

New Empirical Model for the Structural Properties of Silicon

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(Received 21 October 1985)

An empirical interatomic potential for covalent systems is proposed, incorporating bond order in an intuitive way. The potential has the form of a Morse pair potential, but with the bond-strength parameter depending upon local environment. A model for Si accurately describes bonding and geometry for many structures, including highly rebonded surfaces.

PACS number: 61.50.Lt

In recent years there has been growing interest in the structural properties, energetics, and statistical mechanics of complex systems. For some systems, such as condensed rare gases, computer simulations using empirical interatomic potentials have been employed very successfully to study ordering and melting.¹ For semiconductors and other covalent solids, however, even the statics of relatively simple systems poses a formidable problem. This paper proposes a new empirical potential, with which it is feasible to calculate the structure and energetics of complex covalently bonded systems. The advantage of this model potential over traditional approaches is illustrated by applying it to Si.

For small distortions which do not alter the bonding topology, simple models such as the Keating model² can adequately describe the energetics of phonons and elastic deformations of tetrahedral semiconductors.³ For more drastic reconstructions, the Keating model can provide some insight into structure,^{4,5} but the bond lengths of rebonded atoms are inaccurate, and the calculated energies are meaningless. Therefore, the prototypical covalent solid, Si, has been studied primarily through difficult quantum-mechanical calculations,⁶⁻¹⁵ which are currently restricted to a few atoms or tens of atoms per unit cell.

Recently, though, Stillinger and Weber¹⁶ proposed an empirical interatomic potential, incorporating two- and three-body interactions, and used it in molecular-dynamics simulations of molten Si. Another empirical potential was proposed by Pearson *et al.*¹⁷ However, neither of these potentials attempt to describe accurately the properties of nontetrahedral forms of Si. Biswas and Hamann¹⁸ proposed a more general form for the three-body interaction, and determined the eighteen parameters in that model by a least-squares fit to a large data base of calculated energies of real and hypothetical Si structures. Equations of state for these structures were well reproduced. However, relatively few structures outside the data base were calculated, and so it is difficult to evaluate the generality of the resulting potential. Highly undercoordinated systems were apparently not well described.

Here I propose a qualitatively new interatomic po-

tential, which appears to be more transferable and more accurate than conventional two- and three-body potentials. The form of the potential is motivated by intuitive ideas about the dependence of bond order upon local environment. This is apparently the first such potential to attempt to incorporate the structural chemistry of covalent systems, however crudely.

Ferrante, Smith, and Rose^{19,20} recently showed that a large number of calculated binding-energy curves for solid cohesion and chemisorption could be mapped onto a single dimensionless curve by use of a three-parameter rescaling. Abell²¹ showed that this universal behavior was well explained by the assumption of a Morse or Morse-type pair potential, and gave an illuminating discussion of the physical interpretation of the potential parameters, very much in the spirit of the present work. The potential here is constructed so as to guarantee²¹ that this universal behavior is obtained.

Consider the pair potential

$$E = \sum_i E_i = \frac{1}{2} \sum_{i,j \neq i} V_{ij}, \quad (1)$$

$$V_{ij} = f_c(r_{ij}) [A \exp(-\lambda_1 r_{ij}) - B_{ij} \exp(-\lambda_2 r_{ij})], \quad (2)$$

where E is the total energy of the system, E_i is the site energy for site i (introduced to make the asymmetry of V_{ij} more intuitive), V_{ij} is the interaction energy between atoms i and j , r_{ij} is the distance between them, and A , B , λ_1 , and λ_2 are all positive, with $\lambda_1 > \lambda_2$. (The Morse potential is defined by $\lambda_1 = 2\lambda_2$.) f_c is an optional cutoff function to restrict the range of the potential, discussed below. The first term in (2) is repulsive, and is interpreted as due to orthogonalization, etc.²¹ The second term is interpreted as representing bonding. B_{ij} therefore implicitly includes the bond order and must depend upon local environment.²¹ In the present work, rather than introduce three-body terms to describe bond-angle forces, etc., the form (2) is strictly adhered to. All deviations from a simple pair potential are ascribed to the dependence of B_{ij} upon the local atomic environment. Specifically, the bonding strength B_{ij} for the pair ij should be a monotonically decreasing function of the number of

competing bonds, the strength of the competing bonds, and the cosines of the angles with competing bonds. These three factors have been incorporated in the following simple trial potential:

$$B_{ij} = B_0 \exp(-z_{ij}/b), \quad (3a)$$

$$z_{ij} = \sum_{k \neq i,j} [w(r_{ik})/w(r_{ij})]^n \times [c + \exp(-d \cos \theta_{ijk})]^{-1}, \quad (3b)$$

where $w(r)$ is the "bare" bonding potential, $w(r) = f_c(r) \exp(-\lambda_2 r)$. Here z_{ij} is a weighted measure of the number of bonds competing with the bond ij , and b determines how rapidly the bond strength falls off with increasing effective coordination. The first term in (3b) is just the ratio of the unscaled bond strengths of the bonds ik and ij , raised to the power n . The parameter n thus determines how much the closer neighbors are favored over the more distant ones in the competition to form bonds. The final term gives the dependence on bond angle, which is taken as a function of $\cos(\theta_{ijk})$ to insure the proper analytic behavior. θ_{ijk} is the angle between bonds ij and ik . A simple exponential was tried prior to this Fermi-type function, but it did not provide sufficient freedom to describe the entire range of bond angles accurately. Note that this formulation is not symmetric, i.e., $V_{ij} \neq V_{ji}$. This simply means that the energy associated with a given bond is not divided equally between the two atoms in the formal accounting of (1). However, the potential possesses all physically required invariance properties.

In practice this potential can be more short ranged than its functional form would suggest, because bonding with more distant neighbors is effectively suppressed by the competition embodied in (3). As a result, it is reasonable (for large n) to truncate the potential at a very modest distance, e.g., 3 Å, as discussed below. Then the calculation of total energy and forces requires only of order N^2 operations, where N is the number of atoms, as opposed to N^3 for a general three-body force. (Biswas and Hamann¹⁸ discuss an alternative strategy for obtaining N^2 behavior.)

The most important quality an empirical potential should possess is transferability, i.e., applicability to systems very different from the ones used to determine the potential. In order to test the accuracy and transferability of this potential, the parameters have been fitted to a *minimal* set of known high-symmetry structures, and the resulting potential then applied to a large number of low-symmetry systems for which reasonably reliable *ab initio* calculations are available. Specifically, a Morse potential ($\lambda_1 = 2\lambda_2$) is assumed for simplicity. Only the first shell of neighbors is included, so that the parameter n does not yet enter. (The cutoff function f_c is specified more precisely below.) The remaining six parameters are fitted to the

following six data: the cohesive energy, lattice constant, and bulk modulus of bulk Si, and the cohesive energies of the Si_2 dimer and the hypothetical simple-cubic and face-centered-cubic structures, as calculated by Yin and Cohen.⁶ (The parameters are chosen to reproduce the correct energy at the equilibrium lattice constant calculated here.) The resulting values of the parameters are given below. As a first test the resulting bond lengths of these structures are compared in Fig. 1 with the actual values (i.e., experiment²² or *ab initio* calculation⁶) and are found to agree to within 1% in every case, although the bond length varies by more than 20% over this range of structures. Figure 1 also illustrates how both the actual and the model bond energies decrease monotonically with increasing coordination. The weak cohesive-energy minimum for the diamond structure may be viewed as resulting from the competition between decreasing bond strength and increasing number of bonds. From this viewpoint, it is natural that for carbon, the optimum coordination should fall between 3 (graphite) and 4 (diamond), so that these are nearly degenerate in energy, while for Si the optimum coordination is slightly greater than 4, so that the six-coordinated β -tin and simple-cubic structures are the nearest in energy to the diamond structure. This represents a continuous shift toward higher optimum coordination with increasing "metallicity," which for isovalent tin and lead leads finally to the six-fold β -tin structure and twelvefold fcc, respectively.

As a further test, the properties of Si in the graphitic structure are calculated. The resulting bond length of 2.28 Å is substantially shorter than for the diamond structure, in good agreement with Yin and Cohen's⁷ result of 2.25 Å. The cohesive energy of 4.30 eV is in fair agreement with their value of 3.92 eV; accuracy levels of *ab initio* calculations are discussed below. In addition to the above, the calculated Si_2 vibrational

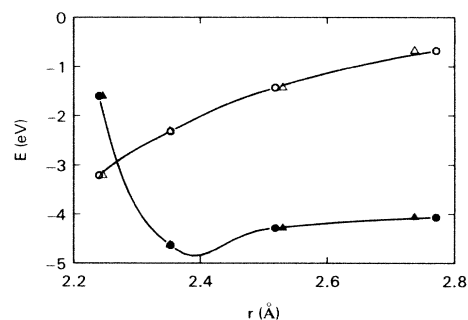


FIG. 1. Cohesive energy and bond energy vs bond length, for the high-symmetry structures used to determine the potential parameters in Table I. Open circles and triangles give model and actual cohesive energy per bond, respectively. Filled circles and triangles give model and actual cohesive energy per atom, respectively. Structures are, from left to right, Si_2 dimer, diamond structure, simple cubic, and face centered cubic. The lines are spline fits to guide the eye.

frequency (15.4 THz) and the graphitic Si isotropic bulk modulus (0.47 Mbar, assuming the same c/a ratio assumed by Yin and Cohen⁷) are in excellent agreement with the actual values^{7,22} of 15.3 THz and 0.50 Mbar. Bulk moduli were not reported for the other hypothetical structures.

Since tests of the present model's accuracy rely largely on *ab initio* calculations using the local-density-functional (LDF) approach, it is appropriate to stress here the uncertainties inherent in those calculations. For formation energies of point defects in Si, where several authors have reported painstaking studies,^{8,9} no one claims accuracy of better than ± 0.5 eV, and even this is basically a guess. Initial and subsequent reports by the same authors have given improvements in accuracy (i.e., revealed initial inaccuracies) of up to 1 eV for point defects,⁸ and 0.7 eV even for simple close-packed bulk structures.⁶ This simply reflects the extreme difficulty of the calculations. More fundamentally, the inherent accuracy limits of LDF are not well known.

Nevertheless, *ab initio* LDF calculations have been invaluable in the understanding of the structure and energetics of semiconductor surfaces and defects. If the present model can give accuracies even a factor of 2 or 3 worse than the best LDF calculations, that is already enough to guarantee it an important role in studies of more complex systems.

To handle more general structures, the remaining parameters, n and f_c , must be specified. n was taken quite large, $n=4$, to insure very short-ranged behavior. Then inclusion of neighbors up to arbitrary distance only changed the lattice constant, cohesive energy, and bulk modulus of bulk Si from the nearest-neighbor value by 2%, -4%, and < 1%, respectively. This change was due entirely to the repulsive term in (2). For the cutoff function f_c , a smooth but relatively abrupt cutoff around $r_{ij} = 3$ Å was used, consistent with the inclusion of only first neighbors in the determination of the potential parameters. The dependence of results here on n and f_c was not systematically tested. The precise form of f_c and the values of all parameters used are given in Table I.

This potential was tested extensively against a large number of structures. For the β -tin structure of Si, the resulting cohesive energy (4.51 eV), c/a ratio (0.52), and atomic volume (15.7 Å³) agree quite well with the actual values⁶ of 4.36 eV, 0.55, and 15.5 Å³, respectively. For the unreconstructed Si(111) surface, a relaxation energy of 0.12 eV/(surface atom) is found, with a reduction of 29% in the first interlayer spacing. This is in excellent agreement with *ab initio* calculations,^{11,12} which give 0.15–0.17 eV relaxation and 29%–37% interlayer contraction. Optimization of the Si(100) 2×1 dimer gives a symmetric dimer with an energy 1.9 eV/dimer below the ideal (100) surface, and a dimer bond length of 2.29 Å, significantly short-

TABLE I. Parameters used in the model potential, Eqs. (1)–(3).

$$A = 2280 \text{ eV}, \quad B_0 = 171 \text{ eV}, \quad \lambda_1 = 2\lambda_2, \quad \lambda_2 = 1.465 \text{ \AA}^{-1}, \\ b = 1.324, \quad c = 6.5, \quad d = 6.02, \quad n = 4,$$

$$f_c = \begin{cases} 1, & r < R - D, \\ \frac{1}{2} - \frac{1}{2} \sin[\frac{1}{2}\pi(r - R)/D], & R - D < r < R + D, \\ 0, & r > R + D, \end{cases}$$

$$R = 3.0 \text{ \AA}, \quad D = 0.2 \text{ \AA}$$

er than the bulk bond length of 2.35 Å. This is in excellent agreement with detailed calculations^{13,14} of energy (1.7–2.1 eV/dimer below the ideal surface) and bond length (2.22–2.25 Å). In contrast, previous model potentials have given dimer bond lengths substantially longer than the bulk bond length.^{4,18}

As another test, structures and energies of $\sqrt{3} \times \sqrt{3}$ arrays of Si adatoms on Si(111) have been calculated, and compared with the results of Northrup.¹⁵ The threefold top site (directly above a second-layer atom) is found to be lower in energy than the threefold hollow site by 0.78 eV/adatom, and the distances between the adatom layer and the second full layer are 2.44 and 2.00 Å for threefold top and hollow sites, respectively. These values compare very well with Northrup's results of 0.62 eV, and 2.49 and 2.12 Å, respectively.

A particularly stringent test of such a model is the π -bonded chain structure proposed by Pandey¹² for the Si(111) 2×1 surface, and supported by a variety of experiments. This structure is highly strained, but the strain energy is compensated for by enhanced π bonding, a rather subtle mechanism. As a result, most models give an energy higher than that of the ideal surface. The present model gives an energy of 0.12 eV/(surface atom) below that of the ideal (111) surface. This is a significantly weaker gain than the 0.35 eV found in more accurate calculations.^{11,12} Nevertheless, the present model is accurate enough to find that, despite the large strain, the π -bonded chain is a reasonable candidate for the Si(111) 2×1 surface.

Results for point defects were reasonably good, with one serious exception. The energies of the simple vacancy and tetrahedral-site interstitial were calculated to be, respectively, 2.7 and 3.6 eV (3.1 and 3.8 eV prior to relaxation). This agrees semiquantitatively with *ab initio* calculations,^{8,9} which suggest a vacancy formation energy of around 3.8 ± 0.5 eV, and around 4.7 ± 0.5 eV for interstitial formation.

During extensive testing, a single case was found where the present model yielded unphysical results. The formation energy of the hexagonal-site interstitial was found to be essentially zero with the parameters listed in Table I. The failure of the model for one case is hardly surprising. Rather, since the parameters were fitted to the energies of a small number of high-

symmetry structures, the reasonable accuracy of the model for the vast majority of cases studied is remarkable, and indicates an unprecedented level of transferability. Even for this pathological case, the *structure* found here was in *quantitative* agreement with the calculated¹⁰ relaxation of 5% around the interstitial.

The potential can be further improved in a systematic way. A more flexible form for (3), combined with a least-squares fit to a large data base (including, e.g., the hexagonal interstitial) would certainly yield improvements, as would a more systematic procedure for determining the optimal value of n . Also, Abell²¹ stressed the advantage of permitting λ_1 and λ_2 to vary independently. The cutoff function f_c could be omitted (albeit at considerable cost in computational efficiency) to eliminate that element of arbitrariness. And the extension to multicomponent systems is straightforward.

Finally, to illustrate the unique utility of an empirical potential, I calculate total energies for three models of the Si(111)7×7 surface. This problem is at present completely inaccessible to *ab initio* techniques. The three models chosen are those of Takayanagi *et al.*,²³ McRae and Petroff,²⁴ and Himpfel²⁵ (see also Ref. 5). Atomic coordinates were relaxed by use of a steepest-descent method, and the surface energies compared. It should be born in mind that the structure obtained could be a metastable state, and that for such complex structures the optimization procedure used here is limited by numerical noise; so the results are only an upper bound on the energy, even within the present model. With this caveat, energies for the three models, per 7×7 cell (relative to the ideal surface), were -6.3 eV (Takayanagi), +1.4 eV (McRae), and +11.9 eV (Himpfel). The difference between the two most favorable models is only 0.2 eV per nominal surface atom (49 atoms/cell), which might easily fall within the uncertainty of the model. Nevertheless, the results certainly favor the model of Takayanagi. The calculated energy is only insignificantly lower than the relaxed surface or π -bonded chain, but this represents an upper bound; in any case, the entropy of this structure is presumably a critical factor driving the high-temperature transition.

The central conclusion of this work is that there are tremendous benefits in replacing the traditional two- and three-body expansion of the interaction energy with a simple pairlike potential (2), where, however, the coefficient B depends upon the local environment so as to incorporate the effect of variable bond order. In this way, structural chemistry is for the first time included in a classical empirical potential. The specific form (3) for that dependence is somewhat arbitrary, and no doubt better forms will be found, either by improved understanding or by trial and error. Nevertheless energies and geometries are described very well for Si, and the unique transferability of the potential

suggests that it may capture some of the essential physics of covalent bonding.

It is a pleasure to thank R. M. Tromp for providing the atomic coordinates used to start the Si(111)7×7 optimization, J. E. Northrup for permission to quote results prior to publication, and D. R. Hamann and R. Biswas for discussions and for providing a preprint of Ref. 18 prior to publication.

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