Application of the Embedded-Atom Method to Covalent Materials: A Semiempirical Potential for Silicon

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The embedded-atom method, a semiempirical theory of metal bonding, is investigated as a method to calculate the bonding in a covalent material. A simple first-neighbor embedded-atom method model is sufficient to explain the geometry and structure of many metastable phases of silicon, but not its shear behavior. To obtain realistic shear behavior of silicon, an angle-dependent electron density is included to model the effects of bond bending. This model uses only the experimental bulk properties of silicon. Calculated properties of metastable phases and point defects are presented.

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Atomistic simulation of a large number of atoms with use of molecular dynamics or Monte Carlo methods is a powerful technique for answering questions about structural transformations. Underpinning these calculations is the assumed atomic interaction potential. It would, of course, be desirable to take these interactions directly from first-principles calculations; however, even with current high-speed computers such calculations are orders of magnitude too slow for the millions of energy evaluations necessary to examine the complex systems of practical interest. Thus in order to obtain useful atomic interactions researchers have developed empirical and semiempirical potentials. Specifically for silicon there has recently been a considerable amount of interest in the development of empirical potentials.[1-6] Most of these potentials have drawn upon the results[7] of density-functional [local-density approximation (LDA)] theory calculations of various structures of silicon. Thus, in contrast to the Keating silicon potential[8] which only fitted equilibrium bulk properties, these potentials are hopefully applicable far from equilibrium and therefore are useful for making structural predictions. In general they work well in the regime of where they were fitted. However, there are a number of problems with these potentials. Since they are strictly empirical, there is no way to easily extend their applicability to more complicated systems, e.g., alloys. In addition, their functional forms are quite complicated, leading to difficulty in computation as well as in basic understanding. No single potential represents all of the properties of silicon well.

At the same time as these improvements were being made in the understanding of the interactions in silicon, Daw and Baskes[9] were developing the embedded-atom method (EAM) to describe interactions in metals. The EAM is a semiempirical method based on local electron density theory which has been shown to accurately describe a large number of properties in metals, e.g., defects,[10] liquids,[11] surfaces,[9,10,12] alloys,[10] mechanical properties,[13] and hydrogen on surfaces.[14] The evaluation of the energy with the EAM is rapid enough so that thousands of atoms may be considered in molecular dynamics or Monte Carlo simulations.

It is the purpose of this Letter to show that a formalism based on the EAM may be used to describe the covalent bonding in a material such as silicon. The fact that the EAM, which was developed to model metallic bonding, is also sufficient to describe covalent bonding is not intuitive; in fact, the success of this relatively simple model is somewhat surprising. Further work is in progress to explain why this model works so well. It should be noted that the LDA, on which the EAM is based, works for both metallic and covalently bonded materials. In fact, silicon itself is metallic in the close-packed structures. With only bulk experimental properties for diamond silicon, the model developed below gives semiquantitative agreement with structural properties of silicon calculated from LDA theory. It is straightforward to extend this model to include the effects of alloying additions or impurities. Thus, the prediction of structural stability of strained layered superlattices is now at hand.

Let us start with a simple first-neighbor model of a *homogeneous* solid. In the EAM[9] the energy, E, of each atom in a monoatomic solid is given by

$$E(r)=F(n_1\rho^a(r))+0.5n_1\phi(r), \qquad (1)$$

where n_1 is the number of first neighbors in this reference structure, ρ^a is the spherically averaged atomic electron density at a distance r from the nucleus, ϕ is the pair interaction, and F is the embedding function. The reader is referred to the EAM references above for more details about the method. For a uniform expansion or contraction, this energy is well described by a universal function,[15] E_r:

$$E_r(a^*)=-E_0(1+a^*)e^{-a^*}, \qquad (2)$$

where $a^*=\beta(r-r_1)$, E_0 is the sublimation energy, r_1 is the equilibrium first-neighbor distance, and $\beta=(9B\Omega_0/r_1^2E_0)^{1/2}$, where B is the bulk modulus and Ω_0 the equilibrium atomic volume. We may use Eqs. (1) and (2) to solve for the pair interaction ϕ.

Let us now calculate the energy, E_n, of a solid in a different crystal structure with n first-nearest neighbors.

Inserting the pair interaction in Eq. (1), we get

$$E_n = \frac{n}{n_1} E_r(a^*) + \left[F(n\rho^a) - \frac{n}{n_1} F(n_1 \rho^a) \right]. \tag{3}$$

At this point we take the embedding function to be given by

$$F(\rho) = E_0(\rho/\bar{\rho}) \ln(\rho/\bar{\rho}), \tag{4}$$

where $\bar{\rho}$ is the density an atom sees at equilibrium in the initial reference structure (n_1 neighbors). The justification for an embedding function with this form will be seen below. Then

$$E_n = (n/n_1) E_r(a^*) + E_0(n\rho^a/\bar{\rho}) \ln(n/n_1). \tag{5}$$

At equilibrium for small changes in first-neighbor distance,

$$r - r_1 \cong [-n_1(\rho^a)'_{r=r_1}/\beta^2\bar{\rho}] \ln(n/n_1). \tag{6}$$

To see if, in fact, this relationship is meaningful, the calculations of Yin and Cohen[7] for silicon are shown in Fig. 1 as the change in first-neighbor distance versus $\ln(n/n_1)$. The reference structure is taken as diamond cubic. As predicted by Eq. (6), the data fall in a straight line. Also shown in Fig. 1 are the results of quantum cluster calculations of silicon single-, double-, and triple-bond lengths,[16] which are seen to fall on the same line. This logarithmic relationship between bond length and number of bonds has been noted previously by Pauling[17] for covalent bonds in both carbon and metals. The simple EAM model explains this relationship nicely. The key to this agreement is the functional form chosen for the embedding function [Eq. (4)]. At this point we use this agreement to justify the specific form we have taken; hopefully, a theoretical justification will follow. With the slope of this curve to determine ρ^a (as a simple exponential, for example), the values of the equilibrium energies [Eq. (5)] are within a few tenths of an electronvolt of the calculated energies of Yin and Cohen[7] for various metastable silicon structures.

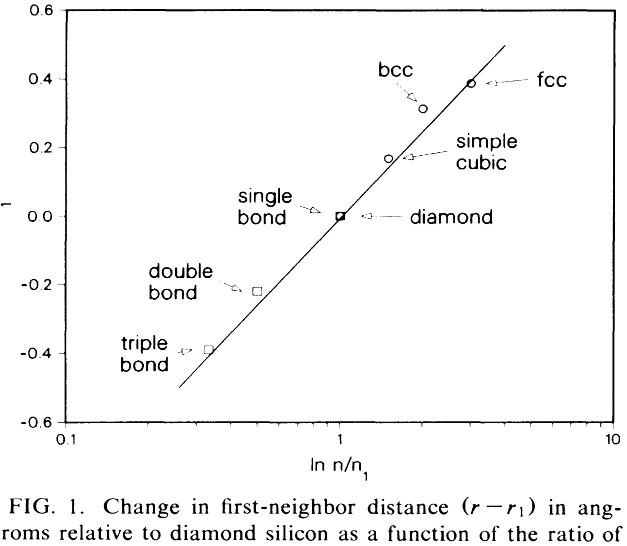

FIG. 1. Change in first-neighbor distance $(r - r_1)$ in angstroms relative to diamond silicon as a function of the ratio of the number of nearest neighbors to that in diamond silicon, n/n_1. The quantum cluster calculations are for single, double, and triple bonds in silicon. The line is drawn as a guide to the eye. Circles are the density-functional calculations (Ref. 7) and squares are the quantum cluster calculations (Ref. 16).

This agreement with structural energies and bond lengths gives one a hope that most of the bonding information is contained in the EAM formalism. However, there are two major problems with the simple treatment just presented. Both problems are related to the elastic shear constants. For the diamond structure, a first-neighbor central-potential model gives $C_{11} = C_{12}$. (See Daw and Baskes[9] for expressions for the elastic constants in the EAM.) This condition is strongly violated for silicon (see Table I). However, by inclusion of additional neighbors in the model, it is easy to satisfy the experimental values of C_{11} and C_{12}.

The second problem is a more difficult one to solve. The Cauchy discrepancy, $C_{12} - C_{44}$, in the EAM is proportional to the second derivative of the embedding function,[9] which from Eq. (4) is positive. The experimental Cauchy discrepancy for silicon is negative (see Table I). This is clearly an unacceptable situation. Addition of more neighbors does not solve this problem at all. The source of the problem lies in the directionality of the bonding in silicon. Since the model, as formulated, spherically averages the electron density, this directionality is lost. However, a small modification of the model may be made to include these bond-bending forces.

To include the effects just discussed, we now recast the model including more distant neighbors and angle-dependent density. The total energy, E, of a solid is given by

$$E = \sum_i F(\rho_i) + \tfrac{1}{2} \sum_{i \neq j} \phi(R_{ij}), \tag{7}$$

$$\rho_i = \sum_{j \neq i} \rho^a(R_{ij}) - a \sum_{\substack{j \neq i \\ k \neq i}} (1 - 3\cos^2\theta_{jik}) \rho^a(R_{ij}) \rho^a(R_{ik}), \tag{8}$$

TABLE I. Values of the parameters in the silicon model. Units are electronvolts for energy, electronvolts per cubic angstrom for elastic constants, and angstroms for distance.

Experimental data	Model parameters
E_0, 463[a]	α, 3.2
B, 0.61[b]	a, 1/3
r_1, 2.351[c]	r_c, 5.0
C_{11}, 1.03[b]	
C_{12}, 0.40[b]	
C_{44}, 0.49[b]	

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.

where R_{ij} is the distance between two atoms i and j, θ_{jik} is the included angle between atoms j, i, and k, and a is a constant to be determined by fitting to the shear moduli. The density is given by two terms, the linear superposition of atomic densities and an angular correction term. The specific angular form for the density was chosen to minimize the total energy under a tetrahedral distortion of the electron density as well as to vanish in ideal cubic structures. It may be considered as the first term in an expansion in spherical harmonics as used by Biswas and Hamann.[1] Since the angle-dependent term must decrease in magnitude as a function of distance, it is natural to use the decreasing atomic electron density to scale this decrease. Other distance scaling was not able to reproduce both shear moduli. The embedding function is given by Eq. (4).

For the monatomic *homogeneous* solid under uniform expansion or contraction, the energy per atom is now

$$E(r)=E_r(a^*)=F(\rho_i(r))+0.5n_1\Phi(r), \tag{9}$$

$$\Phi(r)=\textstyle\sum_s \phi(a_s r)n_s/n_1, \tag{10}$$

where r is the first-neighbor distance, n_s is the number of sth neighbors, and a_s is the ratio of the sth-neighbor distance to the first-neighbor distance. Note that in the expression for ρ_i [Eq. (8)], the angular part sums to zero for cubic structures and $\rho_i=\sum_s n_s \rho^a(a_s r)$. It is straightforward to solve Eq. (9) for Φ, as above, but to obtain ϕ requires a cutoff, r_c, so that beyond r_c all functions are zero. Then

$$\phi(r)=\Phi(r)-\sum_{s\neq 1}\frac{n_s}{n_1}\Phi(a_s r)+\left(\frac{n_2}{n_1}\right)^2\Phi(a_2^2 r), \qquad r>r_c/a_2a_3 \tag{11}$$

which turns out to be a sufficient range for our purposes.

Hence as above, we are able to obtain the pair potential from the universal function[15] for the reference structure and an assumed form for the embedding function. To summarize, the energy is given by Eq. (7) with the embedding function from Eq. (4), the density from Eq. (8), and the pair potential from Eq. (11).

The next step is to determine the parameter a and the atomic density, ρ^a, by fitting to the experimental elastic shear moduli.[19] The results of the fit are given in Table I, where the atomic density was assumed to take the form

$$\rho^a(r)=(r/r_1)^4 e^{-a(r-r_1)}. \tag{12}$$

Since only density ratios are used in the models, the density may be taken to be unity at the equilibrium first-neighbor distance with no loss of generality. Hence the density and the parameter a are dimensionless. This form gives the dominant long-range radial dependence of the $3s$ and $3p$ electron densities for a silicon atom. The atomic density for silicon has $a\cong 4$ Å^{-1}.[21] Previously for metals[9] we were able to use the calculated[21] atomic density. For silicon this density does not seem to work. The value for a implies a more diffuse electron density than is found in the atom. This effect is presumably due to hybridization. The cutoff is chosen large enough (5 Å) to be relatively unimportant. The functions are cut off smoothly over the 0.5 Å before the cutoff. The calculated structural energies may change on the order of tenths of an electronvolt with changes in the cutoff procedure.

The model reproduces the experimental bulk lattice constant, sublimation energy, and bulk modulus of diamond silicon exactly, and the individual elastic constants to within 5% of experiment. The diamond structure is predicted to be the most stable phase. The predicted equilibrium lattice constant and energies for a number of structures are given in Table II and Fig. 2. It may be seen that these results agree with LDA calculations to within a few tenths of an angstrom or electronvolt. This agreement may be considered quite good since there are no free parameters. It is instructive to compare the current results with the recent silicon empirical potentials, some of which were fitted to the LDA data base. In Fig. 2 the energies of the various metastable phases of silicon are shown. Note that the current results (which were not fitted) agree with the LDA calculations to the same extent as the empirical potentials[1,3,4] that were fitted to at least part of the data base. The current agreement is considerably better than those potentials[2,6] which were not fitted.

In order to evaluate the model away from ideal structures the energetics of point defects and surfaces have been calculated. The vacancy formation energy was found to be 3.12 eV compared to the 5–6 eV[23] calculated with LDA. The T_d (hex) interstitial was calculated to be 5.70 (6.70) eV compared to LDA calculations of 5–7 (6–8) eV.[23] Large error bars ($\simeq 1$ eV) have been placed on these LDA calculations by the authors. The

TABLE II. Equilibrium lattice constants of silicon structures. Value of c/a given in parentheses.

	Lattice constant (Å)	
Structure	This work	LDA calculations
Diamond ($A4$)[a]	5.43	5.45[c]
Wurtzite ($B4$)	3.84 (1.63)	3.86[c] (1.63)[b,c]
Cubic (A_h)	2.61	2.53[c]
Hexagonal (A_f)	2.75 (0.95)	2.62[c] (0.93)[c]
β-tin ($A5$)	4.83 (0.62)	4.83[c] (0.55)[c], 4.76[d] (0.53)[d]
fcc ($A1$)	4.19	3.89[c]
bcc ($A2$)	3.25	3.09[c]
hcp ($A3$)	2.96 (1.63)	2.74 (1.63)[b,c]

[a] Experimental lattice constant 5.43 Å (Ref. 20).

[b] c/a held fixed.

[c] Reference 7.

[d] Reference 22.

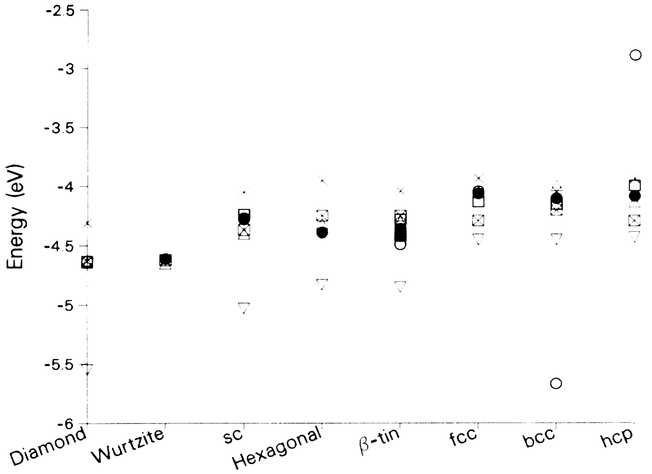

FIG. 2. Calculated energies of various structures of silicon. Both first-principles calculations (LDA) and empirical and semiempirical calculations are presented. The current work, with no free parameters to fit the LDA structural energies, agrees with the LDA calculations as well or better than the other calculations shown. Crosses within squares, current work; open squares, Dodson (Ref. 4); open circles, Tersoff (Ref. 3); triangles, Biswas and Hamann (Ref. 1); crosses, Stillinger and Weber (Ref. 2); inverted triangles, Pearson, Takai, Halicioglu, and Tiller (Ref. 6); filled circles, LDA (Ref. 7); filled squares, LDA (Ref. 22).

surface results indicate similar agreement with LDA calculations and experiment. These results are presently being prepared for publication.

In conclusion, we have shown that a semiempirical model, based on the EAM but including an angle-dependent electron density, can be applied to silicon. The major advantages of this model over previous empirical models are (1) its simplicity and (2) its straightforward application to alloy systems. The model uses the experimental bulk diamond-silicon lattice constant, sublimation energy, and elastic constants. There are no additional free parameters. The LDA structural geometries as well as energies are reproduced quite well.

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