Improvement of the XANAM System and Acquisition of a Peak Signal with a High S/N ratio

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Abstract. We have made remarkable progress in detecting X-ray-induced frequency shift signals, which will promote development of a chemically sensitive NC-AFM. A high-performance controller provides a tenfold higher signal to noise ratio than that previously reported. We confirmed that the frequency shift or complementary Z-feedback signal dependence on X-ray energy has a peak. An important feature of the signal is that it does not follow the absorption spectrum of a surface element. These new findings are important to elucidate this novel X-ray-induced phenomenon.

1. Introduction
Nanoscale chemical analysis is a fundamental issue. Numerous approaches have been actively pursued [1–19]. We previously proposed a new approach aiming at this purpose: X-ray Aided Non-contact Atomic Force Microscopy (XANAM) [20, 21]. After NC-AFM imaging, a cantilever was fixed above an X-ray irradiated Au region. Then the frequency shift of the cantilever was measured as a function of incident X-ray energy. A peak was observed in the cantilever frequency shift dependence around the Au L$_3$ X-ray absorption edge energy. This novel phenomenon is useful to identify surface chemical species under NC-AFM observation and can engender development of a chemically sensitive NC-AFM. We called the method XANAM.

We originally proposed that a mechanism of X-ray-induced frequency shift involving the core electron transition to a bonding or an anti-bonding orbital of the chemical bond [22] between a cantilever tip and a sample surface should modify its electron density and consequently change the force interaction during NC-AFM imaging.

Fig. 1 Basic concept of XANAM
imaging, as shown in Fig. 1. Soon thereafter, we received many comments that the spectrum in the literature [20, 21] might be regarded as an edge jump accompanied with a white line that is a sharp absorption peak appearing at the absorption edge. If that were true, what we observed were absorption coefficients changed by other factors such as electrostatic or thermal effects. However, because of the low S/N ratio, we were unable to definitively answer whether the feature was a peak or an absorption edge. In this paper, we have improved our electronic measurement capabilities by replacing the original instrument with a Nanonis SPM controller, which provided us a remarkably increased S/N ratio. We obtained a high S/N ratio spectrum that depicts the feature as a peak. In this study, we present details of the system and discuss its possible mechanisms.

2. Experimental

Figures 2(a) and 2(b) respectively show a schematic diagram of our experimental setup and its photograph. All measurements were carried out at the beam line 7C of the Photon Factory, Tsukuba, Japan. The ring was operated at 300 mA and 2.5 GeV. The beam line 7C provides $10^{11}$ photons/s at the sample position. The X-ray was monochromatized using a Si(111) double-crystal monochromator with an energy resolution $(\Delta E/E)$ of about 5000. A NC-AFM UHV-chamber (Unisoku Co., Ltd.) was placed in the center of an experimental hutch connected to the beam line. The instrument consisted of two components: an AFM chamber and a pre-treatment chamber. The base pressures for both chambers were $10^{-8}$ Pa. Two Be windows were equipped with the AFM chamber for X-ray beam entrance and exit. The AFM microscope was set on a mobile stage that had three translational axes and a rotational axis to adjust the sample position relative to the X-ray beam pathway, the motion of which was controllable from outside of the hutch. In addition, we were able to monitor inside the AFM chamber using a CCD camera. Figure 3 shows a CCD camera image with the X-ray beam coming from the right side and irradiating the sample surface at a glancing angle. We placed a phosphor screen to confirm the X-ray position on the source side. The X-ray beam was focused along the sagittal direction by bending a monochromator. The X-ray beam’s size in the parallel and perpendicular directions at the sample surface were estimated as less than 1.5 mm. We scanned the incident X-ray energy from -50 eV to +50 eV around the Au L_3 absorption edge.

Fig. 2 (a) Photograph of a NC-AFM chamber installed in the X-ray protective hutch at the beam line at the Photon Factory. (b) A schematic diagram of our experimental setup.
We used the self-sensing piezoelectric cantilever (Nikon Corp.). The cantilever tip apex was made of silicon nitride. The system required no optical components to detect the cantilever deflection. Consequently, we were able to simplify the NC-AFM stage architecture to provide much visibility and aid alignment of the sample position to the X-ray beam.

Typical resonance frequency and the oscillation amplitude of the cantilever were, respectively, 115 kHz and 3.0 nm. The cantilever oscillation amplitude was calibrated by measuring excitation amplitude vs. Z distance curves with applying certain voltages to a dither piezo element.

Figure 4 shows a block diagram of the XANAM measurement system. In this work, we used a high-performance SPM controller (Nanonis; Nanonis GmbH). The signal to noise (S/N) ratio of this system was at least tenfold higher than that of the previous controller. A Z-feedback signal of the piezo sample scanner in the constant Δf mode was recorded as the force interaction together with X-ray incident intensity, which is a complementary signal of the Δf in the constant height mode. The voltage signal was converted to the frequency by the V/F converter (NVF-02B; Tsuji Electronics Co., Ltd.) and accumulated by the pulse counter (ORTEC974; EG&G Ortec). The spatial resolution of the NC-AFM microscope was less than 10 nm under X-ray irradiation conditions. We did not try to obtain atomic resolution images because of beam time limitations. The Z-feedback signal dependence on the X-ray energy was measured as follows. First, we fixed the cantilever position above the certain region while irradiating the sample surface with the X-ray. After waiting for several minutes until the cantilever motion became stable, we started to scan X-ray energy while monitoring the Z-feedback signal of a sample scanner.

Different from the previous work, we used a fully Au-covered Si wafer with 20-nm-thick Au layer. The sample was prepared in a separate high vacuum deposition chamber, VPC-260F (ULVAC, Inc.), and was introduced in the NC-AFM chamber.

![Fig. 4 Block diagram of the XANAM measurement system](image)
3. Results and Discussion

Figure 5 shows the Z-feedback signal during energy scanning of the X-ray. The X-axis is the X-ray energy, whereas the Y-axis is the Z-feedback signal. After approaching the tip to the Au-covered surface, we kept the cantilever over 10 min without any operation. Then the X-ray energy was scanned around the Au adsorption edge. As in the previous experiment, we again found a remarkable sharp peak in a Z-feedback spectrum around the X-ray absorption edge region. Figure 5 shows the Au absorption spectrum of Au foil for reference, too. An inflection point around the Au L₃ absorption edge was at 11919 eV. The peak position in the Z displacement signal was also at 11919 eV. The amount of Z displacement and the full width at half maximum (FWHM) of the peak were 0.62 nm and less than 2 eV, respectively. Results clarified that the signal response was much improved over those of previous data. Note that the Z position after the peak turned back to the nearly original position, meaning that the cantilever change does not follow the absorption spectrum. It is important to understand the mechanism. We originally proposed that the frequency shift occurs because of the electron transition to the unoccupied or occupied state of the chemical bond between the tip and the surface [20, 21]. However, it was pointed out that the photons were too few to excite the Au atom under the tip apex constantly and other possibilities were suggested as follows:

1) Thermal effect induced by X-ray absorption
2) Charge effect induced by X-ray absorption
3) X-ray localization in the nanospace between the tip apex and surface at the absorption energy

The first two possibilities can be denied unambiguously. The frequency shift should have followed the absorption spectrum of Au L₃ but not in the case shown in Fig. 5, if (1) and (2) were correct.

Hence, the third candidate is another possible mechanism. As found in surface-enhanced Raman spectroscopy (SERS), the X-ray electric field can be concentrated around the atomically sharp tip apex. If the tip apex is approached closely to the sample surface in the order of X-ray wavelength (sub-nanometer), the strong electric field might be localized between them and the X-ray absorption might be resonantly enhanced. Although we need further studies by measuring force curve as a function of Z distance or bias voltage to confirm the real mechanisms, this novel phenomenon might open the way to an atomic scale chemical analysis called X-ray aided non-contact atomic force microscopy (XANAM)[20, 21].

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