

## *Ab Initio* Study of Pressure-Induced Restructuring of Nano-Scale Networks made from Carbon or Silicon

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Pressure-induced structural transformations for nano-scale networks of group IV elements (carbon and silicon) are investigated using the first-principles molecular dynamics with constant-pressure scheme. Conditions to change layered  $\text{CaSi}_2$  into cluster solid with 3-dimensional Si network is discussed by comparison with the graphite-diamond transformation. Uni-axial compression is relevant for the former transformation at low temperature, although isotropic compression is able to cause formation of diamond from graphite.

### 1. INTRODUCTION

High pressure technique has been regarded as one of the important methods for synthesis of novel materials. There are many examples of artificially created materials by applied pressure, *e.g.* the diamond synthesis under ultra-high pressure and polymerization of  $\text{C}_{60}$ . This type of structural transformations with formation of new bonds may be regarded as a sort of chemical reaction. Interestingly, frameworks of these materials are rebuilt accompanied with change of their dimensionality as well as bonding character. A key to understand such phenomena should be a microscopic analysis based on detailed investigation of electronic state.

Recent development of the first-principles calculation can satisfy such requirements and we have obtained a new complimentary apparatus for high-pressure experiments. This is called the first-principles molecular-dynamics (FPMD) with constant-pressure scheme.<sup>1</sup> Using this method, we are able to reproduce the pressure-induced structural transformations in the computer and observe reconstruction of nano-scale network before our eyes.

As an example, we focus here on two types of layered structures made from carbon or silicon, *i.e.* graphite and calcium silicide ( $\text{CaSi}_2$ ). Graphite is one of the most familiar 2-dimensional (2D) nano-network. Although Si has no stable layered structure as simple body, we can find several examples in silicides. Actually, 2D silicon network is known to exist in  $\text{CaSi}_2$ .<sup>2-4</sup>

We examine difference between these networks

under high-pressure condition. After introducing FPMD with constant pressure scheme, we first review the graphite-diamond transformation, where isotropic pressure is enough to induce transformation. On the other hand, we will show that uni-axial compression is needed for the transformation of layered  $\text{CaSi}_2$  into 3-dimensional cluster solid at low temperature.

### 2. METHOD

If we consider structural properties of general compound, we should apply the electronic state calculation, which is required to get information about forces on atoms and stress as well. This becomes serious for simulation of transition processes, because character of the material can be variable on the way of the transformation. Although cost of calculation grows, FPMD satisfies these requirements in principle, except for materials with strong electron correlation.

In order to determine the electronic state, we apply *ab initio* pseudo-potential LDA calculations using a plane-wave expansion. By this method, we can easily obtain the Hellmann-Feynman force on atoms and internal quantum stress. The Kohn-Sham equation is solved by the conjugate gradient method at each step of the molecular dynamics.

In actual calculation, MD at a given pressure  $P_{\text{ext}}$  is performed following the next Lagrangian proposed by Wentzcovitch *et al.*<sup>1</sup>:

$$L = \sum_I \frac{1}{2} m_I \dot{\mathbf{q}}_I d \dot{\mathbf{q}}_I - E(\{\mathbf{q}_I\}, \epsilon)$$

$$+\frac{1}{2}W\text{Tr}({}^t\dot{\epsilon}\dot{\epsilon}) - P_{\text{ext}}\Omega_{\text{cell}} \quad , \quad (1)$$

where  $\epsilon$  and  $\Omega_{\text{cell}}$  are the strain tensor and volume of the unit cell, respectively. Energy of the electronic ground state  $E(\{\mathbf{q}_I\}, \epsilon)$  for a configuration of atoms in the real coordinate  $\{\mathbf{r}_I\}$ , together with  $P_{\text{ext}}\Omega_{\text{cell}}$ , gives a potential for MD simulation of atoms and the cell. Here, scaled atomic coordinates  $\{\mathbf{q}_I\}$  are introduced by  $\mathbf{q}_I = (1 + \epsilon)^{-1}\mathbf{r}_I$ , while  $d = {}^t(1 + \epsilon)(1 + \epsilon)$  is the metric tensor. Motion of the cell is determined using a fictitious mass  $W$ . We can generalize the Lagrangian so that uni-axial compression is realized by applying scheme proposed by Parrinello and Rahman.<sup>5</sup>

We use Troullier-Martins's soft pseudo-potential (PP) for each element. For Ca PP, we choose a component for  $s$ -wave as the local part in the Kleinman-Bylander's separable form. Structural parameters of Ca crystal (FCC) are reproduced within 1% error by treating 3p- and 4s-electrons as valence electrons. Total energy of bulk Ca is well converged with cutoff energy above 40Ry. On the other hand, calculation of carbon needs higher cutoff due to localized charge around bonds. We adopt cutoff energy of 40Ry and 60Ry for calculations of Ca compounds and carbon, respectively.

For the integration of the first Brillouin zone of  $\text{CaSi}_2$ , we adopt 8 ( $2 \times 2 \times 2$ ) uniform k-points for the structural optimization and FPMD. While uniform k-points up to 81 points are used for the calculation of carbon. Wigner type exchange-correlation energy is used throughout the calculations. For finite temperature MD, Nosé thermostat is adopted.

### 3. GRAPHITE-DIAMOND TRANSFORMATION

As well-known, graphite undergoes structural transformations into two types of diamond, *i.e.* cubic diamond and hexagonal diamond by applied pressure around 14-20 GPa. FPMD with constant pressure scheme is satisfactorily applied to graphite by Scandolo *et al.*,<sup>6</sup> who showed theoretically that both transformations can happen. We have independently performed constant-pressure FPMD simulation of graphite and obtained change in charge density at the moment of transformation to the hexagonal diamond.<sup>7</sup> In these

simulations, isotropic compression cause reduction of inter-layer distance of graphite, which is followed by inter-layer bond formation.

The 3-dimensional  $sp^3$  framework of the cubic diamond is created by mutual sliding of AB-stacked honeycomb sheets of graphite accompanied with zigzag corrugation of them. This transformation path is indeed confirmed by Scandolo *et al.*<sup>6</sup> On the other hand, the hexagonal diamond is made from formation of local armchair structure without lateral displacement.

In order to compare transition probability of two diamond structures from graphite we calculated activation barriers for these transformation by determining saddle points of the potential surface using a newly developed method for saddle point search.<sup>7</sup> We found that the cubic diamond is obtained with smaller activation energy irrespective of the pressure up to 20GPa. The results indicate that the cubic diamond is favored whenever collective sliding motion of graphite sheet is allowed, although the hexagonal diamond will be obtained if such slide is prohibited.

### 4. LOW- AND HIGH-PRESSURE PHASES OF $\text{CaSi}_2$

We now investigate calcium di-silicide as an example of 2- or 3-dimensional Si-network. There are three polymorphs of  $\text{CaSi}_2$  known experimentally.<sup>4</sup> The most popular one is the layered  $\text{CaSi}_2$ , which consists of double layers of Si sandwiched between trigonal layers of Ca, and vice versa. From two possibilities of stacking sequences, we choose the ABC stacking as a starting material here, which we call "trigonal  $\text{CaSi}_2$ ". (Fig. 1(a)) In this trigonal phase, Si atoms are bonded by  $sp^3$ -like connection.

Another polymorph has a 3-dimensional framework of  $sp^2$ -like bond connection, which we call "tetragonal  $\text{CaSi}_2$ ". (Fig. 1(b)) Experimentally, tetragonal phase is obtained by a structural transformation from the low-pressure trigonal phase by high-temperature/high-pressure treatment. Typical conditions are 4GPa and 1300-1800K.

We have performed structural optimization of trigonal and tetragonal structures in isotropic pressure up to 20GPa. For the trigonal phase, we use orthorhombic unit cell (6 Ca, 12 Si), while primitive unit cell (4 Ca, 8 Si) is used for the

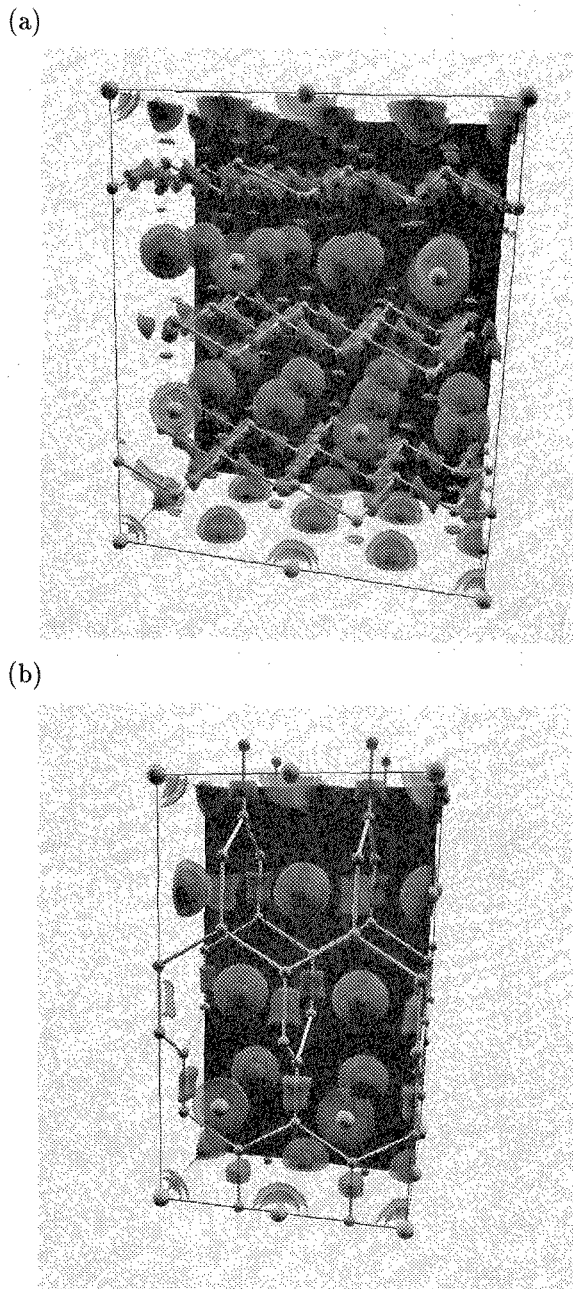


Figure 1: Trigonal (a) and tetragonal phase (b) of  $\text{CaSi}_2$  optimized by FPMD. Smaller spheres represent Si atoms, while larger ones are Ca. Charge density is also shown by a contour.

(a) Trigonal

	Present (0GPa)	Present (20GPa)	Exp. <sup>2</sup>
a-axis	3.88	3.45 (3.71)	3.82
c-axis	15.93	15.33	15.98
c/a	4.11	4.44 (4.13)	4.18
z	0.197	0.198	0.197

(b) Tetragonal

	Present (0GPa)	Present (20GPa)	Exp. <sup>3</sup>
a-axis	4.33	3.839	4.283
c-axis	14.15	14.06	13.52
c/a	3.27	3.662	3.157
z	0.420	0.4196	0.413

Table 1: Optimized structural parameters of trigonal (a) and tetragonal (b) phase of  $\text{CaSi}_2$ . Positional parameter  $z$  for Si is in  $6c$  or  $8e$  for trigonal phase ( $D_{3d}^5-R\bar{3}m$ ) or tetragonal phase ( $D_{4h}^{19}-I4_1/amd$ ). Unit of length is  $\text{\AA}$ . Optimized tetragonal structure has anisotropy on a- and b-axis (shown in parenthesis). (See text.)

tetragonal phase. Obtained structural parameters for 0GPa shows good agreement with the experimentally observed values. (Table 1) Here we should comment that the optimized cell for the trigonal phase has weak anisotropy on a- and b-axis. This may be caused from small number of k-points used for the k-point sampling. This deviation, however, will not change our conclusion in the next section.

Now we discuss structure and charge distribution. Si corrugated sheet for the trigonal phase has almost the same (but slightly smaller) bonding angle as  $sp^3$  connection. Bond length between Si atoms is elongated by about 3.6% compared to that of bulk Si. At the top of each triangular pyramid of Si, a hump of electron density is found, which suggests existence of a lone pair. There is no indication of bonding between Ca and Si.

For tetragonal phase, we may decompose 3D structure into 1D zigzag chains bridged by bonds parallel to c-axis. However, bond length is shorter for inter-chain bond. ( $\text{Si-Si}_{\text{inter}} = 2.27\text{\AA}(2.27\text{\AA})$  and  $\text{Si-Si}_{\text{intra}} = 2.50\text{\AA}(2.41\text{\AA})$  in the optimized (experimental) structure.) We can clearly see bond-charge for each Si dimer parallel to c-axis compared to that in 1D chains. (Fig. 1(b)) The

reason for the difference between two Si-Si bond lengths may come from that charge transfer from Ca to Si network weakens bonds of the 1D zigzag chain. Detailed analysis will be presented elsewhere.

Next we discuss high pressure phase of  $\text{CaSi}_2$ . Two structures are optimized up to 20GPa, *i.e.* they are stable (or meta-stable) phase.  $c/a$  ratio is almost the same as or becomes larger than that at 0GPa for both structures, which means that lattices shrink almost uniformly by isotropic compression. In contrast, we see anisotropic elasticity in graphite, which originates from hard  $sp^2$ -bonded 2D networks weakly combined together by inter-plane van der Waals interaction.

## 5. PRESSURE-INDUCED PHASE TRANSFORMATION OF $\text{CaSi}_2$

If we consider thermal equilibrium condition, relative stability of each phase is determined by comparing enthalpy as shown in Fig. 2. At ambient pressure, trigonal phase is stable against orthorhombic phase by 136 meV/ $\text{CaSi}_2$ . When the pressure is increased, dense orthorhombic structure is stabilized. Thus, phase transformation will occur for high temperature.

However, the result in the last section indicates that the trigonal phase remains to be meta-stable when the static pressure is applied at low temperature. The reasons are the followings. i)  $sp^3$ -bonded corrugated Si sheet is soft against deformation, because Si-Si bonding is rather weak and bond length varies easily. ii) Ionic repulsion between Si and Ca layer inhibits interlayer Si-Si bonding.

In order to induce bond-formation between two Si planes, it seems that uniaxial compression will work as a trigger. We performed FPMD with anisotropic pressure following the generalized scheme mentioned before. Then we observed that Ca atoms gradually keep away from each other and new inter-layer bonds are created between Si atoms. Investigation on character and stability of the structure will be given in future.

## 6. CONCLUSION

As we have shown, the constant pressure FPMD can give much information about pressure-induced phenomena for various materials. Variety of ac-

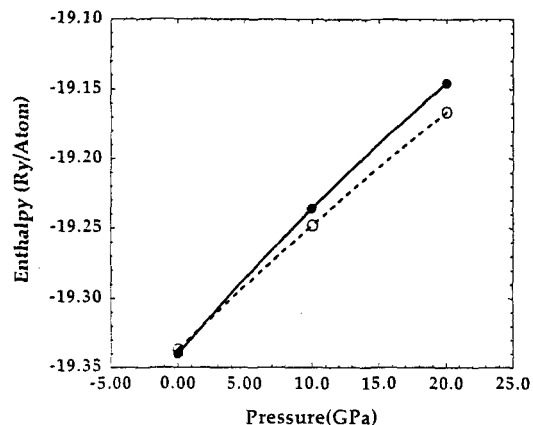


Figure 2: Enthalpy of  $\text{CaSi}_2$  for trigonal (●) and tetragonal (○) phase. Lines are guide to the eye.

cessible knowledge spreads as follows: i) structural information of stable and metastable state at any pressure condition. ii) saddle point structure and activation energy. iii) transformation path. iv) conditions to cause structural transformation. These information would be a seed of synthesis of new materials.

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