Practical X-ray Spectrometry with Second-Generation Microcalorimeter Detectors

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Introduction

X-ray spectroscopy is a widely used and extremely sensitive analytical technique for qualitative as well as quantitative elemental analysis. Typically, high-energy-resolution X-ray spectrometers are integrated with a high-spatial-resolution scanning electron microscope (SEM) or transmission electron microscope (TEM) for X-ray microanalysis applications. The focused electron beam of the SEM or TEM excites characteristic X rays that are emitted by the sample. The integrated X-ray spectrometer can then be used to identify and quantify the elemental composition of the sample on a sub-micron length scale. This combination of energy resolution and spatial resolution makes X-ray microanalysis of great importance to the semiconductor industry.

Conventional energy-dispersive X-ray spectrometers are based on semiconductor detectors, such as lithium-drifted silicon (SiLi) cooled to −180°C (liquid nitrogen) or silicon drift detectors (SDD) that operate at −30°C [1]. The absorption of an X ray by these intrinsic semiconductors results in the creation of a number of electron-hole pairs that are collected on the detector electrodes, giving rise to a charge pulse. The total charge collected is directly proportional to the X-ray energy. Wavelength dispersive spectrometers (WDS) use a curved diffracting crystal to select the X-ray wavelength to be measured by adjusting the crystal such that the Bragg condition is satisfied. To perform a complete scan (for example, from 100 eV to 12 keV), several different diffracting crystals must be used. Although the quantum and geometric collection efficiencies are low, wavelength-dispersive spectrometers have excellent energy resolution of 2 to 20 eV (for full width at half maximum [FWHM]) depending on the X-ray line. The mechanical design and critical geometric requirements inherent to wavelength dispersive spectrometers, however, and the serial mode of operation required to obtain a complete X-ray spectrum, force these spectrometers to be slow, to be difficult to operate, and to require large electron beam currents.

Although wavelength-dispersive spectrometers offer superior energy resolution, semiconductor energy-dispersive spectrometers are the most widely used device for X-ray microanalysis because of their ease of use, lower operating costs, long-term stability, and ability to quickly provide qualitative analysis and quantitative analysis (standards-based). Semiconductor detectors have a serious and fundamental limitation, however. The relatively poor energy resolution (120 to 130 eV FWHM for Mn Kα X-rays) makes it extremely difficult to resolve overlapping peaks at low X-ray energies, such as the W Mα and Si Kα overlapping peaks from tungsten silicide (WSi_2) and the Ba Lα and Ti Kα overlapping peaks from barium titanate ($BaTiO_3$), both of which are technologically important materials.

Superconducting microcalorimeter detectors are now able to achieve better than 2 eV FWHM for the Mn Kα peak [2]. This resolution is sufficient to resolve the strong peak overlaps that occur at low X-ray energies, as well as the subtle energy shifts related to elemental chemical bonding states. This article describes recent advances that have enabled the development of a next-generation cryogen-free microcalorimeter spectrometer that is easy to use, offers higher count rates than available previously, and provides X-ray mapping at low accelerating voltages as well as quantitative X-ray microanalysis.

Microcalorimeter Detectors

A typical X-ray microcalorimeter detector consists of three parts: an absorber that converts the energy of the incident X ray into heat, an extremely sensitive thermometer to measure the temperature rise of the microcalorimeter following absorption of an X ray, and a support and thermo-isolation structure that sets the rate of heat loss from the microcalorimeter. The absorber should have a short X-ray absorption length and a thermalization time that is consistent with the speed of the microcalorimeter. Typically semi-metal films of Bi about 2 μm thick are used for the absorber (see Figure 1).

Detector components. The thermometer for a transition edge sensor (TES) microcalorimeter consists of a superconducting thin film operated at its superconducting transition using a novel negative electrothermal feedback technique [3]. The electrothermal feedback holds the detector at a precise temperature, typically around 100 mK. Following a photoabsorption event, the sudden temperature rise of the microcalorimeter results in a current pulse through the TES (the height of the pulse is proportional to the incident photon energy), which is measured using a low input-impedance
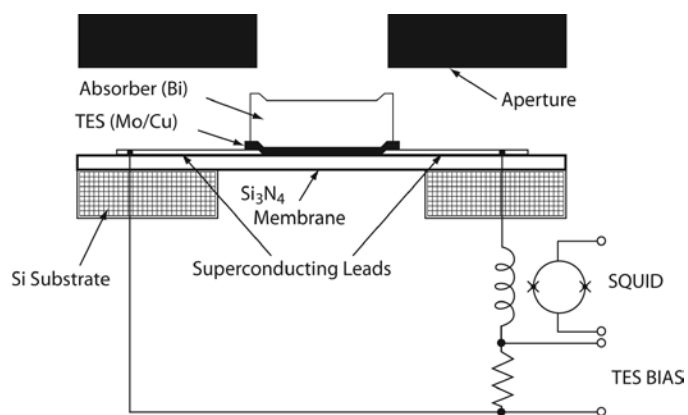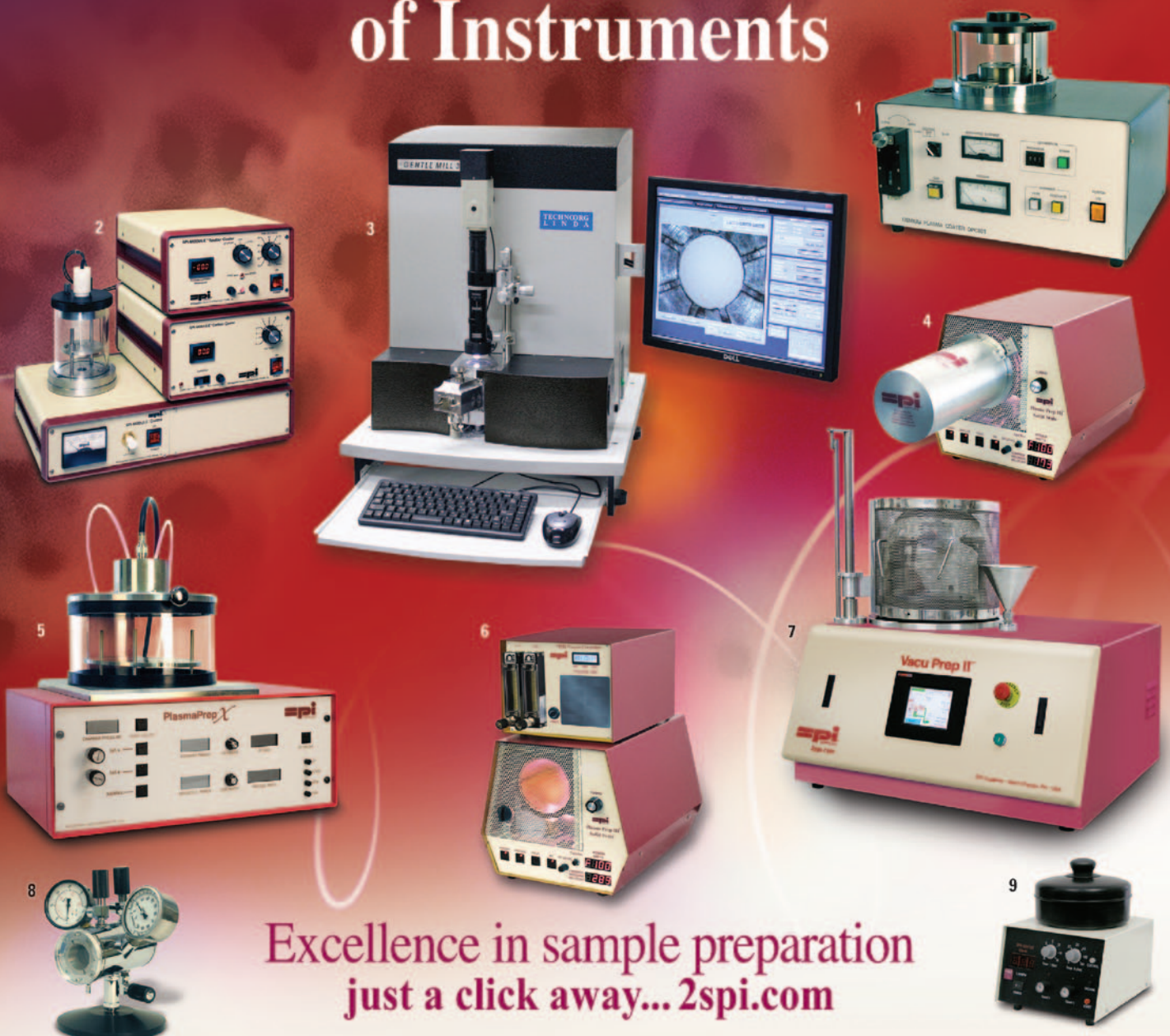

Figure 1: Schematic cross section of a TES microcalorimeter X-ray detector fabricated on a backside micromachined membrane. Also shown are the X-ray absorber material (Bi) and the first-stage SQUID readout amplifier. See text for details.

amplifier such as a dc superconducting quantum interference device (SQUID). The TES is fabricated from superconductor/normal metal. Using such bilayer films, the superconducting critical temperature may be tuned to around 100 mK by adjusting the strength of the proximity-effect coupling, that is, by adjusting the thicknesses of the superconducting and normal metal layers. The use of normal metal films with low resistivity and low thermal conductivity ensure fast thermal response times. Bilayers of Mo/Cu and Mo/Au currently are the most attractive and most commonly used materials for TES fabrication.

The third part of a TES microcalorimeter is the thermal isolation membrane upon which the TES bilayer structure is fabricated. The membrane thermally isolates the TES from the surrounding substrate and determines the rate of heat loss from the microcalorimeter. Micromachined silicon nitride membranes typically are used for this purpose, as shown in Figure 1 [4]. The membrane is formed by depositing a silicon nitride film on an oxidized Si wafer and then etching the backside of the wafer down to the membrane using a deep reactive ion etch (DRIE) process.

Spectrum generation. Signal processing and spectrum generation for microcalorimeter detectors do not differ principally from the methods used for other energy dispersive detectors: an optimal filter and dynamic base line restoration are applied to separate the signal from noise. The digitized and filtered signal is fed to a multichannel analyser (MCA), which successively builds up a spectrum from the individual energy readings for the captured and detected X-ray quanta.

Count-rate enhancements. Although TES microcalorimeters have low intrinsic count rates (up to around 600 cps), one way to increase the collection efficiency and therefore effective count rate is to use a polycapillary X-ray optic. However, polycapillaries require careful mechanical positioning that can shift with mechanical or thermal shock, and they can introduce spectral artifacts. A more attractive approach is to use an array of microcalorimeter detectors, which also increases the collection efficiency and the effective count rate. The state-of-the-art MICA-1600 microcalorimeter spectrometer includes a 16-detector array to enable count rates on the order of 10 kcps.

Spectrometer Design

In order to cool microcalorimeter detectors to 100 mK, an adiabatic demagnetization refrigerator (ADR) is used. The ADR is pre-cooled using a pulse tube cryocooler for cryogen-free operation. The use of a remote rotary valve for the pulse tube cryocooler, three stages of vibration isolation in the spectrometer, and bellows coupling to the microscope column (Figure 2) yields SEM performance with negligible image degradation even at the highest magnifications.

The ADR contains two thermally isolated paramagnetic salt pills that are magnetized and then adiabatically demagnetized to reach a base temperature below 50 mK. This regeneration process is fully automated and takes 1 to 1.5 hours to complete. The magnetic field is used to raise the temperature above the base to the operating temperature of about 100 mK. To stabilize the temperature, which is crucial in order to avoid peak shifts, precision temperature control electronics are required. This is accomplished automatically using a servo loop interfaced with the magnet power supply to precisely and gradually lower the
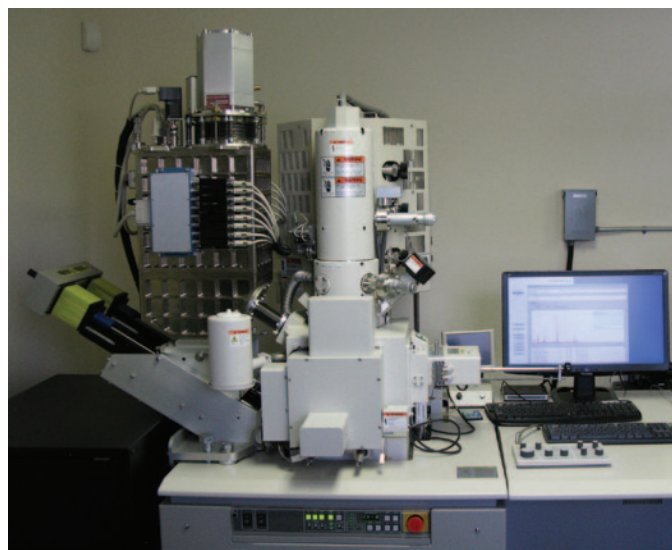
Figure 2: (a) MICA-1600 microcalorimeter X-ray spectrometer mounted on an SEM (Hitachi S-4800). (b) Detail showing the bellows mount where the microcalorimeter is mounted to the standard EDS port on the specimen chamber.

magnetic field in order to offset the increasing temperature drift from heat leaks and the heat load at the microcalorimeter stage. In this way, temperature fluctuations of less than 10 μK can be achieved [5].

The microcalorimeter spectrometer described here, STAR Cryoelectronics' Model MICA-1600, includes a snout with cold finger, at the end of which the TES microcalorimeter detector array and input stage SQUID amplifiers are mounted. The snout includes a standard X-ray vacuum window and three layers of IR blocking windows to reduce thermal loading on the detectors. The spectrometer is supported on a linear translational slide that is bolted to the SEM support plate. The spectrometer snout is installed through a standard port for semiconductor-based energy-dispersive spectrometers, as shown in Figure 2b.

For the MICA-1600 with an array of 16 individual microcalorimeter detectors, the detector output signals are

Table 1: Comparison of X-ray spectrometers.

	Microcalorimeter	WDS	EDS
Energy Resolution	< 10 eV	5–10 eV	125–130 eV
Acquisition Time	Short	Long	Short
Detection Efficiency	~100%	< 30%	~100%
Full Spectral Detection	Yes	No	Yes
Required Beam Current	10 pA–1 nA	1 nA–100 nA	10 pA–1 nA
Sample Damage	Low	High	Low

recorded using a Bruker Nano pulse processor optimized for microcalorimeter pulse shapes and pileup rejection. Spectral analysis is carried out using Bruker's Esprit software with the full range of analytical functions required for X-ray microanalysis at the SEM or TEM, including multi-point analysis, line scans, and mapping with elemental intensity or elemental concentration.

X-ray Spectrometer Comparison

A spectrometer based on microcalorimeter detectors combines the best features of wavelength-dispersive and energy-dispersive spectrometers in a single instrument: high-energy resolution and detection efficiency along with fast and full spectral detection with minimal sample damage. A summary of the key parameters [1] of the three types of spectrometers typically used for X-ray microanalysis is shown in Table 1.

Application Data

Microcalorimeter detectors have sufficient energy resolution to clearly resolve peak overlaps that occur at low

X-ray energies. This can be seen in Figure 3, where a spectrum for a NIST 3670 reference glass is shown along with the equivalent spectrum that would be obtained using a conventional semiconductor-based detector with a typical energy resolution of 120 eV. With the microcalorimeter spectrometer, all peaks are clearly resolved, including the Zn Lα (1.012 keV) and Zn Lβ (1.034 keV) peaks.

The high-energy resolution achievable with microcalorimeter detectors enables the use of very low beam energies to reduce the size of the X-ray excitation volume and probe nanometer-scale features. For example, Figure 4 shows sample spectra for a W (20 nm) over Ta (20 nm) bilayer on Si recorded at 3, 5, and 7 keV beam energies. At all three beam energies, all of the W, Ta, and Si peaks are clearly resolved. At 3 keV, the X-ray excitation volume is almost entirely limited to the top 20 nm W film, and only the W Mα peaks and a weak Ta Mα peak are observable. As the beam energy is increased, the depth of the X-ray excitation volume increases, leading to the emergence of the Ta Mα and Si Kα peaks.

The ability to probe nanometer-scale features using low-beam energies makes it possible to perform X-ray mapping of materials with strong peak overlaps such as W (Mα at 1.775 keV) on Si (Kα at 1.740 keV). Figure 5 shows X-ray maps
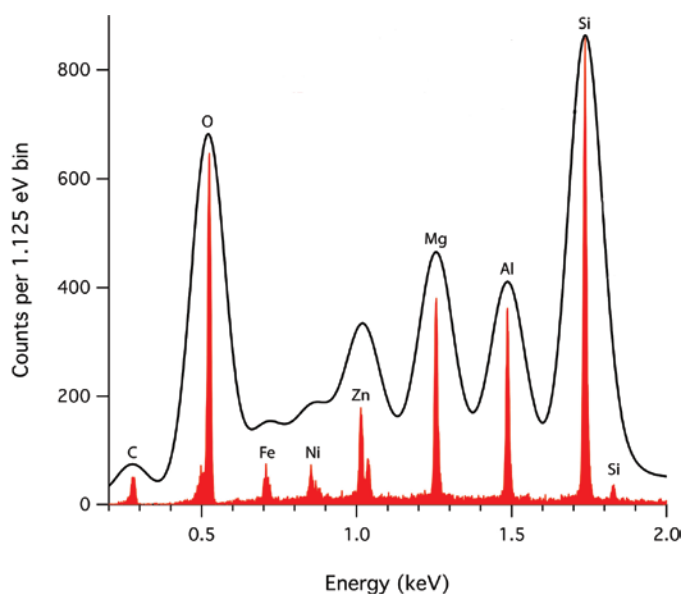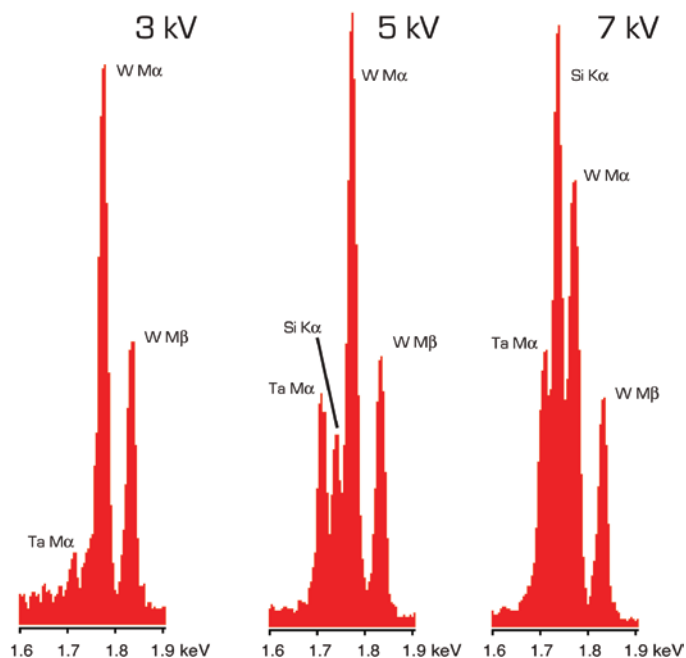

Figure 3: Spectrum from NIST K3670 reference glass (courtesy of D. Newbury, NIST). Red spectrum was acquired with the microcalorimeter at a beam energy of 7 keV. The black line shows the equivalent spectrum calculated for a conventional EDS spectrometer (courtesy of J. Ullom, NIST).

Figure 4: Microcalorimeter spectra for a W (20 nm) over Ta (20 nm) bilayer on a Si substrate. The MICA-1600 clearly resolves the Ta, Si, and W peaks around 1.75 keV and enables surface analysis of nanometer-scale films. The spectra above illustrate how the depth of the X-ray excitation volume increases with increasing beam voltage.
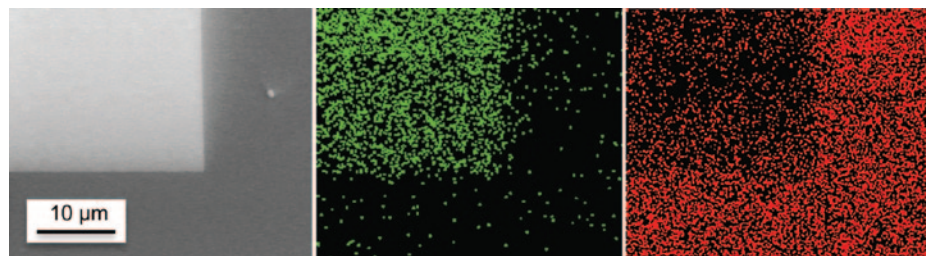
Figure 5: SEM image (left) of a W pad (20 nm thick) on a Si wafer. The microcalorimeter detector resolved the W (Mα at 1.775 keV) and Si (Kα at 1.740 keV) peaks near 1.7 keV (see Figure 4) and enabled the X-ray mapping of W (middle) on Si (right) at 3 keV.

collected at 3 keV from a specimen with a 20 nm W pad on a Si substrate. Low-beam-energy X-ray mapping also provides better lateral and depth spatial resolution and less beam damage during acquisition.

The excellent energy resolution of microcalorimeter detectors enables peak detection and resolution at very low energies, such as the detection of boron Kα at 183 eV as shown in Figure 6. The carbon and nitrogen shown are impurities in the boron or surface species deposited during handling.

Future Trends

The MICA-1600 already is a powerful tool for high-resolution X-ray microanalysis and nanoanalysis. Although the energy resolution of the current model is less than 10 eV, advances in microcalorimeter detector development suggest that multi-detector arrays with a combined energy resolution of better than 2 eV are feasible. The development and fabrication of such detector arrays are 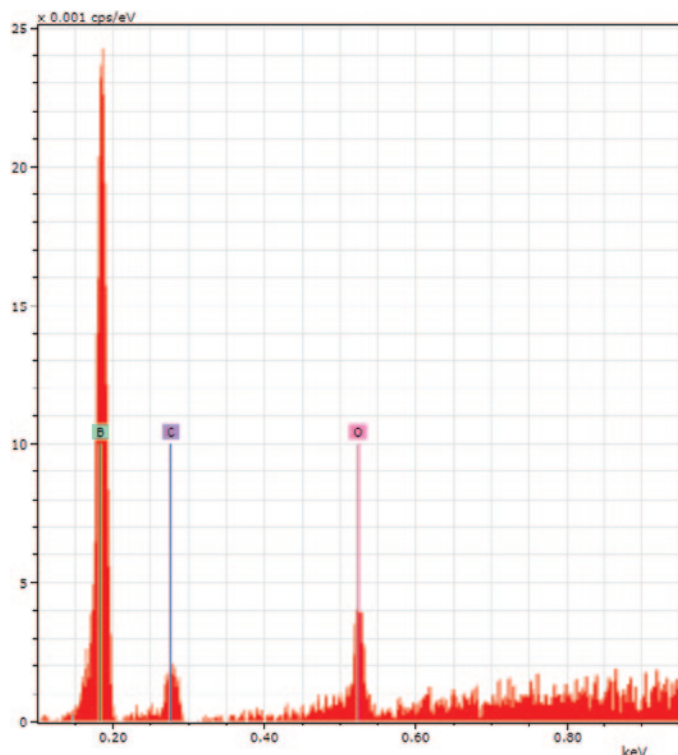currently underway. This is expected to be sufficient to detect the small energy shifts associated with chemical bonding states.

By using more efficient IR blocking windows and eliminating the X-ray vacuum window, it is anticipated that the low-energy X-ray detection range can be extended to Li K Kα at 54 eV. The detection of Li X rays currently is not possible using conventional X-ray spectrometers.

Conclusion

The commercial second-generation microcalorimeter X-ray spectrometer provides an energy resolution of 10 eV on Mn Kα compared to 125 eV with conventional EDS detectors. It also can collect X rays at several thousand counts per second. This technology allows collection of X-ray spectra and maps at low beam energies for improved analysis and X-ray mapping in situations where peak overlaps and beam damage would hamper conventional systems.

References

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Figure 6: Microcalorimeter spectrum from "pure" boron taken at 5 keV. The energy of the B Kα peak is 183 eV. The detected carbon and oxygen may be surface contamination from handling and exposure to air.