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#### UNIVERSITY OF CALIFORNIA, SAN DIEGO

## Shock-Induced Amorphization in Covalently Bonded Solids

A dissertation submitted in partial satisfaction of the requirements for the

degree of Doctor of Philosophy

in

Materials Science and Engineering

by

**Shiteng Zhao** 

Committee in charge:

Professor Marc André Meyers, Chair Professor Farhat Beg Professor Shengqiang Cai Professor Vlado Lubarda Professor Jian Luo Professor Vitali Nesterenko

2017

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This dissertation of Shiteng Zhao is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California, San Diego

2017

## DEDICATION

To my mother and father,

Shiteng Zhao

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#### **Publications**

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#### **ABSTRACT OF DISSERTATION**

Shock-Induced Amorphization in Covalently Bonded Solids

by

Shiteng Zhao

Doctor of Philosophy in Materials Science and Engineering University of California, San Diego, 2017 Professor Marc André Meyers, Chair

Pulsed lasers with a power of the order of terawatts, once deposited on a target surface, will launch a stress pulse that propagates into material. Owing to the ultrashort duration of the laser pulses, unprecedented experimental conditions which combine high pressures (and/or shear stresses), strain rates and temperatures can be generated in materials, yielding a yet unexplored regime of study: materials science at extremes.

High-power, short-duration, laser-driven, shock compression and recovery experiments were carried out on four covalently bonded materials, namely, silicon (Si), germanium (Ge), boron carbide (B<sub>4</sub>C) and silicon carbide (SiC). These materials were

chosen because of their high Peierls-Nabarro stress and negative Clapeyron slope. The profile of the shock waves was measured by a velocity interferometer system for any reflectors (VISAR). The shock deformation microstructure has been revealed by high resolution transmission electron microscopy and all the materials exhibit shock-induced amorphization. For Si and Ge with [001] orientation, two distinct amorphous regions were identified: (i) a bulk amorphous layer close to the surface and (ii) amorphous bands initially aligned with {111} slip planes. The VISAR measurements show that the estimated thresholds for such a crystalline-to-amorphous transition is estimated to be ~10 GPa (for silicon) and ~4 GPa (for germanium). Further increase of the shock stress leads to the crystallization of amorphous domain into nanocrystals with high density of nano-twins. For polycrystalline boron carbide, only amorphous bands inclined to the direction of shock wave propagation have been observed at a shock stress above ~45 GPa. At lower shock stress, planar faults have been seen below the shocked surface. For [0001] oriented monocrystalline silicon carbide, in addition to the amorphous bands inclined to the shock direction, some amorphous bands perpendicular to the direction of shock wave propagation were observed.

We propose that the amorphization is produced by the combined effect of high magnitude hydrostatic and shear stresses under dynamic shock compression. This study reveals that amorphization is a general inelastic deformation mechanisms in covalently bonded elements and compounds subjected to shock compression. Their formation yields a decrease in the overall hydrostatic and deviatoric elastic energy. 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, agree 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 by classical nucleation theory.

#### Chapter 1 Introduction

In 2005, on its 125th anniversary, Science, one of the most prestigious scientific journals in the world, put together a special issue: "*What we don't know*?" 125 questions were raised yet no universally accepted answers were given. In this list, one question that drew my instant attention as it relates closely to this thesis: "*what is the nature of the glassy state*?" Atoms and/or molecules in a glassy/amorphous solid are arranged "randomly", very much alike those in a liquid, albeit more closely packed. On the contrary, in crystalline solids, atoms are arranged periodically and therefore show long range order. Theoretically, every solid may have either crystalline or amorphous structure upon cooling down from its liquid phase. But where is the boundary between crystal, glass and liquid? Physicists have been developing ever more complicated theories, hoping to reveal the hidden order within such a disordered system. For a materials scientist, however, perhaps a more important and practical question is: "*how can we produce amorphous materials and do they behave differently with their crystalline counterparts*?"

Quenching a liquid below glassy transition temperature  $(T_g)$ , thus hindering crystallization, is widely used to fabricate amorphous solids.  $T_g$  is not a thermodynamic parameter and is strongly materials-dependent. The critical quenching rate  $(\kappa_c)$  varies from  $10^{-2}$ K/s to  $10^{10}$ K/s for varied materials. This methodology works well for multi-component systems with slow  $\kappa_c$ , but often fails to yield the glassy state in pure elements whose  $\kappa_c$  are much higher. Specifically,  $\kappa_c$  is estimated to be on the order of  $10^{10} \sim 10^{13}$  K/s for silicon whereas it is  $10^{-2}$  K/s for SiO<sub>2</sub>. Due to technological limitations, it is very challenging to

fabricate bulk amorphous elements through melting and quenching. Alternatively, other processes such as plasma deposition [5], static pressure by diamond anvil cell [6], radiation damage [7], indentation [8], and impact by nanodroplets [9] have been used to produce amorphous silicon (a-Si). Among these techniques, high pressure-induced amorphization is of great scientific interest.

Silicon, similar to H<sub>2</sub>O, melts with a reduction in volume. Thus, its melting temperature decreases as pressure increases. Theoretically, silicon can be melted by application of high pressure and if this pressure is retracted suddenly, the disordered structure may be preserved. However, various high-pressure experiments revealed that, instead of melting, silicon will undergo multiple phase transitions which are summarized in Table 1.1. Once diamond cubic silicon transformed into other phases, its melting pressure increases and therefore pressure induced melting was never observed under quasistatic high-pressure experiments. Dynamic loading, especially shock loading, provides a route to bypass the phase transitions that happen under thermodynamic equilibrium condition. But still, the question remains: can we recover silicon, a notoriously brittle solid, from shock experiments?

In recent years, high power, short pulsed lasers have become an important tool to probe the behavior of matter in an unprecedent regime, that is known as extremes [1–4]. Once the laser impinges on the target (or the ablator in front of it), a thin layer of materials is ablated and transformed into plasma, leading to a volume expansion. A compressive (shock) wave is generated and pressurizes the material as it propagates into the sample. An unprecedented state may be created that is characterized by the combination of high strain

rate  $(10^7 \sim 10^{10}/\text{s})$ , pressure (10s to 100s GPa), and temperature (up to 1000s K), extending our reach of materials science. Due to the extremely high loading rates (much faster than the characteristic time scale of crack propagation), the recovery of brittle solids from laserinduced shock experiment becomes feasible.

#### 1.1 Motivation

The behavior of matter under extreme conditions of high pressure, temperature, strain and strain rate is of fundamental scientific importance. Geophysical processes in the core of the Earth and other planets, matter withstanding hypervelocity impacts from comets, shock-wave compression of materials, detonation of explosives, high-pressure and high temperature synthesis of novel materials, failure of materials reaching their intrinsic limit of performance, all require an understanding of the fundamental mechanisms of materials response at the atomic, microstructural, and continuum levels. Experimental approaches are achieving ever more extreme conditions while applying novel diagnostics to increase the extent and fidelity of the measured data. This leads to a fascinating new territory, materials science at extremes. In order to complete our understanding of extreme deformation of materials, some fundamental questions have to be answered:

1. What is the maximum speed with which dislocations can move?

Do supersonic dislocations really exist?

- 2. Can we use shock experiments to obtain amorphous covalent solids? What is the threshold shock pressure for materials to be amorphized? What is the atomic configuration of amorphous/crystalline interface? What role do lattice defects play in amorphization?
- 3. Are there any recoverable shock-induced phase transformations?

These questions are far from settled due to limitations in experimental techniques. However, over the past decade, using high power lasers, such as the Omega and Janus laser facilities, this unique regime of science, combining high pressures, shear stresses, temperature, and strain rates, is emerging to be realized. On the other hand, large scale atomic simulation has been proven to be a powerful tool to gain great insights into the shock phenomena. By combing state-of-the-art laser shock compression experiments and molecular dynamics simulations, we are proposing to address these questions, both experimentally and computationally.

Covalently bonded materials have been playing an irreplaceable role in the modern technological society. For instance, the majority of semiconductors materials of which the electronic devices are built fall into this category. Here we present the results of our research on four typical covalent solids: silicon (Si), germanium (Ge), silicon carbide (SiC), and boron carbide (B<sub>4</sub>C). Si, Ge, and SiC are widely used as semiconductors whereas B<sub>4</sub>C is a famous light-weighted armor material. We chose these materials for a number of reasons. First, we need very high-quality crystals, so that the source of lattice defects, for shock strengths below the homogeneous nucleation threshold, are on the surface. Second, very high-quality wafers of Si/Ge/SiC are readily available commercially at a reasonable cost. Third, we also need crystals with high enough barriers to create defects that in preparing the samples for post-shot TEM analysis, the defects created by FIB cutting and subsequent polishing do not overwhelm the shock-created defects, which is the subject of study. Covalently bonded materials are ideal in this regard, as well. Finally, the threshold and time scale for the onset of plasticity in these materials has been a topic of debate.

#### 1.2 Research Objectives and Methodology

Special experimental setups were designed for pulsed laser-driven shock recovery experiment of covalent bonded solids. The laser experiments were executed at Omega Laser Facility, Laboratory of Laser Energetics, Rochester University and Janus Laser Facility, Lawrence Livermore National Laboratory. The microstructures of the shocked sample were characterized by various techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), transmission Kikuchi diffraction (TKD), atomic force microscopy (AFM) and Raman spectroscopy.

Special sample holders and heating elements were designed to conduct experiments under various conditions (shock at elevated temperatures, recovery experiment, VISAR, in-situ X-ray diffraction, etc.). Brittle targets (Si/Ge/SiC/B4C) were encapsulated in certain ductile metals which are shock impedance matched with the targets. By doing so, the damage caused by reflected wave was minimized, leading to successful recoveries of the samples. This enabled subsequent post-shock microstructural characterization.

A novel approach for an experimental measurement of average dislocation velocity was implemented. Starting with a high quality single crystal, nano-indentations were made on the front surface of the crystal, then a strong, but short duration shock was driven across this nano-indented surface and into the bulk crystal. The shock strength needs to be high enough to cause plastic deformation, but its duration needs to be short enough that the plastic work induced heating of the sample is low, to reduce as much as possible post-shot annealing of dislocations and other defects. The goal is for the shock-induced defects to be frozen into the recovered sample. The peak shock strength needs to also stay below the homogeneous nucleation threshold, so that the plasticity is evolved from the nanoindentation sources at the surface. In the post-shock TEM of the shock recovered sample, the depth of the plastic zone can be determined. Dividing this by the duration of the shock wave should allow a first experimental bound on dislocation velocity due to high pressure shock waves. The existence of amorphous and new crystalline phases was identified by selected area electron diffraction. The atomic structure of these materials was revealed by high resolution TEM.

#### Chapter 2 Background

#### 2.1 Literature Review on Silicon

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 [5,6]. Silicon is traditionally considered to be an ideally brittle material, lacking dislocation activity at room temperature [6]. It has a low fracture toughness ( $K_1c \sim 1 \text{ MPa} \cdot m^{1/2}$ ) that is comparable to ceramics [7] and shows considerable crystallographic anisotropy [8,9]. 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  $\beta$ -Sn at 10~12 GPa is the most prominent [10–16]. Indentation and scratching investigations reported near-surface amorphization [17-19], Gamero-Castaño and coworkers [20–22] observed surface amorphization by nanodroplet impact and Deb et al. [23] compressed porous silicon film and identified pressure-induced amorphization. In addition to experimental studies, several thermodynamic and kinetic approaches have been presented to study the silicon amorphization mechanisms [24–27].

The shock behavior of silicon was reported as early as 1960s [28]. Various experimental researches were carried out, with foci on shock Hugoniot data[29], high-pressure phase transformation[30], inhomogeneous plastic flow[31], etc. More recently, the shock behavior of silicon has also been studied computationally [32].

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 [5,6]. In this section, the fracture mechanisms, plasticity, polymorphism/amorphization of silicon will be reviewed.

#### 2.1.1 Fracture Mechanisms

Silicon is traditionally considered to be an ideally brittle material, lacking dislocation activity at room temperature [6]. Silicon fractures by rupture of individual atomic bonds, eventually leading to catastrophic failure. Sen *et al.*[33] investigated the crack behavior of silicon by molecular dynamic simulations and drew the following conclusions: (1) at low temperature, dislocation activity is heavily suppressed due to limited plasticity ahead of the crack tip, resulting in a sharp crack surface; (2) at elevated temperatures, however, the crack will be blunted and dislocation emission is observed.



Figure 2-1 Molecular dynamics simulations of crack propagation in silicon at (a) low temperature (200 K) with sharp crack tip, and (b) high temperature (1200 K) with dislocation emission at crack tip [33].

The velocity of the crack is limited by Rayleigh-wave speed. Various studies, both experiments and in computations, have confirmed these phenomena [34,35]. However, most of these researches focus on mode I fracture and in quasi-static loading condition.

Under shock loading, when the deviatoric stress component is significant, the fracture mechanisms of silicon are much less understood.

#### 2.1.2 Defect-Mediated Plasticity

At elevated temperatures, especially above brittle-to-ductile transition temperature, plasticity becomes increasingly predominant. Eremenko and Nikitenko [36] studied the mechanical behavior of monocrystalline silicon by diamond pyramid indenter in the temperature range between 20 to 700°C. They characterized the deformed microstructure by TEM and found that above 400°C, both dislocations and deformation twins appear in the vicinity of indents.



Figure 2-2 Bright field TEM images of silicon indented at elevated temperatures showing (a) dislocations and (b) deformation twinning [36].

More recently, Korte *et al.* [37] performed systematic compression tests on silicon micro-pillars and were able to determine the transition in the deformation mechanisms at a much smaller scale.



Figure 2-3 Micromechanical test of silicon performed at elevated temperatures: (a) initial micropillar; (b) compressed pillar showing a crack; (c) fractured sample; (d) influence of pillar diameter, temperature, on the strength of silicon; (e) dark field TEM image shows deformed microstructure with versatile dislocation structures (partial dislocations, full dislocations and Lomer-Cottrell locks) Figures adapted from [37].

#### 2.1.3 Pressure/Shear Induced Polymorphism

Various materials can transform into novel phases at extraordinary high pressures and temperatures. 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  $\beta$ -Sn at 10~12 GPa is the most prominent [10– 16]. The versatile silicon polymorphism is summarized in the Table 1 below.

Phase	Crystal Structure	Space Group	Existing	Technique	Refs.
			Condition		
Si-I	Diamond Cubic	Fd-3m	Ambient to 10		
			GPa		
Si-II	β-Tin	I41/amdS	10~13 GPa	DAC/Indentation	[38]
Si-III, bc8	BCC	Ia-3			
Si-IV	Diamond	P63/mmc			
	Hexagonal				
	(wurzite)				
Si-V	Simple-hexagonal				
bt8	Tetragonal	I4 <sub>1</sub> /a			
Si-VII	НСР		42 GPa		
Si X	FCC				
Si XI	Body-centered	Imma	13~18 GPa	Synchrotron	[39,40]
	orthorhombic			XRD	
Si XII					

Table 2-1 Polymorphs of Silicon

The various silicon high pressure phases have been a subject of massive research in 1950s-1990s. This topic is rejuvenated in recent years due to the emerging thrust for optoelectronic devices. A thorough graphic review of the P-V diagram is given in Fig. 2-4.


Figure 2-4 Pressure-volume diagram of silicon mapping various phase structures.

It should be mentioned that the boundaries between various high-pressure phases are poorly defined and the conditions for them to appear are extremely difficult to determine. Nevertheless, the existence of silicon polymorphism is of great technological importance.

Phase transitions are typically associated with sharp changes of physical properties. Jamieson [38] showed that the Beta-Tin silicon loses its semiconducting identity and becomes electron conductive. Chang *et al.* [41] reported that simple hexagonal (sh) silicon exhibits superconductivity and the measured superconducting transition temperature is 8.2 K at 15 GPa. Diamond cubic silicon is a semiconductor with an indirect band gap of around 1.14eV, and is normally considered as an inefficient light emitter. However, Raffy *et al.* [42] predicated that the band gap decreases with increasing hexagonality of the polytype. There are also reports showing that hexagonal silicon is actually a direct band gap semiconductor [43]. The unique properties of these silicon phases paved the way to engineer the band gaps of silicon-based devices [44]. However, most of these phases are metastable and only exist either at pressurized states or during the unloading process. Therefore, recovery of novel phases of silicon from high-pressure experiments has been an appealing yet challenging topic. Recently, Hauge *et al.* [45] successfully grew hexagonal silicon crystal on top of a hexagonal gallium phosphide template.

In addition to polymorphism, pressure-induced amorphization of silicon was also reported. Using micro-indentation, Clarke *et al.* [17] first observed crystalline-toamorphous transitions in silicon and germanium. They proposed two possible mechanisms:

(1) diamond cubic silicon transformed directly to an amorphous state; this is because the applied pressure exceeded the extrapolation of the liquidus curve in the P-T diagram. Amorphization takes place upon loading.

(2) During loading, dc-Si was transformed into electron conductive phases. However, the reverse transition is sluggish whereas the unloading rate is relatively fast. Therefore, amorphization happened upon unloading.

Wu *et al.* [18] extracted cross-sectional electron transparent sections directly from the indented area and their observation suggested that the deviatoric stress is a more important driving force than hydrostatic stresses. Nanoindentation was used where the deformation zone is nano-to-submicro scale. The advantage of nano-indentation lies in the fact that the small deformation area enables careful and precise microstructural and mechanical characterization. Various nanoindentation investigations were carried out to probe the phase transition/amorphization in silicon. Jang *et al.* [13] studied the influence of load, rate, and indenter angle on the phase transformation behavior. Chang and Zhang [46] used a Berkovich nanoindenter to study the loading/unloading curve discontinuity in silicon, which are usually referred as "pop-in" and "pop-out" phenomena.

Indentation and scratching investigations silicon reported near-surface amorphization [17–19]. Gamero-Castaño and co-workers [20–22] observed surface amorphization by nanodroplet impact and Deb *et al.* [23] compressed porous silicon film and identified pressure-induced amorphization without experiencing high-pressure polymorphism. They carried out in-situ X-ray diffraction and Raman spectroscopy on a porous silicon sample pressurized by diamond anvil cell. It was shown in Fig. 5 that the diffraction peaks become broader as the pressure increases and above ~13 GPa, the sharp diffraction peak disappear. On the other hand, Raman spectra show a broad peak (480 cm<sup>-1</sup>).



Figure 2-5 (a) In situ synchrotron diffraction and (b) Raman spectra of nanoporous silicon under hydrostatic pressurization and (c) Raman spectra under decompression [23].

The diverse behavior of silicon subjected to mechanical load lie in its unique structure. At ambient environment, silicon shows a firm but not close packed diamond structure. The atoms only occupy 34% of the total unit cell volume. This is a very open structure and there is a large degree of freedom for silicon atom to rearrange under stresses.



Figure 2-6 Deformation map of silicon with the pink region showing the unknown territory.

One can refer to a deformation mechanism map proposed by Ashby and Weeterman to infer the deformation mechanisms of specific materials under various loading conditions. It can be seen from the silicon map (Fig. 2-6) that it does not show prominent plasticity until 600°C. At higher temperatures and low strain rate, silicon also creeps. However, at relatively high strain rates, especially in the region of shock loading, the deformation mechanisms of silicon remain unknown.

#### 2.1.4 Dynamic Behavior of Silicon

How silicon responds to stress waves is of great scientific and practical significance. However, unlike silicon's quasi-static mechanical behavior, our understanding of its dynamic behavior is still immature. The use of shock wave techniques to probe the equation of state of silicon and other covalently bonded solids at extreme pressures and temperatures dates back to 1960s. Pavlovskii [28] shocked silicon up to 200 GPa where he found two kinks in the Pressure-Volume curves, as shown in Fig.2-7. He attributed the first kink to elastic-to-plastic transition whereas the second one to a phase transition. Gust and Royce investigated the orientation dependence of the shock wave propagation in silicon and conclude that <100> shows a higher HEL (~9.2 GPa) than <110> (5 GPa) and <111> (5.4 GPa). They also observed a multi-wave structure which indicates several phase transitions at a shock pressure of 13-14 GPa. [47] Turneaure and Gupta [48] shocked silicon single crystals to stresses between 15.9 GPa and 21.7 GPa and reported inelastic deformation of silicon up to a 23% of compression. They attribute this significant strain to phase transformation. By matching bulk impedance, they postulate the transformed phase is of simple hexagonal. However, using a propellant gun, Kishimura and Matsumoto [30] performed shock-recovery experiments on silicon up to 38 GPa and reported the absence of phase transition. In recent years, high power pulsed laser has become an emerging technique for shock physics. Wark et al.[49] performed laser shock compression on silicon below its Hugoniot elastic limit (HEL) and measured its elastic strain to be 3% by XRD. Loveridge-Smith et al. [29] reported that silicon has an abnormally high HEL when subjected to high amplitude pulsed laser shock, whereas Smith et al. [31] found the inhomogeneous plastic flow, using a similar technique under the same relative conditions.



Figure 2-7 P-V diagram of silicon under shock compression. [28]

Room temperature brittleness makes it experimentally difficult to examine the response of silicon under shock conditions and complicates post-shock microscopy if the sample survives. For these reasons, reports on shock behavior of silicon are scarce and sometimes contradictory: Smith *et al* [50] investigated the microstructure evolution of silicon by repetitive femtosecond-laser doping and found a diverse polymorphism (Si-I, III, XII). 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 and informed computational simulation of the events connecting pre- and post-shock characterization.



Figure 2-8 Schematic drawing of the P-T phase diagram of silicon superposed with shock Hugoniot.

Recovering supercooled silicon from shock experiments has been an outstanding goal. Nesterenko [51] was among the earliest scientists to make this effort. According to the phase diagram of silicon, it is most desirable to achieve this at the triple point, assuming a thermodynamic equilibrium. However, the shock generated heat is not sufficient to homogeneously melt the bulk silicon crystal. Thus, in order to achieve a higher temperature rise at the shock front, porous silicon with a density of one half that of the bulk silicon was used. The porous silicon had an initial particle size of micrometer scale whereas X-ray diffraction of the shocked specimen shows that the grain size of the shock-recovered sample is reduced to a few hundreds of nanometers. This is an indirect evidence for melting followed by crystallization.

# 2.2 Literature Review on Germanium

Germanium sits right below silicon in the periodic table; therefore, they have very comparable properties. For instance, germanium is also covalently bonded and has the diamond cubic structure under ambient conditions. It is semiconducting as well, with a melting temperature of 1211.4 K, which is significantly lower than that of silicon. Its density is  $5.323 \text{ kg/m}^3$ . Germanium is brittle at room temperature with a fracture toughness  $\sim 0.6 \text{MPa}\sqrt{m}$ .

Under pressurization, similarly, Ge also undergoes phase transitions reported as early as 1960s when Jamieson [38] conducted X-ray diffraction and showed that diamond cubic Ge will transforms into white tin structure with a volume shrinkage of 12.5%. The first shock-wave study on Ge was performed by McQueen [52] where multiple waves can be observed with a Hugoniot elastic limit of ~4 GPa and a transition pressure around 12.5 GPa. Later on, there are other studies on shock compression of germanium, showing consistent reports on the HEL of germanium around 4 GPa. However, recovery of Ge from high pressure experiments had not been hitherto realized.



Figure 2-9 Shock Hugoniot of Germanium measured by Gust and Royce [53].

#### 2.3 Literature Review on Boron Carbide

Boron carbide (B<sub>4</sub>C) is one of the hardest materials on earth while extremely low density (2.52 kg/m<sup>3</sup>) at the same time, making it an excellent body armor material [54–57]. The dynamic behaviors of B<sub>4</sub>C under impact/shock loading has been a subject of intensive studies for decades [54,58–65]. The characteristic shock wave profile and shock Hugoniot are displayed in Fig. 2-10, where the post-yield softening can be viewed from Fig. 2-10 (a). Various studies have shown that B<sub>4</sub>C tends to undergo an abrupt shear strength drop at a critical shock pressure around 20~23 GPa, suggesting an deteriorated impact resistance [59]. Historically, this is attributed to some localized softening mechanisms such as shear localization and/or melting. Using transmission electron microscopy (TEM), Chen *et al.* [66] first identified localized amorphization in B<sub>4</sub>C which can be aligned to certain crystallographic planes. However, the sample they took was from some fragmented

powders and therefore lost its connection to the shock/impact surface. Therefore, the relationship between the observed microstructure and the loading information could not be understood. The key factor to fill this gap is to shock the B<sub>4</sub>C sample beyond the amorphization threshold while maintaining the intactness of the shocked sample. In order to achieve this goal, the duration of the stress pulse should be smaller than the characteristic time for crack propagation which is typically in µs scale (limited by Rayleigh wave speed [67]). Traditional dynamic loading methods such as plate impact and split Hopkinson pressure bar cannot deliver the strain rates required since the stress pulse of both techniques are in µs. Therefore, brittle solids such as B<sub>4</sub>C will fail catastrophically by crack nucleation, propagation, and coalescence [68]. Recent studies show that the lateral confinement of the B<sub>4</sub>C sample results in an increased compressive strength, showing that imposing confinement may increase the recoverability of the sample from high pressure experiments[69].



Figure 2-10 Shock wave profile (a) and shock Hugoniot of boron carbide (b) from Grady [59].

Boron carbide possesses a rhombohedral crystal structure, which is shown in Fig. 2-11. The boron atoms tend to form icosahedra which render the stoichiometry of  $B_4C$  complicated. This is shown in the magnified view in the upper right corner of Fig. 2-11. There is one carbon atom in each icosahedron, and nominal stoichiometry of the icosahedron is  $B_{11}C$ , although the exact location of the carbon within the icosahedron is still under debate. Outside the icosahedron, the carbon-boron-carbon (C-B-C) chain connect each icosahedron and forms the skeleton of the rhombohedral lattice. The following figure shows schematically the structure of the boron carbide.



Figure 2-11 Unit cell of the boron carbide with an icosahedron magnified in the upper right corner: boron atoms are marked green whereas the black colored atoms are carbon. The plane intersecting with the unit cell is (113).

The green atoms are boron whereas the black ones are carbon. It has been shown that the linear C-B-C chain is much more compliant than the icosahedron and therefore it is more prone to undergo plastic deformation. This is because the icosahedra are generally thought to be in near-spherical shape and their bonds are highly delocalized (fullerene-like intraicosahedral  $sp^2$  bonds [70]). If a shear stress is applied on a certain plane, e.g. (113) in this case, although it will cut through the icosahedron, they are less likely to break compared with the C-B-C chain. Thus, it has been postulated that the bending/breaking/rotation of the C-B-C chain is the reason for the shock-induced amorphization in B<sub>4</sub>C whereas the boron rich icosahedron may remain intact [71]. However, recent atomic probe study suggest that the icosahedron can be broken when boron carbide undergoes field evaporation [72].

The search for amorphization-resistant boron carbide has been an outstanding goal [73]. Subhash *et al.* [73] suggested three possibilities:

(1) doping  $B_4C$  with foreign atoms. Silicon is a potential candidate. Recent studies shown that silicon dopant increases the amorphization threshold [74] and may improve the fracture toughness of  $B_4C$ .

(2) Fabrication of polymorphs with the greatest thermodynamic stability.

(3) Reducing the grain size down to nano-scale[75].

Note that the stress induced amorphization have also been observed in quasi-static loading. Parsard and Subhash conducted Raman spectroscopy on the post-nanoindented boron carbide and revealed the 3-D mapping of the amorphous zone [76].

## 2.4 Literature Review on Silicon Carbide

The covalent bonding nature provides silicon carbide (SiC) with desirable properties such as high melting temperature, excellent corrosion resistance as well as ultrahigh hardness. As such, it has been used as an important engineering material for loadbearing structures such as engine frame, body armor and fiber/whisker reinforced composites. SiC is also a semiconductor, which can be used in electronic devices. Its hightemperature stability and high breakdown voltage render it a viable alternative for siliconbased devices, especially in harsh service environments. Silicon carbide is known to exhibit various polymorphs which differ in the stacking sequence of the close-packed plane [77,78]. It has been reported that these crystalline phases can transform from one to another under quasi-static pressurization and that the critical pressures for the phase transformations depend on the initial structures [79]. For instance, it was shown that 3C-SiC will transform into the rocksalt-type structure at around 100 GPa [79]. Chen et al. [80] performed in-situ nanopillar compression of 4H-SiC and revealed the phase transformation of 4H (hexagonal) structure to the 3C (cubic) structure at 9-10 GPa. There are also predictions suggesting that SiC may undergo pressure-induced amorphization [81]. Recently, such a phase change is reported by Levitas *et al.* [82] in their diamond anvil cell experiment. Han et al. [83] also report deformation-induced amorphization in SiC nanowire, indicating that such a crystalline-to-amorphous transition gives rise to the observed superplasticity.

In addition to its quasi-static mechanical behavior, the response of SiC to dynamic loading and shock compression/release has also drawn intensive interest. Grady [59] studied the shock-wave properties in polycrystalline silicon carbide and found that it exhibits a high Hugoniot elastic limit (HEL~15-16 GPa), after which it undergoes a postyield hardening region, in contrast with B<sub>4</sub>C. Shih *et al.* [84,85] studied the high rate deformation and shear localization of bulk and powder silicon carbide and found that the fracture mechanism of SiC depends on the particle size distribution. Feng *et al* [86] measured the shear strength of shocked SiC and confirmed that it increases up to twice of the HEL. They also found that at stresses beyond twice the HEL, SiC gradually loses its strength with increasing shock compression. Such anomalous macroscopic behavior maybe due to the complicated microscopic phase changes that are often contradictory in the literature [87,88]. However, the microstructural evidence of these shock-induced phase transitions has not been identified.

#### 2.5 Pressure-induced amorphization

Classical thermodynamics relates the Gibbs free energy, G, to the internal energy (U), pressure (P), temperature (T) and entropy (S) of the system,

$$G = U + PV - TS \tag{2.1}$$

Since amorphous structures show much higher configurational entropy, one might think that they are more stable than crystalline solids. In reality, it is not so since the increase of internal energy required to destroy the long-range order of crystalline solids far exceeds the entropy term in Eq. 2.1 at temperatures much below melting temperature. Therefore, the most common method to produce an amorphous structure is fast quenching of the liquid to prevent crystallization. Alternatively, one can increase the internal energy by introducing massive lattice defects (vacancies, dislocations), through ball milling, ion/neutron radiation, and other means [89] until amorphous structure becomes energetically more favorable. Another possibility lies in the group of materials whose melting curves show downwards trend with increasing pressure. This leads to Mishima's seminal work of "melting" hexagonal ice by pressurizing it to around 1 GPa at 77K [90–92]. Since then, many materials, including silica [93,94],  $Ta_2O_5$  [95], and minerals such as LiKSO<sub>4</sub> and CaSiO<sub>3</sub> [96] have shown evidence of becoming amorphous under static compression.

In terms of dynamic pressurization, interestingly, long before realizing that these are the results of shock-wave compression created by meteorite impacts, geologists have documented glassy states of many mineral materials such as quartz, zircon (ZrSiO<sub>4</sub>) and feldspar (KAlSi<sub>3</sub>O<sub>8</sub>-NaAlSi<sub>3</sub>O<sub>8</sub>-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>) in meteorite craters [97–99]. More careful investigations show that there are two types of amorphous minerals: diaplectic glass and normal glass. The formation of former is considered as a solid-state transition whereas the latter undergo melting and quenching. Later, geophysicists realized that the recovered microstructure depends heavily on the shock pressure and temperature; hence, they named this effect shock metamorphism.



Figure 2-12 (a) Temperature-Shock Pressure map of geological minerals and (b) Planar deformation features (PDFs) in Quartz and (c) Diaplectic glasses in Zircon. Figure adapted from Ref. [100].

Figure 2-12 shows the domains in the P-T diagram of geological materials, distinct by post-impact microstructure characterization. Fig. 2-12 (b) and (c) are examples of planar deformation features (PDF) and diaplectic glass in quartz [98] and zircon [99], respectively. The samples are taken from different meteorite impact craters. Due to their unique morphological features, geologists and geophysicists often use shock metamorphism as a barometer and thermometer for terrestrial impact formations [98,101].

Materials showing pressure-induced amorphization are potentially candidates for density driven first-order amorphous-amorphous transition. The physics underlining is the melting curve maxima which are observed in many systems [102,103].

Normally the melting curves of materials show a positive pressure dependency whereas some exceptions exist where the specific volume is reduced during melting. This results in a melting point maximum in the T (P) curve. If this maximum is in the tensile region (P<0), then an initial negative melting slope is observed as shown in Fig. 2-13. Consider liquid as a mixture of low density (LDL) and high density (HDL) domains; the "concentration" of HDL increases as pressure increases. This explains the turning point of melting curve (change of melting slope) above crystalline phase (density smaller than liquid). Upon fast cooling where crystallization can be bypassed, there exist a (T, P) point below which the liquid mixture undergoes spinodal-type decomposition into two phases, i.e. LDL and HDL, respectively. Such a density-driven transition is therefore a first order phase transformation. LDL and HDL have distinct glassy transition temperatures and below which LDL and HDL will be transformed into two corresponding amorphous structures known as LDA and HDA.



Figure 2-13 Left, Schematic drawing of the pressure-induced amorphization in materials with negative melting slope; right, generic T-P diagram of materials with a melting maxima. Figure adapted from Ref. [96].

# 2.6 Fundamentals of Shock Physics

The study of shock phenomena inevitably requires the understanding of stress wave propagation in materials and structures. At low shock pressures, stresses may be below the rate-dependent yield strength of materials, the Hugoniot elastic limit (HEL). Once the shock pressure exceeds the HEL, inelastic waves as well as elastic waves will be generated. In this section, some basics of stress wave propagation are reviewed.

# 2.6.1 The uniaxial strain state

The uniaxial strain state refers to a situation where a rigid body is subjected to a uniaxial, or one-dimensional deformation, e.g. a plate impact experiment where one thin plate is impacted against another. Such a state is defined as,

$$\varepsilon_{33} \neq 0, \quad \varepsilon_{11} = \varepsilon_{22} = \varepsilon_{12} = \varepsilon_{13} = \varepsilon_{23} = 0$$
 (2.2)

According to the generalized Hooke's law:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} = C_{ij33} \varepsilon_{33} \tag{2.3}$$

For a cubic crystal,

$$C_{ijkl} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}$$
(2.4)

The corresponding strain and stress tensors can be written as,

$$\varepsilon_{ij} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \varepsilon_{33} \end{bmatrix} \text{ and } \sigma_{ij} = \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$
(2.5)

where  $\sigma_{11} = C_{12}\varepsilon_{33}, \sigma_{22} = C_{12}\varepsilon_{33}, \sigma_{33} = C_{11}\varepsilon_{33}.$ 

In the elastic regime,  $\sigma_{11} = \sigma_{22} < \sigma_{33}$ , and so the hydrostatic pressure and maximum shear stress are defined as  $P = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}) = \frac{(C_{11} + 2C_{12})}{3}\varepsilon_3$  and  $\tau_{\text{max}} = \frac{1}{2}(\sigma_{33} - \sigma_{11}) = \frac{(C_{11} - C_{12})}{2}\varepsilon_3$ , respectively.

The Mohr's circle can be drawn and it predicts that the maximum shear stress occurs at an angle 45° to the shock direction. The trajectory of the maximum shear is a cone.



Figure 2-14 Three dimensional Mohr's circle for uniaxial strain sate.

Following von Mises or Tresca yield conditions, the yield stress  $Y_0$  (for uniaxial stress) can be defined as,

$$Y_0 = \sigma_{33} - \sigma_{11} \tag{2.6}$$

For isotropic elastic solids, it can be shown that under uniaxial strain conditions, the stress-strain relationship before the onset of plastic flow can be derived,

$$\sigma_{33} = \left(K + \frac{4G}{3}\right)\varepsilon_{33} \tag{2.7}$$

where K and G are the bulk modulus and shear modulus of the solids, respectively. The Hugoniot elastic limit (HEL) represents the onset of the plastic deformation,

$$\sigma_{HEL} = \left(\frac{K}{2G} + \frac{2}{3}\right) Y_0 \tag{2.8}$$

If we ignore the strain hardening part of plastic deformation, the stress-strain behavior after the onset of plastic deformation is,

$$\sigma_{33} = K\varepsilon_{33} + \frac{2Y_0}{3}$$
(2.9)

In particular,  $K\varepsilon_{33}$  is the hydrostatic pressure (*P*) in uniaxial strain condition, and the maximum shear stress  $\tau_{max} = (\sigma_{33} - \sigma_{11}) / 2 = Y_0 / 2$ . Thus,

$$\sigma_{33} = P + \frac{4\tau_{max}}{3}$$
(2.10)

Therefore, it is obvious from equations (2.7) and (2.9) that the stress-strain relation before and after plastic deformation are different, this leads to the two-wave structure as the stress wave propagates through the solids, which will be elaborate in the following section.

# 2.6.2 Fundamental principles of wave dynamics

Almost all the work in the field of impact mechanics or shock physics concerns stresses wave propagation which is founded on the three fundamental conservation laws: conservation of mass, momentum, and energy.

In a physical system with *n* components, mass is conserved, i.e.

$$m = \sum_{i=1}^{n} \rho_i V_i = const \quad (\text{mass conservation})$$
(2.11)

where  $\rho_i$  is the mass density and  $V_i$  is the volume of the *i*th component of the body.

According to Newton's second law:

$$\sum_{i=1}^{n} m_i v_i = const \qquad \text{(momentum conservation)}$$
(2.12)

 $v_i$  is the velocity of the *i*th component of the system and the energy conservation states,

$$\sum_{i} E_{0,i} + \sum_{i} \frac{1}{2} \rho_{0,i} v_{0,i}^{2} = \sum_{i} E_{1,i} + \sum_{i} \frac{1}{2} \rho_{1,i} v_{1,i}^{2} + W \text{ (energy conservation)}$$
(2.13)

where 0 and 1 denote the initial and final states, E is the internal energy and W represents work done on the system. At high pressures, metals behave as fluids and Bernoulli's equation can be used, which states the change of kinetic energy of a fluid system equal the work done to it (Pressure times the change of volume),

$$P_0 + \frac{1}{2}\rho_0 v_0^2 = P_1 + \frac{1}{2}\rho_1 v_1^2$$
(2.14)

Now considering the force acting on element of a bar in longitudinal direction (x direction), the Newton's second law reads,

$$\frac{\partial \sigma}{\partial x} = \rho \frac{\partial v}{\partial t} \tag{2.15}$$

Let us define the strain,  $\varepsilon = \frac{\partial u}{\partial x}$  and particle velocity,  $v = \frac{\partial u}{\partial t}$ ; then the wave

function (plane wave front) can be written as

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial \varepsilon} \cdot \frac{\partial^2 u}{\partial x^2}$$
(2.16)

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial \sigma}{\partial \varepsilon} \cdot \frac{1}{\rho} \cdot \frac{\partial^2 u}{\partial x^2}$$
(2.17)

Obviously, the slope of the stress-strain curve,  $\sqrt{\frac{\partial \sigma}{\partial \epsilon} \cdot \frac{1}{\rho}} = c(\epsilon)$  define the

propagation velocity of the wave, for elastic wave in isotropic solid,  $\frac{\partial \sigma}{\partial \varepsilon} = E$ , the wave

function become:

$$\frac{\partial^2 u}{\partial t^2} = \frac{E}{\rho} \frac{\partial^2 u}{\partial x^2}$$
(2.18)

As previously stated, the uniaxial strain state results in two-wave structure with an elastic precursor,

$$\frac{\partial \sigma}{\partial \varepsilon} = K + \frac{4G}{3} \tag{2.19}$$

as well as a plastic tail,

$$\frac{\partial \sigma}{\partial \varepsilon} = K \tag{2.20}$$

Therefore, the elastic wave and plastic wave velocities are, respectively,

$$c_e = \sqrt{K + \frac{4G}{3}} \tag{2.21}$$

$$c_{plastic} = \sqrt{\frac{K}{\rho}}$$
(2.22)

and the solution to wave function (Eq. 2.16) reads,

$$u = f(c_0 t - x) + g(c_0 t + x)$$
(2.23)

where f and g are functions depending on the initial conditions where f corresponds to the wave propagate to the right (direction of increasing x) and g describe the wave travelling to the left (decreasing x). It should be pointed out that the above treatment is based on the assumption that the transverse sections of the solids remain plane during the passage of the stress pulses. Thus, the stress distribution is homogeneous on that plane section. However, the longitudinal contractions will necessarily lead to the lateral expansion. The ratio between lateral and longitudinal strains is given by Poisson's ratio, v, and the lateral expansion will cause the non-uniform distribution of stress and distort the plane section.

If we only consider the elastic wave travelling to the right,  $u = f(c_0 t - x)$ , then the differentiation of u with respect t and x are,

$$\frac{\partial u}{\partial x} = -f'(c_0 t - x)$$

$$\frac{\partial u}{\partial t} = c_0 f'(c_0 t - x)$$
(2.24)

Thus,

$$\frac{\partial u}{\partial x} = -c_0 \frac{\partial u}{\partial t} = \frac{\sigma}{E}$$
(2.25)

$$\sigma = -c_0 E \frac{\partial u}{\partial t} = -\rho c_0 u_p \tag{2.26}$$

Eq. 2.26 shows that the longitudinal stress is linearly proportional to the particle velocity, and  $\rho c_0$  is referred as characteristic sound impedance.

Now, imagine we send two compressive wavelets, one ahead of the other, into a perfect elastic solid medium. The wave speed is proportional to the pressure, i.e. the higher the pressure, the faster the compressive wave travels. Therefore, the second wave eventually overtakes the first wave and the waves steepen into a shock, with a velocity higher than the sound speed at this pressure, as schematically shown in the figure 2-15. In reality, however, the material is not a perfectly elastic medium, and dissipative effects have to be taken into account. In metals, the most dominant mechanisms are defect generation and propagation, which leads to viscous flow that limits the increase of the sound speed. The thermal transport also limits the temperature gradient behind the shock front. These dissipative stresses will cancel the compressive stress that eventually leads to a steady state shock.



Figure 2-15 Schematic drawing of compressive waves steepen into a shock, if stability criteria is fulfilled.

2.6.3 Rankine-Hugoniot Conservation Equations Although it cannot be derived, experimental observations indicate a linear relationship between shock velocity,  $u_s$  and particle velocity  $u_p$ ,

$$u_s = c_0 + s u_p \tag{2.27}$$

where  $c_0$  is the bulk sound speed and s is the slope of the shock Hugoniot (P-V diagram).

The conservation of mass, momentum and energy are,

$$\rho_0 u_s = \rho_1 \left( u_s - u_1 \right) \tag{2.28}$$

$$p_1 - p_0 = \rho_1 u_1 \left( u_s - u_1 \right) = \rho_0 u_s u_1 \tag{2.29}$$

$$p_1 u_1 = \rho_0 u_s \left( \frac{1}{2} u_1^2 + E_1 - E_0 \right)$$
(2.30)

Combining (28), (29), and (30) yields the Rankine-Hugoniot condition,

$$p_1 - p_0 = \frac{c_0^2 (v_0 - v_1)}{\left[v_0 - s(v_0 - v_1)\right]^2}$$
(2.31)

Plotting pressure as a function of specific volume, one can construct the so-called Hugoniot curve as referenced in the literature, a typical Hugoniot curve is given in Fig. 2-16.



Figure 2-16 (a) Typical Hugoniot curves of elastoplastic materials and materials with a phase transition; (b) relationship between shock Hugoniot, Rayleigh line and release isentrope.

It has been shown that the velocity of the shock wave is proportional to  $\sqrt{\frac{P}{V}}$ .

Therefore, the shock velocity is an increasing function of the pressure. It should be pointed out here that the Hugoniot curve is not the loading curve but rather the collection of all the possible states that a material can reach by shock compression. For a given shock, we can graphically connect the initial and final states with a chord, called the "Rayleigh line". The Rayleigh line can be treated as the loading path where the change in strain and temperature across the shock front lies on. Since the materials have dissipative mechanisms such as viscosity and heat transport, leading to a component stress adding to the equation of state, so the Rayleigh line must lie above the Hugoniot. The Hugoniot defines the state behind the shock wave in the P-V plane. Thus, the kinks or slope discontinuities are either due to elastic-to-plastic transition or phase transformation. Shock produces entropy which induce temperature rise. Upon shock release, it can be assumed to be isentropic. When the pressure goes back to ambient, the residual temperature is higher than the initial temperature, and so is the volume.

In terms of materials strength under shock, it is more useful to plot longitudinal stress against specific volume, as shown in the figure 2-17.



Figure 2-17 Plot of Pressure and Longitudinal Stress as a function of specific volume, showing the offset between the two curves. The two-wave structure with an elastic precursor followed by a plastic wave is shown in the longitudinal stress vs. volume curve.

A two-wave structure is revealed in the longitudinal stress vs. volume curve: an elastic precursor is followed by a plastic tail. The transition from elastic to plastic is indicated by Hugoniot elastic limit (HEL). Note that the speed of plastic wave will exceed that of the elastic precursor, resulting in the overdriven plastic wave (stable shock). According to Eq. 2.9., the longitudinal stress offsets pressure by two-third of the yield

stress, which forms a gap between the two curves. Such a gap shrinks as the stress increases, indicating that the materials undergo softening during shock loading. It should be mentioned that the HEL is not yield stress, but rather the elastic limit of the longitudinal stress.

#### 2.6.4 Mie-Grüneisen Equation of State

The Rankine-Hugoniot equation cannot reveal the full picture of the equation of state (EOS), which is a surface in the *P*-*V* (or  $\rho$ )-*E* space. There is many EOS in the literature, and the most widely used one is Mie-Grüneisen EOS:

$$\gamma = V \left(\frac{\partial P}{\partial E}\right)_{V} = -\frac{V}{T} \left(\frac{\partial T}{\partial V}\right)_{S} = \frac{\beta K_{s}}{C_{p}}$$
(2.32)

where  $\gamma$  is the Grüneisen parameter, *E* is the internal energy,  $V=1/\rho$  is specific volume,  $\beta$  is the coefficient of thermal expansion,  $K_s$  is the isentropic bulk modulus and  $C_p$  the specific heat at constant pressure. For metals,  $\gamma$  is empirically shown to be only a function of volume:

$$\frac{\gamma(V)}{V} = \frac{\gamma_0}{V_0} \tag{2.33}$$

Considering the conservation equations 2.28-2.30, one can obtain the following equation:

$$P = \frac{\rho C_0^2 \chi}{\left(1 - s\chi\right)^2} \left(1 - \frac{\gamma_0}{2}\chi\right) + \gamma_0 E$$
(2.34)

where  $\chi = 1 - \frac{\rho_0}{\rho} = 1 - \frac{V}{V_0}$  and the subscript 0 denotes the reference state, usually set as 0 K.

# 2.6.5 Shock-Induced Temperature Rise

In materials subjected to shock compression, the volume decrease is accompanied by a temperature rise. Assuming an adiabatic condition at the shock front, one can establish a relationship between temperature and pressure at each point on the shock Hugoniot by means of the Grüneisen EOS and thermodynamic relationships [10].

From the first and second laws of thermodynamics, one arrives at,

$$dE = TdS - PdV \tag{2.35}$$

In which,

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_{V} dT + T\left(\frac{\partial S}{\partial V}\right)_{T} dV = C_{v}dT + T\left(\frac{\partial S}{\partial V}\right)_{T} dV \qquad (2.36)$$

According to Maxwell relationships, one obtains,

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T}$$
(2.37)

Substituting (34) and (33) into (32) yields,

$$dE = C_{v}dT + T\left(\frac{\partial P}{\partial T}\right)_{V}dV - PdV$$
(2.38)

Applying the Grüneisen equation,

$$\frac{\gamma}{V} = \left(\frac{\partial P}{\partial E}\right)_{V} \tag{2.39}$$

Thus,

$$\left(\frac{\partial P}{\partial T}\right)_{V} = \left(\frac{\partial P}{\partial E}\right)_{V} \left(\frac{\partial E}{\partial T}\right)_{V} = C_{v} \frac{\gamma}{V}$$
(2.40)

Substituting (37) into (35) gives,

$$dE = C_{v}dT + T\frac{\gamma}{V}C_{v}dV - PdV \qquad (2.41)$$

Considering the energy conservation for a Hugoniot shock process, we have,

$$\Delta E = \frac{1}{2} (P_1 + P_2) (V_0 - V_1)$$
(2.42)

Therefore, the change of internal energy with volume along Hugoniot gives,

$$\left(\frac{dE}{dV}\right)_{H} = C_{v} \left(\frac{dT}{dV}\right)_{H} + T\frac{\gamma}{V}C_{V} - P$$
(2.43)

$$\left(\frac{dE}{dV}\right)_{H} = \frac{1}{2} \left(\frac{dP}{dV}\right)_{H} \left(V_{0} - V\right)$$
(2.44)

Thus, a differential equation is obtained,

$$C_{\nu} \left(\frac{dT}{dV}\right)_{H} + T \frac{\gamma}{V} C_{V} - P = \frac{1}{2} \left(\frac{dP}{dV}\right)_{H} \left(V_{0} - V\right)$$
(2.45)

The standard solution is,

$$T = T_o \exp\left[\left(\frac{\gamma_o}{V_o}\right)(V_o - V)\right] + \frac{V_o - V}{2C_v}P + \frac{\exp\left(-\frac{\gamma_o}{V_o}V\right)}{2C_v}\int_{V_o}^{V}P \exp\left[\frac{\gamma_o}{V_o}V\right]\left[2 - \frac{\gamma_o}{V_o}(V_o - V)\right]dV$$

(2.46)

# 2.6.6 Influence of Shear in Shock Compression of Solids

The importance of shear stresses in reactions and phase transitions can be significant and, in some cases, dominant [1–4]. 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. Amorphization is usually achieved by quenching liquid matter below its glassy transition temperature to hinder crystallization. For silicon, other processes such as plasma deposition [5], static pressure by diamond anvil cell [6], radiation damage [7], indentation [8], and impact by

nanodroplets [9] 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 decades [10].

The shear component of stress is significant during shock compression of covalently bonded materials. For metals, non-hydrostatic stress is relaxed by yielding, which usually occurs below 1 GPa. For covalent materials, such as Si, a higher elastic limit, between 4 and 10 GPa for high strain rates, dictates that the shear stress is rather significant prior to relaxation. Such a high shear stress, as discussed later in this dissertation, plays a crucial role in the phase transition/amorphization under shock and thus we quantify the relationship between hydrostatic and deviatoric stresses.

A shock wave creates a uniaxial strain state with corresponding stresses that have hydrostatic and deviatoric (shear) components. For purely elastic deformation of a cubic crystal in uniaxial strain condition:

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} = C_{ij33} \varepsilon_{33} \tag{2.47}$$

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

$$\frac{\tau_{\max}}{P} = \frac{3(C_{11} - C_{12})}{2(C_{11} + 2C_{12})}$$
(2.48)

In particular, for silicon,  $C_{11} = 165.7$  GPa and  $C_{12} = 63.9$  GPa [104], yielding  $\frac{\tau_{max}}{P} \approx 0.52$ , assuming zero pressure elastic constants. This value is in agreement with our molecular dynamics simulations where  $C_{ij}$  was determined as a function of pressure and the ratio of maximum shear over pressure decreases with increasing pressure to a value of

0.26 at a pressure of 20 GPa. We note that pressure generally does not produce lattice defects, whereas shear stresses are responsible for plastic deformation and generation of lattice imperfections such as dislocations, stacking faults, and twinning.

#### 2.7 Laser Driven Shock Compression

Shock physics has been an area of intensive study ever since World War II. The first experimental step, naturally, is to create a shock wave. During the past decades, various techniques, including plate impact (accelerated by gas gun or explosives) and Z-pinch have been implemented and well developed to study the shock wave propagation in different media. In the materials science community, scientists are interested in the recovered microstructure of the shocked materials. But there are some limitations embedded in the above-mentioned techniques: (1) the heat generated by shock is hard to diffuse away so that the recovered microstructure is most likely an annealed one; (2) the time scale (duration of pulse) is limited to µs and therefore any phenomenon (e.g. melting and/or phase transformation) with faster kinetics is difficult to be probed. (3) recovery of brittle solids from shock experiments are extremely tricky since these materials tend to undergo catastrophic failure (crack propagation and coalescence) which render successful recovery a challenging mission.

The past decade witnessed the emergence and rapid development of high power pulsed laser as an effective tool for materials science at extremes. Today, laser shock and/or quasi-isentropic compression experiments are used to explore the extreme pressure, strain rate, and temperature regimes inaccessible through other techniques. The significant advantage of this technique over plate impact and detonation of explosives is that the short duration of the stress pulse (ns in our experiments) ensures rapid decay as it propagates through the target, creating a self-quenching mechanism: the heat diffuses from the highpressure to the low-pressure regime, in millimeter and millisecond scale [105]. Therefore, laser-driven shock experiments are an ideal methodology for shock-recovery experiments. Especially, it is probably the only existed technique that allows successful recovery of brittle solids from strong shock experiment since the short duration (ns) of stress pulse helps to minimize crack propagation.

The way in which laser-driven shock compression experiment works is described by the schematic drawing in Fig. 2-18,



Figure 2-18 A schematic illustration of laser ablation process and stress wave generation: the laser is focused on the ablator in front of which a phase plate is placed before the focus point to smooth the laser inhomogeneity; the laser turns the ablator into plasma which causes a volume expansion that eventually lead to a blast wave. Such a blast wave will go through the rest of the target.

We describe below a typical experimental configuration used in our shock recovery

experiments. The high power pulsed laser irradiates onto a transparent ablator, usually a polymer with a very low density, ionizes it into rapidly expanding plasma that flows away

from the energy deposition surface. Based on Newton's third law, the surface experience a reaction force equal to the rate of momentum that is carried away, leading to the establishment of shock wave that propagates radially through the ablator and eventually into the target materials. Such a process is usually termed as laser ablation and involves very complicated energy and mass transport. The ablation pressure is a function of laser parameters. An analytical scaling law was originally proposed by Lindl [106] and calibrated by various laser experiments,

$$P(GPa) = (42 \pm 3) \cdot \left(\frac{I(TW/cm^2)}{\lambda(\mu m)}\right)^{0.71 \pm 0.01}$$
(2.49)

where I=E/At is the laser intensity, A, t and  $\lambda$  are the spot area, laser duration, and laser wavelength, respectively. Using modern large laser facility such as Omega and the National Ignition Facility, extraordinarily high pressures can be produced routinely: using a 3.52 TW (10<sup>12</sup>W) laser with a wavelength of 352 nm, the ablation pressure will be ~210 GPa, which is almost the pressure inside the Earth's core (~350 GPa)! It should also be mentioned here that not all of the laser energy can be absorbed; the coupling efficiency decreases as the wavelength of the laser increases. Another note is that once the laser intensity is above 10<sup>18</sup> W/cm<sup>2</sup>, the relativistic effect must be considered. Moreover, the ponderomotive pressure, which will steepen the density profile of the plasma, grows as the laser intensity increases. It equals the plasma pressure at the critical density at I=10<sup>16</sup> W/cm<sup>2</sup> and thus stops the plasma expansion [107]. In this investigation, the laser intensity was below TW/cm<sup>2</sup>, and all the effects mentioned above may be neglected. A phase plate was placed before the focus of the laser optics to smoothen out the laser non-uniformities. As one can imagine, the shock pulse does not have the temporal and spatial uniformity of pressure as plate impact experiments. Therefore, before the stress waves reach the actual target, a pulse shaper was used (with similar shock impedance) to make the stress pulse more planar (uniaxial strain). To minimize the damage caused by reflected waves, a momentum trap is also used at the rear surface of the target and inserted in an impedance matched tube.

# 2.8 Laser-driven Shockless (Ramp) Compression

Shock compression can reach an extremely high pressure, although it often melts the target at the shock front or release. To avoid melting, ramp compression with a tailored wave profile needs to be adopted to achieve dynamic compression at a relatively lower temperature. A laser-based, experimental platform has been developed to study solid-state material dynamics at ultrahigh strain rates and pressures, relevant to the regimes found in ICF but in planar geometry [108–110]. An intense laser pulse is focused onto a ~200 µmthick plastic foil, launching a several-hundred-GPa shock wave. When this shock breaks out at the back side of the foil, it unloads across vacuum gap as a plasma flow. This plasma stagnates on the far side of the gap, and it launches a ramp wave through the sample being studied. A thin (~10  $\mu$  m thick) CH<sub>2</sub> heat shield isolates the sample from the heat of the stagnating plasma. This ramped "plasma drive" allows the sample to be loaded quasiisentropically, to pressures of many hundreds of GPa. Provided that the ramp wave does not steepen into a shock, the sample temperature does not rise above  $\sim 1/3$  of the melt temperature, allowing materials to be studied at ultrahigh strain rates and pressures in the solid state. The strain rates are very high, on the order of  $10^7$  s<sup>-1</sup>, corresponding to a characteristic strain of ~10% over a characteristic time scale of ~10 ns. One approach to study material deformation dynamics at ultrahigh strain rates is to imprint the metal foil to be studied with a pre-imposed ripple. The ramped plasma drive accelerates this rippled foil, and the interface (between the stagnating plasma drive and the rippled foil) is subject to the Raleigh-Taylor instability. Alternatively, ripple can grow by Richtmyer-Meshkov instability in a slightly modified geometry.

#### **Chapter 3 Experimental Materials and Methods**

# **3.1 Materials**

In this investigation, we have studied four different covalently bonded solids, namely, silicon (Si), germanium (Ge), boron carbide (B<sub>4</sub>C), and silicon carbide (SiC). The most relevant physical properties are summarized in Table 3-1. Silicon, germanium and silicon carbide are important semiconductors and therefore the high-purity crystals can be purchased commercially. We acquired these crystals with a purity of 99.99% from UniversityWafer Inc. (001) orientation is chosen for silicon and germanium and (0001) orientation for silicon carbide. For boron carbide, the growth of monocrystalline materials is extremely difficult and not commercially available. Therefore, polycrystalline materials were used in this study, which are provided by the US Army Research Laboratory. Covalent bonds are typically strong, therefore all the four materials can be categorized as "hard materials". Ranking these materials in terms of hardness yields, B<sub>4</sub>C>SiC>Si>Ge.

Materials	Orientation	Density	$C_l$	HEL	$T_m$	Ε	G	Heat of
			km/s	GPa	K	(Isotropic)	(Isotropic)	Fusion
		kg/m <sup>3</sup>				GPa	GPa	kJ/mol
Silicon*	001	2.33	8.43	4~10	1687	130-	51-80	50.21
						188		
Germanium*	001	5.32	5.4	~4	1211	103	41	36.94
Boron* Carbide	polycrystalline	2.52	13.5	18~20	3036	430	180	71.55
Silicon Carbide [111] (4H)	0001	3.21	12	15~16	3100	347	131.4	

Table 3-1 Summarized properties of materials studied in this investigation

\*Properties adapted from Wikipedia
# 3.2 Laser-driven Shock Compression Experiments

Four laser-shock experimental campaigns have been executed successfully during this study, and they are listed in Table 3-2. The details of the experiments are given in the following sections.

Campaign Time	Materials	Laser System	Key Parameters	Peak Power	Diagnostics
Winter 2014	Silicon	Omega	1 ns duration 3 mm spot size	5.66 TW/cm <sup>2</sup>	Ride-along recovery
Summer 2015	Boron carbide/Silicon carbide	Janus	3 ns duration 1 mm <sup>2</sup> spot size	3.33 TW/cm <sup>2</sup>	VISAR; Recovery; Preheating
Fall 2016	Germanium	Omega	1 ns duration 3 mm spot size	2.83 TW/cm <sup>2</sup>	Ride-along recovery; VISAR
Spring 2017	Olivine/GaAs /High entropy alloy	Omega	1 ns duration 3 mm spot size	7.07 TW/cm <sup>2</sup>	Dedicated recovery plus VISAR

Laser compression experiments were carried out at two laser facilities: (1) Omega Laser Facility, Laboratory of Laser Energetics, University of Rochester; and (2) Jupiter Laser Facility, Lawrence Livermore National Laboratory.

## 3.2.1 The Omega Laser

Omega Laser is one of the most powerful laser sources in the earth. A schematic drawing of the laser facility is shown in Fig. 3-1 (a) and the corresponding target assembly is given in Figure. 3-1 (c).



Figure 3-1 Schematic drawing of the Omega laser facility (a), picture of target chamber (b), schematics of the experimental set-up (c), the target package (d), and a photograph of the assembled recovery tube.

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. To maximize the exposure area and achieve a planar shock, the laser beam was defocused to 3 mm. The target was assembled in a vacuum chamber and was pumped down to a pressure of 10<sup>-3</sup> Pa during working conditions to prevent oxidation of the target and absorption/scattering of the laser.

The target design of the four experimental campaigns are very similar. Taking the Winter 2014 campaign as an example, Silicon [001] single crystal 3mm x 3mm cylinders, were encapsulated in aluminum cups to protect the target from shattering. The close acoustic impedance of aluminum (17.33 MPa s/m) to silicon (19.7 MPa 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. In the case of other materials, equivalent designs were implemented.

The pulsed laser is deposited onto the surface of the 20  $\mu$ m thick polystyrene (CH) ablator turning the polymer into plasma. The rapidly expanding plasma subsequently launches a planar shock wave into the 100  $\mu$ m thick aluminum "piston". The compression wave decays as it traverses the aluminum, upon arriving at the silicon or germanium target surface. It is both transmitted and reflected in accordance with impedances of the target materials. The stress pulse profiles were simulated using HYADES, a 1-D hydrodynamic code.

#### 3.2.2 The Janus Laser

Omega laser is a very stable laser source and the pulse shape is well calibrated. However, it is very difficult to customize the experimental set-up and the proposals to use it are extremely competitive. On the other hand, Janus laser is a user facility, with a flexible target chamber adaptive to various diagnostics. The laser shock experiments on  $B_4C$  and SiC were performed here in the Summer 2015 campaign. The schematic and real experimental set-up was shown in Fig. 3-2.



Figure 3-2 Photograph of the Janus target chamber (a) showing the target mount in the center; the same target mount also has the heating capacity which can heat the target up to 550°C; the schematic drawing of the optics showing the direction of the drive laser and VISAR laser; An fringe recorded by streak camera is shown in (d), the free surface velocity profile can be seen in (d).

### 3.2.3 VISAR Experiments and Analysis

Thermodynamic variables such as pressure and volume are not straightforward to measure in a shock experiment. Instead, one usually measures the velocity of the shocked target and then deduces the shock pressure indirectly. Line-imaging VISAR (velocity interferometer system for any reflector) is a useful diagnostic to measure the shock wave velocity, particle velocity and free surface velocity of the shocked materials, depending on the design of the targets.

Here is an example of a dedicated VISAR (velocity interferometer system for any reflector) shot conducted at Omega laser to calibrate the laser intensity deposited on the target. The experimental set-up was mounted in a vacuum chamber pumped down to a pressure of ~10<sup>-3</sup> Pa to prevent laser absorption. A 3.7 ns pulse of 3 $\Omega$  light (351 nm) at

1.08 TW/cm<sup>2</sup> was used to directly drive a shock into a 6 um CH ablator and a 5 um tantalum witness sample. A line imaging VISAR instrument detects the Doppler shifts of the probe light reflected off the moving portions of the target. The light was imaged through a Mach-Zehnder interferometer onto the slit of an optical streak camera, producing a series of fringes streaked in time. The fringe position, which is proportional to the velocity of the reflecting surface, was measured using Fourier analysis of the streak record. Through an MgO window, VISAR measured an interface velocity of 1.8 + 0.1 km/s, which corresponds to a shock of 110 GPa in the Ta and 42 GPa in the CH by impedance matching. This was confirmed by the excellent agreement between the velocities derived from two independent VISAR channels using etalons with different lengths. Hyades simulations were matched to the VISAR data by setting the fraction of laser energy used in the simulation to 77%. This multiplier was then applied to the simulations of the silicon recovery shots with nominal intensities 0.3-2.0 TW/cm<sup>2</sup>. Holding the laser wavelength constant, the ablation pressure is determined mainly by the laser intensity and is independent of ablator material (for low Z materials) to a first approximation. This is evident in the scaling law measured for diamond ablators on Omega,

$$P(GPa) = (42\pm3) \cdot \left(\frac{I(TW/cm^2)}{\lambda(\mu m)}\right)^{0.71\pm0.01}$$
(3.1)

which gives an ablation pressure,  $44 \pm 3$  GPa, that matches the measured pressure in the CH ablator for our VISAR experiment. This scaling law is then applied to determine the ablation pressure in simulated silicon recovery experiments. HYADES then performs a 1D calculation of the ensuing hydrodynamics of the shock wave propagating through the aluminum piston into the silicon to generate the pressure plots shown in the main text. The

1D approximation is likely valid due to the aspect ratio of the sample and rapid decay of the shock waves limiting their interaction with the aluminum capsule. Based on uncertainties in the driven intensity, ablation pressure scaling, and variations across different shot days, we estimate that the uncertainty in the shock pressure in the silicon is  $\pm 13\%$ .

It should be mentioned that the laser energy is not homogeneously distributed across the entire laser spot, leading to a heterogeneous shock pressure distribution on the target surface. The pressure is higher in the center and decays significantly towards the edge. At Janus laser facility, a similar VISAR system is used.

#### **3.3 Microstructure 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. Atomic Force Microscopy (AFM) was used to map the shocked surface profilometry, especially the surface step caused by shock-induced fracture.

### 3.3.1 Raman Spectra

Raman spectroscopy is considered to be a powerful tool to indicate vibrational, rotational, and other low-frequency modes in materials [112]. 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  $0.3 \text{ kW/cm}^2$ , 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  $\mu$ m.

## 3.3.2 TEM/HRTEM Sample Preparation and Observation



Figure 3-3 TEM sample acquisition methodology and micrographs showing silicon subjected to shock below the threshold for amorphization: (a) secondary electron image of the 50 J laser-shocked Si target prior to FIB thinning of the TEM foil; a carbon film was deposited on the area of interest to protect the sample; (b) schematic of the TEM sample crystallography: the foil is normal to [110] direction and parallel to [1-10] orientation. (c) normal view of the as-FIBed sample under SEM; (d) unshocked reference sample observed by TEM and (e) the sample subjected to weakest laser shock compression (20 J). No defects were identified in either (d) or (e); The "c" marks in (d) and (e) denote carbon films deposited on top of the TEM foil.

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, germanium, and silicon carbide 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, as shown in Fig. 3-3. These cracks, orientated in [110] and  $[1\overline{10}]$  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 are always within ~2° to the  $\{110\}$  zone, indicating that the foil normal is <110>.

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## Chapter 4 Laser Shock Compression of Silicon

#### 4.1 Background and Justification

Silicon is the most studied covalently-bonded element. Covalent bonding results in a high Peierls-Nabarro stress, a direct consequence of the directionality of bonds. Thus, the generation of defects, such as dislocations, stacking faults, and twins is much more difficult. Combined with this, the open structure of Si (diamond cubic) is prone to collapse during melting, leading to an increase density. These two effects motivated the objective set upon this work to shock and then recover silicon to investigate the mechanisms of inelastic deformation. A corollary was to establish the velocity of dislocations in shock compression.

### **4.2 Shock-Induced Amorphization in Silicon**

#### 4.2.1 Raman Spectra

Post-shock Raman spectroscopy was carried out to identify the amorphous silicon at a macroscopic scale. Fig. 4-1 illustrates Raman spectra as a function of laser energy. Beyond a laser energy threshold of 50.4 J (shock pressure threshold of 11.2 GPa), characteristics of amorphous silicon are observed. Both unshocked and 20 J shocked silicon targets show a sharp Raman peak at 520 cm<sup>-1</sup> owing to the transverse optical (TO) phonon band, a characteristic of diamond cubic silicon. 50.4 J shocked targets shows an extra broad peak at 460-480 cm<sup>-1</sup> that is attributed to the amorphous silicon (TO mode [113]) whereas the crystalline 520 cm<sup>-1</sup> peak still exists due to the small thickness of amorphous layer.



Figure 4-1 Raman spectra of the laser shock-recovered silicon targets.

When laser energy increases to 106.8 J, the 520 cm<sup>-1</sup> peak vanishes and the 480 cm<sup>-1</sup> amorphous peak dominates due to the increasing thickness of the amorphous layer (~2  $\mu$ m, see TEM image Fig. 4-2 (a)) exceeding the penetration depth of the illumination laser. The spectrum of the 150 J shocked target shows a single 520 cm<sup>-1</sup> shift due to the full crystallization at the top surface. It is also noted that the 520 cm<sup>-1</sup> Raman peak for the 150 J shocked sample is broadened and shows an asymmetrical configuration compared with the 18.2 J shocked and unshocked sample. This is due to the presence of ultrafine grained/nanocrystalline materials [114] as presented later in Figure 4-20.

### 4.2.2 TEM/HRTEM Observation

In order to probe the microstructure of the shocked silicon, both conventional and high resolution TEM observations were carried out. They show that the crystal-toamorphous transformation proceeds via a clear sequence of events. The recovered samples show several morphological configurations:

- (a) Bulk transformation regions close to surface.
- (b) Transformed bands that decrease in thickness with distance from the surface.
- (c) Small 'feathering' features originating at the bands.
- (d) Transformed regions at intersections of bands.

These different morphologies are shown in Fig. 4-2 and marked A,B,C,D, and E respectively.



Figure 4-2 TEM images of the complex amorphous pattern: (a) broad region of the amorphous material on the top surface, marked by A, below which multiple amorphous bands penetrate into the crystal; (b) pattern of the amorphous bands (B) decreasing in thickness with depth; (c) termination (D), bifurcations and feathering, marked by C, usually observed along with the primary bands and different variants of the bands eventually intersect; (d) the intersection leads to the formation of a jog/kink feature and is indicated by E.

Profuse stacking faults (SFs) and nanotwins are usually found in the vicinity of the amorphous bands, as imaged by HRTEM. These planar defects occur preferentially on {111} planes. Fig 4-3 (a) shows such features with the apparent zigzag displacement highlighted in Fig. 4-3 (b). The thickness of each planar defect varied from 0.6 to 1 nm,

corresponding to 2~3 atomic planes. Figs. 4-3 (c) and (d) show that SFs often intersect to create localized regions of high strain energy. Although these faults occur on {111}, {112} is also a favored twinning plane in silicon [115]. These faults act as precursors and favored nucleation sites for amorphization.



Figure 4-3. High resolution TEM micrographs showing the onset of amorphous bands: (a) a single amorphous band proceeded by one set of stacking faults; (b) inverse FFT image of the boxed region in (a), showing clearly the zigzag feature of multiple SFs, twins and dislocation; (c) nucleation of the amorphization at the SFs intersections; (d) inverse FFT image of the boxed region in (c) shows that the intersected region become less order.

The formation of 'feathers' emanating from bands is best explained by Figure 4-4, which shows a [001] stereographic projection. The maximum shear stress cone is marked by a red dashed circle. The maximum shear stress occurs at an angle of  $45^{\circ}$  to the shock wave propagation direction. The {111} slip planes are also marked in the stereographic

projection (green spots) and only coincide with the maximum shear cone at the orientations [011], [101],  $[0\bar{1}1]$  and  $[\bar{1}01]$ . For other orientations, and specifically for the one from which the current samples were extracted (plane normal = [110]) the angle of (111) with (001) is 54°. For this orientation, the (112) plane (blue spots) makes an angle of 35.3° with the shock propagation direction ([001]). The maximum shear cone straddles these two planes, each 9° away from the maximum in opposite directions. Thus, the resolved shear stresses on the (112) and (111) planes are identical.



Figure 4-4 (a) (001) Stereographic projection with maximum shear cone indicated by red dashed circle. (b) Detail of stereographic projection. TEM samples always show a foil normal of {110} and the corresponding slip and twinning planes are marked by green ({111} planes) and blue ({112}), respectively.

The results indicate that although amorphization can initially take place along {111}, further propagation and growth almost always deviates a few degrees from {111} towards the cone of maximum shear, as evidenced in Fig. 4-5.



Figure 4-5 High resolution TEM image of an amorphous band initiated along  $\{111\}$  slip planes  $(35.3^{0} \text{ with shock direction})$  and spreading towards the direction of the maximum shear  $(45^{0} \text{ with shock direction})$ . Adjoining stacking faults marked SF.

### 4.2.3 Solid State Amorphization Mechanisms

#### 4.2.3.1 Microstructural Considerations

The onset of amorphization is strongly affected by shear stresses and deformation.

All evidence indicates that the transformation is preceded by twins/stacking faults; these defects advance with the shock wave and promote amorphization.

Figure 4-6 shows in schematic fashion how these defects can give rise to amorphized regions that can reorient themselves to seek other directions where their propagation is favored. A set of (1-11) SFs is generated under an applied stress and penetrates into the sample. These stacking faults serve as the nucleation sites for amorphization, as shown in Fig. 4-6 (b). Once the amorphous nucleus is formed, its growth tends to deviate towards the orientation of the maximum shear (Fig. 4-6 (c)). Furthermore, bifurcation of the primary bands into  $(1 \overline{12})$  is shown in Fig. 4-6 (d).



Figure 4-6 Schematic illustration of amorphous band nucleation inside set of stacking faults and growth along maximum shear and  $(\overline{112})$ .

There is also evidence, shown in Fig. 4-2 (c), of nucleation of amorphized regions at intersections of twin/stacking faults. Stacking-fault intersections are regions of higher energy because of the additive nature of elastic strain. Indeed, Lagneborg [116] observed the nucleation of martensite at twin-twin and  $\varepsilon$ - $\varepsilon$  intersections. A similar mechanism is proposed in Figure 4-7, which shows two intersecting groups of stacking-faults/twins giving rise to the initiation of amorphization.



Figure 4-7 Schematic illustration of the amorphous phase nucleated from stacking-fault intersections.

### 4.2.3.2 Thermodynamic Considerations

Assuming that amorphous Si is energetically equivalent to liquid Si, i.e. that their Gibbs free energy curves are identical, amorphization can be treated as melting at lower temperatures as a first approximation.

(*i*) *Amorphization Energetics* Fig. 4-8 (a) shows the Gibbs free energies (energy per unit volume) of amorphous silicon (a-Si) and crystalline silicon (c-Si) as function of temperature in the absence of applied stress [117]. The intersection gives the melting temperature where the Gibbs free energy of a-Si equals that of c-Si. At lower temperatures, c-Si is energetically more favorable and the transformation of c-Si into a-Si will lead to an energy increase, which serves as the energy barrier ( $\Delta G_{c-a}$ ) of the c-a transformation. Assuming the difference between Gibbs free energy curves to be linear,  $\Delta G_{c-a}$  can be expressed by:

$$\Delta G_{c-a}(T) = \Delta G_{c-a}(300 \text{ K}) \left(1 - \frac{T}{T_m}\right)$$
(4.1)

The green solid line in Fig. 4-8 (b) shows  $\Delta G_{c-a}$  as function of temperature (without the application of pressure and/or shear); At 300, K the value of  $\Delta G_{c-a} \approx 41 kJ / mol$ . The

high energy barrier prevents the c-a transformation at lower temperatures. However, this may be overcome by the assistance of external work. It has been shown that stress plays a very important role in solid state phase transformations [118–120]. Patel and Cohen [121] were the first to study the influence different stress states on the martensitic transformation under quasi-static loading and to propose a rationalization. Using the same formalism, Thadhani and Meyers [122] were able to evaluate the martensitic transformation under tensile pulses propitiated by reflected shock waves. This framework is applied here. This is a simplified version of the more general treatment by Eshleby which involves characteristic transformation strains (eigenstrain) and a special methodology.

Analogous to the Patel and Cohen rationalization, the work (*W*) done on the transformation due to the action of applied stress can be separated into two contributions: (1) a hydrostatic pressure term taken as the product of the hydrostatic stress and volumetric strain of the transformed region ( $P\epsilon_v$ ), and (2) a shear energy term taken as the product of the deviatoric shear stress and shear strain producing ( $\tau\gamma$ ). Thus, the total work per unit volume is the sum of the two contributions,

$$W = P\varepsilon_v + \tau\gamma . \tag{4.2}$$

Under shock compression, the high amplitude of pressure and shear stress are coupled and applied simultaneously. The effect of shock compression is shown in Fig. 4-8 (b); the energy barrier shifts downwards due to the contribution of pressure and shear. A general relationship can be expressed as,

$$\Delta G_{c-a}(T; P, \tau = 0) = P\varepsilon_{v} + \tau\gamma + \Delta G_{c-a}(T; P, \tau).$$
(4.3)

If  $P\epsilon_v + \tau\gamma$  is sufficiently high to exceed  $\Delta G_{c-a}(T; P, \tau = 0)$ ,  $\Delta G_{c-a}(T; P, \tau)$  can become zero or even negative, implying that the c-a transformation will occur spontaneously.

The longitudinal shock stress,  $P_{zz}$ , hydrostatic pressure, P, and maximum shear stress,  $\tau_{max}$  are related by[123],

$$P_{zz} = P + \frac{4}{3}\tau_{max}$$
 (4.4)

In elastic compression, the ratio of  $\tau_{max}$  over P , for cubic materials loaded along [001] direction, is given as function of the elastic constants:

$$\frac{\tau_{\max}}{P} = \frac{3(C_{11} - C_{12})}{2(C_{11} + 2C_{12})}$$
(4.5)

 $C_{11}$  and  $C_{12}$  are pressure dependent stiffness, resulting in a pressure dependent relationship between shear stress and hydrostatic pressure.

Transformation of c-Si to high density a-Si at elevated pressures leads to a volume shrinkage  $\Delta V \equiv 0.91 \text{ cm}^3/\text{mole}$ , rendering  $\varepsilon_v = \frac{\Delta V}{V} = 0.075$  [23]. TEM observation shows that amorphization tends to occur in regions of massive stacking faults/nanotwins. Hence,  $\gamma$  can be estimated, as a first approximation, by the characteristic strain of 0.707 for cubic crystals. Thus, *W*, calculated by Eq. 4.2, increases monotonically with shock pressure. The compressive nature of shock loading favors such a c-a transformation by reducing the energy barrier,  $\Delta G_{c-a}$ , as shown in Fig. 4-9 (b), where the solid-dotted lines denote a reduced  $\Delta G_{c-a}$  for three different laser energies corresponding to different shock pressures. The intersections of the solid-dotted lines with the temperature axis indicate c-a transformation temperatures at which  $\Delta G_{c-a} = 0$ . Fig. 4-9 (c) shows the effect of shock pressure on the c-a transformation temperature.

It should be noted that the temperature rise associated with shock can be calculated analytically by Eq. 4.6 [123],

$$T = T_{o} exp\left[\left(\frac{\gamma_{o}}{V_{o}}\right)(V_{o} - V)\right] + \frac{V_{o} - V}{2C_{v}}P + \frac{exp\left(-\frac{\gamma_{o}}{V_{o}}V\right)}{2C_{v}}\int_{V_{o}}^{v}P exp\left[\frac{\gamma_{o}}{V_{o}}V\right]\left[2 - \frac{\gamma_{o}}{V_{o}}(V_{o} - V)\right]dV$$

$$(4.6)$$

 $\gamma_0$  is the Grüneisen parameter and  $C_v$  is the heat capacity. The shock-induced temperature (shock temperature) rise was calculated [124] and is plotted in Fig. 4-9 (c) along with the c-a transformation temperature. The temperature rise at shock front will further facilitate the c-a transformation.

(*ii*) *Nucleation* The nucleation of amorphous phase occurs preferentially in connection with the stacking faulted regions. Note that nucleation of a-Si introduces extra interfaces which lead to energy increase, whereas this event also consumes the stacking faults, resulting in an energy decrease. Assuming an ellipsoidal nucleus with radius *r* and semi-thickness *c*, the aspect ratio  $f = \frac{c}{r}$  defines the shape of the nucleated embryo. Hence,

the net Gibbs free energy gain of amorphization is:

$$\Delta G = \frac{4\pi r^2 c}{3} \cdot G_{c-a} + 4\pi r c \gamma_{ac} - \frac{4\pi r^2 c}{3} \gamma_{SF} \rho_{SF} - \frac{4\pi r^2 c}{3} \cdot \frac{1}{2} \rho_d G_{\{111\}} b_p^2 \qquad (4.7)$$

where  $\gamma_{ac}$  is the interfacial energy,  $\gamma_{SF}$ ,  $\rho_{SF}$ ,  $\rho_{d}$  denote stacking-fault energy, partial dislocation density, and dislocation density, respectively.  $\mathbf{b}_{p}$  is the Burgers vector of the

partial dislocations.  $G_{\{111\}}$  is the shear modulus of the materials on  $\{111\}$  slip plane.  $\frac{1}{2}\rho_d G_{\{111\}} b_p^2$  is approximately the stored elastic energy of dislocations per unit volume. TEM observations, as evidenced in Fig. 4-2,3, suggest that the amorphous structure tends to exhibit a more disc-like than spherical shape, i.e. *f*<<1. It should be mentioned that one stacking fault corresponds to two partial dislocations, rendering,

$$\rho_{\rm d} = \frac{2\rho_{\rm SF}}{l_{\rm SF}} \tag{4.8}$$

Where  $l_{SF}$  is the width of stacking faults, i.e. the distance that a perfect dislocation dissociates. Substituting Eq. 4.8 into Eq. 4.7;

$$\Delta G = \frac{4\pi r^{3}}{3} \cdot f \cdot \left( \Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_{p}^{2} \right) + 4\pi r^{2} \gamma_{ac} \cdot f$$
(4.9)

The  $\Delta G$  vs. r curve has three different configurations, depending on the sign of

$$\Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_p^{2}:$$

(1) If  $\Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_p^2 > 0$ ,  $\Delta G$  is positive and increases monotonically

with r. The Gibbs free energy continues to increase once the amorphous nucleus is formed. Therefore, the solid state amorphization will not happen.

(2) If 
$$\Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_p^2 = 0$$
, the  $r^3$  term on the right-hand side vanishes

and the energy increase of the system is associated with the introduction of the new c-a interfaces. Therefore, the solid state amorphization is unfavorable.

(3) If 
$$\Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_p^2 < 0$$
,  $\Delta G$  vs. r curve becomes convex with the

maximum value at a critical radius. Therefore, once the amorphous nucleus exceeds the critical value, amorphization will take place spontaneously.

Considering f to be constant, classical nucleation theory [125] gives the critical

nucleus size and energy barrier for the condition  $\frac{\partial \Delta G}{\partial r} = 0$ ,

$$\mathbf{r}_{c} = -\frac{2\gamma_{ac}}{\Delta G_{c-a} - \gamma_{SF}\rho_{SF} - \frac{\rho_{SF}}{l_{SF}}Gb_{p}^{2}}$$
(4.10)

and 
$$\Delta G_{c} = f \cdot \frac{16\pi \gamma_{ac}^{3}}{3\left(\Delta G_{c-a} - \gamma_{SF}\rho_{SF} - \frac{\rho_{SF}}{l_{SF}}Gb_{p}^{2}\right)^{2}}$$
 (4.11)

 $\Delta G_{c-a} - \gamma_{SF} \rho_{SF} - \frac{\rho_{SF}}{l_{SF}} G_{\{111\}} b_p^2 = 0$  gives a critical value of the stacking fault density:

$$\rho_{\rm SF} = \frac{\Delta G_{\rm c-a}}{\gamma_{\rm SF} + \frac{G_{\{111\}}b^2}{l_{\rm SF}}}$$
(4.12)

Assuming a linear isotropic elastic medium,  $l_{SF}$  can be estimated by[126]

$$l_{\rm SF} = \frac{G_{[111]} b_p^2}{8\pi\gamma_{\rm SF}} \cdot \frac{2-\nu}{1-\nu} \cdot (1 - \frac{2\nu \cdot \cos 2\Theta}{2-\nu})$$
(4.13)

Where  $\upsilon$  is the Poisson ratio and  $\Theta$  is the angle between Burgers vector and line element of the perfect dislocation. For cubic crystals[127,128],

$$G_{\{111\}} = \frac{3C_{44}(C_{11} - C_{12})}{4C_{44} + C_{11} + C_{12}}$$
(4.14)

For silicon,  $\Theta$  is 60°.  $\upsilon = 0.215 [129]$ ,  $\gamma_{SF} \approx 55 mJ / m^2 [130]$ , and  $G_{\{111\}} \approx 44.3 GPa$ [104] and  $\gamma_{ac} \approx \gamma_{cl} = 0.416J / m^2 [131]$ . At 300 K,  $\Delta G_{c-a} = 41kJ / mol [117]$ , renders a critical stacking fault density of  $\rho_{SF} = 5.7 \times 10^9 m^{-1}$  which corresponds to a critical dislocation density of  $\rho_d |_{P_{ZZ=0}} = 2.84 \times 10^{18} m^{-2} = 2.84 \times 10^{14} cm^{-2}$ . Thus, an extremely high density of stacking faults/dislocations is required to compensate for the energy gain of c-a transformation at room temperature, making the c-a transformation impossible.



Figure 4-8 (a) Gibbs free energy of a-Si and c-Si as function of T from [117], the values of a-Si is assumed to be identical with liquid silicon; the difference between a-Si and c-Si is denoted as  $\Delta G_{c-a}$ , the energy barrier for the c-a transformation. (b) The influence of pressure and shear on the energy barrier. (c) Calculated c-a transformation temperature and shock temperature as function of shock pressure.

Under shock compression, as shown in Fig. 4-8,  $\Delta G_{c-a}$  decreases as pressure and shear stress increases. Additionally, the temperature rise at the shock front further decreases the energy barrier. Correspondingly, the required dislocation density to trigger c-a transformation is also reduced. For instance, at a shock pressure of 11 GPa ( $E_{laser}=50.4$ J),  $\Delta G_{c-a} \approx 5kJ / mol$  at room temperature (as shown in Fig. 4-8 (b)), and Eq. 4.15 gives the required  $\rho_d|_{P_{ZZ=11GPa}} \approx 3.5 \times 10^{13} cm^{-2}$ , which is on the same order of magnitude of the defect density as measured from HRTEM. This explains why amorphization usually initiates either along stacking faults packets or along their intersections, as proposed in the previous section.



Figure 4-9 Influence of defect density (in cm<sup>-2</sup>) on the Gibbs free energy for amorphization nucleation at a constant pressure ( $P_{shock}$ ~11 GPa,  $\Delta G_{c-a}$ ~5 kJ/mol at room temperature).

Figure 4-9 illustrates the effect of defect (partial dislocation) density on the nucleation energy of an amorphous embryo under shock compression. The aspect ratio of

the amorphous nuclei is assumed to be constant and f = 0.01 is taken as a first approximation. Below the critical dislocation density of  $3.5 \times 10^{13} cm^{-2}$  (dark green), nucleation of amorphous structure will always result in an energy increase. Beyond this critical condition, further increase of dislocation density enables amorphization.

Under strong shock compression,  $\Delta G_{c-a}$  may become negative at a sufficient pressure. This is the case of 106.8 J; no lattice defects are required for amorphization to occur. This is supported by a bulk layer of amorphous structure without lattice defects at c-a interfaces. However, as the shock wave propagates through the material, it is rapidly attenuated and therefore  $\Delta G_{c-a}$  increases. Thus, a transition of bulk amorphization to directional amorphization can be expected. In the latter case, shock-induced defect generation plays a crucial role.

The dislocation density at the shock front can be calculated from a homogeneous nucleation mechanism [132],

$$\rho_{d} = \frac{2\pi^{2}}{0.8(1-\nu)k^{3}b_{0}^{2}} \left(\frac{V}{V_{0}}\right)^{-\frac{2}{3}} \left[1 - \left(\frac{V}{V_{0}}\right)^{\frac{1}{3}}\right]^{3}$$
(4.15)

in which k is the orientation factor,  $b_0$  is the Burgers vector V is the compressed specific volume and  $V_0$  is the specific volume in the relaxed state. The specific volume can be related to shock pressure by Rankine-Hugoniot relationship [123],

$$P_{zz} = \frac{C_0^2 \left(1 - \frac{V}{V_0}\right)}{V_0 \left[1 - S \left(1 - \frac{V}{V_0}\right)\right]^2}$$
(4.16)

where *s* and *c*<sub>0</sub> are experimentally-determined parameters characteristic of materials  $(u_s=c_0+su_p)$  and defined in section 2.6.3. Therefore, the shock-induced dislocation density can be expressed as function of shock pressure, as shown in Figure 4-10. It can be inferred that  $\rho_d \approx 1 \times 10^{12} \text{ cm}^{-2}$  when  $P_{zz} = 11GPa (E_{laser}=50.4 \text{ J})$ , which matches reasonably well the previously calculated critical dislocation density of  $\rho_d|_{Pzz=11GPa} \approx 3.5 \times 10^{13} \text{ cm}^{-2}$  for amorphization to be initiated at this shock energy level. We note that Eq. 4-15 gives the "global" dislocation density produced by the shock, and that MD simulated dislocation densities in the localized plastic regions are much higher and extremely close to the critical value estimated above for amorphization.



Figure 4-10 Calculated dislocation density ( $\rho_d$ ) as a function of pressure P assuming homogeneous nucleation of loops behind front [56]. Hugoniot relationship of the modified Tersoff potential used to obtain pressure vs. volume. Experimental laser experiments marked on plot by their energy levels. The shaded cyan area represents the range of the predicted Hugoniot elastic limit (HEL). The dotted lines denote the shock pressure threshold (and corresponding dislocation density at shock front) where amorphization is observed experimentally.

It should be noted that shock-induced defects also affect the activation energy ( $\Delta$ Gc) to form a critical nuclei size, i.e. the higher the defect density, the lower the  $\Delta$ Gc, as shown in Figure 4-10. Under medium to high shock compression, the high defect density and associated heat might enable thermally activated barrier-less nucleation, as proposed by Levitas [133,134]. The formed amorphous silicon is most likely of high density (liquid-like), which is the carrier of plasticity of amorphous silicon, according to Demkowicz and Argon [135].

## 4.2.4 Melting and Quenching Induced Amorphization

The massive faulting activity caused the formation of amorphous bands seems to favor a solid-state process. However, we cannot deny the possibility of melting-andquenching mechanism since quenching a liquid matter below its glass forming temperature is the most widely used technique to fabricate amorphous solids. Besides, considering the melting temperature of silicon decreases monotonically with pressure, melting should be more readily under high pressure. Moreover, a thick amorphous layer (~2  $\mu$ m) appears in the O-100 J shocked sample which covered the entire shock surface as suggested by Raman spectroscopy at different regions on the as-shocked target, indicating "melting" might occur. We will explain this possibility below.

Silicon can be categorized into a group of materials whose melting temperature decreases with increasing pressure[23,136,137]. Thus, melting of silicon would occur at a temperature much lower than the ambient melting point when it is subjected to high pressure (regardless of the phase transitions). This can be described by the Clausius-Clapeyron equation:

$$\frac{dP}{dT_m} = \frac{\Delta H}{T_m \Delta v} \tag{4.17}$$

where  $\Delta H$  is the melting enthalpy of silicon and  $\Delta v$  is the specific volume difference between liquid and diamond cubic silicon. Assuming that  $\Delta H = 40kJ / mol$  [23] and  $\Delta v = -1.12cm^3 / mol$  [138]is independent of pressure and temperature, one can get the integrated Clausius-Clapeyron equation,

$$P_{1} - P_{0} = \frac{\Delta H}{\Delta v} \left( ln T_{m} - ln T_{m0} \right)$$
(4.18)

*P* and  $T_m$  are the pressure and melting temperature while 0 and 1 denote initial and pressurized states, respectively. If  $P_1 >> P_0$  which is the case for laser shock compression, one will have

$$P = \frac{\Delta H}{\Delta v} \cdot ln \frac{T_m}{T_{m0}}$$
(4.19)

We can therefore estimate the pressure required to melt silicon at room temperature (300K), giving a value of P=62 GPa, which is much larger than the peak pressure (P=9.8 GPa) of the laser shock experiment on which the amorphizaition in silicon is observed. One possible explanation of this huge discrepancy is that the melting enthalpy and volume are all dependent on pressure and temperature. In fact, the actual phase boundary between diamond cubic phase and liquid phase is a concave one, as seen in Fig. 3 of ref. 14. The extrapolation of the phase boundary to the room temperature gives a critical pressure of  $P\sim14$  GPa. This value is much closer yet still higher than the experimental value. Moreover, the threshold for the shock-induced amorphization of silicon should be smaller

than 9.8 GPa since the amorphous layer has already formed at this laser energy level. Therefore, other factors must be playing a role to lower the threshold of the amorphization.

As stated before, quenching a liquid below its melting temperature, thus hindering crystal nucleation, is the most commonly used method to fabricate an amorphous solid. For silicon, on one hand, the melting temperature decreases as the pressure increases. On the other hand, the non-equilibrium nature of shock loading leads to massive heat generation in the deformed region. When the shock-induced temperature rise exceeds the melting temperature (at that pressure), silicon will be melted. This brings another question: what is the critical cooling rate above which crystallization can be prevented?

A critical cooling rate,  $\kappa$ , and a glassy temperature,  $T_g$  should be defined for the quenching induced glassy transition. The difficulty to validate this mechanism, however, is during the shock loading and release, the pressure is rapidly changing and consequently the melting temperature is not constant through the loading/unloading path. Therefore,  $T_g$  is poorly defined under shock condition and is a variable of pressure. Hence, we will only estimate the cooling rate. Normally, the average cooling rate  $\bar{\kappa}$  is defined by the supercooling  $\Delta T = T_{m0} - T$  divided by the cooling time  $\Delta t$ . During laser shock compression of silicon, the actual temperature on the materials in the time window between peak pressure and pressure back to ambient can be treated as a constant value ( $T_c$ ). On the other hand, melting initiated when  $T_c \geq T_m$  ( $T_c > T_m$  will cause a superheating condition), whereas the melting temperature rises rapidly as the pressure decays. If we consider the actual melting ceased when  $T_m = T_c$ , then the pseudo supercooling can be expressed as  $\Delta T = T_{m0} - T_c$ . Plotting the pressure profile (100 J-shocked sample) together with the P-T

phase diagram adapted from Deb *et al* [23], one can read the cooling time from the plot, as shown in Fig.4-11a. Therefore, the average cooling rate can be estimated,  $\bar{\kappa} = \frac{\Delta T}{\Delta t} \approx 2.5 \times 10^{10} K s^{-1}$ , which is close to the previous experimental report [139] of the critical cooling rate to amorphize silicon (>10<sup>10</sup>Ks<sup>-1</sup>), but is two orders of magnitude slower than the reports from MD [140] and ab-initio simulation [141].

It should be emphasized that the cooling rate changes drastically during the shock release. In fact, it can be related to the decay rate of the shock pressure. Recall the integrated

Clapeyron equation,  $P = \frac{\Delta H}{\Delta v} \left( \ln \frac{T_m}{T_{m0}} \right)$ , one has,

$$T_m = T_{m0} \cdot \exp\left(\frac{\Delta v}{\Delta H} \cdot P(t)\right)$$
(4.20)

And taking the first derivative of both nominator and denominator of the original Clapeyron equation gives,

$$\frac{dP(t)/dt}{dT_{\rm w}(t)/dt} = \frac{\Delta H}{T_{\rm w}\Delta v}$$
(4.21)

Substitute this Eq. 4.20 into Eq. 4.21 renders,

$$\kappa(t) = \frac{dT_m(t)}{dt} = \frac{T_{m0} \cdot \Delta v}{\Delta H} \cdot \exp(\frac{\Delta v}{\Delta H} \cdot P(t)) \cdot \frac{dP(t)}{dt}$$
(4.22)

Taking the 100 J sample as an example and plotting the cooling rate against time, as shown in Fig. 4-11b, one can see that the cooling rate decreases with time, although it fluctuates back and forth. The maximum cooling rate is  $8 \times 10^{10} K / s$ , half order magnitude higher than the average value that determined above. Although this quenching mechanism

alone probably cannot preserve the disordered structure of silicon from its melted state, it will facilitate the crystalline-to-amorphous transformation. At this point, whether this shock-induced amorphization in silicon is a solid state or whether it undergoes melting process is hard to distinguish by shock-recovery experiments. Further in-situ experiment should be conducted to shed more light on the procedure. X-ray diffraction experiments at a facility such as the LCLS would be very helpful.



Figure 4-11 (a) Double y axis plot of temperature (black) and time (blue) as function of pressure and (b) plot of cooling rate and pressure as function of time.

### 4.2.5 Interfaces between Amorphous and Crystalline Si

The unique morphologies of the amorphous patterns render the interfaces between

a-Si and c-Si complicated, which is shown in Fig. 4-12. In general, the c/a interface between the surface amorphous layer and unshocked crystal is sharp and well defined. One can usually observe stacking faults, lying on {111} planes, emitted from the interface, probably being the precursor of the subsequent directional amorphization. Since all the observations were taken from the [110] projection, two {111} variants will be expected and they can either intersect (b) or diverge (c).

Once the directional amorphization is initiated, two kinds of interfaces can be observed: (1) Strain free interface: the coherence of the lattice is barely interrupted by the formation of amorphous materials. As shown in (d), there is only a slight misorientation ( $\sim 2^{\circ}$ ) between the two sides of the amorphous band. (2) Strained interface: the interface is delineated by lattice imperfections such as stacking faults and/or nano-twins.



Figure 4-12 Various morphologies of amorphous/crystalline interfaces.

## 4.2.6 Bifurcation of the Amorphous Bands

It was shown previously that there might be various "features" associated with the primary amorphous band. These bifurcations, as shown in Fig. 4-13, may be a result of local perturbations.



Figure 4-13 Bifurcation of the amorphous band

#### 4.2.7 Shock-Induced Phase Transformation

In addition to amorphization, silicon is known to exhibit multiple phase transitions upon pressurization and depressurization. Up to thirteen phases have been reported in the literature. In Fig. 4-14, it shows a new crystalline structure of silicon in the laser shockrecovered sample. It is found in the vicinity of the directional amorphous band (with some stacking faults nearby) and therefore might be formed by a shear-driven transformation. A higher magnification image of the transformed region (circled by dashed white line in (a)) is given in (b) which is in contrast to (d) where the initial lattice structure, the diamond cubic silicon, is shown. Only taking the low index diffraction into consideration and perform inverse FFT on (b) gives a sharper image of the new crystalline structure. It seems that the new structure is composed of two sub-lattices which are shifted along a specific displacement vector. The FFT diffraction pattern of the entire area is presented in (e) and has three major characteristics: (1) a [110] zone where the observation is made; (2) Extra spots on {111} streaking which correspond to stacking faults and/or the presence of the new phase; (3) A diffuse ring pattern that is attributed to the amorphous structure shown in this area.

Fig. 4-14(e) shows the interface between diamond cubic silicon and the new phases. Various equal-spaced, parallel dislocations (marked by red symbols) are seen at the phase boundary, indicating the semi-coherence of the interface. The existence of the interface dislocations can be seen clearly in (g) which is an IFFT image of (f) which only takes the transmitted beam and one {111} diffracted beam into account.



Figure 4-14 A potential new phase formed in the vicinity of the amorphous band: (a) a HRTEM micrograph showing the amorphous domain, stacking faults (denoted by white dotted line) and new phase (white circled region). The magnified view of the new phase is shown in (b) and the phase filtered lattice is given in (c) which clearly shows a different atomic arrangement compared with diamond cubic lattice in (d). The diffractography of (a) is presented in (e). The interface of the new phase and the diamond cubic lattice is demonstrated in (f) and its IFFT image in (g) clearly show the dislocation dipoles lying on the interface.

#### **4.3 Shock-Induced Fracture**

The keen thrust for impact-resistant electronic devices to cater ever harsher service environment require better understanding of fracture mechanisms of silicon, which is considered ideally brittle below ductile-brittle transition temperature [33]. It fractures by rupture of individual atomic bonds, eventually leading to catastrophic failure. Dislocation activity is heavily suppressed due to the limited plasticity ahead of the crack tip, a direct result of the high Peierls-Nabarro stress. The speed of the crack is limited by Rayleighwave speed. [67,142–144] Various studies, both experimental and computational, have confirmed these phenomena [34]. However, most of these researches focus on mode I fracture under quasi-static loading conditions. Under dynamic loading when deviatoric stress component is significant, the fracture mechanisms of silicon are much less understood. Especially, the atomic picture in the vicinity of the crack tip is missing. Here we use high resolution transmission electron microscopy (HRTEM) to reveal the microstructure near the crack tip of fractured monocrystalline silicon crystal subjected to nanosecond pulsed laser. There is dislocation emissions at the crack tip, leading to dislocation pile-up and crack bifurcation. The dislocation core seems to be spreads out and hitherto of sessile type. The shock-induced overall temperature rise is negligible in this particular case.

Fig. 4-15 a-f illustrate the crack pattern in the central region of the as-shocked surface of the crystals as a function of laser shock energy. At lower energies of 20 J and 50 J, a well-defined crack network with straight crack lines perpendicular to each other is observed. A 70° tilted view, as shown in Fig. 4-15a, b, indicates that most of the cracks are not "opened" but instead "sheared" within their cleavage planes, leaving a "step" on the shock surface. These observations suggest that mode II crack mode is the predominant fracture mechanism. Furthermore, the straight crack lines, oriented in [110] and [1-10] directions are the traces of the cleavage planes on the (001) shock surface. Subsequent TEM observation confirms that the cleavage planes are mostly of {111} type. At an intermediate energy level (100 J), the crack pattern is less regular with the appearance of wavy crack lines, although the perpendicular network still exists. It also appears that some of the cracks are opened due to a higher shock pressure. At high energies (150 J, 200 J, 450

J), the crack line density decreases, the shear cracks vanish whereas some huge opened cracks are preserved, suggesting a change of the cracking mechanism from mode II to mode I. Besides, a large concentration of tremendous micro/nano-particles were deposited on the shock surface (Fig. 4-15 d,e,f). Although the laser shock experiments were conducted in a vacuum chamber, energy dispersive X-ray spectroscopy indicates that oxidation occurred in some of these particles. Moreover, multiple spherical holes, potentially resulting from shock-induced evaporation, can be identified on the 200 J and 450 J shocked sample.



Figure 4-15 Secondary electron fractography of laser shock compressed silicon monocrystals: (a) 20 J; (b) 50 J; (c) 100 J; (d) 150 J; (e) 200 J; (f) 400 J.

Indeed, Maddox *et al.* [206] observed similar voids in the surface of laser-shocked tantalum. These voids are most likely the results of shock-induced vaporization and deposition and potentially an indicator of the 'hot spots' of the laser beam.


Figure 4-16 (a) Secondary electron image (SEI) of a crack on the shocked surface, (b) 3-D profilometry in the vicinity of crack by AFM, (c) the measured height profile across the crack.

Multiple fracture activity can be observed on the shocked surface, Fig. 4-16 (a). This illustrats one particular crack line. It seems that the crack caused a perturbation to the surface of the shocked crystal. Nanoscale profilometry was carried out by atomic force microscopy (AFM). It shows that this crack was sheared along a particular orientation, leaving a step (~ 2 nm in this case) on the surface. Additionally, the crack was also slightly opened in the direction perpendicular to the crack line. Therefore, the resultant shape is a groove with an asymmetrical wedge-shaped cross-section. These observations suggest that the fracture mechanism is a combination of mode I (open) and mode II (shear). Furthermore, this straight crack line, oriented in [1-10] direction, is the trace of the cleavage plane. Subsequent TEM observation confirmed that the cleavage planes are of {111} type, which is also the most conventional slip plane of dislocations in silicon.



Figure 4-17 Dislocation structure in the vicinity of crack tip: (a) Secondary electron image of as-FIBed region across a crack produced by nanosecond pulsed laser, the cutting direction is perpendicular to that of crack line; (b) cross sectional secondary electron image of the as-FIBed TEM foil; (c) Bright field TEM image showing dislocation pile-ups ahead of the crack tip; (d) a magnified HRTEM image focusing on the dislocated region ([110] zone); (e) lattice image of the boxed region in (d), showing the dislocation substructure.

In order to gain more information on the microstructure near the crack tip, crosssectional TEM/HRTEM observation was carried out. FIB was used to trench an area that cut through the crack line in the 20 J shocked sample, as illustrated in Fig. 4-17a. Fig. 4-17b is a secondary electron image (SEI) of the TEM foil (thinned from the region in Fig. 4-17a) with a clear view of an inclined crack on it. A step can be observed on the top surface of the foil, confirming the mode II cracking mechanism. The inclination angle is measured to be 70° to the (001) shock surface. This is inconsistent with the 54.7° angle of  $\{111\}$ -cleavage plane. However, subsequent HRTEM observations show that the cleavage plane is indeed of  $\{111\}$  type - albeit with a zigzag configuration in microscopic. The crack was deflected at a depth about 4  $\mu$ m. Unlike ideal brittle fracture without dislocation generation, multiple dislocations are seen in front of the crack tip (Fig. 4-17c). These dislocations were generated to relax the stress concentration at the crack tip. Burgers circuit conducted on a magnified lattice image in Fig. 4-17e suggests a  $\frac{1}{2}$  [110] Burgers vector, indicating a Lomer-Cottrell dislocation since it does not lie on any slip planes on this particular [110] projection. Furthermore, the dislocation core spreads into two displacement vectors of  $\frac{1}{4}$  [112] and  $\frac{1}{4}$  [112]. The dissociation of the perfect dislocation results in an energy increase, which is not favorable. Such a process should be the result of highly concentrated stress at the sharp crack tip. Generally speaking, these dislocation substructures are sessile and cannot move. (Peach-Koehler equation, dislocation pile up model)



Figure 4-18 Schematic illustration of the dislocation substructures ahead of the crack tip, core spread was shown in the magnified circle with IFFT image taken from Fig. 4-17 (e). Inverse fast Fourier transformation image (IFFT) at the dislocated region clearly show two dislocations marked by red indicator.

The dislocation distribution in a material subjected to a stress  $\tau_{app}$  in dislocation pileup of length  $l_p$  is [129],

$$n(x) = \frac{2(1-\upsilon)\tau_{app}}{Gb} \left[ \frac{(l_p / 2) + x}{(l_p / 2) - x} \right]^{1/2}$$
(4.23)

where  $\sigma$  is the stress caused by the crack tip. For a given stress and number of dislocations in the pile up, *N*, one has,

$$l_p = \frac{GNb}{\pi (1 - \upsilon) \tau_{app}}$$
(4.24)

Considering pile up as a superdislocation, shown in Fig. 4-18, with a spread core, one expresses the shear stress near the pile up.

$$\tau_{pile-up} \approx \frac{GNb}{2\pi(1-\upsilon)x} \approx \frac{GNb}{\pi(1-\upsilon)l_p}$$
(4.25)

On the other hand, the shear stress to propagate a crack in certain cleavage plane is [145],

$$\frac{\tau_{prop}}{G} \approx A \left\{ \frac{4\gamma}{\pi (1-\nu)Gb} \right\}^{\frac{1}{2}} \left( \frac{r}{b} \right)^{-\frac{1}{2}}$$
(4.26)

Where A is a constant (~1),  $\gamma$  is the free energy of the cleavage plane, and *r* is the radius of the crack. Therefore, the ratio of shear stress caused by the dislocation pile-up over the stress required to propagate a crack is,

$$\frac{\tau_{pile-up}}{\tau_{prop}} = \frac{NbG^{\frac{1}{2}}}{2A \cdot \left[\pi(1-\upsilon)\gamma\right]^{\frac{1}{2}}} \cdot \frac{r^{\frac{1}{2}}}{l_p}$$
(4.27)

In the current study, N=30 was approximately obtained from the TEM figure, b= 0.384 nm, G=44.3 GPa is the shear modulus along {111} pane and  $\gamma = 1$  J/m<sup>2</sup> for {111}

planes. Plotting  $\frac{\tau_{pile-up}}{\tau_{prop}}$  against the dimensionless parameter  $\frac{rb}{l_p^2}$ , one can get the critical

condition,  $\frac{\tau_{pile-up}}{\tau_{prop}} \leq 1$ , for the crack to propagate along the original cleavage plane whereas

 $\frac{\tau_{pile-up}}{\tau_{prop}}$  >1 leads to crack deflection, as shown in Fig. 4-19.



Figure 4-19 Plot of shear stress ratio against dimensionless parameter, showing the crack propagation criteria.

#### 4.4 Nanocrystallization

As laser energy increases, so does the heating effect of shock. Since the amorphous structure is thermodynamically metastable, it can transform into a crystalline structure, upon unloading. Indeed, this was observed in the high energy (150 J) experiment and is analyzed in this section.

# 4.4.1 Grain Size Gradient Along the Shock Direction

As shown in Fig. 4-20, the 150 J shocked sample exhibits a polycrystalline microstructure close to the shock surface, whereas amorphous bands were still seen 10~12 µm below the shock surface. The sharp diffraction ring confirms the polycrystalline nature; the grains are equiaxed. Grain-size distribution was measured by the line intersection method as a function of depth along the shock direction.



Figure 4-20 TEM micrographs of the 150 J-shocked silicon crystal showing crystallization of amorphous structure: a, top surface showing grain size of around one micrometer; b,  $\sim 3 \,\mu m$  below the surface showing a ultrafine grained structure; c,  $\sim 7 \,\mu m$  below the surface showing even finer grain size; d,  $\sim 10 \,\mu m$  below the surface showing a mixture of amorphous band and undeformed monocrystalline crystal.

A grain size gradient emerges with coarse grains on the surface and finer grains within. Depending on the grain sizes, as shown in Fig. 4-21, four different regions can be delineated, namely, (1) coarse grain silicon (CG-Si) with a grain size around 1µm

(corresponding to Fig. 4-20a); (2) ultrafine grained silicon (UFG-Si) with a grain size of  $150\pm60$  nm (Fig. 4-20b); (3) nanocrystalline silicon (nc-Si) with a grain size of  $50\pm20$  nm (Fig. 4-20c); and (4) a mixture of amorphous and monocrystalline silicon (a/m-Si, Fig. 4-20d). The boundaries between different regions, however, are not well defined and some large grains, possibly due to abnormal grain growth, can be observed in the nanocrystalline region. It is also interesting to see a high density of twin structures with nanometer thickness in UFG-Si and nc-Si. Also, various contrasted spots were found on the contrast-free residual amorphous domains, indicating crystalline structures within the amorphous silicon.



Figure 4-21 Grain size distribution of the 150 J-shocked sample as function of depth below the shock surface. Four regions, namely coarse grained (CG-Si); ultrafine grained (UFG-Si); nanocrystalline (nc-Si); and mixture of a-Si and monocrystalline (m-Si), can be classified depend on the grain size.

The amorphous phase can transform into nanocrystalline silicon through two possible mechanisms: (1) crystallization from the molten phase; (2) crystallization directly from the amorphous phase. TEM observations (Fig. 4-20d) seem to favor the second

mechanism since multiple crystalline "islands" can be identified on the preserved amorphous bands, indicating an early stage of nucleation.

#### 4.4.2 Crystallization Mechanism

Crystallization from amorphous materials is akin to recrystallization from heavily cold-deformed metals and alloys; however, they differ in driving force, i.e. in the former, crystallization is driven by the Gibbs free energy difference between amorphous and crystalline states whereas, in the latter, recrystallization is promoted by the stored elastic energy due to previously imposed cold work. Despite this difference, they share common foundations: both are based on nucleation and growth. In light of this, three stages of crystallization can be expected: (1) formation of nuclei with a critical size; (2) grain growth at expense of the surrounding amorphous materials; (3) grain impingement and continuous grain growth via motion of high-angle grain boundaries.

The driving force of crystallization is the Gibbs free energy difference between a-Si and c-Si,  $\Delta G_{a-c}(T) = g_a(T) - g_c(T)$ . Considering a homogeneous nucleation mechanism and spherical nuclei, one has,

$$r_c = \frac{2\gamma_{c-a}}{\Delta G_{a-c}} \tag{4.28}$$

 $\Delta G_{a-c}\left(\frac{T_m}{2}\right) \approx 1.9$  GPa (23.2 kJ/mol) can be obtained from Fig. 4-8 (b), if it is assumed that  $\frac{T_m}{2}$  the crystallization temperature. This is two orders of magnitude higher than the driving force for recrystallization for cold-deformed metals, which is usually on the order of 10 MPa (0.12 kJ/mol) [146,147].  $\gamma_{c-a}$  is the same for crystallization as that for amorphization and has a reported range of  $0.4 \sim 2J/m^2$  [131,148–150], rendering a critical grain size of  $D_c=2r_c=0.4\sim 2$  nm.



Figure 4-22 (a) HRTEM micrograph of a nucleus crystallized from amorphous silicon; (b) magnified view of the black boxed region in (a), showing the crystalline embryo (delineated by white dashed line) with clear twined structure.

Figure 4-22 (a) displays a spherical crystalline nucleus ( $D\sim10$  nm) embedded in an amorphous matrix. A magnified view (Fig. 4-22(b)) of the area enclosed by the box in Fig. 4-22 (a) clearly shows the twinning structure. These are the characteristic growth twins, and not deformation twins. Note that the intersection of the mirror plane with the c/a interface forms a triple junction, which influences the grain growth kinetics.

As the crystallization proceeds, the volume fraction of the amorphous material shrinks, resulting in decrease number of nucleation sites. Nucleation ceases once all the amorphous phase is consumed. After this, grains start to impinge on each other, leading to faceting of the spherical interfaces. Grain impingement also leads to the formation of grain boundaries and the motion of which generates the further grain growth [151].

The crystallized microstructure is influenced by nucleation rate,  $\dot{N}$ , and grain growth rate,  $\frac{dr}{dt}$ . The competition between the two factors determines the final grain size, i.e. the larger  $\dot{N}$  and the smaller  $\frac{dr}{dt}$ , the finer the grain size. The complete randomness of amorphous structure provides plentiful nucleation sites of equal probability. Nucleation at such small critical sizes is readily achievable by thermal fluctuation and thus it is preferred over grain growth before grain impingement, resulting in a very fine grain size. The boundaries between three stages of the crystallization are difficult to delineate. However, since the critical size for homogeneous nucleation is small and the temperature at this stage is sufficiently high, it is postulated that nucleation has fast kinetics and therefore the grain growth after grain impingement is the rate-controlling step.

### 4.4.3 Influence of Triple Junctions on Grain Growth

The specific kinetic and thermodynamic properties of triple junctions strongly affect the microstructure evolution of polycrystals [152]. Gottstein and Schvindlerman [152,153] demonstrated that triple junctions drag the motion of grain boundaries and therefore influence the kinetics of grain growth. Such a phenomenon is especially important when the grain size is in nano-scale.

It is proposed here that triple junctions may play a very important role in the nanocrystallization of amorphous silicon. As mentioned above, nuclei are distributed homogeneously in the amorphous matrix; therefore, numerous triple junctions can be expected. Considering the triple junction effect on the grain growth, one has the modified Nernst-Einstein equation [153],

$$\frac{dr}{dt} = \frac{m_b F}{\left(1 + \frac{1}{\Lambda_{ij}}\right)}$$
(4.29)

where *r* is the grain radius,  $m_b$  is the mobility of grain boundary and/or c-a interface,  $\wedge_{tj} = \frac{m_{tj}}{m_b} \cdot D$  is the dimensionless parameter related to the mobility of triple junction  $(m_{tj})$ 

and  $m_b$ . The driving force of the grain growth is:

$$F = \frac{2\gamma_{gb}}{r} = \frac{4\gamma_{gb}}{D}$$
(4.30)

D=2r is the average grain size.

If  $\wedge_{tj} >> 1$ , grain-boundary mechanism is the controlling process of grain growth kinetics and  $D \propto t^{0.5}$ . This is similar to the Hu-Rath equation [154] that was used by Lu *et al.*[155].

If  $\wedge_{ij} << 1$ , the triple junction is the dominant factor for grain growth kinetics and  $D \propto t$ . One should note that the triple lines in polycrystalline materials not only retard the grain growth by dragging the motion of the grain boundary but also provide extra driving force  $F_{ij} = \frac{36\gamma_{ij}}{\pi r^2}$  [156,157] where  $\gamma_{ij}$  is the triple line tension.  $F = F_{ij}$  gives a critical grain size  $D_c$  at which the driving force contributed by grain boundary equals. The triple line energy of silicon has not been measured experimentally whereas MD simulation gives a value of  $8.6 \times 10^{-8}$  J/m [149]. The grain boundary energy is measured to be  $0.45 \sim 0.5$  J/m<sup>2</sup> [148]. Therefore, a critical diameter,  $D_c \approx 22$ nm is obtained. Thus, the effect of triple line on the grain growth kinetics should be taken into account at least until the grain size reaches 22 nm; this is especially important after the nucleating grains encounter.

Kinetics of melting and crystallization has been studied for a variety of systems [131,158]. The pressure effect on the crystallization from amorphous phase was first proposed by Ye and Lu [159]. Recently, high pressure melting and crystallization into a nanocrystalline structure was simulated for Ta [160], and it was shown that classical nucleation theory can provide a reasonable picture of the crystallization process. Under shock compression, the crystallization will most likely occur during the unloading path due to the rapid decay of the pressure pulse, since the crystalline form is stable at room temperature and pressure.

# 4.5 Shock Melting

Melting occurs when the shoc-induced temperature rise exceeds the melting temperature of silicon; if the cooling rate is slow enough (below critical cooling rate for glassy transition), the molten silicon will undergo conventional solidification process and the resultant microstructure is polycrystalline. This is what happened for the O-200 J and O-400 J shocked sample, as shown in Fig. 4-23.



Figure 4-23 TEM micrograph of 200 J-Omega-shocked sample: (a) multiple nano-spaced twin structures are imaged with a diffracted pattern with characteristic twin spots shown in (b).

Fig. 4-23 shows a TEM image of the microstructure of shock-melted-solidified silicon. Annealing twin structures with nano-scale interspacing were identified with corresponding electron diffraction pattern showing (1-11) mirrored spots. The grain size is in the order of several micrometers and the intersections of twin boundaries with grain boundaries usually form a triple junction.

# 4.6 Summary of the Chapter

Despite the fact that silicon is omnipresent in the modern technological society, our understanding, especially of its mechanical response at extreme pressures and strain-rates, is far from complete. High-power, short-duration, laser-driven, shock compression and recovery experiments on [001] silicon unveiled remarkable structural changes observed by transmission electron microscopy of recovered specimens. Amorphization occurs above a shock energy threshold. Two distinct amorphous regions were identified, including a bulk amorphous layer close to the surface and amorphous bands initially aligned with {111} slip planes. Further increase of the laser energy leads to the re-crystallization of amorphous silicon into nanocrystalline silicon with large densities of nano-twins. It is postulated that the co-existence of high magnitude hydrostatic and shear stresses under dynamic shock compression produces amorphization which occurs below the calculated critical melting pressure of silicon. The shock-induced defects play a very important role in the onset of amorphization.

Chapter 4, in part, is a reprint of the material as it appears in "*Pressure and Shear Induced Amorphization of Silicon*", Extreme Mechanics Letters 2015 5: 74-80. This work is coauthored by S. Zhao, B. Kad , E. N. Hahn, B.A. Remington, C.E. Wehrenberg, C.M. Huntington, H.-S. Park, E. M. Bringa, K.L. More, M.A. Meyers. The dissertation author is the first author of this work.

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# Chapter 5 Laser Shock Compression of Boron Carbide

#### 5.1 Background and Justification

Boron carbide is one of the hardest materials on the Earth (arguably second to the diamond). Owing to its excellent mechanical properties and low density, it has been used as body armors. However, it has been observed that boron carbide suddenly losses its strength immediately after the Hugoniot elastic limit, which restrained its application. Although it has been postulated that this is due to the amorphization, the microstructural mechanisms of such a process remain unclear. In order to resolve this puzzle, we designed a laser shock-recovery experimental apparatus which is implemented in Jupiter laser facility (Janus), Lawrence Livermore National Laboratory. The nanosecond stress pulse effectively prevents materials from shattering under shock compression. Successful recovery experiment enables us to examine the microstructure of the shocked B<sub>4</sub>C.

## 5.2 Preparation of Boron Carbide Samples

The received B<sub>4</sub>C crystals were hot-pressed at 2000 °C with the initial powder size of approximately 1  $\mu$ m. Boron carbide powders (H.C. Starck GmbH, HCS Grade, 1  $\mu$ m average particle size) were hot-pressed to full density without sintering aids at 2000°C and then machined into polycrystalline cylinders (3 mm in diameter and 3 mm in height). The surface of the cylinders was mechanically polished using diamond suspensions with decreasing grade sizes of 5  $\mu$ m, 3  $\mu$ m, 1 $\mu$ m, and 0.5  $\mu$ m, prior to the laser shock experiment. Surface roughness of these crystals are controlled through mechanical polishing by diamond suspensions with decreasing grade sizes of 5  $\mu$ m, 3  $\mu$ m, 1 $\mu$ m, and 0.5  $\mu$ m, 3  $\mu$ m, 1 $\mu$ m, and 0.5  $\mu$ m, 1 $\mu$ m, 1 $\mu$ m, and 0.5  $\mu$ m, 1 $\mu$ 

# **5.3 Laser Shock Compression Experiments**

The green laser (nominal wavelength=528 nm, laser energy= 50 J) has a nominal square pulse shape with duration of 3 ns, resulting in a pulse power of 1.67 TW/cm2. Such a high energy density was deposited onto a target package which is comprised of an aluminum foil (200  $\mu$ m) and B<sub>4</sub>C crystal (3 mm in diameter and 3mm in height) encapsulated in a titanium cup. The aluminum foil has three functions: (1) as an ablator to transform laser energy into stress pulse; (2) as a heat shield which minimizes the preheating induced by laser irradiation; (3) as a pulse shaper to make the shock pulse on the target surface planar (uniaxial strain condition). The rear (free) surface velocity of the aluminum foil to the laser shock is characterized by velocity interferometry (VISAR), which was shown in Fig. 5-1.



Figure 5-1 Free surface velocity interferometry (VISAR) for laser shock compressed aluminum ablator. (a) The temporally resolved VISAR fringe, showing the shock break-out and pull-back features which can be reflected on the determined profile of  $U_{fs}$  vs. t in (b). Two independent VISAR channels with distinctive Etalon length were used to unambiguously determine the free surface velocity. The peak  $U_{fs} \sim 4.2$  km/s, rendering  $U_p \sim 2.1$  km/s. Such a particle velocity is used to conduct impedance matching in Fig. 5-2.

The free surface velocity ( $u_{fs}$ ) can be approximated as twice of the particle velocity ( $u_p$ ),  $u_p \sim 0.5 u_{fs}$ . Conservation of momentum gives the relationship between longitudinal stress (or shock pressure, P) and  $u_p$ ,  $P = \rho_0 u_s u_p$ . The shock pressure on the surface B<sub>4</sub>C is determined by shock impedance ( $Z = \rho_0 u_s$ [123]) matching, as can be seen in Fig. 5-2 where the inset shows the target package of the recovery experiment. The shock Hugoniot data of Al was well measured and documented by LANL SESAME database. For B<sub>4</sub>C, however, there are some discrepancies among data reported in the literature, depending on the

porosity of the material. Fig. 5-2 shows two most representative curves from Pavlovskii et al. [161] and McQueen et al. [52], giving a shock stress ( $\sigma_{33}$ ) range between 45 and 50 GPa.



Figure 5-2 Shock Hugoniot (P vs.  $u_p$ ) of aluminum and boron carbide. At the interface of Al and B4C, shock wave will be reflected and the shock pressure changes as equilibrium is reached. Invert the shock Hugoniot of Al gives the estimation of the reflected curve. And the intersection of the reflected curve with shock Hugoniots of B4C is the shock pressure in B4C. Taking the Up= 2.1 km/s from Fig.1, one gets the shock pressure,  $\sigma_{33}$ = 45-50 GPa.

# **5.4 TEM characterization**

The recovered microstructure was characterized by high-resolution transmission

electron microscopy (HRTEM). The sample was cut directly from the recovered sample

surface by focus ion beam (FIB) with a 30 kV initial high beam voltage and 5 kV final low

voltage to remove the beam damage.



Figure 5-3Bright field TEM image of (a) initial microstructure of as-sintered boron carbide showing absence of deformation features and (b) laser-shocked material showing massive strain contrast, indicating that material is heavily deformed.

Fig. 5-3 (a) shows the low-magnification TEM micrograph of the initial microstructure of boron carbide as the reference. The as-sintered material shows virtually zero-defect contrast, indicating that it has a low defect density. Fig. 5-3 (b), however, shows that the shocked material exhibits a sharply distinct structure, with diffraction contrast throughout the sample, indicating that the material is heavily deformed. The clear microstructural differences between initial and shocked condition confirm that the planar faults (cracks and stacking faults) and amorphous material are indeed the result of shock compression.

The shock-recovered microstructure was depicted in a low magnification bright field TEM image in Fig. 5-4(a). A crack was observed in the center of the TEM foil and multiple planar faults can be imaged. The crack is  $45^{\circ}$  away from the shock direction and therefore coincides with the maximum shear direction. The planar faults deviate (~15°) from the maximum shear, albeit the inclined feature indicates that shear stress played a very important role. These PFs lead to misorientation in their surroundings which can be demonstrated by HRTEM images at different positions of one particular planar fault. Align the electron beam parallel to one set of lattice planes (two beam conditions), one could image the lattice perturbation caused by the planar faults. From region b to d, the misorientation on two sides of the planar fault increases, suggesting a trend of losing long range order. The inverse FFT figures were shown as insets on the bottom left corner of b, c and d, respectively. It is shown in Fig. 41 (b) that the lattice perturbation at the tip of the planar fault is small and is accommodated by dislocation dipoles (Marked by red symbols) at the interface. As being moved to the body of the PF, the interfaces begin to lose its coherence, with Fig. 41(c) being the intermediate stage and Fig. 41(d) being the final stage (the sharp incoherent interface is marked by solid red lines in the insets of Fig. 41 (b) and (d)). The lattice continuity was almost lost completely in the vicinity of the planar fault (region d), suggesting the onset of amorphization.



Figure 5-4 TEM/HRTEM micrographs of recovered B4C from laser shock compression. (a) low magnification TEM image shows the shocked surface with cleaved crack in the center. Multiple planar faults can be imaged. HRTEM images in (b-d) illustrate different part of one particular planar fault in (a) with corresponding inverse FFT images at the interfaces shown in the bottom left insets.

Some amorphous bands can be observed a few  $\mu$ m below the shock surface. These bands (marked by a-B4C in the amorphous region), unlike those observed in silicon [162,163], do not necessarily originate from the shock surface and sometimes terminate on both ends, resulting in an ellipsoidal shape as shown in Fig. 5-4 (a). The amorphous structure was confirmed by the diffused ring in the FFT diffractograph which is shown in the upper right inset of Fig. 5-4 (c). The thickness of the amorphous ellipsoid ranges from 2 nm to 5 nm. Fig.5-4 (b) shows the magnified view of the band termination, a six-degree 'lattice rotation' was observed in the vicinity of the band tip. A zone axis of  $[\overline{7}\overline{13}]$  was

chosen to establish crystallographic relationship between the amorphous domain and the rhombohedral matrix. Choosing (215) to construct the two-beam imaging condition indicates that this amorphous band aligned reasonably well with (215) plane.

It is also evident that the amorphous bands do not always present contiguously with the cleaved fracture surface, but instead are observed all around the sample. Therefore, the amorphization of B4C, although occurred in a localized pattern, should be treated as a random event. The ultra-short stress pulse duration (10s of ns including the shock release) is two orders of magnitude smaller than the characteristic time ( $\mu$ s) for crack propagation effectively preventing the sample from catastrophic failure.



Figure 5-5 HRTEM micrographs of amorphous band far away from the crack. (A) Both ends of the amorphous band, which exhibits an ellipsoidal shape, terminate in material (one end is shown here). (B) Lattice image at the tip of the amorphous band shows clear lattice rotation. (C) Lattice image showing the amorphous region (marked as  $a-B_4C$ ) with inset showing the corresponding FFT diffractograph. (D) Geometrical phase analysis corresponding to (C) shows that the local shear

strain ( $\varepsilon_{xy} = \frac{1}{2}\gamma$ ) is significantly higher in the amorphous region than its surroundings, indicating that shear stress plays a crucial role in amorphization.



Figure 5-6 Additional HRTEM micrographs of boron carbide laser shocked above (A) and below (B) the threshold for amorphization. An amorphous band aligning with (2-21) is identified in A. A planar fault, possibly lying on (021) is seen in (B).

We performed several laser shock compression experiments on boron carbide at different laser energies (and associated shock pressures). Amorphization is only observed in the particular experiment where the maximum shock energy is E~50J and pressure is  $P=45\sim50$  GPa. Fig. 5-6A shows the structure. We have looked at other TEM samples where the amorphous band does not necessarily align with (215) plane. Fig. 5-6A shows an amorphous band lying roughly on ( $2\overline{2}1$ ) plane (as defined in main text). At a lower laser energy (Fig. S4B, E~20 J, P~25 GPa), one planar fault, possibly a stacking fault, was found to formed on (021) plane. The majority of the material behaves elastically. Thus, it can be concluded that amorphization occurs beyond a shock threshold between 25 to 50 GPa.

It was also shown in Fig. 5-7 that there were many nano-grains (10~20 nm) found in the vicinity of some cracks (intergranular), leading to a diffractograph composing of

sharp rings. These nano-grains tend to form a thin film and cover close to the cleavage plane as shown in (c). A high resolution TEM image shows that some lattices are severely curved in the nanocrystalline region. (d) and (e) show the BF and the DF images, respectively, of one nano-grain with size of 10 nm.



Figure 5-7 Nanocrystals showing in the vicinity of an intergranular crack: (a) the low magnification image; (b) the nanograins shows a zigzag configuration and tend to cover the free surface of the crack (c); one nanograin is imaged in bright field mode (d) and dark field mode (e); a HRTEM image of the boxed region in (c) was shown in (f) with curved lattices in everywhere.

#### **5.5 Mechanical and Thermal Interpretation**

Under shock compression (uniaxial strain) before Hugoniot elastic limit (HEL), the

stress-strain relationship can be expressed by generalized Hooke's law,

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} = C_{ijkl} \varepsilon_{33} \tag{5.1}$$

where  $C_{ijkl}$  is the fourth order elastic constant tensor. Therefore, for isotropic solid, the maximum shear stress,  $\tau_{max}$ , and hydrodynamic pressure, P, can be expressed as function

of elastic constants and longitudinal strain and the ratio can be written as,

$$\frac{\tau_{\max}}{P} = \frac{3(C_{33} - \min\{C_{13}, C_{23}\})}{2(C_{33} + C_{13} + C_{23})}$$
(5.2)

For B4C with a low symmetrical rhombohedral Bravais lattice ( $R\overline{3}m$  space group),[164] the elastic constants have different values according to different structure models. Here we adopt the more widely accepted equilibrium B11C-CBC model where the boron carbide primitive cell contains 15 atoms with one linear C-B-C chain surrounded by polarized icosahedrons. Using ab-initio simulation, Aryal et al. [165] reported calculated values of C<sub>33</sub>= 553.1 GPa, C<sub>13</sub>=76.8 GPa and neglecting the tiny difference between C<sub>13</sub> and C<sub>23</sub>, one arrives,

$$\frac{\tau_{\max}}{P} = \frac{3(C_{33} - C_{13})}{2(C_{33} + 2C_{13})} \approx 1$$
(5.3)

Therefore, the shear stress in boron carbide before onset of inelastic deformation is very significant. The shock pressure relates to hydrostatic and deviatoric stresses by,

$$\sigma_{33} = P + \frac{4}{3}\tau_{\max}$$
 (5.4)

Thus, at HEL (around 20 GPa[166,167]),  $\tau_{\text{max}} \approx P = 8.6$  GPa. In this particular case,  $\sigma_{33} = 45 \sim 50$  GPa, where shock pressure is much beyond HEL, the shear stress will be released by inelastic deformation, i.e. amorphization. Shear stress facilitates amorphization in that it gives rise to larger lattice displacement than that of hydrostatic pressure.

Pressure is also postulated to play a role in amorphization of B<sub>4</sub>C. On one hand, it has been proved that B<sub>4</sub>C exhibits a negative melting slope with  $\frac{dT}{dP} \sim 13 \pm 6K / GPa$  [168], rendering a reduction of melting temperature up to 400 K. On the other hand, the

volumetric change caused by hydrostatic pressure and the lattice friction caused by shear stress lead to tremendous heat generation. Localized melting or viscous flow may happen due to the elevated temperature in the localized area and the rapid shock release will trigger a self-quenching mechanism, which eventually gives rise to amorphization.

There are several proposed atomistic mechanisms to explain how  $B_4C$  amorphizes under stressed condition. For instance, destruction of C-B-C chain, [169] transformation into and then collapse of B12-CCC polytype, [170] break of boron-carbon bonds between neighboring icosahedrons, [171] and depressurization amorphization.[172] Despite the complicated nature of atomic displacement during amorphization, it is undisputed that shear stress is vital in the process. Amorphization and cleavage are both energy dissipation mechanisms since they both create extra interfaces. Therefore, they are competitive phenomena of  $B_4C$  under shock loading. However, as the strain rate increases, amorphization is kinetically favored, suggesting a transition of failure mode from crack nucleation/propagation to amorphization.

The material is hot-pressed polycrystalline boron carbide with initial grain/powder size around  $1\sim2 \mu m$ . For laser shock compression, the spot size of the beam is 1 mm, 3 orders of magnitude larger than the grain/powder size. Thus, the polycrystalline solid can be approximated as isotropic where the properties, for example, Young's modulus of each individual grain are averaged. Thus, the assumption that polycrystalline B<sub>4</sub>C behaves isotropically under laser shock compression is still valid since the shock-affected zone covers many grains. TEM observations show that the sample contains grains with varying orientations, confirming the polycrystalline nature of the material. Thus, using the isotropic

assumption to qualitatively estimate the shock-induced pressure and temperature rise is still reasonable.

However, at the grain level, where amorphization takes place, the anisotropy cannot be ignored in the complex picture of the directional amorphization in boron carbide. The evaluation of the anisotropic mechanical behavior (assuming B<sub>4</sub>C is linear elastic) can be carried out by the coordinate transformation, knowing the shock compression direction. It should be noted that boron carbide is a strongly anisotropic material (with anisotropy ratios of  $C_{33}/C_{11}=0.98$ ,  $C_{13}/C_{12}=0.49$ ,  $2C_{44}/(C_{11}-C_{12})=0.8$ ), and, as a result,  $E_{max}/E_{min}=8.1$  [173]. In order to determine the stress state on a specific plane, Voigt's approach to coordinate transformation on stiffness tensor needs to be performed prior to the calculation of the Cauchy normal and shear stresses [174]. If  $C_{iikl}$  is the original stiffness tensor, one can write,

$$C_{mnop} = l_{mi} l_{nj} l_{ok} l_{pl} C_{ijkl}$$
(5.5)

where  $C_{nnop}$  is the stiffness tensor in the new coordinate system and l are the direction cosines. The ratios between the resolved shear stress,  $\tau$ , and shock stress,  $\sigma_s$ , on the observed planar fault (as in Fig. 5-4) and amorphous band (as in Fig. 5-5) are 0.25 and 0.2, respectively. Therefore, the amorphization process is strongly loading-path dependent. The original fourth order stiffness tensor is  $C_{ijkl}$ , where i,j,k,l=1-3. Such a tensor is defined by Cartesian coordinates where the loading axis is collinear with direction [001]. The loading axis for a specific grain can be obtained from the diffraction pattern as shown in Figs. 5-4 and 5-5.

The new constitutive equations, according to the generalized Hooke's law:

$$\sigma_{mn} = C_{mnop} \varepsilon_{op} \tag{5.6}$$

where m,n,o,p are indices that range from 1 to 3. Since shock compression generates a uniaxial strain state (direction of shock propagation in the transformed coordinate aligns with the new  $x_2$  axis), the constitutive equation reduces to,

$$\sigma_{mn} = C_{mn22} \varepsilon_{22} \tag{5.7}$$

Therefore, the stress state of the grain can be obtained. We can calculate the Cauchy normal and shear stresses of an oblique plane with direction cosines l,m,n from the following equations:

$$\sigma_n = \sigma_{11}l^2 + \sigma_{22}m^2 + \sigma_{33}n^2 + 2(\tau_{12}lm + \tau_{23}mn + \tau_{13}\ln)$$
(5.8)

$$\tau = \left[ \left( \sigma_{11}l + \tau_{12}m + \tau_{13}n \right)^2 + \left( \tau_{12}l + \sigma_{22}m + \tau_{23}n \right)^2 + \left( \tau_{13}l + \tau_{23}m + \sigma_{33}n \right)^2 - \sigma_n^2 \right]^{1/2}$$
(5.9)

We can apply this to the amorphous band or planar faults oriented by direction cosines l, m, and n to the new coordinate system. This was done for a planar fault and for two amorphous bands. It is assumed that the plane of the band is perpendicular to the plane of the foil (which is parallel to the shock-wave propagation direction). The ratios of the shear stress to shock stress for the planar fault (1-1-4) and two amorphous bands ((2-21) and (215)) are found to be equal to 0.25, 0.2 and 0.37, respectively. The shear stress is indeed significant and can induce lattice disordering. The directional cosines matrix used for the analysis are attached:

1. For the planar fault shown in Fig. 2 of the main text:

$$l_{ij} = \begin{bmatrix} -0.9103 & -0.1221 & 0.3955 \\ -0.2881 & -0.4991 & -0.8173 \\ 0.2972 & -0.8579 & 0.4191 \end{bmatrix}$$

The resultant stiffness tensor (in matrix notation) and stress state (in tensor notation) are:

$$C_{rs} = \begin{bmatrix} 430.190037760 & 147.472609842 & 147.418536417 & -17.9691083660 & -48.0070061429 & 49.9008393746 \\ 147.472609842 & 350.306812681 & 188.833543809 & -70.5178761540 & 54.8512486818 & -30.2258176869 \\ 147.418536417 & 188.833543809 & 387.378800037 & 114.320905378 & -19.3684556129 & 4.65286147351 \\ -17.9691083660 & -70.5178761540 & 114.320905378 & 163.931504340 & 46.6207163699 & 65.9769711745 \\ -48.0070061429 & 54.8512486818 & -19.3684556129 & 46.6207163699 & 199.591072978 & -29.9378391428 \\ 49.9008393746 & -30.2258176869 & 4.65286147351 & 65.9769711745 & -29.9378391428 & 221.506600620 \end{bmatrix} GPa$$

2. For the amorphous band in Fig. 3 of the main context, the matrix of directional cosines

is:

$$l_{ij} = \begin{bmatrix} -0.2089 & -0.9172 & -0.3392 \\ 0.6701 & -0.3869 & 0.6335 \\ -0.7123 & -0.0949 & 0.6954 \end{bmatrix}$$

The resultant stiffness tensor and stress state are:

$$C_{rs} = \begin{bmatrix} 439.119611225 & 162.936067440 & 126.112141122 & -9.00948200255 & 0.462576312320 & 93.5057674938 \\ 162.936067440 & 309.219353605 & 234.520074655 & 26.3514489096 & 12.3392128014 & -26.1058853788 \\ 126.112141122 & 234.520074655 & 339.768626667 & -50.6173948352 & 4.95793134736 & -51.2084654798 \\ -9.00948200255 & 26.3514489096 & -50.6173948352 & 247.447982999 & -67.0093964785 & -3.48592584217 \\ 0.462576312319 & 12.3392128010 & 4.95793134736 & -67.0093964785 & 112.789858717 & 95.9939539969 \\ 93.5057674938 & -26.1058853788 & -51.2084654798 & -3.48592584213 & 95.9939539969 & 144.703193940 \end{bmatrix} GPa$$

$$\sigma_{mn} = \begin{bmatrix} 162.9361 & -26.1059 & 12.3392 \\ -26.1059 & 309.2194 & 26.3514 \\ 12.3392 & 26.3514 & 234.5201 \end{bmatrix} \varepsilon_{22} \quad GPa$$

3. For another amorphous band shown in Fig. 5-6 the matrix of directional cosines is:

$$l_{ij} = \begin{bmatrix} -0.9307 & -0.3428 & -0.1273 \\ 0.3236 & -0.9342 & 0.1499 \\ -0.1703 & 0.0980 & 0.9805 \end{bmatrix}$$

The resultant stiffness tensor and stress state are:

 $C_{rs} = \begin{bmatrix} 467.120130406 & 187.904152202 & 80.5339125641 & -30.9569683413 & 36.0292757936 & -36.8318802017 \\ 187.904152202 & 468.764682597 & 78.3947757755 & -21.6571979755 & 7.77743988489 & 49.1506099856 \\ 80.5339125641 & 78.3947757755 & 505.479668332 & 41.8262329449 & -34.3249396965 & -10.8900154368 \\ -30.9569683413 & -21.6571979755 & 41.8262329449 & 171.394204076 & -9.77737733700 & -0.607714743596 \\ 36.0292757936 & 7.77743988489 & -34.3249396965 & -9.77737733700 & 176.774888909 & -15.3464401670 \\ -36.8318802017 & 49.1506099856 & -10.8900154368 & -0.607714743596 & -15.3464401670 & 239.304795791 \end{bmatrix} GPa$ 

$$\sigma_{mn} = \begin{bmatrix} 187.9 & 49.15 & 7.78 \\ 49.15 & 468.76 & -21.65 \\ 7.78 & -21.65 & 78.39 \end{bmatrix} \varepsilon_{22} \quad GPa$$

Pressure may also play a role in amorphization of B<sub>4</sub>C. It was shown that B<sub>4</sub>C exhibits a negative melting slope with  $dT/dP \approx -13 \pm 6K/GPa$  [168], resulting in a reduction of melting temperature up of to 200 K at the HEL (~20 GPa). Besides, the elastic stiffness of boron carbide is pressure dependent, indicating that pressure may affect the shear instability of B<sub>4</sub>C, the dominant amorphization mechanism.

The increase in temperature due to shock compression can be evaluated from the Hugoniot relations and experimentally-determined shock parameters. This is shown in Figure 4 (marked as homogeneous shock temperature,  $T_{homo}$ ), in conjunction with the decrease of melting point. Clearly,  $T_{homo}$  is not sufficient for melting at a shock stress of 45 GPa.

### 5.6 Modelling the Localized and Homogeneous Temperature Rise

In addition to the  $T_{homo}$ , there is localized heat generation because of the lattice friction associated with shear localization. It is assumed that shear localization and amorphization start at HEL. The localized temperature rise  $\Delta T_{band}$  in an amorphous band of width  $w_{band}$  can be estimated by assuming that the relaxation in deviatoric strain energy is balanced by the increase in internal energy and heat transfer to its surroundings. The heat extracted from the shear band is modeled assuming that there is a constant heat generation in its symmetry plane, a problem that was solved analytically by Carslaw and Jaeger [175,176] assuming a semi-infinite body on whose surface heat is deposited,

$$\Delta T_{band} = \frac{2}{\sqrt{\pi}} \frac{\beta \tau \gamma w_{band}}{\Delta t} \sqrt{\frac{t}{k \rho C_p}}$$
(5.10)

where  $\beta$  is the fraction of deviatoric strain energy converted to thermal energy (usually taken as 0.9). *k* is thermal conductivity.  $\tau$  and  $\gamma$  are the shear stress and strain inside the band, respectively. The former is approximated as  $\tau_{max}$  at HEL, and assumed to be independent of increasing shock stress. The latter is related to the uniaxial strain ( $\varepsilon_{uniaxial}$ ), width ( $w_{band}$ ) and interspacing ( $w_{spacing}$ ) of bands,  $\gamma \approx \varepsilon_{uniaxial} \left( \frac{w_{spacing}}{w_{band}} + 1 \right)$ , if all the deviatoric strain is relaxed by shear band.  $w_{band} = 2 \sim 10$  nm can be measured from postmortem TEM micrographs and  $w_{spacing} \sim 1 \ \mu m$  is approximated as the particle size since typically there is only one amorphous band per grain.



Figure 5-8 Homogeneous and localized temperature rise as a function of shock compression. The applied shock pressure of 45~50 GPa is significantly below the pressure for homogenous shock-induced melting ( $T_{\text{homo}}$ ), although the melting temperature,  $T_m$ , decreases as pressure increases. Conversion of strain energy inside the amorphization band to heat generated by shear leads to localized temperature increase  $\Delta T_{band}$ . Different values of heat conversion factor,  $\beta$ , are assumed. Note that the localized temperature rise only occurs in the plastic regime ( $\sigma_s >$  HEL). The calculation represents an estimate and incorporates heat extraction from the band; no melting is predicted.

Fig. 5-8 plots  $\Delta T_{hand}$  with varying  $\beta$  at time t = 3 ns which is approximated as the

laser pulse duration  $\Delta t$ . The uncertainties in Eqn. 5 render the accuracy of prediction heavily dependent on these material parameters, especially the strain in the amorphous band and flow-stress dependence of strain softening. In the case of softening, the temperature rise will be decreased. Nevertheless, the physical picture qualitatively captured in Eqn. 5 provides an estimate for localized heating. The localized heating may also lead to formation of nano-crystals in the vicinity of the stress concentration (crack), as evidenced in Fig. 5-7.

The microstructure of the recovered cylinder was characterized by high resolution transmission electron microscopy (HRTEM). HRTEM samples were cut directly from the shocked surface by focused ion beam (FIB) with a 30 kV initial high beam voltage and 5 kV final low voltage to remove beam damage.



Figure 5-9 Schematic drawing of the amorphous band subjected to shock loading (pressure plus shear).

A simple equation based on transformation of strain energy into thermal energy and heat conduction to surroundings is proposed to evaluate the localized temperature rise within the evolving band ( $\Delta T_{hand}$ ). The physical picture is depicted in Fig. 5-9.

The governing equation for the 1-D heat conduction problem is given as,

$$\rho C_p \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} + \dot{q}$$
(5.11)

where  $\rho$ ,  $C_p$ , k are density, heat capacity, heat conductivity of shear band, respectively. Considering a constant heat source (amorphous band,  $\dot{q}$  =constant) at surface of a semiinfinite body (bulk crystal); Jaeger [175,176] gave the temperature rise,  $\Delta T_{band}$ , at the surface (center of amorphous band, x=0) as a function of, t,

$$\Delta T_{band} = \frac{2}{\sqrt{\pi}} \frac{\dot{q}}{k} \sqrt{\alpha t} = \frac{2\dot{q}}{\sqrt{\pi}} \sqrt{\frac{t}{k\rho C_{p}}}$$
(5.12)

where  $\dot{q}$  is the rate of heat generation. In our case, conversion of strain energy into heat leads to,

$$\dot{q} \approx \beta \frac{\tau \gamma w_{band}}{\Delta t}$$
(5.13)

where  $\beta$  is the conversion efficiency,  $w_{band}$  is the width of the amorphous band,  $\tau$  is shear stress,  $\gamma = \varepsilon_{uniaxial} \left( 1 + \frac{w_{spacing}}{w_{band}} \right)$  is shear strain inside the shear band,  $\Delta t = 3$  ns is

approximately the duration of the laser. Thus,

$$\Delta T_{band} = \frac{2}{\sqrt{\pi}} \frac{\beta \tau \gamma w_{band}}{\Delta t} \sqrt{\frac{t}{k \rho C_p}}$$
(5.14)

Eq. 5.14 provides an estimation of the localized temperature rise in the amorphous band. The accuracy of the prediction depends on the material parameters. However, the upper bound of  $\Delta T_{band}$  is established. The local temperature rise may also lead to the formation of a nanocrystalline structure, shown in Fig. 5-7, depending on the local stress state and deformation path. Table 5.1 shows the material parameters used in the model of Fig. 5-8.

Table 5.1 Model Parameter		
Values		
β	-	0.5~0.9
$ ho_{B4C}$	kg/m <sup>3</sup>	2.50E+03
$C_p$	J/kg*K	1.00E+03
α	$m^2/s$	1.00E-6
k	W/m*K	1.00E+01

It should be noted that the bulk temperature rise, as induced by homogeneous shock compression, is significantly below the melting point. Assuming an adiabatic condition at the shock front, one can establish a relationship between temperature, T, and pressure, P, at each point on the shock Hugoniot by means of the Grüneisen EOS and thermodynamic relationships (1):

$$T = T_{o} exp\left[\left(\frac{\gamma_{o}}{V_{o}}\right)(V_{o} - V)\right] + \frac{V_{o} - V}{2C_{v}}P + \frac{exp\left(-\frac{\gamma_{o}}{V_{o}}V\right)}{2C_{v}}\int_{V_{o}}^{V}P exp\left[\frac{\gamma_{o}}{V_{o}}V\right]\left[2 - \frac{\gamma_{o}}{V_{o}}(V_{o} - V)\right]dV$$
(5.15)

T<sub>0</sub> is the reference(initial) temperature, *V* and *V*<sub>0</sub> are the specific and reference specific volumes, respectively,  $\gamma_0$  is the reference Grüneisen constant, and  $C_{\nu}$  is the heat capacity. The localized temperature and homogeneous temperature as a function of shock stress is plotted in Fig. 4 of the main text.

#### 5.7. Summary of the Chapter

Solid state shock-wave propagation is strongly non-equilibrium in nature and hence rate dependent. Using high-power pulsed laser-driven shock compression, unprecedented high strain rates can be achieved and here we report on the directional amorphization in boron carbide polycrystals. At a shock pressure of  $45 \sim 50$  GPa, multiple planar faults, slightly deviated from maximum shear direction, occur a few hundred nanometers below the shock surface. High resolution transmission electron microscopy reveals that these planar faults are precursors of directional amorphization. It is proposed that the shear stresses cause the amorphization and that pressure assists the process by ensuring the integrity of the specimen. Thermal energy conversion calculations including heat transfer suggest that amorphization is a solid-state process. The adiabatic nature of shock compression results in a local temperature rise which may also facilitate amorphization. Such a phenomenon has significant effect on the ballistic performance of B<sub>4</sub>C.

Chapter 5, in part, is a reprint of the material as it appears in "*Directional amorphization of boron carbide subjected to laser shock compression*". Proc. Nat. Acad. Sci. U.S.A. 2016, 113:12088-12093. This work was coauthored by S. Zhao, B. Kad, B. A. Remington, C.E. Wehrenberg, J. Lasalvia, K. Beuler, M.A. Meyers. The dissertation author is the first author of this work.
## Chapter 6 Laser Shock Compression of Germanium

## **6.1 Background and Justification**

Amorphous and nanocrystalline materials draw intensive attention due to their superior functional and mechanical properties [177]. Since they are thermodynamically metastable, amorphous solids can transform into nanocrystals if appropriate heat treatments are applied [178]. To achieve amorphization, quenching liquid at ultrafast cooling-rates is required, which is extremely difficult for most pure elements [179]. Alternatively, it has been shown that application of pressure leads to amorphization of material whose melting line displays a negative Clapeyron slope (dT/dP<0) [23,90,96,180]; germanium (Ge) falls into this category [51]. However, instead of pressure-induced amorphization, numerous studies, in both static [38,181] and dynamic conditions [47,182,183], have shown that Ge undergoes polymorphisms at elevated pressures. Consequently, amorphization has not been unambiguously identified in Ge until Clarke [17] observed the indentation-induced crystalline-to-amorphous transition. More recently, high speed nanodroplet test also showed surface amorphization of Ge in an extremely localized manner [21].

Despite being widely studied, the underlining microstructural mechanisms of pressure-induced amorphization remain vague. Moreover, production of bulk amorphous germanium from high pressure experiments has not been possible. This is due to the notorious brittleness of germanium at room temperature which renders its recovery from high pressure experiments enormously challenging since it shatters catastrophically by crack nucleation, propagation and coalescence in these scenarios. Depositing high-power pulsed laser energy onto a mm-scale target, transient states of extreme stresses and temperatures promptly build up and decay rapidly as the short wavelength pulse propagate through the material. The short duration of the stress pulse preserves the integrity of the target by suppressing the full development of cracks and enables postmortem microstructure characterization. Using this methodology, we have reported shock-induced amorphization in silicon and boron carbide [162,184]. In this study, we demonstrate that extreme deformation by laser shock results in amorphization and subsequently nanocrystallization in germanium. The important, albeit often ignored, role of shear in pressure-induced phase transition [185,186] is clearly evidenced by the directional feature of the amorphous bands.

### **6.2 Materials and Methods**

#### 6.2.1 Laser shock recovery experiments

We performed laser-driven shock-recovery experiments at Omega laser facility, Laboratory of Laser Energetics, University of Rochester. The shock wave is created by the following sequence of processes. First, the high power pulsed laser energy is deposited on the 20 um CH ablator of the target package, ionizing it into plasma. Second, as the plasma flows away, the target surface experiences a reaction force equal to the rate at which momentum is carried away due to the rocket effect. The stress pulse promptly builds up and transforms into a shock wave. Third, the shock wave propagates inwards and quickly decays as the laser duration is very short (1ns). The amplitude of the ablation pressure ( $P_{abl}$ ) can be estimated by the analytical model put forward by Lindl [33],

$$P_{abl} = C \left(\frac{I}{\lambda}\right)^{\beta} \tag{6.1}$$

where *C* is a material-dependent constant and  $\lambda$  is the wavelength of the laser.  $I = \frac{E_{laser}}{At}$  is the laser irradiance and  $\beta$  is the material-dependent exponential (calibrated to be 0.71 for diamond [34], which is similar to our CH ablator). The target package consists of a 20 µm CH ablator, 50 µm Al foil, Ø 3X3 mm cylindrical Ge target and Ti momentum trap. The assembly is encapsulated within a Ti cup. The Al foil has two functions: (1) as a heat shield to minimize the preheating induced by laser irradiation and (2) as a pulse shaper to render the shock pulse on the target surface planar (uniaxial strain state). The laser pulse is nominally a 1ns square pulse of 351 nm (3 omega) laser light. The beam was used without phase plates and defocused to a spot size of 3 mm diameter.

#### 6.2.2 VISAR analysis and impedance matching

Separate VISAR experiments were conducted to measure the particle velocity and further infer the shock pressure. A 532 nm probe laser is reflected from the rear surface of the moving target and then it will pass through collection optics and be routed into two separate streak cameras. Each of them uses a different etalon thickness. The VISAR target is comprised of a 20  $\mu$ m CH ablator, 50  $\mu$ m Al foil, a half-moon Ge sample (100  $\mu$ m thick) and laser-transparent LiF window. This specific geometry of the target allows the measurement of particle velocity of both front and rear surface of the Ge sample, which shows the rapid decay of the shock pressure as function of the depth. A correction factor of 0.775 is applied to the apparent velocity to account for the pressure dependence of the index of refraction of the LiF window. Conservation of mass and momentum give the relationship between the initial density  $\rho_0$  particle velocity  $u_p$ , shock velocity  $u_s$  and shock stress  $\sigma_{33}$ ,

$$\sigma_{33} \approx \rho_0 u_s u_p \tag{6.2}$$

where  $\rho_0 u_s$  is often termed as shock impedance, which can be obtained from the slope of the shock Hugoniot curves ( $\sigma_{33}$  vs.  $u_p$ ) in Fig. 1E of the main text. At the interface between the Al foil and Ge sample, shock wave is reflected and the shock stress changes. The inverted shock Hugoniot of Al (red dotted line in Fig. 1E) gives the estimate of the reflected shock wave and the intersection of this line with Ge curve (black line in Fig. 1E) yield the shock pressure on the front surface of the Ge sample. Such a process is termed as impedance matching [35]. The shock stress at the rear surface of Ge sample can be read directly from the Ge Hugoniot curve.

#### 6.2.3 Radiation-hydrodynamic simulations

Radiation-hydrodynamics simulations were performed using the HYADES code to aid in the design of the experiment and interpretation of the results. The target was modeled as a 1-D stack consisting of 20  $\mu$ m polystyrene ablator, 3  $\mu$ m of glue (approximated as polystyrene), 50  $\mu$ m Al, 3  $\mu$ m glue (polystyrene), and 125  $\mu$ m Ge. In order to simulate VISAR data, an additional layer of glue and LiF were substituted at the corresponding interface (front or back of the Ge). A rate-independent Steinberg-Guinan model was used to model the strength of Al (*36*). The Ge was modeled as elastic-perfectly plastic using the Von Mises yield criterion with Y<sub>VM</sub> = 4 GPa, consistent with observations of the Ge Hugoniot elastic limit.



Figure 6-1 HYADES simulation of shock-wave propagation and decay in Ge: (A) Calibration of the simulation with the experimentally-determined velocity profile at the Ge/LiF interface (rear surface); (B) simulated longitudinal shock stress vs. time profile at different depths below the shock surface, showing the decay of the amplitude of the stress wave as it passes through the material.

#### 6.2.4 TEM sample preparation and observation

Transmission electron microscopy is the ultimate tool to characterize the postmortem microstructure of the shocked target. To prepare TEM samples cite-specifically, a Hitachi NB5000 scanning electron microscope (SEM) equipped with a focus ion beam (FIB) was used to cut TEM samples directly from the laser-shocked germanium monocrystal surface. The TEM foils were ion milled by 30 kV Ga beam and finally polished at 5kV to minimize FIB damage. A Hitachi HF3300 transmission electron microscope operated at 300 kV was employed to characterize the post-shock microstructure. In addition to the results shown in Fig. 6-3 where the Ge target was laser shocked with a high energy ( $E_{laser}$ =100 J,  $\sigma_{33}$ ~33 GPa), Fig. 6-4 shows the microstructure of the Ge target shocked at a low energy ( $E_{laser}$ =20 J,  $\sigma_{33}$ ~10 GPa). The contrast-less feature of the high resolution TEM image suggest the random arrangement of the atoms. The Fourier-transformed diffractograph exhibits a halo-shaped ring pattern, confirming the amorphous nature of the materials.



Figure 6-2 Laser-driven, shock-recovery experimental set-up, velocimetry measurement, and determination of shock stresses: (A) shock-recovery assembly with target package (along the laser path:  $20 \,\mu\text{m}$  CH ablator,  $50 \,\mu\text{m}$  Al pusher and Ø3 X 3mm Ge crystal) encapsulated in Ti and backed by momentum trap (Ti). The assembly is mounted in a recovery tube; (B) VISAR target package is similar to that of the recovery experiment except that a 100  $\mu\text{m}$  thick half-cylindrical Ge foil is used so as to capture the information from both front (Al/LiF) and rare (Ge/LiF) surface of the target. The laser-transparent LiF window is glued to the rear surfaces of Ge target on one side and Al pusher on another side; (C) Temporally resolved VISAR fringes showing the shock break-out at front and rare surfaces of the sample. (D) Measured particle velocity,  $U_p$  as a function of time. (E) Determination of the peak shock stress on the front surface of Ge target by impedance matching. Note that Al and LiF are closely impedance-matched in the regime involved in our study.

## 6.3 Shock-Induced Amorphization and Nanocrystallization

Experiments were performed at Omega laser facility, using a pulsed laser with a nominal square pulse shape (wavelength= 352 nm; laser duration= 1 ns). The nominal laser energy is  $E_{taser}$ =100 J and renders its intensity to be around 1.1 TW/cm<sup>2</sup>. Fig. 6-2A shows schematically the shock-recovery assembly. The high density of laser energy vaporizes the polystyrene (CH) ablator, which drives a compressive wave that eventually propagates into the [001] monocrystalline Ge target. The peak shock stress,  $\sigma_{33}$ =33 GPa, can be inferred

indirectly from the particle velocity ( $u_p$ ) measurement by VISAR (velocity interferometer system for any reflector) experiments (Fig. 6-2B-D) and impedance matching (Fig. 6-2E).



Figure 6-3 TEM/HRTEM micrographs of laser-shock recovered germanium: (A) TEM image shows the hierarchy of the deformation microstructure. (B) Distribution of the grain size in the nanocrystalline domain and (C) amorphous band width and spacing. (D) Zoomed view of nanocrystal. (E) Zoomed view of partially amorphous band with embedded nano-crystals. (F) Zoomed view of a completely amorphous band showing zero contrast inside the band. The corresponding Fourier-transformed diffractions in the boxed regions are shown in the insets. (G) Lattice image in a nanocrystal shows nano-scale twins/stacking faults on {111} planes. The Fourier-filtered image in the red inset reveals the zigzag feature of these planar defects. (H) Amorphous band with stacking faults in its vicinity. (I) Two {111} stacking fault packets intersect, resulting in the early stage of amorphization and two set of twin spots on the diffraction pattern.

Transmission electron microscopy (TEM) was used to inspect the post-shock deformation microstructure. The TEM samples were extracted by focus ion beam cutting from the as-shocked surface and the microstructural hierarchy is displayed in Fig. 6-3A. Along the direction of shock wave propagation (left to right), nanocrystalline material can be observed as deep as  $3 \mu m$  below the shock surface. Statistical analysis (Fig. 6-3B) shows the average grain size is  $62.4\pm31$  nm, whereas much smaller (~10 nm) grains can be seen towards the end of nanocrystalline regime. In addition, profuse nanotwins/stacking faults lying on {111} planes are identified (Fig. 6-3D, G), further subdividing the nanostructure. As one goes deeper, massive deformation bands are observed. It shows that these bands exhibit (Fig. 6-3C) an average width ( $w_{band}$ ) of 25.4+17 nm and interspacing ( $w_{spacing}$ ) of 124.4+63 nm. Fourier-transformed diffraction pattern (inset between Fig. 6-3E and H) in these regions shows a mixture of halo ring and sharp spots, suggesting that these bands are essentially amorphous with nanocrystals embedded. High-resolution TEM reveals the nanocrystalline islands (indicated in Fig. 6-3H) within an amorphous band. In another contrast-free band (Fig. 6-3I), the halo-ring diffraction indicates a complete amorphous structure. These amorphous bands align roughly with {111} planes of the diamond-cubic lattice, which is also close to the maximum shear direction. Most amorphous bands align parallel to each other, albeit other variants can be observed and they tend to intersect and bifurcate, forming a complex network. Dislocations—indicator of plasticity—have not been observed unambiguously by TEM, but identified as the precursor of amorphization in our molecular dynamics simulations (MD).

At a much lower shock stress ( $E_{laser}$  =20 J;  $\sigma_{33}$ =13 GPa), the recovered sample shows bulk amorphization close to the shock surface. The TEM sample (Fig. 6-4) exhibits a completely amorphous state up to 4 µm below the surface without undergoing crystallization.



Figure 6-4 Micrographs of Ge shocked at a lower laser energy (20 J): (A) scanning electron microscopy image of the shocked surface of [001] Ge single crystal. The rectangle indicates the position of the TEM sample cut by focused ion beam technique; (B) SEM image of the TEM sample cross-section; (C) High resolution TEM image shows that the deformed structure is indeed amorphous without long-range order. The amorphous feature can be also confirmed by fast-Fourier transformed diffractography in the bottom-left corner.

To better understand the atomistic mechanisms of amorphization, we have also carried out large-scale MD simulations to mimic laser shock experiments on germanium. The Tersoff [190] interatomic potential was instrumented and executed in the LAMMPS [191] code. MD simulations (Fig. 6-5A) show that amorphization occurs above a critical particle velocity of 1.2 km/s during compression and that the directional features of the amorphous bands agree well with the TEM observation. Interestingly, MD simulations predict massive stacking faults/nanotwin formation before the onset of amorphous banding. 6-5B), suggesting that these planar faults are the precursors of amorphous banding. Moreover, Fig. 6-5C, D illustrate that both amorphous band and stacking fault align with

{111} planes. These stacking faulted areas seem to provide nucleation sites for crystallineto-amorphous transformation and amorphous bands grow at a velocity comparable to shear wave velocity of germanium.



Figure 6-5 Molecular dynamics simulation of partial dislocation propagation and amorphization: (A) 3-D visualization of shocked germanium colored by coordination number. The amorphous bands are colored red. (B) Only the plastically-deformed (defected) atoms are shown, suggesting that the amorphous bands are preceded by partial dislocations (stacking faults). The amorphous band aligns roughly with {111} slip plane. Radial pair distribution functions (inset) distinguish the amorphous domain from crystalline structure. (C-F) Four snapshots showing the evolution of stacking faults and then amorphous bands. (G) Measurement of dislocation/amorphous band speed during shock compression and supersonic burst of dislocation is notified prior to the formation of amorphous band.

## **6.4 Discussion**

#### 6.4.1 Amorphization

Germanium melts with a reduction in volume. Therefore, its melting temperature decreases as pressure increases (dT/dP = -35 K/GPa [192]). By the same token, compressive stresses favor a process such as amorphization where the disordered phase possesses a smaller specific volume than the original crystalline phase, although the amorphous state is energetically less favorable in ambient. In addition, the superposition of shear stress also facilitates amorphization by inducing large lattice displacement [162]. Planar shock compression generates a uniaxial strain condition where the synergy of high amplitude pressures and shear stresses can lead to the crystalline-to-amorphous transition. The shock stress ( $\sigma_{33}$ ), hydrostatic pressure (P) and maximum shear stress ( $\tau_{max}$ ) can be obtained from the generalized Hooke's law for uniaxial strain,  $\sigma_{ij} = C_{ij33}\varepsilon_{33}$  where  $C_{ijkl}$  is the elastic constants and  $\varepsilon_{33}$  is the uniaxial strain and  $x_3$  is the direction of shock wave propagation. Thus, the ratio of  $\tau_{max}$  / P can be expressed as a function of elastic stiffness in voigt notation,

$$\frac{\tau_{\max}}{P} = \frac{3(C_{11} - C_{12})}{2(C_{11} + 2C_{12})}$$
(6.3)

For germanium [193], at ambient pressure,  $C_{11}$ = 129.2 GPa,  $C_{12}$ =47.9 GPa, rendering  $\tau_{max} / P \approx 0.54$ . This is a first approximation since the elastic moduli are pressuredependent as predicted by our MD simulations (Fig. 6-7). Nevertheless, the shear stress is significant before it is relaxed by directional amorphous banding. Applying classical nucleation theory one can obtain the pressure and shear stress dependence of the nucleation barrier, as explained previously by Zhao *et al.*[194],

$$\Delta G_{c-a} = \Delta g_{c-a} \cdot \frac{4}{3} \pi r^3 - \left(P \varepsilon_v + \tau_{\max} \gamma\right) \cdot \frac{4}{3} \pi r^3 + \gamma_{c/a} \cdot 4\pi r^2 \tag{6.4}$$

where  $\Delta G_{c-a}$  is the energy gain of nucleating a spherical amorphous nucleus,  $\Delta g_{c-a} = 14.2$  kJ/mol [195] and  $\gamma_{c/a} = 0.08$  J/m<sup>2</sup> [195] are the volumetric Gibbs free energy barrier and crystalline/amorphous interfacial energy, respectively.  $\varepsilon_v$  and  $\gamma \approx \varepsilon_v \left(1 + w_{spacing} / w_{band}\right)$  are the volumetric and shear strain, which can be obtained by Ge shock-Hugoniot data [52]. The second term on the right-hand side of Eq. 6.4 represents the work done by pressure and shear, which help to overcome the energy barrier and interfacial energy gain of nucleating an amorphous embryo. Such an effect is plotted in Fig. 4A. The monotonically increasing energy curve for zero-stress state (blue) indicates the difficulty of forming amorphous phase at ambient state whereas under shock, the curves (red and yellow) are bended concave-down after passing through a critical condition  $dG_{c-a}/dr = 0$ , corresponding to a critical nucleus size of  $r_c = 2\gamma_{c-a}/(P\varepsilon_v + \tau_{max}\gamma - \Delta g_{c-a})$ .

Shock-generated heat is another important factor in amorphization and subsequent nanocrystallization: (1) the temperature rise at shock front reduces the energy barrier of crystalline-to-amorphous transition; (2) upon further heat transfer, the newly formed amorphous structure can re-transform into energetically more favorable crystalline phase; (3) if the heat is sufficiently high, shock-induced melting may occur; (4) the transient nature of the shock-induced thermal flux results in a self-quenching mechanism which leads to a hierarchical nanostructure.

The increase in temperature due to shock-compression can be evaluated by considering both homogeneous temperature  $(T_{homo})$  resulting from work done by hydrostatic pressure and localized temperature rise  $(T_{local})$  resulting from work done by shear stress. The latter assumes balance between relaxation of deviatoric strain energy and increase in internal energy with heat loss to its surroundings, thus it gives a rough estimation of the temperature inside the amorphous band [184]:

$$T_{local} = T_{homo} + \frac{2\dot{Q}w_{band}}{\sqrt{\pi}} \cdot \sqrt{\frac{t}{k\rho C_p}}$$
(6.5)

where  $\dot{Q} \approx \beta \tau_{\text{max}} \gamma / \Delta t$  is the rate of heat generation by converting deviatoric strain energy,  $\beta$  is the conversion efficiency (usually taken as 0.9),  $\Delta t \sim 1$  ns is the duration of the laser pulse. *k*,  $\rho$ ,  $C_p$  are the heat conductivity, density and heat capacity of the amorphous band, respectively. It should be noted that the shear stress is assumed to be independent of shock stress after Hugoniot elastic limit (HEL~4GPa for Ge [47]) as it well be relaxed by plastic deformation.



Figure 6-6 Thermodynamic analysis of amorphization: (A) Gibbs free energy change associated with nucleation of an amorphous embryo. The presence of shock stress (pressure plus shear) renders it possible to overcome the energy barrier of crystalline-to-amorphous transformation; (B) Pressure-induced homogeneous temperature ( $T_{homo}$ ) and shear-induced localized temperature ( $T_{local}$ ) compared with the decreasing melting temperature ( $T_m$ ) as a function of shock stress (negative Clapeyron slope). The intersections represent the critical shock stresses of crystalline-to-amorphous transition, indicating that shear stress lower the threshold.

Fig. 6-6 shows the plot of shock-induced temperatures together with melting temperature as a function of shock stress. The intersections of  $T_{homo}$  and  $T_{local}$  with  $T_m$  render the critical shock stresses (17.5 GPa for  $T_{homo}$  and 14 GPa for  $T_{local}$ ) for the onset of amorphization. Clearly, the presence of shear stress lowers the threshold for amorphization. These calculations, whose accuracy depends largely on the materials parameters, agree qualitatively with our experimental observations.

## 6.4.2 Supersonic Dislocation

Both our TEM observations and MD simulations show that dislocation (stacking faults) activity occurs prior to the amorphization, suggesting that dislocations are the trigger to the drastic crystalline-to-amorphous transition. Therefore, it is reasonable to infer that the kinetics of dislocation motion determine the kinetics of amorphization. It has been predicated by the theory of linear elasticity that the dislocation velocity is limited by the transverse wave speed ( $C_T$ ) at which the energy associated with the screw dislocation approaches infinity, as shown in Eq. 6.6,

$$\frac{W}{l} = \frac{Gb^2}{4\pi \left(1 - \frac{v_d^2}{C_T^2}\right)^{1/2}} \ln \frac{R}{b}$$
(6.6)

where W is the elastic energy associated with a moving screw dislocation, l is the length and b is the Burgers vector. However, MD simulation by Gumbsch and Gao (25) suggested the existence of supersonic dislocation in tungsten, even above longitudinal sound speed. Gumbsch and Gao (25) proposed that a supersonic dislocation can be obtained if an ultrafast dislocation seed is nucleated at a stress concentrator. An applied stress is required to help the dislocation to overcome the sound barrier. Such a condition can be most-likely achieved in the strong shock experiment where the high stress state (both hydrodynamic and deviatoric components) build up quickly at the shock front. In our MD simulations, supersonic dislocation bursts are identified, as shown in Fig. 6-5, prior to amorphization. The motion of dislocation is non-uniform at this stage and the velocity should be a range instead of a constant. After such a supersonic event, the dislocation velocity quickly falls off when the amorphization is initiated and the motion of dislocation/amorphous band is transonic and uniform. The MD snapshots in Fig. 6-5 show how the partial dislocations nucleate, catch up with the shock front, and eventually give rise to the formation of amorphous bands.



Figure 6-7 (A) Pressure dependency of elastic constant and (B) ratio of maximum shear over pressure (assuming elasticity and no relaxation).

## 6.4.3 Estimation of Sound Speeds and Dislocation Velocity

Travel of acoustic waves in crystal is highly anisotropic and orientation dependent. Germanium is a cubic material and the active slip system is of  $\{111\}<110>$  type. Thus, we need to evaluate the sound speeds along <110> direction to compare them with the dislocation velocity. The corresponding longitudinal sound speed is:

$$C_{L} = \left(\frac{C_{11} + C_{12} + 2C_{44}}{2\rho}\right)^{1/2}$$
(6.7)

The transversal sound speed is polarized in different <110> directions:

$$C_{T \max} = \left(\frac{C_{44}}{\rho}\right)^{1/2}$$

$$C_{T \min} = \left(\frac{C_{11} - C_{12}}{2\rho}\right)^{1/2}$$
(6.8)

It should be noted that the elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{44}$  are a function of pressure, as shown in Fig. 6-7. Thus, the sound speeds also depend on pressure, which are plotted in Fig. 6-8.



Figure 6-8 Pressure dependency of longitudinal sound speed, transverse sound speed (split into two different values due to crystal anisotropy) along <110> slip direction. The intersection of the vertical red dotted line with the black line gives the longitudinal sound speed at the pressure matched with the condition of the MD simulation (roughly agree with experiment as well).

Dislocation velocity ( $V_d$ ) is estimated by tracking the displacement of the defects in time. Multiple snapshots with 1 ps spacing (in MD time) are used and the effective defect length is measured from each snapshot. It should be noted that the motion/growth of these defects are not strictly limited in one particular direction and we also notice the lateral growth of the stacking faults/amorphous bands, suggesting the activation of stacking faults in the adjacent slip planes. Due to these complexities, the defect velocity was measured several times to minimize the errors caused by the uncertainty of the defect length. Despite of the error bars, our measurements show that the partial dislocations nucleate with an ultrafast velocity ( $V_d \sim C_T$ ) right after the shock front passed by. Shortly after their nucleation, the dislocations are still under extremely high stresses and they quickly accelerate to the supersonic ( $V_d > C_L$ ) regime. However, the motion of supersonic dislocations is not steady state, i.e. the velocity should be a range instead of a number. After such an explosive motion/growth, their velocity falls to the transonic regime  $(C_L > V_d > C_T)$ . The supersonic dislocations seem to trigger the amorphization which helps to relax the concentrated deviatoric stress.

In summary, we have shown that germanium undergoes shock-induced amorphization and nanocrystallization under extreme deformation. Although it is difficult, at this stage, to conclude whether these processes are solid-state or the results from melting and quenching, the presence of shear stress is definitely crucial, which enhances the understanding of pressure-induced amorphization and polyamorphisms [136,196,197]. Shock-induced amorphization has been discovered in a variety of materials [66,162,184] and hence should be incorporated in the deformation-mechanism paradigm. More practically, our results suggest high-power, pulsed laser as a new tool to quickly produce substrate-free, micrometer-scale, bulk nanocrystalline and amorphous semiconductors.

### 6.5 Summary of the Chapter

Gradient nanostructures attract renewed interest for their potential to obtain superior structural and functional properties of materials. Applying powerful laser-driven shocks (stresses of up to one-third million atmospheres, or 33 Gigapascals) to germanium, here we report a complex gradient nanostructure consisting, near the surface, of nanocrystals with high density of nanotwins. Beyond there, the structure exhibits arrays of amorphous bands which are preceded by planar defects such as stacking faults (partial dislocations). At a lower stress, the surface region of the recovered target is completely amorphous. It is proposed that germanium undergoes amorphization above a threshold stress and that the deformation-generated heat leads to nanocrystallization. These experiments are corroborated by molecular dynamics simulations which show that supersonic partial dislocation bursts play a role in triggering the crystalline-to-amorphous transition.

Amorphization and nanocrystallization are two powerful methods to tailor material properties by altering their microstructure without changing the overall chemistry. Using powerful laser-driven shocks, we demonstrate that amorphization and nanocrystallization can be achieved within a time scale that is considerably shorter than other conventional techniques. Our results provide compelling insights into pressure/shear amorphization and propose a novel route to fabricate gradient semiconducting nanostructures using lasers. Additionally, shear-driven amorphization is demonstrated as deformation mechanism in this extreme regime.

Chapter 6, in part, is a reprint of the material as it appears in "*Generating Gradient Germanium Nanostructures by Shock-induced Amorphization and Crystallization*" Proc. Nat. Acad. Sci. U.S.A. 2017, 114: 9791-9796. This work was coauthored by S. Zhao, B. Kad, C.E. Wehrenberg, B.A. Remington, E.N. Hahn, K.L. More, M.A. Meyers. The dissertation author is the first author of this work.

# Chapter 7 Laser Shock Compression of Silicon Carbide

Silicon carbide has been predicted to undergo amorphization under extreme pressurization. However, the microstructure evidence of such a drastic structural change is lacking since its brittleness prevents the successful recovery of SiC. In this chapter, we report on pulsed laser-driven shock-induced localized amorphization in SiC at a shock stress of approximately 50 GPa. The ultrashort (tens of nanosecond) loading duration preserves the integrity of the target. Postmortem transmission electron microscopy reveals that the amorphous regimes are extremely localized and are either inclined or horizontal to the direction of shock wave propagation which coincides with the c axis ([0001]) of the crystal. Large scale non-equilibrium molecular dynamic simulations elucidate such a process and suggest that the plasticity on the basal plane may be the precursor of the horizontal amorphization whereas the high amplitude shear stresses are effectively relaxed by the formation of inclined amorphous SiC. Our results provide rationales to the previous reports on the post-yield hardening/softening of SiC subjected to shock loading.



Figure 7-1 Schematics of laser shock recovery experiment (A) and VISAR experiment (B) and post-shot analysis (C-E)

To probe the evidence of phase transition, we performed laser shock recovery experiment at Janus Laser Facility, Lawrence Livermore National Laboratory. The Janus laser can generate large amplitude stress pulses with nanosecond duration, sufficient to shock silicon carbide above its phase transition threshold and to prevent it from shattering under shock compression and release. The  $2\Omega$  laser (~50 J) has a nominal square pulse shape with duration of 3 ns, resulting in a pulse power of 1.67 TW/cm<sup>2</sup>. Such a high energy density was deposited onto a target package which is comprised of an aluminum foil (200  $\mu$ m) placed in front of a [0001] orientated SiC crystal (3mm in diameter and 1mm in height, Fig. 7-1A). The ionization of the Al foil provides the high pressure which drives the shock wave into SiC. Copper capsule and momentum trap are used to capture the reflected tensile

stress waves. The peak shock pressure (~50 GPa) can be determined by a separate VISAR experiment (Fig. 7-1B-D) and subsequent impedance matching (Fig. 7-1E)[123].



Figure 7-2 HETEM images of the (A) horizontal amorphous bands and (B) inclined amorphous band in shock recovered SiC.

High resolution transmission electron microscopy (TEM) revealed the post-shock microstructure. Focus ion beam was used to lift-out the TEM sample from the target surface so that the observation is right below the shock surface where it experienced the peak shock stress. Localized amorphous bands (marked as a-SiC), with a thickness as wide as 5 nm, can be identified. These bands can either horizontal (Fig. 7-2A) or inclined (Fig. 7-2B) with respect to the direction of shock wave propagation, which is in consistent with the c axis of the crystal. For the inclined amorphous band, there seem to be some lattice shifts in the vicinity of the band as shown in the inverse Fourier transformation diagram in Fig. 7-2C, suggesting this regime has undergone drastic shear deformation. Graphic phase analysis (GPA) in Fig. 7-2D confirms that the in-plane shear strain is localized within the

amorphous band. The inclined amorphous band shows a very similar morphology to the ones previously reported in Si, Ge, and  $B_4C$ . However, the horizontal amorphous band is unexpected since the shear effect in the basal plane should be minimal, indicating that the longitudinal shock stress plays a vital role in such a process. Note that these amorphous bands are usually contagious with nanocracks, suggesting that amorphization may be associated with the failure of SiC subjected to shock compression. Another note is that there are more horizontal bands than the inclined ones, based on the observation from three different TEM samples, although they are both scarce.



Figure 7-3 HRTEM images of (A) horizontal planar fault and (B) directional planer fault.

In addition to the two types of amorphous bands, planar faults have been identified as well, which is likely to be the precursors to the amorphization. Fig. 7-3A illustrates the planar faults (indicated by the red triangles and magnified in the inset on the upper right corner) on the (0001) plane, i.e. the basal plane of the SiC. Fig. 7-3B depicts another set of planar faults lying on the (-211-4) planes. The lattice distortion caused by the planar faults is shown clearly in the inverse Fourier transformed diagram in the upper right inset of Fig. 7-3B.

It can be postulated that the shock-induced amorphization in SiC is a synergy of longitudinal shock stress and shear stress. The passage of strong shock wave plastically deforms the crystalline lattice and introduces anisotropic defects such as planar faults, which may harden the materials after HEL. Upon subsequent increment of the loading, the materials will undergo amorphization. The formation of horizontal amorphous band does not contribute to the relaxation of deviatoric stress. However, it has been reported that the amorphous SiC is much more compliant than its crystalline counterpart [198]. Thus, a decrease in its loading sustainability is expected if horizontal amorphization occurs in SiC. In contrast, the inclined amorphous banding is a result of shear localization which corresponds to the softening of the materials. During the release procedure, both horizontal and inclined amorphous bands are more prone to failure, as they create interfaces inside the crystals, which is preferred cites for crack to nucleate and opening when subjected to tensile wave. This explains that the amorphous domains are usually close to the cracks.

Chapter 7, in part is being prepared for publication of the materials. S. Zhao, R. Flanagan, E.N. Hahn, C.E. Wehrenberg, B.A. Remington, M.A. Meyers will be the coauthors. The dissertation author is going to be the first author of this work.

# Chapter 8 Conclusions and Perspectives

Laser-driven shock compression is a powerful tool to probe the deformation mechanisms of solids under extreme regimes of pressures, strain rates, and temperatures. The stress pulse generated by the nanosecond laser is so short that the ultrahigh strain-rate  $(10^{7}/\text{s}\sim10^{8}/\text{s})$  cannot be obtained by any other techniques, yielding new physics in this yet unexplored regime. It has been demonstrated in the previous chapters that four different covalently bonded solids, namely, silicon, germanium, boron carbide, and silicon carbide undergo laser driven, shock-induced amorphization. The major achievements of this dissertation and future perspectives are summarized in this chapter.

## 8.1 Shock-Induced Amorphization as a New Deformation Mechanism

When crystalline solids are stressed, dislocation slip, twinning and phase transformations are the predominant mechanisms to dissipate the imparted elastic energy. These mechanisms are usually triggered by critical stresses and have distinct characteristic time scales, as shown in Fig. 8-1. Dislocation mediated plasticity is usually considered sluggish and therefore is the most important deformation mechanism under the quasi-static loading condition. The critical shear stress (usually the Peierls-Nabarro stress) for the onset of dislocation slip increases with strain rate since the process is thermally activated. Mechanical twinning is independent to strain rate and has a relatively faster kinetics. Thus, it is more favorable under higher strain rate affnd at higher stress states, as evidenced by the observation of slip-twinning transition in many metals subjected to dynamic loading [155]. For some materials such as iron [199–201], phase transformations may occur under either static or dynamic loading. Under shock compression, high hydrostatic and shear stresses

promptly build up at shock front, favoring fast energy dissipation mechanisms. Amorphization, which only involves localized atomic arrangements, is therefore an additional potential deformation mechanism. Shock-induced amorphization has now been reported in various materials and hence should be incorporated as a deformation/damage mechanism of crystals subjected to high-strain-rate loading.



Figure 8-1 Deformation mechanisms as a function of shock stress and strain rate. It should be noted that the boundaries between each domain are strongly materials dependent.

Covalently bonded solids usually have high strength (high bond strength), yet they are intrinsically brittle due to the difficulty to activate slip systems. Since the directional nature of the covalent bonds results in large burgers vector and narrow dislocation width, leading to very high Peierls-Nabarro stresses, as listed in the table 8.1.

	Fe	Cu	Si	Ge	B4C	SiC
$ au_{P-N}$ / MPa	390	0.28	4640	4440	-	19760
$rac{ au_{P-N}}{G}$	5.2x10 <sup>-4</sup>	7x10 <sup>-6</sup>	0.0767	0.0908	-	0.117

Table 8-1 Peierls-Nabarro stress of the four covalently bonded materials and their comparison with Fe and Cu [202].

It can be seen from Table 8-1 that the Peierls-Nabarro stress for covalently bonded solids are orders of magnitude higher than metals such as Fe (bcc) and Cu (fcc). The dislocation is therefore much harder to move in these materials. As such, they fail catastrophically immediately after yielding by crack nucleation, propagation and intersection. Fracture seems to be the only route for these materials to release the energy when subjected to external loading. However, what if the cracking can be suppressed? Early dynamic fracture mechanics studies suggest that the rate of a crack propagation is limited by the Rayleigh wave speed [67,203,204], which is in the order of a few km/s. Our target is in the millimeter scale and the shock velocity is in the order of km/s, so the characteristic time scale for a newly nucleated crack to propagate through the sample is t  $\sim \frac{1mm}{1km/s} = 1 \ \mu s$ , which is significantly longer than the pulse duration of the stress wave that generated by a nanosecond laser. Thus, the crack propagation and interaction can be largely moderated, which allows the stress, especially the deviatoric stress to build up in the materials, promoting other energy release mechanisms.

We have demonstrated that shock-induced amorphization has become a dominant

deformation mechanism in this regime. The occurrence of amorphization somehow inhibits massive cracking. For Si and Ge, both a bulk amorphous layer adjacent to the surface and amorphous bands penetrating the crystal were observed. The amorphous material has the characteristic featureless appearance and displays a halo-shaped diffraction pattern with an absence of spots or sharp rings. The fraction of material amorphized increases as the laser energy rises, i.e. the surface layer becomes thicker (from 100 nm to 1µm) and sub-surface bands broader. The 'islands' of crystalline material isolated between the intersecting amorphous bands are smaller near the surface. The bands appear to be crystallographically aligned and multiple variants are to be expected. Numerous secondary feather-shaped bifurcations originating from the primary amorphous bands are observed. High resolution TEM micrographs reveal the early stage of the amorphous band formation and penetration into the crystalline lattice, indicating that the bands initiate from {111} planes. Abundant {111} stacking faults and/or nano-twinning can be clearly identified in the vicinity of the amorphous band, exhibiting a zigzag configuration. The amorphous bands show an asymmetric growth: the top part of the band is aligned with specific slip plane, whereas the bottom bounding surface is misaligned. This is because the slip planes and surfaces of maximum shear are not coincident. The amorphous band is still in its growth stage, where the staking faults terminate at different depths. Multiple high-resolution TEM observations indicate that amorphous bands initiate preferentially when two different sets of stackingfault variants intersect; the amorphous bands will grow in a direction that reasonably aligns with the predominant stacking-fault variant (not necessarily coincident with the plane of maximum shear).

For B<sub>4</sub>C and SiC, no surface amorphous layer has been observed in the current

investigation. However, the amorphous bands have been identified in both carbides. These bands are usually extremely narrow (<10 nm), suggesting that the deformation is highly localized. Besides, these lenticular amorphous bands are contiguous to the nanoscale crack in the materials, suggesting a transition from fracture to amorphization. In silicon carbide, some amorphous bands are horizontal to the direction of shock wave propagation, which may be due to the tensile waves generated by release. The absence of bulk amorphous layer is probably due to the fact that the amplitude of the shock wave in the current study is not sufficiently high to melt the surface.

The observation of the amorphization pattern in the laser shock-recovered sample reveals a new deformation mechanism that can only be activated at high strain rate. The critical stress for the onset of amorphization scales with the dynamic strength (HEL) of the materials. Such a mechanism is of great significance in understanding matters under extreme loading conditions and is potentially a new method to fabricate amorphous materials by laser-driven, shock loading.

## 8.2 Influence of Shear Stress on Amorphization

It is shown in this thesis that shear stress play a crucial role triggering the crystalline-to-amorphous transition. Shear manifests itself in three possible ways: (1) shear strains cause massive inelastic lattice displacement that can lead to the loss of long-range order; (2) non-hydrodynamic stresses lower the melting temperature of materials significantly as the work done by shear stress provides the driving force for "Virtual Melting"[185]; (3) shear-induced plasticity causes localized heating which lead to localized thermal softening and reduce the mechanical barrier for amorphization. Specifically, the resolved shear stress on slip planes leads to the formation of stacking-

faults in Si and Ge, which is the precursor to the amorphization.

The deviatoric stress is quite significant under shock compression up until the HEL, after which it will be relaxed by the directional amorphization. Since the initial material is crystalline, stress is a tensor and anisotropy plays a very important role, especially in determining the path of the amorphization. The elastic moduli and the related parameters of the materials studied in this investigation is given in Table 8-1.

	Si [104] Diamond Cubic	Ge [193] Diamond Cubic	B <sub>4</sub> C [55] Rhombohedral	SiC [205] 4H
C <sub>11</sub>	165.6	129.2	542.8	507
C33			534.5	547
C <sub>44</sub>	79.5	64.0	164.8	159
C <sub>12</sub>	63.9	47.9	130.6	108
C <sub>13</sub>	—	—	63.5	—
$\frac{\tau max/P}{3(C_{11}-C_{12})/2(C_{11}+2C_{12})} \\ 3(C_{33}-C_{13})/2(C_{33}+2C_{13})$	0.52	0.54	1	0.86

Table 8-2 Elastic moduli and ratio of maximum shear over pressure of the studied materials.

It should be noted that the elastic moduli depend largely on hydrostatic pressure. Another factor that affect the magnitude of the shear stress is the strain rate dependence of the Huginiot elastic limit (HEL). The higher the strain rate, the higher the HEL, and therefore the higher the actual shear stress. All the materials studied in this thesis are covalently bonded, and have a higher HEL (and shear stress) than metals. Dislocationmediated plasticity and twinning are usually inhibited in these materials and the large shear stress needs to be relaxed by a new mechanism, i.e. shear-driven directional amorphization.

### 8.3 Influence of Shock-induced Temperature Rise on Amorphization

The temperature rise at the shock front is another crucial factor for amorphization. When materials undergo shock compression, their volume decreases, and consequently large work is imposed to the system. Therefore, the work is dissipated as heat and the temperature at the shock front is increased. It is natural to conjecture that melting can occur at the shock front if the temperature rise exceeds the thermodynamic melting point of the materials. The negative Clapeyron slope for silicon, germanium, and boron carbide leads to the decrease in melting point with hydrostatic pressure (Fig. 8-2 (a)), whereas the majority of materials exhibits an opposite trend (Fig. 8-2 (b)). Therefore, it is easier for materials with negative Clapeyron slope to undergo shock-induced melting and amorphization.



Figure 8-2 Phase diagram of materials with negative Clapeyron slope (a) and positive Clapeyron slope (b). Blue lines are the melting curves and red lines denote the shock Hugoniot. The intersection of the shock Hugoniot with the melting curve result in shock-induced melting and a plateau.

In silicon, germanium and boron carbide, the experimentally observed amorphization occurs at a pressure lower than the predicted "melting pressure", which is consistent with early estimate by Nesterenko [51]. Since the pressure is not sufficient to generate melting, shear induced local effects must be playing an important role, as explained in the previous section 8.2.

## **8.4 Perspectives**

Powerful laser-driven shock compression experiments have made it possible to probe the unexplored regimes in the pressure-temperature-time space. We have shown that crystalline-to-amorphous transition is a new route to relax the stress in these extremes, enabling many new and exciting scientific questions to be answered:

(1) Does amorphization take place during loading or release?

Whether amorphization takes place under shock loading or release is still under debate. Can we settle this by time resolved X-ray diffraction during shock compression experiments?

- (2) Can we avoid or prevent the crystalline-to-amorphous transition in these materials? Will carefully designed pulse shape affect the recovered microstructure? For instance, ramp compression can be used to "gradually" load the sample to a similar stress state without raising the temperature significantly (quasi-isentropic compression), yielding new path-dependent phenomena (crystalline-to-crystalline phase transitions, dislocation/twinning mediated plasticity, fracture).
- (3) Do amorphous and nanogradient materials acquire unique physical properties? How does grain refinement and amorphization affect the mechanical behavior of covalently bonded materials? Can we develop a powerful laser ablation based technology to make new materials without altering the overall chemistry?
- (4) Is there any polyamorphization? Will the materials undergo low density amorphous-to-high density amorphous phase transition during pressurization (or the reverse transition during stress release)?

(5) Will other covalently bonded materials show the similar feature of shear driven direction amorphization? Is there any generalized law that determine such behavior?

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