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X-ray Energy Dependency of XANAM Spectrum by a qPlus Sensor Probe

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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. SPM is widely used in many studies of surface science related to catalysis chemistry, semiconductor process engineering, fuel cell and solar cell technology, and sensor technology. Additional refinements for the microscopes are in progress in order to make higher level of usability and to append new functionalities. Among them, development of novel chemical imaging techniques with high spatial resolution was still a hot topic. The chemical analysis on semiconductor surfaces at the atomic scale by noncontact atomic force microscopy (NC-AFM) was reported as a prominent answer for the issue [1], showing that the precise analysis of chemical component in the force interaction between a probe and a surface provided locations of atom with their elemental names. On the other hand, our study on X-ray aided noncontact atomic force microscopy (XANAM)[2-4] is potentially expected to provide a possible solution for the analysis on the non-ideally flat surfaces, by using synchrotron X-ray technique for the elemental analysis combined with the NC-AFM. We proposed that HOMO/LUMO localized at the covalent bonding between the probe and the surface play a role of an extremely small detector of photoelectrons excited from the inner core-levels of atoms in the surface, or the energy levels of the orbitals can be resonantly interacted when the electron excitation occurs. As a result, strength of the force interaction can be altered by the effect induced by the X-ray absorption, providing us the chemical information on the surface (Fig. 1). Indeed, we succeeded that the electron excitation were surely detected though the XANAM measurements of force interaction profiles [2-4].

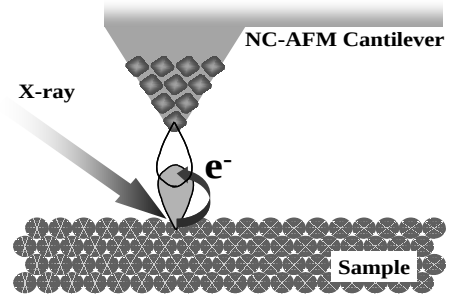

Fig. 1 Basic concept of XANAM

However, the sensitivity to the changes in the covalent bond force was not sufficiently obtained in the previous experiments. From the study on the relationship between a morphological shape of a tip apex and the spatial resolution in NC-AFM measurements, a sharper tip provided a higher resolved image at atomic resolution by increasing the sensitivity to the chemical bonding force [5, 6]. Therefore, sharpening the tip apex was a possible solution for increasing the sensitivity to the chemical bond force in the tip-surface interaction.

In this report, we show an improved results on energy dependency of force spectrum improved by introducing a qPlus sensor [7]. The sample was a gold (Au) deposited Si wafer. We could obtain enhancement of high signal to noise ratio in the XANAM measurements toward enhancing the chemical sensitivity.

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-deposited substrate was used as a sample. The 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. 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 of 11919 eV. The data was recorded by Nanonis control systems

(SPECS Zurich GmbH) for SPM operations and X-ray experimental instruments at the beam line.

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. Under the X-ray irradiation condition, a sharpened W-tip on the qPlus sensor probe effectively suppressed the influence of the electrostatic interaction over the spectral background at the beginning of the spectral measurements. Figure 2 shows a result on a Au surface deposited on a Si wafer. The figure is composed of a 3D contour plot on the X-ray energy dependency of the force spectra (Δf), as well as the absorption spectrum of the Au L3 edge. The data were separately recorded. As previously observed in the papers [2-4], Fig. 2 showed peak-like features around the Au L3 absorption edge, but no significant changes in the electrostatic force

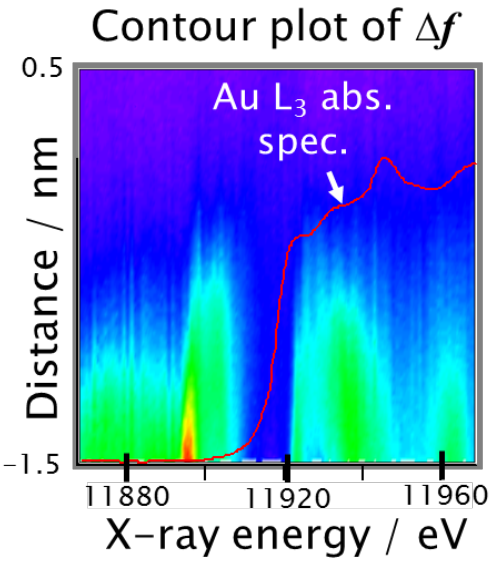

Fig.2 the 3D spectral measurements of X-ray energy dependency of force spectroscopy on the Au surface

components appeared at the higher energies than the absorption edge energy. Thus, the tip-sharpening was also effective to suppress the influence of electrostatic force and was very useful to detect the covalent bond force component preferentially. Indeed, deep reduction of the interaction force component localized at the absorption edge was clearly observed in this spectrum, which was not found in the previous studies. Although the reason why the phenomenon appeared was not clearly elucidated, the covalent bonding might be weakened in the energy region due to the resonantly-occurred excitation from the core-level electrons of Au toward the LUMO state in the covalent bond between the tip and the surface.

4. Conclusion

In order to improve the quality of XANAM measurements, we have introduced a qPlus sensor probe. We carried out the 3D spectral measurements of X-ray energy dependency of force spectroscopy on the Au surface. From the results, the tip-surface interaction force could be recorded with high signal to noise ratio toward enhancing the chemical sensitivity, and consequent results showed more complex features on X-ray energy dependency of the covalent bond force component for the XANAM measurements.

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