A Possibility of XANAM (X-ray Aided Non-contact Atomic Force Microscopy)

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We have measured a frequency shift of the noncontact atomic force microsocpy (NC-AFM) cantilever above Au islands when we scanned the X-ray energy around the Au L_3 absorption edge. We have found a clear peak of the frequency shift just above the Au L_3 absorption edge. This novel phenomenon suggested that the combination of energy-variable X-rays and NC-AFM provides us a new way of nano level chemical mapping of surfaces.

A surface chemical mapping on an atomic level is very important in nanoscience to understand the chemical processes occurring at the surfaces of catalysts, sensors, and electronic devices. Since the invention of the scanning tunneling microscopy (STM)[1] in 1982, atomic-level spatial resolution of conductive material surfaces has been achieved and the invention of the noncontact atomic force microscopy (NC-AFM)[2] in 1995 has made it possible to measure insulator surfaces. However, it is still difficult to distinguish chemical species directly by these STM and NC-AFM. Many efforts have been done to obtain chemical information by developing techniques of scanning probe microscopy (SPM) family such as STM inelastic tunneling spectroscopy,[3] STM light emission spectroscopy,[4,5] infrared scanning near-field optical microscopy,[6] X-ray excited STM.[7] In this brief communication, we report a novel phenomenon that will be a base for a new elemental analysis at the atomic level by SPM, named "X-ray Aided Noncontact Atomic force Microscopy (XANAM)."

The NC-AFM has a wide applicability to insulator inorganic oxides and organic polymers.[8] Atomic level observations of insulating oxide surfaces have recently been reported.[9–13] NC-AFM imaging is attained by detecting the frequency shift of the cantilever, which can simply be explained by the value proportional to the attractive force gradient between a tip of the cantilever and the surface atoms.[14] Theoretical and computational analyses show that the forces are not only physical forces such as van der Waals force and electrostatic force but also chemical bonding force such as a covalent bonding. The chemical bonding force may depend on the electron density of bonding and antibonding orbitals. If the electron density of these orbitals can be controlled, one may control the interaction between the surface atom and the cantilever. X-ray is one way to alter the electron density of bonding or antibonding orbitals by exciting core electron. The core electron has a binding energy specific to elements and their chemical state. Thus one can get a chemical mapping using the NC-AFM aided by X-ray irradiation. To test the above hypothesis, we carried out a simple experiment to see how the frequency shift depends on X-ray energies near the absorption edge. We found a sudden frequency shift of the NC-AFM cantilever just above the Au L_3 X-ray absorption edge described later.

The experiments were performed at BL7C of the Photon Factory, Institute of Material Structure Science, High Energy Accelerator Organization (KEK-IMS-PF). A noncontact atomic force microscope was operated under ultrahigh vacuum (UHV) conditions with a piezoresistive AFM cantilever (NIKON). The tip apex of the cantilever was composed of silicon nitride. A typical resonance frequency and force constant of the cantilever were 88 kHz and $150\,\mathrm{Nm}^{-1}$, respectively. The partially Au-covered sample was prepared by vacuum evaporation of Au on a Si substrate through a 1000 L Ni mesh put on the substrate. The sample was set on the microscope stage with its surface standing vertically. Two X-ray entrance and exit beryllium windows were placed at the front and backside of the UHV chamber. The microscope stage had three kinds of freedom to set the sample surface on the X-ray pass: *x*- and *y*- horizontal movements and a rotation around vertical (*z*) axis. We focused an X-ray beam on the sample position by a sagital focusing Si(111) double-crystal monochromator.[15] Because of the beam time limitation, we could not optimize the NC-AFM imaging conditions. The spatial resolution of the microscope was a few nanometer, which was confirmed by the observation of a PZT layer sample surface composed of fine particles with diameter from 10 to 20 nm, as shown in Figure 1.

The NC-AFM observation of the partially Au-covered Si sample was carried out in a constant frequency shift mode with constant excitation amplitude of the cantilever with X-ray irradiation at 11850 eV. Figure 2 shows a typical NC-AFM image of a sample surface observed at room temperature. Au-deposited region and Si region were clearly distinguished by their height difference. The Si region was probably covered with native Si oxide layer because no treatment to remove oxide layer was done in the UHV chamber. The constant frequency shift of the cantilever was −20 Hz during the observation. Then we put the cantilever above the Au island, as shown in Figure 2 by a square, and stopped the scan feedback routine of the cantilever. We started to measure frequency shift dependency on the X-ray energy around

Figure 1. A NC-AFM image of PZT layer sample under X-ray irradiation, $70 \times 70\,\mathrm{nm}^2$, $\Delta f = -20\,\mathrm{Hz}$, $A_0 = 27\,\mathrm{nm}$.

Figure 2. NC-AFM image of partial Au-deposited Si surface, $3.5 \times 3.5\,\mu m^2$, $\Delta f = -20\,Hz$, $A_0 = 27\,nm$.

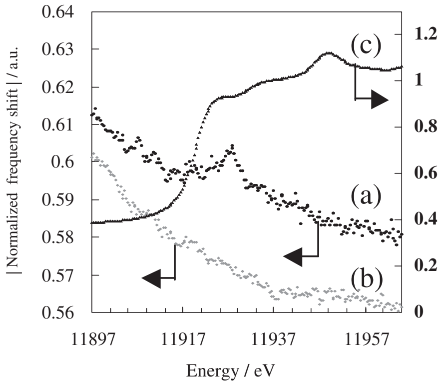

Figure 3. Frequency shift spectra normalized by I_0 on both Au (a) and Si (b) regions together with absorption spectrum of Au foil (c).

the Au L_3 absorption edge. For comparison we carried out the same experiment on the bare Si surface in the same energy range.

Figure 3 shows the frequency shift spectra above both Au and Si regions together with an absorption spectrum of Au foil. The frequency shift signal was integrated by a F–V converter circuit with duel time of 2 s, and was normalized by incident X-ray intensity which was simultaneously recorded by the ionization chamber in front of the NC-AFM chamber. We plotted the absolute value of the normalized frequency shift. Generally, the frequency shift is negative in the attractive force region. Increasing the absolute value of the shift corresponded to the enhancement of attractive force between the cantilever and the sample surface. Each spectrum was recorded with increasing the X-ray energy.

When the X-ray was irradiated, the sample was heated by the X-ray and changed its position gradually related to the tip apex by the thermal drift. Consequently the monotonous variations in the background were found. In addition to these background variations, we found a distinctive peak around the X-ray energy of 11925 eV in the Au region, while no peak was found in the Si region within the same energy range. We observed repeatedly the peak at the same X-ray energy at different Au regions but no peak was found at Si regions. The presence of the peak clearly demonstrates that the X-rays around the absorption edge energy affect the frequency shift of the NC-AFM cantilever. Generally, the frequency shift is negative in the attractive force region. Thus, increasing the absolute value of the shift corresponded to the enhancement of attractive force between the cantilever and the sample surface. Note that the normalized frequency shift did not follow the absorption spectrum of Au foil, namely, the spectral feature of Au region did not have an absorption edge but a peak. It means the phenomenon is not simply related to the photoabsorption process.

The following origins to enhance the attractive force between the cantilever and the sample surfaces can be proposed.

(1) Excitation of photoelectron to a bonding orbital to strengthen the covalent bond, as mentioned above.
(2) Local electric field enhancement around cantilever apex like Surface Enhanced Raman Spectroscopy (SERS).

We are planning to measure element-selected NC-AFM image by this system soon. Although the detailed mechanism and physics are unclear at the moment, the phenomenon suggested that NC-AFM could distinguish Au from Si under the X-ray irradiation tuned at the absorption edge energy. This phenomenon will lead to a new nano-level element-selected imaging method aided by X-ray called as XANAM.

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