A nalytical TEM of Materials using a Large Area Silicon Drift EDS Detector

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INTRODUCTION
Recently, silicon drift detectors (SDD) have been introduced for the analysis of X-rays in the scanning electron microscope, replacing Si(Li) energy-dispersive spectrometry (EDS) detectors [1]. In Si(Li) detectors, a silicon crystal doped with lithium analyses the characteristic X-rays that are produced when an electron beam is focused on a sample in the SEM or TEM. Si(Li) detectors have proved to be very reliable, and they deliver consistent quantitative results over a wide range of elements [2]. However, these detectors have two drawbacks: 1. The detector must be kept at liquid-nitrogen temperature during analysis; 2. The detectors are, to a certain extent, count limited in that quantitative analysis can only be performed at count rates in the order of 5-10 kcps, although with newer Si(Li) detectors it is possible to perform qualitative work at higher count rates [3]. The basic form of the silicon drift detector was described in 1983 by Gatti and Rehak [4]. But now, new large area (up to 80 mm²) silicon drift detectors are revolutionising the energy-dispersive X-ray spectrometry market. Recently, the application of large area SDD detectors to TEMs has improved solid angle – especially beneficial where counts are low in nanoprobe mode [5]. The SDD detector can also handle high count rates, for example when analysing thicker samples or with a larger beam. This improves data collection times and makes fast mapping in the TEM a reality. Also, liquid nitrogen-free operation is safe, convenient and vibration free.

PRINCIPAL ADVANTAGES OF SILICON DRIFT DETECTORS
High Solid Angle
For X-ray analysis of nanoparticles or when a high spatial resolution is required, such as grain boundary segregation studies, an 80 mm² SDD with large solid angle significantly increases the count rate. Figure 1 shows EDX mapping of Cu-Au nanoparticles with an 80 mm² SDD detector. This analysis was performed to ascertain whether this bi-elemental particle exhibited a core-shell structure, or whether the Cu and Au are homogeneously mixed. The collection time was 120 minutes. The Cu and Au mapping shows the obviously homogeneous elemental distribution; this would have been impractical with a Si(Li) detector.

High Count Rates
The 80 mm² SDD sensors can deal with higher count rates than conventional Si(Li) detectors and this can be very useful in the TEM [6, 7]. For example, it may be required that a map be collected within a certain time, due to time constraints, by the limitations of drift or by contamination. Figure 2 shows a high count rate (100 kcps) mapping of a IC6 superalloy with 2 frames (3.5 mins) and 9 frames (18 mins) collection time. Obviously, ‘reasonable’ results can be obtained within 3.5 mins as shown in Figure 2 a-d. In this article the concept of fast and convenient X-ray mapping in the TEM will now be discussed with examples of applications in materials science and engineering.

Figure 1: EDX mapping of Cu-Au nanoparticles using an 80 mm² X-Max SDD. (a) HAADF image of a nanoparticle. (b) Cu map. (c) Au map. (d) O map. (e) X-ray spectrum. From Tran, Johnston, Preece and Jones (to be published).
MATERIALS AND METHODS
Specimen Preparation
The Cu and Au nanoparticles were dispersed in toluene then deposited on a carbon film-coated copper grid. The IC6 superalloy specimens were electropolished to perforation using a twin-jet electropolisher (Struers Tenupol 5). The Nd$_2$Fe$_{14}$B and semiconductor specimens were prepared by focused ion-beam milling.

Transmission Electron Microscopy
The microstructural observations were carried out on a FEI Tecnai F20 TEM at an accelerating voltage of 200 kV in STEM mode.

Energy Dispersive X-ray Microanalysis
EDS X-ray microanalysis was carried out on a FEI Tecnai F20 TEM interfaced to Oxford Instruments Inca EDS software with an X-Max large area (80 mm$^2$) SDD detector. The X-ray maps were obtained with spot sizes from 4 to 8 and condenser apertures from 30 µm to 150 µm.

RESULTS
X-ray Mapping Studies of Microstructures in Engineering Samples
A large area detector and a bright field-emission gun reduce collection time, and this combination is very useful for high spatial resolution microanalysis, as described above. In addition, with thicker specimens and larger beam sizes, the resulting increased count rates can be accessed by the drift detector, but with a subsequent loss in spatial resolution.

The following examples will show how beam size (via C1 lens and C2 apertures) and specimen thickness can be used to control X-ray map quality to fit the user's requirements.

Effect of the Condenser Lens Current (C1)
Figure 3 compares SDD maps obtained with small (spot size 8) and large (spot size 4) beam sizes for a specimen of Nd$_2$Fe$_{14}$B with 1 at% ZrB$_2$. The microstructure consists of three phases: Nd-rich, ZrB$_2$, and Nd$_2$Fe$_{14}$B. The Nd-rich areas oxidise easily and oxygen can be observed with X-ray mapping. Here, the size of the C2 condenser aperture is fixed to 150 µm. The collection time is the same for both beam sizes. The maps obtained with the larger beam size have an adequate spatial resolution for this microstructure and are better than those obtained with the smaller beam. The boron maps show the good soft X-ray capability of the SDD.

Effects of Condenser Aperture (C2)
Figure 4 shows the effects of condenser aperture size on EDX mapping. The specimen is the same as above – Nd$_2$Fe$_{14}$B with 1 at% ZrB$_2$. Figures 4a-4f show the maps obtained with a 30 µm aperture and 4g-4l show the maps with a 150 µm aperture, this time with the C1 current fixed (spot size 5). Again, the better map with more counts and acceptable spatial resolution is obtained with the larger aperture (4g-4l).

Effect of Specimen Thickness
When analysing thicker samples with field emission TEMs, the SDD detector shows a significant advantage by being able to handle high count rates. Figures 6a-6d show X-ray maps of a thin area of the sample and 6e-6h show X-ray maps for a thicker area of the sample. In the thicker area, the acquisition count rate exceeds 30 kcps which exceeds the range commonly handled by TEM-mounted Si(Li)
detectors. The map from the thicker sample is better and has an acceptable spatial resolution for the microstructure in question.

**Quantitative X-ray Mapping**

The large solid angle and the excellent resolution of the SDD detector make the X-ray collection more efficient; the data sets are of sufficient size and spectral quality to enable the use of Quant-mapping to be used to distinguish elements where peaks overlap. For example, Figure 7 shows quantitative X-ray mapping for a semiconductor device sample - a section through the memory array of a 64 MB DRAM. After quantification, elements such as nitrogen in the presence of titanium in TiN and tungsten in the presence of silicon can be distinguished.

**CONCLUSIONS**

Silicon drift detector technology has made enormous advances in resolution and stability in a relatively short time. The drift detector can be run at very high count rates, has a large solid angle and is very efficient in detecting soft X-rays. For more general purposes, X-ray maps can be obtained quickly, controlling the signal intensity within acceptable limits using beam settings or specimen thickness.

The silicon drift detector has made TEM X-ray mapping into an everyday method for materials characterisation, often in preference to SEM because of the much better spatial resolution.

**REFERENCES**

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