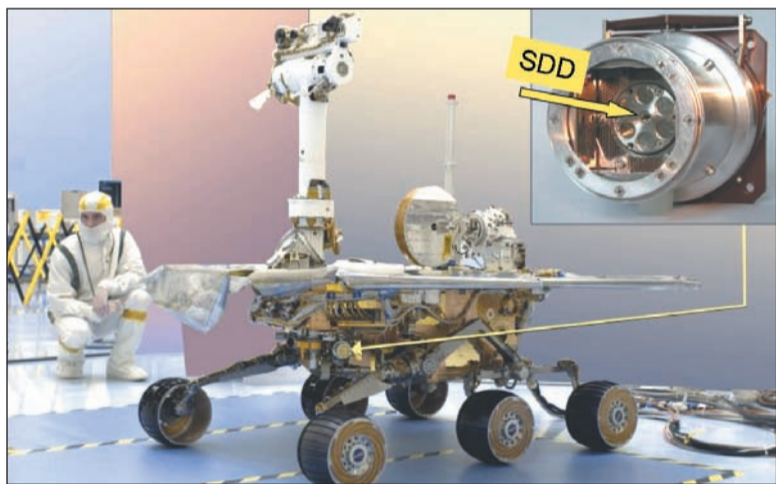


# focus on Microscopy & Microtechniques

## Nanoscience using silicon drift detectors for chemical analysis

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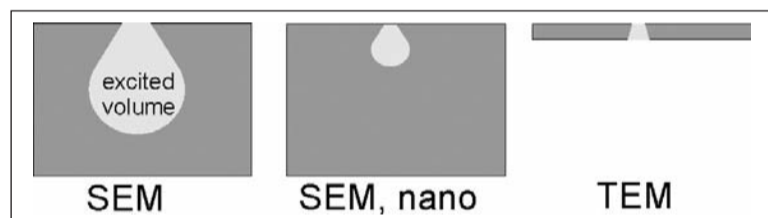
Peltier cooled silicon drift detectors (SDD) were originally developed for space research to avoid the need of liquid nitrogen for cooling X-ray detectors. *Figure 1* shows one of the first SDDs on Mars rover Spirit. Energetic alpha particles and X-rays from a curium-244 source are used here to illuminate Martian material. The SDD placed in the middle of the spectrometer in the inset on the upper right detects the resulting fluorescence. Compared to the simple diode design the SDD-signal readout is based on sideward depletion [1] assisted by a so-called drift field which guides the charge generated in the Si-device by the incoming X-rays towards a small readout node [2]. The reduced size of the readout area is the main reason for cooling by Peltier elements being sufficient in these devices. SDD technology allows much faster and more efficient data collection compared to the diodes cooled by liquid nitrogen. It was introduced for energy dispersive X-ray analysis (EDS) in scanning electron microscopy (SEM) more than a decade ago. In SEM the material of interest is exposed to an electron beam, which causes several types of interaction signals. Backscattered and secondary electrons are used to generate images of the sample. X-rays characteristic for excitations of particular states of the elements present in the sample are used for chemical analysis in EDS. Much effort has been invested into the optimisation of SDD-technology for a high quality element analysis. This includes the improvement of energy resolution, further noise reduction and speed of acquisition. After great success in SEM SDDs are now about to revolutionise EDS in transmission electron microscopy (TEM), which can deliver higher spatial resolution compared to SEM. Main aspects of SDD-EDS analysis in nanoscience are the topic of this contribution.



*Figure 1. Mars rover Spirit with SDD-technology, enlarged inset on the upper right: The Alpha-particle X-ray Spectrometer (APXS). It works by exposing Martian material to energetic alpha particles and X-rays from a curium-244 source and measuring the energy spectra of backscattered alpha- and X-radiation. Image © MPI HLL, Garching, Germany.*

### SDD technology for EDS

To facilitate any application in nm-size and below, whether molecular cages for drug delivery in the human body or a nanostructure for semiconductor industry, it is necessary to have means for nanoanalysis. To successfully realise nm-structures it is vital to be able to control the location of each element on nm and even atomic scale. EDS in combination with electron microscopy is a straightforward method to deliver this. Spatial resolution in SEM is improved by reducing the accelerating voltage of the electron beam to generate a smaller excitation volume. In TEM electron transparent samples are prepared so that the excitation volume is even smaller (*Figure 2*). The problem is though that in this case often the available beam current is smaller and due to this and the reduced excitation volume the generated X-ray signal decreases. Therefore it is crucial to collect X-rays efficiently by covering a large solid angle around the sample. A good estimate for the solid angle  $\Omega$  out of which data can be collected, measured in steradian [sr], is given by  $\Omega [\text{sr}] = A (\cos \delta) / d^2 [\text{sr}]$ .  $A$  is the detector area,  $d$  its distance to the sample and  $\cos \delta$  creates the projection of the detector area onto a part of the sphere around the sample. Therefore,  $\delta$  is the angle between the detector surface normal and the line for the shortest distance between the detector centre and the sample surface. Geometric constraints in the microscope pole piece and ports often complicate the design of large solid angle detectors. At present the manufacturers are exploring various different designs. Side-entry detectors in SEM are mostly inserted at a suitable take-off angle between 30° and 45°. In TEM side-entry detectors are mostly inserted using the horizontal ports, which are generally the only ones available. In that case a particular effort is needed to realise a good take off angle for a good peak to background ratio in the spectra. The TEM side-entry detector has to be placed as high as possible above the sample without sacrificing solid angle. Multi-detector systems can offer much higher solid angles and better take-off angles than single side entry detectors [3]. Additionally they are combining this advantage with using small chip sizes, which compared to large area detector chips, need less cooling to attain good energy resolution, show less pile up and can be read out faster. *Figure 3* shows an annular multiple chip detector, which reaches a solid angle of 1.4sr in SEM. For scanning TEM (STEM) integrated multi-detector systems were recently successfully developed [4].

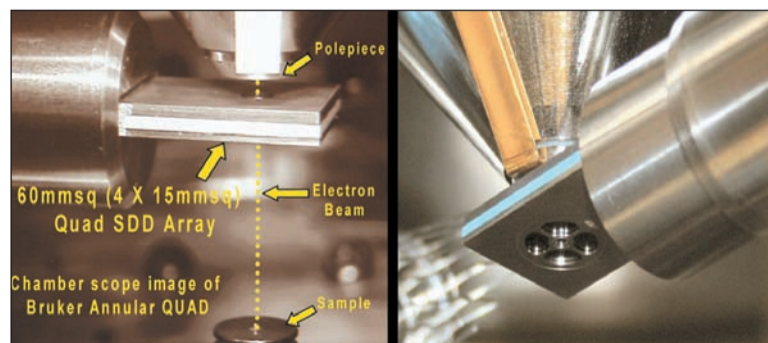


*Figure 2. Excitation volume reduction by lower accelerating voltage in SEM (two left schematics) and using electron transparent samples in TEM (right).*

### Spectroscopy on the nano-scale using side entry detectors in conventional STEM

Employed in TEM, EDS is a valuable compliment to the well-established electron energy loss spectroscopy (EELS). EDS is particularly useful if many elements in a material have to be determined at once. This is the case for many life science applications, one example being the characterisation of environmental pollution in airborne nano-particles, body tissue and plants. *Figure 4* shows another life science example, a yeast cell, which has been osmium stained and silver labelled. The EDS map acquired within 24 minutes at a solid angle of 0.12sr and a take-off angle of 22° clearly reproduces the Ag labelling (which appears as small dark features on the bright field image) but, additionally, EDS delivers the distribution of all the other elements in the cell. For clarity maps of only some of them are displayed in the figure. The following examples show, that much shorter mapping times are sufficient to achieve similar results.

A materials science area where many elements have to be found and quantified at once is mineralogy. Other attractive application areas for EDS in TEM are problems where the EELS signal is detectable only with low efficiency or unfortunate overlaps occur in the EEL spectra. This is the case for materials such as catalysts, heavier elements like Pt, mixed magnetic materials and III-V semiconductors.



*Figure 3. Multichip detector system (Bruker XFlash QUAD 5060F) for high solid angle EDS in SEM.*

*Figure 5* shows EDS data from the epitaxial growth of Pt alloyed NiSi thin films. NiSi is of great interest for nm-sized metallisation structures in semiconductor devices like MOSFETs. Pt alloying of NiSi is used to stabilise the metallic NiSi at elevated temperatures and to avoid transformation into the more stable but less conducting NiSi<sub>2</sub> phase. This works because PtSi is more stable than NiSi and Pt is soluble in NiSi substituting Ni but it is not soluble in NiSi<sub>2</sub>. Ni and Pt were deposited on HF-cleaned (001)Si wafers by magnetron sputtering. The amount of Pt sputtered from a single Pt target was optimised to produce 3 at% Pt in case of a closed NiSi film. The film was rapidly annealed for 30s at 700°C in

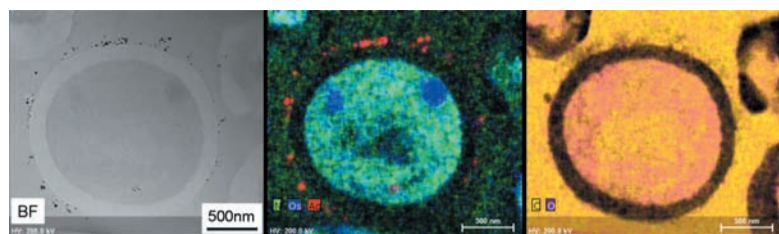


Figure 4. Yeast cell, Os stained, Ag labelled, bright field image and element maps. Map size 328x289 pixel, dwell time 14ms/pixel, measuring time 23.7min, dead time 6.3%, beam current ~700 pA. Other elements in the cell can be found easily by EDS. The following maps show, that much shorter measurement times are feasible. Data courtesy: P. Lasson, Synergie 4, France.

$N_2$ -atmosphere and thereby a mixture of  $NiSi$  and  $NiSi_2$  was produced. A  $0.12sr$ ,  $22^\circ$  take-off angle SDD on a conventional STEM was used for the EDS-data acquisition. The more dense  $NiSi$  appears brighter in Z(atomic number)-contrast of the high angle annular dark field image (HAADF). Unfortunately the Pt content is difficult to quantify by EELS due to the delayed Pt edge. In the EDS map acquired within 7 minutes however, the Pt is clearly depicted. The preferred solution of Pt in  $NiSi$  was confirmed by this EDS experiment. Quantification of the Pt content in the marked area using theoretical Cliff-Lorimer factors delivers the expected 6 at% in case of a mixed  $NiSi/NiSi_2$  film within an error of  $\pm 3at\%$ . The images show the experimental spectra as black outlines and the deconvoluted quantified spectra in colours. Point-measurements or line scans with longer acquisition (dwell) times per pixel would improve statistics and deconvolution results and thus reduce these error bars still keeping the whole measurement within 7 minutes.

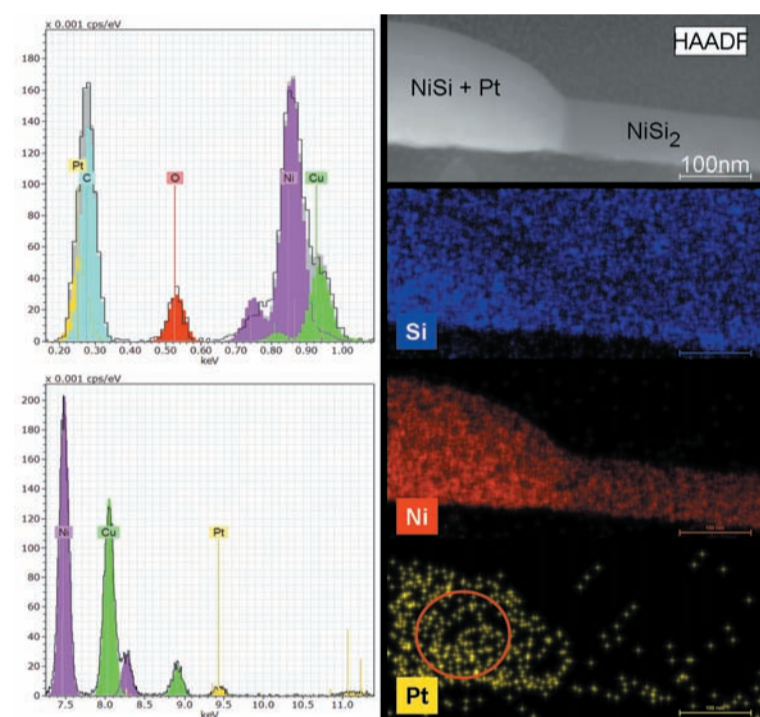


Figure 5.  $NiSi(+Pt)/NiSi_2$  epitaxial thin film. Map size 659x298 pixel, dwell time 2ms/pixel, measuring time 6.7 min, dead time 1.7%, beam current 210 pA. The more dense  $NiSi$  appears bright in z-contrast of HAADF. The qualitative element maps show the solution of Pt in  $NiSi$ . The marked region was quantified using theoretical Cliff-Lorimer factors and found to contain 6at% ( $\pm 3at\%$ ) Pt reproducing the nominal deposition content. The spectra show the deconvolution and quantification result (coloured/gray) in comparison to the experimental spectrum (black line).

Finally, two examples of SDD-EDS for III-V semiconductor nanostructure analysis are discussed. The data were acquired in conventional STEM using a  $0.12sr$  solid and  $22^\circ$  take-off angle for EDS. Particularly the combination of III-V elements often comprises a mixture of several heavy and several light elements. It is ambiguous to conclude the element distribution just from Z-contrast in HAADF images. Thus, III-V semiconductor structures are predestined for spectroscopy and particularly for energy dispersive X-ray analysis (EDS), which allows distinguishing many elements at once relatively easily and straightforward. Furthermore, in EDS the signal from the less delocalised inner-shell ionisations above 2keV can be used with higher efficiency compared to EELS, allowing atom column chemical analysis as shown recently using a low noise  $0.12sr$  Bruker silicon drift detector system on an aberration corrected STEM [5]. It has to be emphasised that atom column EDS is a directly interpretable important complement to the well-established electron energy loss spectroscopy [6].

Figure 6 shows qualitative element maps of an overgrown 3-D nanostructure consisting of Ga, In, As, Al and P used for the development of laser diodes. The maps were acquired in 7 minutes. This example explains well that it would be ambiguous to deduce the element combination just from Z-contrast, since light elements (Al and P) and heavy elements (Ga, As and In) are mixed here. EDS however, after only minutes of mapping time gives a clear and straightforward picture of the local element combination in this material on the nm-scale. The spectrum shows which energy regions were used to display the qualitative element maps. The spectrum of the map has to be evaluated carefully and care has to be taken choosing the energy regions for qualitative analysis to avoid ambiguities in case of line overlaps. This includes also overlaps with lines of the sample support, for example, Cu from the grid, or of carbon contaminants.

As a last example an InAs/InP nanowire heterostructure grown by Au-assisted chemical beam epitaxy was studied. The thinner P-rich regions of various thicknesses down to nominally 1.5nm can be clearly distinguished after a few minutes of element mapping in STEM. A longer measurement time was used for better statistics in quantification. Figure 7 shows the quantified element distribution. The Au-catalyst droplet on the nanowire tip appears clearly after deconvolution of all overlapping lines as shown in the given spectrum. The line scan extracted from this 18 minutes map after 4x4 pixel binning and quantification shows that As and P substitute each other whereas the In concentration remains constant at 50%.

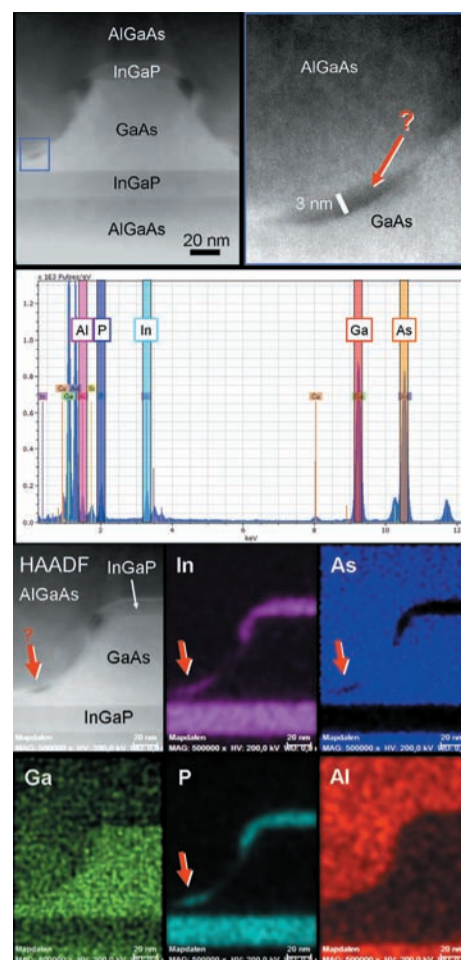


Figure 6. Overgrown 3-D nanostructure comprising several III-V-elements. Map size 195x270 pixels, dwell time 8ms/pixel, measuring time 7 min, dead time 1.7%, beam current 210 pA. Judging the chemical composition from z-contrast in high angle annular dark field images (HAADF) would be ambiguous. EDS reveals the element distribution correctly if the displayed energy regions are chosen carefully, as shown in the spectra.

Sample courtesy: G. Tränkle, Ferdinand Braune Institute for high frequency technology, Berlin, Adlershof, Germany. Data courtesy: A. Mogilatenko, Humboldt University zu Berlin, Germany.

## Outlook

EDS using silicon drift detectors is developing into a powerful tool for nano-scale chemical analysis of electron transparent samples. Large solid angle detectors can be developed, using this modern technology. SDD systems installed on conventional STEM instruments provide quantitative data on nm-scale on a routine basis now. These results provide an idea of what will be possible using this technique combined with aberration correction. First atom column EDS data have been shown employing a low noise SDD for EDS in an aberration (Cs-) corrected STEM instrument [5]. Further developments of high solid angle detectors, suitable for the low signal rates at atomic resolution but also for high speed data analysis in microscopes with high brightness sources, sample stability provided, promise exciting opportunities for the future of EDS in electron microscopy.

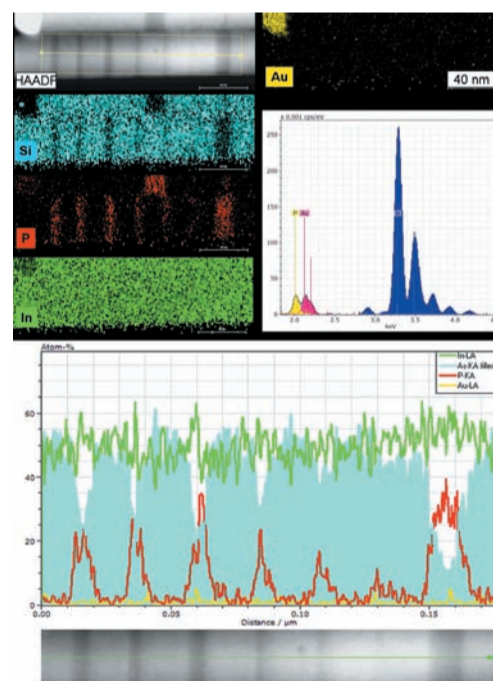


Figure 7. Nanowires with InAs/InP heterostructure. Quantified map, 4x4 pixel binning, map size 755x243, dwell time 6ms/pixel, measuring time 18.4 min, dead time 2.1%, beam current 200 pA. The HyperMap (a spectrum is saved for each pixel) was quantified using theoretical Cliff-Lorimer factors after 4x4 binning. The spectrum part shows the deconvolution result in colours and the experimental spectrum as a black line. The line scan extracted from the quantified HyperMap as shown in the HAADF clearly reproduces all P-rich regions, as visible in the HAADF image, down to the nominal 1.5nm thickness and shows that P and As replace each other, whereas the In concentration remains at 50at%.

Sample courtesy: D. Ercolani, L. Sorba, P. Pingue, V. Piazza, NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silvestro 12, I-56127 Pisa, Italy

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## References

- [1] E. Gatti, P. Rehak, *NIMA* 255:608-621, (1984)
- [2] Strüder L, et al, *Microsc. Microanal.* 4, 622-631, (1999)
- [3] N. J. Zaluzec, *Microsc. Microanal.* 15, 93-98, (2009)
- [4] S. von Harrach et al, *Microsc. Microanal.* 15, suppl.2 (2009) 208
- [5] M.-W. Chu, et al., *PRL* 104,196101 (2010)
- [6] A.J. D'Alfonso et al., *Phys. Rev. B* 81 (2009) 100101(R).