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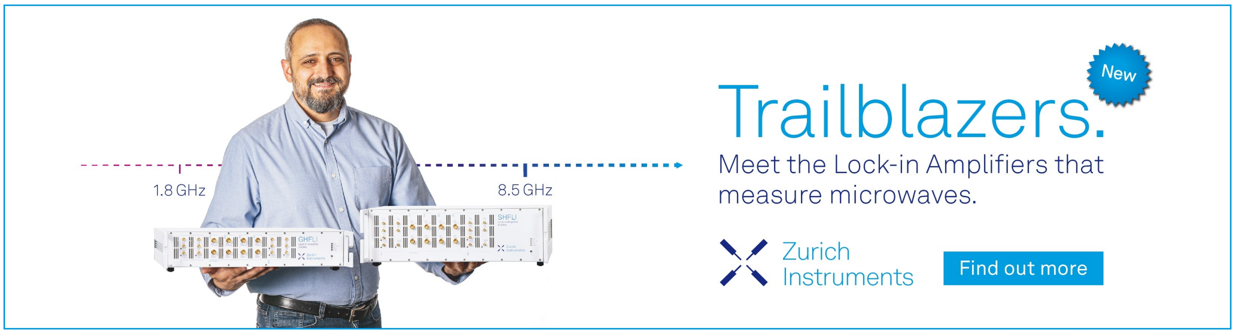

Synthesis of submicron metastable phase of silicon using femtosecond laser-driven shock wave

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We measured the grain size of metastable phase of Si synthesized by shock compression. We analyzed the crystalline structures of the femtosecond laser-driven shock compressed silicon with x-ray diffraction measurements. We found that submicron grains of metastable Si-VIII exist in the silicon. We suggest that the pressure loading time is too short for the nucleated high-pressure phases to grow in case of the femtosecond laser-driven shock compression, therefore Si-VIII grains of submicron size are obtained. We are expecting to discover other unique crystalline structures induced by the femtosecond laser-driven shock wave. © *2011 American Institute of Physics*. [doi:10.1063/1.3673591]

Silicon is one of the most important elements in the field of not only electronic industry but geoscience because it has some high-pressure phases and metastable phases formed during pressure-release. Silicon, which has a diamond type structure at atmospheric pressure, has various allotrope generated by pressure loading.[1–16] The phase transitions of silicon have been studied for around half a century.[1,2,17] There are two kinds of allotropes in silicon. One is the high-pressure phases, which are stable only under pressure, and do not remain after pressure release. The other is metastable phases generated by pressure unloading. The former has six phases which have β-Sn,[1,2] orthorhombic (*Imma*),[4,5,10,11] simple hexagonal,[3,7] orthorhombic (*Cmca*),[3] HCP,[3,8,9] and FCC (Refs. 8 and 9) structures. These high-pressure phases are metallic, unlike the semiconducting diamond type phase.[17] The metastable phases are BC8 (Si-III),[1] R8 (Si-XII),[12,14] Si-VIII,[6] and Si-IX.[6] The β-Sn structure transforms to R8 and BC8 sequentially under slow decompression in the statically compressed silicon.[1,12,14] Both the Si-VIII and the Si-IX are obtained following rapid release of pressure after static compression.[6] The Si-VIII phase is generated after compression to 14.8 GPa where the simple hexagonal structure is stable followed by rapid release of pressure. Si-IX phase is obtained by rapid pressure release after being held at 12.0 GPa for 1 h.[6] The diamond structure of silicon is a semiconductor with an indirect bandgap, while the metastable BC8 structure was predicted to be a semimetal,[18,19] which implies a potential for new technological applications. However, properties of metastable structures have not been cleared experimentally because of its experimental difficulties, therefore simple-creation of metastable structures is important for characterizing their materials' properties.

Semiconductor Si is ablated by irradiation with a femtosecond laser pulse.[20] The recoil impulse force during the ablation drives a mechanical shock wave.[21–24] The effects of the shock wave spread further than the laser induced thermal wave.[21] The temperature rises because of the entropy increase caused by the shock compression in the shock affected region, however the surroundings absorb the heat rapidly in the case of focused femtosecond laser irradiation.[25,26] Furthermore, the femtosecond laser-driven shock wave has a different characteristic from the conventional shock wave such as the compressions induced by flyer impact and longer pulsed laser. The pressure rises sharply over a few picoseconds and decreases quickly over tens of picoseconds.[22,27–29]

Therefore, we expect that there is not enough time for the crystalline grains associated with the high-pressure phases to grow and the grains that do exist grow as dispersed microcrystals because the pressure loading time is ultrashort. The purpose of this study is to investigate the effect of the femtosecond laser-driven shock wave on the synthesis of the

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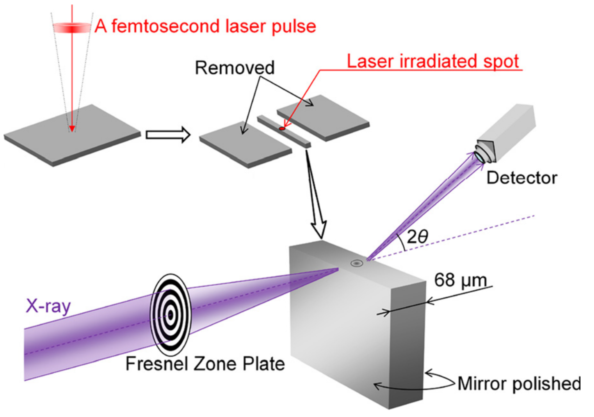

FIG. 1. (Color online) Schematic of the procedure for sample preparation and geometry of the XRD measurements. A femtosecond laser pulse irradiated the silicon surface. The spot was measured by the XRD after the sample preparation.

crystalline grains through measurement of the crystalline grain size of the metastable Si-VIII phase which is generated by the pressure induced phase.

A femtosecond (TSA, Spectra-Physics Inc.) laser pulse with near Gaussian profile was irradiated onto (100) plane of a single crystal silicon chip with purity of 99.999999999% in air at room temperature. The laser wavelength was 800 nm, the pulse width was 130 fs, and the pulse energy was 6.3 mJ. The diameter of the irradiated spot was around 70 μm and the corresponding average laser intensity was 1.3×10^{15} W/cm^2. A schematic of the procedure for sample preparation and geometry of the XRD measurements is shown in Fig. 1. Both sides of the sample for the measurements were removed. Then the cross sections perpendicular to the sample surface were mirror-finished. The thickness of the sample was approximately 68 μm. The polishing processes do not influence the crystalline structures, which are transformed by the shock loading, because the distance between the shock affected region and the polished surfaces has tens of μm. We performed transmission x-ray diffraction measurements in order to investigate the synthesized structures using an x-ray wavelength of 1.240 Å at a beam line for surface and interface structures, BL13XU of SPring-8.[30] The x-ray is focused vertically to 0.7 μm and horizontally to 1.5 μm using a Fresnel zone plate[31] and perpendicularly injected onto the cross section of a laser irradiated spot. The x-ray penetrates the sample because the x-ray attenuation length in silicon is 134 μm. We first performed the measurements at each Bragg angle of the metastable Si-VIII phase, and secondly analyzed the crystalline grain size and the distribution for the observed diffractions in the measurements.

The XRD measurements by varying the detector angle 2θ as shown in Fig. 1 were carried out at several tens of points under the laser irradiated spot. As a result of repetitive measurements, one diffraction peak satisfying Bragg's law was detected as shown in Fig. 2(a). We confirmed that the peak agrees well with the (423) plane of the metastable Si-VIII phase which is formed from high-pressure phases under pressure release. The peak is approximated with Lorentz distribution to estimate the grain size from the full width at half maximum (FWHM) and the fitted curve is shown in

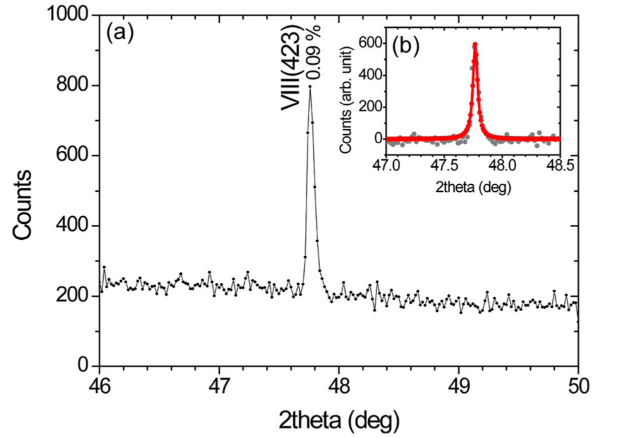

FIG. 2. (Color online) (a) XRD pattern obtained by varying the detector angle with keeping constant the incident angle. X-ray exposure time is 10 s/step. Percentage attached to diffraction indicates difference between observed and theoretical d-spacings. (b) The curve indicates the Lorentzian profile.

Fig. 2(b). The grain size, D, of the synthesized Si-VIII phase is estimated using Scherrer's equation which is expressed as $D = K\lambda/\beta\cos\theta$, where K is a constant equal to 1.107, λ is the x-ray wavelength, β is the FWHM of the diffraction peak, and θ is the diffraction angle. The grain size based on this estimation is 243 nm.

The distribution of the Si-VIII structures was investigated with two-dimensional XRD mapping at a detector angle of 47.76°, at which the diffraction of the Si-VIII (423) plane was obtained. The mapping result is shown in Fig. 3. Several parts of the red colored areas correspond to regions where the diffraction of the Si-VIII (423) plane was observed. The grain, which is estimated as 243 nm using Scherrer's equation, is detected from larger area than the actual grain size using the x-ray beam with diameters of 0.7 μm in vertical and 1.5 μm in horizontal directions. As a

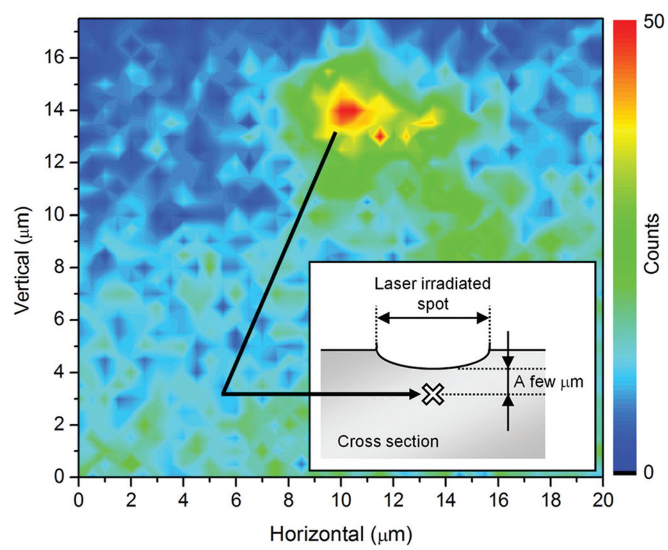

FIG. 3. (Color) 2 D-XRD mapping result fixing the detector angle to 47.76 degree which corresponds to the Bragg angle of Si-VIII (423). A schematic illustration of the measured region is shown in the inset. The Si-VIII phase exists in the red-colored area. The Si-VIII grain exists at a depth of a few microns from the laser irradiated surface. A distance of each point of measurements is 0.5 μm vertically and horizontally.

result of comparison between the two-dimensional XRD mapping of the Si-VIII phase and the sample figure, the grains appear to exist at a depth of a few microns from the laser irradiated surface as shown in the schematic illustration in Fig. 3. The region is affected only by the shock, and without the thermal wave induced by the laser itself. Any other diffractions of Si-VIII structure were not observed by varying the detector angle. Therefore there are no more Si-VIII grains with different orientations in the surroundings of the Si-VIII grains observed in Fig. 3.

We suggest that crystalline grains as small as submicron size are generated because of the ultrashort pressure loading, which is characteristic of the femtosecond laser-driven shock because there is not enough time to grow the nucleated high-pressure phases such as β-Sn structure. The high-pressure phases transformed to the metastable Si-VIII phase under pressure release and the grains remained after the compressions. These results indicate that the femtosecond laser-driven shock is quite effective for synthesizing submicron size crystalline grains with the pressure induced phase transition.

In conclusion, we found that crystalline grains of the metastable Si-VIII phase of silicon with size of 243 nm exist in the femtosecond laser-driven shock compressed silicon as determined by transmission micro-beam XRD measurements. We conclude that the submicron crystalline structure is caused by the ultrashort pressure loading of the femtosecond laser-driven shock wave. We are expecting to discover other unique crystalline structures induced by the femtosecond laser-driven shock wave.

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