

CRYOGENIC MICROCALORIMETERS FOR X-RAY MICROANALYSIS*

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ABSTRACT

We have developed a high-resolution x-ray energy-dispersive spectrometer (EDS) based on cryogenic microcalorimeter x-ray detectors for use in x-ray microanalysis. With an energy resolution of 3 eV at 1.5 keV, count rate of $\sim 500 \text{ s}^{-1}$, and an effective collection area of $\sim 5 \text{ mm}^2$ (using polycapillary x-ray optics), microcalorimeter EDS combines the favorable qualities of commercially-available wavelength dispersive spectrometers (WDS) and semiconductor EDS. After describing the spectrometer system, we present several applications of microcalorimeter EDS to important microanalysis problems, including the analysis of contaminant particles in the semiconductor industry.

INTRODUCTION

We have recently developed a high-energy-resolution x-ray microcalorimeter energy-dispersive spectrometer¹ (EDS) for use in x-ray microanalysis. X-ray microanalysis is a sensitive, nondestructive analytical technique that provides spatially resolved qualitative and quantitative microchemical analysis. The combination of high-energy-resolution x-ray spectrometers with high-spatial-resolution scanning electron microscopes (SEM) has provided powerful microanalysis instruments which are widely used in both industry and academia. In these instruments, a finely focused electron beam is used to excite x rays in a small region of a sample under analysis. The x rays are then analyzed using a commercially-available wavelength-dispersive spectrometer (WDS) or semiconductor energy-dispersive spectrometer (EDS) to obtain an x-ray spectrum. Comparing the integrated characteristic x-ray intensities produced by the sample and elemental standards yields qualitative and quantitative compositional information on a micrometer or even a nanometer length scale.

Unfortunately, neither semiconductor EDS nor WDS fully satisfy the microanalysis requirements facing many technology-intensive industries. In a semiconductor EDS detector, x rays are

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absorbed in a voltage-biased intrinsic semiconductor to create electron-hole pairs, which separate under the applied electric field to yield a collected charge proportional to the x-ray energy. Semiconductor EDS is used in over 90% of installed x-ray microanalysis systems because it is easy to use, inexpensive to operate, and offers both rapid qualitative evaluation of chemical composition and accurate quantitative analysis. However, it is limited by an energy resolution on the order of 100 eV, which is insufficient to resolve many important overlapping x-ray peaks in materials of industrial interest, such as the Si $K\alpha$ and W $M\alpha$ peak overlap in WSi_2 . In contrast, WDS uses Bragg reflection from curved diffracting crystals to achieve the excellent resolution (typically 2 eV to 10 eV) needed to resolve most peak overlaps. However, qualitative WDS analysis is severely limited by the long time needed to serially scan over the entire energy range using multiple diffraction crystals.

There is a need for a new generation of x-ray spectrometer that combines the excellent energy resolution of WDS with the ease of use and the parallel energy detection capability of semiconductor EDS. One such next-generation x-ray spectrometer is microcalorimeter EDS. In this paper, we review the prototype microcalorimeter EDS system¹ developed at NIST, and examine several applications of microcalorimeter EDS to important microanalysis problems. Portions of the research described here have been published previously; in particular, Ref. 1 provides a more detailed overview of the microcalorimeter EDS system.

DETECTOR AND INSTRUMENTATION

An x-ray microcalorimeter consists of an x-ray absorber in thermal contact with a thermometer. When an x-ray photon of energy E interacts with the absorber, the deposited energy is thermalized and measured as a temperature rise $\Delta T = E/C$, where C is the heat capacity of the detector. The temperature of the microcalorimeter returns to the equilibrium temperature with a $1/e$ time constant $\tau = C/G$, where G is the thermal conductance between the absorber and the heat bath. The energy resolution ΔE of a microcalorimeter is limited by thermodynamic temperature fluctuations, such that $\Delta E \propto \sqrt{k_B T^2 C}$, where k_B is Boltzmann's constant and T is the operating temperature of the detector. Microcalorimeters are typically operated at low temperatures ($T \sim 0.1$ K) where materials have low heat capacity (leading to a large temperature rise), thermal and electrical noise sources are reduced, and sensitive thermometers are available. The first x-ray microcalorimeters used semiconductor-thermistor thermometers²⁻⁴ read out using field effect transistors. While these devices obtain energy resolutions sufficient for many microanalysis problems (~ 8 eV at 6 keV), their intrinsically slow response times (typically $\tau \geq 1$ ms) limit widespread application.

The microcalorimeter EDS developed at NIST uses a new type of microcalorimeter⁵ with a superconducting transition-edge sensor (TES) thermometer, which is a superconducting film biased in temperature within its narrow resistive transition from the normal to the superconducting state. The TES is biased with a voltage V , and the current flowing through the film is measured with a low-noise superconducting quantum interference device (SQUID) amplifier. The heat bath is then cooled to well below the transition temperature of the film, typically chosen to be ~ 100 mK. As the TES cools, its resistance R drops and the Joule heating (V^2/R) in the film increases. A stable equilibrium is established when the resistance is reduced to the point where the Joule

heating equals the heat flowing to the heat bath. The TES thus self-regulates in temperature within its transition, an effect referred to as negative electrothermal feedback.⁵

When an x ray deposits its energy in the absorber, the temperature and resistance of the TES increase, leading to a decrease in the current and thus the dissipation of Joule power in the TES, while the heat flowing to the heat bath remains approximately constant. Thus, the x-ray energy is primarily removed by a reduction in Joule heating, which can lead to a thermal response time more than a hundred times faster than the natural relaxation time τ .⁵ This faster time constant significantly increases the output count rate of TES microcalorimeters (to $\sim 500 \text{ s}^{-1}$, at present), making these new microcalorimeters very attractive for microanalysis applications.

Fig. 1 shows a cross-sectional view of a microcalorimeter including the physical layout and the external electrical connections. Using electron-beam evaporation through shadow masks, the TES, Bi absorber, and electrical contacts are deposited on a $0.5 \text{ }\mu\text{m}$ thick freely suspended silicon nitride membrane supported by a micromachined silicon substrate. The thin membrane reduces the thermal conductance from the detector to the bath, prevents the loss of absorbed x-ray energy via high energy phonons escaping into the substrate, and eliminates x-ray absorption in the substrate.⁶ Additionally, the electrical contacts to the TES are made with superconducting aluminum lines, which have very small thermal conductivity. The TES itself is $400 \text{ }\mu\text{m}$ by $400 \text{ }\mu\text{m}$ in lateral area and consists of a 300 nm thick Ag/Al bilayer. Proximity coupling between the normal metal Ag and the superconducting Al provides sharp and reproducible superconducting transitions at temperatures in the range 50 mK to 1 K . The thicknesses of the two metals are chosen to obtain a suitable transition temperature, typically near 100 mK . A $2 \text{ }\mu\text{m}$ Bi film deposited on top of the TES bilayer is used as an x-ray absorber. A $350 \text{ }\mu\text{m}$ diameter circular Pt aperture is used to collimate incoming x rays so that they are incident only on the absorber.

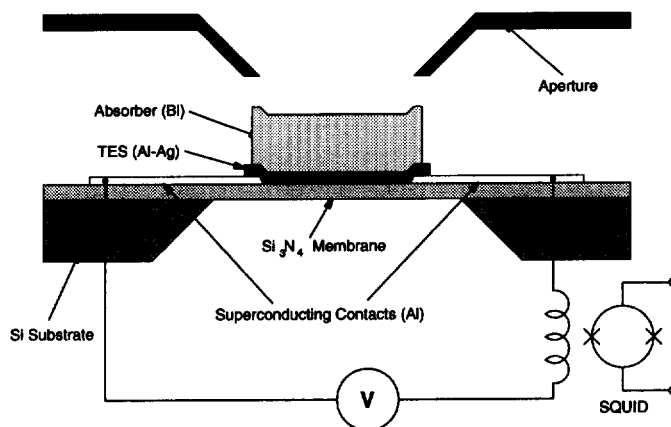


Figure 1. Cross-sectional view of the TES microcalorimeter. An x ray passes through an aperture and is absorbed in the Bi film. The resulting thermal energy pulse raises the temperature of the TES, causing an increase in resistance of the TES, and a pulse of decreased current at the SQUID input.

The use of a superconducting transition as a thermal sensor provides the detector with many of the advantages typically associated with superconducting circuits. Due to their low normal-state resistance ($R_n \sim 30 \text{ m}\Omega$), TES microcalorimeters are far less susceptible to microphonic pickup than high-impedance semiconductor thermistor microcalorimeters. Their low impedance also

allows efficient coupling to low-noise, low-power SQUID amplifiers. Because the detector's electrical bandwidth is limited by the L/R_n time constant of the SQUID input circuit (L is the sum of the stray and SQUID input inductances), improved speed and stability are obtained by mounting a first-stage SQUID at 0.1 K close to the detector chip, thus minimizing stray inductance. The output of this SQUID is amplified by a series-array SQUID⁷ operating at 4 K. The large output voltage (5 mV) and high output impedance (100 Ω) of the series-array SQUID allows the use of simple room temperature amplifiers for read out. At this stage, signal pulses resulting from discrete x-ray photon events are shaped for real-time peak height analysis using a commercially available EDS multichannel analyzer. In addition, pulse pileup rejection circuitry is used to veto x-ray pulses that are coincident in time.

For microcalorimeter EDS to be practical and useful to industry, a convenient and simple refrigeration system is required to reach operating temperatures of less than 100 mK. The refrigerator must be compact enough to be mounted on an SEM, have low vibration, and be very simple to operate. To satisfy these requirements, we have used an adiabatic demagnetization refrigerator⁸ (ADR) installed in a commercial two-cryogen (liquid helium and liquid nitrogen) cryostat to provide cooling from the liquid helium reservoir at 4 K to the detector stage at 100 mK. The ADR consists of two paramagnetic "pills" constructed of ferric ammonium alum (FAA) and gadolinium gallium garnet (GGG) which are supported in the bore of 4 T superconducting magnet by a low thermal conductance mechanical support. A mechanical heat switch is used to thermally ground both pills to 4 K during magnetization. Demagnetization causes the FAA pill to cool to 50 mK and the GGG pill to 1 K. The GGG pill is used as an intermediate heat intercept between 50 mK and 4 K, reducing thermal leakage to the FAA pill, thus increasing the hold-time of the FAA pill. The detector is mounted on a Cu rod which is in thermal contact with the FAA pill. A detector operating temperature of 70 mK can be held for over 12 hours, after which the ADR requires a magnetic "recharge" cycle that takes less than 45 minutes to complete. A cross-sectional view of the ADR cryostat is shown in Fig 2.

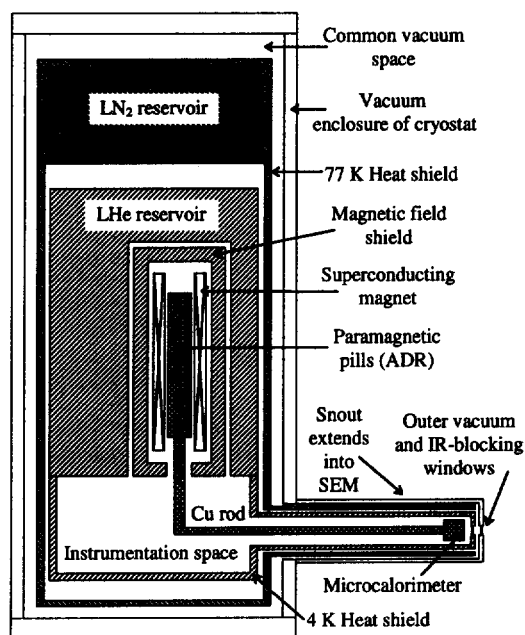


Figure 2. Cross-sectional drawing of the ADR cryostat (not to scale) from Ref. 1. The microcalorimeter is mounted at the end of a Cu rod that extends into the sample chamber of the SEM.

To increase the fraction of x rays collected from the sample, the TES microcalorimeter is placed at the end of a long Cu rod which is surrounded by heat and vacuum shields that protrude from the cryostat and extend into the SEM. A commercial vacuum-tight x-ray window placed at the end of the snout permits x-ray illumination of the detector. Within the snout, two free-standing Al-coated polymer membranes at 4 K are positioned between the x-ray window and the detector, reducing the infrared heat load on the detector. This arrangement allows us to place the detector less than 30 mm from the SEM sample stage.

Although our microcalorimeters have a small collection area ($\sim 0.1 \text{ mm}^2$), we have dramatically increased the effective detector area using polycapillary x-ray optics.^{1,9,10} These optics utilize high-efficiency grazing-angle x-ray reflections to deflect x rays over a wide angle. A polycapillary optic consisting of tens of thousands of fused glass capillaries can collect x rays from a point x-ray source and focus the x rays onto the small area absorber of our detector, as shown in Fig 3. This technique increases the effective area of the microcalorimeter to $\sim 5 \text{ mm}^2$ (relative to an effective sample-detector distance of 25 mm) over a broad range of x-ray energies (200 eV to 10 keV).

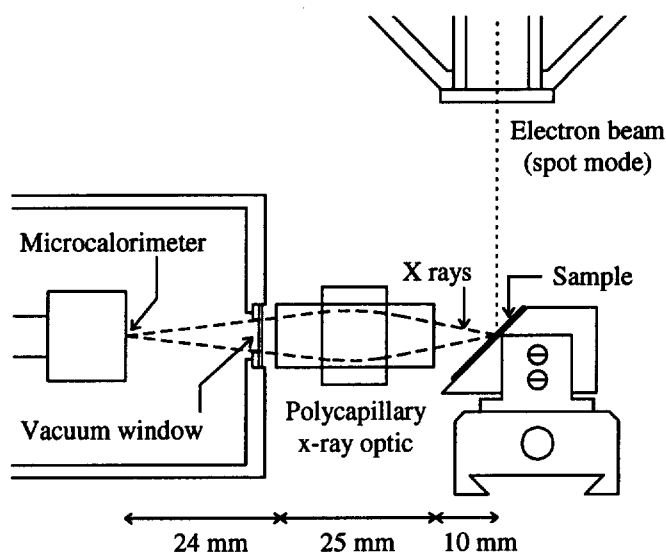


Figure 3. Diagram (approximately to scale) of microcalorimeter, polycapillary x-ray optic, and sample inside the SEM chamber, adapted from Ref. 1. By mechanically positioning the optic, the input and output focal spots of the optic are aligned with the sample and the microcalorimeter. For clarity, translation stages, heat shields and infrared-blocking Al filters are not shown.

MICROCALORIMETER PERFORMANCE AND APPLICATIONS

Microcalorimeter EDS must show significant performance increases over currently available techniques to be of practical value to the microanalysis community. As illustrated in Table 1, the current performance of microcalorimeter EDS approaches that of high-resolution semiconductor EDS in terms of solid angle ($\sim 7 \text{ msr}$ (milliradians) using a polycapillary optic x-ray lens) and maximum count rate ($\sim 500 \text{ s}^{-1}$), while providing improved energy resolution comparable to that of a wavelength-dispersive spectrometer (WDS). The excellent energy resolution of our “general purpose” microcalorimeter EDS ($\sim 10 \text{ eV}$ FWHM over the energy range 0 keV to $\sim 10 \text{ keV}$) allows straightforward identification of closely spaced x-ray peaks in complicated spectra, including

Table 1. X-ray Spectrometer Comparison.^a

Spectrometer Type	Energy Resolution (eV)	Maximum Count Rate (s ⁻¹)	Solid Angle (msr)	Collection Efficiency ^b (msr)
Semiconductor EDS (large area)	175 (at 6 keV) 145 (at 6 keV)	30000 5000	150 150	115 115
Semiconductor EDS (high-resolution)	130 (at 6 keV)	3000	25	19
WDS (several diffracting crystals)	2 to 20	50000	8 to 25	0.8 to 2.5 ^c
Microcalorimeter EDS (NIST, with polycapillary x-ray optics)	7 (at 6 keV) 3 (at 1.5 keV)	150 500	4 7	2 4

^a A more complete table, including a comparison to other low temperature detectors, is presented in Ref. 1.

^b Collection efficiency is defined as the product of solid angle and the overall spectrometer efficiency at 1.7 keV.

^c Because a WDS accepts only x rays of a narrow energy band, its practical collection efficiency is further reduced (up to several orders of magnitude) when scanned over the entire energy range.

overlapping peaks in important materials (such as TiN and WSi₂) which cannot be resolved by semiconductor EDS. Recently, we have developed a TES microcalorimeter¹¹ with an instrument-response energy resolution of 3.1 eV $\pm$ 0.1 eV FWHM (digital processing) and ~4 eV FWHM (analog processing) over the energy range 0 keV to ~2 keV. The ability to resolve severe peak overlaps using this detector is clearly observed in Fig. 4, in which we show an x-ray spectrum of TiN acquired in real time with our microcalorimeter EDS mounted on a SEM. The impressive increase in resolution over semiconductor EDS, coupled with reasonable output count rates and solid angle, demonstrates the usefulness of microcalorimeter EDS for x-ray microanalysis.

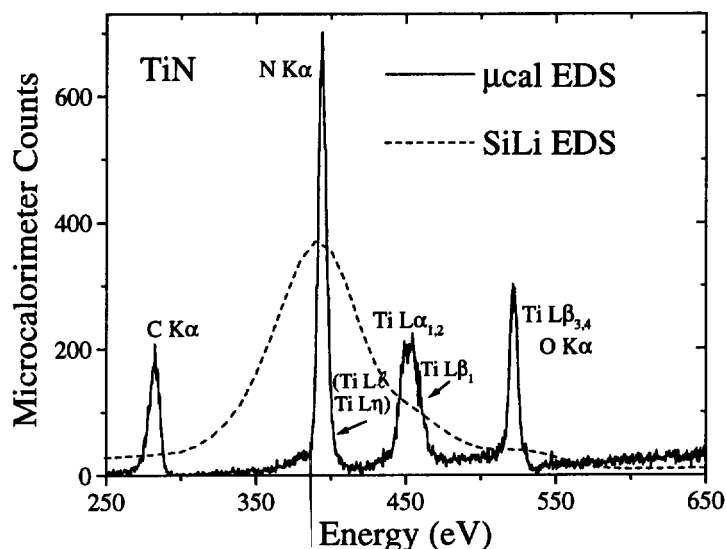


Figure 4. Microcalorimeter (μ cal) and semiconductor (SiLi) EDS x-ray spectra of TiN, from Ref. 12.

PARTICLE ANALYSIS IN THE SEMICONDUCTOR INDUSTRY

A difficult microanalysis challenge facing the semiconductor industry is the chemical identification of the small particles and defects that occur in the manufacture of integrated

circuits.¹² As circuit dimensions continue to shrink, it becomes impossible to perform this task efficiently with either EDS or WDS systems. To obtain x-ray spectra of a small particle, the electron-beam energy must be substantially reduced so that the majority of x rays originate from the particle and not the underlying substrate. The low energy electron-beam greatly reduces the x-ray flux per unit beam current, while increasing the likelihood of unresolvable peak overlaps. Because of this, both high energy resolution and efficiency are required, so that neither WDS nor semiconductor EDS are good detector choices. Additionally, the small x-ray flux imposes only modest requirements on detector count rate, making the microcalorimeter EDS very attractive in this analytical situation.

In Fig. 5 we show a microcalorimeter EDS spectrum of a 0.3 μm diameter W particle on Si. Such particles cannot be analyzed using semiconductor EDS due to the severe peak over-laps between the Si-K and W-M x-ray lines. The ability of microcalorimeter to analyze small Al oxide particles has also been investigated. In Fig. 6 we show microcalorimeter EDS spectra of Al oxide particles as small as 0.1 μm in diameter. In all cases, peaks from the Al oxide particles are clearly observable and are a significant fraction of the Si substrate peaks. In the case of the smallest particles (0.1 μm and 0.14 μm) the electron beam diameter was larger than the particle, leading to increased substrate peaks. This problem can be alleviated in the future through the use of a high-spatial-resolution field-emission SEM.

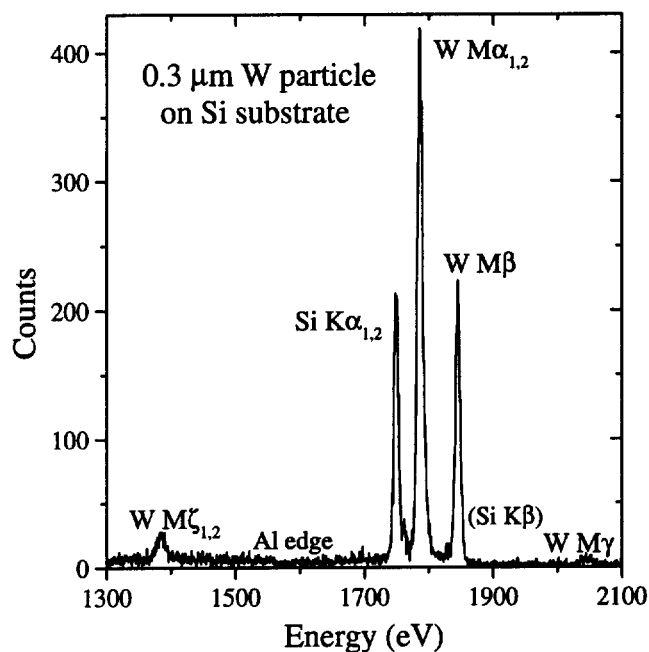


Figure 5. Microcalorimeter EDS x-ray spectrum of a 0.3 μm diameter W particle on a Si substrate (from Ref. 12), acquired under the following conditions: 5 keV beam energy, 50 pA beam current, 63 s^{-1} input count rate, 60 s^{-1} output count rate, 5% dead time, 400 s live time, and a 45° x-ray takeoff angle.

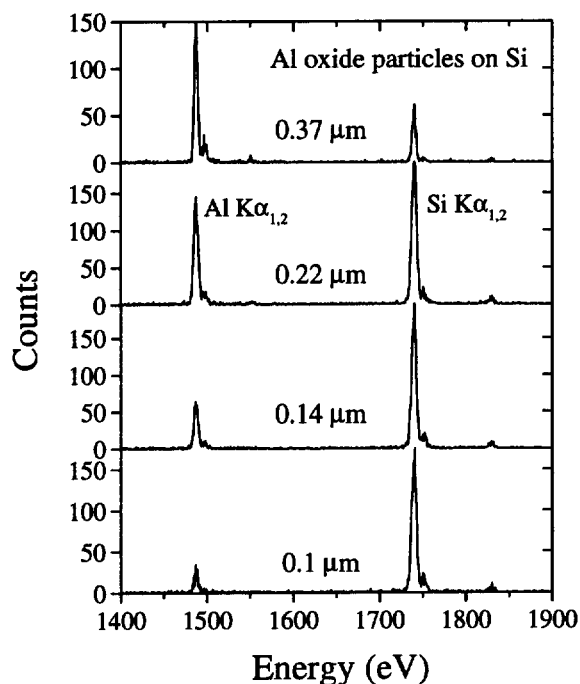


Figure 6. Microcalorimeter EDS x-ray spectra of several sized Al_2O_3 particles on a Si substrate (from Ref. 12), acquired under similar conditions as the spectrum in Fig. 5. The average diameter of each particle is displayed directly above its spectra. The electron beam diameter was estimated to be larger than the diameters of the two smallest particles.

CHEMICAL SHIFT MEASUREMENTS

Chemical shifts result from changes in electron binding energies with the chemical environment of atoms. Measurements of chemical shifts in analytical techniques such as x-ray photoemission spectroscopy (XPS) and Auger electron spectroscopy (AES) have been demonstrated to provide valuable chemical bonding state information.¹³ For example, the ability to identify particle composition by distinguishing different oxidation states (for example, Al and Al₂O₃) using AES has been demonstrated to be useful in determining sources of contamination in semiconductor processing tools.¹⁴

While chemical shift measurements are not as well established in x-ray spectroscopy, chemical shifts have been observed in WDS x-ray spectra as changes in x-ray peak positions, relative peak intensities, and peak shapes.¹⁵ These chemical shift effects can be significant (with x-ray peak shifts on the order of 1 eV), particularly for x-ray lines resulting from transitions involving valence electrons of light elements¹⁶ such as C. However, chemical shift measurements are not routinely performed in WDS analysis due to the extreme time penalty of scanning.

The improvement in energy resolution of our most recent TES microcalorimeter now allows microcalorimeter EDS measurements of chemical shifts¹⁷ in x-ray spectra, as shown in Fig. 7 for Fe and FeO-OH. The EDS operation of the microcalorimeter ensures that all peak shapes and integrated peak intensities are readily accessible. With further improvements in the energy

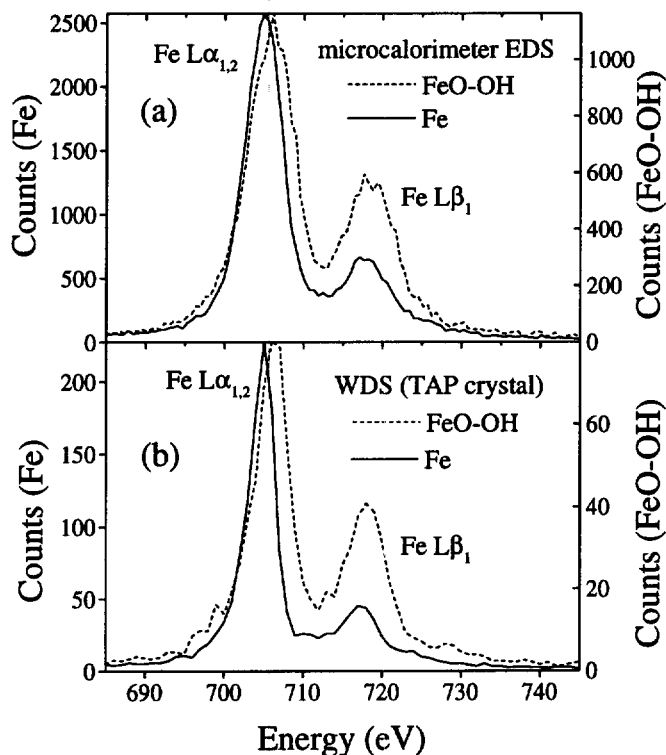


Figure 7. (a) Microcalorimeter EDS spectra and (b) WDS spectra of Fe (solid line) and FeO-OH (dashed line), from Ref. 17. The observed changes in the Fe-L peak positions and intensities result from chemical bonding effects. Good agreement is observed between microcalorimeter EDS and WDS spectra.

resolution of microcalorimeter EDS, analysis using x-ray peak shapes and positions may become practical and provide valuable chemical bonding state information for particle analysis and other applications.

CONCLUSION

Microcalorimeter EDS is a next-generation spectrometer for x-ray microanalysis with the energy resolution of a WDS and the parallel energy detection of an EDS. The excellent energy resolution of microcalorimeter EDS will allow many new applications to important microanalysis problems, including the analysis of contaminant particles on semiconductor surfaces and chemical shift measurements. With commercialization and further development, microcalorimeter EDS will help to meet the analytical requirements for x-ray microanalysis in the future.

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