Improvement of Low-Energy PIXE System for Precise Surface Analysis

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A particle induced X-ray emission (PIXE) system was improved for the analysis of the very thin surface of a material. We developed a precise low-energy proton irradiation system with a compact X-ray detector set near a sample. The energy of protons was varied from 30 to 100 keV for the analysis of the thin surface of a sample. It was confirmed from experimental results on some standard samples that the present PIXE analysis system had sufficient statistics on the counting for characteristic X-rays. Also this PIXE system was successfully applied to the analysis of the thin surface of the multi-layer films and the particulate sample.

Key Words: PIXE, surface analysis, low-energy proton beam, particulate sample

1. Introduction

Techniques on the particle induced X-ray emission (PIXE) have been developed to determine accurate elemental concentration of particulate samples such as aerosols and others 1,2. Generally, a MeV-class ion beam is necessary for an effective PIXE analysis3). However, such high-energy ions penetrate into the deep region of a sample target and they induce the X-ray emission even in the deep region. It is, therefore, very difficult to analyze the elemental concentration of only a limited surface layer of a sample by using the normal PIXE system 4,5. On the other hand, low-energy ion beams penetrate into only the surface of a target, and moreover they cause much lower background X-ray emission due to the bremsstrahlung effect. Thus the PIXE with a low-energy proton beam is effective for the surface analysis, though there is a problem of the low counting rates for the characteristic X-rays induced by low-energy protons 5,6.

To cope with the problem, we developed a precise low-energy proton irradiation system with a compact X-ray detector set near a sample target. At first, this paper describes the low-energy proton irradiation system for the PIXE analysis and, then, shows the results of some surface analysis experiments performed with this PIXE system.

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2. Ion accelerator and its related components

2.1 Precise ion irradiation system

Fig. 1 shows a schematic drawing of the configuration of the components of the ion irradiation system for the PIXE analysis. The ion beam system was constructed by using the principal components for a 200 keV ion implanter. The maximum power of the ion accelerator is 200 kV x 5 μA and an extremely low-energy ion beam is produced by using a deceleration power supply in place of an acceleration power supply. The low-energy ion beams of H⁺, He⁺, He⁰ and other ions are available in this system 7. The proton beam with an energy less than 100 keV is mainly used for the PIXE analysis on the thin surface layer of a sample. The vacuum level of the target chamber is kept at better than 1 x 10⁻⁵ Pa.

Fig. 1 Configuration of components of ion irradiation system for PIXE analysis
A water-cooled copper plate with 4 different-sized apertures (0.5, 1, 5 and 10 mm) was placed to collimate the beam. According to the requirement for a beam size for the precise irradiation, an ion beam is transported to the position of the fittest aperture.

2.2 X-ray detector and ion beam monitor

A thermoelectrically cooled Si-PIN photo diode was used for the characteristic X-ray measurement in the PIXE analysis with a low-energy proton beam. Fig. 2 shows a schematic drawing of the detector arrangement and the block diagram of the measurement system. The detector was set 35 mm away from a sample target. The energy resolution of the detector was about 230 eV FWHM for the 5.9 keV peak of $^{55}$Fe. This detector satisfactorily measured characteristic X-rays in the energy range from 2 to 20 keV.

![Fig. 2 PIXE analysis system with low-energy ion beam](image)

Before the start of the beam irradiation for the PIXE analysis, the ion beam profile was observed with a beam monitor made of a fluorescent screen. Fig. 3 shows an example of a proton beam spot of about 0.40 mm$^2$ on the fluorescent screen. After the adjustment of the beam positioning and focusing, the target sample was set in front of the fluorescent screen.

![Fig. 3 Example of proton beam spot observed with fluorescent screen (E$_p$, 100 keV, I$_p$, 1 μA)](image)

2.3 Preparation of standard samples

Some standard samples were prepared to evaluate the X-ray energy spectra in the PIXE analysis with a low-energy proton beam. Thin films of pure metals such as Au, Ag, Cu and others were made on clean glass plates by an evaporation process. The thickness of the foils ranged from 5 to 1000 nm. Measured spectral data were compared with the fundamental data on these standard samples. Non-conducting samples were covered with nets of metal meshes before irradiation. This is for the prevention of the inductive noises due to the electrical discharge in the sample. Fig. 4 shows examples of X-ray energy spectra for the standard samples, which were measured by using the present PIXE system with a 100 keV proton beam. It is suggested from the figure that the counting rates of the characteristic X-rays are sufficiently obtained with this PIXE system.

![Fig. 4 X-ray energy spectra for standard samples](image)

3. Characteristics of PIXE analysis system with low-energy proton beam

3.1 X-ray counting rate vs. proton beam current

We examined several basic characteristics of the present PIXE analysis system with a low-energy proton beam. First, we checked the relation between beam currents and X-ray counting rates measured with this system.

![Fig. 5](image)
3.2 Sensitivity vs. atomic number

In order to examine the sensitivity of this PIXE system, the standard samples made of pure metal films were irradiated with a 100 keV and 1 μA proton beam. Fig. 6 shows the sensitivity of this PIXE system for several typical elements. It was confirmed from the figure that this PIXE system had sufficient counting rates for X-rays characterized by the L-shell and/or M-shell electrons and also had fairly higher sensitivity for elements with larger atomic number.

3.3 Sensitivity vs. proton energy

We examined the relation between the proton energy and the counting rates for the characteristic X-rays. Fig. 7 shows an example of the relation between the sensitivity and the proton energy. The standard sample made of 5 nm thick Au films was irradiated with a proton beam in the energy range from 30 to 120 keV and Mα X-rays from Au were measured. The equation in the figure was obtained by a non-linear regression.

4. PIXE system for precise surface analysis

4.1 PIXE analysis of multi-layer films

In the point of the analysis on the thin surface, we performed several experiments to examine the performance of the present PIXE system. A normal PIXE analysis system with a MeV-class ion beam has a high sensitivity but it does not always give sufficient data on the thin surface of a sample, because the higher energy ion beam makes the area of the X-ray emission the deeper. The thin surface can be effectively searched with the low-energy proton beam, though the sensitivity is not so high.

Four layers of different kinds of metal films were made on a clean glass plate by an evaporation process. The element type and the thickness of each layer are shown in Table 1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Element</th>
<th>Thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>First layer</td>
<td>Ti</td>
<td>50</td>
</tr>
<tr>
<td>Second layer</td>
<td>Al</td>
<td>100</td>
</tr>
<tr>
<td>Third layer</td>
<td>Ag</td>
<td>200</td>
</tr>
<tr>
<td>Fouth layer</td>
<td>Cu</td>
<td>600</td>
</tr>
</tbody>
</table>

This standard sample made of the multi-layer films was irradiated with a low-energy proton beam. Fig. 8 shows the X-ray energy spectra for the standard sample irradiated with 80 ~ 100 keV proton beam. As shown in Fig. 8, the peaks corresponding to the characteristic X-rays of Al Kα (1.58 keV), Ag Lα (2.96 keV) and Ti Kα (4.54 keV) were well measured with this PIXE system.

Fig. 9 also shows the relation between the proton energy and the counting rates of characteristic X-rays from the standard sample. All data on the counting rate were normalized with the data at the energy of 100 keV. The counting rate of Ag Lα X-rays decreased more sharply with the proton energy than Ti and Al. It is suggested from these results that the thin surface can be effectively analyzed with the variation of the proton energy.
4.2 PIXE analysis of particulate sample

To confirm the performance of this surface analysis system, we performed elemental analysis of a particulate sample of calcium phosphate, which is expected to be useful for the separation of fluoride from sludge. The particulate sample of calcium phosphate was fixed on Ag films made on a clean glass plate. Fig. 10 shows the energy spectra of X-rays from the particulate sample irradiated with a proton beam in the energy range from 60 to 100 keV. It is suggested from the clear peaks of Ca Kα (3.60 keV), P Kα (2.01 keV) and Ag Lα (2.96 keV) X-rays that the purity of the sample is sufficiently high.

Fig. 11 shows the relation between the proton energy and the counting rates of Ca Kα, P Kα and Ag Lα X-rays. As shown in Fig. 11, the tendency of P slightly differs from that of Ca and the PIXE system with a low-energy proton beam may be useful for the analysis of the particular sample, though the results obtained in this analysis experiment are too little to discuss the details of the particulate sample of calcium phosphate.

5. Conclusion

We developed the PIXE system with a low-energy proton beam to analyze the thin surface of a sample. It was confirmed from the experimental results on the standard samples that this PIXE analysis system had sufficient statistics on the counting of characteristic X-rays from a sample. Also this PIXE system was successfully applied to the analysis of the thin surface of the multi-layer films and the particulate sample.

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References


