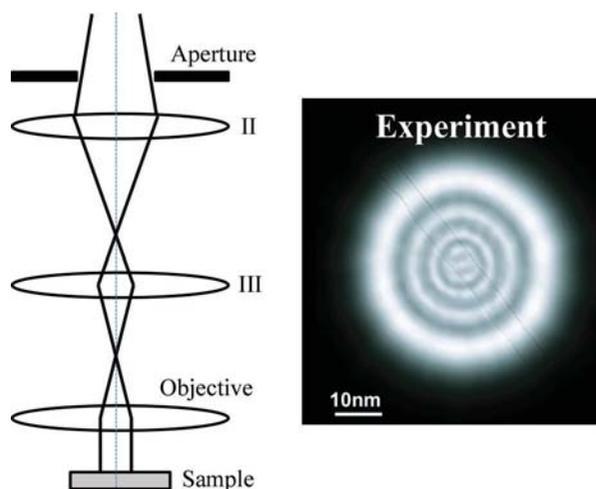


2. INSTRUMENTATION AND SAMPLE PREPARATION

**Figure 2.4.4**

Schematic illustration of electron nanoprobe formation using a combination of condenser lenses (II and III) and the objective lens. The beam divergence angle is kept at a minimum by forming a crossover at the front focal plane of the objective lens. An image of an experimental electron nanoprobe is shown on the right with a carbon nanotube contained inside the probe.

limited by the aberrations of the illumination lenses. A beam convergence angle as small as ~ 0.05 mrad has been reported (Zuo *et al.*, 2004). A diffraction pattern recorded using NAED is similar to one recorded by SAED. The major difference is that the diffraction volume is defined directly by the electron probe in NAED. Since all electrons illuminating the sample are recorded in the diffraction pattern, NAED in an FEG microscope also provides higher beam intensity than SAED (the probe current intensity using a $10\ \mu\text{m}$ condenser-II aperture in a JEOL 2010F is $\sim 10^5\ \text{e s}^{-1}\ \text{nm}^{-2}$) (Zuo *et al.*, 2004).

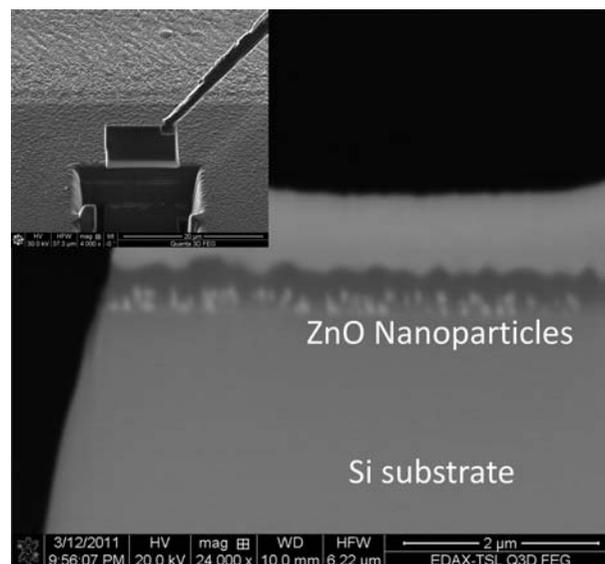
The small probe size is most useful for studying a small section of thin films or for selection of nanoparticles for powder diffraction. The small beam size reduces the background in the electron diffraction pattern from the surrounding materials.

2.4.3.3. Sample preparation

The success of an electron powder diffraction experiment to a large extent depends on sample preparation. The powder sample has to be suitable for electron-beam observation, and the sample also needs to be compatible with the vacuum environment of the microscope. *In situ* experiments can be carried out using special holders for cooling, heating and cryogenic or environmental transfer. Special microscopes are also available to provide a gaseous or ultra high vacuum environment for the investigation of structures under a gas or at ultra low pressure, or *in situ* sample preparation.

The observed area of the sample must be electron transparent, *i.e.* have a thickness of less than or comparable to the inelastic mean free path of electrons. The inelastic mean free path increases with the electron voltage (Egerton, 2011). The typical sample thickness ranges from a few tens to hundreds of nanometres for 200 kV high-energy electrons (see Table F.1 in Zuo & Spence, 2017).

The sample-preparation techniques can be divided into three categories: (i) bulk-based for bulky materials and supported thin films, (ii) powder-based techniques and (iii) free-standing thin films over a supporting grid prepared by vacuum evaporation or sputtering.

**Figure 2.4.5**

Sample preparation and lift-out using a focused ion beam (FIB). A thin section of the sample is cut out using the FIB and attached to a mechanical probe for lift-out (inset). The image shows the lift-out section containing ZnO nanoparticles in bright dot-like contrast supported on an Si substrate.

The bulk-based techniques involve mechanical cutting, thinning/polishing and perforation. An ion beam is typically used in the last step of perforation to create a thin area around the edge of a hole for electron-beam observation. Chemical and electrolytic methods are also often used for preparing electron-transparent samples. While these methods have been applied to a broad range of materials, they are mostly used for metals or semiconductors to create smooth sample surfaces free from defects or sample heating caused by ion-beam irradiation. Mechanical thinning and polishing are sometimes done with a wedge angle with the help of a tripod. The thin region next to the edge only requires a brief ion-beam bombardment to make it electron transparent. A detailed description of traditional sample-preparation techniques for TEM can be found in Barna & Pécz (1997). The above techniques are applicable to both thin films and bulk nanocrystalline materials. The powder-based techniques use dispersion of powders on thin supporting films placed on metal grids specially made for TEM observations. This technique is most suitable for nanoparticles. For micron or larger-sized powders, additional grinding is used to produce smaller particles. The most commonly used supporting films are continuous amorphous carbon films, holey carbon films, networked carbon fibres (lacey carbon), amorphous silicon nitride and SiO_x . For amorphous carbon films, an ultra thin version is available which is especially useful for nanoparticle samples.

A recent development in TEM sample preparation is the use of a focused ion beam of Ga^+ ions for cross-sectioning a sample. The focused ion beam can drill a precise hole in the sample. The same ion beam can also be scanned over a sample surface to form an image by collecting the secondary electrons or ions generated by the beam. The ion column can be integrated into an electron column in a scanning electron microscope in the so-called dual-beam configuration. An image can be formed using either electrons or ions. Most often the electron beam is used for sample inspection, while the ion beam is used for patterning and milling. This allows precise control over the position and thickness of the cross section, which is very practical for characterization of

2.4. ELECTRON POWDER DIFFRACTION

semiconductor devices or failure analysis in general (Fig. 2.4.5). Further details about ion-beam techniques can be found in Lábár & Egerton (1999) and Orloff *et al.* (2002). For a comprehensive review of sample-preparation techniques for TEM, see Ózdöl *et al.* (2012).

2.4.3.4. Diffraction data collection, processing and calibration

Experimental electron powder diffraction data are collected using two-dimensional area electron detectors. Experimental issues involved in the diffraction-pattern recording procedure are electron optical alignment, diffraction-pattern collection and calibration, with particular care taken in adjusting the specimen height position (eucentric position), selection of a suitable illumination-beam convergence angle and diffraction-camera length, and finally projector-lens focusing. The diffraction-camera length is determined by the setting of intermediate and projector lenses in combination with the objective lens. To calibrate the diffraction-camera length, a standard sample is placed in the eucentric position of the objective lens at the standard focus. At this setting, the specimen plane is conjugate to the selected-area aperture (Fig. 2.4.3) and the sample image appears in focus. To obtain a sharp diffraction pattern, the detector plane must be conjugate to the back focal plane of the objective lens. This can be achieved by setting up a parallel-beam illumination and adjusting the intermediate-lens focus length to bring the direct beam into a sharp focus.

Currently available area electron detectors are CCD and CMOS cameras, imaging plates (IPs) and photographic film. While photographic film has a long history of use in electron microscopy, its limited dynamic range makes it less useful for electron diffraction data collection. Both CCD cameras and IPs are digital recorders capable of collecting electron intensity over a large dynamic range. The crucial characteristics of digital recording systems are the gain (g), linearity, resolution, detector quantum efficiency (DQE) and the dynamic range. The gain of a CCD or CMOS camera can be normalized using a flat-field illumination; the gain in IPs is assumed to be constant. The detector resolution is characterized by the point-spread function (PSF), which is roughly the detector's response to a point-like illumination. These characteristics for CCDs and IPs have been compared by Zuo (2000). The intensity of an electron diffraction pattern recorded with a digital detector is given by

$$I^{\text{recorded}}(i, j) = g(i, j)H(i, j) \otimes I^{\text{original}}(i, j) + n(i, j), \quad (2.4.14)$$

where $g(i, j)$ is the detector gain image, H is the PSF of the detector, n is the detector noise and I^{original} is the intensity of scattered electron beams originally received by the detector. The i and j are the pixel coordinates of the detector. The PSF is experimentally characterized and measured by the amplitude of its Fourier transform, or the so-called modulated transfer function (MTF). The effects of the PSF can be removed by deconvolution. The Richardson–Lucy method is specifically targeted for Poisson processes, which can be applied to CCD images (Zuo, 2000). The alternative to the removal of the PSF is to treat it as part of the peak broadening that can be used to fit the powder pattern.

The noise in the experimental data is characterized by the DQE:

$$\text{var}(I) = \frac{m\bar{g}I}{\text{DQE}(I)}. \quad (2.4.15)$$

Here I is the experimentally measured intensity, var stands for

the variance, m is the area under the MTF and \bar{g} is the average gain of the detector. Once the DQE is known, this expression allows an estimation of the variance in measured intensity, which is essential for quantitative intensity analysis where the variance is often used as the weight for comparing experimental and fitted data.

The performances of CCDs and IPs for electron diffraction pattern recording are different at different electron dose rates. At low dose rates, the DQE of the CCD camera is limited by the readout noise and the dark current of the CCD. IPs have better performance in the low dose range due to the low dark current and low readout noise of the photomultipliers used in IP readers. At medium and high dose rates, the IP signal is affected mostly by the linear noise due to the granular variation in the phosphor and instability in the readout system, while for CCDs the noise is mostly linear noise in the gain image.

Electromagnetic lenses are not perfect and have aberrations affecting the collected data. In most transmission electron microscopes, electron diffraction patterns are produced using the post-specimen magnetic lenses. For electron diffraction, the most important aberration is the distortion of the projector lens, causing a shift of an image point. There is no blurring in diffraction patterns associated with the lens distortion. However, the distortion affects the overall shape of diffraction patterns. The distortion is most obvious at low camera lengths, where the pattern may seem stretched or twisted at high scattering angles. There are three types of distortion of the same order as the spherical aberration of the lens. They are called pin-cushion, barrel and spiral distortions (Reimer, 1984). A distortion can also arise from the use of an electron energy filter, where a lower order of distortion can be introduced with the use of non-spherical lenses (Rose & Krahl, 1995).

For quantitative analysis an electron powder diffraction pattern recorded on an area detector needs to be integrated into one-dimensional powder diffraction data (Fig. 2.4.6). The integration involves four separate steps: (i) identifying areas of the diffraction pattern for integration, (ii) centring the diffraction pattern, (iii) applying a diffraction pattern distortion correction, if there is any, and (iv) integrating intensities for a constant diffraction angle. Electron powder diffraction patterns can be recorded on a crystalline support film, which gives sharp diffraction spots distinct from the powder diffraction rings. The sharp diffraction patterns from the support film can be excluded from the powder diffraction intensity integration in step (i) by using a mask. The same approach can be used to eliminate any alien features from a diffraction pattern caused, for instance, by the aperture or the energy filter. The diffraction pattern centring is based on the analysis of the transmitted beam in the centre of the pattern. As the transmitted beam is usually very strong and is often overexposed, finding its centre may be a non-trivial task. In order to prevent detector damage in the area of the transmitted beam a beam stop is often used. In this case, the central area in the pattern may have an irregular shape not suitable for the centring procedure. Non-distorted diffraction patterns can be centred by finding the centre of the concentric diffraction rings either by locating the position of the maximum diffraction peak intensity along the ring and using these positions to determine the centre of the ring, or by searching for the centre that gives the maximum correlation between $I(g)$ and $I(-g)$. For distorted diffraction patterns, the centring and the distortion correction must be carried out simultaneously.

The distortion correction requires a powder sample with known d -spacings. The amount of distortion can be obtained by