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High-Density Liquidlike Component Facilitates Plastic Flow in a Model Amorphous Silicon System

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Molecular dynamics simulations show that plastic deformation of amorphous Si modeled by the Stillinger-Weber potential is very sensitive to the density of the initial unstressed state. Low-density systems exhibit a pronounced yield phenomenon, strain softening, and a dramatic drop in pressure during deformation at a constant volume. This behavior is explained by the presence in every system of a certain concentration of solidlike and liquidlike components, the latter being denser and more amenable to plastic flow.

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Below grain sizes of about 10 nm, bulk nanocrystalline metals are known to soften significantly due to the relative ease of accumulating large amounts of plastic strain in disordered material present in between neighboring crystallites [1]. Nevertheless, some covalently bonded materials with grain sizes around 2–6 nm have exhibited hardness levels often in excess of those of polycrystalline diamond films [2]. Since plastic deformation in these nanocrystalline materials is also expected to localize mainly in a disordered intergranular component [3], their ultrahardness implies that covalently bonded disordered solids exhibit plastic flow that differs significantly from that of their metallic cousins. (Covalently bonded amorphous materials are intrinsically brittle at room temperature, but they can nonetheless deform plastically when free of fracture-producing flaws.) While plastic deformation in glassy metals and polymers has been studied before [4–6], the work presented here broadens our understanding of the phenomenon in directionally bonded disordered network solids deformed to large strains well exceeding their yield strain.

Because of a lack of crystalline order in amorphous covalently bonded solids, atomic-scale investigations of their plasticity have remained—with few exceptions [7]—outside the capabilities of experimental techniques. Computer simulations have played a deciding role in the study of these materials [8–10]. We chose to simulate a model covalently bonded system of silicon based on the Stillinger-Weber (SW) potential [8] because it exhibits well the strong directional bonding that distinguishes it from metallic glasses. The SW potential consists of sums of 2- and 3-body terms, the latter accounting for bond bending. More complex models that reproduce the specific low temperature behavior of silicon were also considered [11] as was a modified version of the Stillinger-Weber potential [12]. Nevertheless, the SW potential was chosen to study amorphous silicon (*a*-Si) due to its simplicity and because, unlike other potentials [13], it exhibits good agreement with the behavior of the modeled material across all temperature ranges and in both solid and liquid states.

Amorphous samples were created by melting the diamond cubic crystal and then quenching the liquid by constant pressure molecular dynamics [10]. As expected, the system shrunk upon melting. Some of this volume loss, however, was recovered upon quenching. The extent of volume recovery depended on the quench rate with lower rates yielding lower density amorphous structures. This behavior is typical of tetrahedrally bonded materials [14] and stands in stark contrast to the behavior of most metals, which expand upon melting and yield glasses of increasing density as the rate of quenching decreases [15]. By quenching molten Si at rates between 2.01×10^{10} and 5.17×10^{13} K/s, we were able to obtain disordered silicon samples of differing densities. The properties of the best relaxed (most slowly quenched) of these samples were in good agreement with previous simulations [9,10] and experiments [16,17].

Plastic deformation simulations were conducted at constant volume and temperature on systems of 4096 atoms under periodic boundary conditions. The system size was chosen large enough to ensure that individual plastic shear events—as identified by aggregation of atomic deviatoric strains [18]—were well confined in the simulation cell and could be associated uniquely with sudden drops in deviatoric stress. Samples were deformed to plastic strains much larger than the yield strain by repeatedly applying volume-conserving plane-strain [19] increments of 0.1%. The system was relaxed by molecular dynamics after each strain increment. To avoid any contribution to stress relaxation from temperature-activated phenomena, all simulations were conducted at 300 K, i.e., well below the melting temperature of ~1690 K [20]. The full stress tensor for each deformed configuration was calculated from the chosen potential [21]. Since *a*-Si is isotropic, the plastic deformation resistance was characterized through the deviatoric stress (σ_{dev}) and pressure (P) components of the stress tensor τ, defined as usual

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[19] as

$$P = -\tfrac{1}{3}\mathrm{tr}(\tau), \qquad \sigma_{\mathrm{dev}} = |\tau - \tfrac{1}{3}\mathrm{tr}(\tau)I|,$$

where tr stands for the tensor trace and I for identity. Deviatoric stress accounts for all shearing stresses and excludes all dilatational stress components. Deviatoric strain is computed from the strain tensor analogously to deviatoric stress.

Deformation of as-quenched structures of differing densities [Figs. 1(a) and 1(b)] shows that plastic behavior is crucially dependent on density. For the system of lowest density (◇, created by slowest quenching), elastic loading (albeit nonlinear) terminates with a sharp yield phenomenon, initial yield is followed by significant strain softening [Fig. 1(a)], and plastic deformation is accompanied by a dramatic drop of pressure well below zero [Fig. 1(b)]. The first two of these phenomena have also been observed in simulations of aged metallic glasses [5], but the third is entirely novel. The pressure drop during deformation at constant volume corresponds to volume contraction in a constant pressure simulation and stands in stark contrast to the behavior of metallic glasses, which expand during deformation. Figure 1(a) also shows no well-defined yield point for high enough initial densities (○, created by fastest quenching). Furthermore, high-density systems do not exhibit the pressure drop apparent during deformation of low-density systems. Instead, their pressure increases drastically, corresponding to a system dilatation under constant pressure. Unlike in metallic glasses where the pressure and deviatoric stress attain steady state at the same strain, the pressure in these dense structures stabilizes at higher strain than does the deviatoric stress. Finally, deformation of all structures is accompanied by irreversible average coordination changes that correlate well with system pressure.

The behavior described above suggests that the disordered systems undergo some structural evolution as they deform. First, the strain softening and pressure drop of systems with low initial density indicates a gradual transition to a denser, easily flowing state. Lack of sharp yielding for initially dense systems reinforces this view. Meanwhile, the prolonged change in pressure during deformation of these systems indicates that in the flow state, kinetic equilibrium is established between structural components of varying density. Last, evolution of average coordination points to qualitative changes of local atomic environments. Describing the structural changes taking place in the material as it deforms requires characterization of local bond ordering. A suitable one was found based on the means and standard deviations of bond angles for each atom; i.e., every atomic environment was described by the two numbers

$$\mu = \frac{1}{n}\sum_{n}\theta_n, \qquad \sigma^2 = \left(\frac{1}{n}\sum_{n}\theta_n^2\right) - \mu^2,$$

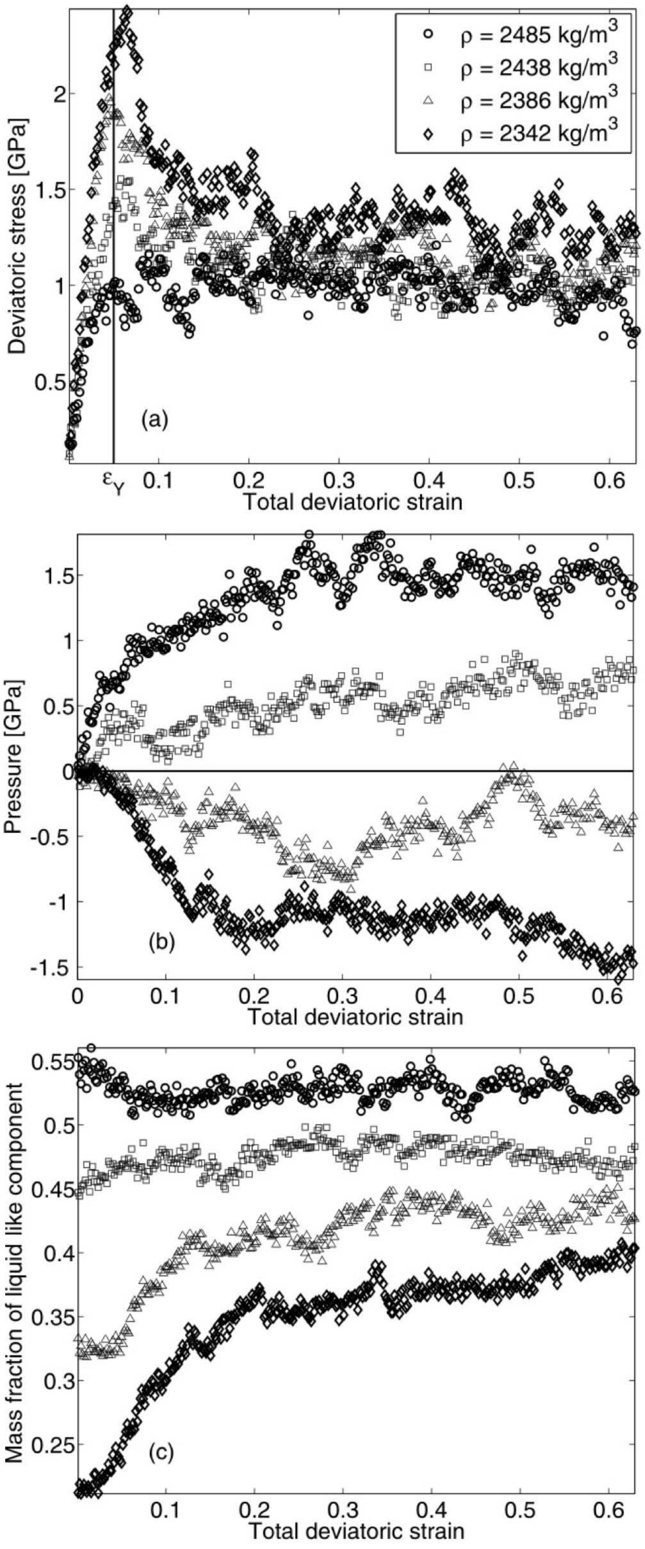

FIG. 1. The amorphous covalent network material studied exhibits a range of plastic deformation behaviors depending on the density of the initial unstressed state. (a) Deviatoric stress [19] vs deviatoric strain; (b) system pressure vs deviatoric strain; (c) mass fraction of liquidlike component vs deviatoric strain. The legend in (a) applies to (b) and (c) as well. ε_Y is the yield strain.

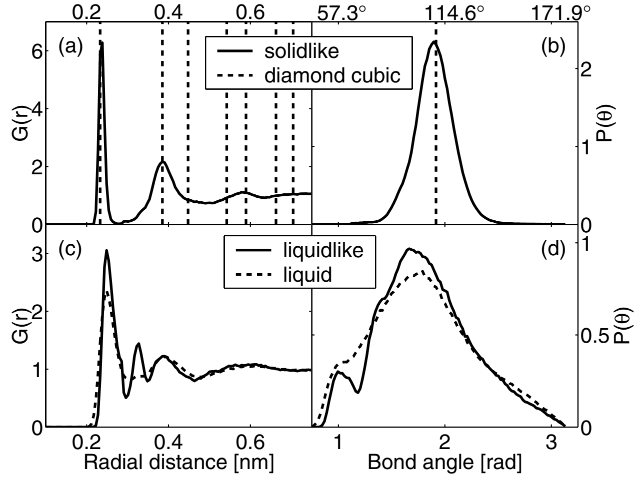

FIG. 2. Comparison of solidlike component with diamond cubic Si and liquidlike component with liquid Si based on RDFs [$G(r)$] and ADFs [$P(\theta)$].

where the sums are taken over the n bond angles θ_n between the atomic site of interest and its nearest neighbor atoms. Distributions of these quantities for all atoms in the system were clearly bimodal and the height of the distribution peaks changed in proportion to system pressure during deformation. Thus, two distinct structural components can be distinguished based on this bimodality. These components do not form phase domains, but are not entirely isolated, either: they exhibit a coherence that spans about two or three atomic dimensions.

After partitioning the system based on the analysis above, the structure of the two components was characterized by radial and angular distribution functions (RDFs and ADFs). Comparison of the results reveals clear differences between the two components [Fig. 2]. One component [Figs. 2(a) and 2(b)] has a very well-defined and narrow nearest neighbor peak in the RDF. Its distribution of bond angles is symmetric and centered on 108.9°, i.e., almost precisely on the tetrahedral angle of 109.5°. The configuration of this component, therefore, is that of a continuous random network, a form of amorphous covalent structure with local atomic environments that resemble those of atoms in a diamond cubic crystal [22]. Meanwhile, the RDFs and ADFs of the other component [Figs. 2(c) and 2(d)] bear a striking resemblance to those of the system in its liquid state. The split second peak in the RDF of the amorphous component is characteristic of configurations with ill-defined second nearest neighbors and is commonly observed in random close-packed structures such as metallic glasses and ball bearing packings [23]. Because of the above structural characteristics, we refer to the first of these components as "solidlike" and to the other as "liquidlike." The densities, coordinations, and 2- and 3-body potential term contributions of the components, each of which is remarkably close to that of their crystalline solid or liquid counterpart, reinforce this distinction [Table I].

The plastic flow characteristics of the two components can be deduced from the variation in their concentration during deformation [Fig. 1(c)]. The large proportion of liquidlike component at steady state plastic flow and an increase in its concentration during strain softening show that this form of disordered covalently bonded material is involved in plastic deformation more easily than the solidlike form. High initial yield stresses for structures with large concentrations of solidlike component and no discernible yield phenomena for structures with large concentrations of liquidlike component buttress this conclusion. Therefore, the characterization described lends dramatic support to the idea [24] that pockets of easily flowing material in amorphous solids are better distinguished by their similarity to the structure of the material in its liquid form rather than by free volume alone [4]. In metals, the "free volume" and "similarity to liquid" conditions happen to coincide, since metals have lower densities in their liquid state and the flow state of metallic glasses is therefore dilated. In the case of the covalent network material studied here, however, the liquid state is denser than the solid at the melting point. Thus, the flow state of the material in its amorphous form is contracted.

The liquidlike component described above can be viewed as a "plasticity carrier" in a-Si systems, much like dislocations are "plasticity carriers" in crystalline materials [19]. Like dislocations, pockets of liquidlike component are stable structures and not just transitional configurations that the system achieves while in disequilibrium during plastic flow. In both cases, aging by bond angle reordering removes plasticity carriers resulting in a material that exhibits a high initial yield stress.

TABLE I. Comparison of diamond cubic Si and liquid Si with solidlike a-Si and liquidlike a-Si via average coordination, density, and binding energies (E_b). The Stillinger-Weber potential is a sum of 2- and 3-body terms, so the overall binding energy was decomposed into contributions from these two components.

	Diamond cubic Si ($T = 0$ K)	Liquid Si ($T = 1690$ K $\approx T_m$)	Solidlike a-Si ($T = 300$ K)	Liquidlike a-Si ($T = 300$ K)
Coordination	4	5.13 ± 0.86	4.00 ± 0.06	4.97 ± 0.40
Density	2324 kg/m^3	2386 kg/m^3	2256 kg/m^3	2554 kg/m^3
E_b 2-body	-8.67 eV	-9.93 ± 0.95 eV	-8.82 ± 0.37 eV	-10.45 ± 0.52 eV
E_b 3-body	0 eV	3.60 ± 1.21 eV	0.91 ± 0.54 eV	4.16 ± 0.89 eV

Meanwhile, plastic deformation at temperatures well below the glass transition creates plasticity carriers in a process sometimes referred to as "rejuvenation" in that its effect is opposite to that of aging: the resulting material is more amenable to plastic flow.

In summary, we have shown that amorphous silicon as modeled by the Stillinger-Weber potential undergoes plastic flow more easily when it is contracted (denser) and that this phenomenon is a consequence of the high density of an easily flowing liquidlike component. This result serves as a clear indication that free volume considerations cannot account for the plastic flow behavior of some disordered solids. An explanation based on plasticity carriers distinguished by their similarity to the material in its liquid form appears more robust.

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