PHYSICAL REVIEW B VOLUME 53, NUMBER 17 1 MAY 1996-I

# Expanded-volume phases of silicon: Zeolites without oxygen

Alexander A. Demkov
*Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504*

Wolfgang Windl
*Center for Solid State Science, Arizona State University, Tempe, Arizona 85287-1704*

Otto F. Sankey
*Department of Physics and Astronomy, Arizona State University, Tempe, Arizona 85287-1504*

(Received 31 January 1996)

By reducing the (4;2)-connected regular three-dimensional nets of zeolites to 4-connected nets, we introduce a variety of new expanded structures of elemental Si. An *ab initio* molecular dynamics method is used to determine the optimized geometries, energetics, and electronic properties of the proposed structures. It is found that Si structures derived from those of group-6 (5-ring) zeolites are particularly low in energy ($\sim 0.1$ eV/atom above the ground state) and semiconducting (with band gaps varying $\pm 0.7$ eV about the 1.17 eV gap of diamond Si). [S0163-1829(96)02318-1]

Silicon, whose ground state equilibrium phase is the diamond structure, is at the heart of the semiconductor industry; as such, it is one of the most thoroughly studied materials. Of high scientific interest have always been possible new phases of this widely used semiconductor, as such new phases may have applications in electronics if they were to have desirable or novel electronic properties. This has led, e.g., to high-pressure research on Si, where new phases such as $\beta$-tin have been discovered. These new phases have been found not to be semiconducting, however, but rather are metallic or semimetallic.

A common approach to search—theoretically—for new materials is to start with a simple structure and hypothesize more complex materials by analogy.[1] For example, starting with carbon in the ''simple'' diamond phase, one might hope to synthesize isoelectronic symmetrical analogs such as BN, BeO, and LiF in a structure similar to diamond. Even more complex compounds can be derived by forming asymmetrical analogs such as $B_2O$, $BeN_2$, or $LiN_3$.

Of course, an alternate approach consisting of inverting this idea can also be chosen: The knowledge of complex compound structures might be exploited to predict possible new phases for simpler or even elemental materials. Recently, this idea was used to search for new phases of carbon by two different groups.[2,3] Unfortunately, no experimental evidence for the existence of such materials has yet been reported. We follow this approach here using known complex silicate phases to predict new structures for elemental silicon, where such evidence *does* exist.

Framework alumino-silicates, which form a dazzling array of complex structures, are (4;2)-connected nets with 4-coordinated Si or Al atoms and 2-coordinated oxygens. Perhaps the most beautiful group of them is the class of structures known as zeolites, which are often composed of polyhedral cages interconnected by channels. Because of their ability to transport atoms or molecules through the channels and to house guest molecules within the cages, zeolites have been exploited for several industrial applications as, e.g., petroleum cracking, drug delivery, as ion exchangers, or as gas separators.

The idea is now that the (4;2)-connected nets of alumino-silicate structures can be reduced to the 4-connected ones of common semiconductor materials such as Si, C, Ge, and III-V's by stripping off the oxygen atoms.

In this work we present such a ''stripping'' as a systematic procedure to generate 4-coordinated low-energy and large-volume elemental silicon structures which are analogous to zeolites. Thus our new silicon structures amount to *zeolites without oxygen*—only the framework of $T$ atoms remains. These $T$ sites can be occupied not only by Si as is studied in the present work, but in principle also by, e.g., carbon,[2,3] germanium, or in suitable structures by alternating heteropolar species likely to form 4-connected nets such as Ga and As.

To test the stability and to determine the cohesive energies of these new structures and their ground state properties, we have performed *ab initio* electronic structure local density approximation (LDA) calculations within the framework of the local orbital approach.[5,6] We found that these new silicon materials are insulators with varying band gaps and, most importantly, that the formation energies of these materials with respect to the ground state diamond structure are comparable to those of true (oxygen-containing) zeolites above the $SiO_2$ ground state $\alpha$-quartz. This curious and important observation introduces a connection between two distinct groups of silicon-based materials: silicates, which are important in mineralogy and in many technological applications, and elemental silicon, which is used in most semiconductor electronic devices.

The *1991 Atlas of Zeolite Structure Types*[7] lists 85 different zeolite structures, and this number has been increasing rapidly in recent years. The impressive variety of zeolite structures is mostly due to the large number of possible ways to link $TO_4$ ($T$=Al,Si) tetrahedra in a (4;2)-connected alumino-silicate framework or, alternatively speaking, to the

0163-1829/96/53(17)/11288(4)/$10.00

relative flexibility of the angle about the bridging oxygen which varies in framework silicates from 130° to 180°. On the other hand, the $TO_4$ tetrahedra are known to stay fairly regular with the O-$T$-O angle close to the ideal tetrahedral angle of 109° as this angle is ensured by the $sp^3$ nature of the $T$-atom bonding.

After stripping off the bridging oxygens, the (4;2) net reduces to a 4-connected net of $T$ atoms. The new net, of course, has lost its flexibility as it has direct $T$-$T$ bonds instead of $T$-O-$T$ connections. Therefore, because of their angular distribution which contains many angles far from the ideal tetrahedral one, the majority of 4-connected nets derived from the (4;2)-connected ones are unsuitable for our purposes. Looking for ‘‘good candidates,’’ structures consisting mainly of planar pentagons resulting in a bond angle of 108° which is very close to the tetrahedral angle could be a good choice. Unfortunately, there are no 4-connected nets consisting of just planar pentagons. However, nets exist that are built of 5-rings and a structural unit known as 5-1 [a 5-ring with a ‘‘leg’’; see, e.g., the basis of bikitaite shown in Fig. 2(a)]: First, there are clathrate structures such as melanophlogite (MEP), dodecasil 3C (MTN), dodecasil 1H (DOH), deca-dodecasil 3R (DDR), and nonasil (NON). All clathrate structures involve a combination of 5-rings and 5-1 units (with the exception of nonasil containing 5-rings and 6-rings). Second, there are group-6 zeolites,[8] for which 5-1 is the only secondary building unit. Group 6 combines a variety of different structures such as zigzag structures (BIK, CAS, MTT, TON, ZSM-12, NAPO-36), pentasils (MFI, MEL), and sawtooth nets (MOR, DAK, FER, MFS); we have chosen several structures from these families as examples in the present work.

Besides group-6 zeolites there exist many common zeolites based on different linkages of the sodalite $\beta$-cage. This cage, which is also known as Kelvin’s polyhedron, contains six squares and eight hexagons. Different stacking of these polyhedra leads to different structures like, e.g., sodalite (SOD), linde A (LTA), or faujasite (FAU). The squares have bond angles of 90°, which, for Si, is energetically undesirable since Si prefers the tetrahedral angle due to its $sp^3$-bonding. However, if the number of such 90° angles remains small, the Si structure may still have a relatively low energy overall. We have chosen SOD, LTA, and FAU structures as examples of this class in this work.

We have performed electronic structure molecular dynamics simulations[5,6] on several example structures from the families mentioned above. The method employs the local orbital basis using the periodicity of the lattice (Bloch states). A large set of special **k** points was used for all structures and checked for convergence of the Brillouin zone integration. Both internal and external coordinates (cell shape and size) were fully relaxed using constant zero-pressure damped molecular dynamics techniques. From these calculations we obtain the total energy of the structure, the electronic band structure and band gaps, the optimized geometry including bond lengths and bond angles, and its vibrational phonon modes. In addition to zeolite-derived phases, we have examined the all-silicon equivalents of quartz, tridymite, and cristobalite in order to explore the lower-volume region of the phase diagram also.

The results of our calculations are summarized in Fig. 1, where we display the energy per atom for each of the pure silicon structures vs the volume per atom relative to the ground state Si diamond phase. For comparative purposes, we define the energy of the Si-diamond structure to be zero. In the regions of volume less than that of diamond, we have plotted values from the literature[9] for the compressed phases of Si $\beta$-tin, simple cubic (sc), face-centered-cubic (fcc), and BC8 (the BC8 phase is a metastable phase that is quenched in upon release of pressure from the $\beta$-tin phase).[10] It can clearly be seen how the energy of the compressed structures increases rapidly with decreasing volume.

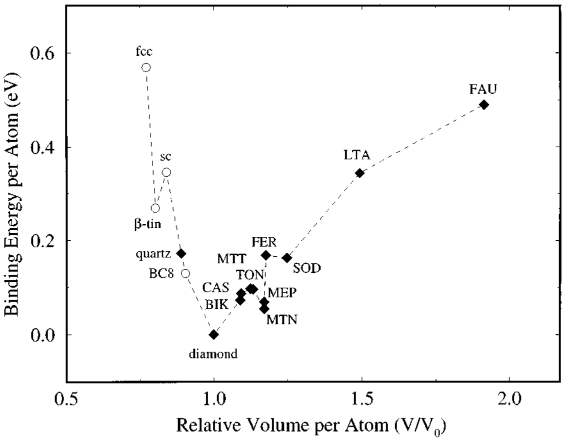

FIG. 1. Binding energy per atom with respect to diamond for elemental silicon structures as a function of relative volume per atom. The zeolite- (and quartz-) derived structures of silicon are indicated by the solid diamonds, while open symbols represent high-density phases from Refs. 9 and 10.

Looking for new phases derived from silicates on the high-pressure side, we examined the common $SiO_2$ polymorphs quartz, cristobalite, and tridymite.[11] We find the Si-quartz structure to be a possible high-pressure phase. The structure of Si-cristobalite simply reduces to that of the diamond phase of Si, while the Si-tridymite structure is that of lonsdaleite (wurtzitelike) and is virtually degenerate in energy with that of diamond (thus is not displayed in the figure).

The most important feature of Fig. 1, however, is the appearance of a number of new zeolitelike phases of Si which are expanded in volume in comparison to diamond. We find the very surprising result that all the structures derived from group-6 zeolites and clathrates with rings of five or more atoms (BIK, CAS, FER, MTT, TON, MEP, and MTN) are relatively low in energy. They cluster around a 15% volume expansion, and have an energy cost of around 0.1 eV/atom or even less. Therefore, these structures are all *far lower* in energy than the first stable high-pressure structure $\beta$-tin.

The examined structures with 4-rings (SOD, LTA, and FAU) have larger volumes, and have energies which seem to grow in proportion to their volume. It is notable that SOD, with one-third (1/3) of its rings being 4-rings and 2/3 being 6-rings, has an energy even lower than FER which has no rings smaller than 5-rings. Therefore, the energy appears to correlate best to the volume and the overall distribution of bond angles.

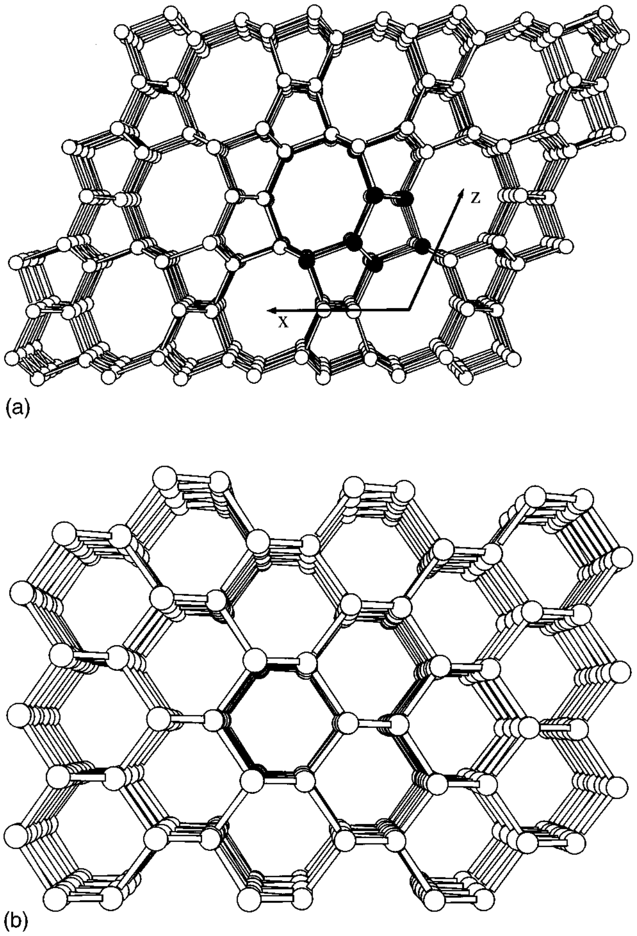

FIG. 2. The $T$-atom framework of the bikitaite (BIK) structure viewed along the (a) $y$ axis (the black circles denote the basis atoms, the arrows the two in-plane lattice vectors) and (b) $z$ axis. Note that (b) is undistinguishable from the (111) perspective of the diamond structure.

All the expanded structures are found to have a distribution of bond lengths located near the diamond phase bond length, but with a skew towards slightly longer bond lengths. The ''dip'' in energy for MEP and MTN may be attributed to the fact that unlike the other examined structures, both of them have planar pentagons, and therefore bond angle distributions concentrating on a narrow region around the tetrahedral angle. A very similar behavior was previously found for the carbon analogs of these structures.[2,3]

By way of example, we show the structure of the all-Si bikitaite (BIK) phase in Fig. 2 whose energy was also found to be particularly low. The lattice is monoclinic with six Si atoms per unit cell. Figures 2(a) and (b) show two orthogonal views of the structure: The view down the $y$ axis [Fig. 2(a)] shows zigzag chains of linked 5-rings separated by rows of 8-rings. This view is typical for group-6 zeolites. Notice that neither the 5- nor the 8-rings are planar, nor are they in the plane of the projection. The projection along the $z$ axis [Fig. 2(b)] reveals quite a different situation consisting of a honeycomb structure similar to that found in diamond.

Our *ab initio* band structure calculations predict that the expanded Si structures studied are insulators. Their band gaps vary from about 0.7 eV below the Si diamond band gap (expt. 1.17 eV) to about 0.7 eV above it. In addition, the highest-frequency optic vibrational modes at zone center vary from approximately 25 $\mathrm{cm}^{-1}$ below the Si diamond frequency (expt. 521 $\mathrm{cm}^{-1}$) to about 130 $\mathrm{cm}^{-1}$ above it.[12]

Furthermore, there is an interesting similarity between the energetics of the expanded volume silicon phases and that of the corresponding oxygen-containing $SiO_2$ zeolite structures. This can be seen by comparing Fig. 1 with Fig. 3 of Ref. 13 where the experimental excess enthalpy of several silica ($SiO_2$) zeolites as a function of volume is shown. The comparison shows that the energy scale for both expanded materials is ~ 0.10 eV per molecule or atom (0.1 eV = 10 kJ/mol). Furthermore, both materials have energies which rise rapidly for their compressed structures. An important difference, however, appears for the very large-volume structures: $SiO_2$ materials appear to saturate in energy, while elemental Si structures appear to rise continually.

Both Si and $SiO_2$ materials have been extensively studied, and a connection between these two opens several new avenues to explore as, e.g., the possibility of band-gap engineering not by means of changing the composition of diamond–zinc-blende-structure materials like $Ga_{1-x}Al_xAs$ or $Si_{1-x}Ge_x$ but rather by changing the structure of *elemental* silicon towards the desired band gap. Furthermore, this new way of band-gap engineering by tailoring the structure and not the composition could make the band-gap region *above* the Si gap more accessible. Up to now, it is technically very demanding to increase the band gap in Si by straightforward alloying. For example, addition of small amounts of the large-band gap material carbon to Si does not increase but rather decrease the gap,[14] whereas larger amounts of carbon cannot be added because of the small solubility of C in Si. In addition, the new structures proposed here may have very interesting electron or even ion or atom transport phenomena due to the channel-and-cage structure of these materials.

Perhaps the reason that this ''obvious'' analogy between Si and $SiO_2$ materials seems to have been missed in the past may in part be due to two reasons: (i) Reliable electronic-structure-based calculations of such complex systems have become possible only within the last few years. Therefore, speculations in this direction could not be checked theoretically. (ii) The structures described here (just as zeolites) have a volume per atom larger than their absolute ground state structure. Experimentally there is no simple way to apply negative pressure. This problem is circumvented in natural zeolites by the use of guest impurities. These impurities act as templates around which the polyhedron cage can nucleate. The expanded Si structures or ''silisils'' (as they may be called in analogy with silacious zeolites referred to as zeosils) could be made in a similar way. In fact, this has been done in the case of the two ''best'' expanded structures from Fig. 1, MEP and MTN. These structures can be synthesized in the presence of ''templating atoms'' like, e.g., alkali (or other) metals.[4,15] The size of the metal atom is important in determining which of these structures form. Furthermore, metal doping can lead to interesting effects and recently has been shown to produce the first tetrahedral Si-based superconductors.[16]

Many years ago Kamb[17] noticed a similarity between structures of water (ice) and silicas. This similarity was based on the observation that both materials have a tendency to form tetrahedrally linked framework structures. Silica polymorphs are constructed out of near-rigid $SiO_4$ tetrahedra, and structures of water form in which an oxygen atom is surrounded by four hydrogen atoms. We can now take this analogy one step further: There may exist low-energy near-tetrahedral structures of elemental silicon which mimic the structures found in both $H_2O$ and $SiO_2$.

The main result of our work is therefore that by using analogies from complex $SiO_2$ structures, we are able to show that there exists a number of possible new low-energy expanded structures of pure silicon, and possibly for other materials also. The energetics of these systems is surprisingly favorable, and in fact several have energies far less than that of any high-pressure phases obtained in the laboratory. A characteristic energy scale of 0.1 eV/atom (or ~10 kJ/mol) is found for our ‘‘silisils,’’ which is quite comparable to the energies of the zeosils[13] of $SiO_2$. Furthermore, we believe that these materials could offer new applications like, e.g., band-gap engineering *via* structure tailoring, and should possess very unusual physical properties. Clearly, the challenge now goes to the experimentalist to invent novel synthesis routes and experiments to probe this unique volume region of such an important material.

We thank the Office of Naval Research (Grant No. ONR 00014-90-J-1304), the NSF High Pressure Material Synthesis group (MRG Grant No. DMR-9121570), and the Si-Ge-C project (AFOSR DARPA F49620-93-C-0018) for support. It is our pleasure to thank Michael O’Keeffe and Paul McMillan for many insightful discussions that we had in the course of this work. We also thank Jan Gryko for lively discussions, and for his dedicated efforts in synthesizing new samples of MEP and MTN for further study.

---

[1] H. T. Hall and L. A. Compton, Inorg. Chem. **4**, 1213 (1965).

[2] R. Nesper, K. Vogel, and P. Blöchl, Angew. Chem. Int. Ed. Engl. **32**, 701 (1993).

[3] G. B. Adams, M. O’Keeffe, A. A. Demkov, O. F. Sankey, and Y.-M. Huang, Phys. Rev. B **49**, 8048 (1994).

[4] A. A. Demkov, O. F. Sankey, K. E. Schmidt, G. B. Adams, and M. O’Keeffe, Phys. Rev. B **50**, 17001 (1994).

[5] A. A. Demkov, J. Ortega, O. F. Sankey, and M. Grumbach, Phys. Rev. B **52**, 1618 (1995).

[6] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).

[7] W. Meier and D. Olson, *Atlas of Zeolite Structure Types*, 3rd ed. (Butterworth-Heineman, London, 1992).

[8] D. W. Breck, *Zeolite Molecular Sieves, Structure, Chemistry, and Use* (J. Wiley and Sons, New York, 1974).

[9] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[10] R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, Phys. Rev. B **35**, 9559 (1987).

[11] The distinction between $\alpha$ and $\beta$ phases is irrelevant once we remove the oxygen.

[12] W. Windl, A. A. Demkov, and O. F. Sankey (unpublished).

[13] I. Petrovic, A. Navrotsky, M. Davis, and S. I. Zones, Chem. Mater. **5**, 1805 (1993).

[14] A. A. Demkov and O. F. Sankey, Phys. Rev. B **48**, 2207 (1993).

[15] J. S. Kasper, P. Hagenmuller, M. Pouchard, and C. Cros, Science **150**, 1713 (1965).

[16] H. Kawaji, H. Horie, S. Yamanaka, and M. Ishikawa, Phys. Rev. Lett. **74**, 1427 (1995).

[17] B. Kamb, Science **148**, 232 (1965).