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Transition Edge Sensor-Energy Dispersive Spectrometer (TES-EDS) and Its Applications

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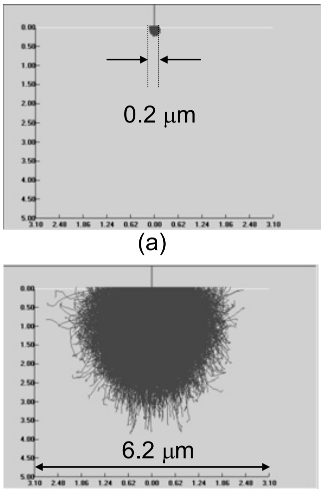
SUMMARY The Transition Edge Sensor (TES)-Energy Dispersive Spectrometer (EDS) is an X-ray detector with high-energy resolution (12.8 eV). The TES can be mounted to a scanning electron microscope (SEM). The TES-EDS is based on a cryogen-free dilution refrigerator. The high-energy resolution enables analysis of the distribution of various elements in samples under low acceleration voltage (typically under 5 keV) by using K-lines of light elements and M lines of heavy elements. For example, the energy of the arsenic L line differs from the magnesium K line by 28 eV. When used to analyze the spore of the *Pteris vittata L* plant, the TES-EDS clearly reveals a different distribution of As and Mg in the micro region of the plant. The TES-EDS with SEM yields detailed information about the distribution of multi-elements in a sample.

key words: *energy dispersive X-ray detector, scanning electron microscope, superconducting transition temperature, dilution refrigerator, high energy resolution*

1. Introduction

A Scanning Electron Microscope (SEM) is a powerful tool used to observe the image of the surface of millimeter- and nanometer-size samples. When the primary electron is diffused in the sample, secondary electrons, X-rays and Auger electrons are emitted from the sample. Elements in the sample can be determined by measuring the energy of the characteristic X-ray of each element.

An SEM under low acceleration voltage (typically 5 kV) is advantageous because the region of secondary electron generation is limited to near the surface, thus yielding a clear, definitive surface image. When a low-voltage SEM is used, the elemental composition is usually analyzed under low voltage (< 5 kV) without a need to increase the excitation voltage that is typically required in conventional X-ray analysis (20 kV). Figures 1(a) and 1(b) show simulated electron trajectories in a silicon substrate for 3 kV and 15 kV. Based on these simulation results, the diffusion range is 0.2 μm for 3 kV and 6 μm for 15 kV. Energy Dispersive X-Ray Spectroscopy (EDS) identifies the elemental composition of materials simultaneously imaged with an SEM. The EDS can analyze the material by using a solid-state detector (SSD) and has a large solid angle (typically 10 msr.), thus requiring only a short measurement time for a wide energy range (0–20 keV). However, the energy resolution of conventional EDS (130 eV for Si(Li) at 6 keV) is inadequate to separate the K lines of light elements, L lines of transition metal and M lines of heavy elements. For example, the difference between the Si-Kα line and the W-Mα line is only 35 eV. A Wavelength Dispersive X-ray Spectrometer (WDS) can separate the X-ray spectra below 5 keV with high-energy resolution (typically 10 eV at 6 keV) by using multiple crystals [1]. A high probe current (e.g., 1 nA to 1 μA) is required to compensate the low collection efficiency of WDS compared to EDS but degrades the SEM image due to the large beam diameter (e.g., 10 nm at 0.1 nA and 40 nm at 10 nA for 10 kV) and damages the sample due to the electron beam. Another disadvantage in using WDS for analysis is the extended time required for the movement of the analyzing crystals.



(b)

Fig. 1 Trajectories of electrons in a silicon substrate for 3 kV and (b) 15 kV.

A Transition Edge Sensor (TES) is an Energy Dispersive X-ray Spectrometer with high-energy resolution ($<$ 5 eV at 6 keV) and can analyze a wide energy range (0–10 keV) with only one detector [2]. Due to its high-energy resolution, the SEM-TES with low voltage can evaluate the sample surface and analyze its elements. The large solid angle of SEM-TES (from 2 msr. to 4 msr.) enables analy-

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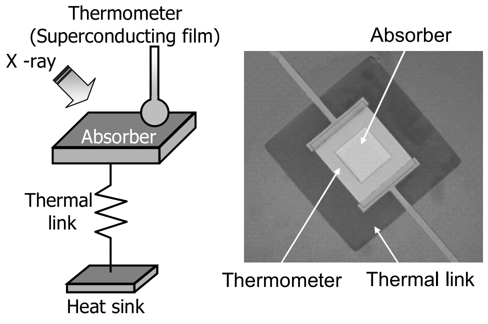
sis under low probe current (typically 1 nA), thus not only reducing damage to the sample but also enabling detailed visualization of nanoparticles. The SEM-TES can analyze nanoparticles and precipitates on a surface because the excitation volume that is less than 5 kV is limited to around the nano materials on the surface. Here, we report our SEM-TES system, the performance and its applications.

2. Transition Edge Sensor (TES) and SQUID Array Amplifier

The TES is a microcalorimeter that measures the incident photon energy as a change in temperature in the TES. The TES is composed of an absorber to detect X-rays, a thermometer to measure the change in temperature, and a thermal link to regulate the heat flow from the thermometer to the heat sink (Fig. 2(a)). A superconducting film is used as a thermometer to utilize the steepness of Resistance vs. Temperature curve at super conducting transition. The absorber is located at the center of the thermometer, which is stacked on the thermal link. Figure 2(b) shows a photo of the TES. The thermometer is a bilayer of gold/titanium (Au/Ti) and is 350 μm × 350 μm, and the absorber is gold (Au) is 150 μm × 150 μm. The thickness of the bilayer is adjusted to Au(120 nm)/ Ti (50 nm) so that the transition temperature is between 150 mK and 200 mK. The thermal link is a 1-μm-thick silicon nitride film, and the thermometer is located at the center of the silicon nitride film.

A constant voltage is applied to the TES to keep the operating voltage within the transition range by the heat balance between the Joule heating in the thermometer and the heat that escapes from the thermometer to the heat sink. The shunt resistor (typically under 10 mΩ), which is designed parallel to the TES, has a typical operation resistance from 40 mΩ to 50 mΩ that ensures a constant voltage because most of the bias current flows to the shunt resistor. When an X-ray is absorbed, the Joule heating is decreased by the increase in resistance of the thermometer, and thus a pulse current is generated. The electrothermal feedback function improves the pulse decay time from milli-seconds to microseconds [2]. The energy of an incoming X-ray can be determined by the integral of the pulse shape as follows:



(a) (b)

Fig. 2 (a) Schematic and (b) photograph of TES.

$$E = V_0 \int_{-\infty}^{\infty} I dt = V_0 \Delta I \tau_{eff} \tag{1}$$

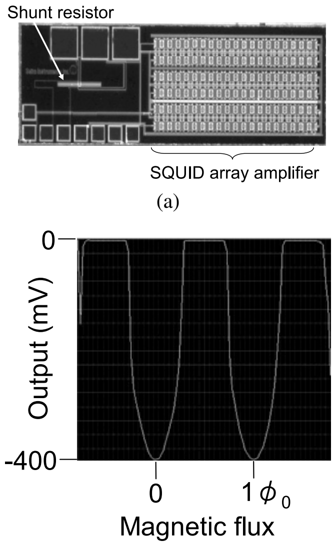
where, E is incoming energy, ΔI is pulse height and τ_{eff} is pulse decay time. The incoming X-ray energy is determined by the measured pulse height because the operation voltage and pulse decay time are constant.

The electrothermal feedback can improve the energy resolution by $\xi = 2\sqrt{(n/2)/\alpha}$ compared to that without electrothermal feedback, and is expressed as follows:

$$\Delta E = 2.355\xi\sqrt{k_B C T^2} \tag{2}$$

where, C is the heat capacitance, k_B is the Boltzmann constant, and T is the operating temperature. The parameter n is concerned with the thermal conductance between the TES and the heat bath. In this case, the value is 3. The theoretical energy resolution is within 1 eV when $C = 1$ pJ/K, $\xi = 0.17$ and $T = 100$ mK.

Figure 3(a) shows a photograph of a SQUID array amplifier in which 240 single SQUID elements are connected in a series on a 2.4 mm × 7.5 mm chip. A gold shunt resistor (also mounted in the chip) is used to operate the SQUID under 1 K. Figure 3(b) shows a typical output voltage-current curve [3]. Operating the SQUID array amplifier under a Fluxed Locked Loop (FLL) condition produces linearity in the magnetic flux-voltage curve. Although the maximum output voltage was about 600 mV, setting the voltage from about 400 mV to 500 mV enables stable operation of the SQUID array amplifier. The current flowing to the TES can then be measured based on the voltage output of the SQUID array amplifier under FLL.



(a)

(b)

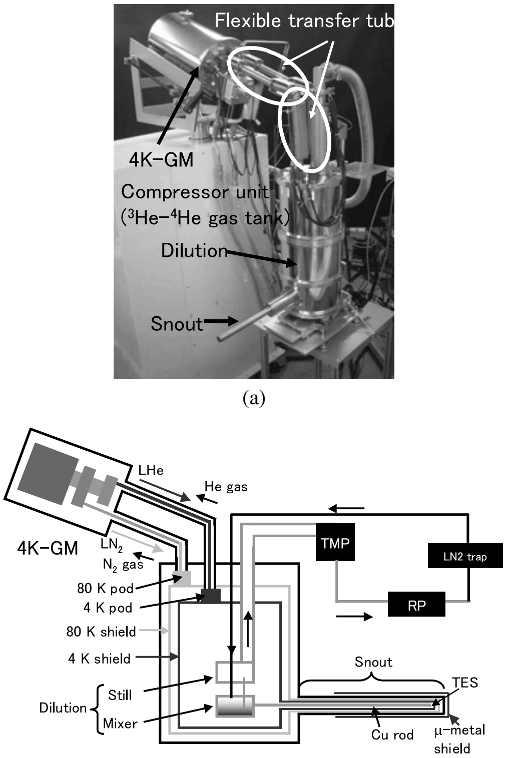
Fig. 3 (a) Photograph of SQUID array amplifier containing 240 single SQUID elements in series and (b) V-phi curve.

3. Transition Edge Sensor (TES) System for Microanalysis with Scanning Electron Microscope (SEM) — Energy Dispersive Spectrometer (EDS)

3.1 TES System Based on a Dilution Refrigerator

The energy resolution of the TES depends on the operating temperature. Based on Eq. (2), a temperature less than 200 mK is needed to achieve an energy resolution that is less than 20 eV. Either a dilution refrigerator or adiabatic demagnetization refrigerator (ADR) [4] is commonly used to achieve a temperature that is less than 200 mK. In our system, we adopted a dilution refrigerator because it can continuously maintain the minimum temperature, whereas an ADR is discontinuous due to its regeneration cycle.

A dilution refrigerator typically uses cryogen (liquid helium and nitrogen) to cool the mixing and still from room temperature to 4.2 K and to continuously cool the thermal shields. In our TES- EDS system (Fig. 4), a mechanical cooler is used instead of cryogen, and the dilution refrigerator has a snout, such as that in a conventional SSD system. The Cu-rod in the snout is in contact with the mixing chamber in the dilution refrigerator. The TES and SQUID array amplifier are mounted on the top of the Cu rod. A Gifford-McMahon refrigerator (4 K-GM) is used as a precooler to cool the dilution refrigerator from room temperature to 4 K and to cool the two thermal shields (4 K, 80 K) in the dilution refrigerator. A flexible transfer tube between the dilution refrigerator and the 4 K-GM refrigerator is used to transfer liquid helium and liquid nitrogen from the 4 K-GM to the dilution refrigerator via gravity. The cryogen draws heat from the 4 K and 80 K thermal shields. The vaporized helium and nitrogen gas are recondensed in the 4 K-GM refrigerator. The 4 K-GM refrigerator can continuously cool the 4 K thermal shield. The Cu-rod stably maintains the temperature at 100 mK because the radiation heat from the 4 K thermal shield is always less than 1 μW, which is much smaller than the cooling power of the mixing chamber, which is the coldest part in the dilution refrigerator. During X-ray detection, the temperature of the Cu-rod is controlled at 130 mK by a temperature controller (Lakeshore 370). The temperature controller can adjust the heat balance between the Joule heat of the resistance heater embedded in the Cu-rod and the cooling power of the mixing chamber. The temperature stability at the top of the Cu rod is within ±20 μK. X-rays emitted from the sample are introduced and detected by the TES via thin film windows (polyimide films with evaporated aluminum) located in the 4 K and 80 K thermal shields and in the room temperature shield. The spectrometer efficiency is defined as the transmittance efficiency of the thin film windows multiplied by the absorption efficiency of the Au absorber of the TES. Figure 5 shows the typical transmittance efficiency curve for our system.



(a)

(b)

Fig. 4 Photograph and (b) schematic cross view of TES -EDS.

The detection area (about 0.04 mm^2) of the TES-EDS system has to be improved because the solid angle is three orders smaller than that for conventional EDS. A polycapillary lens composed of a bundle of thousands of parallel glass tubes that are tapered at both ends [5] was added to the system to increase the solid angle by two orders compared with that without the capillary. The solid angle was 2–3 msr. The sample holder was tilted 45° from the axis of the primary electron beam. The snout with the X-ray lens was inserted in the SEM chamber parallel to the SEM stage. The distance between the sample and the intake edge of the X-ray lens was 27 mm.

3.2 System Operation and TES Properties

Figure 6 shows the SQUID output-bias current curve when the heat sink temperature was 150 mK. Table 1 summarizes

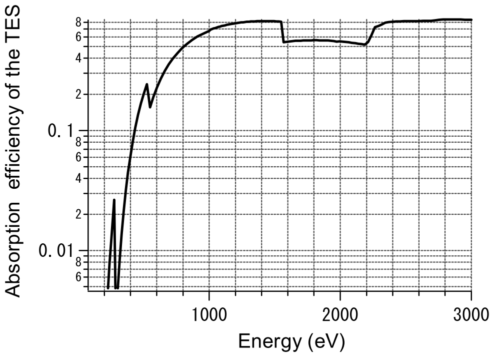


Fig. 5 Absorption efficiency of the TES with transmittance efficiency of the thin window for incoming X-ray energy.

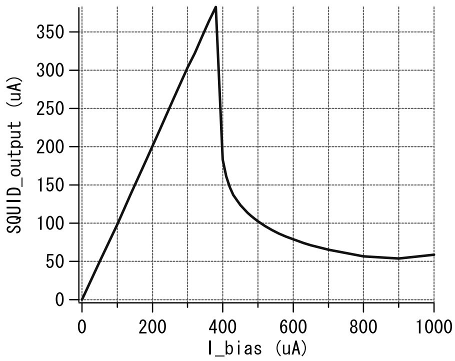


Fig. 6 SQUID output-bias current curve.

Table 1 TES parameters.

TES size (μm)	350 X 350
Absorber size (μm)	150 X 150
Transition temperature (mK)	240
Heat capacitance (pJ/K)	1.57
Thermal conductance (nW/K)	3.4
Normal resistance (mΩ)	100
Temperature of the heat sink (mK)	150
Operation resistance (mΩ)	40
Decay time without ETF (μs)	462

the specifications of our device. We designed the TES parameters not only to obtain high-energy resolution but the high-count rate. The target count rate was over 500 cps because the high-count rate was needed to make the analysis time shorter. The pulse decay time needed to be within 50 μs to achieve the destination with count rate empirically. We designed the normal thermal conductance without electro thermal feedback under 500 μs. When the bias current decreases from 1000 μA to 900 μA, the TES current decreases linearly because the TES is under normal resistance. However, when the bias current is decreased from 900 μA to 400 μA, the TES current increases because the TES is under the superconducting transition and thus the TES resistance decreases. When the TES is in the superconducting state, the bias current (under 400 μA) and the TES current are equal. Figure 7 shows the response pulse for the photon of Al-Kα (1487 eV) when the bias current is 650 μA. The pulse rise is 4.8 μs, decay time is 17.1 μs, and the pulse height is 2.6 μA. The loop gain ($L_0 = P\alpha/GT$) of the electrothermal feedback can be estimated from the pulse decay time as follows:

$$\tau_{eff} = \frac{\tau_0}{1 + L_0} \tag{3}$$

where, P is the power in the TES, α is the sharpness of the superconducting transition, G is the thermal conductance, and τ_{eff} and τ_0 are the pulse decay time with and without ETF, respectively. Based on this equation, $L_0 = 25.1$ and $\alpha = 100$. The energy resolution calculated from the base line noise was 9.53 eV. Figure 8 shows the experimentally obtained noise current (solid line) and the calculated noise current (dashed line). The calculated noise current is composed of phonon noise, Johnson noise, SQUID noise and constant voltage noise [6]. Comparison between the experimental and calculated noise current at 15 kHz reveals that a constant voltage noise of 1.8 pV/$\sqrt{\text{Hz}}$ would exist in the TES. The experimental noise current below 4 kHz (phonon noise region) does not coincide with the calculated noise current because the harmonic noise of 50 Hz might actually continue up to 1 kHz, which is not accounted for in the calculation. The energy resolution can be estimated at 7.4 eV if the noise current below 4 kHz decreases from the solid line to the dotted line in Fig. 8. Based on the X-ray spectrum of Al-Kα (Fig. 9), the energy resolution was 12.8 eV and the total counts were 20,000 pulses. Fluctuation in the TES current (typically 0.07 μA) might explain the difference between the energy resolution calculated based on the signal-to-noise ratio (9.53 eV) and that based on the measured X-ray spectrum (12.8 eV) because this TES current fluctuation was observed using an oscilloscope. Therefore, the empirically estimated peak shift in the spectrum was about 5 eV when the TES current fluctuation was 0.07 μA.

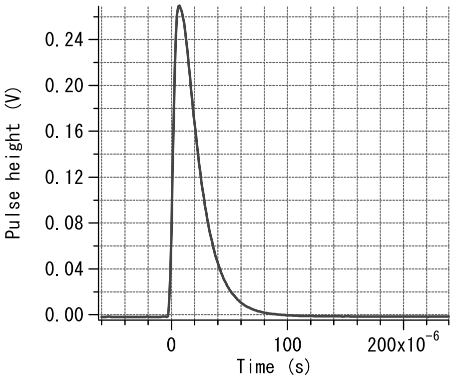


Fig. 7 Response pulse for Al-Kα.

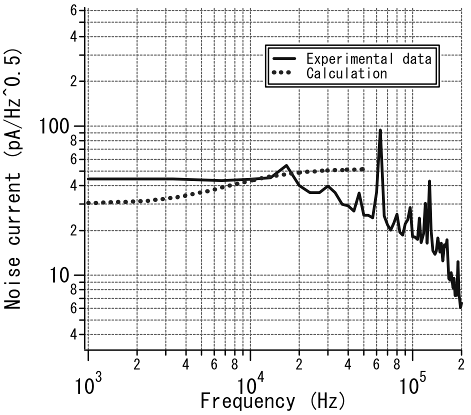


Fig. 8 Noise current of experimental data (solid line) and calculation (dotted line).

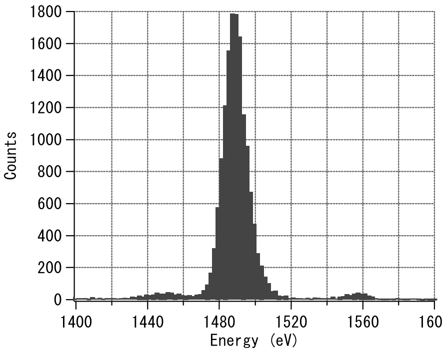


Fig. 9 X-ray spectrum for Al-Kα.

4. Element Analysis of the Plant *Pteris vittata L.* and Particles Composed of Light Elements on an Aluminum Substrate Using TES-EDS

The high X-ray collection efficiency of the TES in our system (4 msr.) compared to that of WDS (typically less than 0.1 msr.) enables analysis of material under low current (e.g., 1 nA). The high probe current (> 10 nA) causes heat damage to the sample during the inelastic scattering of the incident electrons against the sample. The heat in the particle is proportional to the probe current and the probe voltage. For minimal damage to a sample, the TES is ideal because it can operate under low voltage (< 5 kV) and low probe current (< 1 nA).

The fronds of *Pteris vittata L.* can absorb and accumulate a high concentration of arsenic. Contaminated soil can be cleaned through the use of this plant in a procedure called "Phytoremediation." Figure 10(a) shows a photograph of the spore of Pteris vittata L. and Figs. 10(b) and (c) show the X-ray spectra measured with the TES at points "A" and "B" in Fig. 10(a). The acceleration voltage was 5 kV and the probe current was 1 nA. X-ray peaks generated by essential elements in the plants are clearly observable: C-Kα (277 eV), O-Kα (525 eV), P-Kα (2.014 keV), S-Kα (2.398 keV), and K-Kα (3.313 keV). These elements (C, P, S, and K) are concentrated at the center of the spore rather than outside of the spore. An essential elemental for chlorophyll is Mg. The Mg-Kα peak is 1.254 keV, while that of As-Lα peak at 1.282 keV. The energy difference between Mg-Kα and As-Lα is only 28 eV. Figure 10(d) shows enlarged spectra between the 1 keV and 1.6 keV region extracted from Figs. 10(b) and (c). The ratio between the peak height of As and the height of the continuous X-ray at 1.2 kV is the same between points A and B whereas the ratio between the peak height of Mg at point B and the height of the continuous X-ray at 1.2 kV is smaller than that of point A. In this experiment, the energy resolution degraded from 12.8 eV to 25 eV because of the instability of the refrigerator. The high-energy resolution and capability of multi-element analysis can separate neighboring X-ray peaks and yield accurate information about the element concentration.

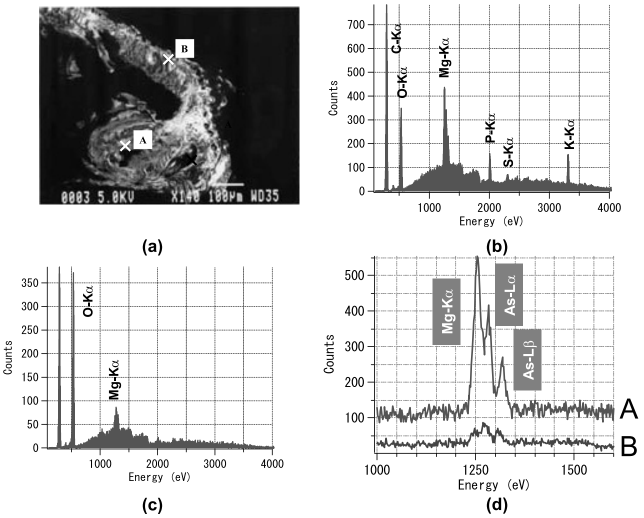


Fig. 10 (a): Photograph of spore of the plant *Pteris vittata L.* (b) and (c): X-ray spectra measured at points "A" and "B" in (a). (d) Enlarged spectra between 1 keV to 1.5 keV for both (b) and (c).

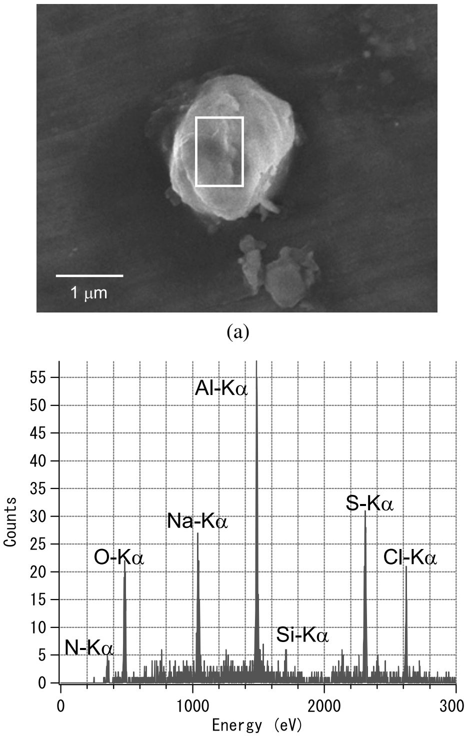


Fig. 11 Photograph of a particle on an aluminum substrate. (b) X-ray spectrum for rectangular area in (a).

Low voltage and low beam current is beneficial for elemental analysis of a sample that is easily damaged by an electron beam. Such easily damaged samples are mainly composed of light elements (primarily carbon). Figure 11 is a photo of a particle on an aluminum substrate. The white rectangle indicates the area analyzed under the area scan mode. For elemental analysis of the particle, we usually use the spot mode in which an electron beam is fixed at a designated position from the start of analysis to the end. Part of the energy of the electrons is converted to heat and released from the particle to the aluminum substrate. If the electron beam irradiates at a fixed position, the temperature at the beam position increases locally and the sample is destroyed at the beam position, yielding a small spot. An area scan at low voltage effectively prevents increasing temperature because the electron beam constantly moves and the irradiation time at any one spot is reduced. Figure 11(b) is an X-ray spectrum for the white rectangular area in Fig. 11(a). The acceleration voltage was 5 kV, the probe current was about 250 pA, and the measurement time was 60 s. The spectra for light elements (N, O, Na, Al, Si, S, Cl) were clearly evident and no sample damage was observed after the measurement. This particle might be a piece of skin because Na and Cl were detected. The peak for C was not observed because we had cut the X-ray with energy less than 300 eV to emphasize the X-ray peaks of the minor element.

5. Conclusion

The performance and application data of a TES-EDS with SEM have been described in detail. Advantageous characteristics of this system include (1) high-energy resolution, (2) low voltage (< 5 kV), and (3) low beam current (< 1 nA), and 4) peak separation between light elements and heavy elements. This SEM-TES is an energy dispersive type detector that can detect multi-elements simultaneously. Analysis of nanoparticles through the use of this TES-EDS with SEM will be reported elsewhere.

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