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LATEST DEVELOPMENTS OF THE SOFT X-RAY EMISSION SPECTROMETER

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Shogo Koshiya is a development engineer of a soft X-ray emission spectrometer, which can be mounted on a scanning electron microscope and/or electron probe microanalyser. His background is the spectroscopy (SXES, EELS, and EDS) and the microscopy (STEM and HR-TEM) based on electron microscope. He received his PhD in Physics from the Tohoku University, Japan in 2012. After his PhD, he worked as a Postdoc at IMRAM, Tohoku University and NIMS and as a development engineer at JEOL Ltd. JEOL's SXE spectrometer was launched in 2012, and he joined the development team of SXES in 2018. Currently, he develops the commercial and prototype SXE spectrometers for electron microscopes. He authored or co-authored about 20 scientific papers.

1. INTRODUCTION

An electron-beam induced wavelength-dispersive type grating spectrometer for soft X-ray emission spectroscopy (SXES), which can be mounted on a transmission electron microscope (TEM), was firstly developed by Terauchi *et al.* [1]. The spectrometer used a varied-line-spacing (VLS) grating and a charge-coupled device (CCD) detector. It enables microscopic chemical bonding state analysis of solids because of sufficiently high energy resolution of the spectrometer and nanometre-size of an electron-beam. After some improvements of the spectrometer [2, 3], a national project to commercialise the spectrometer, which can be mounted on JEOL scanning electron microscope (SEM) and electron probe microanalyser (EPMA) [4]. The spectrometer can simultaneously acquire spectra in a certain energy range depending on the grating. Recently, these spectrometers have been applied in various fields such as batteries, metals, and minerals [5].

There are several important issues to be resolved in improving the spectrometer performance, such as sensitivity, energy resolution, data acquisition rate, and acquisition energy range, etc. In this paper, we present the improvement of energy resolution. The commercial SXES spectrometer had to be designed so as not prevent the function of electron microscopes. The compact design of the mechanical system in this spectrometer resulted in a limited energy resolution in the energy range from 500 eV to 2 keV. This energy region includes K-emissions from third-period elements such as Mg, Al and Si, and L-emissions from 3d transition metal elements such as Fe and their surrounding elements. For realising a better energy resolution in the energy region, a larger dispersion power of VLS gratings and/or a finer pixelated detector are necessary. In recent years, the performance of complementary metal oxide semiconductor (CMOS) detector for scientific measurements has improved significantly and they are replacing CCDs. CMOS has been developed not only for high-speed and high-sensitivity measurements, but also for larger sensor sizes keeping a finer pixel size than that of CCD. Therefore, to improve the energy resolution, a prototype CMOS detector was applied to a commercial SXES spectrometer. The detectability of K- and L-emission spectra of light elements and 3d transition metal elements were evaluated. Furthermore, the newly observed spectral structures were discussed [6].

2. EXPERIMENTAL

The CCD detector of a commercial SXES-ER (SS-94040SXSER, JEOL Ltd.) was changed to a prototype CMOS image sensor, which has a pixel size smaller than the half of CCD, 13.5 × 13.5 μm^2, used in commercial SXES spectrometers. A VLS grating of JS2000 used in the commercial spectrometer was applied, which allows the acquisition energy range from 350 eV to 2,300 eV in commercial SXES-ER. The modified spectrometer was attached to an electron probe microanalyser JXA-8230 (JEOL Ltd.). Magnesium (Mg), magnesium-oxide (MgO), iron (Fe), iron oxides (FeO, Fe_3O_4, Fe_2O_3, and $MnFe_2O_4$), pyrite (FeS_2), and zinc (Zn) were used as specimens, which were commercially available as reagents.

The accelerating voltage of the instrument was set to 7 kV. The probe current and the exposure time were typically 100 nA and 1,500 s, respectively. The probe current and the exposure time were adjusted to obtain the sufficient signal to noise ratio in the case for weak peaks, of which intensities are 1/100 to main peak. The electron beam size on the specimens were less than 1 μmφ in diameter.

3. *Mg K-EMISSION SPECTRA*

Figure 1 shows SXES Mg K-emission spectra of magnesium (Mg) detected using CCD and CMOS detectors. The VLS gratings used were the same JS2000 type ones. In this energy range, Mg-Kα (K-$L_{2,3}$) and -Kβ (K-$M_{2,3}$) emissions are observed. The spectral shape of the main peak of K$\alpha_{1,2}$-emission is considered symmetrical due to the core-level (2p) to core-level (1s) transitions. On the other hand, Kβ-emission should indicate asymmetrical shape due to the valence electron (M-shell) to core-level (1s) transitions. Furthermore, it is known that satellites called non-diagram-lines are seen on the higher-energy side of the main peak [7]. Satellites are defined as X-rays arising from a one-electron jump in a multi-hole configuration.

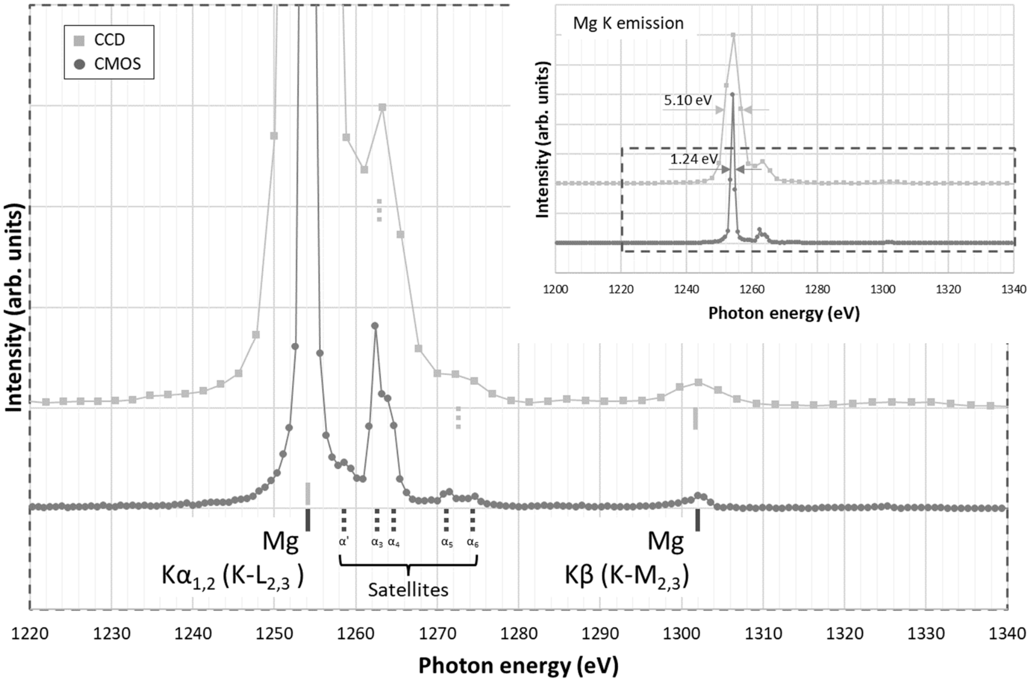

Figure 1. Mg K-emission spectra of Mg using CCD and CMOS detectors.

The full width at half maximum energies of Mg-K$\alpha_{1,2}$-emission main peaks are 5.10 eV and 1.24 eV for CCD and CMOS, respectively (inset of Fig. 1). This result reflects the small aberration of VLS grating. Therefore, it can be said that the energy resolution performance improvement of current commercial spectrometers can be achieved by replacing the detector. The E/ΔE value of CMOS achieved more than 1,000.

Satellites could not be observed separately with CCD due to insufficient spatial resolution of the detector. In contrast, the use of CMOS as a detector allowed the satellite to be clearly observed. The lines are labelled α', α_3, α_4, α_5, and α_6, respectively, from the low-energy side. The detailed analysis of satellites may lead the transition probabilities of multi-hole in relaxation processes [8, 9]. Those results show that the energy resolution performance of the commercial spectrometer with JS2000 can be improved by replacing the detector.

4. 4th PERIOD ELEMENT L-EMISSION SPECTRA

Figure 2 shows Lℓ,η and Lα,β-emission spectra of iron (Fe) and zinc (Zn). Basically, the spectral shape of the Lℓ,η-emissions (Figs. 3a and 3c) are considered symmetrical due to the core-level (3s) to core-level (2p) transitions. On the other hand, the Lα,β (Figs. 3b and 3d) emissions are associated with valence electron (3d) to core-level (2p) transitions, so the spectrum is asymmetric, reflecting the chemical bonding states of specimens. The shoulder-structures at higher energy side are indicated by arrows in Zn-Lα,β emission spectra (Fig. 3d). The shoulder-structures were identified at about 3 eV and 4 eV higher energy to the main peak of Lα-emission at 1,012 eV and at about 4 eV higher energy to the peak of Lβ-emission at 1,035 eV. The electronic structure calculation results in the ground state of Fe and Zn did not indicate such shoulder-structures. These shoulder-structures of Zn-Lα,β emission spectra are similar to the satellites of Mg-K emission. This is due to the relaxation of multiple excitations [10, 11]. On the other hand, the shoulder-structure is not clearly observed in the Fe-Lα,β emission spectra. The Fe-Lα,β emission spectra with their satellites was reported by Sepúlveda *et al.* [12]. Essentially, satellites due to multi-holes are considered to exist. Nevertheless, all these transitions are not always observable separately due to the natural linewidths involved and because of the finite spectrometer energy resolution.

L-emission spectra were measured using this detector for scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), cobalt (Co), nickel (Ni), copper (Cu), gallium (Ga), germanium (Ge) and arsenic (As), although spectra are not shown here. The results show that no shoulder-structure is clearly observed in the Lα,β-emission spectra of Sc ($Z = 21$) to Co ($Z = 27$), whereas shoulder-structure is clearly observed in Ni ($Z = 28$) to As ($Z = 33$). Co and Ni were the boundary between observability and non-observability in this spectrometer.

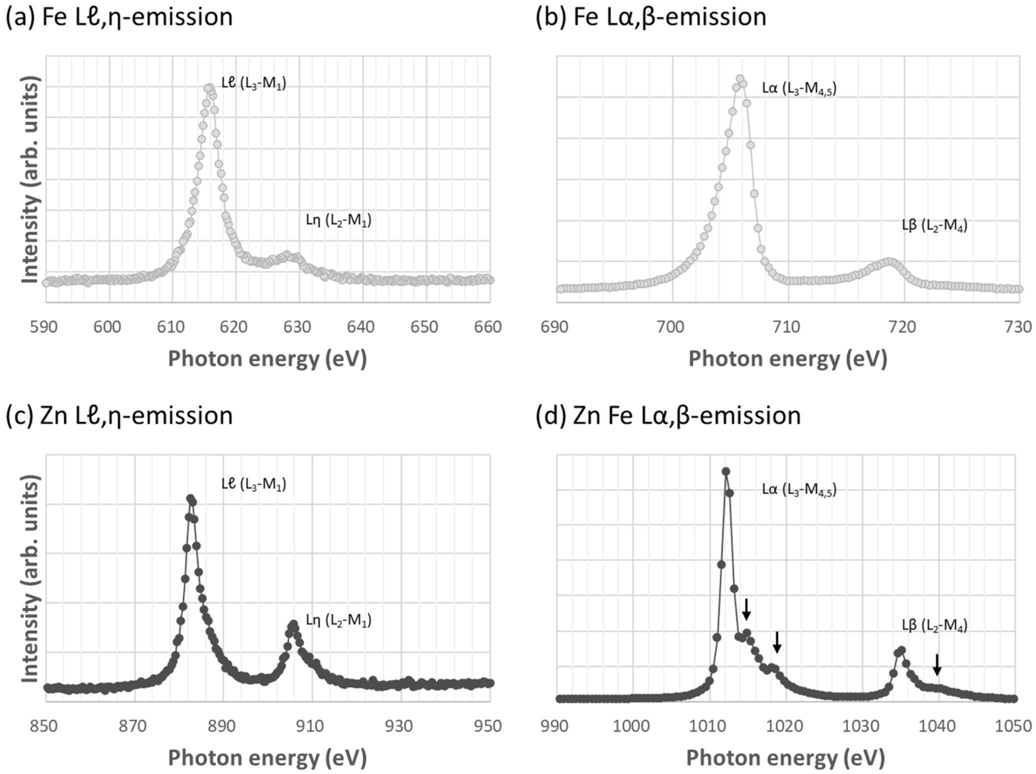

Figure 2. L-emission spectra of Fe and Zn. A and c) Lℓ,η-emission spectra. b and d) Lα,β-emission spectra.

Figure 3 shows Fe-Lα,β emission spectra of iron (Fe), iron-oxides (FeO, Fe_3O_4, Fe_2O_3, and $MnFe_2O_4$), and pyrite (FeS_2). In contrast to Fe, the main peak positions of Lα- and Lβ-emissions are clearly shifted to higher energy side for iron oxides of Fe_3O_4, Fe_2O_3 and $MnFe_2O_4$. The shoulder structure for Fe_2O_3 and $MnFe_2O_4$ about 709 eV of Lα-emission may be attributed to the satellite. The peak positions of FeO are observed at almost the same position as Fe, but the spectral shape and peak ratio are clearly different. The surrounding atoms of Fe for iron-oxides can be understood as O. A distinct peak shift originates from the valency of Fe atom site, which reflects the different chemical bonding states. Lα-emission spectra of FeS_2 shows not only the peak shift but also the spectral shape. From these results, it can be said that the present spectrometer can easily discriminate the different bonding states of Fe.

5. *CONCLUSION*

Measurements were made with a fine pixel pitch large sensor size CMOS detector to obtain electron beam-excited microscopic SXES spectra with high energy-resolution. The change in the detector from CCD to CMOS allowed the acquisition of high energy-resolution spectra. In Mg-K emission spectra, separated satellites are clearly observed. The high energy-resolution

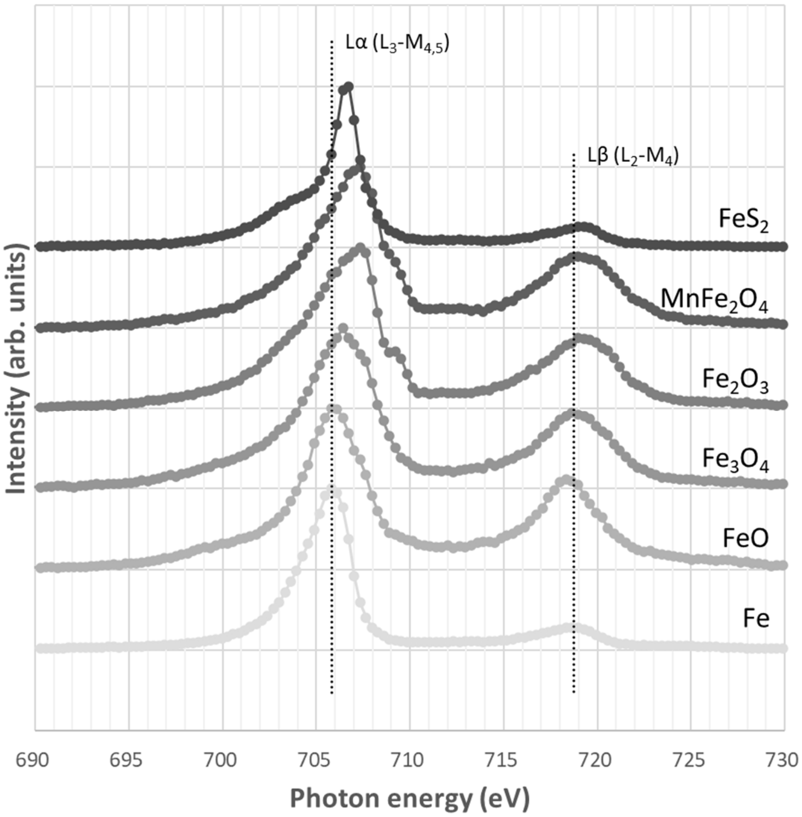

Figure 4. Fe-Lα,β emission spectra of Fe, FeO, Fe_3O_4, Fe_2O_3, $MnFe_2O_4$, and FeS_2.

spectra of 4th period elements L-emissions were measured. The shoulder-structures on the higher-energy side of Lα,β-emission peak were observed in some spectra. These are due to the relaxation of multiple excitations. The obtained spectra are close to the data that can be obtained in synchrotron radiation facilities. Furthermore, the spectrometer enables the chemical bonding state identification of iron-based materials. Although faster and more sensitive acquisition of spectra is an issue for the future, the results in this study show the potential for expanding the range of applicability of microscopic SXES measurements.

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