

# Separating Non-linear Optical Signals of a Sample from High Harmonic Radiation in a Soft X-ray Free Electron Laser

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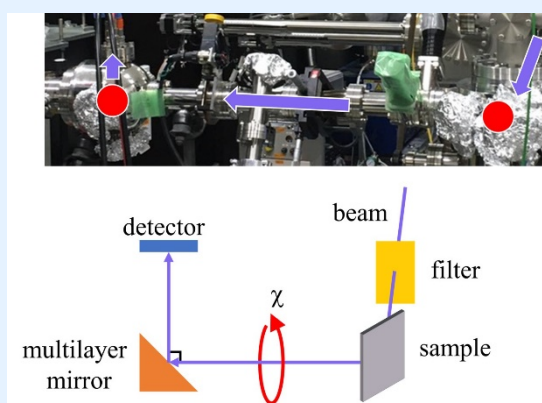
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Second harmonic generation (SHG) is a unique non-linear optical effect that can be used to investigate chemical states of molecules at surfaces/interfaces. By the use of soft X-rays, SHG gains element selectivity through the inner-core excitation resonance. However, it is challenging to observe SHG signals separately from the second-order light generated from the undulator. Here, we report a new ellipsometry method for soft X-ray SHG to suppress the contribution of second-harmonic radiation from the light source. Through measurements of a GaAs(100) crystal, we demonstrate that pure SHG signals can be obtained for the horizontally polarized component. The present method is generally applicable regardless of the incident photon energy and hence the absorption edge of the targeted materials. If combined with optical filters blocking the second-harmonic radiation and equipped with soft X-ray phase shifters, the method allows one to obtain further information from SHG signals such as tensor components of second-order non-linear susceptibility.

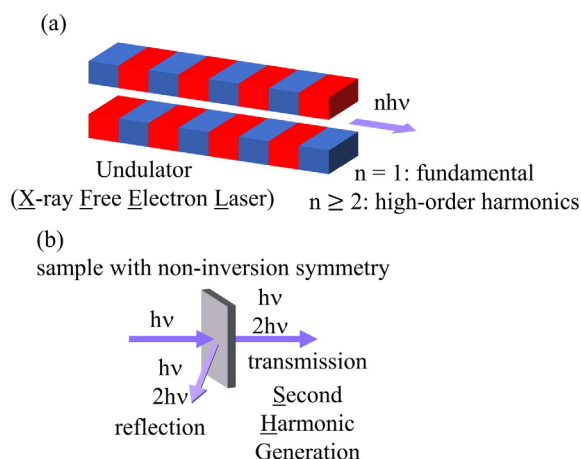


**Keywords** Non-linear spectroscopy; Soft X-rays; Extreme UV; X-ray free electron laser; Multilayer mirror

## 1. INTRODUCTION

Second-order non-linear optical response, such as second

harmonic generation (SHG), has been used in various fields, for example, physics [1], chemistry [2], and physiology [3]. SHG is a phenomenon where second-order-harmonic light ( $2h\nu$ ) is produced by interactions between the fundamental



**Figure 1:** Generation of high-order harmonic light. (a) A schematic drawing of fundamental and high order harmonic beams generated in the undulator. (b) Two optical configurations for measuring SHG from a sample: transmission and reflection geometry.

light ( $h\nu$ ) and materials with broken inversion symmetry. To date, SHG of visible light has been used to reveal chemical states of molecular at surfaces/interfaces where inversion symmetry is broken [2, 3] and to convert light to higher frequencies [4, 5].

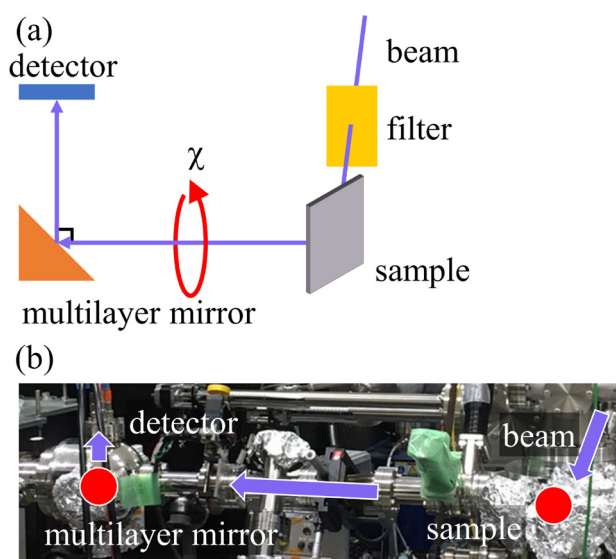
Recently, by the development of soft X-ray free electron laser (SXFEL) such as SPring-8 Angstrom Compact free-electron LASER (SACLA) [6, 7], SHG became observable also in the soft X-ray range. As shown in Figure 1(a), SXFEL beam is generated at the undulator section by use of self-amplification of spontaneous emission (SASE) [8, 9]. In the range of soft X-rays, SHG acquires element selectivity by inner-core excitation resonance. Such soft X-ray SHG

has been observed in the transmission geometry at Free Electron laser Radiation for Multidisciplinary Investigations (FERMI) @ ELETTRA [10, 11] and at a table-top soft X-ray laser (SXRL) [12] and in the reflection geometry at SACLA [13–15] [Figure 1(b)]. In the reflection geometry, the reflected fundamental light and SHG signals from a sample are separated by a grating and detected using a two-dimensional detector [13–15]. However, it is often difficult to acquire pure SHG signals since second-harmonic radiation generated by off-axis effects at the undulators [16–18] is also reflected by the sample and mixed into the SHG signal at the detector. Such contamination is harmful for discussing genuine properties of SHG, and therefore, an efficient experimental method to selectively detect SHG signals has been desired.

In the present technical note, we report a new ellipsometry method for soft X-ray SHG experiment to suppress the contribution of second-harmonic light from the beamline. We installed an ellipsometer unit [19] and performed soft X-ray SHG measurements of a GaAs(100) crystal, which is a representative non-linear crystal in the range of visible light. From analysis of the polarization of the  $2h\nu$  component, we found a suppression of the second-harmonic radiation at a specific polarization, thereby succeeding in extracting essential SHG signals. By combining with appropriate optical filters, the present method will further enhance the capability of soft X-ray SHG.

## II. SYSTEM

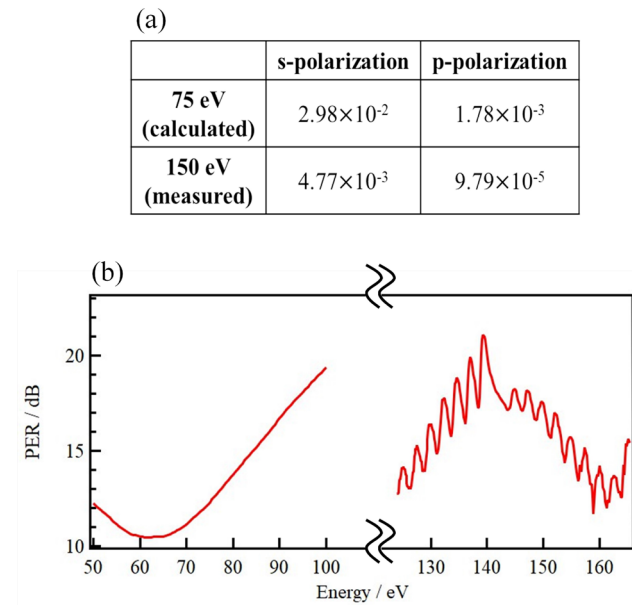
Figure 2(a) shows a schematic drawing of the experimental setup for the soft X-ray SHG measurement and the optical paths. A SXFEL beam travels through a filter, installed at the beamline, to select the fundamental and/or the second-harmonic radiation from the beamline. The fundamental photon energy was set at  $h\nu = 75$  eV so that the SHG energy of 150 eV ( $= 2h\nu$ ) coincides with the As M absorption edge in the GaAs(100) crystal. Filters are thin films of Sn (thickness: 0.1  $\mu\text{m}$ ) and Si (thickness: 0.1  $\mu\text{m}$ ) for blocking the first-order light ( $h\nu = 75$  eV) and the second-order one ( $2h\nu = 150$  eV), respectively (Table 1). An Al filter was also used to adjust the photon flux to prevent beam damage on a sample. The incident and reflection angle at the sample were set at  $45^\circ$  from the surface plane. A beam from the sample is led to a Ru/B<sub>4</sub>C multilayer mirror whose reflectivity and polarization extinction ratio (PER) are shown in Figure 3, and reflected into a detector, as shown in Figure 2(a). The multilayer mirror and the detector were set in an



**Figure 2:** The optical setup for soft X-ray SHG. (a) A schematic drawing and (b) a photo of the ellipsometry setup for soft X-ray SHG measurements assembled at SACLA SXFEL beamline BL1. The optical paths are traced by purple arrows.

**Table 1:** Calculated transmittance of Al, Si, and Sn filters at 75 eV ( $h\nu$ ) and 150 eV ( $2h\nu$ ).

| filter | 75 eV ( $h\nu$ )     | 150 eV ( $2h\nu$ )   |
|--------|----------------------|----------------------|
| Al     | $2.2 \times 10^{-2}$ | $4.5 \times 10^{-3}$ |
| Si     | $7.9 \times 10^{-1}$ | $1.0 \times 10^{-1}$ |
| Sn     | $1.9 \times 10^{-4}$ | $5.8 \times 10^{-1}$ |



**Figure 3:** The property of the Ru/B<sub>4</sub>C multilayer mirror. (a) Reflectivity values of the multilayer mirror for s- or p-polarized lights with the photon energy of 75 eV (calculated value) or 150 eV (measured value). The incident angle is set to 45°. (b) Polarization extinction ratio (PER) of the multilayer mirror with the photon energy between 50 and 100 eV (calculated value), and between 125 and 165 eV (measured value). The incident angle was set to 45°.

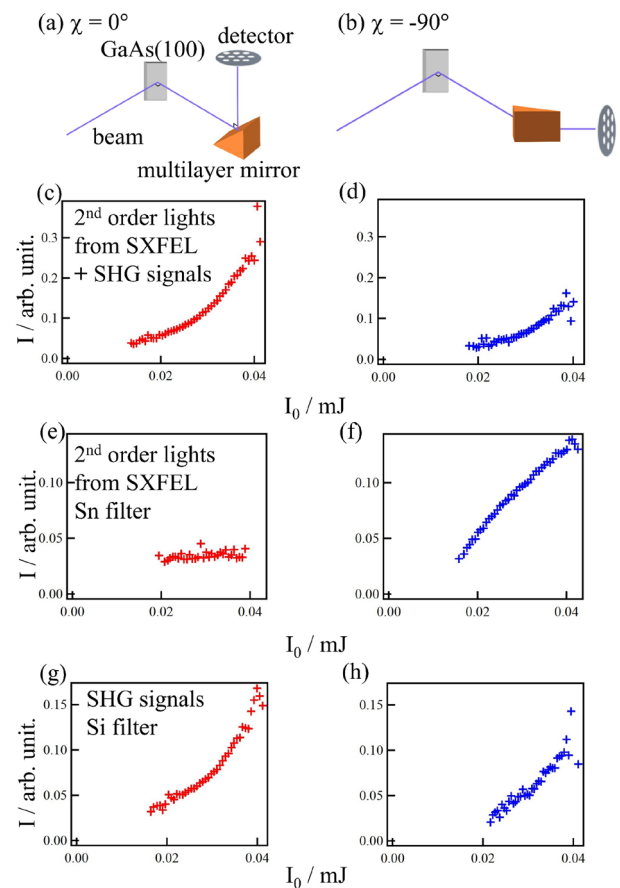
ellipsometer unit that rotates around the optical path. We define the positive angle,  $\chi$ , as counter-clockwise direction seen from the downstream of the optical path [Figure 2(a)].

The whole system for the soft X-ray SHG measurement was installed at SFXFEL beamline BL1 at SACLA, as presented in Figure 2(b). The  $\chi$  rotation of the ellipsometer unit was controlled by a stepping motor. Technical details of the unit are described elsewhere [19].

### III. DEMONSTRATION

Figure 4 shows changes of the detected signals  $I$  with respect to the incident intensity  $I_0$  for the GaAs(100) crystal under the various measurement conditions and the ellipsometer rotation angles  $\chi$ . The fundamental photon energy was set at  $h\nu = 75$  eV so that the SHG energy of 150 eV ( $= 2h\nu$ ) coincides with the As M absorption edge in the GaAs(100) crystal. Figure 4(c, d) shows the intensity plots of the reflected light at the detector with only an Al filter. In this case, the  $I_0$  dependence of the signal intensity clearly deviates from the linear one. Although this non-linearity is characteristic of SHG [13–15], it is unclear whether the signal is purely from SHG or in a mixture with second-harmonic radiation.

By adopting a Sn filter at the beamline, one can block the fundamental beam of SFXFEL and introduce the second-harmonic radiation ( $2h\nu = 150$  eV) alone to the sample. Intensity plots of the reflected light obtained by the detector



**Figure 4:** Soft X-ray SHG data for a GaAs(100) crystal recorded with the ellipsometry method. (a, b) The measurement geometries for the rotation angles  $\chi = 0^\circ$  and  $-90^\circ$ , respectively. (c, d) Intensity of the  $2h\nu$  signal containing both second-order light from SFXFEL and SHG from a sample, plotted with respect to the incident beam ( $h\nu = 75$  eV) intensity  $I_0$  at  $\chi = 0^\circ$  and  $-90^\circ$ , respectively. (e, f) The same as (c) and (d) but for the selectively extracted second-order light from SFXFEL using a Sn filter. (g, h) The same plots for SHG signal obtained by blocking the SFXFEL second-harmonic radiation using a Si filter.

show a linear dependence [Figure 4(e, f)], assuring that the signal arises from the reflection of the second-harmonic radiation. The slight downward bending in Figure 4(f) around  $I_0 \sim 0.02$  mJ is likely due to larger error bars arising from weaker intensity and the smaller number of events. Remarkably, the intensity is much larger at  $\chi = -90^\circ$  than at  $\chi = 0^\circ$ . This is probably because the second-order light arising from off-axis effects are mainly composed of vertical polarization [17, 18]. Furthermore, the p-polarized (hori-

**Table 2:** Calculated reflectivities of GaAs crystal for p- or s-polarized light with 75 or 150 eV at the incident angle of 45°.

|                    | p                     | s                     |
|--------------------|-----------------------|-----------------------|
| 75 eV ( $h\nu$ )   | $2.05 \times 10^{-6}$ | $1.43 \times 10^{-3}$ |
| 150 eV ( $2h\nu$ ) | $2.04 \times 10^{-7}$ | $4.51 \times 10^{-4}$ |

zontally polarized in the present case) component is generally suppressed through reflection compared to the s-polarized (vertically polarized in the present case) one [20]. As shown in Table 2, this consideration indeed applies to the GaAs crystal. These observations in turn give a clue for the composition of the  $2h\nu$  intensities plotted in Figure 4(c, d): whereas the  $\chi = 0^\circ$  data [Figure 4(c)] consists almost fully of the SHG signal, the  $\chi = -90^\circ$  data [Figure 4(d)] may contain a substantial contribution from second-harmonic radiation. This setup is thus capable of delivering a highly pure SHG signal for the horizontally polarized component. Importantly, it is for material-independent reasons that the horizontally-polarized part of the reflected second-harmonic radiation is weak. Therefore, the present methodology is applicable to any kind of materials even when optical filters that match the specific energy of second-harmonic radiation are not available.

For  $h\nu = 75$  eV, with a Si filter at the SXFEL beamline, one can cut the second-harmonic radiation ( $2h\nu = 150$  eV) from the light source. In other words, the sample is exposed only with the fundamental light. In this case, the non-linear signals can be regarded as genuine SHG from the GaAs crystal irrespective of the polarization [Figure 4(g, h)]. These figures show that the intensity of the SHG light is larger at  $\chi = 0^\circ$  than at  $\chi = -90^\circ$ . This suggests an inequivalence in the tensor components of the second-order non-linear susceptibility which contributes to SHG in each geometry. As such, by combining the ellipsometry method with filters that cut-off the second-harmonic radiation, one can determine the amplitude of the polarization component irrespective of its direction. By further adopting a soft X-ray phase shifter that functions at the resonance energy, one could make full polarization analysis and thus disentangle tensor components of the non-linear susceptibility. The present work will, thus, open up the capability of soft X-ray SHG and enhance its applicability in modern material science.

## IV. CONCLUSIONS

We developed a new ellipsometry method to measure soft X-ray SHG signals without influence by second-harmonic radiation from the light source. By utilizing characteristics that (i) second-harmonic radiation from the beamline mainly consists of vertical polarization and (ii) p-polarized (horizontally polarized in the present case) light is generally suppressed through reflection compared to the s-polarized (vertically polarized in the present case) one, we demonstrated on the GaAs(100) crystal that the ellipsometry method can deliver almost pure SHG signals for the horizontally polarized component. This method is applicable to any samples irrespective of their resonance photon energy. If combined with appropriate filters that cut-off the second-harmonic radiation and equipped with soft X-ray phase shifters, complete polarization analysis of SHG can be realized. The present work would thus boost the capability of soft X-ray SHG and stimulate future application to complex materials.

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