

Thermodynamic Criterion for the Stability of Amorphous Intergranular Films in Covalent Materials

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(Received 26 March 1996)

The thermodynamic origin of disordered intergranular films commonly found in covalent ceramic materials is studied by molecular-dynamics simulation. Our studies show that all high-energy grain boundaries in a model covalent material, silicon, exhibit a universal amorphous structure, whereas low-energy boundaries are crystalline. This allows the identification of a thermodynamic criterion for the existence of stable disordered intergranular films based on the relative energies of the atoms in the grain boundaries and in the bulk amorphous phase. [S0031-9007(96)01285-9]

PACS numbers: 61.43.Dq, 61.72.Mm

The frequently observed existence of thin intergranular disordered films typically of nanometer thickness represents one of the most intriguing features in the atomic structures of grain boundaries (GBs) in mostly covalent ceramic materials. For example, Si_3N_4 -based ceramics prepared by liquid-phase sintering usually contain approximately 1 nm thick silicate-based glassy intergranular layers. The presence of such films provides a path for rapid diffusion and hence controls high-temperature properties, such as the strength of the material and its creep and oxidation resistance. Because such disordered, impurity-based intergranular films are usually formed during high-temperature (liquid-phase) sintering of the ceramic, at first sight their presence at room temperature appears to be a strictly kinetic, nonequilibrium phenomenon. However, various experimental observations raise the intriguing possibility that these films may be in a state of thermodynamic equilibrium. Most importantly, Clarke's early experimental observations (summarized in Ref. [1]) showed that the thickness of these disordered films is apparently constant independent of grain misorientation. Furthermore, recent high-resolution-microscopy observations in Si_3N_4 ceramics [2–4] demonstrated that the uniform thickness of intergranular films varies systematically with the overall chemical composition of the sample. It was also found that some special low-energy boundaries in Si_3N_4 do not contain disordered films at all. These experimental observations suggest that basic thermodynamic concepts, such as the GB energy, may control the existence, structure, and properties of such intergranular films. In this paper, using molecular-dynamics (MD) simulations, we elucidate the thermodynamic origin of these films and address the question of whether they can exist even in the absence of impurities.

In order to investigate the thermodynamic nature of these films, it is desirable to eliminate any impurity-related effects as well as to avoid any (kinetics- or thermodynamics-based) effects of interfacial chemistry.

In experiments even the purest ceramic materials inevitably contain identifiable levels of impurities. By contrast, computer simulations can be performed in the complete absence of impurities, and any role of interfacial chemistry can be eliminated by studying a *one-component* covalent model material, such as silicon. Our simulations reveal that high-energy GBs disorder and broaden upon high-temperature equilibration, whereas low-energy GBs remain crystalline. Furthermore, this disordering is driven by a lowering of the GB energy and the structures of the disordered intergranular films thus obtained are shown to be the same for all high-energy GBs and very similar to that of bulk amorphous Si. This demonstrates that, in principle, (a) amorphous grain-boundary films can be the result of purely thermodynamic rather than kinetic factors and (b) their formation does not necessarily require the presence of impurities.

For several reasons silicon represents an ideal choice of a one-component model material for this study. First, a well-tested interatomic potential due to Stillinger and Weber (SW) [5] is available for Si which provides not only a good description of the diamond and amorphous phases but also of the melting temperature (of 1690 ± 20 K [6], remarkably similar to the experimental value 1683 K) and the six-coordinated structure of the liquid [5,6]. Second, the structure and excess energy of the bulk amorphous phase are well reproduced by the SW potential [7,8]. Third, a significant amount of information is also available on GBs, crystal/liquid, and crystal/amorphous interfaces [9–11]. We believe this combination of relevant phase information reproduced at least semiquantitatively by the SW potential makes Si an ideal model material for this simulation study.

In our search for disordered GB films we study symmetrical *twist* boundaries which usually have higher energies than symmetrical *tilt* boundaries [12] and are thus more likely to lower their energy by disordering. The simulation cell is depicted in Fig. 1(a). It contains two

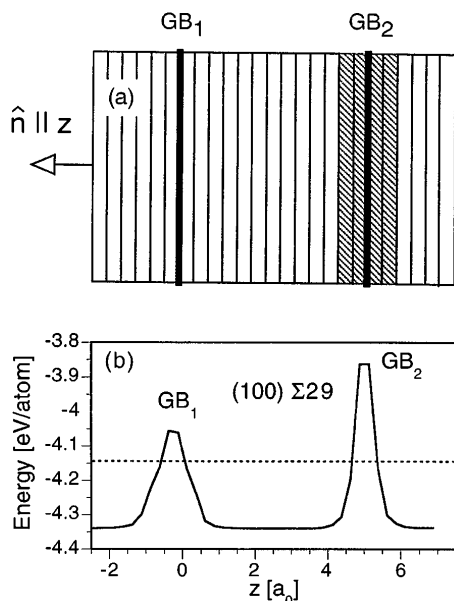


FIG. 1. (a) Three-dimensionally periodic simulation cell containing two grains. GB_1 and GB_2 are twist boundaries obtained by a rotation of two symmetrically aligned semicrystals about the common GB-plane normal $\hat{n} \parallel z$. (b) Average energy per atom in (100) slices of thickness $0.25a_0$ as a function of z for the (100) $\phi = 43.60^\circ$ ($\Sigma 29$) twist GB in Si. The dashed line indicates the cohesive energy of bulk amorphous Si.

grains misoriented with respect to each other by a twist angle, ϕ , about the common GB-plane normal (directed along the z direction). Because of the periodic border conditions in all three dimensions, the simulation cell contains *two* crystallographically identical twist boundaries, labeled GB_1 and GB_2 . The distance between the two GBs was chosen to be close to $5a_0$ ($a_0 = 5.43 \text{ \AA}$ is the zero-temperature lattice parameter of Si), which is sufficiently large for their interaction to be negligible. Their fully relaxed zero-temperature starting structures were obtained by iterative energy minimization. To enable the unit-cell volume to respond to the internal pressure, during all our MD simulations a constant-stress algorithm was applied in the z direction. To mimic the effect of embedding the GB between semi-infinite *bulk* crystals, the dimensions of the simulation cell in the GB (x - y) plane were kept fixed at the previously determined perfect-crystal lattice constant at the simulation temperature.

To find a lower-energy grain-boundary structure, the material in GB_1 [unshaded region in Fig. 1(a)] was subjected to two distinct high-temperature treatments, whereas the atoms in GB_2 [shaded region in Fig. 1(a)] were kept fixed. In the first treatment GB_1 was melted at 3000 K. The temperature was then lowered below the melting point to 1350 K and a new grain boundary was allowed to form in the GB_1 region on crystallization from the planar seeds provided by GB_2 . Crystallization requires typically about 15 000 MD time steps ($\Delta t = 2.76 \times 10^{-15} \text{ s}$) after which the system is kept at that temperature for an additional 10 000 Δt . The final structure was then obtained by cooling the system down

to zero temperature at a rate of 1 K per 50 Δt , i.e., at a cooling rate of $7.25 \times 10^{12} \text{ K/s}$ (which is rather "slow" on an MD time scale but many orders of magnitude higher than experimental cooling rates).

In the second treatment GB_1 was simply annealed at $T = 1500 \text{ K}$ (180 K below T_m) for 20 000 Δt and then also cooled down to zero temperature. In all cases these two treatments yielded structures for GB_1 with practically the same overall characteristics (radial and bond-angle distribution functions at the GB and energy profiles), although the detailed atomic structures and GB energies were not completely identical. To verify that structures thus obtained were, indeed, fully equilibrated they were reheated up to 1500 K, kept at this temperature for an additional 20 000 Δt , and then again cooled down, revealing no changes in these structural characteristics.

We first present in some detail results for the (100) $\phi = 43.60^\circ$ ($\Sigma 29$) twist GB which has a relatively high zero-temperature relaxed energy of 1464 ergs/cm^2 [9]. (Although this value represents the lowest-energy rigid-body translation of this particular GB, we found that it is rather insensitive to such translations.) Profiles of the plane-by-plane average energy per atom are shown in Fig. 1(b). While the energy profile of this GB_2 structure is rather narrow with a maximum value of -3.87 eV , the profile of GB_1 is broader but its peak value is only -4.05 eV . (For later reference, the cohesive energy of bulk amorphous silicon prepared by slow cooling of the liquid phase [9] is -4.15 eV ; as indicated by the dashed line in Fig. 1, this value is 0.185 eV above the perfect-crystal cohesive energy of -4.335 eV .) Despite the GB_1 energy profile being broader, the related GB energy of $1300\text{--}1340 \text{ ergs/cm}^2$, given by the integral under the peak, is approximately 10% lower than the energy of GB_2 (1464 ergs/cm^2). This demonstrates that high-temperature relaxation lowers the energy, suggesting a thermodynamic origin for this restructuring.

The lowering of the energy is accompanied by disordering of the GB structure as revealed in Figs. 2(a) and 2(b) showing projections of the atom positions onto the x - z plane for GB_1 and GB_2 . Whereas GB_2 [Fig. 2(a)] exhibits a clearly identifiable planar structure even right at the GB, individual atomic planes cannot be clearly defined in the center of GB_1 [Fig. 2(b)].

The loss of crystalline order in GB_1 is also evident from the related *local* radial distribution function for the atoms in the most disordered part of GB_1 and the local bond-angle distribution function [Figs. 3(a) and 3(b)]. They reveal only short-range order and are strikingly similar to the corresponding distributions obtained for bulk amorphous Si (also shown). Furthermore, consistent with results for bulk amorphous Si using the same potential [8], in the disordered region of GB_1 only about 1.5% of the atoms are threefold coordinated (i.e., atoms with dangling bonds), while 83.5% are fourfold and 15% are fivefold coordinated. By comparison the GB_2 structure is considerably less well coordinated, with 6% of the atoms having dangling bonds.

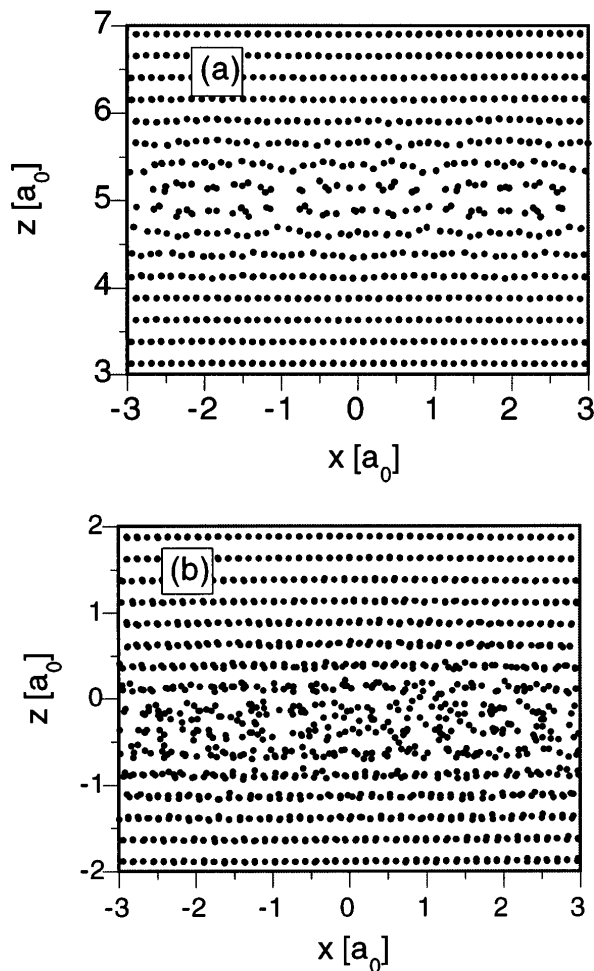


FIG. 2. Positions of the atoms projected onto the x - z plane for the $\Sigma 29$ boundary in Si; (a) zero-temperature-relaxed GB_2 region and (b) high-temperature-relaxed GB_1 region.

For the following reasons we believe that the amorphous film at this particular GB, indeed, represents its lowest-energy structure. First, two fundamentally different high-temperature treatments (growth from the melt and high-temperature anneal) yield practically the same amorphous GB structures. Second, subjected to further annealing these structures were found to be stable on a MD time scale. Third, these amorphous GB films are far better coordinated than the corresponding zero-temperature relaxed GBs.

The origin of the driving force for the GB disordering is apparent from Fig. 1(b). The peak energy of -3.87 eV/atom for the GB_2 structure far exceeds the average energy for bulk amorphous Si of -4.15 eV (dashed line). By contrast, in the most disordered plane of GB_1 the average energy is only of -4.05 eV/atom, much closer to the cohesive energy of amorphous Si. More importantly, the GB energy (i.e., the integral under the peak) is lowered during disordering despite a broadening of the GB. These observations allow us to identify a criterion for the existence of an equilibrium disordered GB film: If atoms in an ordered GB have energies higher than the atoms in the bulk

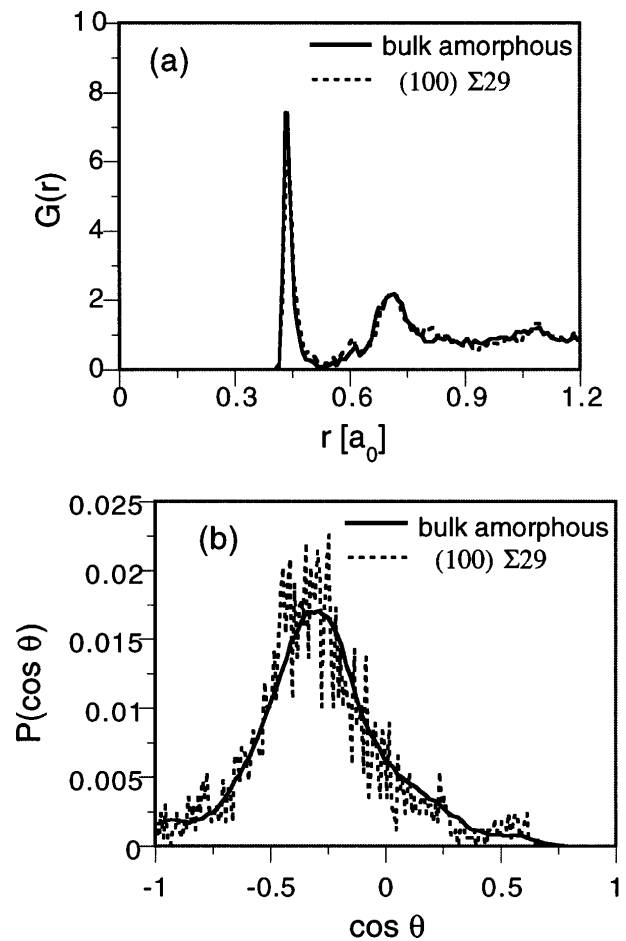


FIG. 3. (a) Radial distribution function $G(r)$ for the most disordered plane in the GB_1 region of the $\Sigma 29$ GB and for bulk amorphous Si. (b) Angular distribution functions $P(\cos \theta)$ (in arbitrary units) for the same structures as in (a).

amorphous phase, the introduction of an amorphous film into the crystalline interface is energetically favorable. By contrast, as we show later, if the atoms in an ordered GB have energies similar to, or lower than, the energies of the atoms in the amorphous phase, the GB will not disorder.

Although the structure of the intergranular disordered film is very similar to that of *bulk* amorphous silicon (see Fig. 3), the film is nevertheless highly confined between the two crystalline grains. Because of this confinement, the energy of the atoms in the most disordered plane of GB_1 does not decrease all the way down to the bulk amorphous value [see Fig. 1(b)]. Moreover, detailed analysis of the related plane-by-plane structure factor (not shown) reveals the presence of a small—but stable—signal of residual crystallinity in the most disordered planes of GB_1 , which is not surprising given the adjacent crystalline material.

Based on these insights, one might expect that all high-energy GBs should have similar, “confined-amorphous” structures. To test this prediction we investigated three other high-angle, high-energy twist boundaries: $(100) \phi = 61.93^\circ$ ($\Sigma 17$), $(110) \phi = 44.00^\circ$ ($\Sigma 57$), and $(112) \phi = 35.26^\circ$ ($\Sigma 35$) with qualitatively different zero-temperature relaxed structures. We found that

high-temperature relaxation lowers the energies of all these GBs to values in the range of 1300–1370 ergs/cm². Moreover, despite being sandwiched between different crystallographic surfaces, all GBs were found to be disordered and very similar to each other, as is also apparent from the related energy profiles in Fig. 4. As in the case of the (100) Σ 29 GB the local radial and bond-angle distribution functions for all GBs (not shown) are very similar to those of amorphous Si.

By contrast with these disordered structures for high-energy GBs, one might expect that a low-energy GB should not lower its energy upon high-temperature equilibration and hence should not disorder. To confirm this prediction we studied the (111), $\phi = 42.10^\circ$ (Σ 31) twist GB, also a *high-angle* GB; however, on the most widely spaced (and hence, lowest-energy [12]) plane in the diamond structure, with a zero-temperature relaxed GB energy of only 638 ergs/cm² [9]. Indeed, as expected, neither its structure nor its energy change during high-temperature annealing and the GB remains crystalline right up to the GB plane.

It is interesting to note that tight-binding calculations for Si also indicate the possibility of GB disordering in that the energies of atoms in GBs are typically larger than the cohesive energy of the amorphous phase. These calculations yield GB energies that are typically about (30–50)% higher [13,17] than those obtained from the SW potential, while the energy of the amorphous phase is only about 20% higher [14]. This implies that GB disordering is even more likely for Si described by tight-binding calculations than for Si described by the (empirical) SW potential. Consistent with this, fully quantum-mechanical calculations for the (100) $\phi = 36.87^\circ$ (Σ 5) twist boundary in germanium yielded a disordered structure remarkably similar to that of amorphous Ge [15].

An obvious question we have to address is why such amorphous GB films have not been observed experimentally in Si. While we can only speculate, one reason might be associated with the rather similar densities of the amor-

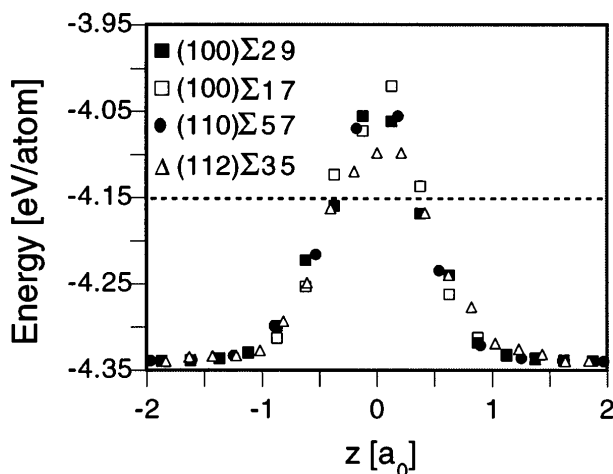


FIG. 4. Energy profiles along the z direction for four different high-energy, large-angle GBs.

phous phase and the perfect crystal, rendering it difficult to identify a thin, perhaps less than 1 nm thick amorphous film by electron-microscopy techniques which, in essence, probe the electron density. Another reason might arise from the fact that most GB studies in Si and Ge, particularly those involving high-resolution microscopy (see, for example, Ref. [16]) have dealt with *tilt* boundaries, which are known to have a generally lower energy than twist boundaries. Nevertheless, based on the fact that the experimentally determined excess energy of 0.13–0.16 eV/atom [17] for amorphous Si is even lower than that calculated for the SW potential (0.185 eV/atom), it seems possible that disordered GB films could, in fact, exist in Si, although a more conclusive assessment of this possibility requires experimental values for the GB energy.

The generic similarity of the simulated behavior of Si grain boundaries to the observed behavior of the impurity-based films usually present in covalent ceramics suggests that such GB films do not require impurities for their stabilization and that their existence in high-energy boundaries as an equilibrium “constrained-amorphous GB phase” of uniform thickness may be attributable to thermodynamics alone.

P. K. acknowledges support from the Max-Planck Research Award program. S. R. P. and D. W. are supported by the U.S. Department of Energy, BES-Materials Science under Contract No. W-31-109-Eng-38.

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