Since the discovery of X-rays in the 19th century, scientists have continuously endeavored to develop brighter X-ray sources. One of the most remarkable breakthroughs is the emergence of synchrotron light sources, which generate brilliant X-ray beams with intensity many orders of magnitude higher than those of X-rays generated previously. Such brilliant X-rays have provided a pathway to the measurement of high-quality X-ray scattering data, which has enabled the structure determination of complex systems including giant proteins, functional units of living organisms, and viruses. However, the increase in brilliance is also accompanied by the severe problem of X-ray radiation damage to the samples. For precise structure determination, a sufficient scattering signal should be recorded before the samples are severely damaged. The problem of radiation damage was considered to be an intrinsic issue associated with X-ray scattering experiments, setting a fundamental limit on the resolution in X-ray structure determination.

X-ray Free Electron Lasers (XFELs), which generate femtosecond X-ray pulses, may completely avoid the problem of radiation damage. In the first several femtoseconds after the irradiation of an X-ray beam, it has been predicted that atoms do not change their positions owing to inertia [1]. Thus, the ultrashort pulse duration of XFEL light allows us to use intense X-ray radiation beyond the conventional X-ray dose limit. This innovative concept, known as ‘diffraction before destruction’ has paved a clear way to the high-resolution structure determination of weak scattering objects, including nanometer-size protein crystals and non-crystalline biological particles. Moreover, structural determination of a single biomolecule with atomic resolution is expected as an ultimate application of XFELs.

Despite the potential impact of XFELs on structure determination, a detailed understanding of the femtosecond X-ray damage processes has been lacking. In particular, evaluation of the ignition time of the atomic displacement, which is crucial for realizing advanced XFEL applications, has not yet been investigated. Although improving our knowledge of the X-ray damage processes is essential for all aspects of XFEL science, experimental verifications have not been realized owing to the extreme difficulty of carrying out observations with ultrahigh space (Ångstrom) and time (femtosecond) resolutions. As a new approach to investigating the femtosecond X-ray damage processes, we have developed an X-ray pump–X-ray probe scheme at SACLA BL3 and investigated the femtosecond X-ray damage processes in diamond [2].

A schematic illustration of the experiment is shown in Fig. 1. We operated the XFEL source in a two-color twin-pulse mode [3]. Here, the eight upstream undulators were tuned to generate a 6.1 keV X-ray pulse to excite (i.e., pump) the sample. The remaining undulators generated a 5.9 keV X-ray pulse to probe the temporal changes in the crystalline structure of diamond through Bragg reflection. The time interval between the twin pulses was controlled by a magnetic chicane located downstream of the eighth undulator. The X-ray intensity was increased up to ~10^19 W/cm^2 with a two-stage focusing system [4]. Note that this intensity is almost the highest value achievable at current XFEL facilities. We set a thin diamond film at the focal point and measured the Debye-Scherrer rings of the 111 and 220 reflections with two multiport MPCCD detectors.

Fig. 1. Schematic illustration of X-ray pump–X-ray probe experiment at SACLA BL3. Twin XFEL pulses with tunable time separation were generated by the two-color twin pulse mode of SACLA. The XFEL pulses, which were focused with X-ray mirrors, irradiated a thin film of diamond powder crystals. Debye-Scherrer rings of 111 and 220 reflections in the horizontal direction were measured using two MPCCD detectors.
charge-coupled device (MPCCD) detectors.

Figure 2 shows MPCCD images of the 111 and 220 reflections, which were averaged over multiple shots with specific fluences of the pump and probe pulses. For both the 111 and 220 reflections, the pump diffraction intensities were almost constant regardless of the time separation between the twin pulses, which indicates that little radiation damage occurred during the irradiation of the pump pulse. In contrast, the probe diffraction intensities gradually decreased as the time separation increased. We consider that these changes were indicative of X-ray-induced atomic displacement.

To quantitatively analyze the X-ray damage processes, we assumed that the displacements of the carbon atoms were independent and random with a mean of zero. Under this assumption, the diffraction intensity of Bragg reflection is reduced by a factor of \( \exp(-q^2\sigma^2) \), where \( q \) is the scattering vector and \( \sigma \) is the root-mean-square displacement perpendicular to the Bragg plane. Using this representation of the diffraction intensities, we evaluated temporal changes in the atomic displacement perpendicular to the (111) and (220) planes (\( \sigma_{111}, \sigma_{220} \)). Figure 3 shows the temporal changes in \( \sigma_{111} \) and \( \sigma_{220} \) for three different pump pulse fluences. In all cases, \( \sigma_{111} \) and \( \sigma_{220} \) rapidly increased 20 fs after irradiation of the pump pulse, indicating that the critical time for the ignition of the X-ray-induced structural changes was 20 fs for the present fluences of the pump pulses. This result proves that sub-10-fs XFEL pulses enable damageless structural determinations and supports the validity of the theoretical predictions of ultraintense X-ray–matter interactions.

The X-ray pump–X-ray probe scheme demonstrated here is expected to be a highly effective way of exploring femtosecond X-ray–matter interactions due to its ultrahigh time and space resolution. This scheme should contribute to verifying and improving the theory of X-ray interactions with matter and stimulate advanced XFEL applications, as well as the investigation of exotic states of matter generated by intense X-ray irradiation.

Ichiro Inoue\textsuperscript{a}\textsuperscript{*} and Makina Yabashi\textsuperscript{a,b}

\textsuperscript{a}RIKEN SPring-8 Center
\textsuperscript{b}Japan Synchrotron Radiation Research Institute (JASRI)

\*Email: inoue@spring8.or.jp

References