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STRUCTURES OF Si AND Ge CLUSTERS UNDER MODIFIED STILLINGER-WEBER POTENTIAL

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Structural behaviors of silicon and germanium clusters under the recently proposed modified Stillinger-Weber (SW) potential have been studied by molecular dynamics method along with the conjugate-gradient optimization. Since the SW potentials have been derived from the properties of bulk materials, it gives relatively large discrepancy when the cluster number is small, e. g. $n=3$ and 4. When $n>4$, the ground-state structures under the modified SW potential are close to that from the first-principle calculation. The binding energies are also improved under the modified SW potential. These results may be attributed to the relative enhancement of the two-body term over the three-body term in the modified SW potential, which leads to structures with a preferential coordination number 4. Structural behaviors of germanium clusters are similar to those of silicon.

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I. INTRODUCTION

Clusters, as the primary stage forming bulk materials from atoms, have their own distinct structual properties. For example, the ratio of surface atoms to bulk atoms is larger than that of bulk materials; the structures of clusters change with the number of atoms in the cluster; structures with specific stability appear at certain cluster numbers, the so-called "magic number"[1], etc. Theoretical studies have been active in recent years, including *ab inito* type calculations based on quantum molecular orbital method or local density approximation[2-6], model potential calculation[7-9], and semiempirical tight-bonding calculation[10, 11]. The results of *ab inito* type calculations are believed to be more reliable, but the calculation work involved is enormous. The model potential method with its empirical analytic potential form is very efficient for conducting various kinds of calculations; however, the correctness of the results depends upon comparison with experiments or *ab inito* type calculations.

The model potential method has been used with great success in rare-gas system with additive two-body potential, e.g. the Lennard-Jones potential[12]. Since the two-body potential leads to close-packed structures, it is not adequate for describing covalent system with strong directional bonding and valence saturation. It is necessary to include three-body and other many-body interactions in calculation. Several such model potentials have been proposed[7, 13-15] for silicon, e.g. by fitting experimental data, such as cohesion energy, lat-

tice constants, and elastic constants, etc. The Stillinger-Weber (SW) potential is one of the successful model potentials which has been extensively studied for many purposes[7, 16 – 18]. Since the original SW potential did not give satisfactory lattice dynamics behavior[19], Zi Jian *et al.*[20] have recently modified the potential based on fitting to lattice dynamics data. In this paper, we report the structural behaviors of Si and Ge clusters under the modified SW potential, which are studied by molecular dynamics technique along with optimization.

II. METHOD

A. Modified Stillinger-Weber potential

The modified SW potential keeps the form of the original SW potential, i.e.

$$V=\sum_{\substack{i,j\\ i<j}} V_2(r_{i,j})+\sum_{\substack{i,j,k\\ i<j<k}} V_3(i,j,k), \tag{1}$$

where

$$V_2(r_{i,j})=\varepsilon f_2(r_{i,j}/\sigma), \tag{2}$$

$$f_2(r)=A(Br^{-p}-r^{-q})\exp[\delta/(r-a)], \quad \text{for } r<a$$
$$=0, \qquad \text{for } r\geqslant a, \tag{3}$$

$$V(r_i,\ r_j,\ r_k)=\varepsilon f_3(r_i/\sigma,\ r_j/\sigma,\ r_k/\sigma), \tag{4}$$

$$f_3(r_i,\ r_j,\ r_k)=h(r_{ij},\ r_{ik},\ \theta_{jik})+h(r_{ij},\ r_{kj},\ \theta_{ijk})+h(r_{ik},\ r_{jk},\ \theta_{ikj}), \tag{5}$$

$$h(r_{ij},\ r_{ik},\theta_{jik})=\lambda\exp[\gamma(r_{ij}-a)^{-1}+\gamma(r_{ik}-a)^{-1}](\cos\theta_{jik}+1/3)^2, \text{ for } r_{ij}<a \text{ and } r_{ik}<a$$
$$=0, \qquad \text{for } r_{ij}\geqslant a \text{ or } r_{ik}\geqslant a. \tag{6}$$

The parameters ε and σ reduce the units of energy and length, and they are so chosen as to give the correct atomization energy and density of the crystalline silicon at zero temperature and pressure. Parameter a is the cutoff distance which makes the potential and its derivative approach zero continuously as the distance r is close to a. The magnitude of a is set to keep only the nearest-neighbor interaction in diamond silicon. The parameters ε, σ, γ, p, q, and a are kept unchanged in the modified SW potential. The parameter δ is the additional parameter introduced, while in the original SW potential it is equal to 1. After fitting to the lattice dynamics data, the parameters are modified, as shown in Table 1.

Table 1. Parameters of the modified SW potential.

	Si	Ge
ε	2.17	1.93
σ	2.0951	2.181
A	6.865464121	6.768571075
B	0.611445848	0.616574299
λ	9.11	8.37
δ	0.9757	0.9625
	p=4, q=0, γ=1.2,	a=1.8

B. Molecular dynamics and optimization

First, we describe the method briefly. The cluster configuration changes in the way of molecular dynamics, i.e. every atom follows a trajectory in real space calculated according to Newton's equation of motion. The instantaneous atomic configurations are periodically mapped onto their local minima of the potential energy surface by optimization. The ground-state structure (the global minimum) is then the lowest of all the local minima.

Newton's equation of motion is integrated by Beeman's algorithm, that is

$$x(t+\mathrm{d}t)=x(t)+v(t)\mathrm{d}t+[4a(t)-a(t-\mathrm{d}t)]\mathrm{d}t^2/6 \tag{7}$$

and

$$v(t+\mathrm{d}t)=v(t)+[2a(t+\mathrm{d}t)+5a(t)-a(t-\mathrm{d}t)]\mathrm{d}t/6. \tag{8}$$

The time step $\mathrm{d}t$ is in unit of $\sigma(m/\varepsilon)^{1/2}=7.6\times10^{-14}$ s and the magnitude of it is chosen between 0.01 and 0.1. The acceleration $a(t)$ is obtained as the minus derivation of the potential in the reduced unit. Initial positions and velocities are chosen randomly, only they are set to ensure the linear and angular momenta equal to zero. The temperature is set by scaling the velocity.

Optimization is conducted every 50 or 100 time steps, and Flectcher-Reeves' conjugate-gradient optimization method[21] is used. At low temperature and small $\mathrm{d}t$, the configuration evolves slowly or oscillates about a local minimum of potential energy surface, the optimization results may then be unchanged. At a sufficiently high temperature, fragmentation to a few smaller clusters may occurs. Since our goal is to find the ground-state structure or the lowest of all the local minima, to let cluster undergo as many local minima as possible in a limited computer time (typically 50000 time steps), an adequate temperature and time step $\mathrm{d}t$ are chosen by trial and error method before running.

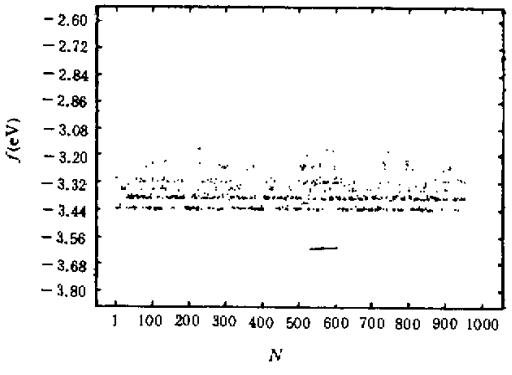

Fig. 1. Typical optimization records along with molecular dynamics simulation for Si_8. Successive point has a delay of 50 time steps.

Figure 1 is a typical trajectory of the optimized energy per atom during a molecular dynamics run for Si_8. From such records, different local minima corresponding to stable or metastable structures of the system can be identified and the frequency of visiting a certain structure under the given condition can also be extracted.

III. RESULTS AND DISCUSSION

Figure 2 displays the ground-state structures of Si under the modified SW potential, and for comparison the results of the original SW potential and Raghavachari and Rohlfing (RR)'s molecular orbital results[3] are also presented. Table 2 lists the corresponding binding energy per atom of the structure. The structural behaviors for Si and Ge are qualitatively the same. In the following, only the behaviors for Si are discussed.

Table 2. *Binding energies per atom for Si and Ge clusters under modified SW potential in unit of eV.*

n	2	3	4	5	6	7	8	9	10
Si	1.08	1.83	2.35	2.72	3.06	3.28	3.44	3.59	3.65
Ge	0.96	1.48	2.15	2.49	2.81	3.02	3.16	3.29	3.36

For the dimer Si_2, the only possible structure is trivially linear. The experimental bond length and energy per atom are 0.244 nm and 1.62 eV, respectively. The results of modified SW potential are 0.236 nm and 1.08 eV, which are almost the same as the original SW potential.

For Si_3, the ground-state structure is an equilateral triangle, which is the same as that under the original SW potential, though there is difference in bond length and energy as in the case of $n=2$. In addition, there is also a metastable isosceles triangle with an apex bond angle of 109.4° (with a binding energy per atom 1.44 eV). This angle is inherent in the three-body term of SW potential from the consideration of diamond structure of Si, i.e. this angle makes the contribution of the positive three-body term of SW potential in diamond structure Si equal to zero. The ground-state structure of RR is an isosceles triangle with an apex bond angle of 77.8°.

For Si_4, the ground-state structure under the modified SW potential is a tetrahedron, while that of the original SW potential is a square and that of RR is a rhombus with an apex angle 117°. A rhombus with an apex angle 114° under modified SW potential is metastable with a higher energy −2.23 eV. Since the parameters in the potential are derived from bulk-material property, one cannot expect it to describe the small cluster as well. The discrepancies with the believed more exact quantum mechanical results imply that some fundamental structural law in building the small cluster have been overlooked in the model potential.

For Si_5, the ground-state structure under the modified SW potential is a trigonal bipyramid. The side of the base triangle is 0.27 nm. The bond length connecting the apex atom to that lying on the base plane is 0.251 nm. The result of RR is a similar structure with the corresponding bond lengths 0.326 and 0.234 nm. So, it looks more compressed.

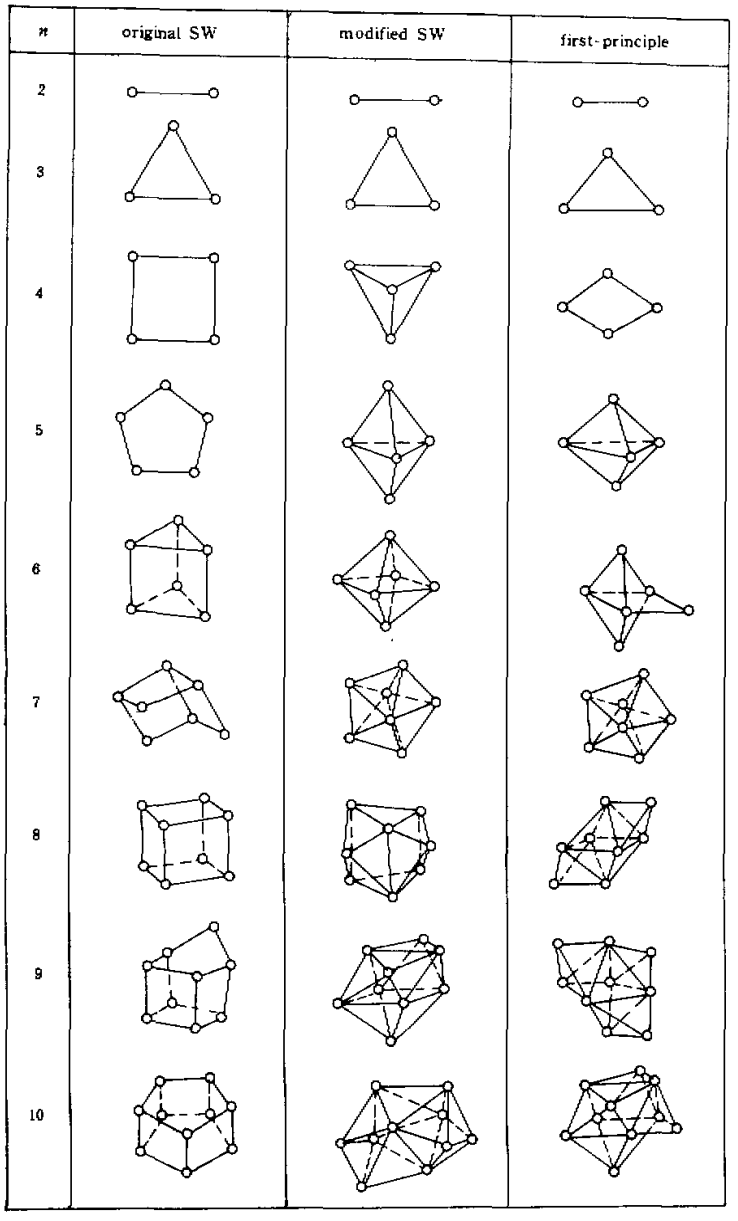

Fig. 2. Ground-state structures of Si cluster with $n=2-10$ under modified SW potential. For comparison, the results of original SW potential and first principle calculation of RR[7] for $n=2-9$ and Ballone *et al.*[5] for $n=10$ are also presented.

The ground-state structure under the original SW potential is a pentagon.

For Si_6, the ground-state structure under the modified SW potential is an octahedron with bond length 0.255 nm. The result of RR may be considered as a distorted octahedron with two apex atoms biased to one of the base atoms. However, the local density approximation result of Ref.[6] gives the ground-state structure as a compressed octahedron. The disagreement in different *ab inito* methods may be in part due to the different approximations used, and in part due to the limited search of possible atomic configurations. The empirical potential given in Ref. [8] also gives octahedron as the ground-state structure. However, the result of original SW potential is a trigonal prism.

For Si_7, the ground-state structure under the modified SW potential is a pentagonal bipyramid. The bond length within the pentagon is 0.25 nm, while the bond length connecting apex atom to that lying on the base plane is 0.261 nm and the distance connecting the two apexes is 0.302 nm. The result of RR is similar, with the corresponding bond lengths being 0.248, 0.247, and 0.258 nm, respectively. It looks a little more compressed than that of the modified SW potential. Local density approximation of Ballone *et al.*[5], semiempirical tight-bonding calculation of Ref.[11], and empirical potential given in Ref.[8] all got similar ground-state structures. However, the ground-state structure of the original SW potential is a far different complicated structure.

For Si_8, the ground-state structure of the original SW potential is a perfect cube. The result of RR is an oppositely facecapped octahedron. The results of empirical potential given in Ref. [8] gives adjacently bicapped octahedron. The oppositely facecapped octahedron under modified SW potential is metastable with a cohesion 3.35 eV per atom. The ground-state structure of modified SW potential is a distorted adjacently bicapped octahedron, and the four atoms forming a square in octahedron now form a rhombus with an apex bond angle around 109°. The structure is more like a bi-tetracapped distorted trigonal prism. It should be noted that the minimum coordination number in such a configuration is 4, while in RR's structure the capped atoms has only a coordination number 3.

For Si_9, the ground-state structure of the modified SW potential is a tri-tetracapped trigonal prism. The calculation by RR showed that the distored tricapped octahedron has an energy slightly lower than the tri-tetracapped trigonal prism structure by 0.04 eV/atom (or 3 kcal/mol). The results of the semiempirical tight-bonding calculation of Ref.[11] and empirical potential given in Ref.[8] also give tri-tetracapped trigonal prism as the ground structure. Comparing these with the original SW potential and RR's quantum mechanical results, one finds that the modified SW potential prefers a coordination number 4 to 3. This result is due to the relative enhancement of two-body term over the three-body term in the modified SW potential, which leads to a more compact structure. For example, λ in the modified SW potential is 9.11 while in original SW potential 21.

With the increase of the cluster number, the number of metastable configurations increases greatly. The structures are often complicated and with energies close to each other. Local density approximation of Ref.[5] determined the ground-state structure of Si_{10} to be

the one in which the three rectangular faces and one of the triangular faces of the prism are caped, as shown in Fig.2. The calculation of RR cannot determine whether this structure or the tetracapped octahedron is more stable. The ground-state structure of the modified SW potential is close to the result of empirical potential given in Ref.[8]. Compared with the result of local density approximation, the model potential again favors structures with minimum coordination number 4 but not a structure having a triangle face capping with coordination number 3. The structure can be regarded as having the triangle face capping atoms distorted to a more compact configuration. The original SW potential for Si_{10} can be obtained by stacking two Si_5 planar pentagon rings.

In conclusion, since the modified SW potential is derived from the properties of bulk materials, it gives relatively large discrepancy when the cluster number is small, e.g. $n=2$, 3 and 4. The results of $n=5$, 6 and 7 of the modified SW potential is close to those of the first-principle calculation. Though the detailed structures for $n=8$, 9 and 10 under modified SW potential are different from those of the first-principle calculation, they show similar compactness and alternatively close to the slightly high lying metastable structures of each other. The characteristics of ground-state structures under modified SW potential is that the structures with minimum coordination number 4 are more favored. This may be attributed to the relative enhancement of the two-body term over the three-body term in the modified SW potential. In addition, the binding energies under modified SW potential are improved over that of the original SW potential.

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