ABNORMAL X-RAY EMISSION FROM INSULATORS BOMBARDED WITH LOW ENERGY IONS

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ABSTRACT
An abnormal phenomenon, low energy ion induced X-ray emission from insulators is reported and discussed. Irradiation with He⁺, Ga⁺, Ar⁺, and Xe⁺ ions in energy from 5 to 100 keV induces strong characteristic X-ray emission from insulator targets but not from conductive ones. The phenomenon is different from the high energy ion induced X-rays, such as PIXE (particle induced X-ray emission) in several aspects, such as very low energy of the used ions, existence of upper limit energy for the ion to induce X-rays. It is implied that the phenomenon relates not only to plus charging-up on surface of the irradiated specimen but may also to ion irradiation related process, such as sputtering. However, further study has to be done for a precise mechanism of the phenomenon. Features, such as high X-ray yields, suggest the phenomenon has potential applications in element analysis and studying ion-solid interaction.

INTRODUCTION
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. On the other hand, it is known that characteristic X-rays can be induced by high energy ions irradiating on a target. One of the applications is the particle induced X-ray emission (PIXE), which is known to be a high sensitive analysis method1). The typical energy of the ions is in order of MeV. A high energy incident ion collides with and transfers an amount of energy to an inner shell electron of a target atom. The amount of transferable energy reduces with decreasing energy of the incident ion. When the transferred energy is lower than that needed to stimulate an inner shell electron, no characteristic X-ray emission takes place. However, in the present work, X-ray emission is induced from insulator targets by low energy ions, such as 10 keV, 20 keV He⁺ ions, or 5 to 30 keV Ga⁺ ions, or other low energy ions. The present paper describes the experiment results, discusses the mechanism and potential applications of the phenomenon.

EXPERIMENT
Transmission electron microscope (TEM) and focused ion beam (FIB) instruments were used for the experiment. The TEM was a high-voltage TEM (HVTEM), JEM-ARM1000, made by JEOL Co. Ltd. to which a dual-ion implanter system and a Si(Li) energy dispersive X-ray spectroscopy
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(EDS) system made by EDAX were attached. Plus ions with energy up to 100 keV were used. Ions with a required energy were selected by a magnet analyzer. The size of the ion beam was about 1.5 mm in diameter. The ion beam was aimed to the center of a target specimen at an angle of 15 degrees to the normal of the specimen surface. He$^+$ ions with energy of 10, 20, 50, or 100 keV, Ar$^+$ and Xe$^+$ ions of 100 keV were used. Current of the ion beam was adjustable from 1 to 80 nA. One of the FIB instruments was a JEM-9310FIB made by JEOL with a focused Ga$^+$ ion source and a Si(Li) EDS system made by JEOL. Another FIB instrument was a JFS-9855S with dual-beams of a focused Ga$^+$ ion source and an electron source, and a Si(Li) EDS system made by Oxford instrument Co. Ltd. The energy of Ga$^+$ ion source and electron source was up to 30 keV for the FIB instruments. The Ga$^+$ ions irradiated to a specimen in a direction normal to surface of the specimen. The area irradiated by Ga$^+$ ions was adjustable from a size of 2.0 mm x 2.6 mm to smaller sizes. The Ga$^+$ ion beam irradiated to a specimen in a spot or a scanning mode, which made no difference as to delectability of X-rays. All the incident ions were plus ions. The experiments were performed at room temperature.

Insulator specimens of Al$_2$O$_3$, ZrSiO$_4$, etc. and conductor or semiconductor specimens of Al and Si, etc. were used. The specimens were in disk shape in diameter of 3 mm or a square shape with an edge of 2.1 mm, and thickness of about 0.2 mm. Surface of specimens were mechanical mirror-polished, or electro-polished (Al). A specimen was set in a specimen holder made of metals which was grounded during the ion irradiation. The take-off angle was 30 degrees for the EDS detector attached to JEM-ARM1000, and 40 degrees for the EDS detectors attached to the FIBs.

RESULTS AND DISCUSSIONS

Fig. 1 shows a set of X-ray spectra detected from an Al$_2$O$_3$ and an Al specimen which were irradiated with 10 keV He$^+$ ions. A spectrum detected with the same EDS system from the same Al$_2$O$_3$ specimen irradiated with 400 keV electrons is also shown for comparison. The Y axis displays X-ray counts induced by ions or electrons. Two peaks at 0.53 keV and 1.49 keV in the
spectrum from Al$_2$O$_3$ bombarded with 10 keV He ions were considered as characteristic X-rays of O-K and Al-K, respectively, since their peak energies were very close to O-K$_\alpha$ of 0.525 keV and Al-K$_\alpha$ of 1.486 keV, respectively. The X-ray yields of O-K and Al-K peaks induced with 10 keV He$^+$ ions had comparable values (X-ray photons per ion) with those induced with 400 keV electrons (X-ray photons per electron). Similar results were obtained from the above specimen-pair irradiated with 20 keV He$^+$, 100 keV Ar$^+$, 100 keV Xe$^+$, and 5 to 30 keV Ga$^+$ ions. The ion irradiations to other insulator and conductive specimens of ZrSiO$_4$, MgO, Si, etc. were also carried out with ions and energies mentioned above. It is evidenced that characteristic X-rays of target elements were stimulated from insulator specimens but not from conductive ones.

However, characteristic X-rays were not detected from even the insulator specimens of Al$_2$O$_3$ and ZrSiO$_4$ bombarded with He$^+$ ions in energy of 50 keV or 100 keV. Fig.2 shows a spectrum from an Al$_2$O$_3$ specimen irradiated with 100 keV He$^+$ ions. A continues background X-ray was recognized but no characteristic X-rays were identified. These results indicated that at least for He$^+$ ions, there was a upper limit energy for the ion to induce X-ray emission from the experimented specimens. The limit should be less than 50 keV for the above specimens.

The present phenomenon 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. 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$^3$), considering the target dependence and the ion energy dependence of the X-ray emission.

It has been reported that in PIXE works when insulators, such as CuF$_2$, were irradiated with high energy protons or He$^+$ ions in energy from about 400 keV to several MeV without electric neutralization for charging-up of the sample surface, strong enhancements of characteristic X-ray emission were observed$^{4-6)}$. A similar phenomenon was also reported in 1968, in which X-ray of Al-K or Si-K were observed from Al$_2$O$_3$, or SiO$_2$ irradiated with protons in energy from 10 keV to 120 keV$^7)$. The present results were similar to the reported ones at some aspects. However, it was different from the reported ones in several features, such as the energy range of ions and the dependence of X-ray emission on energy of ions.

It is known that the behavior of an insulator target under charged particle or photon irradiation is quite different from that of a conductive one$^{8,9)}$. One of the reasons is the charging-up produced on surface of the insulator target during the irradiation. It is considerable that the present X-ray emission was resulted from some indirect energy transfer processes from the incident ions to atoms of the target. This process may relate to charging-up on surface of a target produced in the irradiation, since charging-up takes place on an insulator target and not on a conductive one.

In order to clarify the relation of X-ray emission and charging-up, secondary electron (SE)
images of irradiated specimens were observed during and after Ga⁺ ion irradiation. Fig. 3 shows a typical image observed with JEM-9310FIB during an irradiation with 30 keV Ga⁺ ions with a current of 200 pA. An electric grounded Al sample and an Al₂O₃ sample were put nearby on a specimen holder. The Al₂O₃ sample looked dark while the Al one looked bright. This image revealed that SEs emitted from the Al₂O₃ specimen were very few comparing to the SEs from the Al one. This may be due to a plus electric field built by a plus charging-up on the Al₂O₃ surface during the irradiation. The plus electric field may suppress the emission of SEs from the specimen. Therefore, this image confirms that a plus charging-up was built on the Al₂O₃, an insulator specimen.

Fig. 4 shows change of SE image observed with the dual-beam instrument JFS-9855S after switching off the 30 keV ion source in current of 4 nA and simultaneously switching on a 10 keV electron beam in current of 300 pA (at relative time 0 second). Fig. 4a and 4b were taken at relative time 0.5 second and 8.5 second, respectively. Though there was no injection of plus ions and there was an injection of electrons, the surface of the Al₂O₃ sample looked blur and dark as seen in fig. 4a. The specimen looked brighter and brighter, and the structure on surface became clearer and clearer with the time passing. At 8.5 second, as shown in fig. 4b, the SE image of the specimen became a brightness of a normal SE image and the surface morphology can be seen. It
was considered that because of the injection of electrons the charging-up became weaker and weaker with the time, therefore intensity of the plus electric field on surface also became weaker and weaker, and the SEs emitted from the target increased with the time. At about 8.5 second, SE emission reached to a value close to the normal level of a SE image. It was confirmed again that charging-up hence building of an electric field took place on the surface of the bombarded target.

In order to investigate further the relation of the X-ray emission and the ion irradiation, time dependence of X-ray emission was analyzed. The EDS detector was switched on before the start of ion irradiation, switched off after the stop of the irradiation. A typical result was shown in fig. 5, in which X-ray intensity of O-K peak from an Al₂O₃ target irradiated with 30 keV Ga⁺ ions was graphed via the time. The ion irradiation was started at 60 second with a current of 3.0 nA. X-ray emission started almost at the same time when the irradiation was started. The emission continues during the irradiation, while it stopped at almost the same time when the irradiation was stopped at 360 second. It was evidenced that strong X-ray emission took place only during the ion irradiation. Since the charging-up and the built electric field existed on the target for several seconds even after switching off the ion beam as concluded from above discussion, these results implied that the X-ray emission did not only relate to the charging-up and the built electric field. This argument could be also obtained from the fact that the emission of characteristic X-rays were not observed from the above discussed specimens when they were irradiated with 50 or 100 keV He⁺ ions, though charging-up should also take place in the cases. Detailed discussion on other features of fig. 5, such as the high pulse X-ray emission observed in the spectrum, will be carried out elsewhere.

The fact that the X-ray emission depends on the energy of incident ions suggests that the present phenomenon relates to surface- or near-surface-process, since low energy ions could only stimulate processes near surface, while the high energy ions enter a target deep and stimulate less surface processes. These may include processes such as sputtering and backscattering, and their combination with surface charging-up and the built electric field. However, some of the present
results were not fully understood yet, such as why the continuous spectrum in fig. 3 was induced by the low energy ions. The detailed mechanism on the X-ray emission and surface processes is needed to be studied further.

The high X-ray yield as observed in fig. 1, especially in low energy range, suggested that the present phenomenon, low energy ion induced X-ray emission, may be used as an analytical method for light elements, such as N, O, and lighter ones, which are commonly contained in insulators and biomaterials, and are difficult to be analyzed. Noticing that low energy ions are used widely in SIMS, FIB and other instruments and methods, this phenomenon may be easily used as an independent or companied material analysis method. The present phenomenon may also supply a tool for us to get more understanding of the ion-surface interaction, since it results from the interaction between low energy ions and a target.

CONCLUSION
A phenomenon, low energy ion induced X-ray emission was reported. The X-ray emission was only induced from insulator targets, not from conductive ones. This X-ray emission was confirmed to relate to ion irradiation induced charging-up, and relates to ion energy with a feature that there is an upper limit energy for ions to induce X-ray emission. The high emission rate of characteristic X-rays, especially in low energy range, suggests that these X-ray may be used to analyze light elements. Also, it supplies a new approach to study ion-surface interaction.

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