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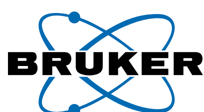
Nanoscience in SEM and TEM

Energy Dispersive X-ray Analysis with High Spatial Resolution



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Nanoscience in SEM and TEM

Energy Dispersive X-ray Analysis with High Spatial Resolution

The development of modern technology affects the science of small objects in two ways. On one hand better means for handling, imaging and analysis of miniature objects are provided, which means we can try and understand our world on a much smaller scale. On the other hand further miniaturization in manufacturing necessitates the control of technological processes at a minimum of one order of magnitude below the aspired device size. The need for rapid and efficient nanoanalysis is growing very quickly. The next generation 22 nm node in microelectronics architecture is approaching. New solutions for electronic interconnects, capacitors, denser data storage and solar cells are currently under development. This requires atomic scale analysis of a wide range of materials such as functionalized carbon nanotubes (CNTs), various perovskites and three-dimensional nanostructures. Another important field of miniaturization is modern medicine. It strives to identify toxic nanoparticles and transfer medication and operation tools precisely to the place where they are needed in the body. For all of this nanoanalysis is irreplaceable. To understand and control the function of miniature sized natural and artificial objects we need to know their element distribution.

The task for scientists and manufacturers is to find the most efficient way to characterize small objects with high quality data at high spatial resolution. One of many steps in this direction in analytical electron microscopy (AEM) is aberration correction. Instead of turning to higher and higher accelerating voltages in larger and larger microscopes the correction of the spherical and chromatic aberration has become reality now and atomic resolution below 80 keV is possible. This is necessary for the investigation of radiation sensitive materials like CNTs. AEM employs different types of spectroscopy. Energy dispersive X-ray analysis (EDS) is used to distinguish between different elements in the sample utilizing the generated X-rays. In both scanning and transmission electron microscopy (SEM/TEM) the aim is to acquire EDS spectra with high signal to background ratio in a short time from small sample areas. This article discusses an efficient way to meet these requirements.

Challenge

For EDS with high spatial resolution, the excited sample volume generating the radiation needs to be small. Unfortunately, the smaller the excited volume the smaller the total EDS signal is, providing the electron dose stays the same. This is the case in SEM, where lower accelerating voltages are used to decrease the excited sample volume and to an even larger extent in TEM, where only the neck of the tear drop shaped scattering volume is available for X-ray generation in the electron transparent sample slices (fig. 1). Among the obvious solutions are higher current density in the probe – which is limited by the beam sensitivity of the samples –, longer measurement times – which are limited by the stability of the microscope and detector system as well as the beam sensitivity – or a larger solid angle for X-ray collection. A comprehensive overview about how the detection limit is influenced by these factors is provided by M. Watanabe and D.B. Williams [1]. O. Krivanek et al. explain how aberration correction contributes to the improvement of the peak to background ratio, which is so important for advancing the detection limits [2].

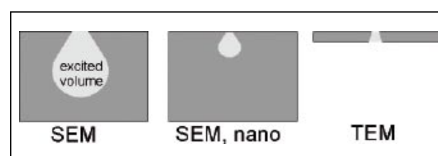


Fig. 1: Excitation volume that contributes to initial X-ray generation.

Solutions

Conventionally, lithium drifted liquid nitrogen cooled silicon devices (Si(Li)) were used to convert X-ray quanta into electric charge. Recently Peltier cooled silicon drift detectors (SDD) were developed and Bruker Nano (formerly RÖNTEC) was the first to use and optimize this new liquid nitrogen free technology for commercial EDS analysis in SEM [3]. This has several advantages compared to conventional Si(Li) technology, particularly for nanoanalysis. SDDs provide a drift field, generated by drift rings on the back side of the active crystal, to guide and collect the charge cloud generated by each photon (fig. 2).

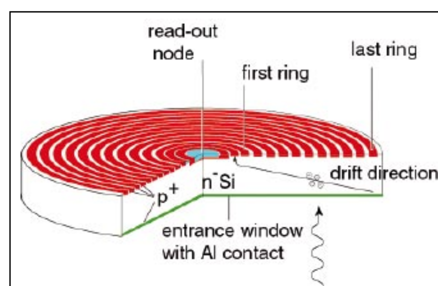


Fig. 2: 30 mm² chip used in TEM-detectors.

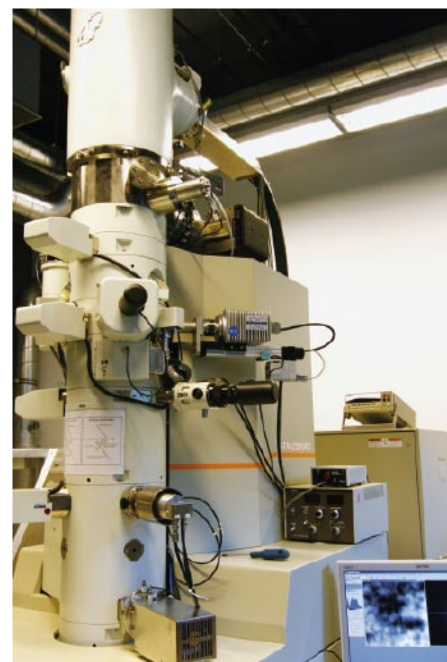


Fig. 3: SDD technology in TEM: Bruker XFlash 5030 installed on a Jeol2200 FS, Humboldt University, Berlin.

Data can be collected much faster and much more efficiently than with conventional Si(Li) detectors. Bruker's hybrid signal processing unit developed especially for SDD readout makes sure the superb collection capabilities of the detectors are properly exploited. XFlash Silicon Drift Detectors show very little dead time, extreme count rate capabilities, and are – unlike most Si(Li) – immune to overload conditions. Furthermore they don't require liquid nitrogen for cooling, making vibrations associated with heavy dewars on the microscope column, microphony and icing problems obsolete. Additionally, the smaller temperature gradient between the ambient

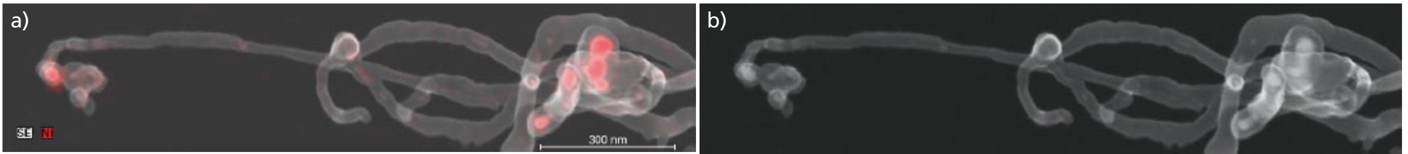
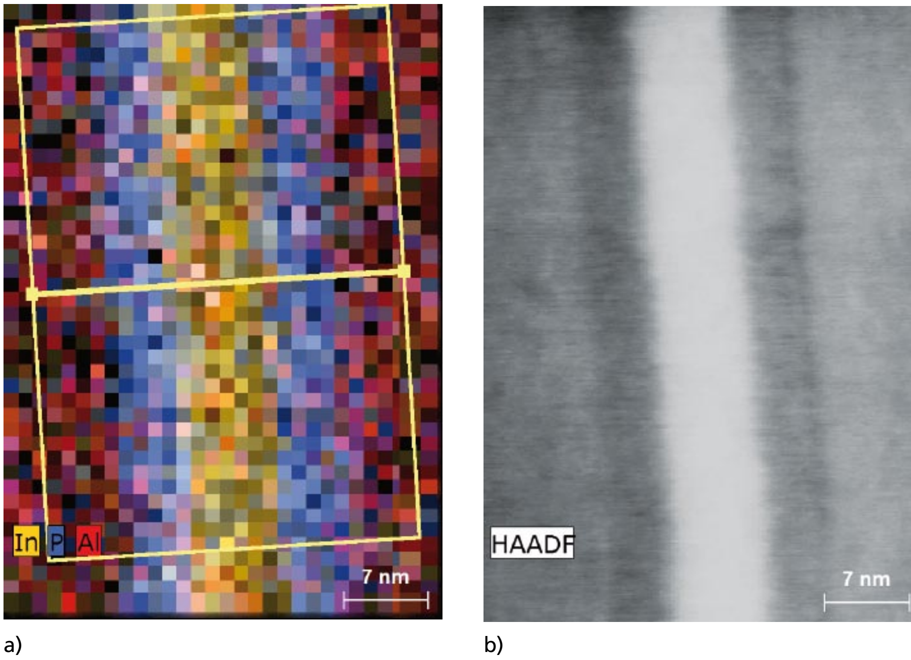


Fig. 4: Ni catalyst particles in carbon nanotubes. Ni-Kα lines were used for identification in the HyperMap (4a). 4b shows a secondary electron image. Sample courtesy of: S. Hermann, T. Geßner, Center for Microtechnologies at the Chemnitz University of Technology.



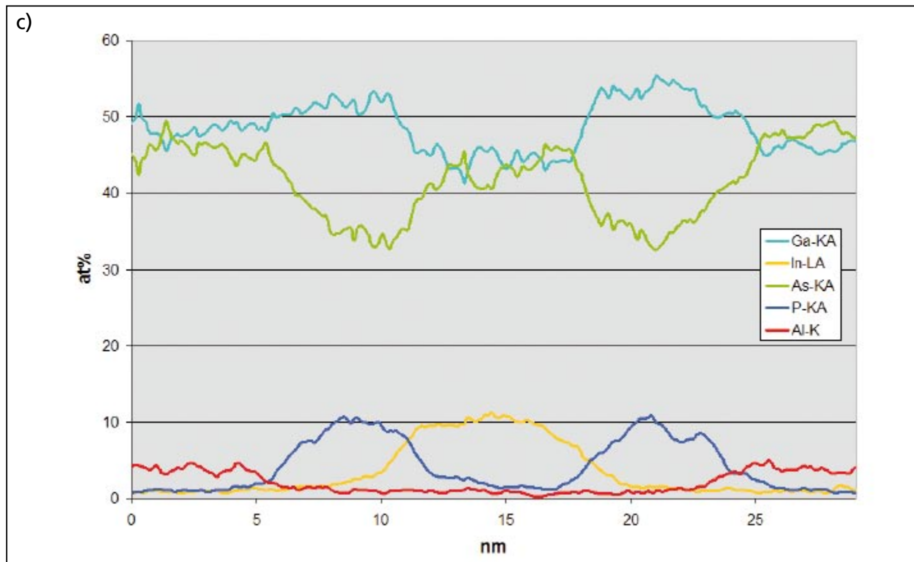


Fig. 5: Quantum well research sample. AlGaAs (P, In) as deposited: AlGaAs, 5 nm GaAsP, 7 nm InGaAs, 5 nm GaAsP, AlGaAs. 5a: Elemental distribution of In, P and Al. 5b: The corresponding HAADF image. 5c: Elemental profile. Sample courtesy of: G. Tränkle, Ferdinand Braun Institute, Berlin and A. Mogilatenko, W. Neumann, Humboldt University, Berlin.

area and the detector chip, which only needs to be cooled down to –25 to –30 °C for 30 mm² XFlash SDDs, ensures high stability and very little drift. These are the reasons why Bruker decided to adapt its XFlash Detectors for TEM as well (fig. 3).

Today, the challenge in EDS is to maximize the solid angle for radiation detection in such a way that fast and complete charge collection as well as energy resolution don't suffer. The solid angle (Ω) can be described as $\Omega = A (\cos \delta)/d^2$. *A* is the active detector area, *d* its distance to the sample and δ is the angle between the normal of the detector surface and the line of shortest distance between sample surface and detector centre. If the detector is tilted towards the sample so that $\delta = 0$, the solid angle equals A/d^2. One approach for improving the solid angle for radiation collection is to increase the active detector area. Since larger chip areas are difficult to readout, this has shortcomings like pile up, incomplete charge collection, the necessity of stronger cooling, worse energy resolution and geometric constraints. Hence Bruker favors employing smaller detector areas closer to the sample or several small detectors at once, as both are much more efficient.

In this way a high count rate efficiency with almost no pile up, low dead time and no peak broadening is achieved, resulting in a clean high throughput and a count rate capability of up to several million counts per second (cps). This makes the approach ideal for high brightness electron sources, radiation sensitive samples and in-situ analysis. Excellent elemental mapping for all count rates and therefore all magnifications is also guaranteed. Superior energy resolution supports the analysis of light elements. Heavy elements with N-lines in the same low energy range can be identified using the company's comprehensive atomic data library. Furthermore the low temperature gradient between the environment and a small chip area provides stable experimental conditions.

Examples

The first example shows nickel catalyst particles (with a diameter of 20 nm) in carbon nanotubes. The sample was analyzed in a Zeiss Supra55 SEM at 20 keV in transmission using a 10 mm² XFlash SDD at a solid angle of 0,01 sr and a beam current of 500 pA. The 1024 x 220 pixel HyperMap [4] was acquired in 15 minutes using a pixel dwell time of 4096 µs. Mirroring the well resolved EDS HyperMap the nickel particles are evident as strong emitters in the secondary electron image (fig. 4).

An experimental result of an AlGaAs (P, In) quantum well research project is shown in figure 5. The data was acquired using a 30 mm² XFlash 5030 SDD for TEM with a 0.12 sr solid angle in a Jeol2200FS TEM. A 210 pA probe current in a 0.7 nm spot was used. The 244 by

342 pixel map was acquired in 6 minutes using 4096 µs dwell time per pixel. The distribution of the heavy element indium (shown in yellow) correlates well with the high angle annular dark field (HAADF) signal. The latter increases with the atomic number of the scattering elements, provided the whole mapped area is equally thick. The quantification of the element map was performed using 8 by 8 pixel binning and theoretical Cliff-Lorimer factors. The elemental profile was generated by adding up all the 8 by 8 pixel data perpendicularly to the layers in the marked region. Just like the acquired raw data the profile provides nm resolution. In order to deliver even more precise data Bruker also offers drift correction options for longer acquisition times and AutoPhase (its principle component analysis solution).

Conclusions

High spatial resolution EDS results using SDD technology in electron microscopy were described above. It is evident that a combination of electron dose and detection efficiency influences the data quality. A large solid angle using small active detector areas guarantees good detector performance, which includes fast readout, low dead time, no pile up, high energy resolution, a stable instrumental environment and excellent performance at high and low count rates. A good detector performance at high count rates is very useful for elemental imaging and for finding the right sample area in low magnification mode. It is also ideal for employing high brightness electron sources and for elemental mapping in in-situ experiments. In addition fast high quality readout is important when low electron doses have to be used for beam sensitive samples and when large data sets for 3-D-characterization need to be acquired. On the nano-scale in high magnification mode, where the number of generated X-rays drops dramatically, such detectors deliver excellent results as well.

References

[1] M. Watanabe, D.B. Williams, *Ultramicroscopy* 78, 89–101 (1999)

[2] For details in analogy to EELS detection limits see: Advances in Imaging and Electron Physics, Volume 153, ISSN 1076–5670, Elsevier, Chapter 3 by O. Krivanek (2008)

[3] Strüder, L., et al., *Microsc Microanal* 4, 622–631 (1999)

[4] HyperMap is Bruker's version of position-tagged spectrometry, where a complete spectrum is acquired and stored for each pixel of the mapping, allowing offline analysis from the database even after the specimen has been archived.

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