Acta Materialia 103 (2016) 519–533

Contents lists available at ScienceDirect

Acta Materialia

journal homepage: www.elsevier.com/locate/actamat

Full length article

Amorphization and nanocrystallization of silicon under shock compression

S. Zhao [a], E.N. Hahn [a], B. Kad [a], B.A. Remington [b], C.E. Wehrenberg [b], E.M. Bringa [c, d], M.A. Meyers [a, *]

[a] University of California, San Diego, La Jolla, CA 92093, USA
[b] Lawrence Livermore National Laboratory, Livermore, CA 94550, USA
[c] Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Cuyo, Mendoza 5500, Argentina
[d] CONICET, Mendoza 5500, Argentina

ARTICLE INFO

Article history:
Received 29 June 2015
Received in revised form
25 August 2015
Accepted 12 September 2015
Available online xxx

Keywords:
Laser shock compression
Silicon
Amorphization
Nanocrystalline
Nano-twinning

ABSTRACT

High-power, short-duration, laser-driven, shock compression and recovery experiments on [001] silicon unveiled remarkable structural changes above a pressure threshold. Two distinct amorphous regions were identified: (a) a bulk amorphous layer close to the surface and (b) amorphous bands initially aligned with {111} slip planes. Further increase of the laser energy leads to the re-crystallization of amorphous silicon into nanocrystals with high concentration of nano-twins. This amorphization is produced by the combined effect of high magnitude hydrostatic and shear stresses under dynamic shock compression. Shock-induced defects play a very important role in the onset of amorphization. Calculations of the free energy changes with pressure and shear, using the Patel-Cohen methodology, are in agreement with the experimental results. Molecular dynamics simulation corroborates the amorphization, showing that it is initiated by the nucleation and propagation of partial dislocations. The nucleation of amorphization is analyzed qualitatively by classical nucleation theory.

1. Introduction

Silicon is an archetypal semiconductor with physical and chemical properties that continue to draw massive research interest. The mechanical behavior of silicon under quasi-static loading is well established as the result of several systematic investigations including mechanical testing and microstructural characterization [1,2]. Silicon is traditionally considered to be an ideally brittle material, lacking dislocation activity at room temperature [2]. It has a low fracture toughness that is comparable to ceramics [3] and shows considerable crystallographic anisotropy [4,5]. Silicon is also known to exhibit pressure-induced polymorphism and amorphization. Up to 13 different crystal structures of silicon have been reported among which the transition from diamond cubic to β-Sn between 10–12 GPa is the most prominent [6–12]. Indentation and scratching investigations reported near-surface amorphization [13–15]. Gamero-Castaño et al., [16–18] have observed surface amorphization by nanodroplet impact, and Deb et al. [19] compressed porous silicon films and identified pressure-induced amorphization. In addition to experimental studies, several thermodynamic and kinetic approaches have been implemented to study silicon amorphization mechanisms [20–23]. Demkowitz and Argon [24] performed MD simulations and predicted various amorphous silicon phases whose density depends largely on the cooling rate. Levitas [25] developed a kinetic and thermodynamic theory for strain-induced phase transitions, including amorphization, indicating that superposition of plastic work leads to a significant reduction in pressure required for strain induced chemical changes. Levitas [20] also proposed a virtual melting mechanism for crystalline-disordered transitions.

Unlike silicon's quasi-static mechanical response, our understanding of its dynamic behavior is still immature. Room temperature brittleness makes it experimentally difficult to examine its response under shock conditions and complicates post-mortem microscopy if the sample survives. For these reasons, reports on shock behavior of silicon are scarce and sometimes contradictory: Loveridge-Smith et al. [26] reported that silicon has an abnormally high Hugoniot elastic limit (HEL) when subjected to high amplitude pulsed laser shock, whereas Smith et al. [27] found inhomogeneous

---

* Corresponding author.
E-mail address: mameyers@eng.ucsd.edu (M.A. Meyers).

http://dx.doi.org/10.1016/j.actamat.2015.09.022
1359-6454/

plastic flow, using a similar technique under the same relative conditions. There is also research indicating that silicon undergoes one of several phase transitions at equivalent pressures [28,29]. The large discrepancy of experimental results as well as computational simulations begs the question: what does silicon look like under shock loading? To definitively answer this question, two requirements are needed: successful recovery of shocked silicon samples from shock experiments and informed computational simulation of the events connecting pre- and post-mortem characterization.

In a preceding letter [30], we reported that laser shock, at a strain rate of ~10^7 s^{-1}, induced amorphization in monocrystalline silicon. A bulk amorphous surface layer and amorphous bands along favorable crystallographic directions were observed, both under transmission electron microscope (TEM) and in molecular dynamics (MD) simulation. It was proposed that large shear stress coupled with high pressure leads to the amorphization. In this investigation, we address this phenomenon, analyzing it quantitatively using thermodynamic parameters. Additionally, we evaluate the crystallization process from the amorphous state.

2. Experimental procedure

2.1. Laser compression experiment

Laser compression experiments were carried out at Omega Laser Facility, Laboratory of Laser Energetics, University of Rochester. A pulsed neodymium glass laser with a wavelength of 351 nm was used. The full width half maximum pulse duration was 1 ns and nominal laser energies were 20, 50, 100, 150, 200, and 450 J. The lasers have a spot size of 3 mm and no phase plates were used in order to maximize the exposure area on the target. The target was assembled in a vacuum chamber and was pumped down to a pressure of 10^{-3} Pa during working conditions to prevent oxidation of the target and prevent absorption/scattering of the laser.

Silicon [001] single crystal 3 mm × 3 mm cylinders, purchased from Universitywafer LLC., were encapsulated in aluminum cups in order to protect the target from shattering. The close acoustic impedance of aluminum (17.33 $MPa \cdot s/m$) to silicon (19.7 $MPa \cdot s/m$) serves to minimize reflection of shock waves at interfaces/free surfaces, reducing damage and aiding successful recovery. Additionally, a 1 mm thick momentum trap was used to trap the shock wave at the rear surface. A dimensioned schematic of the target assembly is shown in Fig. 1.

The pulsed laser impacts the surface of the 20 μm thick polystyrene (CH) ablator turning the polymer into a plasma. The rapidly expanding plasma subsequently launches a planar shock wave into the 100 μm thick aluminum “piston”. The compression wave decays as it traverses the aluminum, ultimately arriving at the silicon target surface. The stress pulse profiles were simulated using HYADES, a 1-D hydrodynamic code. Peak pressure as a function of laser energy is shown in bottom-right panel of Fig. 1. For clarity, targets recovered from laser shock compression are denoted by their nominal laser energy followed by “shocked”, e.g. 20 J shocked, 50 J shocked, etc.

2.2. Microstructural characterization

Post-shock multi-scale microstructure analyses were carried out using different techniques. Scanning electron microscopy was used to characterize the surface morphology of the as-shocked target. Raman spectroscopy was applied to identify the existence of amorphous silicon in bulk regions. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were used to characterize the microstructure evolution as a function of depth along the shock direction.

2.2.1. Raman spectroscopy

Raman spectroscopy is considered to be a powerful tool to indicate vibrational, rotational, and other low-frequency modes in materials [31]. Thus, it is an extremely useful tool to distinguish between amorphous and crystalline phases. A cooled Princeton Instruments CCD detector equipped with a Spex 270M spectrometer was used to obtain Raman spectra on the as-shocked silicon targets. The specimens were mounted under a Nikon Optiphot microscope. Laser illumination was performed by focusing a 0.3 kW/cm^2, 532 nm (wavelength) argon ion laser beam onto the top surface of specimens (adjacent to the area where TEM foils were extracted). The penetration depth of the illumination laser is approximately 0.5 μm.

2.2.2. TEM sample preparation

The focused ion beam (FIB) technique was used to cut TEM foils directly from the as-shocked surface. For consistency and comparison, TEM foils of equivalent orientation are preferred. This is achieved by aligning the FIB cutting direction with the crack pattern observed on the surface plane. TEM foils were prepared in Oak Ridge National Laboratory using a Hitachi NB5000 scanning electron microscope with a dual beam FIB apparatus to cut TEM samples directly from the laser-shocked silicon monocrystal surface. The TEM foils were ion milled by 30 kV Ga beam and finally polished at 5 kV to minimize FIB damage. Before cutting the sample, the area of interest was aligned with the micro-crack network. These cracks, oriented in [110] and $[1\bar{1}0]$ directions, are most likely the traces of {111} and/or {110} cleavage planes. Three foils were prepared for each target in order to ensure the consistency of the results. Zero tilt electron diffraction patterns of all the samples were always within ~2° of the {110} zone, indicating that the foil normal is <110>.

2.2.3. Molecular dynamics simulations

Simulations were accomplished with the LAMMPS package [32] utilizing a modified Tersoff interatomic potential [33] previously shown to have acceptable transferability to high pressure regimes [30]. Shock conditions are generated via infinite piston impact at a given particle velocity [34]. An impact orientation of [001] was selected for consistency with experimental work and transverse directions ([010] and [100]) have periodic boundary conditions applied. All MD snapshots were visualized using OVITO [35].

Our simulations are carried out with the MOD interatomic potential [33], which predicts a melting T of 1680 K at $P = 0$ GPa. Simulations by Lane and coworkers [36] display completely elastic behavior for [001] propagation in a perfect crystal up to ~32 GPa, with a relatively small temperature increase. Some amorphization can be observed at high pressures when nanovoids are added to the sample as pre-existing porosity. Recent simulations by Mogni et al. [29] report shock melting of single crystal Si starting above 35 GPa due to the nature of the modified Tersoff potential they used, which likely overestimates melting temperature.

3. Results and discussion

The successful recovery of silicon from high shock pressures enabled subsequent microstructure characterization. In order to make the analysis consistent, all the TEM images were taken from the [110] zone axis and arranged in a way such that the shock wave travels from left to right (shock direction = [001]), unless noted otherwise.