

Chemical order in amorphous silicon carbide

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While ordering in alloy crystals is well understood, short-range ordering in amorphous alloys remains controversial. Here, by studying computer-generated models of amorphous SiC, we show that there are two principal factors controlling the degree of chemical order in amorphous covalent alloys. One, the chemical preference for mixed bonds, is much the same in crystalline and amorphous materials. However, the other factor, the atomic size difference, is far less effective at driving ordering in amorphous material than in the crystal. As a result, the amorphous phase may show either strong ordering (as in GaAs), or weaker ordering (as in SiC), depending upon the relative importance of these two factors.

Chemical ordering plays a crucial role in determining the properties of binary crystals, and has been studied extensively. Recently there has been great interest in another class of materials, *amorphous* binary compounds such as amorphous GaAs (*a*-GaAs) and amorphous SiC (*a*-SiC). It is hoped that these may have technological applications, in analogy with amorphous Si and C. However, the understanding of such materials poses a new challenge. Unlike the crystalline phases, amorphous materials have no long-range order, so ordering cannot occur on distinct sublattices. Nevertheless, some materials preserve strong short-range chemical ordering even in the amorphous phase. For example, in *a*-GaAs, the Ga is surrounded primarily by As, and vice versa.¹

Aside from III-V compounds, perhaps the most studied amorphous covalent alloy is *a*-SiC. Yet, despite intense interest in *a*-SiC, its structure has remained controversial.²⁻⁴ The characterization of a binary amorphous system represents a formidable challenge; and experimental studies have differed widely in their conclusions, even on such basic aspects as the carbon coordination and the fraction of homonuclear bonds.⁴

In view of the experimental uncertainties, it is particularly disturbing that recent theoretical studies have reached conflicting conclusions. Finocchi *et al.*³ found that C atoms in *a*-SiC are primarily fourfold coordinated, and that *a*-SiC has negligible chemical ordering. In contrast to this, Kelires² found stronger chemical ordering, but with half the C atoms threefold coordinated. While the *ab initio* approach of Ref. 3 is expected to be more reliable, the conclusion that ordering is negligible in *a*-SiC is so counterintuitive as to require some explanation.

Here, we explain the origin of the discrepancy between these theoretical studies,^{2,3} resolving their differences. More important, we isolate the factors determining the degree of ordering in the crystalline and amorphous phases. In this way we explain *why* *a*-SiC is weakly ordered compared with the crystal.

Specifically, we show that there are two separate factors controlling the ordering: the chemical preference for Si-C bonds, and the atomic size difference between the two constituents. The chemical preference contributes to ordering in much the same way whether the system is crystalline or amorphous. However, the size difference

between the constituents acts as a strong driving force for ordering in the crystal, while having much less effect on chemical order in the amorphous material. Thus in *a*-SiC, where the atomic size difference is large and the enthalpy of formation is small, the amorphous system exhibits far weaker ordering than the crystal. This is in contrast to GaAs, where the size difference is smaller and the enthalpy larger, giving strong ordering even in the amorphous phase.^{1,5}

We begin by computationally generating a "sample" of *a*-SiC, much as in Refs. 2 and 3. Our samples have 108 C atoms and 108 Si atoms per cell, with periodic boundary conditions. The unit cell is simple cubic, with a volume corresponding to the density of crystalline SiC. The atomic interactions are modeled with a classical interatomic potential.⁶ The many-body form of the potential reproduces the behavior of Si, C, and SiC rather well.⁷⁻¹⁰ Relevant aspects of the potential are discussed further below. While the potential is not as accurate as the *ab initio* approach of Ref. 3, it has other advantages, which will be apparent below.

Using a continuous-space Monte Carlo method, we first thoroughly equilibrate the liquid at 8000 K. The sample is then quenched at a rate of ~ 8 steps per atom-K, to 300 K. We have checked that our results are not very sensitive to the quench rate or sample size.

The resulting structure can be characterized in part by its radial distribution function (RDF), which is shown in Fig. 1. To better show the structure, the RDF is decomposed into probabilities of C-C, C-Si, and Si-Si pairs at distance r . The C-C RDF has a peak at 1.55 Å, and a second maximum at 2.58 Å. The area under the first-neighbor peak (based on several samples as discussed below) corresponds to $n_{cc} = 1.33$, i.e., each C atom has 1.33 C neighbors. The C-Si RDF has a peak at 1.93 Å, and a second peak at 2.91 Å, with $n_{cs} = 2.67$. Thus, each C atom has a total of 4.0 neighbors on average, as in the crystal. These peak positions are similar to those of Ref. 3.

The Si-Si RDF has a broad range of neighbor distances, as in Ref. 3, so n_{ss} is not well defined. The sharpness of the dip in the Si-Si RDF at around 2.8 Å is an artifact of the cutoff of the potential, and has been discussed elsewhere.⁸⁻¹⁰ While this dip is unrealistic, it

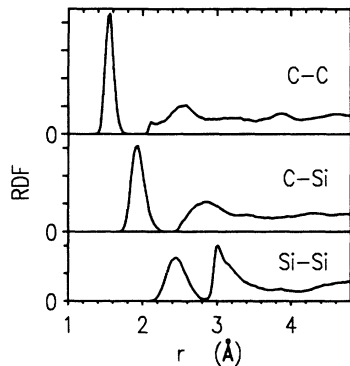


FIG. 1. Calculated radial distribution function (RDF) for *a*-SiC. Separate contributions from C-C, C-Si, and Si-Si pairs are shown. The deep dip between first and second peaks for the Si-Si distribution reflects an artifact of the potential, as discussed in the text.

does not appear to significantly affect the overall structure or chemical ordering.

Our central concern here is with the chemical ordering in *a*-SiC. The short-range order is a fundamental aspect of the structure, and is particularly important in determining the electronic properties.¹¹ A convenient measure of *disorder* is

$$\chi \equiv n_{cc} / n_{cs} . \quad (1)$$

For perfect chemical order, as in crystalline SiC, there are no C-C bonds so $\chi=0$ (no disorder). For a perfectly random system, $n_{cs} = n_{cc}$, so $\chi=1$ (complete disorder).

The simulation results give $\chi \approx 0.5$, midway between random and fully ordered. Comparable ordering was found by Kelires.² This would appear to be in substantial disagreement with the *ab initio* simulations of Finocchi *et al.*,³ who found $\chi \approx 0.9$, and concluded that there was no significant chemical ordering. However, in that work roughly 15% of the carbon atoms had apparently segregated into graphitic regions.^{3,12} Thus, the result $\chi \sim 1$ does not indicate a lack of chemical order; rather it reflects averaging over two regions of opposite order, segregating ($\chi \gg 1$) versus ordering ($\chi < 1$). If we exclude the 15% of graphitic carbon from the counting, the degree of disorder in the SiC-like regions in Ref. 3 is estimated to be roughly $\chi \sim 0.6$. Thus, our result $\chi \approx 0.5$ is in reasonable accord with the *ab initio* simulation, which we interpret as indicating moderate chemical order in *a*-SiC. However, we emphasize that the absolute degree of ordering is not the central result here. This is better determined by *ab initio* methods, once heterogeneity is properly accounted for. Rather, the principal result here is the mechanism determining the ordering, discussed below.

(The potential used here does not include π bonding, as discussed below, so it cannot describe segregation of graphitic carbon. It is not yet clear whether the graphitic regions of Ref. 3 are a universal feature of *a*-SiC. In equilibrium, as SiC is cooled from a liquid, up to 60% of the C segregates as graphite from the Si-rich liquid before reaching 2800 K, where SiC becomes stable.¹³ Since graphite can segregate from the liquid much faster than it

can recombine with the solid Si-rich SiC, the presence of graphitic C could be an artifact of the kinetics of quenching. On the other hand, the formation of graphitic C could actually lower the energy in *a*-SiC by relieving stress, analogous to the effect of hydrogenation on *a*-C.¹⁴)

The large number of threefold-coordinated C atoms in Kelires's model² is apparently an artifact of an earlier potential which I originally proposed for SiC.⁷ That potential (like the one used here) is too short ranged to discriminate π bonding. Since the C potential was fitted to graphite, among other structures, it produces energies for threefold-coordinated C atoms which are appropriate for π -bonded structures. This has proven acceptable in contexts where essentially all threefold C atoms are π -bonded, such as *a*-C and fullerenes. However, for the vacancy in diamond, where π bonding cannot occur, that potential underestimates the formation energy substantially.^{8,15}

Similarly, in the present context that potential underestimates the energy of threefold-coordinated C atoms. π bonding generally cannot occur in *a*-SiC (other than in segregated graphitic regions). A carbon atom, even if threefold coordinated, cannot form a proper π bond with a fourfold-coordinated C atom, or with any Si atom. Here we therefore use a recent alternative parametrization of the potential. This version is fitted only to non- π -bonded structures, and gives an excellent description of C defects in Si.⁶

Our principal goal here is not to simulate the structure of *a*-SiC, which has already been done with more accurate methods.³ It is rather to determine what factors or mechanisms control the degree of chemical order in the amorphous material. We begin by considering a grossly simplified statistical model for chemical ordering. A given C atom has equally many ways of forming C-C and C-Si bonds. In equilibrium, the probability of forming a bond is weighted by a Boltzmann factor $e^{-E/kT}$. If we neglect any geometric constraints, then the only energy difference comes from the chemical preference for Si-C bonds, and the ratio of C-C to C-Si bonds becomes $n_{cs} / n_{cc} = e^{-\Delta H/kT}$. Here ΔH is the enthalpy *per bond* of SiC, i.e., the energy of a Si-C bond (-0.19 eV) relative to the average of a Si-Si bond and a C-C bond in the diamond structure. Then the degree of disorder expected in equilibrium would be

$$\chi = e^{\Delta H/kT} . \quad (2)$$

However, we cannot expect the material to actually be in equilibrium, nor can we assume geometric constraints to be negligible. To see the actual dependence of disorder on ΔH , we generate a *series* of hypothetical materials, which differ from SiC *only* in having different values of ΔH . (The potential used here has a single parameter which controls ΔH .⁷) The ability to isolate a single factor in this manner is a key advantage of our empirical model for the atomic interactions. Such a study would be impossible using *ab initio* methods.

For each hypothetical material, we perform a complete simulation as above, generating an amorphous "sample." From the RDF, we extract n_{cs} and n_{cc} , and thence the disorder χ . The results of these extensive calculations are summarized in Figs. 2 and 3.

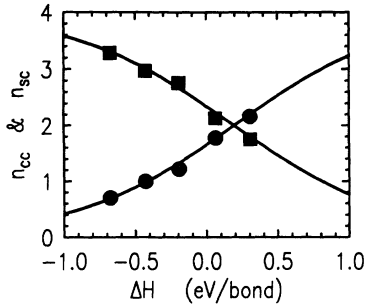


FIG. 2. Average number of neighbors of carbon atoms, for a series of hypothetical materials differing from *a*-SiC only in the value of ΔH . C-C coordination n_{cc} (circles) and C-Si coordination n_{cs} (squares) are shown vs enthalpy of formation ΔH (in eV per bond, for SiC relative to pure C and Si, with each in the diamond structure). Solid lines are fitted (Ref. 16), as discussed in text.

Figure 2 shows the average number of C-C and C-Si bonds formed by a C atom, for each sample studied, versus the value of ΔH . There is a clear trend towards more C-C bonds and fewer C-Si bonds with increasing ΔH . There is also clearly some statistical noise in addition to the systematic variation with ΔH . The values of n_{cc} and n_{cs} quoted above were therefore actually determined from a fit¹⁶ to the entire data set, shown as solid lines in Fig. 2.

The disorder $\chi \equiv n_{cc}/n_{cs}$ for each sample is shown in Fig. 3. In close analogy with Eq. (2), $\ln(\chi)$ varies linearly with ΔH . However, the slope is much smaller than expected from Eq. (2), and the data do not pass through the origin. Thus, the simplest equation that can describe the data is

$$\chi = e^{(\Delta H + \epsilon)/kT^*} \quad (3)$$

It is possible to assign physical interpretations to both ϵ and T^* , which shed considerable light on the ordering in *a*-SiC.

The slope in Fig. 3 corresponds to an effective temperature of $T^* \sim 6000$ K, rather than to the actual temperature (300 K) of the sample. Evidently, as we cool the sample, the structure remains in quasiequilibrium down

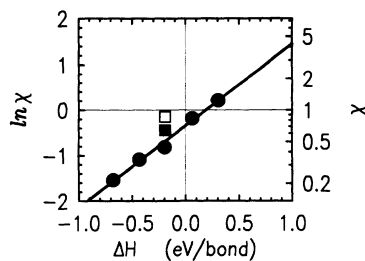


FIG. 3. Logarithm of the calculated order parameter $\chi \equiv n_{cc}/n_{cs}$ vs enthalpy of formation ΔH , for a series of hypothetical materials differing from *a*-SiC only in the value of ΔH . Line is a least-squares fit. Filled and open squares refer to results of Ref. 3, with and without a correction to exclude graphitic regions, as discussed in text.

to $T \sim T^*$, at which point it falls out of equilibrium. (Really T^* is an upper bound on the temperature at which the system falls out of equilibrium; the actual temperature may be somewhat lower.¹⁷) This temperature should be weakly dependent on the cooling rate.

Analogous behavior was seen previously in the simpler case of *a*-Si. There, Kelires and Tersoff¹⁸ showed that the distribution of local environments is determined by quasiequilibrium at the temperature T^* at which the system falls out of equilibrium during cooling. For *a*-Si, this presumably corresponds roughly to the melting point of the amorphous material. In the case of *a*-SiC, the interpretation of T^* is less clear, since SiC does not melt into a stoichiometric liquid. In any case, the quantitative value of T^* is expected to be overestimated, since our potentials tend to overestimate melting points.^{8,19}

The simulation results in Fig. 3 clearly support the simple statistical interpretation embodied in Eq. (3). From this perspective, the surprising thing is not that *a*-SiC exhibits considerable chemical disorder. The weak ordering follows naturally from the small value of ΔH . The question, rather, is why the crystal is almost perfectly ordered.

The answer lies in geometric constraints. (The topological constraints imposed by ring statistics appear not to play an important role here.^{5,20}) In the SiC crystal, every bond is equivalent, and there is no strain. However, if any atom sits on the wrong sublattice, it creates several Si-Si or C-C bonds, which cannot be accommodated without large local strains. In contrast, in the amorphous material the structure can adjust to accommodate the chemical disorder to some extent, reducing the cost in energy.

Figure 3 suggests that size effects persist in *a*-SiC, but to a much smaller degree than in the crystal. If ΔH were the sole factor driving chemical order, then for $\Delta H = 0$ there should be no order, and the solid line in Fig. 3 would pass through the origin. Instead, for $\Delta H = 0$ there is still significant ordering ($\chi \sim 0.7$), which can be modeled via Eq. (3) as an energetic preference $\epsilon \sim -0.2$ eV for Si-C bonds in addition to the chemical preference ΔH . This extra ordering arises because, even in the amorphous state, the system can best eliminate local strain by alternating Si and C atoms.

We have directly confirmed this picture by calculating the atomic-scale stresses, as in Ref. 21. Si and C atoms in *a*-SiC are under compressive and tensile stress, respectively, just as for antisite disorder in crystalline SiC. In the crystal, however, the atomic stresses that we calculate for antisite disorder are 3–4 times greater than the stresses found in *a*-SiC. Since the energy scales as the square of the stress, the characteristic energies associated with chemical disorder are an order of magnitude smaller in *a*-SiC than in the crystal. This is the fundamental reason for the weaker ordering in *a*-SiC.

Thus in *a*-SiC, the chemical preference $\Delta H \approx -0.2$ eV for Si-C bonds is comparable to the contribution $\epsilon \approx -0.2$ eV from the atomic size difference. In contrast to this, in the crystal the size effect is an order of magnitude stronger, and provides by far the dominant driving force for order. In the crystal, the chemical term ΔH is essen-

tial only in fixing the ground state.

In conclusion, we have identified two factors that determine the ordering in amorphous covalent compounds such as *a*-SiC. The chemical preference for mixed bonds plays a similar role in the amorphous and crystalline structures. However, the atomic size difference is a powerful driving force for ordering in the crystal, while playing a greatly reduced role in the amorphous system. Similar effects should be seen in alloys

which segregate rather than ordering, with size-driven segregation suppressed in the amorphous structure, while chemically driven segregation remains as effective as in the crystal.

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¹D. Udron, M.-L. Theye, D. Raoux, A.-M. Flank, P. Lagarde, and J.-P. Gaspard, *J. Non-Cryst. Solids* **137/138**, 131 (1991); E. Fois, A. Selloni, G. Pastore, Q.-M. Zhang, and R. Car, *Phys. Rev. B* **45**, 13 378 (1992).

²P. C. Kelires, *Europhys. Lett.* **14**, 1 (1991); *Phys. Rev. B* **46**, 10 048 (1992).

³F. Finocchi, G. Galli, M. Parrinello, and C. M. Bertoni, *Phys. Rev. Lett.* **68**, 3044 (1992).

⁴The experimental situation is nicely summarized in Ref. 3. Since no conclusion is possible at present, experiments are not further discussed here.

⁵An amorphous system can never exhibit perfect chemical ordering because of the presence of odd-numbered rings. For a given network topology, this constraint places an upper bound on the possible chemical ordering.

⁶The Si-C potential used here is that of J. Tersoff, *Phys. Rev. Lett.* **64**, 1757 (1990), which is appropriate for systems where π bonding does not play an important role. The abrupt cutoff used in that publication is not appropriate for unconstrained simulations, so we take the values proposed previously (Ref. 7) for the parameters *R* and *S*. The value of the parameter χ_{SiC} has been adjusted to 1.0086 to improve the accuracy of the SiC enthalpy of formation.

⁷J. Tersoff, *Phys. Rev. B* **39**, 5566 (1989).

⁸J. Tersoff, *Phys. Rev. Lett.* **61**, 2879 (1988).

⁹J. Tersoff, *Phys. Rev. B* **38**, 9902 (1988).

¹⁰For more background on this approach for generating potentials, see J. Tersoff, *Phys. Rev. B* **37**, 6991 (1988); *Phys. Rev. Lett.* **56**, 632 (1986).

¹¹P. C. Kelires and P. J. H. Denteneer, *Solid State Commun.* **87**, 851 (1993).

¹²G. Galli (private communication).

¹³*Binary Alloy Phase Diagrams*, edited by T. B. Massalski (American Society for Metals, Metals Park, Ohio, 1986).

¹⁴J. Tersoff, *Phys. Rev. B* **44**, 12 039 (1991).

¹⁵J. Bernholc, A. Antonelli, T. M. Del Sole, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. Lett.* **61**, 2689 (1988).

¹⁶Equation (3) for $\chi \equiv n_{cc}/n_{cs}$, plus the fact that $n_{cc} + n_{cs} = 4$, are sufficient to determine n_{cc} and n_{cs} as functions of ΔH . The results are shown as solid lines in Fig. 2. The values of the constants ϵ and T^* in Eq. (3) are discussed in the text.

¹⁷Because of the presence of odd-numbered rings in the bond network, which frustrate ordering, the degree of disorder even in true equilibrium decreases more slowly with decreasing ΔH than implied by Eq. (2). In a lattice-gas model with equal numbers of even and odd rings, we found that for *equilibrium*, a fit to Eq. (2) gives $T^* \approx T$ for $\chi > 0.3$, but $T^* \sim T/2$ for $\chi < 0.2$. However, the linear behavior in Fig. 3 argues against a large effect for *a*-SiC in the regime studied here.

¹⁸P. C. Kelires and J. Tersoff, *Phys. Rev. Lett.* **61**, 562 (1988).

¹⁹S. J. Cook and P. Clancy, *Phys. Rev. B* **47**, 7686 (1993).

²⁰The principal evidence for this conclusion is the result here, that increasing the chemical driving force leads to exponentially decreasing chemical disorder, without any evidence of saturation in the regime of interest.

²¹P. C. Kelires and J. Tersoff, *Phys. Rev. Lett.* **61**, 562 (1988). This formulation must be adapted slightly for multicomponent systems, subtracting the (physically meaningless) atomic stresses arising from the nonunique decomposition of energy into atomic contributions, where there are inequivalent atoms as in SiC.