

BOOK OF TUTORIALS AND ABSTRACTS



European Microbeam Analysis Society

EMAS 2009

11th

EUROPEAN WORKSHOP

on

MODERN DEVELOPMENTS

AND

APPLICATIONS

IN

MICROBEAM ANALYSIS

10 to 14 May 2009

at the

Hotel Spa Faltom

Gdynia/Rumia, Gdansk, Poland

Organized in collaboration with
Silesian University of Technology
Polish Society for Microscopy (PTMi)
Polish Academy of Sciences:
Committee of Materials Science, Institute of Physics,
Institute of Materials Science and Metallurgy



APPLICATIONS OF FAST HIGH RESOLUTION AND HIGH SENSITIVITY EDS ANALYSIS

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Professor Edward D Boyes has appointments in the Departments of Physics and Electronics, and is Co-Director of the York Jeol Nanocentre, at the University of York (UK). Before this, for nearly 20 years he was a Senior Research Fellow in the Central Research and Development Department of the DuPont Company in Wilmington, DE, as a corporate leader in the materials and analytical sciences, and in the development of management policies. He has been a long standing member of the Technical Advisory Group (TAG) for the (US) President's Council of Advisors for Science and Technology (PCAST) reviews of the National Nanotechnology Initiative (NNI) and as a reviewer for DOE, EPA, CDC and NSF. Ed's Ph.D. is in Materials Science from Cambridge University, leading to a faculty position in the Oxford Materials Department and a Fellowship at Wolfson College in the 1980's. He has been an invited speaker at scientific meetings in 17 countries, with over 100 technical publications. His research interests are focused on novel instrumentation for new application driven nanoanalytical methods using FIM, TEM, STEM, ETEM, SEM, ESEM and related chemical and crystallographic analyses; most recently for the development of low voltage SEM for the highest levels of ultrahigh resolution imaging and chemical analysis of 'bulk' sample surfaces, with ~ 1 nm resolution, and in-situ methods. The new purpose built York Nanocentre is focused on aberration corrected electron microscopy for both TEM and STEM to greatly increase information in dynamic in-situ experiments and other applications at and below 1 Å spatial resolution, as outlined in the Materials Research Soc. Bulletin review article in Dec. 2007 (Vol. 32, p. 1044-1050).

1. ABSTRACT

The development of high resolution low voltage (towards 1 nm at 1 kV) SEM systems and much higher (> 15 x) sensitivity medium to low voltage (~ 5 kV) SEM-EDS [1, 2] has demonstrated new capabilities of SEM-based methods in defect review tools and for surface analysis requiring minimum detectable mass and high lateral spatial resolution of nanometre scale features.

The improved methods appear to be particularly important in the analysis of crystallographically specific or other patch field coatings on sub-micron substrate particles, including nanoparticles, with complex three dimensional geometries. These are considered to be not well matched to wider area surface analyses or scanning probe approaches, especially where re-entrant or otherwise steep surfaces are involved, and TEM analyses have their limitations. But these features may have great practical importance in promoting desirable surface properties, both protective and active, and their practical effectiveness can only be evaluated, and as it turns out improved, with the improved characterisation.

The data have been calibrated with wide area thin films on planar substrates with thicknesses monitored by accepted methods such as quartz crystal thickness monitors. The classical crystallographic symmetry of some substrate particles has provided an elegant cross-check with related and chemically deposited (and therefore we expect not deposition direction dependent) surface patches accessible in both plan view and profile with gratifying consistency in results.

It is necessary to have high sensitivity of analysis under minimally invasive conditions with respect to a clean dry high vacuum system and low beam currents. The proof-of-principle system [1, 2] combines superior imaging capabilities at low beam energies with greatly improved access for a custom EDS detector to provide both imaging (to < 0.4 nm and more importantly close to 1 nm at 1 kV) and chemical analysis sensitivity (0.3 sr) at the highest levels so far attained in an SEM accepting a bulk sample, defined in this context as a piece of unthinned Si wafer, and up to 7.5 mm wide. The EDS detection geometry is at least 15x more effective than in regular SEM geometries and some are much worse than that (> 50x).

The high detection efficiency (50 kcps per nA for Al at 5 kV with a 2 nm imaging probe and more typically deployed as 10 kcps from 0.2 nA [2]) can be exploited, as here, for high sensitivity analysis (~ 1 nm) of small area thin films of C or Al₂O₃, or for very high speed analysis (especially for spectral imaging maps), or for low intensity and minimally invasive data collection from delicate samples; or some suitable application specific compromise between these various attributes. One way in which the new capabilities can be focused is for the detection and analysis of small particles on bulk sample surfaces; both as intentional nanoparticles and as inadvertent or incidental ones, such as those which are defect review tool

targets. The demonstrated successful detection and analysis of 28 nm SiO₂ particles on an Al substrate by the Si K-line fingerprint translates into a sensitivity for < 20 nm particles for the single element variety and meeting with an extension of SEM-EDS the current published ITRS Roadmap [3] requirements for next generation semiconductor process defect review tools (Fig. 1). Taking the measured sensitivity of the existing data and processing for both a minimised P/B set at 1.0 and allowing that less than half the mass of the SiO₂ particles analysed is made of Si (residual O), leads to the conclusion the threshold sensitivity of the current method will be about 15 nm for particles of Si on a Al or equivalent base. The projection is this result will be similar, or indeed slightly better, for the more interesting practical application with the cations reversed, i.e., with Al in the particle as alumina and Si as the wafer substrate. And doing it in a minimally invasive way which could be engineered to extend to full wafer analyses; although then, as so often, target discovery and acquisition would inevitably be an issue. The test targets used here in the proof of principle analyses are much simpler to analyse in this regard.

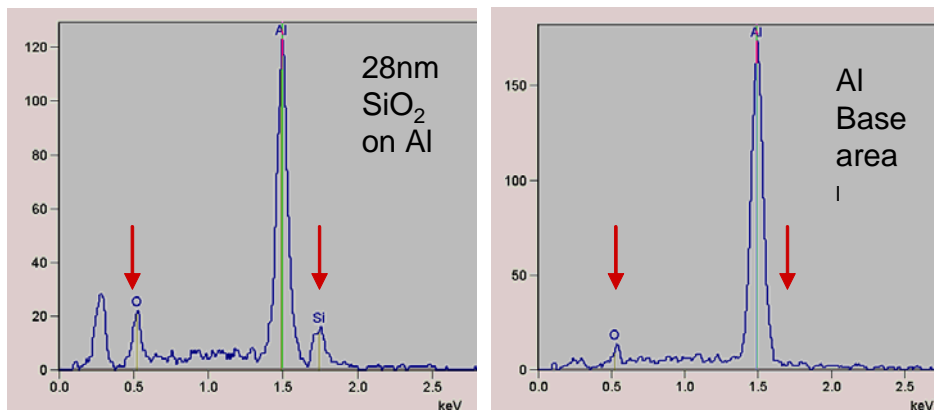


Figure 1. EDS spectra (a) acquired from an identified silica particle 28 ± 1 nm in diameter using 3 kV beam energy at 100000x and the comparable data (b) from the related Al base area showing sensitivity for nanoparticle analysis to ITRS next generation defect review tool specification with demonstrated Si elemental analysis sensitivity equivalent to < 20 nm single element particle detection, as required for the ITRSI Roadmap for future technology; achieved using incremental improvements of current technologies in custom form [5]. Acquisition times used were 5 seconds per spectrum using the normal high resolution imaging probe of < 1 nm at 3 kV beam energy in a custom instrument designed for purpose.

Further improvements in analytical sensitivity, of at least 2x in linear dimensions, to $\ll 10$ nm, or 8x in minimum detectable mass (MDM) analytical sensitivity can be predicted by using X-ray detectors with higher P/B, e.g., conventional wavelength dispersive spectrometers, parallel beam devices or microcalorimeters [4]; although none of these devices would be easy to integrate efficiently into a high spatial resolution instrument and the methods might then prove slower and more invasive. It seems the immediate goals, with identification of incidental

particles down to < 20 nm in size (with some adjustments for different and more complex types of X-ray lines such as W(M), can be achieved with imaginative incremental improvements (I³) to established SEM-EDS methods and that target discovery and acquisition is likely to be the more substantial problem than basic detection efficiency for small particle analyses.

However, the data here were obtained with a novel instrument designed for purpose to improve substantially the detection efficiency and analytical sensitivity and speed of analysis compared to conventional instruments. This system is indeed limited by the conventional EDS detectors fitted to it and would (and hopefully will) benefit from being outfit with new technology detectors for both (if not together) much higher data rates and also higher energy resolution analysis. The ports for these are already prepared. The inescapable conclusion is that the real success lies in optimising the integration of the analysis with high performance imaging and similar rethinking will be necessary more widely if we are to benefit fully from the new detector and processing opportunities now before us. Analytical aspects of instrument design need to be put front and centre – much as they were for the microprobe – if we are to see the benefits of recent developments in detector technology. It should be possible to adapt the design used here for other purposes; for example to analyse full wafers with similar high spatial resolution and analytical sensitivity. It is ‘just’ an engineering problem. The old approach of using a fat probe with masses of current to achieve high count rates is generally unacceptable in that it is incompatible with the image resolution needed for target acquisition and tracking, and the idea of simply beating hell out of samples to get high count rates is impractical, especially where light elements are involved. It is well documented there is too much damage and contamination in many examples, but in other more favourable cases, examples of which will be presented, it is now possible to produce X-ray spectral imaging maps with a depth of information which is convincing as an ‘image’, as distinct from the previous spotty ‘maps’. In addition, spectral imaging is transformed by being able to accumulate much larger data sets than hitherto as the basis for the application of statistical data analysis and extraction procedures, and thereby to mine data further down in the PCA chain to more minor components. With high data rates, X-ray imaging/mapping also moves much closer to real time display; or at least to useful evaluative data within seconds and results in minutes which would previously have taken hours to acquire. The prospects with optimised new technology integrated systems, which we don’t really have yet, are tantalising in the impactful contribution to science which is in prospect.

In summary much higher sensitivity analysis can be deployed for:

- Analysis of smaller incidental particles well down into the nanoparticle range
- Faster analysis in general for better statistics, wider area surveys etc, to the extent of being transformational in application prospects
- Greater information in individual spectra
- As input to spectral imaging and statistical analysis to ‘find’ minority features and phases
- Minimal exposure analyses for speed (faster and more responsive)

- Minimum exposure and therefore minimally invasive (gentler) analyses
- A custom combination of the new analytical attributes configured application specifically for different purposes

A number of incidental attributes of the system used here are also considered important; especially the clean dry vacuum system, scan controls to minimise any residual contamination and target tracking or drift correction software. Protected transfer or in-line applications are also being considered. Comparisons with STEM analyses will be shown; both in terms of the data obtained and in ensuring it is related to the technological context through complementary analyses.

2. REFERENCES

- [1] Boyes E D (2001) *Inst. of Physics (UK) Conference Series* **186**: 115.
- [2] Boyes E D (2002) *Mikrochimica Acta* **138**: 225.
- [3] International Technology Roadmap for Semiconductors (2007) <http://www.itrs.net/>.
- [4] Newbury D, Wollman D, Irwin K, Hilton G and Martinis J (1999) *Ultramicroscopy* **78**: 73
- [5] Hitachi S5000SPX FESEM with Thermo Noran 30 mm² ATW EDS detector at 0.3 sr.

