# X-Ray Absorption Microspectroscopy with Electrostatic Force Microscopy and its Application to Chemical States Mapping

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**Abstract.** A new technique named X-EFM that measures the x-ray absorption fine structure (XAFS) of nanometer objects was developed. In X-EFM, electrostatic force microscopy (EFM) is used as an x-ray absorption detector, and photoionization induced by x-ray absorption of surface electron trapping sites is detected by EFM. An EFM signal with respect to x-ray photon energy provides the XAFS spectra of the trapping sites. We adopted X-EFM to observe Si oxide thin films. An edge jump shift intrinsic to the X-EFM spectrum was found, and it was explained with a model where an electric field between the trapping site and probe deepens the energy level of the inner-shell. A scanning probe under x-rays with fixed photon energy provided the chemical state mapping on the surface.

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## **INTRODUCTION**

X-ray absorption fine (XAFS) structure measurements are an established method for local structure analyses of various materials. In a conventional XAFS measurement, the object size is determined by the x-ray beam size, which is normally greater than a hundred micrometers. However, advanced materials have included artificial structures in the nanometer range. This trend towards smaller materials makes analyses in the hundreds of micrometers insufficient. The conventional XAFS measurement for these advanced materials provides a typical electronic state and atomic coordination in the materials. In general, the information does not correspond with the actual electronic state and coordination of the nano structures. Obviously, an XAFS measurement of a single nano structure is mandatory.

We developed a new technique that performs XAFS measurements at the nanometer level. The technique involves using scanning probe microscopy (SPM) as a XAFS signal detector. Because SPM can observe nanometer objects, we can keep the probing area of XAFS measurements at the nanometer level. However, detecting x-ray absorption is not common even though various physical properties have been

detected with SPM systems. Scanning tunneling microscopy (STM) was used for photocurrent detection in XAFS measurement [1]. However, because bias voltage was applied to the tip, photocurrent is collected from an x-ray irradiation area broader than the probing area. Therefore, measuring high spatial resolution measurement was difficult.

In this paper, we introduce an idea on detecting electrostatic force instead of a photocurrent. Electrostatic force microscopy (EFM) can detect a local electric force independent of the photocurrent, thereby enabling high spatial resolution.

## **EXPERIMENTS**

Figure 1 shows the conceptual figure of our experimental system. EFM was used under the x-ray irradiation. In the discussion, this EFM with an x-ray source is denoted as X-EFM. On the actual surface, electron trapping sites, such as defects, are evident. X-ray absorption at the electron trapping sites induces photoemission of trapped electrons. It corresponds to photoionization of the trapping sites. The photoionization can be detected by X-EFM, allowing for XAFS spectra to be obtained from the X-EFM signal depending on photon energy.

Experiments were performed with a custom-made apparatus produced by UNISOKU Co., Ltd. The X-EFM signal was detected with a lock-in technique using an AC bias applied to a sample. The AC bias voltage and frequency were 2 V and 3-10 kHz, respectively. The EFM probe was coated with Cr (5 nm)/Au (20 nm) for grounding the probe. The details of the system are described in a previous paper [2]. The x-ray source for X-EFM was a MPW6.1 beamline [3] of a synchrotron radiation source (SRS) at the Daresbury laboratory in the UK. This beamline has a multi-pole wiggler that provides soft x rays with a photon energy range of 40-400 eV. The x rays were monochromatized by a grating.

The sample was an n-type (111) oriented Si wafer. The sample was installed in the X-EFM system as prepared, and it was covered by nanometer-thick native oxide. The sample was mounted on a vertical scanning stage opposite to the probe. From a conventional EFM study, electron trapping was formed at the interface between the Si wafer and the native oxide [4]. X-EFM selectively observes this trapping site.



FIGURE 1. Conceptual figure of X-EFM measurement.

#### **RESULTS AND DISCUSSION**

Figure 2(a) indicates an X-EFM signal with respect to photon energy around the Si L absorption edge. As shown in this figure, the edge jump at 107.1 eV and the following absorption peaks were observed. As explained in Fig. 1, Fig. 2 indicates the x-ray absorption spectrum of the electron trapping site. As a reference, an x-ray absorption spectrum obtained with the conventional method probing the total electron yield (TEY) is shown in Fig. 2(b). The TEY from the whole x-ray irradiation area indicates an x-ray absorption spectrum of major Si atoms without an electron trapping level. Obviously, the major Si atoms are SiO<sub>2</sub>. As shown in this figure, the edge jump at 104.5 eV, and the following peaks were observed. A comparison between Fig. 2(a) and (b) reveals that the edge jump of the X-EFM shifts by 2.6 eV. Other absorption peaks in the X-EFM spectrum also tend to shift to a higher energy. These peaks are identified with their absorption energy, and the energy shift

value is indicated in parentheses. The energy shift values are distributed from 2.0 to 3.1 eV. This distribution means that the electronic state modulation is dependent on a molecular orbital.

The edge jump shift to higher energy observed in Fig. 2(a) cannot be explained with chemical shift owing to SiO<sub>x</sub> (x<2). Therefore, we introduced a new model where an electric field owing to a trapped electron deepens the Si 2p (*L*-shell) energy level. The inset of Fig. 3 is the cone model used for an electric field calculation. As shown in this figure, the virtual charge ring with a  $\delta a$  width on the sample surface induces a partial electric field  $\delta E$  at *z*. Here, *z* is the distance between the X-EFM probe and the sample surface, *a* is the radius of the base of the cone, and  $\lambda$  is the charge density of the trapping sites. The partial electric field perpendicular to the sample surface dEcos $\theta$  can be calculated from this cone model:

$$dE\cos\theta = \frac{\lambda za}{2\varepsilon_0 (a^2 + z^2)^{\frac{3}{2}}}$$
(1)

where  $\varepsilon_0$  is the dielectric constant of the vacuum. Therefore, the total electric field E<sub>total</sub> at the probing tip integrated over the sample surface ( $0 < \theta < \pi/2$ ) is  $\lambda/2\epsilon_0$ . This result indicates that  $E_{total}$  is constant for a given value of  $\lambda$ . In the X-EFM experiment, because no DC bias was applied, the E<sub>total</sub> should have been balanced with the edge energy shift  $\Delta E$  in Fig. 2. This balance can be expressed as  $\Delta E/z = \lambda/2\epsilon_0$ . Therefore,  $\lambda$ can be estimated to be  $2\varepsilon_0 \Delta E/z$ . On the other hand, we experimentally obtained a  $\Delta E$  of 2.6 eV, as shown in Fig. 2. The typical z in the SPM is a few nm. The substitution of  $\Delta E/z \sim 1 \times 10^9$  V/m and  $\varepsilon_0$  of 8.854×10<sup>-</sup> <sup>12</sup> F/m leads to  $\lambda \sim 1.6 \times 10^{-2}$  C/m<sup>2</sup>. Assuming that a single electron was trapped at this site, the density of the trapping site can be estimated to be  $\sim 1 \times 10^{17}/m^2 =$  $1 \times 10^{-1}$ /nm<sup>2</sup>. This density indicates that the trapping centers are statistically distributed within a ~3 nm period. This period is consistent with the experimental results with the conventional EFM [4].



**FIGURE 2.** (a) X-EFM spectrum at Si L absorption edge. (b) X-ray absorption spectrum obtained with a conventional method probing total electron yield (TEY).



**FIGURE 3.** (a) Normalized partial electric field dEnorm vs. normalized distance z/a calculated with Eq. (1). (b)-(d) dEnorm calculated from Eq.(2) for various normalized tip radii  $0 < r/z \le 2$ .

For the  $E_{total}$  estimation, we took into account the electric field owing to infinitely distant trapped electrons. It apparently contradicts the nano spectroscopy of X-EFM. However, a detailed analysis supports the nano scale spatial resolution found in this method. Figure 3(a) shows a normalized partial electric field  $dE_{norm}$  defined as  $dE\cos\theta/E_{total}$  with respect to normalized distance z/a. As shown in this figure,  $dE_{norm}$  has a sharp peak and rapidly decreases as z/a increasing. The maximum peak position  $(a/z)_{max}$  was 0.71, and the variance  $\sigma$  was 0.0115. The trapped electrons within z/a < 2.77 determine 2/3 of the  $E_{total}$ . This indicates that distant trapped electrons are negligible; X-EFM can distinguish chemical states on the surface within a nm spatial resolution.

The cone model is idealized. In the actual system, a chipped tip increases the  $(a/z)_{max}$  and  $\sigma$  of dE<sub>norm</sub>. The chipped tip can be formulated with a fluctuation of  $\theta$  at *z*. We defined the fluctuation as  $\Delta\theta$ .  $\Delta\theta$  increases as radius *r* increases in the chipped tip. The  $\Delta\theta$  can be convoluted into dE<sub>norm</sub> as

$$dE_{norm} = \frac{\int_{\Delta\theta} dE \cos\theta}{E_{total}}$$
(2)

Figure 3(b)-(d) indicate  $dE_{norm}$  calculated from Eq.(2) for various normalized tip radii  $0 < r/z \le 2$ . The r/z = 0 corresponds with the ideal tip, as shown by Fig. 3(a). This figure shows that the spatial resolution degenerates as r/z increases For r/z=2,  $(a/z)_{max}$  and  $\sigma$  were estimated to be 2.16 and 0.0854, respectively. Obviously, a sharp tip is a key factor for a high resolution measurement.

Note that  $E_{total}$  is  $\lambda/2\varepsilon_0$  independent of r/z, i.e., the tip shape. Therefore, the estimation of  $\Delta E$  discussed in Fig. 2 can be adopted for any r/z.

Figure 4 indicates a scanning image of X-EFM on the sample surface. For this figure, x rays of 100 and

115 eV were alternatively irradiated during one frame scanning of a demonstration. These photon energies correspond with levels below and above the edge jump energy in Fig. 2(a). As shown in Fig. 5, although a small contrast picture was obtained below the edge jump energy, a large contrast picture can be taken above the edge jump energy. An x-ray absorption tat is dependent on the chemical states provides the contrast. Although the tip shape was not be ideal, we achieved chemical states mapping of the Si oxide film with nano-scale spatial resolution. Moreover, from comparison of the X-EFM with atomic force microscopy, we found that the chemical composition  $SiO_x$  (x < 2) depends on the oxide thickness.



**FIGURE 4.** Scanning image of X-EFM on  $SiO_x$  (x<2) sample surface.

### SUMMARY

We create new x-ray absorption fine structure (XAFS) measurement technique that uses electrostatic force microscopy (EFM) called the X-EFM method. This method detects x-ray induced photoionization on a surface electron trapping site; an X-EFM signal dependent on x-ray photon energy provides the XAFS spectra. The X-EFM spectrum of Si oxide film indicates an absorption edge energy shift. The shift can be reproduced by a model where an electric field is induced between the probe tip and Si oxide surface. One application of X-EFM involves obtaining chemical states mapping with probe scanning under a fixed energy photon above the Si *L*-edge energy.

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