Low-energy Ion Induced X-ray Emission from Insulators and Development of an Instrument for its Measurement*

M. Song,† M. Takeguchi, and K. Furuya
High Voltage Electron Microscopy Station, National Institute for Materials Science, 3-13, Sakura, Tsukuba, Ibaraki 305-0003, Japan

T. Kitamura, M. Kawai, K. Miyazaki, and H. Soejima
Shimadzu Corporation, 1, Nishinokyo-Kuwabaracho, Nakagyo-ku, Kyoto 604-8511, Japan
(Received 15 October 2005; Accepted 4 January 2006; Published 3 February 2006)

Low energy ion induced X-ray emission (LIIXE) from insulators is presented and discussed. Ions of light, such as He\(^+\) ions, or heavy, such as Ga\(^+\) ions, in energy from lower than 1 keV/AMU (atomic mass unit) to several keV are demonstrated to induce characteristic X-ray emission effectively from insulator samples. Features of LIIXE, such as using very low energy ions, no needs for conducting coating on surface of samples, and relatively high X-ray yields for low energy characteristic X-rays, make it prospective for being applied in materials analysis, especially for insulator materials containing light elements. A proto-type instrument under developing for measurement of the X-ray is introduced. [DOI: 10.1380/ejssnt.2006.144]

Keywords: Low energy ion; Irradiation; X-ray; insulator; Material analysis

I. INTRODUCTION

Characteristic X-rays are widely used in elemental and chemical analysis of materials, since their energy characterizes the elements from which they come from. High energy ion irradiation can induce characteristic X-ray emission from a sample. One example of the application is Particle Induced X-ray Emission (PIXE), which uses ions with energy in MeV order to induce characteristic X-ray emission from bombarded samples. PIXE is known to be a high sensitive analysis method [1], and is utilized for analyzing many kinds of substances, such as medieval stained glass [2], magnesium aluminate spinel [3], human skin sections [4], mineral assemblages and ores [5], proteins [6], trace elements inside plants [7], and etc. However, since PIXE uses high energy ions, the system is very expensive and complicated compared with commonly used analytical methods, such as electron probe microanalysis (EPMA), X-ray photoelectron spectroscopy (XPS). On the other hand, low energy ion irradiation to a target is widely used in materials science work and technology, such as secondary ion mass spectrometry (SIMS), focused ion beam (FIB) for preparing electron microscopy samples, etc. X-ray emission is not much considered in these cases. In the present work, it is demonstrated that characteristic X-ray emission can be induced from insulator targets by ions with energy as low as less than 1 keV per atomic mass unit (keV/AMU). The features of low energy ion induced X-ray emission (LIIXE) include using a low energy ion source, no needs for conductive coating for insulator samples, high X-ray yields for low energy characteristic X-rays, etc. These features suggest that it may be used as a material analysis method. It is introduced here that for measurement of such X-rays and developing LIIXE to an analytical method, an instrument is under development.

II. EXPERIMENTAL FOR LIIXE

The experiment is carried out in two instruments. One is a high-voltage transmission electron microscope (HVTEM), JEM-ARM1000, made by JEOL Co. Ltd., to which a dual-ion implanter system and a Si(Li) energy dispersive X-ray spectroscopy (EDS) system made by EDAX are attached [8]. Plus ions with energy up to 100 keV are used. Ions with a required energy are selected by a magnet analyzer. The size of the ion beam is about 2.0 mm in diameter on the target surface. Current of the ion beam is adjustable from 1 to 80 nA. The pressure of the specimen chamber during ion irradiation is lower than 3 × 10\(^{-6}\) Pa. He\(^+\) ions with energy of 10, 20 keV, Ar\(^+\) ions and Xe\(^+\) ions of 100 keV are used for the present work. Ions irradiated a sample in angle of 15 degrees to the normal of the sample surface. Another instrument is a focused-ion-beam (FIB) instrument, which uses a focused Ga\(^+\) ion beam gun with energy from 5 to 30 keV. A Si(Li) X-ray energy dispersive spectrometer (EDS) made by Oxford instrument Co. Ltd. is mounted to the system. Ga\(^+\) ions of 5, 10 or 30 keV are used for the present work. Ga\(^+\) ions irradiated a sample in a direction normal to the sample surface. The pressure in specimen chamber of the FIB is in order of 1 × 10\(^{-4}\) Pa. All the experiments are performed at room temperature.

Insulator samples of MgO and SiO\(_2\), and conductive samples of Si are used. The samples are in disk shape in diameter of 3 mm, and thickness of about 0.2 mm. Surface of samples are mechanical mirror-polished.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Characteristic X-rays were induced from insulator samples by irradiation with ions of He\(^+\) ions in energy of 10 keV or 20 keV, Ga\(^+\) ions in energy of 5 to 30 keV, Ar\(^+\) or Xe\(^+\) ions in energy of 100 keV. Figure 1 shows several

---

*This paper was presented at International Symposium on Surface Science and Nanotechnology (ISSS-4), Saitama, Japan, 14-17 November, 2005.
†Corresponding author: Minghui.SONG@nims.go.jp
FIG. 1: X-ray spectra from MgO and SiO$_2$ samples. (a) a spectrum from MgO irradiated with 100 keV Xe$^+$ ions in current of 3.8 nA for 200 seconds collection; (b) a spectrum from MgO irradiated with 400 keV electrons in current of 1.1 nA for 100 seconds collection; (c) a spectrum from a SiO$_2$ sample irradiated with 10 keV Ga$^+$ ions in current of 1.1 nA for 100 seconds collection; (d) a spectrum from a Si sample irradiated with 10 keV Ga$^+$ ions in current of 1.1 nA for 100 seconds collection.

typical X-ray spectra. (a) is an X-ray spectrum measured from a MgO sample irradiated with 100 keV Xe$^+$ ions in current of 3.8 nA for 200 seconds collection; (b) is a spectrum from the same MgO sample with the same EDS detector as in (a) but irradiated with 400 keV electrons in current of 1.1 nA for 100 seconds collection. Two peaks in the spectrum of Fig. 1(a) are considered as characteristic X-rays of O-K and Mg-K, respectively, since they have peak positions of 0.53 keV and 1.26 keV, the same values of O-K and Mg-K peaks in the spectrum shown in Fig. 1(b). The O-K and Mg-K peaks induced with 100 keV Xe$^+$ ions have comparable intensities with those induced with 400 keV electrons, but have different relative intensities. A broad peak observed in the range from about 0.16 to about 0.3 keV in the spectrum of Fig. 1(a). This peak was commonly observed in spectra of ion induced X-rays using the dual-ion implanter system. The relative intensity of the broad peak decreased when the intensity of peaks of sample elements increased, therefore it was considered that it was mainly a background noise. Figures 1(c) and (d) are spectra from a SiO$_2$ sample and a Si sample, respectively, during the samples irradiated with 10 keV Ga$^+$ ions in current of 1 nA for 100 seconds collection. O-K peak and Si-K peak were observed in Fig. 1(c) but not from Fig. 1(d), because the Si sample was a semiconductor one. The dependence of characteristic X-ray emission on conductivity of samples was also the same for SiO$_2$ and Si pair samples irradiated with Ga$^+$ ions in energy of 5, or 30 keV, and with He$^+$ ions in energy of 10 keV. A peak at energy of 0.28 keV is observed in Fig. 1(c). It has the same energy as that of C-K, and is considered as the C-K peak. Carbon may come from hydrocarbon molecules remained in the chamber and the vacuum system. Carbon contamination is always a problem in microanalysis of materials in vacuum condition when the pressure is higher than $\sim 10^{-6}$ Pa [9]. Another peak centering at 0 keV in Figs. 1(c) and (d) was an instrument noise, its intensity linearly increased with collection time. The above results evidenced that characteristic X-rays of constituent elements of an insulator sample can be effectively induced by irradiation of ions in energy of several keV to 100 keV, but no characteristic X-rays can be effectively stimulated from a grounded conductive or semiconductor sample. It was also observed that characteristic X-rays with lower energy appeared larger yields. These features of the X-ray emission indicate that this X-ray emission is different from conventional X-ray emission, such as the X-ray emission in PIXE and the X-ray emission induced by electron beam in EPMA, since no such relation on conductivity of samples are observed in
from SiO with protons in the same energy from 60 to 120 keV. This could only be observed from Al samples irradiated with protons in energy from 10 to 120 keV [10]. The Al-K peak was induced from Al samples which were irradiated with ions in energy higher than 60 keV/AMU. The present work evidenced that the abnormal X-ray emission may relate to electrons produced in ionization process inside samples [20], or, relates to discharge of the accumulated charges on the irradiated samples [12, 15], or relates to charged state of the irradiated samples [19]. The present work supplied some new results for the phenomenon, but the detailed mechanisms will be discussed elsewhere.

As discussed above, the low energy ion induced X-ray emission (LIIXE) has following features as it is considered as an analytical method. 1) characteristic X-rays of a sample can be induced with ions in much lower energy than in PIXE; 2) it is not necessary to coat a conducting layer on sample surface. Otherwise, this coating may absorb X-rays, especially soft X-rays, from the analyzed sample; 3) there are high X-ray yields in low energy range, noting that the energies of characteristic X-rays of light elements such as C, N, O, etc., commonly contained in organic and insulator materials, are in the range. Therefore, it is expected to be used in analysis of insulator for elements, especially for light elements.

Electron induced X-rays are commonly used in materials analysis, such as electron probe micro analysis (EPMA) and X-ray energy dispersive spectrometry (EDS). Because electron beam is easy to be focused to a very small size, electron induced X-rays are used in micro-area analysis. However, in order to analyze an insulator sample, it is necessary to coat a conductive layer on surface of the sample. This layer may absorb X-rays from the sample, especially soft X-rays. This absorption results in difficulties in analysis of insulator samples. Contrast to the analysis using electron induced X-rays, LIIXE can analyze insulator samples without conductive coating, therefore, it is convenient to be used in analysis of insulator samples. Furthermore, the low energy ions sputter samples during irradiation; hence the LIIXE can be used to analyze depth profile of elements in a sample.

It is noted that low energy ion sources up to energy of several tens keV are used in several kinds of commercial obtainable instruments, such as SIMS and FIB. It is possible to utilize the LIIXE to perform analysis by just combining an X-ray detector in such an instrument. However, the optimum instrumental configuration and conditions for analyzing a sample for utilizing LIIXE is not yet established. For this reason, an instrument for measuring the LIIXE and establishing the optimum conditions for materials analysis is under developing.

| Ion | Energy (keV) | E/AMU (keV) | X-rays from insulator | Reference |
|-----|-------------|-------------|----------------------|-----------|
| He  | 10          | 2.5         | Abnormal emission    | This work |
| He  | 20          | 5           | Abnormal emission    | This work |
| Ar  | 100         | 2.5         | Abnormal emission    | This work |
| Xe  | 100         | 0.76        | Abnormal emission    | This work |
| Ga  | 30          | 0.43        | Abnormal emission    | This work |
| Ga  | 10          | 0.14        | Abnormal emission    | This work |
| Ga  | 5           | 0.07        | Abnormal emission    | This work |
| H   | 10          | 10          | Abnormal emission    | [10]      |
| H   | 60          | 60          | Abnormal emission    | [10]      |
| H   | 120         | 120         | Enhancement          | [10]      |
| H   | 1333        | 1333        | Enhancement          | [11]      |
| \(^3\)He | 2000       | 666.67      | Enhancement          | [11]      |

PIXE or EPMA.

An abnormal X-ray emission induced by ion irradiation relating to insulator samples has been reported by several researchers. Terasawa reported in 1968 that Al-K X-rays were induced from Al\(_2\)O\(_3\) samples which were irradiated with protons in energy from 10 to 120 keV, but Al-K peak could only be observed from Al samples irradiated with protons in energy from 60 keV to 120 keV [10]. The Al-K from an Al\(_2\)O\(_3\) sample shown much larger intensity than that from an Al sample even the two samples irradiated with protons in the same energy from 60 to 120 keV. This abnormal X-ray emission from insulator was also observed from SiO\(_2\) samples. In PIXE work, abnormal enhancement of X-ray emission related to non-grounded insulator samples were first reported by Peisach, et al. in 1993 [11] and then after by other researchers [12–20]. In Peisach's work, metal-fluoride and pure metal samples were irradiated for comparison with protons or \(^3\)He\(^+\) ions in energy from 1333 keV to 2 MeV [11]. Characteristic X-rays were found to be enhanced. They observed that characteristic X-rays of metal elements from metal-fluorides were from 1.6 to 12.8 times more intense than the same X-rays but from pure metal samples.

Table I lists some data for comparing the present results with the typical reported results. As observed in Table I, the abnormal X-ray emission appeared as an abnormal enhancement of X-ray emission when the insulator samples were irradiated with ions in energy higher than 60 keV/AMU. The present work evidenced that the abnormal X-ray emission from insulator samples can be induced from ions in energy much lower than 1 keV/AMU.

This abnormal X-ray emission could obviously not be explained with the binary elastic collision mechanism, both from the target dependence and the value of transferable energy in the collision of low energy ion irradiation. It is also not probable to be considered as due to the quasi-molecule mechanism, which has been accepted as a model to explain X-ray emission during low energy heavy ions collisions [21], considering the target dependence of the X-ray emission.
IV. DEVELOPMENT OF AN INSTRUMENT FOR MEASURING LIIXE

In order to measure the X-ray in high sensitivity and high resolution, and to make it applicable in technology, a new instrument is being developed. There are two factors to develop the new tool: a compact ion beam gun with energy less than 30 keV, which makes a sub-micron sized ion beam using gas sources such as He and Ar, and a new high-sensitive and high-energy-resolution X-ray analyzer equipped with a multi-capillary X-ray lens (MCX) \[22, 23\] and wavelength-dispersive spectrometer (WDS) using flat crystals. As a first step, a proto-type is under developing, the schematic structure is shown in Fig. 2. A gas ion source using \(\text{He}^+\), or \(\text{Ar}^+\) ions is assembled, which is used to produce a fine focused ion beam in energy from 5 to 30 keV. A focused electron beam gun in adjustable energy and beam current is used for comparative study of the ion induced X-ray emission and the electron induced X-ray emission. A Si(Li) crystal X-ray energy dispersive spectrometer (EDS) is mounted for detecting X-ray from samples. The EDS is mounted so that the EDS can detect X-ray from a sample in the same geometry condition no matter the sample is irradiated by the ion beam or the electron beam. The other constitutes of the instrument can be seen from the figure. The final type of the instrument will be equipped with a multi-capillary X-ray lens (MCX) and wavelength-dispersive spectrometer (WDS) using flat crystals. Using a WDS makes it possible to achieve a much higher energy resolution than a Si(Li) EDS. A good enough energy resolution is necessary for analyze chemical state of elements in an organic or an insulator sample. An MCX can collect X-rays from a sample in much larger solid angle compared with a conventional X-ray collecting configuration used in conventional EPMA. Since no window film is used in an MCX, much higher sensitivity for soft X-ray is expected for an MCX than for a conventional X-ray collecting configuration. The final type instrument is expected to be a powerful tool to analyze light elements from organic and insulator materials.

V. CONCLUSION

Low energy ion induced X-ray emission (LIIXE) from insulator was demonstrated. Ions with energy lower than 1 keV/AMU stimulated effectively characteristic X-rays from insulator samples. The LIIXE has features such as using low energy ion source, no needs for conducting coating for insulator samples and high X-ray yields for light elements. A proto-type instrument for applying LIIXE in materials analysis was introduced.

Acknowledgments

The present work has been supported by Japan Science and Technology Agency through a research project.

[1] S. A. E. Johansson, and J. L. Campbell, *PIXE: A novel technique for elemental analysis*, (John Wiley & Sons, Chichester, 1988).
[2] M. Vilariques, and R. C. Dasilva, Appl. Phys. A 79, 373
[3] V. Bandourko, N. Umeda, and N. Kishimoto, Nuclear Instruments and Methods in Physics Research B 190, 146 (2002).

[4] J. Pallon, M. Garmer, V. Auzelyte, M. Elffman, P. Kristiansson, K. Malmqvist, C. Nilsson, A. Shariff, and M. Wedgén, Nuclear Instruments and Methods in Physics Research B 231, 274 (2005).

[5] G. C. Wilson, J. C. Rucklidge, J. L. Campbell, Z. Nejedly, and W. J. Teesdale, Nuclear Instruments and Methods in Physics Research B 189, 387 (2002).

[6] H. N. Luz, D. Spemann, W. M. Klaucke, and W. Tröger, Nuclear Instruments and Methods in Physics Research B 231, 308 (2005).

[7] E. Baklaus, B. Gouget, J. P. Gallien, H. Khodja, and F. Carrot, Nuclear Instruments and Methods in Physics Research B 231, 350 (2005).

[8] N. Ishikawa, and K. Furuya, Ultramicroscopy 56, 211 (1994).

[9] J. I. Goldstein, D. E. Newbury, P. Echlin, D. C. Joy, A. D. Romig, C. E. Lyman, C. Fiori, and E. Lifshin, Scanning Electron Microscopy and X-ray Microanalysis, (Plenum Press, New York, 1992), p.109.

[10] M. Terasawa, J. Phys. Soc. Jpn. 25, 1199 (1968).

[11] M. Peisach, A. E. Pillay, and C. A. Pineda, Nuclear Instruments and Methods in Physics Research B, 75, 14 (1993).

[12] M. Peisach, C. A. Pineda, and A. E. Pillay, J. Radioanalytical and Nucl. Chem. 178, 387 (1994).

[13] M. Peisach, C. A. Pineda, and A. E. Pillay, Nuclear Instruments and Methods in Physics Research B 85, 100 (1994).

[14] R. C. M. Mboweni, C. A. Pineda, M. Peisach, and A. E. Pillay, Nuclear Instruments and Methods in Physics Research B 85, 138 (1994).

[15] A. E. Pillay, and M. Peisach, J. Radioanalytical and Nucl. Chem. 246, 291 (2000).

[16] J. Kawai, K. Maeda, N. Sakauchi, and I. Konishi, Spectrochimica Acta B 50, L1 (1995).

[17] Z. Szokefalvi-Nagy, I. Demater, K. Hollos-Nagu, and I. Kovacs, Nuclear Instruments and Methods in Physics Research B 109/110, 59 (1996).

[18] H. Hamanaka, K. Hasegawa, and K. Maeda, Nuclear Instruments and Methods in Physics Research B 109/110, 203 (1996).

[19] A. P. Jesus, M. A. Reis, and L. C. Alves, Nuclear Instruments and Methods in Physics Research B 136-138, 837 (1998).

[20] A. P. Jesus, M. A. Reis and L. C. Alves, Nuclear Instruments and Methods in Physics Research B 161-163, 120 (2000).

[21] U. Fano and W. Lichten, Phys. Rev. Lett. 14, 627 (1965).

[22] H. Soejima, Japanese patent 1995-11600 (1995); Japanese patent 1995-40080 (1995).

[23] H. Soejima, and T. Narusawa, Advances in X-ray analysis 44, 320 (2001).