MICRO-XRF INSTRUMENT DEVELOPED IN COMBINATION WITH ATOMIC FORCE MICROSCOPE

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ABSTRACT

A new micro-XRF instrument was developed in combination with an atomic force microscope (AFM). A small pinhole of 5 or 10 µm was made on the AFM cantilever. The center of the micro X-ray beam generated by a polycapillary X-ray lens was passed through the pinhole. The present experiment demonstrated that the size of the original X-ray beam of 48 µm produced by the polycapillary lens was reduced to about 10 µm. This instrument enables both observation of the surface morphology by the AFM and elemental analysis by micro-XRF.

INTRODUCTION

Almost all surface analytical methods are used under an ultra-high vacuum. However, in nano science, materials that are not stable under ultra-high vacuum conditions, such as bio-related materials, are increasing in importance. In addition, when electrons and charged particles are used for the excitation beam in surface analysis, damage to the samples poses a serious problem. Therefore, a non-destructive elemental analytical method that can be applied at ambient air pressure is desired. One such method is X-ray fluorescence (XRF). However, it is not easy to analyze small regions by XRF because it is difficult to obtain a small-diameter X-ray beam. Synchrotron radiation provides a suitable beam for micro-region XRF. Actually, a sub-micro X-ray beam has been obtained at a synchrotron radiation facility [1]. However, micro-XRF analysis at the synchrotron radiation facility has difficulties such as machine time, availability, location, etc. Therefore, the development of micro-XRF instruments in laboratories as a fundamental tool for general science is very important. In the present article, we discuss the laboratory based micro-XRF instruments.
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A polycapillary X-ray lens provides useful optics for obtaining an intense micro X-ray beam, especially in laboratories [2-6]. The polycapillary lens consists of more than several hundreds thousand capillaries. The X-rays generated at the target in the X-ray tube are introduced to the polycapillary lens and are totally reflected on the inner wall of each capillary. The X-rays are then focused on a small area of the sample. However, the minimum spot size obtained by the polycapillary lens is a few tens of micrometers, for example, 15 µm for Mo Kα [7].

One of the methods used to reduce beam diameter is to apply an additional pinhole [8]. That is, both the polycapillary lens and the pinhole are placed on the same axis, and the center of the micro beam generated by the polycapillary is positioned so that it passes through the pinhole. The problem in using this method is that the X-rays that pass thorough the pinhole immediately diverge. Therefore, the sample must be placed near the pinhole.

A scanning probe microscope (SPM, scanning tunneling microscope: STM, or atomic force microscope: AFM) is a useful tool for observing surface morphology of samples with atomic resolution [9]. An SPM has similar advantages to XRF in that the SPM enables nondestructive observation at ambient air pressure. However, it is still difficult to obtain chemical information (elemental identification) by an SPM. Thus, we have investigated several possibilities of combining an SPM with X-ray analysis. It has been found that an additional STM tip current was observed under X-ray irradiation [10-14]. This tip current was caused by X-ray-induced photoelectrons. At the SR facility (Photon Factory at Tsukuba, Japan), the STM tip current was measured as a function of X-ray energy resulting in the first instance of obtaining EXAFS-like spectra to the best of our knowledge [15]. These preliminary results indicate that localized elemental analysis will be possible by combining STM and X-ray analysis.

In this article, we have introduced the concept of a pinhole made on an AFM cantilever. AFM is a unique tool applied to electrically non-conductive materials. The focused ion beam (FIB) technique enables the creation of a small hole of several tens of nanometers on a silicon substrate although, in the present study, we made a pinhole of 5 or 10 µm. As mentioned above, the pinhole is used to reduce the size of the micro X-ray beam generated by the polycapillary lens, as shown in Figure 1. Under normal conditions of AFM observation, the distance between the AFM cantilever and the sample surface is about 1 nm. Therefore, the influence of X-ray divergence after the X-ray beam passes through the pinhole is extremely small.
Figure 1. Micro X-ray beam distributions obtained by normal polycapillary X-ray lens and combination of polycapillary X-ray lens and AFM cantilever.

EXPERIMENTAL DETAILS

Figure 2 shows a cross section of an AFM cantilever. A small pinhole of 5 or 10 µm in diameter was made by the FIB technique on the tetragonal cantilever. The position of the pinhole was shifted from the top center of the tetragonal cantilever in order to take an AFM image of this cantilever. Figure 3 shows scanning electron microscopic (SEM) images of the AFM cantilever with the pinhole. Figure 4 shows a typical AFM image (3 µm × 3 µm) of polystyrene beads (50 nm in diameter) with the cantilever having a pinhole of 5 µm. After the pinhole is made, a Au layer about 2 µm thick was coated on the back of the cantilever. This Au layer was prepared to stop the primary X-ray beam and to determine the position of the pinhole.

Figure 2. Pinhole made on the AFM cantilever.
Figure 3. Scanning electron microscope images of pinholes on the AFM cantilevers.

Figure 4. AFM image (3 µm × 3 µm) of polystyrene beads (50 nm in diameter) with the cantilever having a pinhole of 5 µm.

Figure 5 shows the experimental setup for micro-XRF combined with AFM. An X-ray generator was operated at a tube voltage of 40 kV and a tube current of 30 mA. X-rays emitted from the Mo X-ray sealed tube (spot size: 1.0 × 10 mm²) were introduced to the polycapillary X-ray lens, which was produced at Beijing Normal University. The output focal distance was 17 mm. The spot size of the micro X-ray beam was evaluated to be 48 µm using a W wire [16]. As shown in Figure 5, the AFM sample was placed on x-y-z stage 1. The AFM unit with the cantilever and the sample stage was placed on x-y-z stage 2. Six stepper motor stages were controlled with a minimum step of 0.5 µm by a personal computer. Of course, the AFM sample holder had an x-y-z piezo actuator for AFM observation. The X-ray tube and the polycapillary lens were fixed. Therefore, by using x-y-z stage 2, the position of the pinhole on the cantilever was adjusted to be at the center of the micro
X-ray beam generated by the polycapillary lens.

Y$_2$O$_3$ powder, used as the sample, was deposited homogeneously on a Si substrate. X-ray fluorescence of Y K$\alpha$ is effectively excited by Mo K$\alpha$ emitted from Mo X-ray tube. X-ray fluorescence was measured by a silicon drift detector (SDD, X Flash Detector Type 1201, RÖNTEC, Germany, sensitive area: 10 mm$^2$, <150 eV FWHM at 5.9 keV). As shown in Figures 5(a) and 5(b), two experimental configurations were used. To confirm the irradiation position of the focused primary micro beam on the cantilever, X-ray fluorescence from the AFM cantilever was measured under the experimental configuration shown in Figure 5(a).

X-ray fluorescence from the Y$_2$O$_3$ sample must be measured from the narrow gap between the cantilever and the sample. This experimental configuration suggests grazing-exit XRF analysis (GE-XRF) [17-19]. In GE-XRF, X-ray fluorescence is measured at very small takeoff angles, namely grazing angles. Similarly to the total reflection XRF (TXRF), the observation depth is only a few nm under grazing exit conditions [20]. This indicates that surface analysis is possible by GE-XRF. Furthermore, if the “micro” X-ray beam is applied at an incident angle of about 90°, then “localized” surface analysis is possible. Since the continuous X-rays emitted from deep within the sample are not detected, trace analysis is also possible with low background noise [20, 21]. When GE-XRF was applied, the SDD detector was placed on a translation stage, as shown in Figure 5(b). The exit angle was changed by moving the SDD using the translation stage. A slit (300 µm wide) was also attached at the top of the detector.
RESULTS AND DISCUSSIONS

First, elemental maps were obtained for the cantilever having a pinhole of 10 µm to find the position of the pinhole. The AFM unit including the cantilever and the sample was scanned with the fixed micro X-ray beam. This measurement was performed in the experimental configuration shown in Figure 5(a). The cantilever consists of Si and the Au coating on the cantilever. Therefore, the X-ray elemental mappings of Au Lα and Si Kα were clearly observed, as shown in Figure 6. The strong signal of Ti Kα on the left side of the Ti mapping in Figure 6 was produced from part of the cantilever. In addition, the Ti signal on the right side of the same map was produced from the sample holder, which was made of Ti. The dimple is clearly observed in the map of Au Lα and Y Kα, which were emitted from the sample. This dimple indicates the position of the pinhole.

The X-ray elemental mappings of the Y₂O₃ sample were next measured in the grazing exit configuration shown in Figure 5(b). The takeoff angle of X-ray fluorescence was set at less than about 1 degree, and the slit was attached between the sample and the SDD detector. Therefore, the X-rays emitted from the sample and the sample holder were selectively detected. Actually, X-ray fluorescence of Au Lα and Si Kα, which was emitted from the cantilever, is not shown in Figure 7. The strong X-rays on the right in the Ti mapping in Figure 7 were generated by the Ti sample holder. In the mapping for Y in Figure 7, the strong point indicated by the arrow indicates the Y Kα generated from the sample by the primary X-rays that passed through the pinhole. Thus, the X-ray fluorescence spectrum was measured after the cantilever was fixed at this position. The spectrum in Figure 8 was measured by using the X-rays that passed through the pinhole (10 µm) of the cantilever.
Figure 7. X-ray elemental mappings for Au L\(\alpha\), Y K\(\alpha\), Si K\(\alpha\), and Ti K\(\alpha\) obtained for the sample (Y\(_2\)O\(_3\) oxide layer) using experimental setup shown in Figure 5(b).

Figure 8. X-ray spectrum excited by the primary X-rays that passed through the pinhole of the AFM cantilever.

CONCLUSIONS

A small pinhole of 5 or 10 \(\mu m\) was made on an AFM cantilever. Through the use of this cantilever, a normal AFM image was successfully obtained. X-ray elemental maps were obtained by scanning the AFM cantilever. As a result, it was demonstrated that the original X-ray beam size of 48 \(\mu m\) produced by a polycapillary lens could be reduced to about 10 \(\mu m\) in the present (preliminary) experiment. This experimental study of the combination of AFM and X-ray analysis will be useful in obtaining both the AFM image of a sample surface and its elemental distribution by micro-XRF.
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