Pressure and Shear Induced Amorphization of Silicon

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Abstract

Here we report that high-power, pulsed, laser-driven shock compression of monocrystalline silicon produces directional amorphization, revealed by high-resolution transmission electron microscopy and confirmed by molecular dynamics simulations. Shear-induced lattice defects (stacking faults and twins) on crystallographic slip planes play a crucial role in the onset of amorphization. The typical high-pressure solid-solid phase transitions of silicon are not observed whereas the high shear stresses are relaxed by localized dislocation motion/interactions and eventually by directional amorphization, which occurs below the critical hydrostatic pressure for melting of silicon in shock compression. It is therefore proposed that the combined effects of hydrostatic and shear stresses lead to directional amorphization.

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1. Introduction

The importance of shear stresses in reactions and phase transitions can be significant and, in some cases, dominant¹⁻³. During laser-shock compression, the co-existence of strong hydrodynamic and deviatoric stresses often produces mechanical responses unique to the extreme stresses and timescales involved. Recently, Levitas and Ravelo⁴ showed the role of fast, non-hydrostatic compression in generating “virtual melting” in metals subjected to high strain-rate loading. Amorphization is usually achieved by quenching liquid matter below its glassy transition temperature to hinder crystallization. For silicon, other processes such as plasma deposition⁵, static pressure by diamond anvil cell⁶, radiation damage⁷, indentation⁸, and impact by nanodroplets⁹ have been used to produce amorphization that is either highly defective or severely localized. Recovery of amorphous silicon from high-pressure experiments has been an outstanding goal for decades¹⁰. Here we present successful recovery of laser-shocked silicon. We identify bulk amorphization in addition to directional amorphous bands penetrating into the sample. The latter mechanism, directional amorphization, has never before been observed.

2. Shear Stresses in Shock Compression

Laser shock creates a rapid uniaxial strain state with corresponding stresses that have hydrostatic and deviatoric (shear) components. For purely elastic uniaxial deformation:

$$\sigma_{ij} = C_{ijkl} \epsilon_{kl} = C_{ij33} \epsilon_{33} \quad (1)$$

where $i, j=1, 2, 3$ and 3 represents the loading direction coincident with the [001] orientation of the crystal. Therefore, $\tau_{\max}$ is related to P by,

$$\frac{\tau_{\max}}{P} = \frac{3(C_{11} - C_{12})}{2(C_{11} + 2C_{12})}. \quad (2)$$

For silicon, the ambient elastic moduli, $C_{11}=165.7$ GPa and $C_{12}=63.9$ GPa¹¹, render $\frac{\tau_{\max}}{P} \approx 0.52$.

This value is in agreement with molecular dynamics simulations of pressure-dependent C_{ij} and $\frac{\tau_{\max}}{P}$ (see SM Fig. S1). Although the ratio decreases to 0.26 at 20 GPa, this value is still significant. Critically, hydrostatic pressure does not produce lattice defects, whereas shear stresses are responsible for plastic deformation and generation of lattice interruptions such as dislocations, stacking faults, and twinning.

3. Experimental Setup

A schematic of the experiment can be seen in Fig. 1 (a), with cylindrical single crystal silicon targets encapsulated in aluminum. Aluminum has a similar sonic impedance and serves to minimize any tensile reflections, limiting fragmentation of the silicon target. Laser experiments were conducted at Omega Laser Facility, Laboratory for Laser Energetics, University of Rochester. The sources are pulsed neodymium glass lasers, frequency tripled to give a 351 nm wavelength. Laser energies for the experiment were 20, 50, 100, and 150 J, each with full width half max pulse duration of 1 ns and nominally square pulse shape in time. No phase plate was used in order to widen exposure to the laser and lessen lateral pressure gradients. The laser spot size focused on the target package was approximately 3 mm in diameter. Radiation-hydrodynamic simulations were used to infer shock wave propagation through the aluminum and into the silicon samples. The shock pressure profiles at the Al/Si interface are given in Figure 1(c). The values of peak pressures should be taken as first-order reference points. Rigorous methods were undertaken to produce these values, but given uncertainties in the driven intensity, ablation pressure scaling, and variations across shot days, we estimate that the uncertainty in the shock pressure at the Al/Si interface is $\pm 13\%$. The pressure calibration is enumerated further in the SM (Fig S2). Nevertheless, the intricate target package allowed for successful recovery of shocked silicon crystals and the subsequent direct microstructural characterizations are of primary focus here.

4. Characterization of Shock-Recovered Silicon

Characterization of the recovered silicon targets by transmission electron microscopy (TEM) and high resolution TEM (HRTEM) is shown in Figure 2. Electron transparent thin foils were extracted from the approximate center of the as-shocked surface by focused ion beam (FIB) and full details are supplied within the SM (Fig. S3). At the lowest laser energy, 20 J ($P_{peak} \sim 4$ GPa), silicon exhibits purely elastic behavior, i.e., neither phase transitions, nor defects were observed, consistent with previous reports of elasticity at such pressures.^{12,13} No discernable difference between a reference unshocked specimen and the laser-shocked sample substantiates that subsequent observations are not artifacts of sample preparation using focused ion beam. This comparison is provided in the SM (Fig. S3) for curious readers.

At intermediate energy levels of 50 J ($P_{peak} \sim 11$ GPa) and 100 J ($P_{peak} \sim 22$ GPa), conventional bright field TEM shows that the laser-shocked region has both a bulk amorphous

silicon layer adjacent to the surface and amorphous bands penetrating into the crystal. The amorphous material shows a characteristic featureless appearance, displaying a halo-shaped diffraction pattern, as shown in the upper left inset in Fig. 2(b), with an absence of spots or sharp rings. The quantity of amorphous material increases as the laser energy rises from 50 J (Fig. 2(a)) to 100 J GPa (Fig. 2(b)), i.e. the surface layer becomes thicker (from 100 nm to 1 μ m) and sub-surface bands broaden. The ‘islands’ of crystalline material isolated between the intersecting amorphous bands become smaller near the surface. The bands appear to be crystallographically aligned and multiple variants are to be expected, given the symmetry of the [001] crystal orientation. Numerous secondary feather-shaped bifurcations originating from the primary amorphous bands are observed in Fig. 2(b). This is also illustrated later in the molecular dynamics (MD) simulation (Fig. 3(b,c)) as secondary {111} growth variants.

The high resolution TEM micrograph, Fig. 2(c), reveals what appears to be an early stage of the amorphous band’s formation and penetration into the crystalline lattice, indicating that the bands initiate from {111} planes. Abundant {111} stacking faults and nano-twins are identified in the vicinity of the amorphous band, exhibiting zigzag configurations as seen in the red box and upper right inset. The amorphous band shows an asymmetric growth: the top part of the band is aligned with {111} plane, whereas the bottom bounding surface is misaligned by approximately 10%. The fast Fourier transformations (FFT) at the amorphous, bulk crystalline and heavily faulted regions adjacent to the amorphous bands are also given. The faulted region shows extra twin spots and streaking normal to {111} reflections, consistent with the planar directionality of staking faults and/or nano-twins. Fig. 2(d) shows a late-stage amorphous band at about 4 μ m depth below the shock surface. In this particular case, the 5 nm thick band deviates approximately 10-15° from {111} planes, consistent with the previously observed misorientations seen in conventional TEM images, Fig. 2(a, b).

At the highest laser energy explored here, 150 J ($P_{peak} \sim 28$ GPa), the recovered sample shows a nanocrystalline microstructure near the surface. The grain size ranges from ~ 100 nm to just several nm, decreasing with increasing distance from the energy deposition surface. Amorphous bands are preserved at depths greater than 10 μ m below the shock surface. Notably, nanotwins with spacing of several to tens of nanometers can be observed in the newly formed grains (SM, Fig. S4).

5. Molecular Dynamics Simulations

In order to elucidate the formation of directional amorphous bands, large-scale molecular dynamics simulations of Si were carried out using LAMMPS¹⁴ under uniaxial shock compression¹⁵. There are many interatomic potentials used to describe Si under different conditions. We select a modified parameterization¹⁶ of the Tersoff potential¹⁷, which describes reasonably well crystalline, liquid, and amorphous silicon, including the kinetics of the crystal to liquid transition¹⁸. The potential also provides a good extrapolation of the elastic constants with pressure, the Hugoniot, and stacking fault energies (see SM).

The sequence of molecular dynamics snapshots shown in Fig. 3 display the same features seen in Fig. 2: dislocations/stacking faults, amorphous bands in intersecting patterns at angles close to 45° to the shock direction, and, at for higher pressures and/or longer times, fully amorphous material. The sample behaves elastically until ~ 10 GPa and at slightly higher pressures, partial dislocations and stacking faults are first emitted from the surface (light blue lines in Fig. 3(a)), consistent with a previous report that dislocations are more aptly to nucleate at the surface¹⁹. Driven by the high-amplitude stress pulse, these defects travel from the surface inwards along specific crystallographic orientations and intersect, leading to further defect creation and additional plastic work. Simulations by Phillpot *et al.*^{20,21} found that melting would typically initiate at surfaces or grain boundaries in Si. It is clear that defects may facilitate disordering and this is further supported by Gomez *et al.*²², who found that dislocations mediated melting in a model solid. Figure 3(a,b) snapshots are taken during loading and a snapshot of simulated unloading is given in Figure 3(c). The unloading procedure is carried out over 50 ps and shows similar structural characteristics to the shock-loaded condition. The most evident microstructural difference is the retraction of unpinning stacking faults and a decrease in the coordination of the transformed amorphous material.

Figure 4 details the increase in shock temperature and the attendant decrease in melting point for Si with increasing pressure; both molecular dynamics and analytical calculations are shown and place the critical pressure between 11 and 17 GPa^{6,10,23}. Earlier calculations by Nesterenko¹⁰ indicate a value of 11.5 GPa. The negative Clausius-Clapeyron slope ($\frac{dT_{melt}}{dP} < 0$) for silicon²⁴ is responsible for the decrease in melting point with hydrostatic pressure, whereas the majority of materials exhibit an increase with pressure. The experimentally observed

amorphization occurs at a pressure lower than the “melting pressure” predicted above.

6. Conclusions

As pressure alone is not sufficient to produce amorphization under such conditions, localized effects due to shear must play an important role. Shear strains cause inelastic lattice displacement above the elastic-plastic transition. In particular, the resolved shear stress on $\{111\}$ planes leads to stacking-fault formation. Multiple high-resolution TEM observations indicate that the amorphous bands initiate when two different sets of $\{111\}$ stacking-fault variants intersect and that they grow in a direction that reasonably aligns with the predominant stacking-fault variant, not necessarily coincident with the plane of maximum shear. MD simulations indicate that a few ps after formation, the amorphous bands are still under uniaxial compression, which leads to a slight deviation from the equilibrium $\{111\}$ lattice plane towards the maximum shear direction (approximately 10° away). The motion of dislocations also results in localized plastic work, which may be quite large for covalently bonded silicon. Furthermore, non-hydrodynamic stresses can lower the melting temperature of materials under strong shock compression.

The pressure-induced diamond cubic to β -Sn and other phase transitions^{25–29} are considered kinetically unfavorable in laser shock compression due to the rapid stress pulse decay, within nanoseconds. However, varying the laser pulse conditions might lead to a phase transformation. As the laser energy increases, the amorphous bands can be observed deeper into the material due to the higher peak pressure/shear stress whereas the shock-generated heat is sufficient to nanocrystallize the layer close to the surface.

We refer to this phenomenon as rapid pressure and shear driven amorphization. Dynamic uniaxial loading produces large shear stresses that lower the threshold amorphization pressure as previously reported under conditions of static compression⁶. Fabrication of fully-dense amorphous and nanocrystalline silicon can be accomplished within extremely short timescales by appropriate choice of laser shock parameters, yielding a new method to design amorphous/nanocrystalline silicon micro/nano-electrical-mechanical-phonic systems³⁰.

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Figures and Captions

Figure 1. **Experimental setup using high-energy pulsed lasers to launch a short duration (~few ns) blast wave through single crystal Si.** (a) Overall experimental setup showing the target package and recovery tube. Si single crystal is [001] oriented and has dimensions of $\varnothing 3\text{mm} \times 3\text{mm}$. (b) Magnification of the target package, showing a CH ablator (polystyrene) used to produce a plasma under laser irradiation, an Al heat shield that also tamps the Si sample from the front, an Al “encapsulation” to laterally confine the sample on the sides, and a rear Al momentum trap. (c) Calculated pressure-time plots at four energy levels corresponding to the four laser shock experiments. The x axis denotes time in ns, given from the shock traveling from the CH/Al interface. The inset illustrates the simulated shock pressure versus depth into the silicon sample relative to the Al/Si interface for the 50 and 100 J laser shots.

Figure 2. **Characterization of laser shock compressed [001] silicon single crystal (shock wave from left to right):** (a) TEM micrograph of laser shock-recovered sample at 50 J, $P_{peak} = 4$ GPa, showing amorphous layer at surface, from which an amorphous band is emitted. (b) At 100 J, $P_{peak} = 11$ GPa, the recovered silicon sample shows much broader amorphous regions, marked “a-Si” with corresponding diffraction pattern on upper left inset; crystalline “islands” are marked by “c-Si” with diffraction pattern in lower right inset. The appearance of (002) spot is due to the strong double diffraction effect of {111} planes. (c) High resolution TEM micrograph indicating the shear-originated amorphous bands surrounded by stacking faults/micro (nano) twins. (d) High resolution TEM image at a deeper site of the sample showing that the amorphous band deviates away from {111} plane. (c) and (d) are taken from the same TEM sample as in (a) and (b), respectively, and the faulted regions are highlighted in red box with inverse FFT view in the upper right box. Three insets, marked 1, 2, 3, show the fast FFT diffraction patterns of amorphous, crystalline and heavily faulted regions, respectively.

Figure. 3. **Visualization of molecular dynamics simulations using OVITO**³¹ Uniaxial impact loading of $\langle 001 \rangle$ single crystalline silicon. Color indicated by coordination number. Snapshots taken under various loading conditions: (a) 0.85 km/s, 12 GPa, and 25 ps, (b,c) 1.1 km/s, 16 GPa, 25 and 75 ps respectively. Associated transitions from (a) stacking faults, (b) disordering along bands produced by shear strain, and (c) growth of amorphization region. The microstructure of (b) after shock wave release is presented in (c) where unloading reduces unstable stacking faults and decreases the average coordination from 6.7 to 5.1 within the amorphous region.

Figure. 4. **Comparison of pressure dependence of shock-induced temperature rise and decrease of melting temperature.** The temperature rise at the shock front can be determined analytically³² (solid red line) as well as by MD simulation (dashed purple line and triangles). The detailed derivation of temperature rise is given in the SM³³ and the Rankine-Hugoniot relationship of silicon was adopted from reference.³⁴ The MD-predicted T_m vs. P (dashed black line and squares) is compared with the T - P phase diagram (solid blue line) re-plotted from Ref. 7.