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Measurements of 2D force map on Ni nanoparticles on HOPG for XANAM imaging

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1. Introduction

X-ray aided noncontact atomic force microscopy (XANAM) is a scanning probe microscopy combined with synchrotron X-ray designed for elemental analysis in the nanoscale. We reported previously on 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]. From the previous 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 with respect to the tip-sample separation) was measured, and component analysis of the force was performed. As a result, it was found that force components in the change could be classified into the electrostatic force and the covalent bond force. Furthermore, we examined the establishment of imaging procedure for the elemental mapping at the nanoscale, proposed as the extended-force spectroscopy in two dimensions with X-ray energy scanning. Previously, X-ray energy dependency of the force on a gold (Au) partially deposited silicon (Si) surface was recorded successfully. Although the spatial resolution of the obtained image was not so high, it could be regarded that the procedure was established as one of the imaging technique for XANAM. Here, as the remaining problem, we have pursued how the imaging procedure could be optimized for XANAM using a sample of Ni nanoparticles deposited on an HOPG substrate.

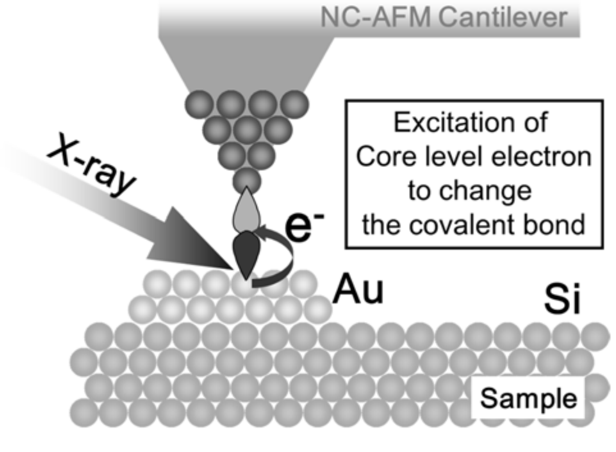

Fig. 1 Basic concept of XANAM

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 Ni deposited HOPG substrate was used as a sample. 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 [2]. 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 [3]. All the measurements were carried out with irradiating the X-rays at the Ni-K absorption edge energy. The data was recorded by Nanonis control systems (Nanonis, SPECS Zurich GmbH).

3. Results and Discussion

Fig. 2(a) and (b) show results obtained from XANAM imaging. Fig. 2(a) shows a contrast difference of force calculated from the force spectra measured in each pixel. The values in Fig. 2(a) were corresponded to the values at the same distance from the sample surface in the force spectra (The red crosses in A and B, as shown in the right column). The height differences on the nanoparticles and bare regions of HOPG were corrected using the topographical information of the nanoparticles, resulting in the cancelation of the origin of the separation in Fig. 2(a). The image in Fig. 2(b) was an NC-AFM image of the same area obtained in Fig. 2(a), showing the Ni nanoparticles formed on an HOPG surface. Compared with two images of Fig. 2(a) and (b), the contrasts in Fig. 2(a) shows the similar tendencies to the corrugations of nanoparticles in Fig. 2(b). Thus, it was confirmed that the 2D force map in Fig. 2(a) was obtained for the area observed in Fig. 2(b).

In this trial, Fig. 2(a) only have 256 (= 16x16) pixels, which corresponds to 6.25 nm / pixel. Because the time interval of measuring force spectra was ~10 s, the time of scanning a frame was 43 min for the 2D force map. To evaluate how far the spatial resolution could be obtained, it was necessary to increase the number of pixels and shorten individual force spectrum measurement time, although another factor of X-ray energy scan should be considered. Further overall improvements of the measurements are in progress to evaluate the spatial resolution of XANAM imaging with X-ray energy scan.

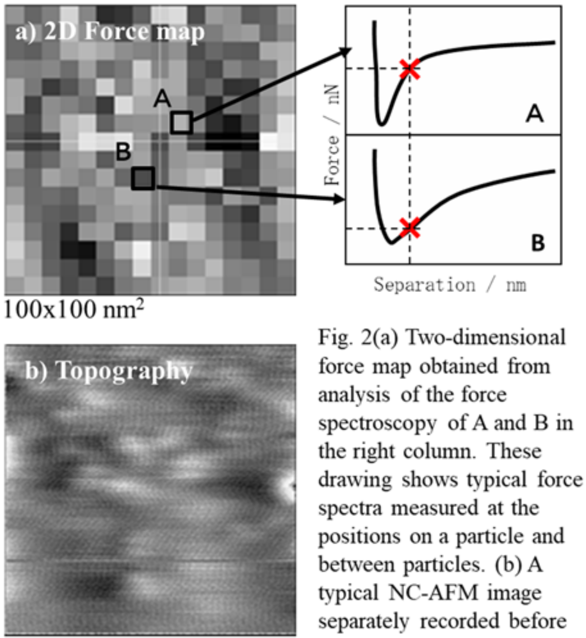

Fig. 2(a) Two-dimensional force map obtained from analysis of the force spectroscopy of A and B in the right column. These drawing shows typical force spectra measured at the positions on a particle and between particles. (b) A typical NC-AFM image separately recorded before the measurement of a).

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 image data of XANAM for estimation of the spatial resolution, we adopted the two-dimensional force spectroscopy measurements as XANAM imaging under X-ray irradiation. Although the number of pixels were not enough to conclude the spatial resolution, the same tendencies of image contrasts were obtained on the Ni nanoparticles on the HOPG surface.

Acknowledgements

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