New Low-Energy Crystal Structure for Silicon

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A minimum-energy path in strain space has been determined which takes cubic silicon into itself. Energies are computed using the Stillinger-Weber model potential and first-principles total-energy calculations. The energy along this path has an additional minimum, corresponding to a crystal structure with a body-centered-tetragonal lattice and fivefold-coordinated atoms. Lattice-dynamics, molecular-dynamics, and elastic-constant calculations show the structure is stable.

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For any Bravais lattice, physically allowed (symmetric) shear strain tensors can be derived which transform the lattice into itself [1]. When such transformations, so-called "magic strains," are accompanied by special translations of the basis vectors, then any crystal can be so transformed. The possible physical relevance of this novel concept is just beginning to be explored [2-5]. Here we focus on a particular application of the magic-strain concept which is of interest for silicon and materials with related structures.

Using the magic-strain concept, we have explored extensively the strain space of silicon and uncovered an interesting transformation which takes the diamond structure into a body-centered-tetragonal (bct) structure with each atom having five near neighbors. Our results are based on the Stillinger-Weber (SW) model potential [6] and first-principles total-energy calculations using a local-density plane-wave pseudopotential (PS) method [7]. The density of silicon in this structure lies, like the coordination number, between that of the diamond structure (low density, fourfold coordination) and that of the high-pressure β-Sn phase (high density, sixfold coordination); its energy is nearly degenerate with β-Sn. We refer to the new structure as bct5, the 5 to distinguish it from β-Sn, which is also bct, and the denote the fivefold coordination. Our results suggest that nonhydrostatic pressure could transform cubic silicon to the bct5 structure. Once in this phase, it could well be stable at ambient conditions.

We describe first the minimum-energy path in strain space that transforms diamond into itself and passes through the bct5 structure. Let $\mathbf{x}_1$ denote the positions of atoms in the fcc lattice and $\mathbf{x}_2$ be the positions of the basis atoms for the diamond structure; $\mathbf{x}_2=\mathbf{x}_1+a_0(1,1,1)/4$, where coordinate axes are the usual cube axes and a_0 is the lattice constant. Employing Van de Waal's method [1], we generate a magic strain (s_m) with A and B matrices having rows (1,1,0), (1,0,1), and (0,1,1) for A, and (1,1,0), (1,0,1), and $(-1,0,1)$ for B:

$$s_m=\begin{pmatrix} 0.5169 & -0.2377 & -0.3773 \\ -0.2377 & -0.3359 & -0.0491 \\ -0.3773 & -0.0491 & 0.1641 \end{pmatrix}. \qquad (1)$$

A and B denote two different types of primitive unit cells for the fcc lattice. s_m is a physically allowed (symmetric) strain which transforms from type A to B. The positions of atoms in the corresponding magically strained diamond are $\mathbf{y}_1=(I+s_m)\mathbf{x}_1$ and $\mathbf{y}_2=\mathbf{t}+(I+s_m)\mathbf{x}_2$ where I is the identity matrix and $\mathbf{t}=a_0(0.1599,0.0533,-0.0533)$. Diagonalization of s_m reveals a strain of $g_0\equiv0.7850$ along the $(0.8493,-0.1581,-0.5037)$ direction, a strain of $f_0\equiv-0.4398$ along the (0.3347,0.8991, 0.2822) direction, and zero strain along the $(1,-1,2)$ direction (eigenvalues and eigenvectors of s_m). To facilitate subsequent discussion, we write the diagonal elements of a *general* strain in the coordinates which diagonalize $I+s_m$ as $s_{11}=-1+(1+f)^{-1/3}(1+g)^{2/3}$, $s_{22}=-1+(1+g)^{-1/3}(1+f)^{2/3}$, and $s_{33}=-1+(1+f)^{-1/3}\times(1+g)^{-1/3}$. When f and g have the magic values f_0 and g_0, then $s_{ii}+1$ are the eigenvalues of $I+s_m$.

We obtain a minimum-energy path between the unstrained and magic-strained structures by stepping f or g, whichever produces the smallest increase in energy, by some fraction of their magic values, while allowing the basis and volume V to relax with each step. For example, a step size of 0.02 requires 100 steps to go from $f=g=0$ to $f/f_0=g/g_0=1$. Results so obtained for the energy and structure using the SW potential are shown in Fig. 1. Also shown are energies calculated by the PS method using the structures obtained from the SW calculation. We see that although there are substantial differences between the results of the two calculations, both show a minimum in energy at the midway point. Starting from the structure at this minimum, the SW energy is further lowered (triangle in Fig. 1) when the lattice is allowed to relax with respect to all possible strains, i.e., by including nonzero off-diagonal elements of s. The structure at the minimum, with a suitable coordinate transformation, is seen to be body-centered-tetragonal, space-group *I4mmm*, with atoms occupying the *e* sites (Wyckoff notation) [8]. Once the symmetry of the new structure was determined, we then carried out PS calculations to minimize the energy within the constraint imposed by the *I4mmm* symmetry. This lowered the PS energy to that given by the plus symbol in Fig. 1.

The lattice parameters predicted for bct5 silicon from

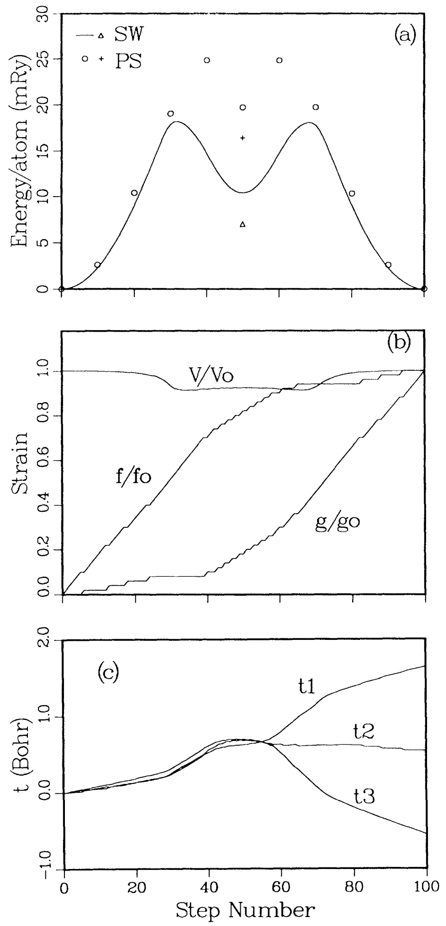

FIG. 1. Energy and structural parameters as a function of step number (steps of f/f_0 and g/g_0 of 0.02): (a) SW energy (solid curve), PS energy for the SW structure (open circles), fully relaxed SW bct5 structure (triangle), and the fully relaxed PS bct5 structure (plus); (b) strain parameters V/V_0, f/f_0, and g/g_0 corresponding to the solid curve and open circles in (a); and (c) the corresponding values for basis-vector translation **t** with respect to standard Cartesian coordinates along principle axes of the unstrained (cubic) structure.

SW (PS) calculations are $a=6.329$ (6.26) bohrs and $c=12.292$ (11.26) bohrs, and the internal structure parameter [8] $z=0.1810$ (0.194). In this structure, illustrated in Fig. 2, each atom has four near neighbors at a distance of 4.786 (4.60) bohrs, with the fifth at a distance of 4.450 (4.37) bohrs. Each atom is at the approximate center of a pyramid with corners occupied by the five near neighbors.

The analogous structure for binary compounds has lower symmetry (*I*4*mm*), resulting in a polar, in principle, ferroelectric, crystal. Three compounds (GeP, GeAs, and SnP) are known to form with this structure when prepared at elevated temperatures and pressures [9]. These are metallic systems. Our calculations predict bct5 silicon would also be metallic.

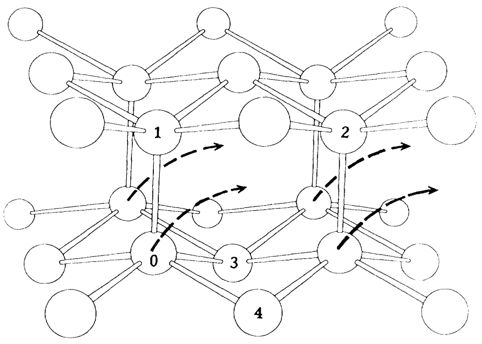

FIG. 2. The bct5 structure with structural parameters as indicated. Two sixfold rings lying in perpendicular (110) planes are denoted by solid and dashed bonds.

To investigate the stability of bct5 silicon we have calculated its elastic constants using both the SW model and PS results (Table I). The SW values were computed using the long-wave method [10], while the finite-strain approach [11] was employed for the PS results. Total energies, with basis-vector relaxation included, were calculated for selected strains (~4% in magnitude) and substituted into the corresponding lowest-order expansions to solve for the elastic constants. The increase in energy for such strains, typically, 2-8 mRy, was calculated to an accuracy of ~0.2 mRy in the energy differences. The finite-strain approach was also employed with the SW potential to check the formulation and estimate errors resulting from the use of 4% (rather than infinitesimal) strains. The overall uncertainty in the PS values reported in Table I, due to finite strains and imperfect convergence, is estimated to be less than ~15%. While large differences exist between the SW and PS elastic constants, the conditions for elastic stability [10] are satisfied for both SW and PS values. In our case the stability conditions are $C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $C_{11}-C_{12}>0$, and $C_{33}(C_{11}+C_{12})-2C_{13}^2>0$. The fact that these conditions are satisfied implies that if cubic silicon is strained (as in Fig. 1) to some point in the vicinity of the bct5 structure, it will tend to relax to the bct5 structure.

TABLE I. Elastic constants (in Mbar units) for the bct5 structure of silicon as predicted from the Stillinger-Weber (SW) model and from first-principles pseudopotential (PS) calculations.

	SW model	PS
C_{11}	4.15	1.44
C_{12}	2.43	1.24
C_{13}	1.39	0.45
C_{33}	2.08	1.60
C_{44}	0.40	0.35
C_{66}	1.01	0.63

The softest PS strain is the one corresponding to $C_{11}-C_{12}$. This particular strain results from equal amounts of stretching and compressing along [100] and [010] directions in the basal plane. We carried out calculations which show that the low value of $C_{11}-C_{12}$ is not an indication of a nearly unstable structure. Specifically, we find that the energy associated with $C_{11}-C_{12}$-type distortions increases monotonically for strains larger than 2%, to about 8 mRy/atom for a 20% strain, the largest strain considered. An explanation for the low value of $C_{11}-C_{12}$ is suggested by the structure. The sixfold rings lying in (110) planes can be quite rigid, as their structure is similar to that of single graphite layers, but cross-ring interactions can be soft. To lowest order, the $C_{11}-C_{12}$ distortion does not change the ring structure, and thus, is soft.

Lattice-dynamics calculations for the SW model in the bct5 structure produce positive real frequencies for all modes, indicating complete stability. Zone-center optic-mode frequencies were also computed from PS total energies using the standard "frozen phonon" technique. These modes (Raman active) have E_g and A_{1g} symmetries with predicted frequencies, respectively, of 603 and 385 cm^{-1} (SW) and 520 and 340 cm^{-1} (PS). For comparison, the triply degenerate Raman-active mode in the cubic phase is 523 cm^{-1} (Expt.), 600 cm^{-1} (SW) [12], and 521 cm^{-1} (PS) [13]. We have not carried out frozen-phonon PS calculations for short-wavelength (zone-boundary) modes. If a zone-boundary mode were unstable, the resulting distortion would further stabilize the fivefold-coordinated structure by relaxing to a new bct5-like structure of lower symmetry.

Molecular-dynamics simulations were performed for SW silicon in the bct5 and β-Sn structures. In each case the computation employed periodic boundary conditions on a cell containing 432 atoms. The simulations were carried out for conditions of zero pressure and temperatures ranging from 0 to 2520 K. At each temperature the simulation was allowed to proceed for 11 000 time steps (5000 for equilibration and 6000 for averaging) of duration 0.000 38 ps each. The bct5 structure transformed to the liquid during the equilibration from $T=2020$ K to $T=2270$ K. This is similar to the case of cubic silicon [12]. On the other hand, the β-Sn structure was found to be less stable, transforming to liquid between 1510 and 1760 K. The melting of bct5 occurs with very little change in density, less than 1%, while the β-Sn form is denser than the liquid by ~6%. The latent heat, however, is greater for bct5; 20.9 kJ/mole compared with 6.3 kJ/mole for β-Sn.

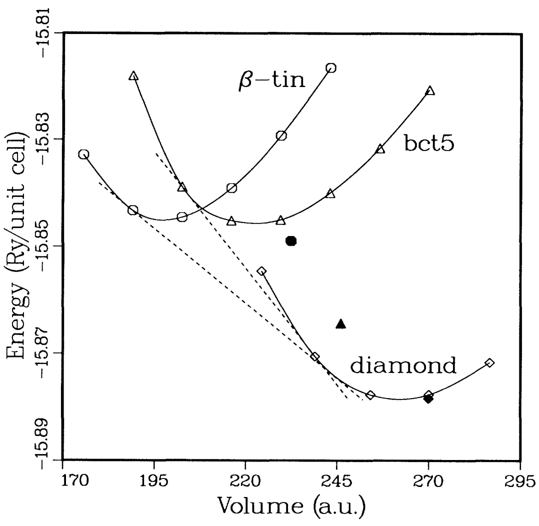

FIG. 3. Energy as a function of volume for the β-Sn (○), bct5 (△), and diamond (◇) structures. Solid lines are fitted to results of PS calculations (open symbols). Solid symbols are SW results for minimum energy and corresponding volume, with the energy scale shifted to match that of the PS diamond structure. Slopes of the dashed lines give transition pressures for cubic to β-Sn (84 kbar) and cubic to bct5 (126 kbar).

Volume-dependent energies are shown in Fig. 3 for the cubic, bct5, and β-Sn structures as derived from PS calculations. Energy differences between *different* structures are estimated from convergence studies to be correct to within 2 mRy. Also shown are results for minimum energies and corresponding volumes for these structures obtained from the SW model. For each volume the remaining structural parameters were relaxed to minimize the energy. Our results for cubic and β-Sn silicon are in good agreement with earlier PS calculations [14,15]. Reference [15] considered another low-energy form of silicon (BC-8) which is quite unlike bct5, having exclusively fourfold coordination and an equilibrium volume closer to cubic silicon than that of the β-Sn form. From the common tangent construction we find a transition pressure of 84 kbar for cubic to β-Sn (compared with 99 kbar in Ref. [14]) and 126 kbar for cubic to bct5.

Having demonstrated the stability of the bct5 structure, we now consider the prospects for making it experimentally. The magic-strain path (Fig. 1) starts out primarily as a contraction along the (0.3347,0.8991,0.2822) direction relative to the usual axes of a cubic crystal. Thus, we propose applying uniaxial stress along this special direction. Since the magic-strain path is a minimum-energy path, the remaining structural parameters should, in principle, follow approximately that predicted in Fig. 1. The difficulty will likely be in preventing fracture before reaching the bct5 structure. Thus, a sudden application of stress, as in a shock experiment, may be preferable. Hydrostatic pressure, in combination with uniaxial stress, might help produce the desired transformation and prevent fracture.

Finally, we note that phenomenological models used for simulating liquid and amorphous silicon should be tuned to give reasonably accurate results for the bct5 structure, since this structure is accessible from thermal energy available in the liquid phase. In this regard, we also note that fivefold coordination is not far from that found in liquid silicon (6.4) [16] and is conjectured to be important in the structure of amorphous silicon as well [17].

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