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Fractional bond model for silicon clusters

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Si_6 and Si_7 are the two largest clusters with confirmed geometries experimentally. The apex atoms in the pentagonal bipyramidal structure for Si_7 have a coordination number of 6, completely different from the tetrahedral structure of the diamond lattice, and never given a definite explanation so far. In this paper, we suggest that atomic bondings in small silicon clusters be the unsaturated covalent, rather than covalent-bond. We introduce the number of bond order and defined it as the ratio of the number of valence electron of an atom to the effective coordination number of the ith atom, which can be smaller than 1 or greater. An *ad hoc* tight-binding model (fractional bond model) for silicon clusters is constructed by explicitly incorporating the dependence of hopping integrals between two atoms on the number of bond order, and their ground state structures of silicon clusters are performed. The results indicate that this model is successful in determining the structures of free small silicon clusters. [S0163-1829(99)00839-5]

An enormous effort has been devoted to determining the structures of free silicon clusters,[1–17] but one has not paid sufficient attention to the problem why some atoms in silicon clusters have a coordination number greater than 4. For example, the ground-state structure of Si_7 is a pentagonal bipyramid with D_{5h} symmetry experimentally confirmed.[18] The apex atoms in the pentagonal bipyramidal structure have a coordination number of 6, completely different from the tetrahedral structure of the diamond lattice. It virtually reflects the micromechanism of atomic bonding in silicon clusters. Therefore, it is necessary to give a concise but clear physical picture for understanding such system.

Theoretical methods used to describe the structural properties of silicon clusters can be classified into the three groups: (i) *Ab initio* quantum-chemical techniques (Hartree-Fock + electron correlation)[19–23] and density-functional methods.[24–26] However, they are time consuming. (ii) Various types of interatomic potentials beyond pair potentials,[27–30] where the many-body terms or the dependence on the local environment are incorporated. This type of method cannot deal directly with the change in electronic structure. (iii) Semiempirical tight-binding schemes,[31–34] such as nonorthogonal tight-binding (NTB) molecular-dynamics technique, and improved versions.[31,32] This group is acceptable for the larger number of tractable atoms and the consumption of computing power. It can give the information of electronic structure as well. Here, we propose the fractional bond model proposed, which is completely different from the known tight-binding schemes. The hopping integrals between two atoms are assumed to depend on four factors: number of bonding electrons, number of bonds, bonding strength of per atom, and interatomic distance, in which the number of bonding electron has something to do with the number of bond order.

On the basis of Pauling's suggestion for understanding bulk-metal systems,[35] we define the number of bond order as

$$n_{\mathrm{bo}}=\frac{n_{\mathrm{ve}}}{Z_i}, \tag{1}$$

where n_{ve} and Z_i denote the number of valence electrons of an atom and the effective coordination number of the ith atom, respectively. The bonding strength per atom is defined as

$$b_s=\left(\frac{f}{N}\right)^{\delta}, \tag{2}$$

where N is the atomic number of a cluster, δ an adjustable parameter, and f the bonding power. According to the theory of orbital hybridization, for the spd hybrids, the bonding power f can be written as

$$f=\sqrt{\alpha}+\sqrt{3\beta}+\sqrt{5\gamma}, \tag{3}$$

where α, β, and γ are the components of orbitals s, p, and d, respectively. For example, $\alpha=\frac{1}{4}$, $\beta=\frac{3}{4}$, $\gamma=0$, and $f=2$ for the sp^3 hybrids.

The cohesive energy of the cluster E_{coh} can be written as a sum of the band-structure energy E_{bs} and the repulsive energy E_{rep} (Refs. 2 and 36)

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TABLE I. Parameters used in the present scheme for silicon clusters.

	Hopping integrals			
	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
ν^{a}	4	3	2	2
μ	1.20	1.40	0.85	0.60
$C_{\alpha\beta}(\mathrm{eV}\ \ \mathrm{\AA}^{\nu})$	-1.15	1.05	0.90	-0.50
$\epsilon_s(\mathrm{eV})=-13.55$ [b]	$\epsilon_p(\mathrm{eV})=-6.52$ [b]	$d_0(\mathrm{\AA})=2.36$ [b]	$\lambda_1(\mathrm{\AA}^{-2})=1.086$ [a]	$\lambda_2(\mathrm{\AA}^{-1})=8.511$ [a]
$\delta=0.095$	$\alpha(\mathrm{\AA}^{-1})=1.6$	$\chi_0(\mathrm{eV})=0.19$		

[a] Reference 34.

[b] Reference 31.

$$E_{\mathrm{coh}}=E_{\mathrm{bs}}+E_{\mathrm{rep}}. \tag{4}$$

The band-structure energy is given by

$$E_{\mathrm{bs}}=\sum_{\alpha} n_{\alpha}\epsilon_{\alpha}-N\sum_{\alpha} n_{\alpha}^{0}\epsilon_{\alpha}^{0}, \tag{5}$$

where ϵ_{α}^{0} are the atomic levels. The n_{α} and n_{α}^{0} are the occupancy of the orbital α of the cluster and of the isolated atoms, respectively. The electronic levels ϵ_{α} of the cluster can be obtained from a tight-binding Hamiltonian of the form

$$H_{\mathrm{tb}}=\sum_{i,\alpha} \epsilon_{\alpha}^{0}a_{i\alpha}^{\dagger}a_{i\alpha}+\sum_{i,\alpha}\sum_{j,\beta} t_{i\alpha,j\beta}(a_{i\alpha}^{\dagger}a_{j\beta}+\mathrm{H.c.}), \tag{6}$$

where $t_{i\alpha,j\beta}$ denote electronic hopping integrals between different sites i and j. They are assumed to have the following form:

$$t_{i\alpha,j\beta}=C_{\alpha\beta}n_{\mathrm{be}}^{\mu}r_{ij}^{-\nu}b_{s}Z_{i}, \tag{7}$$

where n_{be} is the number of bonding electrons and is read as

$$n_{\mathrm{be}}=2\times n_{\mathrm{bo}}=2\times\frac{4}{Z_i}. \tag{8}$$

Here, numbers 2 and 4 represent the electronic number per bond and the number of valence electrons of an atom, respectively. r_{ij} is a distance between the ith and jth atoms and the exponent ν is dependent on the orbitals α and β. Z_i is the effective coordination number of the ith atom and is written as[34]

$$Z_i=\sum_{j\neq i} \exp[-\lambda_1(r_{ij}-R_i)^2], \tag{9}$$

where R_i is the minimum interatomic distance of the neighbors of ith atom and is given by

$$R_i=\sum_{j\neq i} r_{ij}e^{-\lambda_2 r_{ij}}\left[\sum_{j\neq i} e^{-\lambda_2 r_{ij}}\right]^{-1}. \tag{10}$$

The repulsive energy E_{rep} is assumed to have the form[31]

$$E_{\mathrm{rep}}=\sum_{i}\sum_{j>i} \chi(r_{ij}), \tag{11}$$

and $\chi(r)$ is taken to be short-ranged for scaling exponentially with distance

$$\chi(r)=\chi_0 e^{-4\alpha(r-d_0)}, \tag{12}$$

where the parameter d_0 is taken from Ref. 31, α and χ_0 are adjustable parameters. The values of the parameters are listed in Table I.

In order to test present model, an unbiased global search for the ground-state structures of small silicon clusters has been carried out by means of genetic algorithms (GA's),[37,38] an optimization strategy based on modeling of biological evolution. The results of the cohesive energies of the ground-state structures for the Si_N from $N=2$ to $N=10$, together with the calculated second finite difference of the total minimum energy, $\Delta_2E(N)=E(N+1)+E(N-1)-2E(N)$, are summarized in Table II, and compared with the previous *ab initio* values[20,21] and the NTB calculations.[31] The optimized geometries of Si_N $(N=6-10)$ clusters are displayed in Fig. 1.

The minimum energy structure for Si_3 is found to be an isosceles triangle with C_{2v} symmetry, in agreement with *ab initio* results.[20] For Si_4, the stable structure in our case is a distorted tetrahedron rather than a planar rhombus. In the case of Si_5, the lowest energy configuration is found to be a face-capped tetrahedron with C_{2v} symmetry, not in agreement with the *ab initio* results. This structure is the lowest triplet for Si_5 lying on only 0.607 eV higher in energy than the ground-state singlet (compressed trigonal bipyramid) at the MP4/6-31G* level.[21] For the Si_6 cluster, we have shown two energy structures in Fig. 1: an octahedron and its distorted form. However, the distorted octahedron with D_{4h}

TABLE II. Cohesive energies $\langle E\rangle$ (eV/atom) and second finite difference Δ_2E (eV) for Si_N clusters from $N=2$ to $N=10$, and compared with the previous *ab initio* values and the NTB calculations.

	Ab initio [a]		NTB [b]		Present work	
N	$\langle E\rangle$	Δ_2E	$\langle E\rangle$	Δ_2E	$\langle E\rangle$	Δ_2E
2	1.56		1.55		1.568	
3	2.54	-0.56	2.48	-0.74	2.363	-0.89
4	3.17	1.24	3.13	0.80	2.982	0.32
5	3.3	-1.28	3.36	-0.70	3.289	-0.53
6	3.6	0.10	3.63	0.09	3.582	0.13
7	3.8	2.40	3.81	1.32	3.773	0.81
8	3.65	-0.60	3.78	-1.29	3.815	-1.53
9	3.6	-2.60	3.90	0.06	4.018	0.95
10	3.82		3.99		4.085	

[a] Reference 21.

[b] Reference 31.

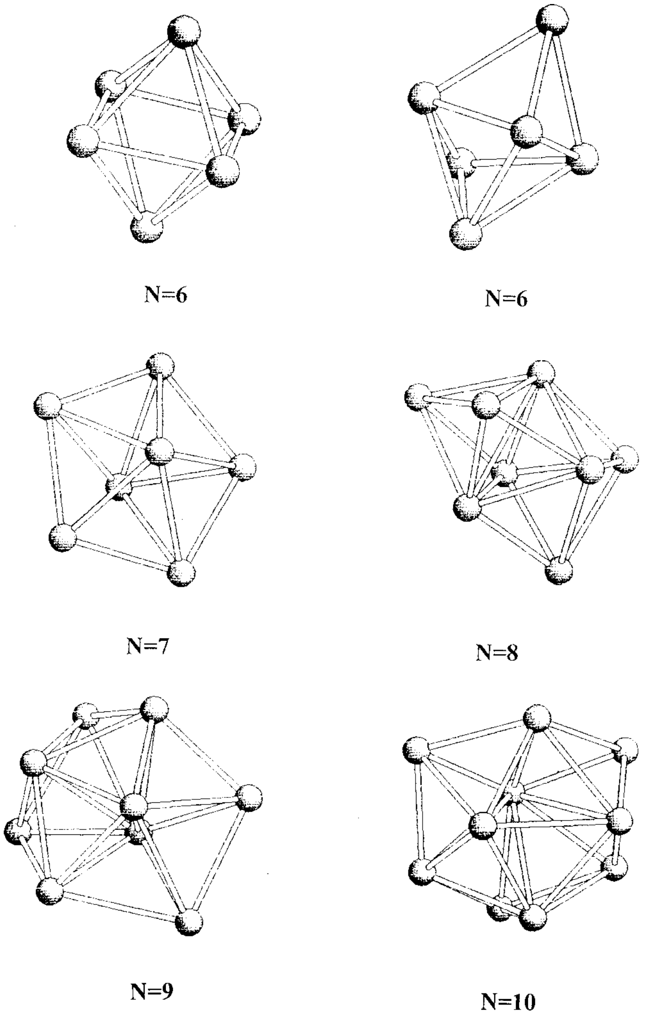

FIG. 1. Geometries of the lowest energy structures of small silicon clusters from $N=6$ to 10 obtained using the fractional bond model.

symmetry has an average energy lower compared with the undistorted octahedron, which means that the distorted one is more stable due to Jahn-Teller effects. The lowest energy structure for Si$_7$ is the pentagonal bipyramid with D_{5h} symmetry, containing silicon atoms with coordination number greater than four. These are in excellent agreement with experimental observations.[5,18]

For Si$_8$, the lowest energy structure is a distorted bicapped octahedron, and this octahedron is capped on adjacent faces. *Ab initio* calculation indicates that the most favorable arrangement corresponds to capping two opposite faces. It is likely that electron correlation effects are not fully included at the Hartree-Fock level. For Si$_9$, the C_{2v} distorted tricapped trigonal prism is its minimum energy structure, in agreement with the result suggested by Ordejón and collaborators.[32] Meantime, they have pointed out that this structure is also a minimum at the Hartree-Fock level as well as that in approximate density-functional theory. For Si$_{10}$, we find that the lowest energy structure is a distorted tetracapped trigonal prism, which is a Jahn-Teller distortion of the structure considered in Ref. 21. In fact, the lowest energy structures of Si$_9$ and Si$_{10}$ clusters can be derived from a pentagonal bipyramid with D_{5h} symmetry. The Si$_7$ cluster, therefore, can be visualized as the building block of Si$_9$ and Si$_{10}$ clusters.

Recently, Vasiliev *et al.*[17] have carried out *ab initio* calculations for the polarizabilities of small semiconductor clusters, and confirmed the ‘‘metalliclike’’ nature of small semiconductor clusters, i.e., these species tend to have higher coordination number than that in the crystalline state. In addition, their work has still shown that Si$_7$ is the most stable one among Si$_N$ ($N=3-10$) clusters since there is a minimum at $N=7$ in the plot of the average polarizabilities versus cluster size. From the calculated second finite difference of total energy $\Delta_2 E$ (see Table II) we have also shown that Si$_N$ clusters with $N=4$, 7, and 9 are particularly stable, which are in good agreement with *ab initio* results[21] and NTB calculations[31] except for $N=9$. It may be deduced that there is a competition between the distorted tricapped trigonal prism and the distorted tricapped octahedron for Si$_9$. The former prevails due to containing a building block with size $N=7$. For Si$_{10}$, similar competition may exist, too. Very recently, Ho *et al.*[38] have found that in $12\leqslant N\leqslant 18$ size range, the cluster geometries can be built on a structural motif consisting of a stack of Si$_9$ tricapped trigonal prisms. This also indicates that Si$_9$ tricapped trigonal prism is stable. Therefore, the maximum of the $\Delta_2 E$ for Si$_9$ is reasonable. Moreover, the geometries obtained for the other small silicon clusters by this model also appear ‘‘metalliclike’’ with the coordination number of some atoms more than 4. This kind of ‘‘metalliclike’’ nature for small silicon clusters comes from the unsaturated covalent bond. It must be pointed out that our model fails to give a planar rhombus for the lowest energy structure of Si$_4$, which has been proved by the experiments.[5,18] A possible reason is that quantum effect may be so significant to dominate the lowest energy structure of Si$_4$. However, a quantum effect cannot be considered sufficiently in the tight-binding approximation.

In summary, we have presented the fractional bond model together with a genetic algorithm, to perform the lowest energy structures of Si$_N$ clusters up to $N=10$. Our results indicate that the distorted octahedron of Si$_6$ and pentagonal bipyramid of Si$_7$, are in excellent agreement with those verified experimentally. The geometried structures given by this model imply that small silicon clusters are of the ‘‘metalliclike’’ nature, i.e., these species give preference to compact structures. This behavior is ascribed to the unsaturated covalent bond in such systems. In addition, the stability of Si$_9$ with distorted tricapped trigonal prism indicates that it can be viewed as a building block of clusters with larger size.

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