Development of surface sensitive DXAFS measurement method by applying Kramers-Kronig relations to total reflection spectra

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Abstract. Total reflection XAFS spectra are obtained combining with dispersive XAFS (DXAFS) configuration. A total reflection DXAFS spectrum of 30 nm Co layer on Si substrate was measured in 4 ms. Kramers-Kronig analysis was applied to extract XAFS signal from total reflection spectra. Spectra obtained by this method are comparable to usual XAFS spectra in terms of signal-to-noise ratios and peak positions in Fourier transformed EXAFS functions. The development of this Kramers-Kronig relations based DXAFS method is useful to study the variation of the surface state with the time resolution of millisecond.

1. Introduction
X-ray absorption fine structure (XAFS) is a useful technique to study local structures and electronic states of elements. XAFS is one of the important methods to examine catalysts especially under the conditions of reactions, and time-resolved XAFS techniques are widely used to observe them in a real time manner. Quick XAFS (QXAFS)[1, 2] and dispersive XAFS (DXAFS)[3, 4] are the two methods usually used to perform time-resolved XAFS measurements.

QXAFS techniques are widely used at XAFS experimental stations in the world. It is relatively easy to install the system to perform QXAFS because the same hardwares as usual step scanning XAFS can be used. Dispersive XAFS (DXAFS) is a powerful technique to obtain time-resolved XAFS spectra, though the setup and detection would be difficult relative to QXAFS. Since a DXAFS spectrum is recorded at once without scanning the x-ray energies by moving monochromators, it has a better capability of time resolution and is suitable to study time evolutions of chemical reactions and transient species. Chemical reactions and other fast processes have been studied by DXAFS methods[5, 6, 7].

We would like to expand this DXAFS technique to the field of surface science, for example, in order to study fundamental mechanisms of surface chemical reactions. We have tried to obtain surface sensitive spectra by detecting signals of total reflection. A total reflection spectrum is so surface sensitive that bulk signals should be eliminated. The total reflection measurements are key to obtain information on surface. Absorption spectra are required to be analyzed by XAFS method, and reflection spectra are transformed to “absorption” spectra by Kramers-Kronig relations.
This kind of method was formerly named ReflEXAFS by G. Martens and P. Rabe[8, 9], and some groups had tried to develop the method[10, 11, 12, 13]. R. Frahm’s group reported film deposit processes observed by the method[14, 15].

We have combined this method with the DXAFS technique. The DXAFS system provides a better time resolution to the total reflection XAFS method, which has a surface sensitivity.

2. Experiment
Usual step scanning XAFS measurements were performed at BL-9C of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization. A 30 nm Co film deposited on a Si wafer was used as a test sample, and a Co foil was used as a standard. Reflection spectra were measured by using stages for grazing incident measurements. The sample was aligned to realize a total reflection condition. The total reflection critical angle of Co is ~7 mrad in this energy range. The incident angle was set to be ~3 mrad, which is well below the critical angle. Total reflection XAFS experiments combined with a DXAFS system were carried out at NW2A of PF-AR. All the measurements were performed under the air atmosphere.

The total reflection spectra were converted to “absorption” spectra via Kramers-Kronig relations. Kramers-Kronig relations are defined with integration of unlimited regions. It is, however, impractical to integral unlimited regions, and the integrations in our analyses of Kramers-Kronig relations were performed in the limited regions as wide as possible for the data until the oscillations can be almost null. It is helpful and usual to adopt this approximation in practice. All the spectra were processed through a standard XAFS analysis procedure.

3. Results and Discussion
The validity of the Kramers-Kronig relations based XAFS method was confirmed by measuring usual step scanning XAFS spectra at BL-9C. A standard Co foil was measured by a standard transmission mode. “XAFS” spectra via Kramers-Kronig relations were obtained from total reflection spectra of the Co(30 nm)/Si film. The reflection spectrum of Co(30 nm)/Si is shown in Fig. 1(a) with that of Co foil.

EXAFS oscillations $k^2\chi(k)$ are shown in Fig. 1(b). The Kramers-Kronig analysis was applied to the total reflection spectrum. The smooth EXAFS oscillations were observed at least until 15 Å$^{-1}$. The structures of the oscillations are roughly similar to each other, and they contain structural information on metallic cobalt. There’s a characteristic difference between the two around 2–4 Å$^{-1}$. The difference would reflect some specific features at anomalous dispersion at the absorption edge. The features at the edge are generally complicated, and discussions on the point are beyond this paper. We would like to focus on the similar oscillations above ~5 Å$^{-1}$. The same frequency corresponds to the same local structure, such as atomic distances.

The EXAFS oscillations were processed through Fourier transformation as shown in Fig. 1(c). The characteristic peak structures of the two[16] resemble well, which are the first peak at 2.2 Å$^{-1}$ and the double peak structure around 4–5 Å$^{-1}$. Though further analyses and careful treatments are required, the whole structures are in good agreement each other.

We had combined the Kramers-Kronig relations based XAFS method with a DXAFS system. The first trial spectra of reflection DXAFS are shown in Fig. 2. They were measured in 4 ms every 10 ms. The specific features are seen in the spectra, and the good reproducibility was observed. We have developed a Kramers-Kronig relations based DXAFS method. It is confirmed that the reflection DXAFS measurements are useful to obtain surface sensitive XAFS spectra via Kramers-Kronig relations. This surface sensitive technique can be applied to study the field of surface science with a good time resolution.
4. Summary

Total reflection XAFS spectra are obtained combining with DXAFS configuration in order to study the variation of the surface state. Total reflection DXAFS spectra of Co(30 nm)/Si were measured in 4 ms every 10 ms. Kramers-Kronig analysis was applied to extract XAFS signal from total reflection spectra. XAFS spectra obtained from the analysis were comparable to usual XAFS spectra in terms of signal-to-noise ratios and peak positions in Fourier transformed EXAFS functions. The obtained spectra showed a possibility to apply this Kramers-Kronig relations based DXAFS method to the field of surface science with the time resolution of millisecond.

Figure 1. (a) A total reflection spectrum of Co(30 nm)/Si (solid line) and absorption one of Co foil (dashed line). Their (b) EXAFS oscillations and (c) Fourier transforms.

Figure 2. Reflection spectra of Co(30 nm)/Si measured by DXAFS method. Each spectrum was recorded for 4 ms.
Acknowledgments
Prof. H. Kondoh is appreciated for fruitful discussions. We are grateful to Mr. T. Nakayama for his support. This work was performed under the approval of PF-PAC No. 2011G116. The authors are grateful for the financial support Grant-in-Aid for Young Scientists (B) (No. 24710102).

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