is set to zero for r_{ij} greater than or equal to a convenient cutoff a; its derivative also approaches zero continuously as r_{ij} nears the cutoff a. Bulk properties, such as the cohesive energy for the diamond lattice, the melting temperature of diamond, and the nearest-neighbor distance, determined from this potential, are in good agreement with experimental values. A few authors have studied the structural properties of small silicon clusters, up to 32 atoms, with this potential;[4] the resulting structures are ringlike, contrary to compact structures obtained from *ab initio* calculations.

For a better description of small silicon clusters, Mistriotis, Flytzanis, and Farantos[12] have tried to include a four-body term in the SW model potential. With the four-body term, they have calculated the structures of a few silicon clusters. When $n\geq 7$, the clusters are more compact than those from the SW potential, but only a limited qualitative agreement with results of LDA was obtained. Moreover, including the four-body term costs a lot of computer time, and prohibits the application to the bigger clusters.

The potential that we are trying to develop should retain the advantages of the SW model and also give the correct ground state for small silicon clusters. The modifications we made on the SW potential are guided by the following physical considerations. Comparing the bond-angle distributions of silicon clusters obtained from SW potentials and LDA calculations,[9,13] we find that in the results of the LDA, there is a large peak at 60° and a smaller peak at about 100°, but in the results of the SW potential, there is only one broad peak at 90°. In the bond-angle distribution of liquid and amorphous silicon, there is also a big peak at 60°.[14] We need the new potential to have a lower energy for a small angle at $\theta\sim 60°$. This could not be described by the SW three-body term $(\cos\theta+\frac{1}{3})^2$ (shown in Fig. 1), since the three-body term of SW has a large value at $\theta\sim 60°$. Therefore, we choose a more complicated function $\lambda_1(\cos\theta+\frac{1}{3})^2[(\cos\theta+c_0)^2+c_1]$ as the angular part of the new potential,

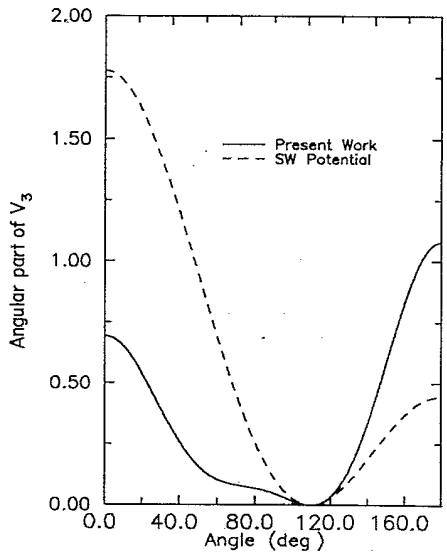

FIG. 1. Angular part of the three-body term of the SW potential and of the new potential.

where c_0 and c_1 are new parameters which are determined by fitting to the phase diagram of bulk silicon and making the structures of small clusters close to the results of CI and LDA calculations. We have used the same values for A, B, p, q, a, and γ as in the SW potential; only λ_1, c_0, and c_1 are adjusted to fit the bulk phase and cluster data. The angular part is shown in Fig. 1. We see that the main change from the SW potential is that the small-angle part is lowered. The lattice constants, bulk moduli, and total energies for various phases of silicon obtained using the present potential are given in Table I. For comparison, results from the SW potential and data from the density-functional theory (DFT) are also shown. Because the energy per atom calculated with the SW potential for diamond structure is -4.13 eV, we scaled the energy unit of the SW potential from 2.17 to 2.32 eV in order to get a cohesive energy of -4.63 eV/atom for diamond in agreement with experiment. We can see that the diamond structure has the lowest energy with this new potential. The total energies of other phases are reason-

TABLE I. Some equilibrium properties of bulk silicon; a_0 (Å) is the lattice constant and B (Mbars) is the bulk modulus.

	Present calculation			SW			DFT		
Phases	a_0	E_0	B	a_0	E_0	B	a_0	E_0	B
diamond	5.43	−4.63	1.08	5.43	−4.63	1.08	5.45	−4.67	0.98[a]
simple cubic	2.76	−3.88	2.43	2.61	−4.32	2.07	2.53	−4.32	
bcc	3.22	−4.31	6.34	3.25	−4.30	7.71	3.09	−4.15	
β-tin	4.95	−4.10	4.54	4.97	−4.42	4.43	4.82	−4.40	1.19[b]
simple hexagonal	2.76	−4.05	3.86	2.83	−4.20	3.60	2.64	−4.38	1.06[b]
fcc	4.11	−4.50	7.60	4.15	−4.21	7.70	3.87	−4.10	

[a]M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).
[b]R. J. Needs and R. M. Martin, Phys. Rev. B **29**, 5390 (1984).

ably close. The lattice constant and bulk modulus are also very similar to results of the SW potential.

With this new potential, the structural properties of small silicon clusters have been studied by the molecular-dynamics method. To obtain the equilibrium structure at zero temperature, the simulated annealing technique is also employed. For comparison with results of other methods, some atomic configurations with high symmetry are relaxed by the steepest descent method.

In the Si_4 cluster, we find that a tetrahedron and a flat rhombus have almost the same energies, instead of a square obtained from the SW potential. CI and LDA calculations predicted that the equilibrium structure of Si_4 is a flat rhombus. The square structure, which is the lowest-energy structure in the SW potential, is no longer stable. The ground-state configuration of Si_5 is a trigonal bipyramid, consisting of an almost equilateral triangle with one atom above the plane of triangle and one atom below. CI and LDA calculations yield exactly the same structure. The lowest-energy structure of Si_5 from the SW potential is a pentagon. We find that the pentagon structure is metastable. The energy of the pentagon is 0.33 eV/atom higher and the pyramid is not stable in our new potential.

The equilibrium structure of Si_6 is found to be an octahedron. This agrees with what is found by combined density-functional–tight-binding methods, and also the LDA. Raghavachari and Logovinsky,[1] however, found the ground-state structure of Si_6 to be an edge-capped trigonal bipyramid. The total energy difference between the face-capped trigonal bipyramid and the edge-capped trigonal bipyramid is extremely small ($\sim$0.10 eV/atom), and these two structures are more or less isoenergetic. In our calculation, a capped distorted trigonal bipyramid is really a stable structure with a total energy only 0.04 eV/atom higher than that of the octahedron. The LDA has also predicted that the capped trigonal bipyramid and octahedron structures are quasidegenerate isomers ($\sim$0.01 eV/atom). In particular, the trigonal prism structure, predicted to be the lowest-energy structure of Si_6 by the SW potential, is no longer stable in this potential. This trigonal prism structure is also not a low-energy structure, either in CI or in LDA calculations.

The ground-state structure for Si_7 is a bicapped pentagon, consisting of a pentagon capped on the top and bottom. This structure is exactly that predicted by CI and LDA calculations. The capped octahedron is an iosmer of the lowest-energy structure of the bicapped pentagon with only 0.05 eV/atom higher energy.

In the case of the eight-atom cluster, the lowest-energy structure has a C_{2h} symmetry. The results of CI calculations indicate a similar structure for Si_8 upon distortion of the two-capped octahedron. We find that a transcapped octahedron is favored over the other high-symmetry structures; its total energy is only 0.05 eV/atom less than the lowest-energy structure, and this transcapped structure is a little bit more stable (0.005 eV/atom) than the skewed-capped octahedron. In LDA results, the transcapped octahedron is the lowest-energy structure and the skewed-capped octahedron is only 0.36 eV higher. We find that the antiprism and bicapped trigonal prism for Si_8, which have very high energy in CI calculations, are also not stable structures in our new potential. It is interesting to note that the capped octahedron can be a metastable minimum in other empirical potentials, but previously proposed empirical potentials cannot describe the relative energy position between the transcapped and skewed-capped octahedrons; for instance, in the potentials of Tersoff and Chelikowsky, the transcapped octahedron is a metastable structure, its energy is much higher than the energy of the most stable structure, and the skewed-capped octahedron is not stable. But we find that the capped octahedron is very close to the ground state and, importantly, the correct relative energy position has been obtained by using the new potential.

In the Si_9 cluster, we find the squashed tricapped trigonal prism is the lowest-energy structure and the tricapped octahedron structure is about 0.09 eV/atom less stable than the tricapped trigonal prism. In the CI calculations, the lowest-energy structure is the tricapped octahedron and the distorted tricapped trigonal prism is almost isoenergetic with the tricapped octahedron.

In our simulated annealing studying of the Si_{10} cluster, we found that a few geometries appeared quite often. A tetracapped trigonal prism and a bicapped tetragonal antiprism have almost the same energies. The tetracapped octahedron is about 0.10 eV/atom higher. In the LDA calculation, the tetracapped trigonal prism has the lowest energy, the tetracapped octahedron, bicapped tetragonal antiprism, and planar zig-zag chain lie a little bit higher in energy. In the CI calculations, the tetracapped trigonal prism and tetracapped octahedron have almost the same energy, the tetragonal antiprism is less stable than the tetracapped trigonal prism and the tetracapped octahedron. We have also done preliminary calculations for bigger clusters; we find that the structure is different from icosahedronlike structures obtained from the empirical potential of Chelikowsky.

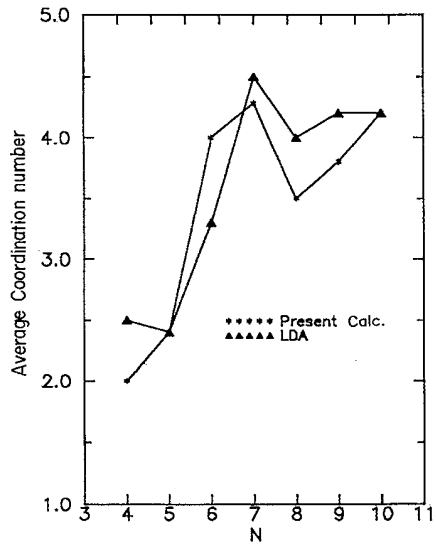

FIG. 2. Size dependence of the average coordination number.

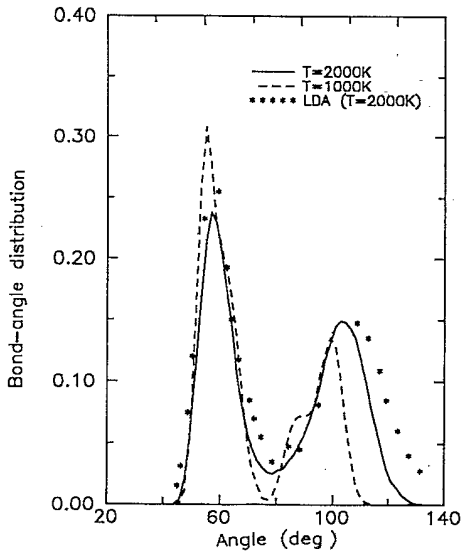

FIG. 3. Bond-angle distribution for the Si_{10} cluster with $R_{cut}=5.0$ a.u.

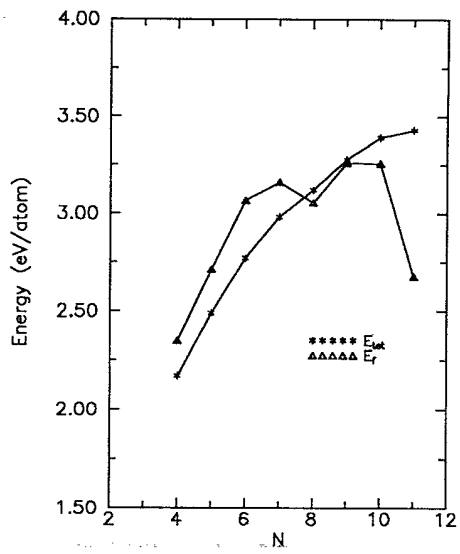

FIG. 4. Size dependence of the total and fragmentation energies.

For a more detailed comparison of the results of the present calculation with LDA, we have calculated the average coordination number of small silicon clusters, and the results are shown in Fig. 2. From the figure, we can see that the obtained average coordination number, with the same $R_{cut}=5.0$ a.u. as in the LDA, is quite close to the results predicted by the LDA method. But other empirical-potential results are not in agreement with LDA results.[10] We have also checked the dynamical properties of small silicon clusters in our new potential and compared them with LDA results.[13] In Fig. 3, the bond-angle distributions of the Si_{10} cluster at $T\sim2000$ and 1000 K have been presented and the results from the LDA are also replotted. We can see that the agreement is quite good. On the other hand, the bond-angle distribution from the SW potential contains less structure, and it is not similar to that obtained with LDA. The bond-angle distributions obtained by the methods of Tersoff and Chelikowsky are also different from those calculated using LDA methods; the first peak is too sharp and there is more structure at large angle. In Fig. 4, the total energy for silicon clusters and the size dependence of fragmentation energy are shown. Similar to LDA results, our potential predicts Si_7 and Si_{10} to be the most stable clusters.

As discussed above, the alternative empirical silicon potential, based not only on the data from crystalline phases, but also from the amorphous and liquid phases, can be used to obtain structural properties of small silicon clusters which are close to CI and LDA results. The ringlike structures from the SW potential have completely disappeared, although only the angular part of the SW potential is changed. Much improvement is achieved over the previously proposed empirical potentials.

In conclusion, it is shown that the modified SW potential can be used to predict the structure of small silicon clusters. The locations of the local minima are much better than those obtained with other empirical potentials.

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