Effect of shock compression on single crystalline silicon

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Abstract. A series of shock-recovery experiments were performed on single crystals of silicon and germanium using a propellant gun and the laser-driven miniflyer method. Characterizations of the recovered samples by X-ray diffraction (XRD) analysis and Raman spectroscopy revealed the absence of additional constituents such as metastable phases and high-pressure phases. The XRD patterns for shocked samples are consistent with a powder XRD pattern corresponding to the cubic-diamond phase. The formation of copper silicide (Cu₃Si) was confirmed in the sample shocked at 38 GPa. The formation of an additional band and the deviation of a center frequency peak from the cubic-diamond phase of silicon and germanium were evident in the Raman spectroscopy results. The results of XRD and Raman spectroscopy indicated that crystalline size reduction, rather than the formation of metastable phases, occurred.

1. Introduction
Revealing high-pressure crystal structures and the related phase transitions is a challenging task. The phase diagram of silicon has been revised on many occasions. Upon compression at a pressure of 11-12 GPa, the cubic-diamond structure of silicon (Si-I) undergoes a phase transition to a metallic β-tin structure (Si-II) [1, 2]. Upon further compression, silicon is transformed, via the Imma phase, to a simple hexagonal structure. When the pressure is reduced, the Si-II phase of silicon typically does not return to the Si-I phase but tends to transform to other metastable phases. A rhombohedral structure (Si-XII) and a body-centered-cubic structure (Si-III) are formed upon pressure release at approximately 9 and 2 GPa, respectively, while two tetragonal phases (Si-VIII, Si-IX) are obtained upon rapid pressure release [3]. Germanium undergoes similar phase transitions under pressure loading and unloading [1].

Under shock loading, silicon undergoes a phase transition to high-pressure phases at approximately 13 GPa [4-6]. It has been shown that the onset pressure of metallization is approximately 10 GPa and that shock-compressed silicon is highly defective and far from equilibrium [7]. In particular, no phase transitions have yet been observed in experiments on laser-induced shock compression [8-10]. Shock recovery experiments on Si [11] and Si and Ge [12] have been performed. No metastable or high-pressure phases were clearly obtained from the shock-recovered samples.

In a recent study, silicon shocked to 16-22 GPa appeared to fully transform to a high-pressure phase [13]. In contrast to earlier studies, the compression of silicon was greater than that
previously reported for silicon shocked to similar pressures. Furthermore, metastable Si-III and a high-pressure phase of silicon produced by ultrafast laser irradiation have been found using synchrotron X-ray diffraction (XRD) and electron diffraction [14]. However, no other studies on germanium have been performed by the shock-recovery method and only X-ray analysis has been used to characterize the recovered samples. A more elaborate study is needed to discuss the behavior of silicon and germanium under shock loading.

In this paper, we report the characterization of shock-recovered monocrystalline silicon and germanium. We present the results of investigating samples by XRD and Raman spectroscopy.

2. Experimental
A target assembly placed in an evacuated chamber was composed of a sample sandwiched between two copper plates of 1.0 mm and 40 mm side lengths, a mild-steel holder, and a momentum trap [11, 15]. The samples used were Si(100) and Ge (100) plates of 1.0 mm thickness. A 30-mm-diameter copper or tungsten plate of 1.5 or 3.0 mm thickness was accelerated toward the target assembly. The shock pressure and temperature were estimated by computer simulation using a two-dimensional hydrocode, AUTODYN®-2D (Century Dynamics Inc.).

Additionally, a shock-recovery experiment was performed on silicon by the laser-driven miniflyer method. The flyer plate used was mounted on a 3.0-mm-thick, 19-mm-diameter BK7 substrate that was coated with a thin-film composite of carbon, aluminum oxide, and aluminum. Copper foil of 25 μm thickness and 3.2 mm diameter was glued to the substrate using a low-viscosity epoxy. A piece of silicon wafer with (100) orientation, and 370 μm thickness backed with a BK7 substrate of 3.0 mm thickness was placed at a distance of 225 μm from the flyer. A laser beam with 1064 nm wavelength generated by a 3J Nd:YAG laser was focused on to the substrate to a spot diameter of 3.2 mm. An 8 mm aperture was used to form a pseudo-top-hat beam. The intensity of the laser beam before irradiating the substrate was 1.07 J and the estimated flyer velocity was 650 m/s. According to the simulation, a peak pressure of 7.4 GPa was generated by the impact of the laser-driven miniflyer on silicon.

The crystal structures of the recovered samples were studied by XRD using a Rigaku RINT-2200 diffractometer with CuKα radiation. θ–2θ scans were taken between 25° and 110° at 0.02° steps. Raman spectra were measured using a JASCO NR-1800 microscopic Raman spectrometer equipped with a charge-coupled device. All measurements were performed at room temperature.

3. Results and Discussion
Representative XRD patterns of the Si and Ge plates shocked at various pressures are shown in Fig. 1. Powder XRD patterns corresponding to the cubic-diamond phase of Si and Ge were obtained. This indicates that shock loading leads to polycrystallization. There are no obvious peaks derived from high-pressure phases or metastable phases in the XRD patterns. Both Si and Ge, the widths of the peaks for the shocked sample are broader than those of the unshocked sample. The XRD data obtained from the Si sample shocked at 38 GPa show that copper silicide (Cu3Si) is formed [16]. Only the strongest line of Cu3Si is observed.

In the XRD patterns of the Si sample shocked at 11 GPa, although the 400 reflection at 2θ = 69° is still the strongest peak, the other reflections are consistent with the peaks of the Si-I phase. Unlike the XRD patterns of the other shots, an additional unknown peak appears at 2θ = 33° in the XRD patterns of the Si sample shocked at 11 GPa. One possible explanation for this peak is that it corresponds to the 200 reflection of the Si-I phase. Because X-ray reflections from a perfect crystal are governed by the dynamical diffraction theory, the 200 reflection, which is not observed in the powder X-ray diffraction of the Si-I phase, can be observed in the XRD pattern of a mostly perfect Si crystal. Another possible explanation is that the additional peak can be identified as the metastable phases of Si such as Si-III and/or Si-IX. Because the additional peak is much broader than the 400 reflection at 2θ = 69° (width β=0.29 for peak at
$2\theta = 69^\circ, \beta = 1.15$ for peak at $2\theta = 33^\circ$), it may indicate that tiny crystallites of a metastable phase are formed.

![Figure 1. XRD patterns of recovered samples. Si-I (♦), Ge-I (■), Cu$_3$Si (○), and Cu (△).](image1)

![Figure 2. Raman spectra of pristine and shocked samples. a) Silicon and b) germanium.](image2)

The observed Raman bands of the shocked Si and Ge samples are shifted to a lower wavenumber side and divided into two components: the main peak and an asymmetric broad band (Fig. 2). For example, the spectrum for Si shocked at the pressure of 13 GPa shows a Raman peak at 519 cm$^{-1}$ and an additional band at 507 cm$^{-1}$. The Raman peak of the shocked Ge is centered at 295 cm$^{-1}$ and an additional weak component at 287 cm$^{-1}$ appears. The additional band may be attributed to a nanocrystalline [17] and/or the metastable phase. Because no other peaks corresponding to the metastable phases are shown in any shocked sample, it is inferred that small crystals are the dominant product under the shock-loading conditions in the present study.

On the XRD pattern of silicon impacted by the laser-driven miniflyer, only the broadened peak for the 400 reflection is observed. Also, no additional peaks appeared in the Raman spectra of flyer-impacted silicon. These results indicate that the formation of metastable phases and the polycrystallization were not induced by miniflyer impact.

In a shock-recovering experiment, the effects of uniaxial and radial release waves and multiple shock loadings on a sample should be considered. These waves may cause complex deformation, including shear and tensile deformation, and these effects are superimposed on the result originating from uniaxial shock loading on a sample. These waves may have an appreciable effect on the polycrystallization of silicon and germanium. However, polycrystallization is not confirmed for silicon impacted by the laser-driven miniflyer. The poor polycrystallization may imply that the release waves cannot be attributed mainly to polycrystallization. It is suggested that the reasons behind the poorly polycrystallization are the shortness of the duration of shock loading by miniflyer impact and the lowness of the peak pressure generated on the sample.
4. Summary
A series of shock-recovery experiments were performed on Si and Ge using a propellant gun and the laser-driven miniflyer method. The XRD patterns and the Raman spectra of the shocked samples revealed the absence of unquestionable proof of the existence of additional constituents such as metastable phases and high-pressure phases of Si and Ge. The Raman spectrum and XRD pattern of each shocked sample indicate a decreasing crystalline size of the cubic-diamond phase rather than the formation of metastable phases.

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