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Depth-selective X-ray absorption spectroscopy by detection of energy-loss Auger electrons

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ABSTRACT

A unique X-ray absorption spectroscopy (XAS) method is proposed for depth profiling of chemical states in material surfaces. Partial electron yield mode detecting energy-loss Auger electrons, called the inelastic electron yield (IEY) mode, enables a variation in the probe depth. As an example, Si K-edge XAS spectra for a well-defined multilayer sample ($Si_3N_4/SiO_2/Si$) have been investigated using this method at various kinetic energies. We found that the peaks assigned to the layers from the top layer to the substrate appeared in the spectra in the order of increasing energy loss relative to the Auger electrons. Thus, the probe depth can be changed by the selection of the kinetic energy of the energy loss electrons in IEY-XAS.

1. Introduction

X-ray absorption spectroscopy (XAS) has become one of the most powerful techniques for investigating local structures and chemical states of atoms in different environments [1]. The chemical states such as the valence states can be obtained by X-ray absorption near edge structure (XANES) spectroscopy [2]. Furthermore, the local structure parameters such as interatomic distances and coordination numbers can be derived from extended X-ray absorption fine structure (EXAFS) spectra [3]. XAS has several measurement modes with different probe depths. The most widely used XAS modes are the electron yield (EY) and the fluorescence yield (FY) modes in the soft X-ray region. The probe depth of the EY mode is generally smaller than that of the FY mode [4]. Therefore, the EY mode is often applied to surface analysis for samples such as semiconductor devices [5–7] and rechargeable battery materials [8–10]. Recently, nondestructive depth profiling of chemical states is increasingly being sought for evaluation of the surfaces of these materials. However, since the XAS probe depth is mainly determined on the basis of the elements present in the materials and on the detected absorption edges, it cannot be set to an arbitrary desired value.

Electrons emitted from the sample surface by X-ray irradiation mainly comprise Auger electrons with a specific energy and energy-loss electrons with a variety of energies due to inelastic scattering. The photoelectrons are certainly emitted as well. Tougaard [11] has performed detailed investigations of the relationship between the electron path length in the solid and the energy loss. It was found that the energy distribution resulting because of an electron with a specific initial energy shifted to higher loss energy with increasing path length. This indicates that electrons originating from the deeper regions of the material lose more energy upon reaching the surface and suggests that the probe depth can be changed by selecting the energy of the detected electrons. In the EY mode, the partial EY (PEY) mode detects the electrons emitted from the sample surface and is surface sensitive compared with the total EY (TEY) mode that measures the sample drain current [4]. Amemiya et al. [12,13] developed a depth-resolved XAS technique in X-ray magnetic circular dichroism, using an imaging-type multichannel plate (MCP) detector. In their studies, various probe depths were obtained by collecting the emitted electrons at various detection angles. Subsequent studies showed that the probe depth could be changed by the application of a retarding voltage and the use of a PEY detector based on the MCP [4,14]. However, in these cases,

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specially designed experimental setups were required. In a different approach, Gao et al. [15] used an electron energy analyzer to select the energy of the emitted electrons. This device is widely used to detect electrons with a high energy resolution, and is often available in the same experimental station in which the absorption measurements are conducted. It was attempted to obtain depth-resolved magnetic information for Fe films grown on Co/Cu(0 0 1) using the PEY mode for the detection of the inelastically scattered electrons at several fixed kinetic energies; this was named the inelastic electron yield (IEY) mode. However, even when measured at different energies, the IEY mode probe depth was similar to that of the TEY mode. This may be because of the fact that the Fe film thickness (18 ML; about 3.4 nm) was small relative to the IEY and TEY mode probe depths. Thus, as of now the IEY mode probe depth has not been thoroughly investigated. Therefore, in this study, XANES spectra for a well-defined $Si_3N_4/SiO_2/Si$ multilayer sample have been investigated using the IEY mode at several kinetic energies corresponding to energy loss to pave the way for the development of depth-selective XAS measurements.

2. Experimental

The experiments were performed at the soft X-ray XAFS beamline BL6N1 of the Aichi Synchrotron Radiation Center (AichiSR) [16,17], which has an electron storage ring with a circumference of 72 m and is operated at an electron energy of 1.2 GeV with a current of 300 mA.

Quasi-monochromatic light from a bending magnet was monochromatized by an InSb(1 1 1) double-crystal monochromator (DCM). The X-ray beam was horizontally focused by the Ni-coated 1000 mm-long bend-cylindrical mirror with an incident angle set to 9.49 mrad. The front-end slit size was 7.0 mm in the horizontal (h) and 3.0 mm in the vertical (v) directions. The downstream slits after the DCM were set wide enough so that the X-ray beam was not obstructed. The beam size at the sample position was 2 mm (h) × 1 mm (v). The horizontal size of the irradiated region of the sample surface depended on the sample tilt. Energy calibration was performed relative to the S K-edge for the first K_2SO_4 peak located at 2481.70 eV.

The electron analyzer (PHOIBOS 150, SPECS GmbH) operated over a range of kinetic energies (from 1 eV to 3.5 keV) and comprised a hemispherical energy analyzer with a mean radius of 150 mm, a pre-retarding combined second-order focusing lens system, and a two-dimensional event-counting detector equipped with an MCP, a phosphor screen, and a CCD camera. The entrance slit of the analyzer was rectangular with dimensions of 7 mm in the energy-dispersive direction and 20 mm in the energy-nondispersive direction. The pass energy was 10 eV and the total energy resolution $E/\Delta E$ were 2600 at 3000 eV. The analyzer input lens axis, with the acceptance angle of $\pm 22^\circ$, was aligned 35° to the incident X-ray beam and parallel to the polarization vector. The take-off angle (TOA) of the analyzed electrons was set to 90° (normal to the surface). In PEY-XAS measurements, the electrons emitted from the sample surface are detected by the electron analyzer during X-ray energy sweeps because of the XAS measurements. The base pressure of the main chamber was approximately 5×10^{-8} Pa.

The sample structure was Si_3N_4(14 nm)/SiO_2(28 nm)/Si(1 0 0). The SiO_2 film was grown at 900 °C in dry O_2 ambient on a Si(1 0 0) substrate. Subsequently, the Si_3N_4 film was deposited by low-pressure chemical vapor deposition (LPCVD) at 800 °C using SiH_2Cl_2 and NH_3 as the source gases. The layer thicknesses were measured by an ellipsometer (L115C, Gaertner Scientific Co.) with an accuracy of ±0.3 nm. To perform the curve-fitting analysis using the ATHENA program [18], we used amorphous Si_3N_4 and amorphous SiO_2 thick films, and Si(1 0 0) as the standards for each of the layers.

The sample drain current in the TEY mode measurements for Si K-edge was approximately 0.3 nA, where incident photon flux is 6×10^9 photons/s on the beamline specifications.

3. Results and discussion

Fig. 1 shows Si K-edge XAS spectra for (a) $Si_3N_4/SiO_2/Si$, (b) Si, (c) Si_3N_4, and (d) SiO_2, measured using the TEY mode. Peaks at 1842, 1846, and 1848 eV were observed for Si, Si_3N_4, and SiO_2, respectively; the peak positions are essentially identical to the results in the previous studies [19]. Peaks or shoulders at those energies were also observed for the multilayer $Si_3N_4/SiO_2/Si$ sample, indicating that the spectrum for the multilayer sample ($Si_3N_4/SiO_2/Si$) is because of a combination of the Si_3N_4, SiO_2, and Si spectra.

Fig. 2 shows X-ray photoelectron spectroscopy (XPS) spectra for $Si_3N_4/SiO_2/Si$ under irradiation at the photon energy (PE) of 1860 eV. Auger and photoelectron peaks that can be assigned to the Si, N, and O elements contained in the sample are observed. The presence of the C 1s peak suggests that contamination or impurity was present within the sample at the photoelectron detection depth. As shown in the inset of Fig. 2, the Si KLL peak energy was 1612 eV and is assigned to the Si_3N_4 layer [20]. The values of kinetic energy (E_k) set in the IEY mode are chosen to avoid the photoelectron peaks such as C 1s, N 1s, and O 1s cross during the X-ray

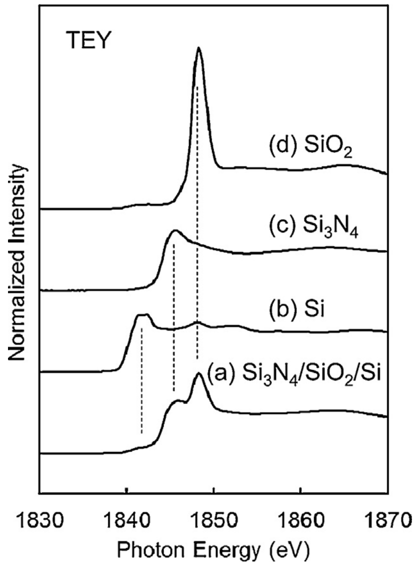

Fig. 1. Si K-edge X-ray absorption spectroscopy spectra for (a) $Si_3N_4/SiO_2/Si$, (b) Si, (c) Si_3N_4, and (d) SiO_2, measured using the TEY mode.

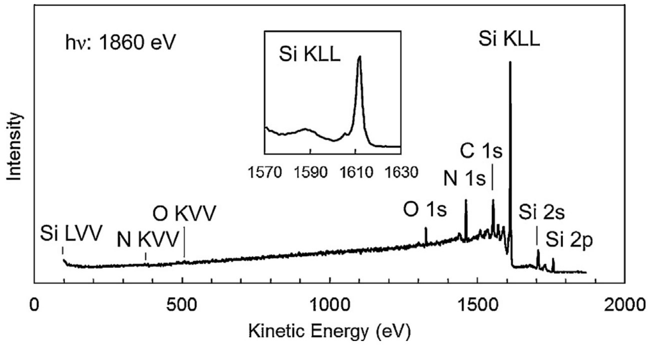

Fig. 2. X-ray photoelectron spectroscopy spectra for $Si_3N_4/SiO_2/Si$ under irradiation at the photon energy of 1860 eV.