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Theoretical possibility of stage corrugation in Si and Ge analogs of graphite

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The planarity of the aromatic stage of two-dimensional Si and Ge layers are theoretically investigated by first-principles total-energy calculations. While a C atom prefers to form the flat aromatic stage, i.e., graphite, Si and Ge prefer to form the corrugated aromatic stage. Si can be said to be the critical element by which the corrugated stage is formed.

I. INTRODUCTION

Recent developments in organosilicon chemistry[1] have led to the synthesis of Si materials of novel structure, such as Si linear quasi-one-dimensional (1D) chains of single and ladder forms, two-dimensional layered materials, and three-dimensional clusters having curious structures. With the discovery of porous Si, which produces a significant visible luminescence, these newly structurized Si materials are being eagerly studied both experimentally and theoretically.

On the consideration of these newly structurized Si materials, the corresponding structures of carbon analogs are the fundamental bases. Many types of Si-saturated skeletons analogous to those C polymers have been synthesized. Aromatic Si compounds, however, remain to be studied. The recent success in synthesizing Si-Si double-bonded compounds[2] has also attracted attention to this field. Thus, attention is now being given to the study of the possible existence of Si aromatic compounds and their electronic structure.

Typical aromatic Si model compounds are a Si finite system of hexasilabenzen, Si_6H_6 (HSB), and an infinite system of Si 2D aromatic stage (AS). The former is the Si complete analog of benzene, and the latter is that of graphite. Although several theoretical calculations on HSB have been reported,[3-7] little theoretical work has been performed on the infinite 2D Si AS system. In this paper, we report the results of a total-energy calculation on the infinite 2D Si aromatic stages and discuss their electronic structures. The calculations were carried out for two types of Si stages having different symmetries; the D_{6h} flat stage (Si complete analog of graphite) and the D_{3d} corrugated stage [(111) plane of crystalline Si]. The geometrical stability of these two 2D Si stages was investigated theoretically.

An understanding of the similarities and differences among the group-IV elements C, Si, and Ge is essential to clarify the structural stability as well as the electronic structures. For this purpose, the calculation was extended to the C aromatic stage and Ge aromatic stage. The present infinite 2D Si AS is a hypothetical material, but it is an important model for investigating the aromaticity of Si elements as well as HSB. The study might connect to that on the electronic properties of metal-disilicide compounds with alkali-earth metals,[8] which have Si-layered stages.

II. CALCULATION METHOD

Present calculations are performed using the first-principles local-density functional (LDF) method.[14,15] We use the norm-conserving pseudopotential introduced by Hamann, Schluter, and Chiang and Bachelet, Haman, and Schluter,[17] in which the core basis functions are neglected. The exchange-correlation energy is, here, approximated by the functional form of Ceperley and Alder's[18] potential parametrized by Perdew and Zunger.[19] In addition to this, the calculation using the $X\alpha$ expression and Wigner's representation[20] are also carried out for a comparison.

The Bloch function is expressed here in two forms. The first is the linear combination of atomic orbitals (LCAO) form of the pseudoatomic wave function, which is obtained numerically in terms of the sum of Gaussian-type orbitals (GTO's).[21,22] We determined the parameters of the expansion coefficients and the Gaussian exponent α_i by the least-squares-fit method. These values have been reported in our previous paper.[23,24]

The second expression for the Bloch function is the plane-wave expansion.[25-27] Plane waves with a kinetic energy of up to 12.25 Ry (Ref. 28) for Si and Ge stage are included in the expansion of the wave functions. However, a larger number of expansion terms are needed for C's atomic orbital (AO) expansion, because AO's of carbon are localized compared with those of Si and Ge. Therefore, plane waves with a kinetic energy of up to 64.0 Ry are included in the expansion of the wave function for C-stage calculations.

The potential gradients and the geometry optimization are, here, carried out by the guide of Hellmann-Feynmann force:[29,30] The geometry optimization for the C stage was checked by the D_{6h} flat stage, i.e., graphite structure. The present optimized bond length (1.43 Å) agrees well with the experimental result (1.42 Å) within a 1% error, independent of the Bloch-function expansion with the plane waves or with the LCAO-GTO basis.

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III. Si AROMATIC STAGE

The geometrical optimization of the aromatic flat-stage structure (Si complete analog of graphite) can be performed only in terms of varying one parameter of the lattice constant A_0, if the D_{6h} symmetry is maintained during the optimization. Figure 1 shows the change in the total energy of the Si 2D flat stage with varying the lattice constant A_0. The minimum value of the total energy is found when the lattice constant is 3.855 Å. The same or similar optimized lattice constants are also obtained by using the $X\alpha$ or Wigner's exchange-correlation representations, respectively. This optimized value of 3.855 Å is accidentally coincident with that for the Si 2D corrugated stage found in $CaSi_2$.[9,13]

On the contrary, in the optimization of the corrugated-stage structure having the D_{3d} symmetry, the deformation angle θ (Ref. 31) should be included as an optimized geometrical parameter, in addition to the above lattice constant. Figure 2 shows the change in the total energy when these two parameters vary. The calculation is based on the LCAO expansion of the Bloch function with a GTO basis, and the functional form of Ceperley-Alder's potential parametrized by Perdew and Zunger is used for the exchange-correlation term. The energy values in the figure are taken from that of the optimized Si flat stage. The negative region surrounded by the solid line, therefore, corresponds to those where the Si corrugated stage is more stable than the Si flat stage. A similar negative region is also found in Fig. 3, in which the Bloch function is expanded with the plane waves and the $X\alpha$ exchange-correlation potential is adopted.

In Fig. 4, we show the calculated z components[31] of the Hellmann-Feynmann forces working at two Si atoms, A and B, of the unit cell, whose lattice constant is assumed to be the optimized value of 3.855 Å. When the deformation angle is small, the Si A atom is moved to the positive direction of the z axis because the z component of the Hellmann-Feynmann force working at the atom A is positive. Contrary, the Si B atom is moved to the negative direction because of its negative z-component value. Therefore, these two forces play as a puckering force to corrugate the Si stage and increase the deformation angle. However, when the value of the deformation angle exceeds 10°, the force directions working at these two atoms are changed to be quite opposite, so that the restoring force to reduce the deformation is induced. Thus, based on the total-energy calculation within the LDF approach and using the present pseudopotential, it is theoretically suggested that the infinite 2D Si AS prefers to pucker its stage plane and that the corrugated stage (at least having the D_{3d} symmetry[32]) is more stable than the flat stage having the D_{6h} symmetry.

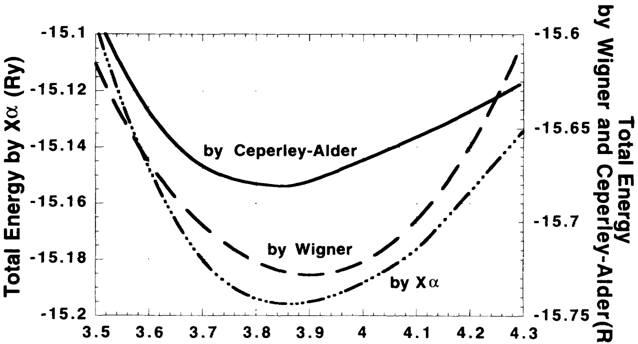

FIG. 1. Change in the total energy of the Si flat stage with varying lattice constant. The exchange-correlation potential is estimated by three different approaches, the functional form of Ceperley and Alder's potential parametrized by Perdew and Zunger, the $X\alpha$ method with $\alpha=0.7$, and Wigner's representation. The D_{6h} symmetry is maintained through the optimization.

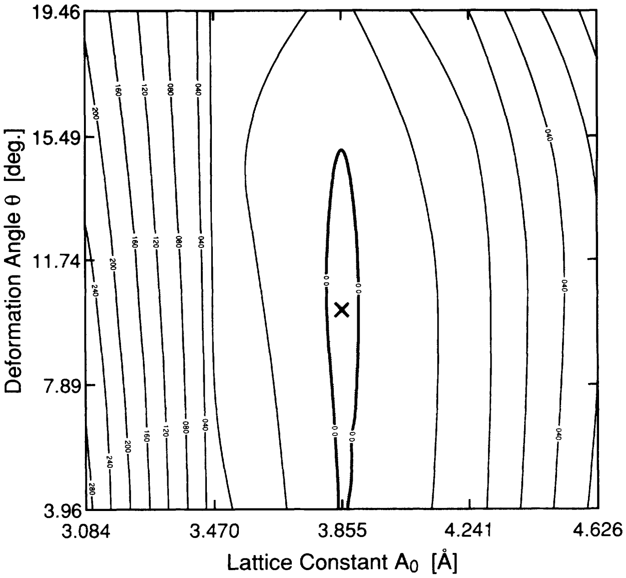

FIG. 2. Change in the total energy of the Si-corrugated stage with varying lattice constant and deformation angle. The D_{3d} symmetry is maintained through the optimization. The shadowed region corresponds to the area where the corrugated Si stage is more stable than the flat one. Values of the total energy are taken from that of the optimized Si flat-stage structure and the contour is shown from zero to 0.29 Ry with an interval of 0.01 Ry (right side) and 0.04 Ry (left side). The local minimum point is shown by ×. The calculation is based on the LCAO expansion of the Bloch function with GTO basis, and the Ceperley-Alder functional form with Perdew and Zunger's parameters is used for the exchange-correlation term.

This feature is in large contrast to the C AS system: We similarly calculated the total energies of the C aromatic stages having two different symmetries, D_{6h} and D_{3d}. The C AS system does not produce such a region where the corrugated stage is more stable than the flat one. The calculated Hellmann-Feynmann forces working at C atoms indicate that C atoms always form a planar skeleton, i.e., a *graphite* structure.

The estimation of the exchange-correlation term is one of the most serious problems in the LDA calculation. The degree of the stage corrugation is slightly different between Figs. 2 and 3. It depends on the expression of the exchange-correlation potential, while the optimized flat stage is obtained independently of the differences in

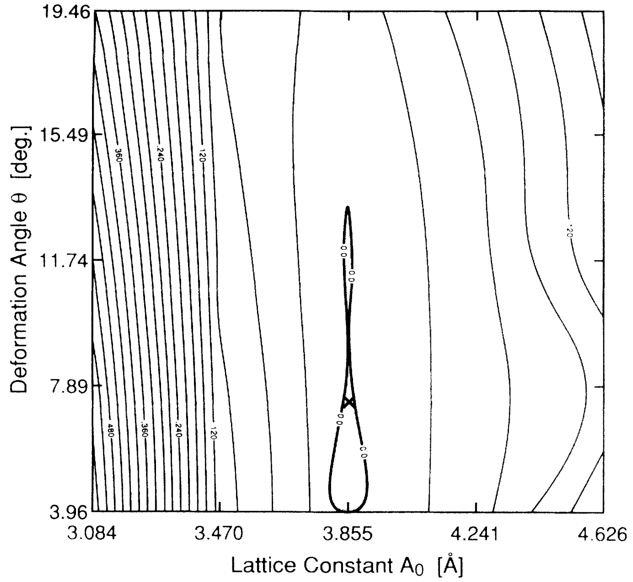

FIG. 3. Change in the total energy of the Si corrugated stage with varying lattice constant and deformation angle. The D_{3d} symmetry is maintained through the optimization. The shadowed region corresponds to the area where the corrugated Si stage is more stable than the flat one. Values of the total energy are taken from that of the optimized Si flat-stage structure and the contour is shown from 0 to 0.54 Ry with an interval of 0.03 Ry. The local minimum point is shown by ×. The Bloch function is expanded with the plane waves, and the $X\alpha$ ($\alpha=0.7$) exchange-correlation potential is used in the calculation.

the exchange-correlation potential as well as in the basis (Fig. 1). Here, we investigate this problem by varying the α value of the $X\alpha$ approach parametrically from zero to 1.5 (Ref. 34) and discuss how the electron-correlation changes the stage corrugation. This is because the study on the relation between the electron correlation and the geometry of the Si stage is another purpose of the present work. The present *ad hoc* $X\alpha$ procedure is a crude way to investigate the nature of the electron correlation and results in a qualitative tendency only. Keeping in mind the applicability of this approach, however, the result might mean something. Figure 5 shows the change in the total energy of the corrugated stage with varying α values. The resulting values are expressed in terms of subtracting the value of the flat stage at each corresponding α value.[35]

In the weak correlation region, the corrugated stage is more stable than the flat stage. This relation maintains up to α of 0.76, but is changed so that the D_{6h} flat stage tends to be more stable than the corrugated stage when the correlation is strengthened. Since the α value of 0.7 is reported to describe a good exchange-correlation potential, the corrugated Si stage could be concluded to be stable. This feature is confirmed by the result using the Ceperley-Alder potential (Fig. 2), but is in sharp contrast with that of the C-stage as shown in Fig. 6, where the D_{6h} flat plane of the graphite stage is more stable than the D_{3d} corrugated stage[36] independent of the α values.

By subtracting the total energy of the optimized Si flat stage from that of the optimized Si corrugated stage, the stabilization energy due to the skeleton puckering can be obtained. This stabilization energy is comparable to that of the Si finite HSB system. The present calculation by using the LCAO-GTO expansion and the Ceperley-Alder potential gives the value of 0.69 kJ/mol per each Si atom for the infinite Si 2D AS system. A similar value of 0.34 kJ/mol is also obtained by the calculation with the plane-wave expansion and the $X\alpha$ potential. Nagase, Teramae, and Kudo[4] showed that the finite HSB system gives values from 0.082 kJ/mol at the Hartree-Fock (HF) level calculation with the polarized 6-31G^* basis sets (HF/6-31G^*) to 1.175 kJ/mol by using the Möller-Plesset perturbation approach with 6-31G^* basis sets on the HF/6-31G^* optimized structure calculation, per each Si-H diatom.

Let us discuss the bond lengths of the flat and corrugated stages. The optimized Si infinite corrugated stage (D_{3d}) also gives the lattice constant of 3.855 Å, which

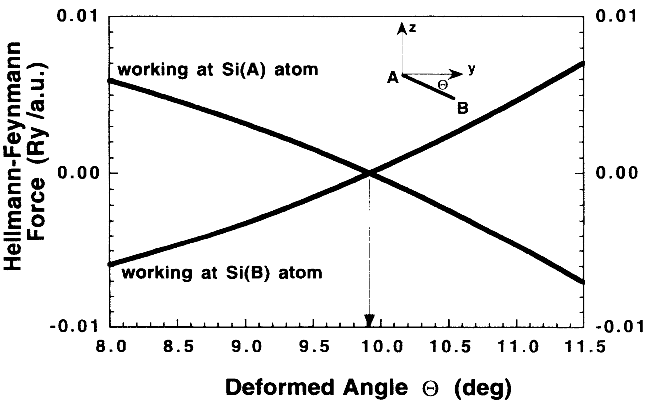

FIG. 4. z components of calculated Hellmann-Feynmann forces working at Si atoms A and B in the unit cell. The lattice constant is fixed to be the optimized value of 3.855 Å. The arrow shown in the figure gives the deformation angle where z components of both Hellmann-Feynmann force are to be zero.

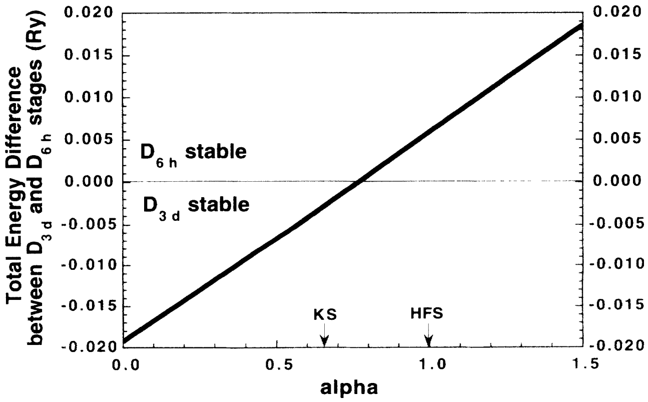

FIG. 5. Change in the total energy of the Si corrugated stage with varying α. Values are taken from that of the Si flat stage at each same α. KS shows the value $\alpha=\frac{2}{3}$ by the Kohn-Sham approximation and HFS shows that of 1 by Hartree-Fock-Slater approximation.

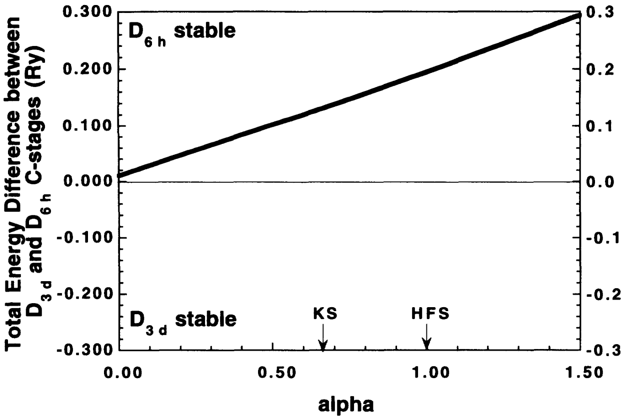

FIG. 6. Change in the total energy of the C corrugated stage with varying α. Values are taken from that of the C flat stage at each same α. KS shows the value $\alpha = \frac{2}{3}$ by the Kohn-Sham approximation and HFS shows that of 1 by the Hartree-Fock-Slater approximation.

coincides with that observed in $CaSi_2$.[9,13] Thus, two types of Si 2D stages having the different symmetries D_{6h} and D_{3d} give the same optimized lattice constants. However, the inter-Si-Si bond lengths are different between them; the corrugated stage gives 2.247 Å but the flat stage gives a shorter one of 2.226 Å (Table I). This means that the puckering deformation from the D_{6h} to D_{3d} symmetry lengthens the bond lengths. This is because this type of the deformation causes the sp^3 hybridization and weakens the double-bond nature between Si atoms. The bond elongation estimated in the Si infinite 2D stage is about ten times larger than that of the Si finite system of HSB, in which the D_{3d} deformation lengthens the Si-Si bond by only 0.004 Å, relative to the D_{6h} structure.[4] Thus, the infiniteness of the Si 2D-stage strengthens to reduce the double-bond character, and results in the longer bond elongation compared with the H-terminated finite system.

In order to consider how the energy parts contribute to the stage corrugation, we decompose the total energy into several energy parts; the lattice (intercore) repulsive potential,[33] Hartree repulsive potential, (ion) core-electron attractive potential, kinetic-attractive potential, and the exchange-correlation potential. These values of the D_{3d} optimized corrugated stage are represented in Fig. 7 in terms of subtracting those corresponding values of the optimized D_{6h} flat stage from them. The negative values, therefore, prefer to form the corrugated stage while the positive values prefer to form the flat stage.

TABLE I. Comparison of the optimized lattice constant A_0/ and bond length d for C, Si, and Ge stage. Both values are in angstroms.

	C stage	Si stage	Ge stage
D_{6h}	2.485/1.435	3.855/2.226	3.985/2.301
D_{3d}	2.455/1.503	3.855/2.247	3.890/2.331
diff.	4.7%	0.94%	1.3%

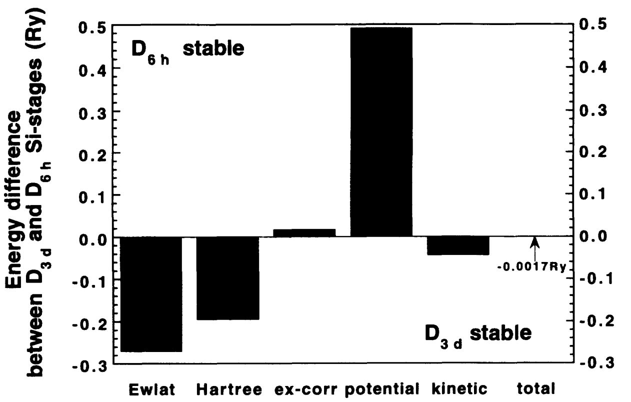

FIG. 7. Contribution of the lattice repulsive potential (Ewalt), Hartree repulsive potential, core-electron attractive potential, kinetic-attractive potential, and the exchange-correlation potential to the formation of D_{6h} and D_{3d} Si stages. The calculation is carried out by the plane-wave expansion and using the $X\alpha$ exchange-correlation potential, for comparison with those results for the Ge and C stages.

Based on the negative value of the intercore repulsive lattice potential, this energy term prefers to form the corrugated stage rather than the flat stage. This is because the corrugated stage has a larger Si-Si bond length than that of the flat stage and produces the smaller intercore repulsive potential. Since the stage corrugation results in a larger effective "volume" of the lattice size, electrons in this stage are able to delocalize toward out of stage as well as toward in stage. Therefore, the corrugated stage produces the smaller interelectron repulsive energy. This feature is confirmed by the fact that the Hartree term prefers to form the corrugated stage rather than the flat stage. On the contrary, the slightly localized character in the flat stage causes the larger potential energy between ion cores and electrons in the local-density-approximation (LDA) approach and tends to form the flat stage rather than the corrugated stage. The electronic delocalization also produces larger stabilization due to the kinetic energy in the corrugated stage compared with that in the flat stage.

According to the resulting positive value of the exchange-correlation term as shown in Fig. 7, it can be said that the electron correlation in the Si infinite 2D stage plays a role in the flat-stage formation rather than in the corrugated-stage formation. This feature is opposite to the molecular orbital result on the Si finite plane of HSB reported by Nagase, Teramae, and Kudo.[4] They found that the restricted HF solutions of HSB are singlet stable but undergo a significant triplet (nonsinglet) instability at both D_{6h} and D_{3d} structures, and are less stable than the spin-density-wave solution. Based on these results, they explain the preference of the D_{3d} corrugated HSB over the D_{6h} flat HSB in terms of some "multiradical" character of the skeletal bonding, i.e., the antiferromagneticlike localization of electrons onto each Si atom.

Thus, the electron correlation functions on the stage formation differently between the 2D stage and HSB systems. This difference might be caused from the difference in the system size, because HSB is a finite system terminated by H atoms but the aromatic stage is an infinite system, in which electrons can delocalize on the stage infinitely: The Bloch states are formed and the well-dispersive E-**k** relations are found in the band structure (Fig. 8).

Si corrugated planes are found in the metal-disilicide compared with Ca atoms ($CaSi_2$), in which a Ca layer is placed between Si_2 corrugated layers.[9,13] The electronic structure of this compound has been intensively investigated by Bisi *et al.*[10] and Fahy and Hamann.[11] According to their results, the strong hybridization is found among Ca $3d$ levels and Si $3p$ levels at the Fermi level, and the significant charge transfer (CT) occurs between the Si corrugated stage and Ca layer. This CT changes the electronic structure from semimetallic (Fig. 8) to metallic.[10,11] Of course this CT plays an important role in establishing the Si-corrugated layers. However, one should notice that the puckering feature of the Si 2D plane is essential and originates from the weakness of the Si skeleton's aromaticity itself. In this sense, it should be said that the CT among Si and Ca atoms works to enhance the puckering nature of the Si 2D skeleton.

IV. Ge AROMATIC STAGE

This investigation is extended to the Ge aromatic stage for comparison. After the optimization on the flat-stage structure having the D_{6h} symmetry (Fig. 9), the total energies of the D_{3d} corrugated stage are similarly mapped by varying both the lattice constant and the puckering angle (Fig. 10). The energy value is taken from that of the optimized D_{6h} flat stage of Fig. 9. The Ge stage also has the possibility of preferring the corrugated stage rather than the flat stage. The characteristic difference from the Si stage is that the corrugation and the stabilization of the Ge stage are more strengthened.

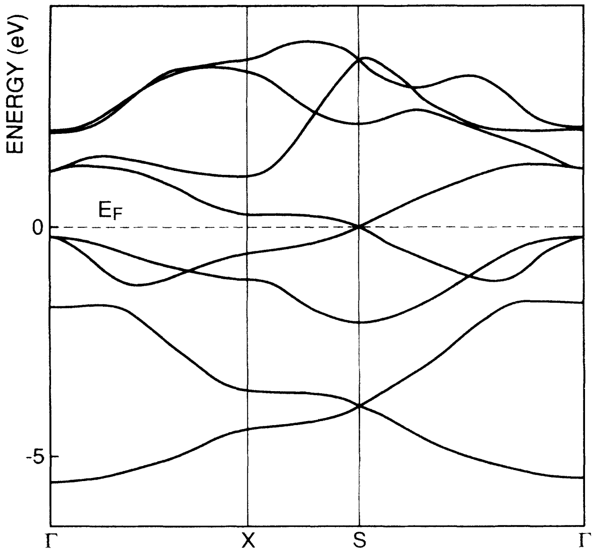

FIG. 8. Calculated energy-band structure of the Si corrugated stage having optimized atomic geometry.

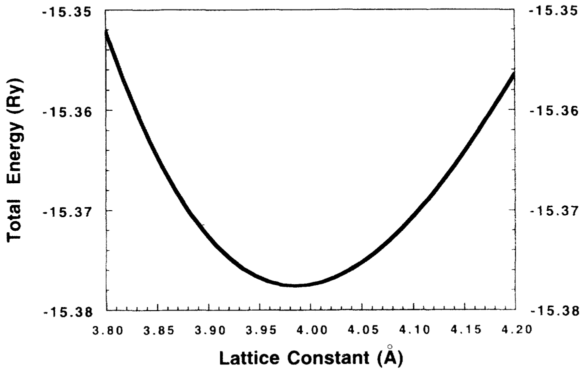

FIG. 9. Change in the total energy of the Ge flat stage with varying lattice constant. The D_{6h} symmetry is maintained through the optimization. The calculation is carried out by the plane-wave expansion and using the $X\alpha$ exchange-correlation potential with $\alpha = 0.7$.

We decompose the total energy into several parts and show those of three kinds of materials in Fig. 11. For the consideration on the similarity and/or the difference among the C, Si, and Ge stage, it is important to note that the D_{3d} corrugated stage provides the interatomic bond length that is longer than that of the D_{6h} flat stage independent of the kind of elements, as shown in Table I. It should be also noticed that the difference in the bond lengths between the optimized corrugated (D_{3d}) and flat (D_{6h}) stages ($\Delta d_{D_{3d}\text{-}D_{6h}}$) is reduced in the order of [C (Ref. 37)]-Ge-Si. This order is important in interpreting

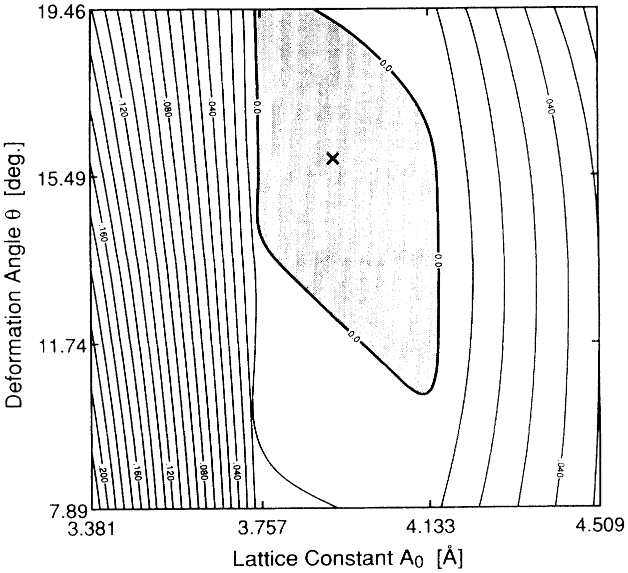

FIG. 10. Change in the total energy of the Ge corrugated stage with varying lattice constant and deformation angle. The D_{3d} symmetry is maintained through the optimization. The shadowed region corresponds to the area where the corrugated Ge stage is more stable than the flat one. Values of the total energy are taken from that of the optimized Ge flat-stage structure and the contour is shown from 0 to 0.22 Ry with an interval of 0.01 Ry. The local minimum point is shown by ×. The calculation is carried out by the plane-wave expansion and using the $X\alpha$ exchange-correlation potential with $\alpha = 0.7$.

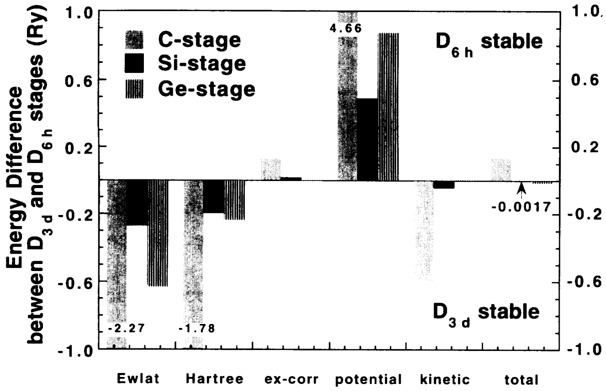

FIG. 11. Contribution of the lattice repulsive potential, Hartree repulsive potential, core-electron attractive potential, kinetic-attractive potential, and the exchange-correlation potential to the formation of D_{6h} and D_{3d} C, Si, and Ge stages. Results are calculated by the $X\alpha$ method with $\alpha=0.7$ and using the plane-wave expansion for a comparison with those for Si and C.

the stage corrugation among these group-IV stages.

Independent of the difference of the elements, the intercore lattice repulsive potential prefers to form the D_{3d} corrugated stage rather than the D_{6h} flat stage. This is because the former's interatomic distances are longer than the latter's, and they cause the smaller intercore repulsive energies. Let us discuss the difference among the C, Si, and Ge elements. The smallest D_{3d} stabilization due to this lattice repulsive potential is found in the Si stage, and this stabilization increases in the order of the Ge and C stage. This tendency originates from the difference in the values of the optimized interatomic bond lengths, $\Delta d_{D_{3d}\text{-}D_{6h}}$.

A similar characteristic is found in the Hartree repulsive energy. The spatial extension due to the stage corrugation lets electrons delocalize toward out of stage as well as within in stage. This electron delocalization weakens the interelectron Coulomb repulsive energy.

On the contrary, the core-electron potential energy acts oppositely, because this energy is the attractive one. Since the electrons in the D_{6h} flat stages can be said to localize compared with those in the D_{3d} corrugated stage, the larger stabilization due to the core-electron potential energy occurs in the former stage. The delocalized electrons in the D_{3d} corrugated stages also stabilize their corrugated forms by the kinetic energy. The degree of the stabilizations are in the order of $\Delta d_{D_{3d}\text{-}D_{6h}}$ except for that due to the kinetic term in the Ge stage.

Thus, each energy term functions similarly to contribute to stage formation among the group-IV elements (C) Si and Ge. However, the resulting total energies are different. Only a C atom prefers to form the D_{6h} flat aromatic stage, while Si and Ge prefer to form the D_{3d} corrugated aromatic stage. C's preference of the flat stage, i.e., *graphite* structure, is a result of the extremely large stabilization due to the ion core-electron attractive potential, whose large values might be originated from the strong electron-localized property due to the shortest interatomic distance among the group-IV elements.

In conclusion, Si can be said to be the critical element among the group-IV elements, which form the corrugated stage. The difference in the role of the electron correlation in the stage formation among the finite and infinite systems might originate from the difference in their sizes, where the electron delocalization is different. Therefore, further studies on the larger finite systems, e.g., naphthalene, should be carried out.

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[31] The puckering of the skeleton plane is, here, defined by the angle θ which is determined as follows: In the calculation, the unit cell includes two atoms, A and B. One of them (A) is placed at origin. The other (B) is able to be placed on the y axis and the two atoms are in the xy plane, when the skeleton maintains the D_{6h} symmetry. When skeleton puckering occurs, atom B varies its position to be out of the xy plane (z direction). The puckering angle θ is, then, defined by the angle between line AB and the y axis.

[32] Performing a total-energy calculation on a structure with a number of externally imposed constraints such as the space group symmetry and translational invariance does not guarantee that the lowest-energy structure found within those constraints is most stable. For the prediction of the existence of a new phase of Si, these constraints should be relaxed and also all the phonon frequencies should be shown to be real in order to distinguish the state from the transition states. This new phase of Si has been intensively investigated by L. L. Boyer, E. Kaxiras, J. L. Feldman, J. Q. Broughton, and M. J. Mehl, Phys. Rev. Lett. **67**, 715 (1991). However, here, we limit the stability between the flat aromatic stage and the corrugated one.

[33] The lattice repulsive potential is calculated in terms of Ewalt's sum method here.

[34] In the present *ad hoc* $X\alpha$ procedure, the interelectron interaction of the correlation as well as exchange is included in the scheme of the LDA. The strength of the electron correlation is expressed by varying the α value. Thus, α values used in the calculation are out of $\frac{2}{3}$ by the Kohn-Sham approximation (small correlation), and of 1 by the Hartree-Fock-Slater approximation (strong correlation).

[35] When varying the value of α, the optimized structure slightly changes. In the present calculation, however, we carried out the single-point calculation on the optimized structures with α of 0.7.

[36] In a 2D infinite C AS system, there is no stable D_{3d} corrugated stage. However, for comparison with the other 2D infinite AS systems of Si and Ge, we introduce a hypothetically "optimized" C corrugated stage having D_{3d} symmetry. All bonds are bonded with tetrahedral angles. Only the lattice constant A_0 is "optimized" and its value is 2.455 Å. This "optimized" corrugated-stage is more unstable than that of the optimized D_{6h} flat stage, i.e., graphite, by 0.7768 Ry/C.

[37] The C stage shows the most significant difference in the bond length between the two optimized stages with D_{6h} and D_{3d} symmetry. This significant difference is, however, meaningless, because the C stage has no stable D_{3d} corrugated stage. This value is estimated by using the hypothetically "optimized" corrugated-stage structure (Ref. 36).

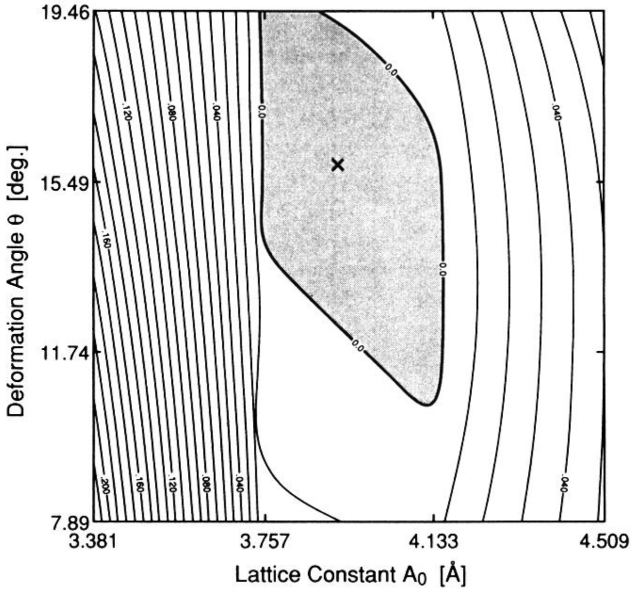

FIG. 10. Change in the total energy of the Ge corrugated stage with varying lattice constant and deformation angle. The D_{3d} symmetry is maintained through the optimization. The shadowed region corresponds to the area where the corrugated Ge stage is more stable than the flat one. Values of the total energy are taken from that of the optimized Ge flat-stage structure and the contour is shown from 0 to 0.22 Ry with an interval of 0.01 Ry. The local minimum point is shown by ×. The calculation is carried out by the plane-wave expansion and using the $X\alpha$ exchange-correlation potential with $\alpha = 0.7$.

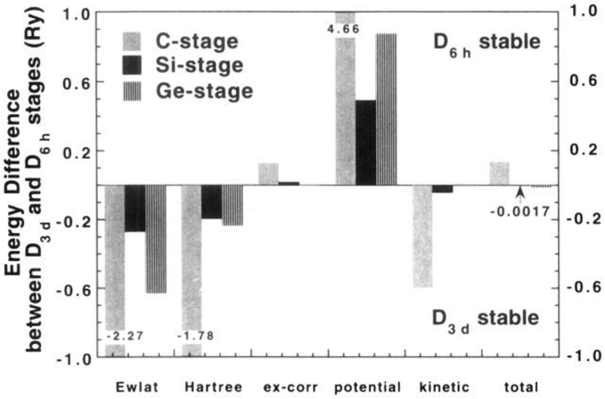

FIG. 11. Contribution of the lattice repulsive potential, Hartree repulsive potential, core-electron attractive potential, kinetic-attractive potential, and the exchange-correlation potential to the formation of D_{6h} and D_{3d} C, Si, and Ge stages. Results are calculated by the $X\alpha$ method with $\alpha=0.7$ and using the plane-wave expansion for a comparison with those for Si and C.

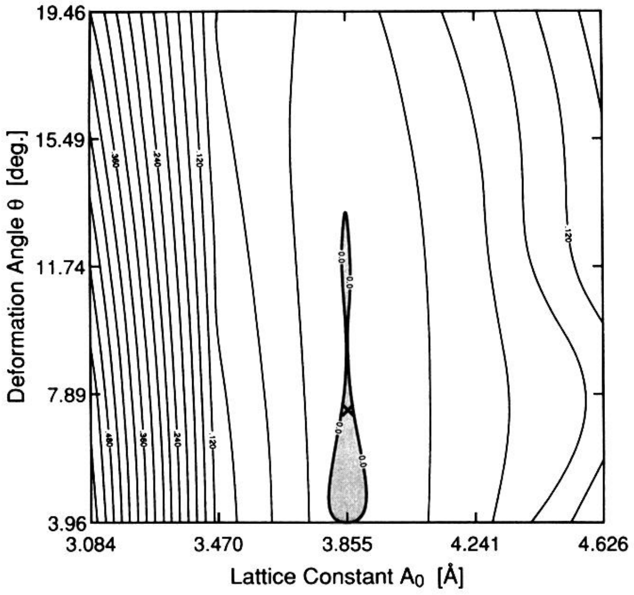

FIG. 3. Change in the total energy of the Si corrugated stage with varying lattice constant and deformation angle. The D_{3d} symmetry is maintained through the optimization. The shadowed region corresponds to the area where the corrugated Si stage is more stable than the flat one. Values of the total energy are taken from that of the optimized Si flat-stage structure and the contour is shown from 0 to 0.54 Ry with an interval of 0.03 Ry. The local minimum point is shown by ×. The Bloch function is expanded with the plane waves, and the $X\alpha$ ($\alpha=0.7$) exchange-correlation potential is used in the calculation.