Scanning transmission electron microscopy and microdiffraction techniques

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Abstract. At the moment scanning transmission electron microscopy (STEM) instruments are not competitive with conventional TEM instruments for high resolution bright field imaging. For studies of the structure and defects of crystalline materials, their special virtues lie in the application of dark field imaging modes combined with observations of microdiffraction patterns from regions of diameter comparable with the microscope resolution limit (currently about 5 Å). They also offer capabilities for microanalysis by use of energy dispersive x-ray spectroscopy (EDS) or electron energy loss spectroscopy (ELS). In principle the spatial resolution of these microanalysis methods is comparable to that of the imaging modes but in practice it is limited by poor signal-to-noise ratios or by the nonlocalized nature of the inelastic scattering process.

The capabilities for microdiffraction are illustrated by sequences of diffraction patterns obtained as the incident beam is moved within the unit cell of a crystal of large (20 Å) periodicity. Applications of more immediate practical significance include diffraction studies of small crystallites of gold 20 to 50 Å in diameter and of the near-amorphous, thin oxide layers formed on chromium and iron films at room temperature.

Microdiffraction, combined with reflection electron microscopy and ELS analysis, provides a powerful new approach to the study of the surface structure of crystals, including bulk samples, and the investigation of surface reactions. In particular, if a beam of small diameter (10–20 Å) is made to run along the face of a small crystal, the diffraction pattern and ELS curves are very sensitive to the form of the potential distribution at the surface and the excitations of the surface states of the crystal.

Keywords. Convergent beam electron diffraction; microdiffraction; surface studies.

1. Introduction

For many areas of application of electron microscopy, STEM does not offer any particular advantage over the conventional TEM. When only bright field images or dark-field images of the standard type are required from specimens which are not too thick, use of STEM is inconvenient because the instruments have not been developed commercially to the same extent, specimen interchange takes longer because of the requirements for better vacuum and the images tend to be noisy and of limited size relative to the resolution, *i.e.* the number of usable picture elements per image is relatively small.

On the other hand the use of STEM has opened up an important new range of possibilities which are having increasing impact in electron microscopy, providing information previously inaccessible and allowing new approaches to a number of important problems of solid state science. New bright field and dark field imaging modes are available, largely because with the STEM configuration it is possible to choose any selected part or parts of the diffraction pattern to form the image. Several different image signals can be obtained simultaneously and combined to emphasize particular

types of information concerning the specimen (Crewe *et al* 1970; Cowley and Au 1978). The STEM imaging mode lends itself particularly well to digital recording of data so that with a minicomputer coupled to the system it is possible to perform a variety of image processing procedures on-line or else the images may be stored conveniently for off-line processing (Strahm and Butler 1981).

For many areas of solid state science, the most important innovations associated with STEM are those which depend directly on the fact that at any one time the specimen is irradiated by an electron probe of very small diameter. For every probe position a microdiffraction pattern is produced from an area of the specimen of diameter comparable with the resolution limit of the STEM images. The energy losses of the transmitted electrons may be observed as a basis for microanalysis by the EELS techniques or microanalysis may be performed by detection of the emitted characteristic x-rays using EDS. Other signals which may be used to provide information on chosen parts of the specimen or else to form images include the emitted light, secondary electrons and acoustic waves. In each case the spatial resolution which can be achieved depends on the nature of the electron-specimen interaction, the efficiency of production of the detected signal and the efficiency of the detection system. At least in microdiffraction and EELS for small energy losses, spatial resolutions approaching 5 Å have recently been reported.

In this review we concentrate our attention on these techniques having high spatial resolution and their relationship to the high resolution STEM imaging modes and provide a few examples to illustrate the potential of these methods for the solution of problems of immediate relevance for research in solid state science.

2. Bright fields and dark field images

In order to obtain the STEM equivalent of the high resolution bright field TEM images of thin crystals, which are proving increasingly valuable for crystallographic studies, it is necessary to illuminate the specimen with a large objective aperture angle (figure 1). The beam which converges on the specimen must be coherent, *i.e.* the illumination falling on the objective aperture must come from a source which is so small that the coherence width is greater than the objective aperture diameter. According to the reciprocity relationship, the detector aperture must be small in order that the geometry be equivalent to TEM with a well-collimated incident beam. Hence only a very small proportion of the incident electrons can be detected and consequently, in order to produce a strong enough signal to form an image in a conveniently short time, it is

Figure 1. Diagram showing the objective aperture and detector aperture angles for STEM.

necessary to use a very bright, small source such as is given by a cold field emission gun.

For the currently available commercial STEM instrument, the HB5 from VG Microscopes Limited, England, the pole piece dimensions for the objective lens have been made relatively large in order to accommodate an EDS detector. Hence the bright field image resolution is about $4.5 \text{ \AA}$ as compared with $3 \text{ \AA}$ for contemporary 100 keV TEM instruments. Figure 2c is a bright field STEM image of the thin edge of a crystal of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ with the incident beam parallel to the short ($3.8 \text{ \AA}$) b axis. The crystal was aligned by observation of the microdiffraction patterns, such as figure 2a obtained using a small ($10 \mu\text{m}$) objective aperture. Then the objective aperture of the correct diameter for optimum bright field image resolution ($60 \mu\text{m}$) was inserted and the scan was switched on. The small black spot in figure 2a is the detector aperture which is actually a small mirror in the optical system attached to our HB5 instrument (Cowley and Spence 1979).

The resolution in figure 2c is noticeably poorer than that in the historically significant images of the same material taken by Sumio Iijima (1971), in which the rows of metal atoms parallel to the beam and separated by $3.8 \text{ \AA}$ (figure 2b) were clearly resolved. This is consistent with the results of calculations of image intensities made using the spherical aberration coefficients of the objective lenses used in the two cases (O'keefe *et al* 1978).

It is interesting to note that in the dark field STEM image of figure 2d obtained with an annular dark field detector, these atom rows, $3.8 \text{ \AA}$ apart, are clearly resolved as white spots and the representation of the structure is good. This is in striking contrast to the dark field images formed in TEM with the usual "high resolution" tilted-beam dark field geometry. For such images, although some fine detail is visible, the structure of the crystal projection is not reproduced in a recognizable form and even the symmetry of the image is strongly perturbed in a manner depending on the tilt of the incident beam (Sumio Iijima, private communication).

It has been argued by Crewe *et al* (1970) and Hanssen and Ade (1976) that dark field images from annular detectors have better resolution than bright field images. These arguments are valid for very thin, weakly scattering objects for which the weak phase object (kinematic scattering) approximation (the wPOA) applies, although modifications of the theory are necessary for imaging near the resolution limit (Cowley 1976). By extension of this theory it has been argued (Cowley 1978) that the same improvement of resolution should apply for thin, strongly scattering objects such as the crystal used for figure 2, for which the strong phase object approximation (POA) is valid. The symmetry of the experimental annular aperture configuration ensures that, in contrast to the TEM case, the symmetry of the dark field image will be maintained.

It seems clear that when, in the near future, the same ultra-high resolution pole pieces are used in STEM as in TEM instruments, important advances in the imaging of crystal structures will be possible.

3. Resolution enhancement by holography and coherent CBED

In his original paper on holography, Gabor (1949) proposed that a very small source of electrons should be placed close to a thin specimen to form a highly magnified shadow image which could be regarded as a hologram from which the object would be reconstructed, with correction of the aberrations of the lenses forming the source. This idea was abandoned because sufficiently small electron sources of the necessary

Figure 2. a. Convergent beam diffraction pattern from a thin crystal of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$. b. A diagram of the structure of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$, projected down the b -axis. The squares are oxygen octahedra, surrounding metal atoms, on two different levels indicated by the line width. c. A bright-field STEM image obtained with a small detector aperture. d. A dark-field STEM image obtained using a large annular detector excluding the zero beam.

brightness could not be formed at that time. Recently with the use of field emission guns and efficient two-dimensional detector systems, the proposal has become more nearly feasible. Shadow images formed in a STEM instrument have demonstrated that the essential requirements have been met (Cowley 1980).

Figure 3, for example, shows a series of shadow images of the thin edge of a MgO smoke crystal. The prominent fringes are given by the (200) lattice plane spacings ($d_{200} = 2.1 \text{ \AA}$). The shapes of the fringes result from the effects of spherical aberration and defocus. Astigmatism would distort the shapes but has been corrected to high accuracy by removing this distortion. The shapes are similar to those of the Ronchigrams used for the detection of aberrations of large telescope mirrors and observed when a diffraction grating is placed near the focus of the mirror (Ronchi 1964). The fringe patterns observed when thin crystals are placed near the focal point of an electron lens have therefore been named "electron Ronchigrams".

When the shadow images such as those of figure 3 are observed on the tv screen, movements of the Ronchi fringes are clearly seen for movements of the incident beam or of the crystal by much less than $1 \text{ \AA}$. The shadow images, regarded as holograms, therefore contain information on a scale of small fractions of $1 \text{ \AA}$ and this information could in principle be retrieved by a suitable reconstruction process. Suggestions have been made on methods by which the reconstruction process could be carried out in practice (Cowley and Walker 1981).

For thin crystals having large unit cell dimensions when projected in the direction of the incident electron beam, it is interesting to observe the transition from the convergent beam microdiffraction patterns (CBED) (figure 2a) to the shadow image as the objective aperture size is increased and, as a consequence, the diffraction spots become larger. As the spots begin to overlap, strong interference effects become apparent in the regions of overlap. When the objective aperture size is so large that many diffraction spots overlap at any point of the diffraction pattern, the distinction between spots is no longer clear. At this stage, the diameter of the electron probe on the specimen is much smaller than the unit cell dimensions. Only a small part of the unit cell is illuminated and the diffraction pattern intensities reflect the arrangement and symmetry of the group of atoms in the beam. Then, as the electron beam is moved across the unit cell, the changes in the diffraction pattern can be observed and recorded (figure 4).

The extent of the diffraction pattern is such that it contains information on spacings as small as $0.5 \text{ \AA}$ or less. Interpretation of the patterns would allow structure analysis showing details in this scale.

4. Practical microdiffraction

While the large-aperture CBED patterns and shadow images have great potential which may be realized in the future, the patterns obtained with smaller objective apertures have immediate practical applications and are increasingly used for gathering data on small specimen areas not otherwise attainable. Patterns such as those of figure 2a and figure 5 have relatively large and poorly defined spots, as compared with the sharply-focussed selected area diffraction patterns commonly obtained with TEM instruments and cannot be used in the same way to give accurate measurements of lattice parameters. Nor can they show the same enormous range of relative intensities, ranging from strong sharp Bragg peaks to weak diffuse scattering. On the other hand, they can

(a)

(b)

(c)

Figure 3. Shadow images of a thin crystal of MgO showing Ronchi fringes due to the 200 lattice planes ($d = 2.1 \text{ \AA}$) taken from a through-focus series.

be obtained from specimen regions only 10–20 Å in diameter and provide information otherwise inaccessible on the structures of very small particles, the ordering in local domains of near-amorphous materials and the environments of individual crystal defects.

Small particles of face-centred cubic metals having diameters less than 100 Å are currently being investigated intensively because of their role in catalysts. Various electron imaging and diffraction techniques have been used to show that the particles are usually not single crystals but are multiply twinned on (111) planes, forming assemblies which commonly contain five or twenty tetrahedral regions related in this way. The evidence on these structures is reasonably clear for the size range down to about 50 Å. Information on smaller particles is needed to confirm the theoretical predictions that this multiply twinned form is in fact the equilibrium form for the smallest sizes and provides the nuclei from which larger particles grow.

The possibility of obtaining diffraction patterns from regions less than 20 Å in diameter is therefore significant in this context. Patterns have been obtained from gold particles formed by cōsputtering with polyester or alumina and having diameters of 20 to 30 Å (Cowley and Roy 1981) (figure 5). The incident beam may lie completely within one single crystal region, (figure 5a) or include a single twin plane or two twin planes (figure 5b,c). The relative intensities and shapes of the spots may be used within limits to derive detailed information on the configurations (Cowley and Roy 1981). Series of patterns taken as the incident beam scanned over a particle could be applied to make complete analysis of its form. It is anticipated that this method of analysis may be extended to the 15–20 Å size range, beyond which difficulties arise because the individual single crystal regions between the twin planes are too small to give clearly recognizable patterns.

In another application of the method (Fumio Watari and Cowley 1981), it has been shown that single crystal patterns may be obtained from the microcrystals in the oxide layers formed when chromium is heated in air. The oxide layers give only very blurred arcs or rings in selected area diffraction patterns so that detailed analysis has previously not been possible. Single crystal microdiffraction patterns from individual microcrystals revealed that in addition to the known rhombohedral Cr_2O_3 , a second form of oxide exists, forming a very thin layer on the surface and having a spinel-type structure which was previously unknown for chromium.

The epitaxial relationship in which this oxide grows on chromium could be established and, from this, models for the growth process could be proposed. It was deduced that the spinel crystallites never grow to more than about 10 Å thick or 50 Å wide but form an intermediate stage in the oxidation which is later dominated by the growth of the rhombohedral form as the oxide layer thickness increases.

Microdiffraction shows that the thin protective oxide layer formed on chromium in air at room temperature is almost completely amorphous (Fumio Watari 1983), having less local order than other so-called amorphous materials such as the amorphous forms of silicon or carbon for which the microdiffraction patterns from 15 Å diameter regions show considerable spottiness, reflecting the extent of the local positional correlations of the atoms (Cowley 1981). Comparison of the pattern from the chromium oxide, (figure 6a) with that from amorphous silicon (figure 6b) suggests that the degree of order in the former is much less.

This comparison of spottiness of the microdiffraction patterns provides at best a very qualitative and subjective measure of the degree of local ordering. However con-

4(a)

4(b)

4(c)

4(d)

Figure 5. Microdiffraction patterns from small particles of gold, 20 to 50 Å in diameter showing the effects of twinning. The incident beam of diameter 15 Å illuminates no twin plane in **a**, one twin plane in **b** and two planes in **c**.

Figure 4. A series of microdiffraction patterns obtained as an electron beam of diameter 5 Å is moved across one unit cell of a $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ crystal. The black spots and the other features are mirrors and a beam stop in the optical system.

Figure 6. a. Microdiffraction pattern from a region 15 Å diameter of a thin oxidized chromium film. b. Similar microdiffraction pattern from a thin film of amorphous silicon. c. ELS spectrum from a thin oxidized chromium film showing the oxygen K edge and the chromium L edge.

siderable conceptual and operational problems have, to date, prevented the development of a more satisfactory, quantitative basis for measurement of the relevant parameters.

Further information may be derived concerning the thin amorphous protective layer on chromium by use of the STEM instrument in that the ELS method provides some indications as to its composition. The ELS curve of figure 6c shows the adjacent peaks due to the oxygen K-edge and the chromium L-edge. From observations of the ratios of the heights of these peaks for oxides of known composition and for films of different thicknesses it is possible to conclude that the oxide layer has a thickness of 10 Å on each side of the chromium and has a composition in the chromium-rich side of Cr_2O_3 (Fumio Watari 1981). Parallel determinations have been made for the thicker oxide layer which forms on iron.

5. Surface studies

To some extent all TEM and STEM studies of very thin specimens can be regarded as studies of surfaces since the surface layers constitute a large proportion of the sample. For special specimens and imaging modes the information on surface structure is explicitly sought and clearly obtained. Such cases include the imaging of atom-high surface steps (Moodie and Warble 1971), the observation of the movements of single heavy atoms on the surface (Crewe 1978; Iijima 1977) and the study of the structure and reactions of surface monolayers (Yagi *et al* 1979).

For most transmission specimens the scattering of electrons by the internal structure dominates the image. For these and for bulk specimens an alternative method for high resolution surface study has been found in reflection electron microscopy (REM). The initial experiments with this method were made with TEM instruments (Nielsen and Cowley 1976) and spectacular results on the surfaces of semiconductors have been obtained when an ultra-high vacuum instrument, with facilities for specimen treatment, has been used (Osakabe *et al* 1981).

STEM instruments have special capabilities for this type of surface research in that the imaging by scanning reflection electron microscopy (SREM) may be correlated with microdiffraction and microanalysis from any chosen small part of the imaged region (Cowley 1980). The vacuum in the specimen chamber is good enough for some surface work (10^{-9} torr or better) and allows surfaces to be kept reasonably clean and free from contamination.

The microdiffraction patterns obtained from surfaces in this mode are similar to the well-known RHEED (reflection high energy electron diffraction) patterns with the incident beam making glancing angles with the plane of the surface. With a convergent incident beam, the diffraction spots become lines and these are frequently seen to be doubled (figure 7a). The outer component of each spot is given by transmission through projections or crystal edges. The inner component comes from flat surface areas and so is displaced by refraction at the surface. By placing the collector aperture in a STEM instrument on one or other of these components, the transmission and reflection images can be formed separately. Figure 7b, for example, is the image of the surface of a small octahedral NiO crystal having overall dimensions of about $1\text{ }\mu\text{m}$. The image is strongly foreshortened because the incident beam makes an angle of about 5×10^{-2} rads with the surface but a useful picture of the surface structure may be obtained. In such images surface steps of height 2–3 Å have been detected and a lateral resolution of about 10 Å has been achieved (Cowley 1982). The technique has obvious applications for the study of surface reactions and the effects on surfaces of various treatments.

In principle the diffracted beams from a surface may be used for ELS microanalysis or microanalysis may be achieved by spectroscopy of the emitted x-rays. Since, when a strong diffracted beam is produced, the penetration of the electrons into the surface may be as little as 10–20 Å, these methods should provide an important new possibility for the chemical analysis of thin surface layers. As yet these methods are not well developed.

Some striking results have been observed with a slightly different geometry. If a crystal such as that of figure 7 is turned so that the face of the crystal is exactly parallel to the incident beam, a diffraction pattern is produced which suggests that electrons have been channelled along the surface. They are deflected towards the crystal by the

Figure 7. **a.** Convergent beam microdiffraction pattern from the surface of a crystal of MgO showing the doubling of diffraction spots due to refraction effects. **b.** Scanning reflection electron microscopy image of the (111) face of a small octahedral NiO crystal using the (444) reflection.

potential field extending from the crystal into the vacuum. Then in striking the crystal they are reflected out by Bragg diffraction but cannot escape the potential field and so continue in an oscillatory path along the surface (Cowley 1981a).

Because electrons which have been channelled in this way have travelled for large distances close to the surface they show strong peaks in the energy loss spectra corresponding to the electronic excitations and radiations generated at surfaces. For example figure 8 shows an ELS spectrum obtained by transmission through the edge of a crystal of NiO and spectra obtained when the electrons traverse a crystal face. For the

Figure 8. a. ELS spectrum obtained in transmission through a NiO crystal. b. Series of ELS spectra obtained as a beam of about 15 Å diameter, running parallel to the flat face of a NiO crystal, is moved successively closer to the face. The total lateral movement of the beam is about 50 Å.

latter, the energy losses associated with bulk excitations are scarcely visible. Instead there are strong new peaks in the 0–30 eV energy loss range.

Some of these peaks are undoubtedly due to the excitation of surface electronic states. Others, and especially the prominent peak at about 14 eV energy loss have been attributed to the generation of transition radiation at a frequency corresponding to the periodic oscillations of the electrons in and out of the surface as they are channelled along the face (Cowley 1981b). Transition radiation has been observed in other contexts and is associated with the fluctuation of the polarization field created by a charged particle at the surface of a dielectric. Its generation at a particular frequency due to an oscillatory motion is, however, a new and interesting phenomenon.

It now appears that the use of high voltage electrons in TEM and STEM instruments will provide a valuable new range of techniques for the study of surfaces, complementing the established methods of LEED, AES, SIMS, etc. In comparison with these well-known techniques, high spatial resolutions are possible, on the Å or nm scale rather than the μm scale. So far the interpretation of the high energy reflection diffraction intensities

has not progressed as far as for LEED and the sensitivity of the surface microanalysis techniques does not match those of the established techniques but the fact that some diffraction and analytical data can be derived from very small areas of a surface and can be related to information from images of quite high resolution suggests that efforts to refine and develop these techniques will be amply rewarded in the near future.

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