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Detecting X-ray induced change in the tip-surface force on Ge by XANAM

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1. Introduction

In recent years, with the progress in research on the application of single atoms and nanoclusters to electronic devices, the demand for surface / interface elemental analysis at the nanoscale has increased. We have developed X-ray aided noncontact atomic force microscopy (XANAM), a scanning probe microscopy combined with synchrotron X-ray designed for elemental analysis at the nanoscale. We reported that Au and Ni surfaces could be identified by detecting the force change in the tip-surface interaction induced by X-ray absorption, which occurs at those element's edge energy [1]. Based on the NC-AFM experimental and theoretical studies, it is well-known that the tip-surface force includes covalent bond force in addition to van der Waals force, electrostatic force. We expected that if the electron density of the orbital in the covalent bond changed with X-ray core-level electron excitation, it could be used for the elemental analysis on an atom beneath the tip from the X-ray absorption edge energy (Fig. 1). By extracting the change in the covalent bond force, the atomic resolution could be achievable. Therefore, the force spectrum of the NC-AFM (interatomic force dependence concerning the tip-sample separation) was measured, and component analysis of the force was performed by caculations based on the theory. As a result, it was found that force components in the change could be classified into the electrostatic force and the covalent bond force. However, the direct proof showing the involvement of covalent forces is still ambiguous, because there have been no experimental results on semiconductor surfaces except the metals

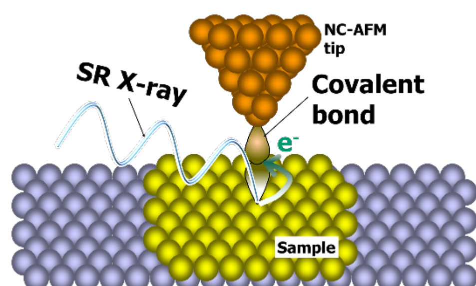

Fig. 1 Basic concept of XANAM

mentioned above. Here, we report that the spectroscopic measurements on a Ge surface. It is well known that the NC-AFM tip can intera ct with the surface atoms on the semiconductor surface with the covalent bonding; thus we expected to detect of the changes in the force induced by X-ray at the Ge-K absorption edge energy, resulting in the direct proof of the issue.

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 the vertical (Z) axis. We focused an X-ray beam on the sample position by a sagittal focusing of Si(111) double-crystal monochromator.

As a sample, a Ge(001) single crystal was used as a sample. The sample surface was cleaned before use by sputtering and annealing [2]. An AFM-probe was fabricated by using a quartz tuning fork and electrochemically-etched tiny tungsten (W) tip with the similar configuration of the qPlus sensor [3]. The typical resonance frequency of the sensor was ~30 kHz. As the force signal, frequency shift (Δf) from the resonance frequency was recorded and converted to the values of force using the Sader-Jarvis equation [4]. All the measurements were carried out with irradiating the X-rays with the energies around the Ge-K absorption edge. The data was recorded by Nanonis control systems (Nanonis, SPECS Zurich GmbH).

3. Results and Discussion

Fig. 2(a) shows a result obtained by force spectroscopy measurements with scanning X-ray energy around the Ge-K edge absorption edge. The vertical and horizontal axes are the tip-surface separation and X-ray energy, respectively. The color contrast indicates the strength of the force detected by the tip. For instance, the force from -5 to -8 nN was observed as the color range from green to

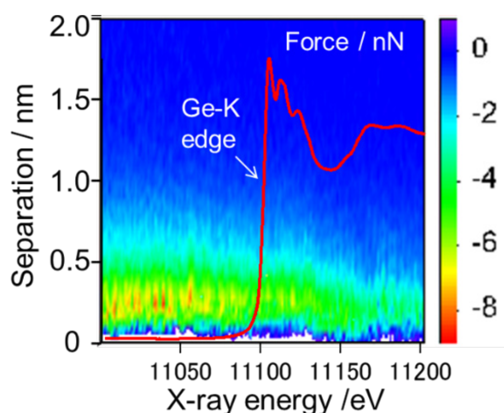

Fig. 2 A set of force spectra on Ge(001) measured with scanning X-ray energy around the Ge-K edge absorption edge. The red curve is the absorption spectrum of Ge, separately-measured.

red via yellow, as shown in the bar graph at the right side. The negative force means the attractive force in the figure. Besides, the X-ray absorption spectrum of Ge-K in the same energy range is superimposed on the figure as a reference, which was separately obtained in the transmission mode using a thin film (3 μm) sample made of Ge. The energy of 11103 eV is used as the absorption edge energy of Ge-K in this report.

First, at the energies below the X-ray absorption edge, the shape of the force curve was almost maintained. The magnitude of the attractive force was kept around -7 ~ -8 nN. Then, the force curve started to change its shape from the absorption edge energy with decreasing the attractive force.

By analyzing the force curve change, a small gap was found near the X-ray absorption edge energy. The state of the gap could be considered as the change-induced by electron excitation from the core level electron to the electron states of the covalent bond between the tip and the surface. Thus, we tentatively concluded that the change restricted to the absorption edge energy was observed experimentally as the covalent bond force. However, the background of the change decreased gradually, too. It seemed to cover the net change of the gap. Although we cared for the measurements with enough sensitivity to the covalent bond, the current result shows that detecting X-ray induced electrostatic forces was still inevitable, because the force involves van der Waals force and electrostatic force. For increasing the sensitivity to such energetically-limited change, it is important to understand the background changes. Thus, it is necessary to analyze the force components to attribute the origins of the changes in the force curves as the next step.

4. Conclusion

We have developed XANAM to obtain elemental information on surfaces at the nanoscale using NC-AFM combined with SR X-ray. To obtain the direct proof of the force change surely involving the covalent bond force, we adopted the force spectroscopy measurements to Ge(001) with scanning X-ray energy around the Ge-K edge absorption edge. As a result, we observed the X-ray induced changes as the small gap over the gradual background change. We concluded tentatively the gap presumably related to the X-ray induced change in the covalent bond force.

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