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Spatial Resolution Limits for X-ray Microanalysis of Bulk Samples

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The ability to perform high quality x-ray microanalysis of very fine structural detail depends on many factors. They include specimen preparation, the ability to focus an electron beam to a very fine probe, the interaction volume from which the x-ray spectrum is generated, the intensity of the particular characteristic x-rays measured, the kind of detector system used and subsequent data processing procedures. In addition, the electron beam position on the sample must stay fixed over the course of the analysis and the level of contamination at the point of impact must be held to a minimum. While all of these factors have been examined at various levels of detail since the origin of x-ray microanalysis [1] worldwide attention on nanotechnology as well as recent advances in instrumentation and modeling have strongly rekindled interest in improving the limits of spatial resolution as it is becoming increasingly important to establish chemistry/structure/property relationships for ever smaller devices and material systems.

Castaing, in his Ph.D. thesis, referred to a limit of about 1 μm determined by the scattering and diffusion of electrons [2]. This limit was based primarily on the need for high accelerating voltages (typically 15-30KV) required to efficiently excite and measure characteristic lines of interest. Since its initial development, x-ray intensity measurements with the electron microprobe have been done with curved crystal diffraction spectrometers. Counting times are selected to be long enough to ensure adequate x-ray counting statistics and thus a reasonable level of precision in quantitative measurements. Unfortunately, the use of high voltages results in excitation volumes around 1 μm in diameter even if the actual electron probe size is less than 10% of that size. It was also well recognized that for instruments with tungsten or LaB6 sources that the probe current decreases as the beam diameter to the 8/3 power [3]. Therefore even if the excitation volume is comparable to the beam diameter, small probes correspond to low currents and since the x-ray signal is proportional to the probe current the x-ray signal generated would be inadequate for good counting statistics. Stated another way, much of microprobe analysis using curved crystal diffraction spectrometer is done with probe current of 10 to 100 nA and at voltages such that the excitation volume is around 1μm.

The emergence of energy dispersive detectors (EDS) in the late 1960's for use on scanning electron microscopes (SEM's) meant much higher detector collection efficiencies were available and therefore x-ray spectra could be collected even at currents 0.1 nA or lower corresponding to very fine electron probes of less than 50nm at probe currents of 1 nA and beam voltages of 30KV for tungsten sources and 20 nm for LaB6. The problem remained, however, that the electron range in the sample at 30 KV still restricted the spatial resolution and that only by decreasing the beam voltage can the excitation volume be decreased in most materials to the 100 nm range. This drop in KV is typically to less than 5 KV and may for

some systems be less than 3 KV. The penalty for using such low voltages is fairly severe and includes some of the following:

- The K lines and L lines for many elements either are not excited or are weakly excited.
- The current associated with W, LaB6 and even cold field emitters may be too low to give adequate counting statistics in a reasonable time period.
- EDS spectrometer resolution may be insufficient to result in the clear separation of the many possible line overlaps that can occur at low energies.
- Contamination effects at the sample surface become more important at low voltages.
- Sample or electron beam drift may make it difficult to keep the point of interest fixed.

The complex interplay of the source type used, beam voltage, beam current, sample composition, probe current and instrument geometry can often be described by Monte Carlo calculations [4] which allow the analyst the opportunity to visualize just what the excitation volume and x-ray spectra will look like for a given set of experimental conditions.

Several relatively recent developments can help overcome some of the barriers described previously. Schottky electron sources can give stable high currents even with small probes at low beam voltages, e.g. 10nA at 3 KV in a 20 nm probe. Such higher currents at low voltage and small probe diameters can be capable of generating sufficient x-rays that can be detected by diffraction spectrometers. Parallel beam spectrometers have been developed that use a combination of x-ray reflection optics and capillary optics to increase the solid angle of the spectrometer and thus further increase count rates [5]. The potential for higher count rates is also being increased by high current mode operation in Schottky based systems in which modifications to the electron optics increase the collection of the number of electrons going down the column without dramatically reducing probe sizes. Even if currents cannot be improved significantly to provide adequate signals for diffraction spectrometers, advances continue to be made in x-ray detectors. X-ray microcalorimeters offer the promise of better than 5 eV resolution which would greatly aid peak separation in the low energy portion of the spectrum [6]. Count rates for these systems are low, however, often less than a few hundred counts per second, and operation and maintenance can be very challenging . Spatial resolution can also be explored in three dimensions (3D) by combining focused ion beam (FIB) techniques with x-ray microanalysis. Work in our laboratory is now underway to obtain serial sections of a sample in the FIB and simultaneously store high resolution SEM images and x-ray images from each section. Data is processed and 3D reconstruction techniques used to examine the 3D nature of different phases based either on their morphology, composition or both. The ability to examine fine structure in three dimensions makes it much easier to look for how things are interconnected and determine how uniform structures are. All of the considerations of how to improve 2D spatial resolution apply to 3D imaging as well.

References

[1]. J. I. Goldstein, et.al. Scanning Electron Microscopy and X-ray Microanalysis, Kluwar Academic/Plenum Press, New York, 2003
[2]. R. Castaing, Thesis University of Paris, 1951
[3]. K. C. A. Smith, Ph.D. Dissertation, Cambridge University, 1956
[4]. E. Lifshin and R. Gauvin, Microsc and Microal 4, 232-233, 1998
[5]. Private communication with ThermoNORAN
[6]. D. A. Wollman, et.al., J. Microscopy, 188, 196

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