Superconducting Transition-Edge Microcalorimeters for X-ray Microanalysis

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***Abstract*— We have developed high-performance x-ray microcalorimeters based on superconducting transition-edge sensors. These superconducting detectors, which are cooled by a compact adiabatic demagnetization refrigerator mounted on a scanning electron microscope, provide significant new capabilities for x-ray microanalysis. The performance characteristics of these detectors are nearly ideal for many applications in x-ray microanalysis, attaining an energy resolution of 3-4 eV at a counting rate of 500 s^{-1} and an effective collection area of 4 mm^2. The excellent energy resolution enables measurements of chemical shifts in x-ray spectra caused by changes in electron binding energy due to chemical bonding. Another important application of these detectors is analysis of contaminant particles and defects for the semiconductor industry. We present data demonstrating the analysis of particles on Si wafers, including 0.3 μm tungsten particles and 0.1 μm alumina particles.**

I. Introduction

We have recently developed an x-ray spectroscopy system for microanalysis applications which is based on superconducting technologies [1]. This prototype not only demonstrates significant new microanalysis capabilities, but also shows that such an instrument is practical to construct and operate. The x-ray detector, or microcalorimeter, measures the thermal energy deposited by an absorbed x-ray, using a superconducting transition-edge sensor (TES) as a thermometer. The microcalorimeter and an adjacent superconducting quantum inteference device (SQUID) preamplifier are cooled to an operating temperature of 0.1 K by a two-stage adiabatic demagnetization refrigerator (ADR). The detector signal is then further amplified by a series-array SQUID operating at 4 K. The large magnetic field (4 T) necessary for operation of the ADR is produced by a low current (10 A) superconducting solenoid also operating at 4 K. High T_c BSCCO/Ag conductors are used as magnet current leads in order to minimize the thermal heat load on the 4K bath.

X-ray microanalysis is a powerful and widely used technique for providing spatially resolved chemical analysis. In such an instrument, a scanning electron microscope (SEM) creates a finely focused electron beam which excites characteristic x-rays from the sample under analysis. A spectrometer then analyzes the x-rays to give information about the chemical composition of the sample. While two types of spectrometers, energy dispersive (EDS) and wavelength dispersive (WDS) spectrometers, have been widely used for many years, neither type of instrument fully meets the microanalysis requirements facing a variety of industries. Even at this early stage of development, our microcalorimeter spectrometer performs better than existing technology for a variety of difficult microanalysis applications.

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II. Detector and Instrumentation

An x-ray microcalorimeter consists of an x-ray absorber in thermal contact with a thermometer. The energy E of an incident x-ray is converted to heat in the absorber, leading to 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 $\tau_0 \propto C/G$, 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, so that $\Delta E \propto \sqrt{k_B T^2 C}$, where k_B is Boltzmann's constant and T is the detector operating temperature. Low temperature ($\sim$ 100 mK) operation improves detector performance by reducing thermal and electrical noise, and by reducing C. Reduced heat capacity improves detector sensitivity and reduces τ_0.

Several groups have constructed x-ray microcalorimeters using semiconductor thermistors as thermometers [2], [3], [4]. While these devices obtain energy resolutions sufficient for many microanalysis problems ($\sim$ 7 eV at 6 keV), their intrinsically slow response time limits widespread application. The use of higher sensitivity TES thermometers [5] permits construction of detectors with improved energy resolution, and permits the use of strong negative electrothermal feedback for better detector response time.

Fig. 1 shows a cross sectional view of a microcalorimeter including the physical layout and the external electrical connections. The detector is fabricated on a micromachined membrane substrate, formed by anisotropic etching of a Si wafer coated with a 0.25 μm thick film of low-stress silicon nitride. The thin membrane reduces the thermal conductance from the detector to the bath, prevents the loss of absorbed x-ray energy via high en-

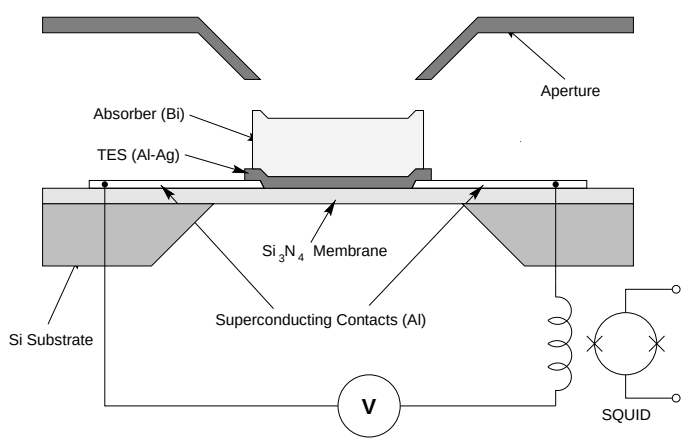

Fig. 1. Cross-sectional view of the TES microcalorimeter. An x-ray passes through an aperture and is absorbed in the Bi film. The resulting thermal energy pulse raises the temperature of the TES, causing an increase in resistance of the TES, and a pulse of decreased current at the SQUID input.

ergy phonons escaping into the substrate, and eliminates x-ray absorption in the substrate [6]. The electrical contacts, TES, and absorber are deposited on the substrate chips by electron-beam evaporation through shadow masks. Electrical contacts to the TES are made with superconducting aluminum lines which have a very small thermal conductivity. The TES consists of a 300 nm thick bilayer of Ag and Al. 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 120 mK. A 2 μm Bi film deposited on top of the bilayer is used as an x-ray absorber. The area of the TES and absorber are both roughly 400 μm by 400 μm. The detector films are deposited without breaking vacuum between evaporation steps. This method has proven to be a simple, and reliable method of detector fabrication.

The use of a superconducting transition as a thermal sensor provides the detector with many of the advantages typically associated with superconducting circuits. Owing to their low normal-state resistance ($R_n \sim 30$ mΩ), TES microcalorimeters are far less susceptible to microphonic pickup than high-impedance semiconductor thermistor microcalorimeters. Low impedance also provides efficient coupling to quiet, 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 further amplified by a series-array SQUID [7] operating at 4 K. The large output voltage (5 mV) and high output impedance (100 Ω) of the series-array SQUID permit the use of simple room temperature amplifiers. This arrangement has several practical advantages. First, the connections from the detector to the first-stage SQUID (which requires low stray inductances and resistances) are made by very short superconducting Al wire bonds. Also, the large signals and relatively high source impedance (1 Ω) of the first-stage SQUID permit signal connection from the 0.1 K first stage to the 4 K series-array to be made using connectors and simple twisted pair wiring. This method increases system reliability and has small thermal loading onto the 0.1 K stage.

Construction of a practical prototype system requires careful consideration of the refrigeration necessary to reach the operating temperature of 100 mK. The refrigerator must be compact enough to be mounted on an SEM, have low vibration, and be simple to operate. To achieve these goals, we use an adiabatic demagnetization refrigerator [8] to provide cooling from the liquid He reservoir at 4K 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. 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. A mechanical heat switch is used to thermally ground both pills to 4K. 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, at which time the ADR requires a magnetic "recharge" cycle which takes less than 45 minutes to perform. A commercial two-cryogen (LHe and LN_2) cryostat provides a 4 K bath for the ADR. The complete cryostat is shown mounted on the column of an SEM in Fig 2.

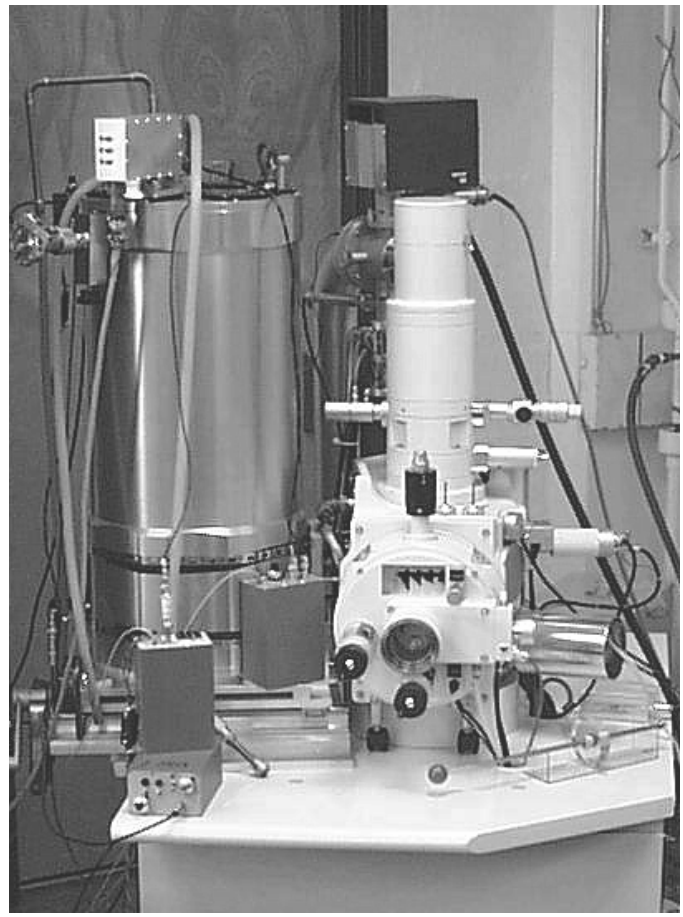

Fig. 2. Photograph of the ADR cryostat mounted on a commercial scanning electron microscope column. The microcalorimeter is mounted near the end of a snout that extends into the sample chamber of the microscope.

As in any SEM-based x-ray spectrometer, the detector is mounted as close as possible to the sample under study to increase the fraction of x-rays collected. To achieve this goal, the TES microcalorimeter is placed at the end of a cold finger which is inside a snout that protrudes from the cryostat and extends 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, we can dramatically increase the effective detector area by using polycapillary x-ray optics [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 thou-

TABLE I
X-RAY SPECTROMETER COMPARISON

Spectrometer Type	Energy Resolution (eV)	Maximum Count Rate (s^{-1})	Solid Angle (msr)	Collection Efficiency[a] (msr)
Semiconductor EDS (high resolution)	130 (at 6 keV)	3000	25	19
WDS (several crystals)	2-20	50 000	8 to 25	0.8 to 2.5[b]
Microcalorimeter EDS with	7 (at 6 keV)	150	4	2
polycapillary x-ray optics[c]	3 (at 1.5 keV)	500	10	5

A more complete table is presented in [1].
[a] Collection efficiency is defined as the product of solid angle and overall quantum efficiency at 1.6 keV.
[b] Because WDS accepts x-rays from only a narrow energy band, its practical collection efficiency is further reduced (up to several orders of magnitude) when scanned over the entire energy range.
[c] The microcalorimeter results presented in this table reflect data taken from two detectors of different design using different optics.

sands 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. This technique increases the effective area of the microcalorimeter by a factor of nearly 300 for a broad range of x-ray energies (200 eV to ∼10 keV).

III. MICROANALYSIS APPLICATIONS

TES microcalorimeters must show significant performance increases over currently available techniques to be of practical value to the microanalysis community. In semiconductor EDS, which constitutes over 90% of installed x-ray microanalysis systems, the detector consists of a voltage-biased semiconductor crystal. Absorbed x-rays create electron-hole pairs which separate under the applied electric field and yield a collected charge proportional to the x-ray energy. High-resolution EDS spectrometers achieve an energy resolution of roughly 130 eV full-width at half maximum (FWHM), at a count rate of 3000 s^{-1}, and have a relatively large collection area (25 msr for typical conditions). In WDS system, an x-ray wavelength is selected for measurement by mechanically adjusting the incident angle of a curved diffracting crystal to satisfy the Bragg reflection condition. The resulting x-rays are then measured using a proportional counter. While WDS can achieve energy resolutions in the range of 2-20 eV at count rates of up 50000 s^{-1}, they can measure only one x-ray energy at a time, thus requiring mechanical scanning of the crystal in order to obtain a complete spectrum. These systems have significantly smaller collection areas and efficiencies than EDS systems, and are susceptible to systematic errors due to variations in spectrometer efficiency with energy. With our TES microcalorimeter we combine the energy resolution of WDS with the ease of use and applicability of EDS. In Table I, we summarize typical performance characteristics of the conventional and microcalorimeter-based spectrometers. Another new high resolution x-ray detector, the superconducting tunnel junction [11], can achieve much higher count rates than the microcalorimeter, but has worse energy resolution and suffers from potentially serious spectral artifacts.

A. High Resolution Energy Dispersive Analysis

Microcalorimeter EDS can already solve many difficult materials analysis problems in the semiconductor industry. Currently, performance of microcalorimeter EDS approaches that of high-resolution semiconductor EDS in terms of solid angle (4 msr using an polycapillary optic x-ray lens) and maximum count rate (500 s^{-1}; over 1000 s^{-1} using a beam-blanker), while providing energy resolution comparable to that of a WDS. The energy resolution of our first-generation microcalorimeter EDS (∼10 eV FWHM over the energy range 0 keV to 10 keV) allows straightforward identification of closely spaced x-ray peaks in complicated spectra (such as the technologically important materials TiN and WSi_2) which cannot be resolved with semiconductor EDS. Recently, we have developed a TES microcalorimeter with an energy resolution of 3-4 eV over the energy range 0-2 keV. The ability to resolve severe peak overlaps using this detector is clearly observed in Fig. 3, which compares an x-ray spectrum of TiN acquired in real time with our microcalorimeter EDS to a spectrum obtained by conventional semiconductor EDS.

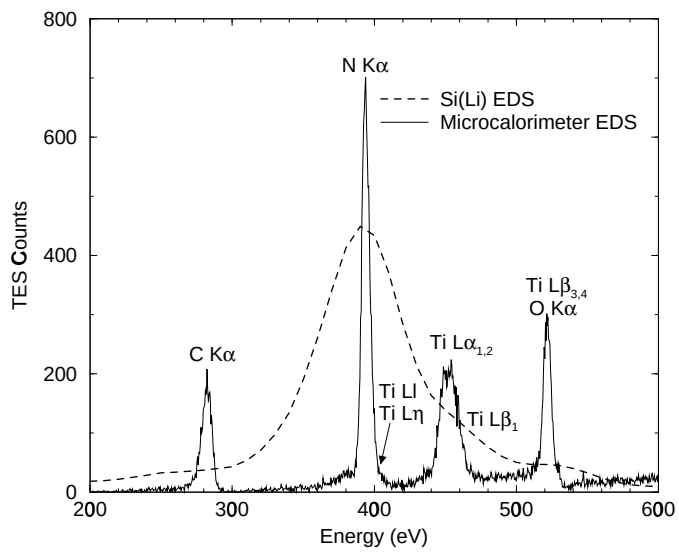

Fig. 3. Microcalorimeter EDS x-ray spectrum of TiN. The original spectrum was corrected for energy nonlinearity, resulting in a constant energy binwidth of 0.45 eV per channel over the energy range presented.

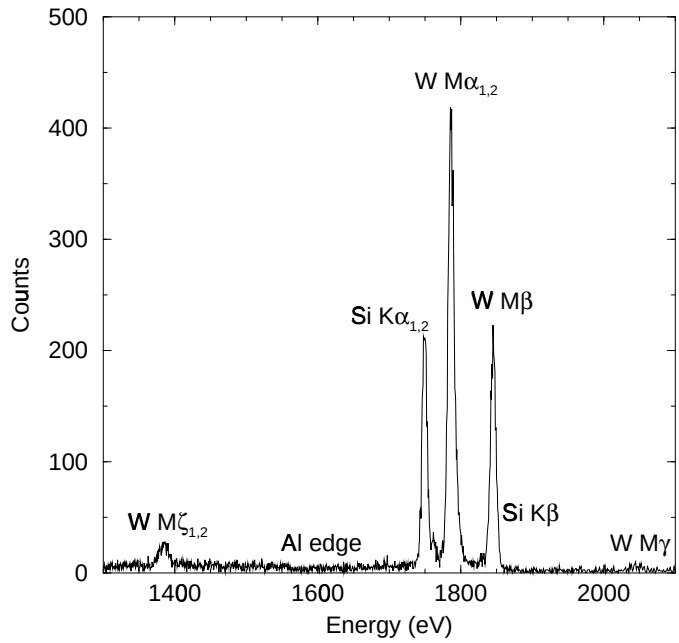

Fig. 4. Microcalorimeter EDS x-ray spectrum of a 0.3 μm diameter W particle on a Si substrate. The original spectrum was corrected for energy nonlinearity, resulting in an energy binwidth per channel that increases from 0.7-1.1 eV over the energy range presented. The electron beam diameter was estimated to be less than the particle diameter. The good energy resolution of this detector enables easy identification of the closely spaced Si-K and W-M lines.

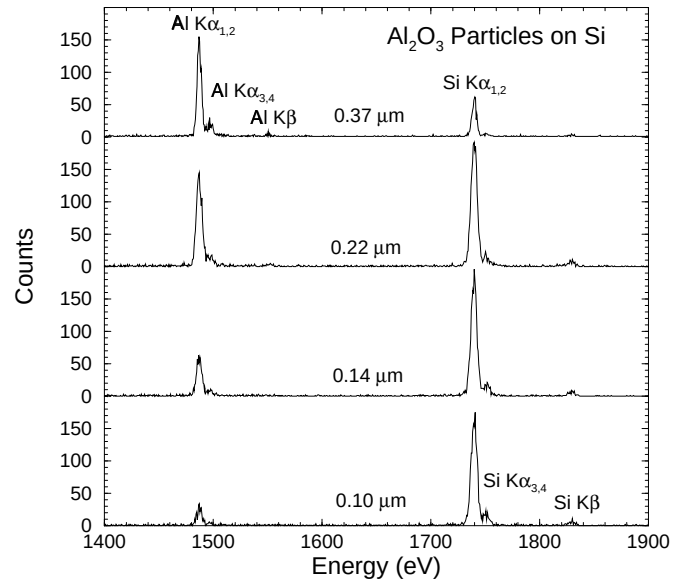

Fig. 5. Microcalorimeter EDS x-ray spectra of several differently sized Al_2O_3 particles on a Si substrate. The average diameter of each particle is displayed directly above its spectra. The original spectrum were corrected for energy nonlinearity. The electron beam diameter was estimated to be larger than the diameters of the two smallest particles. In all cases we see clear signals from both the alumina partice and the Si substrate.

B. Particle Identification

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 large 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.

In Fig. 4 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 overlaps between the Si-K and W-M x-ray lines. The ability of microcalorimeter EDS to analyze small Al_2O_3 particles has also been investigated. In Fig. 5 we show microcalorimeter EDS spectra of Al_2O_3 particles as small as 0.1 mm in diameter. In all cases, peaks from the Al_2O_3 particles are clearly observable and are a significant fraction of the Si substrate peaks. In the case of the smallest particles (0.1 and 0.14 μm) the electron beam diameter was larger than the particle, leading to increased substrate peaks. This problem can be alleviated through the use of a field-emission SEM.

C. Measurement of Chemical Shift

Chemical shifts in x-ray spectra result from changes in electron binding energies due to chemical bonding. Chemical shift measurements with analytical techniques such as x-ray photoemission spectroscopy and Auger electron spectroscopy (AES) have long been demonstrated to provide chemical bonding state information. The ability to identify particle oxidation state (for example, Al and Al_2O_3) using AES has been demonstrated as a means of determining sources of contamination in semiconductor processing tools [13].

The improved energy resolution of our most recent TES microcalorimeter should allow routine microcalorimeter EDS measurements of chemical shifts in x-ray spectra. In Fig. 6 we compare the chemical shift observed between these two compounds with both microcalorimeter EDS and WDS [14]. While chemical shifts have been measured with WDS, these measurements are not routinely performed because of systematic difficulties and the extreme time penalty of scanning. The EDS operation of the microcalorimeter ensures that all peak shapes and integrated peak intensities are readily accessible. With further improvements in the energy resolution of the microcalorimeter, analysis of the chemical bonding state of small particles may become practical.

IV. Conclusions

We have constructed a prototype high-performance x-ray spectrometer system, an achievement made possible by a number of developments in superconducting and cryogenic tech-

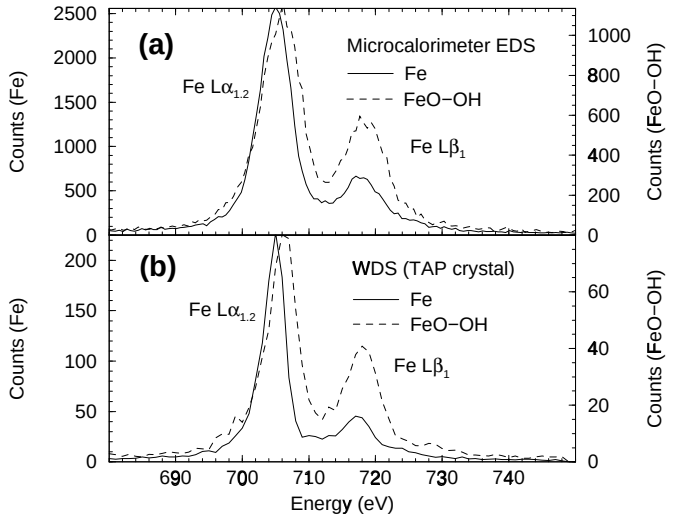

Fig. 6. (a) Microcalorimeter EDS spectra and (b) WDS spectra of Fe (solid line) and FeO-OH (dashed line). The observed changes in the Fe-L peak positions and intensities result from chemical bonding effects. Good agreement is observed between the microcalorimeter EDS and WDS spectra.

nologies. Our spectrometer demonstrates new capabilities for a variety of important microanalysis applications.

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