a. PRF#59408-ND6
b. Project Title: Characterization of the Liquid Phase of Carbon by X-ray Scattering with Free Electron Lasers
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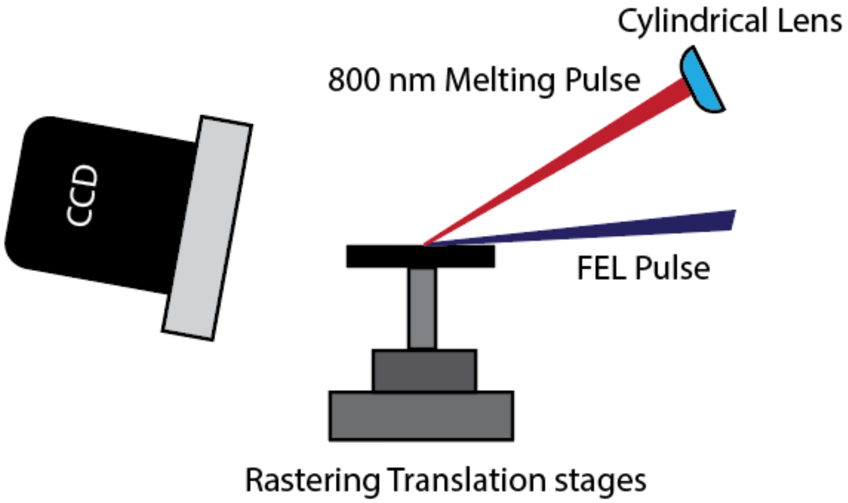
As a first step toward implementing the proposed studies of liquid carbon, we performed prototype experiments on the better characterized liquid state of silicon. We performed grazing incidence x-ray scattering experiments on liquid silicon ablation plumes after melting with an 800 nm 100 fs laser pulse. Liquid silicon was chosen over liquid carbon as the sample due to its relative structural simplicity, with tetrahedral coordination rather than the liquid carbon mixture of different coordination sites. As such, it was hoped might prove to be a good model system for testing the viability of employing ultrafast x-ray scattering to study the nucleation of carbon nanomaterials in the post-irradiation ablation plume, as there is a growing interest in understanding and controlling the nucleation of nanostructures that takes place in the interior of these ablation plume as it expands and cools.

In this study, we sought to observe the earliest dynamics in the femtosecond ablation of silicon by time-resolved grazing incidence X-ray scattering measurements with the X-ray free electron laser at the SACLA facility in Japan. . The femtosecond pulses available from the XFEL also have the requisite time resolution and intensity to directly observe the earliest stages of the ablation process. We overcome the penetration depth mismatch problem by carrying out the measurement in a total external reflection grazing incidence geometry. By doing so, we limit the penetration depth of the x-ray pulse to the uppermost few nm of the laser irradiated sample, allowing direct observation of only the ablation plume and the formation of particles on a timescale previously unavailable to x-ray scattering.

Experiments were carried out at the Beamline 3 of the SACLA (SPring-8 Angstrom Compact Free Electron LAser) XFEL at the SPring-8 facility. The figure below shows a schematic of the experimental set-up. The 1 mm thick silicon wafers used as samples in the experiment were mounted on a diffractometer stage with XYZ translation capability. X-ray pulses (10 fs, 10 keV) from SACLA were impinged on the sample silicon's (100) face at a 0.1^o incident angle, well below the calculated critical angle of 0.17^o, ensuring total external reflection of the x-ray beam. For the 10 keV x-ray used in the experiment we estimate our penetration depth to only be 4-6 nm into the sample. The diameter of the incident x ray beam was 2 um, which spread to a final on-sample footprint of ~1 mm length. The shallow angle of incidence also introduced ~1 ps of temporal smearing.

Ablation of the silicon target was carried out using a Ti:Sapphire laser (λ = 800 nm, τ = 40 fs, F = 1.0 J/cm^2). The laser pulses were focused onto the sample at a 70^o angle relative to surface normal using a cylindrical lens, resulting in an optical spot size that was 2mm long by 35 µm wide, sufficiently large to ensure complete spatial overlap with the x-ray pulse. The incident fluence of the optical laser was sufficient to ensure complete melting of the probed region. Between each laser shot, the silicon sample was rastered to ensure that each measurement was conducted on a pristine surface. Optical and XFEL repetition rates were restricted to 1 Hz to ensure sufficient time between shots for sample translation.



3.4.3 Results/discussion

Scattering intensity in this region is associated with the development of inhomogeneity on the nanoscale, associated with nanoparticles and structures. The large increase in scattering intensity at t=20 ps is thus assigned to nanoscale sized objects that form in the ablation plume. Due to experimental limitation, we did not collect data at q values low enough for accurate modeling, which precludes a complete analysis and characterization of the scattering objects. Nevertheless, the magnitude of the intensity increase is compelling, and we can infer some details as to the carrier of the observed scattering signal. Based on similarities to other studies, we assign the scattering intensity increase seen at 20 ps to the formation of large liquid silicon droplets in the ablation plume as it expands. It has been observed that after laser irradiation of sufficient intensity, silicon transitions to a liquid metallic state, as evidenced by the increase in the sample optical reflectivity for laser fluences above ~0.14 J/cm^2. Initially in a high temperature and pressure state, the plasma expands and cools, eventually crossing the spinoidal line in the phase diagram, which results in fragmentation via the homogenous nucleation of gaseous bubbles throughout the liquid This process, known as *phase explosion*, is well-known to be important in the ablation of semiconductors after femtosecond irradiation, and has been observed in both experiments and theoretical investigations of the ablation process. The 20 ps timescale observed in this experiment for the appearance of ablation-derived droplets agrees well with previous experimental observations of silicon ablation, wherein it was also observed that reflectivity loss due to the ablation occurred between 10 and 50 ps for the silicon (111) surface. Additionally simulations of femtosecond laser ablation of solids find that when the ablating laser fluence is significantly above the ablation threshold, the onset of fragmentation due to void coalescence occurs on a similar 10's of ps timescale. Thus, it is quite probable that we observed the very earliest steps in the liquid ablation process, with the observed droplets being related to the subsequently formed nanoparticles. As semiconductor ablation plumes are known to maintain optically smooth interfaces throughout the ablation process, it is possible to maintain the grazing incidence condition throughout the entirety of the material ablation. As such, the experiment is only sensitive to a narrow slice at the outermost surface of the ablation plume. In future experiments, this fact may be of aid in modelling thermodynamic condition plume and relating them to the evolution of nanoparticles in the plume as probed by the x-ray scattering. While the two time points collected in this experiment are insufficient for an in depth analysis of the plume dynamics, the experimental techniques developed here establish the viability of applying an XFEL-based grazing incidence small angle x-ray scattering experiment as a tool for studying ablation dynamics. The use of a grazing incidence geometry results in a probe that is highly sensitive to the plume itself, while mitigating interference from the sample bulk. As small angle scattering is a sensitive tool for studying both nanoparticle size and morphology, it is well-suited to studying the formation dynamics of nanostructures in the plume on the ultrafast timescales enabled via use of an XFEL. Additionally, by tuning parameters such as laser fluence, gas pressure around the sample, and the nature of the substrate, a more complete understanding of how these interesting properties affect shape and properties of the resulting nanostructures can be achieved.

Conclusions

In order to gain experience and insight into performing and interpreting the novel experiments proposed for the study of liquid carbon and carbon nanostructures with the new generation of X-ray free electron lasers, we have employed grazing incidence hard x-ray scattering using an ultrafast free electron laser source to study the earliest time points in the laser ablation of a silicon target. The dramatic rise in scattering intensity observed at low q in the experiment is attributed to the formation of nanoscale droplets of liquid silicon, resulting from phase explosion in the laser-prepared liquid. Grazing incidence x-ray scattering shows considerable promise as a tool for studying the ablation dynamics of laser irradiated substrates and the formation of nanoparticles. The technique can now be extended to other materials, conditions, and time delays. This is significant, as very few experiments have been able to directly measure the properties of these ablation plumes on ultrafast timescales.

Building on the knowledge gained in this study, new students funded by this project will next investigate the scattering of a liquid carbon plume over a broader angle and time range, effecting the direct study of both the growth and structural composition of nanomaterials formed in the ablation plumes, which will facilitate a deeper understanding of the factors controlling the properties and morphology of carbon nanoparticles produced by laser ablation, and will provide a valuable complement to the femtosecond second harmonic generation and two-photon absorption experiments that we recently performed with free electron laser sources in the soft X-ray region.