High-Resolution Microcalorimeter Energy-Dispersive Spectrometer for X-ray Microanalysis and Particle Analysis*

D. A. Wollman,† G. C. Hilton,† K. D. Irwin,† L. L. Dulcie,† N. F. Bergren,† Dale E. Newbury,‡ Keung-Shan Woo,§ Benjamin Y. H. Liu,§ Alain C. Diebold,§§ and John M. Martinis†

† National Institute of Standards and Technology (NIST), Boulder, Colorado 80303
‡ National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899
§ University of Minnesota, Minneapolis, Minnesota 55455
§§ SEMATECH, 2706 Montopolis Drive, Austin, Texas 78731

We have developed a high-resolution microcalorimeter energy-dispersive spectrometer (EDS) at NIST that provides improved x-ray microanalysis of contaminant particles and defects important to the semiconductor industry. Using our microcalorimeter EDS mounted on a scanning electron microscope (SEM), we have analyzed a variety of specific sized particles on Si wafers, including 0.3 μm diameter W particles and 0.1 μm diameter Al_2O_3 particles. To compare the particle analysis capabilities of microcalorimeter EDS to that of semiconductor EDS and Auger electron spectroscopy (AES), we report measurements of the Al-Kα/Si-Kα x-ray peak intensity ratio for 0.3 μm diameter Al_2O_3 particles on Si as a function of electron beam energy. We also demonstrate the capability of microcalorimeter EDS for chemical shift measurements.

INTRODUCTION

Improved x-ray detector technology has been cited by SEMATECH's Analytical Laboratory Managers Working Group as one of the most important metrology needs for the semiconductor industry. In the Metrology Roadmap section of the 1997 National Technology Roadmap for Semiconductors (NTRS) (1), improved x-ray detector technology is listed as a key capability that addresses analysis requirements for small particles and defects. The transition-edge sensor (TES) microcalorimeter x-ray detector (2) developed at NIST has been identified as a primary means of realizing these detector advances, which will greatly improve in-line and off-line metrology tools that currently use semiconductor energy-dispersive spectrometers (EDS). At present, these metrology tools fail to provide fast and unambiguous analysis for particles less than approximately 0.1 μm to 0.3 μm in diameter. Improved EDS detectors such as the TES microcalorimeter are necessary to extend the capabilities of existing SEM-based instruments to meet the analytical requirements for future technology generations. With commercialization and continued rapid development, microcalorimeter EDS should be able to meet both the near-term NTRS goal of analyzing particles as small as 0.08 μm in diameter and the longer-term requirements of the semiconductor industry for improved particle analysis.

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MICROCALORIMETER PERFORMANCE

Microcalorimeter EDS can already solve many materials analysis problems in the semiconductor industry. As illustrated in Table 1, the current 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 (3)) and maximum count rate (500 s^{-1}; over 1000 s^{-1} using a beam-blanker), while providing improved energy resolution comparable to that of a wavelength-dispersive spectrometer (WDS). The excellent energy resolution of our "general purpose" 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, including overlapping peaks in important materials (such as TiN and WSi_2) which cannot be resolved by semiconductor EDS. Recently, we have developed a TES microcalorimeter with an instrument-response energy resolution of 3.1 eV ± 0.1 eV FWHM (digital processing) and ~4 eV FWHM (analog processing) over the energy range 0 keV to ~2 keV (4). The ability to resolve severe peak overlaps using this detector is clearly observed in Fig. 1, in which we show an x-ray spectrum of TiN acquired in real time with our microcalorimeter EDS mounted on a SEM.

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)	30000	150	115
	145 (at 6 keV)	5000	150	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	7 (at 6 keV)	150	4	2
polycapillary x-ray optics)	3 (at 1.5 keV)	500	10	5

[a] A more complete table, including a comparison to other low temperature detectors, is presented in (2).
[b] Collection efficiency is defined as the product of the 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.

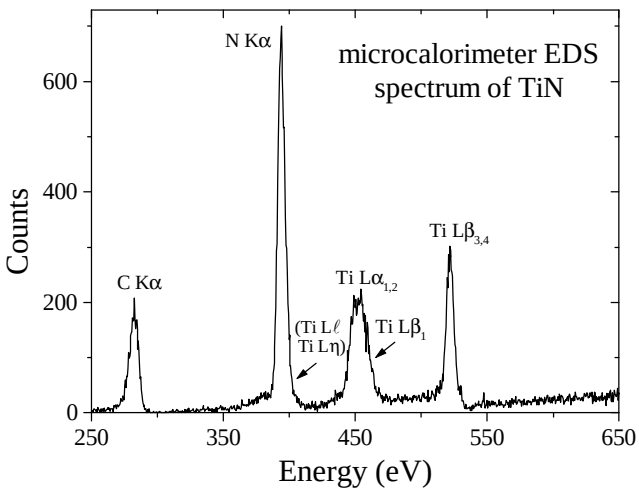

FIGURE 1. Microcalorimeter EDS x-ray spectrum of TiN, acquired under the following conditions: W filament, 2 keV beam energy, 320 s^{-1} input count rate, 230 s^{-1} output count rate, 27% dead time, 400 s live time, and a 45° x-ray takeoff angle. The original spectrum was corrected for energy nonlinearity, resulting in a constant energy binwidth of 0.45 eV per channel over the energy range presented. A significant C contamination peak developed during acquisition of all spectra reported in this work.

PARTICLE ANALYSIS

To demonstrate the usefulness of microcalorimeter EDS for particle analysis, we analyzed a variety of sub-micrometer particles produced at the University of Minnesota. This work was motivated by a SEMATECH project on detector development for particle analysis. As in previous particle analysis comparisons (5, 6), uniform particles of the desired size (0.3 μm diameter and 0.1 μm diameter) and material (Al_2O_3, W, and TiO_2) were selected using an electrostatic classification system and deposited on pieces of Si wafers under cleanroom conditions. These particles were then imaged and analyzed at NIST using SEM/microcalorimeter EDS.

In Fig. 2 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. In Fig. 3 we present a microcalorimeter EDS spectrum of a 0.3 μm diameter TiO_2 particle, another particle type that is difficult to analyze using semiconductor EDS.

In order to compare the particle analysis capabilities of SEM/microcalorimeter EDS to that of other analytical methods, we analyzed 0.3 μm diameter Al_2O_3 particles on

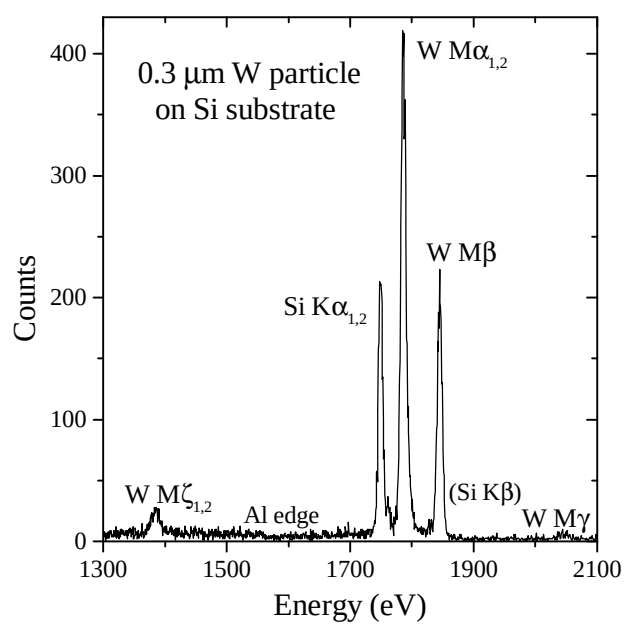

FIGURE 2. Microcalorimeter EDS x-ray spectrum of a 0.3 μm diameter W particle on a Si substrate, acquired under the following conditions: LaB_6 filament, 5 keV beam energy, 50 pA beam current, 63 s^{-1} input count rate, 60 s^{-1} output count rate, 5% dead time, 400 s live time, and a 45° x-ray takeoff angle. The original spectrum was corrected for energy nonlinearity, resulting in an energy binwidth per channel that increases from 0.7 eV to 1.1 eV over the energy range presented. The electron beam diameter was estimated to be less than the particle diameter.

Si to determine the Al-Kα/Si-Kα peak intensity ratio as a function of electron beam energy. This particle-to-substrate ratio has been proposed as a figure of merit for particle analysis and has been useful in the semiconductor industry to determine optimum beam conditions for particle analysis. Particle-to-substrate ratios have been used previously to compare the particle analysis capabilities of field-emission SEM/semiconductor EDS (FE-SEM/EDS) and field-emission Auger electron spectroscopy (FE-AES) (5, 6).

The Al_2O_3 particles were imaged using a SEM and categorized by size and morphology. Compact (preferably round) Al_2O_3 particles with average diameters between 0.26 μm and 0.34 μm were selected for analysis. In Fig. 4 we show a microcalorimeter EDS spectrum of a typical 0.3 μm diameter Al_2O_3 particle acquired at a beam energy of 5 keV. All particle analyses were performed in spot mode with the electron beam at the approximate center of the particle. The smallest SEM electron probe sizes (corresponding to beam currents of 10 pA to 40 pA) were selected to keep the diameter of the electron beam less than that of the particle. This condition was difficult to satisfy

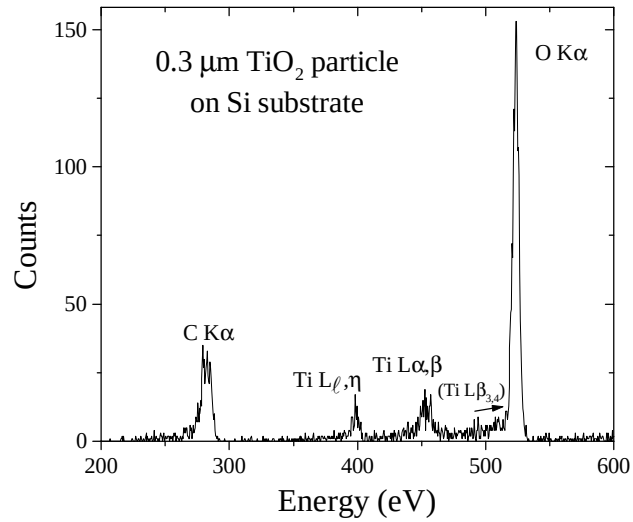

FIGURE 3. Microcalorimeter EDS x-ray spectrum of a 0.3 μm diameter TiO_2 particle on a Si substrate, acquired under the following conditions: LaB_6 filament, 1.8 keV beam energy, 0.53 nA beam current, 30 s^{-1} input count rate, 29 s^{-1} output count rate, 1% dead time, 400 s live time, and a 45° x-ray takeoff angle. The original spectrum was corrected for energy nonlinearity. The electron beam diameter was larger than the particle diameter.

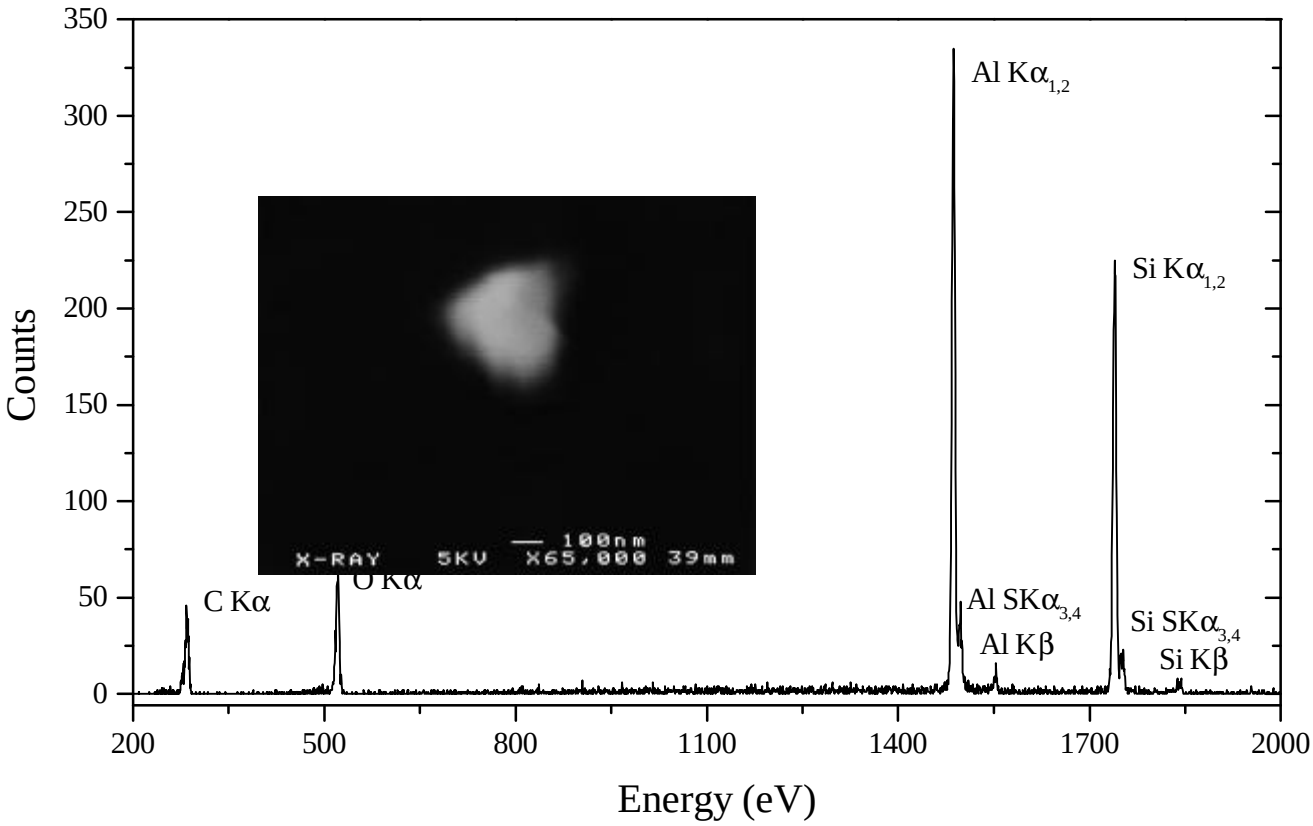

FIGURE 4. Microcalorimeter EDS x-ray spectrum of a 0.3 μm diameter Al_2O_3 particle on a Si substrate, acquired under the following conditions: LaB_6 filament, 5 keV beam energy, 40 pA beam current, spot mode, 200 s live time, 57 s^{-1} input count rate, 54 s^{-1} output count rate, 5% dead time, and a 45° x-ray takeoff angle. The spectrum was corrected for energy nonlinearity, resulting in a nonuniform energy binwidth per channel increasing from 0.4 eV to 0.9 eV over the energy range presented. Note the ability of the microcalorimeter EDS to resolve the Kα and satellite peaks of Al and Si. The electron beam diameter was estimated to be less than the particle diameter. A SEM micrograph of this particle obtained directly before analysis under the same SEM operating conditions is shown in the inset.

at low beam energies (less than ~3 keV) using our LaB_6-filament SEM operating at a working distance of 39 mm. As a result, analyses of 0.3 μm diameter Al_2O_3 particles were performed only at beam energies of 3 keV and higher.

In Fig. 5 we present background-subtracted Al-Kα/Si-Kα x-ray peak intensity ratios obtained from SEM/microcalorimeter EDS analyses of 0.3 μm diameter Al_2O_3 particles on Si. The Al/Si ratios from individual particle analyses at the selected electron beam energies were then averaged and are plotted on a logarithmic scale in Fig. 6.

Using the Al/Si ratio as a figure of merit (as suggested in (5, 6)), SEM/microcalorimeter EDS compares favorably with FE-SEM/EDS and FE-Auger for particle analysis in this analytical situation. For both SEM/microcalorimeter EDS and FE-SEM/EDS, the use of lower electron beam energies resulted in smaller x-ray generation volumes that were better matched to particle volumes, thus producing

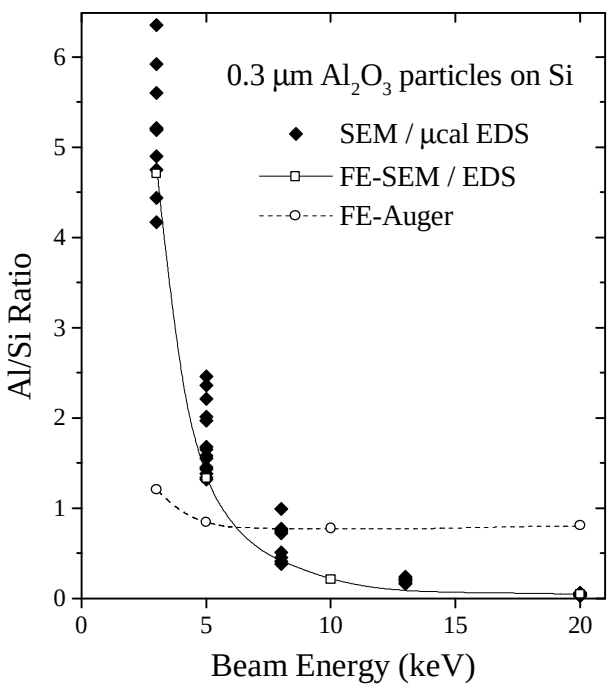

FIGURE 5. Comparison of SEM/microcalorimeter EDS (SEM/μcal EDS), FE-SEM/semiconductor EDS (FE-SEM/EDS), and FE-Auger analyses of 0.3 μm diameter Al_2O_3 particles on Si wafers. The SEM/microcalorimeter EDS data consist of background-subtracted Al-Kα/Si-Kα integrated peak intensity ratios from individual particle analyses, while the FE-SEM/EDS and FE-Auger data are averages over several particles (5, 6). The FE-Auger data were obtained using a whole-wafer field-emission scanning Auger system. The solid and dashed lines connecting the FE-SEM/EDS and FE-Auger data are provided as guides to the eye. The spread in the SEM/microcalorimeter EDS data is greater than that expected from counting statistics and is likely caused by differences in particle shape and electron beam position during analysis.

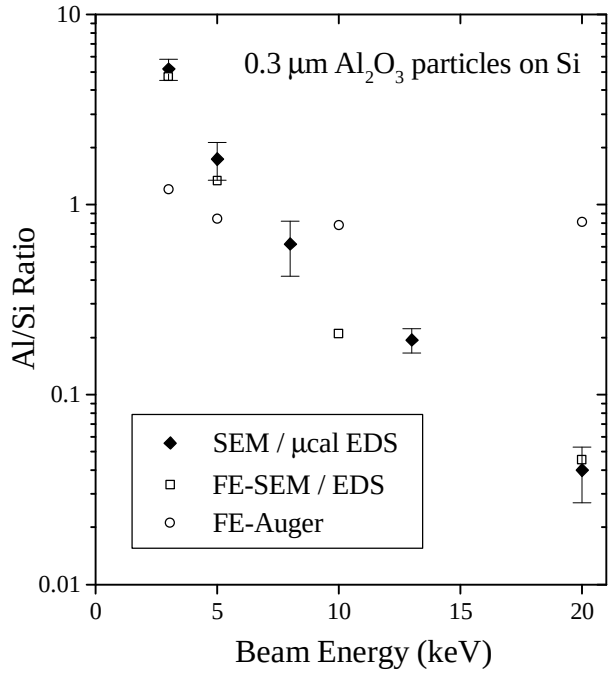

FIGURE 6. Comparison of average Al/Si ratios for SEM/microcalorimeter EDS (SEM/μcal EDS), FE-SEM/EDS, and FE-Auger analyses of 0.3 μm diameter Al_2O_3 particles on Si wafers. The SEM/microcalorimeter EDS data are averages of individual particle data presented in Fig. 5, with error bars equal to corresponding standard deviations. The average Al/Si ratio for SEM/microcalorimeter EDS is greater than that for FE-SEM/EDS by a factor of approximately 1.3. This factor is consistent with the difference in overall spectrometer efficiency (between microcalorimeter EDS and semiconductor EDS) caused by the presence of additional Al infrared-blocking x-ray windows in the microcalorimeter EDS.

high particle-to-substrate ratios. In comparison, the Al/Si ratio for FE-Auger does not have such a strong dependence on beam energy. Unlike x-rays, Auger electrons have very limited range (on the order of a few nanometers) and are collected only from the surface layer of the particle and substrate. The resulting particle-to-substrate ratio for FE-Auger is less dependent on the electron interaction volume (and thus beam energy) and can be greater than that of FE-SEM/EDS for smaller particles (5). A more complete understanding of the measured Al/Si ratios for x-ray and Auger particle analysis as a function of beam energy requires extensive modeling of the electron-beam/particle-substrate interaction (5) and is beyond the scope of this paper.

The ability of SEM/microcalorimeter EDS to analyze smaller Al_2O_3 particles was also investigated. In Fig. 7 we show microcalorimeter EDS spectra of Al_2O_3 particles as small as 0.1 μm in diameter. SEM/microcalorimeter EDS analysis of the 0.1 and 0.14 μm diameter Al_2O_3 particles was limited by the nonoptimal SEM performance at low beam energies, in which the diameter of the electron beam was larger than that of the particles. This limitation can be

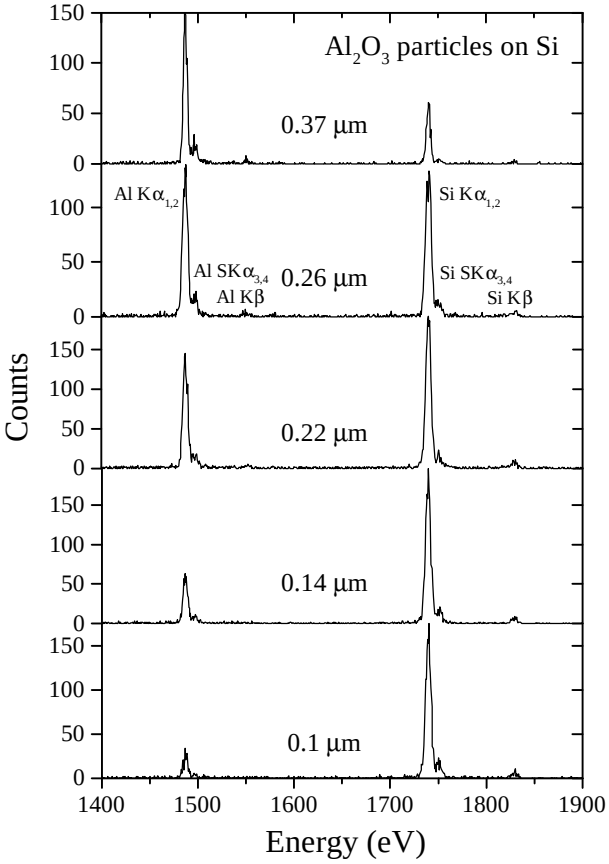

FIGURE 7. Microcalorimeter EDS x-ray spectra of several sized Al_2O_3 particles on a Si substrate, acquired under the following conditions: LaB_6 filament, 5 keV beam energy, 40 pA beam current, ~40 s^{-1} input count rate, ~40 s^{-1} output count rate, ~1% dead time, 150 s live time, and a 45° x-ray takeoff angle. The average diameter of each particle is displayed directly above its spectra. The original spectra were corrected for energy nonlinearity. The electron beam diameter was estimated to be larger than the diameters of the two smallest particles.

avoided in the future with the use of FE-SEM/micro-calorimeter EDS.

By examining the role of x-ray and Auger particle analysis tools in microfabrication facilities, we may be able to project the future use of microcalorimeter EDS in the semiconductor industry. At present, after initial identification and mapping by light scattering, contaminant particles and defects are typically imaged and analyzed using whole-wafer FE-SEM/EDS defect review tools to characterize particle size, location, morphology, and composition (if possible, depending on particle size). Significant statistical information is gathered to characterize large numbers of contaminant particles, of which a representative subset is selected for exhaustive analysis by FE-SEM/EDS, FE-Auger (including depth profiling of particle composition in conjunction with ion sputtering), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and other techniques. Often, particles/defects are observed at several process steps, and thus buried under the subsequent process layers, before a wafer is sent for detailed analysis. These samples are sent to whole-wafer focused ion beam (FIB) tools that prepare cross sections of particles for subsequent characterization by *in situ* SEM/EDS and *ex situ* TEM/EDS.

In the future, microcalorimeter EDS will provide significant benefits for all of the instruments described above (and others) that currently use semiconductor EDS. For example, commercialization of microcalorimeter EDS will allow the direct replacement of semiconductor EDS in existing defect review tools. At this initial stage of particle analysis, automation of analysis is critical to obtain as much statistical information as possible to characterize the contaminant particles and defects. The higher energy resolution of microcalorimeter EDS will provide easier qualitative identification of particle constituents, which in turn should allow improved autoclassification of particle x-ray spectra. In addition, the use of FE-SEM/micro-calorimeter EDS during later stages of particle analysis will benefit from the new capability of microcalorimeter EDS to measure chemical shifts in x-ray spectra, as will be described in the following section.

CHEMICAL SHIFT MEASUREMENTS

Chemical shifts result from changes in electron binding

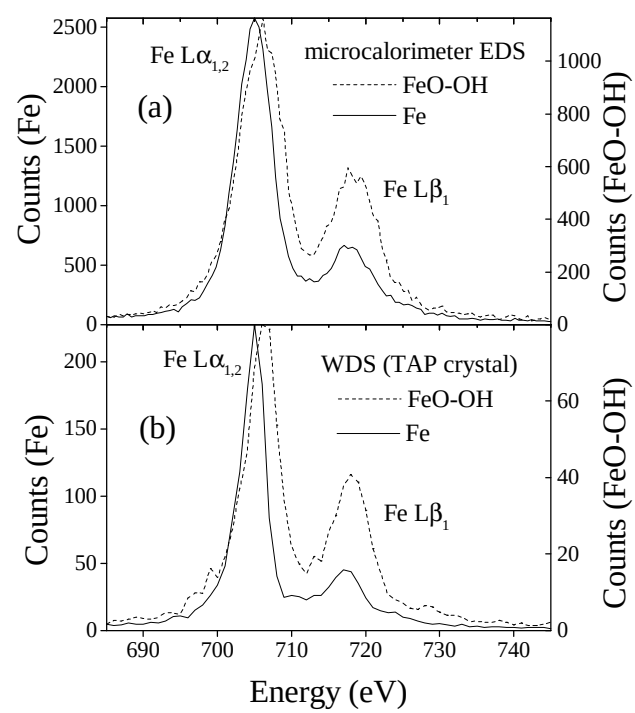

FIGURE 8. (a) Microcalorimeter EDS spectra and (b) WDS spectra of Fe (solid line) and FeO-OH (dashed line), from (7). The observed changes in the Fe-L peak positions and intensities result from chemical bonding effects. Good agreement is observed between the microcalorimeter EDS and WDS spectra.

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 (7). For example, the ability to identify particle composition by distinguishing different oxidation states (for example, Al and Al_2O_3) using AES has been demonstrated to be useful in determining sources of contamination in semiconductor processing tools (8).

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 (9). 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 elements such as C (10). 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 TES microcalorimeter (4) now allows microcalorimeter EDS measurements of chemical shifts in x-ray spectra, as shown in Fig. 8 for Fe and FeO-OH (11) and in Ref. (4) for Al and Al_2O_3. 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 microcalorimeter EDS, analysis using x-ray peak shapes and positions to provide may become practical and provide valuable chemical bonding state information for particle analysis.

CONCLUSION

The excellent energy resolution of microcalorimeter EDS provides improved capability for x-ray microanalysis of contaminant particles and defects, including the potential to provide valuable chemical bonding state information. With commercialization and further development, micro-calorimeter EDS will extend the capabilities of SEM-based x-ray microanalysis instruments to help meet the analytical requirements for future technology generations.

ACKNOWLEDGMENTS

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REFERENCES

1. The National Technology Roadmap for Semiconductors (1997), The Semiconductor Industry Association, 4300 Stevens Creek Boulevard, Suite 271, San Jose, CA 95129.
2. Wollman, D. A., Irwin, K. D., Hilton, G. C., Dulcie, L. L., Newbury, D. E., and Martinis, J. M., *J. Microscopy* **188**, 196-223 (1997).
3. Wollman, D. A., Jezewski, C., Hilton, G. C., Xiao, Q.-F., Dulcie, L. L., and Martinis, J. M., *Microscopy and Microanalysis* **3** (Supplement 2), 1075-1076 (1997).
4. Irwin, K. D., Wollman, D. A., Hilton, G. C., Dulcie, L. L., Bergren, N. F., Martinis, J. M., and Huber, M. E., in preparation.
5. Childs, K. D., Narum, D., LaVanier, L. A., Lindley, P. M., Schueler, B. W., Mulholland, G., Diebold, and A. C., *J. Vac. Sci. Technol. A* **14**, 2392-2404 (1996).
6. Diebold, A. C., Childs, K., Lindley, P. M., Viteralli, J., Kingsley, J., Liu, B. Y. H., and Woo, K.-S., *J. Vac. Sci. Technol. A*, in press.
7. Briggs, D. and Riviere, J. C., *Practical Surface Analysis, Vol.1: Auger and X-ray Photoelectron Spectroscopy*, New York: John Wiley and Sons, 1990, pp. 85-141; Waddington, S. D., *ibid*., pp. 587-594.
8. Brundle, D., Uritsky, Y., and Pan, J. T. *Micro* **13**, 43-56 (1995).
9. Fabian, D. F., Watson, L. M., and Marshall, C. A. W., *Rep. Prog. Phys*. **34**, 601-696 (1971).
10. Holliday, J. E., *J. Appl. Phys*. **38**, 4720-4730 (1967).
11. Wollman, D. A., Newbury, D. E., Hilton, G. C., Irwin, K. D., Dulcie, L. L., Bergren, N. F., and Martinis, J. M., *Proceedings of Microscopy and Microanalysis '98*, Altanta, GA (1998), in press.