

## Data analysis methods of force spectra for XANAM

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### 1. Introduction

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, noncontact atomic force microscopy (NC-AFM) measurements is a powerful tool to reveal physical aspects of surface structures, as well as surface atomic structures. The most prominent part in NC-AFM is applicability to insulator surfaces. However, there have been still an issue on chemical analysis with highly versatile ways for many users, though extremely precise measurements of force spectroscopy in NC-AFM measurements already overcome the issue in 2007[1]. In order to provide the high versatility on the chemical analysis at the nanoscale for various surfaces, we introduced the Synchrotron radiation (SR) X-ray absorption spectroscopy into the NC-AFM measurements[2], called as X-ray aided NC-AFM (XANAM). The SR X-ray can excite the core-level electrons at X-ray absorption edge energies of atoms on sample surfaces. Thus, if the electron or absorption can be detected by a NC-AFM tip, the atom species can be known beneath the tip. In our strategy, we proposed that the covalent bonding involving the tip-surface interaction can be utilized for the detection, since electron density of the covalent bonding should be changed through the electron excitation from the core-level states in an atom on a sample surface at its X-ray absorption edge energy (Fig. 1). Actually, force spectra of a gold (Au) partially deposited silicon (Si) surface showed two 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, the strength of overall forces reduced compared to the one around the near-edge energy region. However, the analysis relied on the sample bias voltage (Vs) dependencies of signals, providing an indirect proof of a presence of the covalent bond as a component with no Vs dependency. Thus, there had been no direct proof of the changing on covalent bonding induced by X-ray absorption of the sample surface beneath the tip. Based on

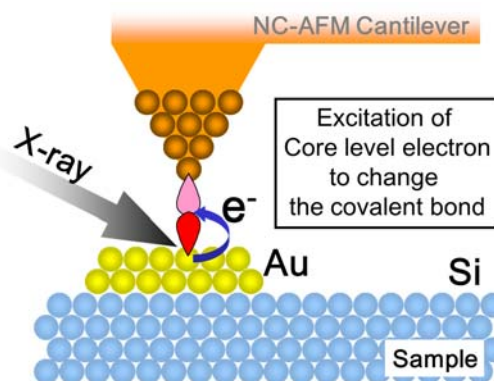


Fig. 1 Basic concept of XANAM

the NC-AFM theory[3, 4], analysis of force components in NC-AFM measurements can be applied to XANAM measurements. The following experiments and analysis were made for the analysis on the changing of the force components induced by the Au-L3 X-ray absorption on a Au sample 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-built 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. 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. Typical Q value and resonance frequency of a fabricated qPlus sensor were ~525 and ~28 kHz, respectively. All the measurements were carried out with irradiating the X-ray beam with energies around the Au L3 absorption edge

energy. The data was recorded by Nanonis control systems (SPECS Zurich GmbH). Analysis on force components was carried out by force spectroscopy on a single point on a sample surface, followed by numerical calculations on original programs coded by Mathematica language (Wolfram).

### 3. Results and Discussion

The force spectra were obtained with X-ray energy scan around the Au-L3 absorption edge. A set of bundled force spectra against the X-ray energy is shown in Fig. 2(a). A contrast in the figure indicates differences in the tip-surface force which was converted from the signal of frequency shift of the oscillated qPlus sensor through the method proposed by J.E. Sader et al[5]. Based on the NC-AFM theory, the force spectroscopy data can be divided into components related to electrostatic force, van der Waals force, and covalent bond force. In addition, X-ray induced another force component related patch charge or image potential induced by X-ray was considered for XANAM experiments. On these components, numerical fitting with using certain functions was done until obtaining a minimum of residual errors as  $\chi^2$  for each force spectrum. For a force spectrum, 4 models described for the functions of electrostatic force, van der Waals force, X-ray induced force, and Morse force were adopted to extract the covalent bond component as a final result. In the model, the tip shape was assumed to have a shank, which was proposed as a good solution for describing electrostatic force[6] and van der Waals force[7] as the tip-surface interaction. In case the Morse force component could not be fitted properly, the other fitting processes were recalculated until obtaining a consistent result on all force components.

Fig. 2(b) shows a result of the covalent bond force extracted from the original data as shown in Fig. 2(a). The data in Fig. 2(b) contains force change depending on the X-ray energy, as well as the tip-surface distance. Around the Au-L3 absorption edge region, the changes in Fig. 2(b) showed a similar tendency with the changes in Fig. 2(a),

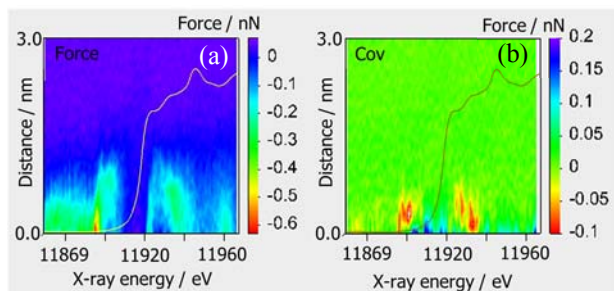


Fig. 2 X-ray energy dependency of force spectrum on a Au-deposited Si substrate. (a) Measured-data (total force), (b) Covalent force component extracted from (a).

although such dependencies were not observed in the force components related to electrostatic force and van der Waals force. Consequently, we obtain the results indicate a clear proof of the mechanism proposed for XANAM as shown in Fig. 1 on the theoretical basis.

### 4. Conclusion

In order to obtain elemental information on surfaces at the nanoscale by using NC-AFM with high versatility, we have developed a noncontact atomic force microscope with SR X-ray absorption spectroscopy, called as X-ray aided NC-AFM (XANAM). In this report, we established the way of analysis on force components in the tip-surface interaction under X-ray irradiation and found a clear evidence of the force change around the Au-L3 absorption edge energy. Based on the NC-AFM theory, the results were divided into 4 components including covalent bond force. By comparing the profiles of force components depending on the X-ray energy, we obtained the change in the covalent bond force was regarded as a major component of X-ray induced force changes which were observed apparently in the original profile of the total force.

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