PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

New crystalline structures for Si and Ge

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(Received 6 May 1985)

A new class of crystalline structures for group-IV materials is proposed. The basic building block for all the new structures is a two-dimensionally ordered slab of atoms which can be stacked together in several distinct ways. The most stable structure obtained in this way has a 20-atom *orthorhombic* unit cell. For Si, the total energy for this structure is calculated to be $\simeq$30 meV per atom higher, and the atomic density 1.3% lower, than in the diamond structure. Other structures with 16, 18, and 32 atoms per unit cell are constructed and their energetic, atomic, and electronic properties are examined. The 32-atom structure is closely related to the recently discovered *allo*-Ge phase.

I. INTRODUCTION

It is well known that, under pressure, diamond-structure Si and Ge undergo a number of structural transformations. Crystalline structures with a body-centered-cubic cell containing eight atoms,[1-3] a simple-tetragonal cell with twelve atoms,[1,2] a β-Sn phase with four atoms per cell,[4] a $4H$ hexagonal cell with eight atoms,[5] and simple-hexagonal[6,7] and hexagonal-close-packed[6] cells each with a single atom have been obtained. The structural, electronic, and energetic aspects of these forms have been extensively studied.[8-12] Recently, a novel crystalline form with an orthorhombic unit cell containing 128 atoms, named *allo*-Ge, has been added to this list.[5] A chemical process and not a high-pressure technique was used in the preparation of *allo*-Ge. Structural phase transformations, first from the *allo*- to the $4H$ phase and then to the diamond structure were observed at $T=420$ and 720 K, respectively.

The essential building block of the new structure consists of a two-dimensionally periodic array of (Ge) atoms shown in Fig. 1. The unit cell contains eight atoms which form planar and puckered fivefold rings. In this paper the question of the types of structure that can be obtained from the layer-type building block shown in Fig. 1 is addressed. It is shown that by varying the stacking order of the building blocks, unit cells with 16, 18, 20, 32, and larger numbers of atoms can be constructed. In *allo*-Ge, evidence for disorder in the stacking direction has been observed in the x-ray data.[5]

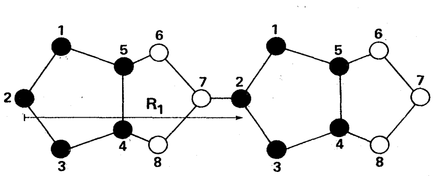

FIG. 1. Side view of a two-dimensionally periodic slab geometry used in the construction of several new crystalline structures for Si and Ge. The unit cell has eight atoms as shown. Atoms 8, 4, 5, and 6 form sixfold rings of bonds when viewed from the top. Dark- and light-colored atoms lie in different planes and are separated by $\pm 0.5R_2\hat{\mathbf{y}}$ normal to the projection plane, where $\mathbf{R}_2$ is a lattice vector.

In the intermetallic $\mathrm{Li_7Ge_{12}}$ crystal from which *allo*-Ge is prepared,[5] the basic building units are stacked on top of each other to form a three-dimensional structure. The Ge atoms on different stacks, however, are separated from each other by an atomic plane of Li atoms. Extraction of the Li intercalate brings the Ge rings into contact, resulting in bond formation between adjacent stacks which makes all atoms fourfold coordinated. The 128-atom *allo*-Ge unit cell presumably results from a stacking together of four layers. The unit cell is large because of a quadrupling of the fundamental translation vector along the y direction of Fig. 1, as indicated by x-ray measurements.[5] This results from a relaxation of interlayer bonds.

The results of calculations on the atomic structure of novel crystalline forms of Si and Ge containing 16, 18, 20, and 32 atoms per unit cell are discussed in the following section. The electronic structure and relative stability of these new crystals are also examined. The most energetically favorable structure is found to have a 20-atom orthorhombic unit cell. The reason why experiment gives a $16n$- instead of a $20n$-atom unit cell is shown to be related to the atomic geometry in $\mathrm{Li_7Ge_{12}}$ from which *allo*-Ge is prepared.

II. NEW CRYSTALLINE PHASES

A. Building block

The essential building block for the class of crystalline structures discussed in this section is shown in Fig. 1. There are eight atoms in the two-dimensional unit cell forming planar and puckered fivefold rings. The primitive translation vectors (in units of bond length in the ideal diamond structure[13]) are approximately

$$\mathbf{R}_1=3.28\hat{\mathbf{x}},\quad \mathbf{R}_2=1.64\hat{\mathbf{y}}\ . \tag{1}$$

The atomic coordinates $\mathbf{r}_i=(r_x,r_y,r_z)$ determined from a minimization of the energy for a Keating-type model[14] are given by

$$\mathbf{r}_1=(0.58,0.00,0.82)\ ,\quad \mathbf{r}_2=(0.00,0.00,0.00)\ , \tag{2}$$

$$\mathbf{r}_3=(0.58,0.00,-0.82)\ ,\quad \mathbf{r}_4=(1.53,0.00,-0.50)\ , \tag{3}$$

$$\mathbf{r}_5=(1.52,0.00,0.50)\ ,\quad \mathbf{r}_6=(2.05,0.82,0.75)\ , \tag{4}$$

$$\mathbf{r}_7=(2.71,0.82,0.00)\ ,\quad \mathbf{r}_8=(2.05,0.82,-0.75)\ . \tag{5}$$

Maximal variations in bond lengths of 0.5% and in bond angles of 12° occur at atom 7. The bond-angle distributions on atoms 6 and 8 are 99.1°, 99.1°, and 109.4°; all other angles are within 5° of the ideal tetrahedral angle of 109.47°.

B. 16-atom orthorhombic cell: *O*-16

The smallest three-dimensionally periodic unit cell that can be constructed from the basic eight-atom building block of Fig. 1 is the one shown in Fig. 2. It contains two stacks arranged to give a 16-atom orthorhombic unit cell which we will refer to as the *O*-16 structure for convenience. The stacking leads to sevenfold rings of atoms between the layers. The total energy of this structure was minimized with respect to both lattice translation vectors and atomic positions using a Keating valence-force-field model. The translation vectors (in units of the ideal-diamond-structure bond length) are given by

$$\mathbf{R}_1=3.324\hat{\mathbf{x}},\ \ \mathbf{R}_2=1.600\hat{\mathbf{y}},\ \ \mathbf{R}_3=4.494\hat{\mathbf{z}}\ . \tag{6}$$

The *O*-16 structure has inversion symmetry as well as a mirror-reflection symmetry which takes z to $-z$. The atomic coordinates (r_x,r_y,r_z) of the first eight atoms are similar to those given for the layered structure in Sec. II A. They are

$$\mathbf{r}_1=(0.592,-0.081,0.832)\ ,\quad \mathbf{r}_2=(0.000,0.000,0.000)\ , \tag{7}$$

$$\mathbf{r}_3=(0.592,-0.081,-0.832)\ ,\quad \mathbf{r}_4=(1.503,0.101,-0.495)\ , \tag{8}$$

$$\mathbf{r}_5=(1.503,0.101,0.495)\ ,\quad \mathbf{r}_6=(2.040,-0.678,0.705)\ , \tag{9}$$

$$\mathbf{r}_7=(2.736,-0.768,0.000)\ ,\quad \mathbf{r}_8=(2.040,-0.678,-0.705)\ . \tag{10}$$

The remaining eight coordinates can be obtained from those above through the relation

$$\mathbf{r}_{i+8}=(1.060,0.593,2.247)-\mathbf{r}_i,\ \ i=1\text{--}8\ . \tag{11}$$

The 16-atom orthorhombic unit cell contains large stresses. Maximal variations of ±20° in bond angles and ±4% in bond lengths are calculated to occur. The possibility of interlayer bond relaxations giving rise to a doubling of the periodicity in the y direction was examined. No such relaxation was found to occur.

The density of electronic states[15] for the *O*-16 structure is shown in Fig. 3 and compared to that of diamond-structure Si. Taking the valence-band maximum (VBM) of the latter to be at zero, the VBM of *O*-16 is at 0.38 eV. The conduction-band minimum occurs at 1.57 eV at the corner point $\pi(1/R_1,1/R_2,1/R_3)$ of the Brillouin zone. The density of states was obtained from a calculation of the electronic levels at 128 (408) points in the irreducible Brillouin zone for Si in the *O*-16 (diamond) structure. The density of states is very similar to that obtained previously[16] for a 12-atom simple-tetragonal structure (ST-12) which also contains five- and sevenfold rings of atoms.

An orthorhombic structure is not the only way in which two building blocks (Fig. 1) can be put together to form a 16-atom unit cell. The layers can be placed relative to each other to form a 16-atom *monoclinic* structure for which the lattice translation vectors $\mathbf{R}_1$ and $\mathbf{R}_2$ are

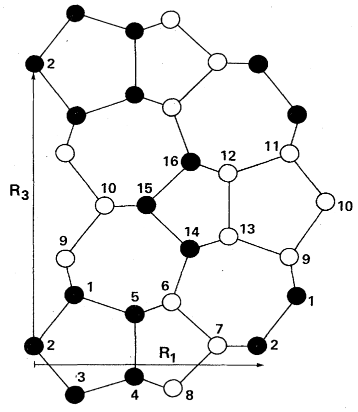

FIG. 2. Side view of the orthorhombic unit cell containing 16 atoms (*O*-16). The structure consists of two stacks of the unit slabs shown in Fig. 1.

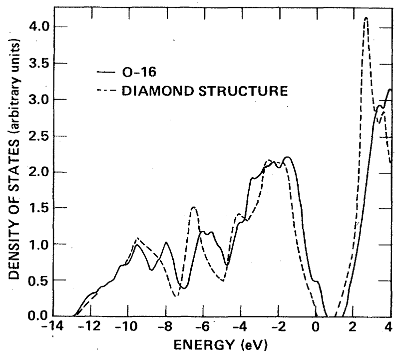

FIG. 3. Density of electronic states for the *O*-16 structure (solid line) is compared to that for diamond-structure Si (dashed line). At each energy the curves have been broadened by Gaussians with a standard deviation $\sigma=0.15$ eV.

nearly the same as in *O*-16, but where $\mathbf{R}_3$ is displaced by $0.5\mathbf{R}_2$. The Keating energy for this structure is calculated to be 10% higher than in the *O*-16 phase.

C. 20-atom orthorhombic cell: *O*-20

The atomic positions for the *O*-20 structure are shown in Fig. 4. The stacking of the building blocks is such as to give rise to six- and eightfold rings of atoms between the layers. Extra atoms labeled as atoms 9, 10, 19, and 20 in Fig. 4 are needed to accomplish the bonding between the stacks. *O*-20 is found to have the lowest energy of any of the structures examined in this study. Maximal bond-angle deviations from 109.47° of $-11.4°$ (on atoms 7 and 17) and $+8.4°$ (on atoms 8 and 18), and bond-length changes of $+2.4\%$ (between atoms 4-5 and 14-15) and -1.6% are found to occur. Optimization of the total energy with respect to the magnitude of lattice translation vectors yields values of $\mathbf{R}_1$ and $\mathbf{R}_2$ which, for the case of Ge, agree with the experimental results for *allo*-Ge to better than 0.5%. Optimization of the structure was carried out with both the Keating[14] and tight-binding[17] models for the total energy. In fact, it is possible that the atomic structure of *O*-20 also occurs in the *allo* phase. The *O*-20 structure has inversion symmetry as well as three mirror planes. The calculated lattice translation vectors are (in units of the ideal bond length in the diamond structure)

$$\mathbf{R}_1=3.194\hat{\mathbf{x}},\quad \mathbf{R}_2=1.644\hat{\mathbf{y}},\quad \mathbf{R}_3=5.870\hat{\mathbf{z}}\ . \tag{12}$$

This gives an atomic density 1.3% lower than in the diamond structure. The atomic coordinates (r_x,r_y,r_z) are given by

$$\mathbf{r}_1=(0.554,0.000,0.827)\ ,\quad \mathbf{r}_2=(0.000,0.000,0.000)\ , \tag{13}$$

$$\mathbf{r}_3=(0.554,0.000,-0.827)\ ,\quad \mathbf{r}_4=(1.497,0.00,-0.512)\ , \tag{14}$$

$$\mathbf{r}_5=(1.497,0.000,0.512)\ ,\quad \mathbf{r}_6=(2.006,0.832,0.743)\ , \tag{15}$$

$$\mathbf{r}_7=(2.652,0.832,0.000)\ ,\quad \mathbf{r}_8=(2.006,0.832,-0.743)\ , \tag{16}$$

$$\mathbf{r}_9=(0.336,0.832,1.352)\ ,\quad \mathbf{r}_{10}=(2.538,0.832,4.287)\ , \tag{17}$$

and

$$\mathbf{r}_{i+10}=(2.874,0.0,2.935)-\mathbf{r}_i,\quad i=1-10\ . \tag{18}$$

The first eight atoms have coordinates similar to those for the atoms in Fig. 1 given by Eqs. (2)—(5). Atoms 9 and 10 (and their counterparts, atoms 19 and 20) are extra atoms that have to be added in order to form the *O*-20 structure.

The total energy of the *O*-20 structure is calculated to be, in the tight-binding scheme,[17] within 30 meV/atom of the energy of the diamond structure. In the Keating-model approximation the strain energy of *O*-20 is one-quarter that of the BC-8 body-centered-cubic cell and a *tenth* of the simple tetragonal ST-12 structures.[8]

The density of electronic states for *O*-20 is shown in Fig. 5. The valence-band maximum is at 0.75 eV with respect to that of diamond-structure Si; the fundamental gap of 1.04 eV is indirect and is between the Γ and $\pi(1/R_1,1/R_2,0)$ points of the Brillouin[15] zone. The possibility of an increase in unit-cell dimensions resulting from bond relaxation in the *y* direction was examined. No such relaxation was found to occur.

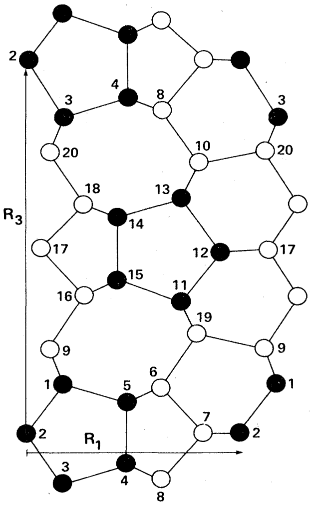

FIG. 4. Side view of the orthorhombic unit cell containing 20 atoms (*O*-20). The structure can be obtained from the slab units shown in Fig. 1, but requires the addition of atoms 9, 10, 19, and 20. Dark- and light-colored atoms are separated by $\pm 0.5R_2\hat{\mathbf{y}}$ normal to the projection plane.

D. *allo*-Ge structure: *O*-128

The *allo*-Ge structure has an orthorhombic unit cell with 128 atoms. The lattice translation vectors deter-

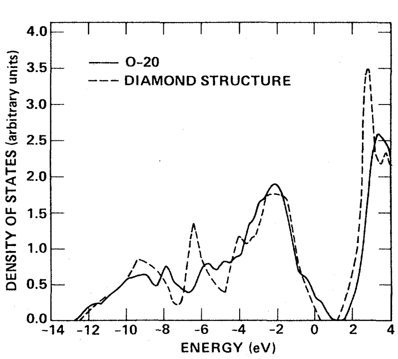

FIG. 5. Density of electronic states for the *O*-20 structure (solid line) is compared to that of diamond-structure Si (dashed line). At each energy the curves have been broadened by Gaussians with a standard deviation $\sigma=0.15$ eV.

mined from x-ray analysis are (in units of bond length in the diamond structure)

$$\mathbf{R}_1=3.18\hat{\mathbf{x}},\ \ \mathbf{R}_2=4\times1.66\hat{\mathbf{y}},\ \ \mathbf{R}_3=9.75\hat{\mathbf{z}}\ . \tag{19}$$

The magnitude of $\mathbf{R}_2$ is 4 times larger than a primitive translation vector probably as a result of a small relaxation of the interlayer bonds. Disregarding this relaxation reduces the unit cell to one containing only 32 atoms. This number suggests a structure consisting of four stacks of the basic eight-atom building block shown in Fig. 1. The stacking sequence is very similar to that for *O*-16 discussed above. Optimization of the *O*-32 structure with respect to lattice translation vectors and atomic coordinates yields values of $R_1=3.25$ and $R_2=1.66$ in good agreement with the x-ray results. The calculated optimal value of 8.95 for R_3 is, however, appreciably smaller than the experimental value of 9.75. This may have been affected by the considerable stacking disorder present in the sample examined, or alternately, *allo*-Ge may correspond to a different stacking arrangement than that assumed here. The density of *allo*-Ge changes from being 4.5% less dense to 2% denser than the diamond structure depending on the choice of R_3. After optimization of the atomic coordinates of *O*-32 no tendency towards extra relaxations leading to an enlargement of the unit cell in the *y* direction is found when a larger cell is used in the calculations. The band gap, for Si, is calculated to be 0.91 eV and indirect, despite the relatively large size of the unit cell. For Ge, the measured Raman spectra of *allo*-Ge has been found to be closer to that of diamond-structure Ge than to that of amorphous Ge.[18]

The energy of Si in the *O*-32 structure is calculated to be higher by 0.12 eV per atom than in the *O*-20 phase. This raises the question of why the latter structure is not seen experimentally. The formation of an *O*-32— and not an *O*-20—type structure is directly related to the atomic arrangement in crystalline Li_7Ge_{12} from which the *allo*-Ge phase is obtained. The stacking units contain only eight Ge atoms, per two-dimensional unit cell, in positions very similar to that shown in Fig. 1. Two additional atoms per unit cell (atoms 9 and 10 in Fig. 4) are needed in order to create the *O*-20 structure. The chemical technique employed in obtaining *allo*-Ge does not allow extra Ge atoms to enter the growth process. If an *allo*-Ge surface were to be used as a substrate for an atom-by-atom growth, as in molecular-beam epitaxy, then an *O*-20 structure is predicted to be the most likely to occur.

E. Other structures

Many other structures, in addition to those already shown above, can be obtained by varying the relative stacking positions of the basic building blocks (Fig. 1). An equal admixture of the stacking geometries in *O*-16 and *O*-20 gives the structure shown in Fig. 6, which has an 18-atom *triclinic* unit cell. Five-, six-, seven-, and eightfold ring geometries are present in this structure. The total energy per atom for this structure, after optimization of the atomic coordinates, is similar to that of *O*-16, which is appreciably higher than that of *O*-20 because of larger angular strains.

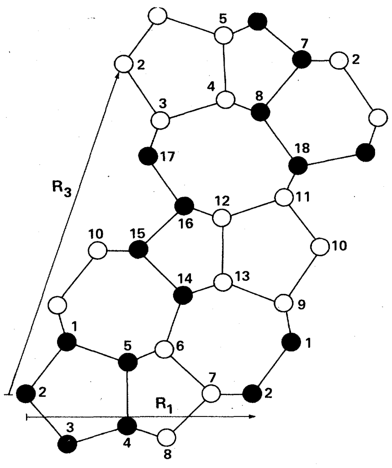

FIG. 6. 18-atom *triclinic* cell with a stacking sequence alternating between those of the *O*-16 and *O*-20 structures.

In general, structures with N atoms per unit cell where N is given by

$$N=8m+10n,\ \ m+n\geq2 \tag{20}$$

can be constructed. In Eq. (20) m and n are non-negative integers. Per unit cell such a structure would have m *O*-16 (with sevenfold rings) and n *O*-20 (with eightfold rings) types of bonding between adjacent slabs. If *allo*-Ge has exactly 128 atoms per unit cell, then Eq. (20) would predict that only *O*-16—type bonding is present in the structure, i.e., n cannot have any value other than zero. Figure 1 of Ref. 5, which may be only schematic, shows, however, eightfold rings of bonds characteristic of the *O*-20 structure.

The observation of stacking disorder in *allo*-Ge is consistent with the various possibilities for the arrangement of building blocks relative to one another. In addition to one-dimensional disorder in the *z* direction, a two-dimensionally disordered structure can also be created from the structures discussed above. An example of this is shown in Fig. 7, where *O*-16 and *O*-20 structures are

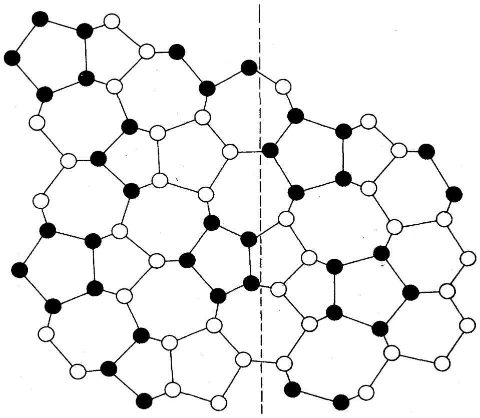

FIG. 7. Two-dimensionally disordered arrangement of atoms is shown. The atoms on the left-hand side of the dashed line have an *O*-16 ring topology; the ones on the right-hand side have an *O*-20 type of stacking. Dark- and light-colored atoms lie in different planes.

joined side by side (instead of vertically), creating a grain boundary represented by the dashed line. Over the limited region shown the atoms on the two sides of the boundary can be joined without large strains building up. It is not possible, however, to maintain the distinct ring geometries of the *O*-16 and *O*-20 structures over a more extended region without introducing broken bonds.

III. CONCLUSIONS

Complex crystalline structures with 16, 18, 20, and 32 atoms per unit cell derived from a common building block were constructed. The building block consists of a two-dimensionally periodic slab of atoms arranged in fivefold rings (Fig. 1). This type of ring geometry has been realized experimentally[5] in Li_7Ge_{12} and *allo*-Ge. For Si and Ge, the most energetically favored structure is predicted to have an orthorhombic unit cell with 20 atoms (*O*-20). Two extra Ge atoms (per slab) would be required to obtain this structure instead of the observed *allo*-Ge phase from the Li_7Ge_{12} intermetallic compound. The electronic and atomic structure of *O*-20 as well as several other structures were investigated.

ACKNOWLEDGMENTS

I would like to thank John Northrup and Richard Martin for several useful discussions. This work is supported in part by the U.S. Office of Naval Research through Contract No. N00014-82-C-0244.

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[16] The density of states in Fig. 3 for *O*-16 is similar to that for the 12-atom simple-tetragonal structure given in Fig. 8 of Ref. 8. Both structures have five- and sevenfold rings of atoms.

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