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A challenge toward surface elemental mapping by 3D XANAM spectroscopy

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1. Instructions

Scanning probe microscopy (SPM) is one of the powerful techniques to obtain information on surface structures on solid substrate surfaces. In addition to the function, spectroscopic usages of SPM are continuously developed for pursuing physical and chemical properties of surfaces/interfaces at the nanoscale. Especially, force spectroscopy in noncontact atomic force microscopy (NC-AFM) measurements is a powerful tool to reveal fundamental aspects of long range and short range physical and chemical interactions. In 2007, through precise measurements on difference in the covalent bonding force between a tip and a surface, elemental species on individual atoms observed in NC-AFM images were distinguished on a silicon surface with two other elemental species [1].

The above spectroscopy study does not use Synchrotron radiation (SR) X-ray and proved that the chemical sensitivity can achieve atomic level by means of SPM tips, although it requires a specialized setting to observe surfaces with atomic resolution on a flat surfaces. On the other hand, there are many techniques on elemental analysis developed in the X-ray experiments, such as XPS, XRF, and XAFS. Basics on them for elemental analysis are recognizing energy in relation to excitation of core-level electrons, emission of photoelectrons and fluorescent X-ray. The techniques are applicable to samples with various morphologies, for instance, a surface with humps. If such flexibility in the applicability can be implemented into NC-AFM and force spectroscopy, more versatile usages, which are accessible to fabrication of semiconductors, catalysts, and sensors, are expected.

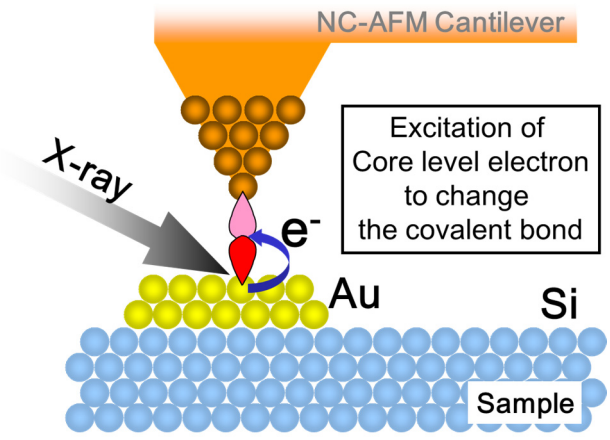

Fig. 1 Basic concept of XANAM

On this point, our study on X-ray aided noncontact atomic force microscopy (XANAM) [2-4] is potentially expected to provide a possible solution for the issue on applications to non-ideally flat surfaces. To the present, a customized NC-AFM for SR X-ray experiments was developed and was tuned for the experiments on some lithographed samples, nanomaterials-fixed surfaces, etc. Recently, the probe system on this apparatus has been refined to a new one adopting a qPlus sensor type probe [5]. The qPlus sensor type probe is very sensitive to the covalent bonding force, or chemical interactions which appears in force spectra, as well as van der Waals force and electrostatic force interactions. Thus, we proposed that HOMO/LUMO states localized at the covalent bond play a role of an extremely small detector of electron excitation from the core-level states of a sample surface when the surface was irradiated with the SR X-ray tuned at the absorption edge energy of the elements beneath the tip. Detecting the excitation of electrons at certain X-ray energy by the tip, we expected to obtain an elemental or chemical map of the sample surface with structural information at the nanoscale (Fig. 1). Actually, force spectra of a gold (Au) partially deposited silicon (Si) surface showed two distinctively-different spectral features on Au and Si regions by irradiating with X-ray tuned at Au L3 absorption edge energy. Near the edge energy region, strength of overall forces reduced compared to the one around the near-edge energy region. Although the spectra should be treated theoretically to divide force components [6, 7], the performance of the XANAM apparatus achieved a certain level of providing sufficient energy dependencies of force spectra for elemental analyses. Thus, we examined to expand the force spectroscopy in two dimensions as an XANAM imaging technique. Three dimensional data matrix for the force along the horizontal and vertical directions of near the surface with an additional axis of incident X-ray

energy was obtained. In this report, we show a concept how the XANAM images could be measured and a tentative data on the Au-partially deposited Si surface.

2. Experimental

The experiments were performed at BL-7C of the Photon Factory, Institute of Material Structure Science, High Energy Accelerator Organization (KEK-IMS-PF). A non-contact atomic force microscope was operated in a home-build ultrahigh vacuum (UHV) chamber equipped with two beryllium windows for X-ray penetration through the chamber. The microscope stage had four kinds of freedom to set the sample surface on the X-ray pass: X-, Y- and Z- movements and a rotation around vertical (Z) axis. We focused an X-ray beam on the sample position by a sagittal focusing of Si(111) double-crystal monochromator. In this measurement, a Au partially-deposited substrate was used as a sample. A qPlus sensor was fabricated by using a quartz tuning fork and an electrochemically-etched tiny tungsten (W) tip. A prong of the fork was fixed on a cantilever holder, followed by sticking the W tip on the other side of the prong with wiring for connecting to a current-to-voltage converter (DLPCA200, FEMTO Messtechnik GmbH) in order to measure the current signal. In this case, the qPlus sensor was oscillated by applying the ac voltage to electrodes on the prongs directly. Typical Q value and resonance frequency of a fabricated qPlus sensor were ~500 and ~27.5 kHz, respectively. All the measurements were carried out with irradiating the X-ray beam tuned around the Au L3 absorption edge energy. The data was recorded by Nanonis control systems (SPECS Zurich GmbH).

Three dimensional images were carried out by repeating the force spectroscopy measurements on virtual grid points in two dimensions on the sample surface. An area of 2×2 μm^2 was divided into 64×64 points of the grid in this experiments. As a result, the 3D data matrix of the force was obtained along two horizontal and one vertical directions on the sample surface.

3. Results and Discussion

The performance of the qPlus sensor was confirmed in respect to signal to noise ratio for the measurements on frequency shift (Δf), amplitude, phase, excitation, and electric current. Sharpness of an apex of the tip was very important for suppressing the level of background signal related to the electrostatic force. Generally in the case of normal operation without irradiation with light, influence of the electrostatic force can be reduced by choosing certain bias voltage between the tip and the surface by compensating the contact potential difference (CPD) between them. Besides, previous paper showed a sharpened tip is fundamentally-insensitive to the electrostatic force, compared to a rounded-shaped tip [8]. However, under X-ray irradiation condition, the X-ray induces positive and negative charge states at random in both of the tip and the sample, and varied the CPD with energy scanning. Since it is very difficult to reduce those influence properly, sharper tip is more profitable to obtain data. Actually, although the influence of the induced-electrostatic force could not be eliminated completely in most measurements in this term, some data were successfully obtained with reducing the influence.

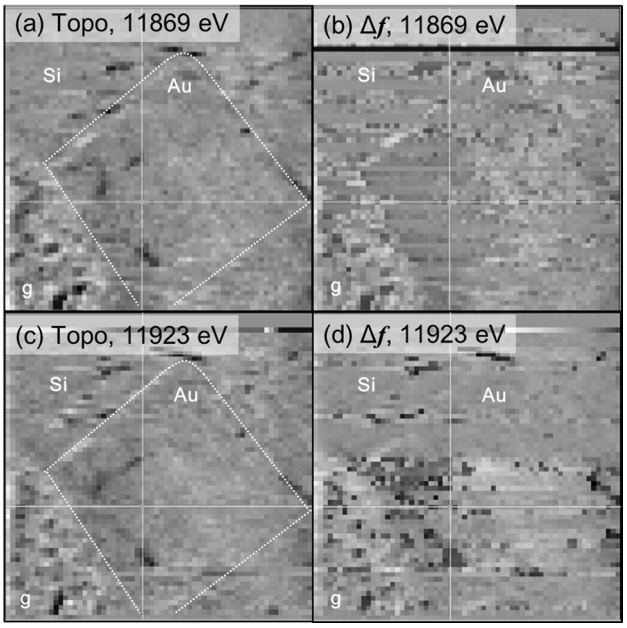

Fig. 2 XANAM (NC-AFM) Images obtained by force spectroscopy measurements on 64×64 grid points on 2×2 μm^2 of a partially Au-deposited Si(O_x) surface. (a): Topography, 11869 eV, (b): frequency shift, 11869 eV, (c): Topography, 11923 eV, (d): frequency shift, 11923 eV.

Fig. 2 shows results of (a) topography and (b) Δf obtained by repeating the force spectroscopy measurements on the virtual girds under X-ray irradiation tuned at 11869 eV. Besides, Fig. 2(c) and (d) were the above signals obtained in the same area under X-ray irradiation tuned at 11923 eV. The Δf images were a slice of the 3D data matrix at certain tip position from the surface. The surface position was defined as a position where decay of the oscillation amplitude of qPlus sensor begun. At an intersection of lines in each image, the tip position is approximately 0.5 nm far from the Au surface. Besides, image contrast are adjusted to be common between a pair of each signal. In the image, a square-shaped Au deposited region, a bare naturally-oxidized Si area, and unknown garbage adsorbed on the surface before starting the measurements. These species were labelled as “Au”, “Si”, and “g”, respectively. Besides, a guide for the

Au region was described as a white square with dotted lines in Fig. 2(a) and (c). In these images, morphologies in the Au region and the garbage were observed in a similar fashion. The fact indicates the tip-shape on the qPlus sensor was maintained during the measurements, and guaranteed the quality of data on Δf images in Fig. 2(b) and (d).

Comparing the two images in Fig. 2(b) and (d), morphologies in the Au region were observed in a different manner, while the garbage were observed similarly in both images. Since the topographical change were not observable as mentioned above, the difference in the Δf images can be interpreted as X-ray induced phenomenon detected in two dimensions. In accordance with the previous results [9], the force interaction were weakened by X-ray near the absorption edge region. In this experiments, X-ray energies of 11869 eV and 11923 eV correspond to lower and higher energies than the Au L3 absorption edge energy of 11919 eV, respectively. Thus, the force weakening possibly occurred and the contrast formation in the Au region might be disrupted in Fig. 2(d). No such variations were found in the bare Si region and the garbage. Consequently, the presence of Au atoms were visualized directly in two dimensions.

4. Conclusion

A challenge to obtain elemental maps has been carried out by the grid measurements of continuous force spectroscopy in two dimensions on the sample surface. By irradiating the X-ray tuned near the Au L3 absorption edge energy, weakening the force signal in a square Au region was visualized in two dimensions. On the contrary, the signal in other parts were not changed. Although further examinations for other X-ray energies and influence of thickness of the Au layer are needed to consider the spatial resolution of XANAM, the results proved the availability of two dimensional force spectroscopy combined with X-ray irradiation for elemental mapping on individual structures on surfaces.

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