

Transformation strain by chemical disordering in silicon carbide

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Swelling is observed in radiation-induced amorphization of SiC, which can be attributed to both structural and chemical disordering. By first-principles calculations, an attempt is made to separate the two factors by creating complete chemical disorder with no initial structural disorder in a 64-atom supercell. By relaxing all stresses and internal forces, significant transformation strains, both hydrostatic and shear, are observed. The relaxed configurations are found to be metallic. Softening of the bulk modulus is found to correlate closely with volume expansion, regardless of whether the expansion is caused by structural or chemical disordering, or with no disorder at all. It is postulated that partial chemical disordering contributes significantly to the internal residual stresses and macroscopic swelling of amorphous SiC. © 2004 American Institute of Physics. [DOI: 10.1063/1.1690093]

I. INTRODUCTION

Near room temperature, silicon carbide (SiC) has the tendency to undergo solid-state amorphization under moderate doses of neutron, ion, or electron irradiation. Snead *et al.* showed that at 340 K, 2.56 dpa of neutron irradiation caused complete amorphization of 6H-SiC single crystal, along with 12.1% expansion in volume (swelling) and about 45% reduction in modulus and hardness.¹ Measurements of XPS and IR spectra^{2,3} and cascade simulations^{4,5} reveal that the structural disordering in the amorphized configurations is accompanied by significant chemical disordering as well, characterized by the proportion of homopolar nearest-neighbor bonds, at ~20%–30% of the total number of bonds. The interplay between chemical disorder and solid-state amorphization has long been conjectured.^{6–12} In this work, the theoretical limiting case of complete chemical disorder in SiC is investigated by density functional theory (DFT) calculations, where the starting configuration is β -SiC perfect crystal but with atoms completely randomly permuted,¹² and then the stresses and atomic forces are relaxed. It is expected that results extracted from β -SiC are qualitatively applicable to other SiC polytypes, such as 2H, 4H, and 6H-SiC.

II. FORMULATION

Swelling may not just be a symptom of amorphization, but a cause as well. Accumulation of knocked-out antisite and Frenkel defects leads to local residual strains due to the large difference in atomic sizes between Si and C, creating significant compressive and fluctuating shear stresses that may drive the eventual collapse of the lattice.¹⁰ Eshelby formulated the theory of elastic inclusion¹³ in terms of the transformation strain $\eta \equiv (\mathbf{J}^T \mathbf{J} - \mathbf{I})/2$, where \mathbf{J} is the transformation Jacobian. Here, it makes sense to regard the calculation supercell as Eshelby's inclusion, which is originally cubic and containing N atoms under periodic boundary conditions

(PBC), but after the random permutation and relaxation at $\sigma_{ij}=0$ will take a new size and shape. η has 6 components which are difficult to analyze simultaneously, so we focus on the hydrostatic and shear strain-tensor invariants

$$I_1 \equiv \frac{1}{3} \text{Tr} \eta, \quad I_2 \equiv \sqrt{\frac{1}{2} \text{Tr}(\eta - I_1 \mathbf{I})^2}, \quad (1)$$

where \mathbf{I} is the identity matrix, and Tr is the trace operator. In the calculations, $I_1 \in (-0.5, \infty)$ and $I_2 \in [0, \infty)$ are no longer deterministic but have distributions that depend on N . Based on symmetry considerations, when N is large, the probability densities should have the following asymptotic behaviors:

$$\begin{aligned} \rho_1(I_1; N) &= \sqrt{N} f_1(\sqrt{N}(I_1 - \bar{I}_1)), \\ \rho_2(I_2; N) &= \sqrt{N} f_2(\sqrt{N}I_2), \end{aligned} \quad (2)$$

which is to say that the hydrostatic invariant has a mean swelling \bar{I}_1 plus a fluctuation proportional to $N^{-1/2}$, whereas the shear transformation strain invariant only has a statistical fluctuation proportional to $N^{-1/2}$. $f_1(x)$, $f_2(x)$ may now be interpreted as the probability distribution of hydrostatic and shear transformation strain fluctuations *per atom*, in an effective sense.

III. CALCULATION RESULTS

The VIENNA AB-INITIO SIMULATION PACKAGE (VASP)¹⁴ is used with Cepley–Alder local density approximation (LDA) exchange–correlation density functional,^{15,16} and ultrasoft (US) pseudopotentials¹⁷ supplied in VASP for Si and C. The plane-wave basis set has cutoff energy of 286.6 eV, and $4 \times 4 \times 4$ Monkhorst–Pack \mathbf{k} sampling¹⁸ is used for the 64-atom supercell. Because of possible semiconductor-to-metal transitions, the Methfessel–Paxton smearing scheme for density of states (DOS) integration¹⁹ is used with smearing width of 0.2 eV. Electronic relaxation stops after $\Delta E_{\text{tot}} < 10^{-4}$ eV. Ionic and supercell relaxations stop after $\Delta E_{\text{tot}} < 10^{-3}$ eV. For easy verification, input and output files are placed at a publicly accessible website.²⁰

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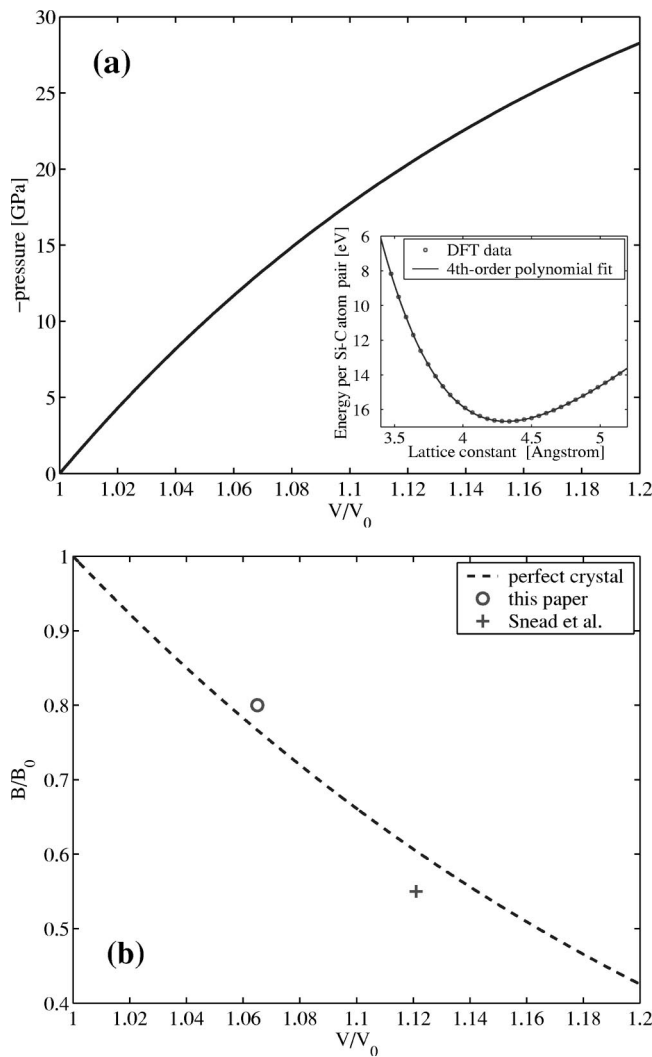


FIG. 1. (a) Pressure–volume relation of β -SiC perfect crystal: V_0 is the equilibrium volume. The inset shows the DFT cohesive energies from which the pressure is derived. (b) “Universal” softening of the bulk modulus with volume expansion. The dash curve plots the bulk modulus of β -SiC perfect crystal as a function of volume expansion. The “o” symbol shows the average volume expansion and bulk modulus of the chemically disordered configurations. The “+” symbol shows the experimental results of Snead *et al.* (see Ref. 1) for neutron-amorphized 6H-SiC.

A β -SiC perfect crystal is studied first. The relaxed supercell ($N=64$) has $L_0=8.622 \text{ \AA}$ (the equilibrium lattice constant $a_0=L_0/2$), and small hydrostatic tension/compression calculations show that the equilibrium bulk modulus $B_0=223.2 \text{ GPa}$, in good agreement with experiments and similar calculations.²¹ The band gap is 1.2 eV, much smaller than the experimental value of 2.3 eV for β -SiC, but this is a common problem in DFT-LDA calculations.²²

A total of $M=65$ chemically disordered samples are relaxed, each starting from a completely randomly permuted configuration. I_1 's sample mean is 0.0217, with standard deviation 0.005 26. I_2 's sample mean is 0.0362. These convert to the following “effective single atom” transformation strains:

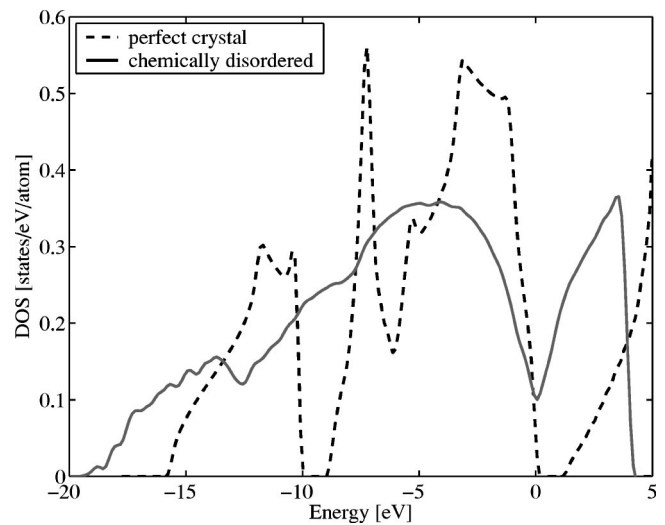


FIG. 2. Average electron density of states (DOS) of the chemically disordered configurations (after relaxation) as compared to that of the perfect crystal. Zero indicates the Fermi level.

$$\bar{I}_1 = 0.0217,$$

$$\sqrt{\int_{-0.5-\bar{I}_1}^{\infty} dx x^2 f_1(x)} \approx \sqrt{N} \times 0.005\ 26 = 0.0421, \quad (3)$$

$$\int_0^{\infty} dx x f_2(x) \approx \sqrt{N} \times 0.0362 = 0.289.$$

The above shows that local shear transformations are as significant as hydrostatic transformations, even though their supercell average tends to zero as $N \rightarrow \infty$ because the local shear transformations largely cancel each other out by the directional nature of shear.

Bulk moduli of the relaxed configurations are calculated by applying additional $\pm 0.2\%$ hydrostatic strains, then relax the atoms, compute the hydrostatic stress invariants, and do central difference. The sample mean bulk modulus is 180 GPa, with standard deviation 19.8 GPa. This is on average -20% softer than the perfect crystal, following the same trend as the experiments. It appears that the amount of volume expansion is a good predictor of modulus change: the present -20% softening is associated with $\sim 3\bar{I}_1=6.5\%$ volume expansion, whereas experimentally, -45% softening in modulus and hardness of neutron-amorphized 6H-SiC is associated with 12.1% volume expansion.¹ This correlation is somewhat striking because the experimental swelling may likely be caused by both structural and chemical disordering. To verify that this is indeed a robust trend insensitive to the details of the disordered structure, we compute the pressure–volume relation of β -SiC perfect crystal [Fig. 1(a)], and the corresponding instantaneous bulk modulus $B \equiv -dP/d \log V$ as a function of volume expansion [Fig. 1(b)]. The results of the two *disordered* materials fall almost right onto the softening trend of the *perfect crystal*. This “universal” softening response for both ordered and disordered SiCs is probably related to the universal binding energy relation (UBER)²³ for all solids and solid–solid interfaces.

In Fig. 2 the electron DOS averaged over $M=65$

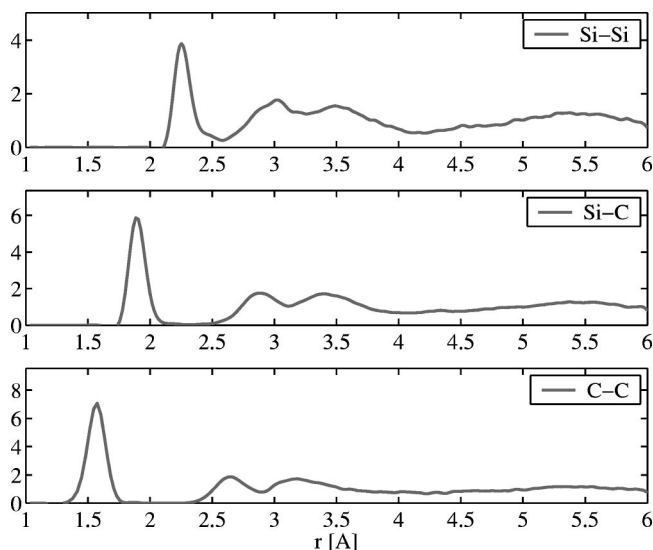


FIG. 3. Si-Si, Si-C, and C-C pair distribution functions in the chemically disordered configurations (after relaxation).

samples with the Fermi energy pinned at 0 is shown in comparison with perfect crystal DOS. Apparently, complete chemical disorder would cause the system to become metallic, consistent with previous calculations.^{24–26} Yet amorphous SiCs produced by quenching from liquids show tendencies to form semiconducting band gap,²⁷ and there is no experimental evidence of metallic amorphous SiC existing for the macroscopic time scale, so it may be concluded then that “real” amorphous SiCs would possess at least partial chemical order. It may be further conjectured that the initial cascade products could be somewhat similar to the configurations studied here with almost complete chemical disorder, but these high-energy metastable configurations are eventually annealed out. The large residual shear stresses found above may be manifestations of Jahn–Teller distortions in the system and a driving force behind the annealing process.

Figure 3 shows the Si-Si, Si-C, and C-C pair distribution functions, with split second peaks clearly seen. Table I lists the coordination number distributions, broken down by the number of Si neighbors, the number of C neighbors, and the number of total neighbors, with neighbor distance cutoffs quite arbitrarily chosen to be Si-Si: 2.58 Å, Si-C and C-Si:

TABLE I. Coordination number statistics of the chemically disordered samples (relaxed): $R_{\text{cut}}(\text{Si-Si})=2.58 \text{ \AA}$, $R_{\text{cut}}(\text{Si-C})=2.16 \text{ \AA}$, $R_{\text{cut}}(\text{C-C})=1.74 \text{ \AA}$.

		Si's coordination number distribution:						
		0	1	2	3	4	5	6
Si		6.30%	23.70%	35.77%	23.08%	8.56%	2.36%	0.24%
C		4.95%	25.19%	39.23%	24.81%	5.82%	0.00%	0.00%
Si+C		0.00%	0.00%	0.05%	2.45%	83.65%	11.92%	1.88%
		C's coordination number distribution:						
		0	1	2	3	4	5	6
Si		6.15%	24.81%	36.92%	25.77%	6.35%	0.00%	0.00%
C		6.44%	29.13%	43.37%	18.65%	2.40%	0.00%	0.00%
Si+C		0.00%	0.05%	0.19%	16.68%	83.08%	0.00%	0.00%

2.16 Å, C-C: 1.74 Å. It indicates that even if one begins with a perfect structure, just by randomly permuting the atoms, one gets an imperfect structure back after relaxation (~17% of the atoms are not fourfold coordinated). In this sense, chemical disordering and structural disordering are not completely “orthogonal.”

IV. CONCLUDING REMARKS

The above calculations continue our previous work of modeling the thermomechanical and transport properties of SiC^{28,29} before and after irradiation. It characterizes a possible intermediate state in radiation-induced amorphization, that of a completely chemically disordered state. Very large local shear stresses are found, alongside a significant net swelling. The chemical disorder may be *partially* annealed out rather quickly, during which a semiconducting band gap will open up. During the conjectured annealing process, it is expected that no long-range order can survive in the system (if there is some to start with), after collapse of the lattice driven by the very large locally fluctuating stresses. Last, it seems reasonable to postulate that if *partial* chemical disorder still exists in the final amorphous state, then it will contribute significantly to the internal residual stresses and macroscopic swelling of that amorphous state.

ACKNOWLEDGMENTS

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