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Scanning microdiffraction of polymers

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Scanning transmission electron microscopy (STEM) has been suggested to have advantages over conventional transmission electron microscopy (CTEM) for the observation of diffraction contrast features and diffraction patterns from radiation-sensitive crystalline polymers. For many applications it is desirable to obtain successive diffraction patterns from very small adjacent areas. Several microarea diffraction techniques are available using CTEM and STEM. The most useful technique is scanning microarea diffraction used in conjunction with STEM dark-field imaging. Using this technique we have obtained diffraction patterns from regions as small as 100 nm × 100 nm for a 12 nm thick polyethylene single crystal. Adjacent microarea diffraction patterns can be obtained while only radiation-damaging the diffracting region. This allows mapping of the specimen crystallography on a very fine scale as well as allowing one to obtain a diffraction pattern for selecting various STEM dark-field conditions while only damaging a small portion of the specimen before the dark-field image is recorded.

1. Introduction

The chief limitation to the use of electron microscopy for the study of crystalline polymers is the radiation damage produced in the polymer by the electron beam. Early workers were quick to discover that polyethylene crystals changed contrast and their diffraction patterns faded in a fraction of a second when viewed under an intense electron beam [1]. Observations of diffraction contrast features (such as dislocations and fold domain boundaries) and recording of diffraction patterns are possible but are severely limited due to the damage of the crystalline lattice by the electron beam [2, 3]. Scanning transmission electron microscopy (STEM) has been suggested to have an advantage over conventional transmission electron microscopy (CTEM) for two principal reasons: (1) the collection efficiency of scattered electrons is higher for STEM than for CTEM [which results in higher S/N ratios in the image for a given incident electron dose (or equivalently a reduced specimen dose is possible for the same quality image)] and (2) microarea diffraction patterns may be obtained without cumulative radiation damage to adjacent areas.

For many problems of interest in material science, it is desirable to know the local crystal structure and orientation and to be able to follow changes in the sample structure and orientation into adjacent areas. Recently, Low *et al.* [4], have successfully obtained STEM *fixed* beam microarea diffraction patterns from adjacent areas with beam diameters as small as 0.1 μm in 300 to 700 mm thick spherulitic polyethylene films. In this paper we demonstrate the usefulness of STEM *scanning* beam microdiffraction for radiation sensitive polymers and determine the minimum sample volume of polyethylene required for suitable diffraction patterns of single crystals.

2. Experimental technique

It is informative to briefly review three techniques now available for obtaining diffraction patterns from limited sample areas. The first two techniques are possible with a CTEM; the rocking beam microdiffraction technique requires an STEM.

Conventional selected-area diffraction (SAD) patterns are obtained in CTEM by using a large diameter, parallel beam of incident electrons on the sample with a field limiting aperture (the SAD

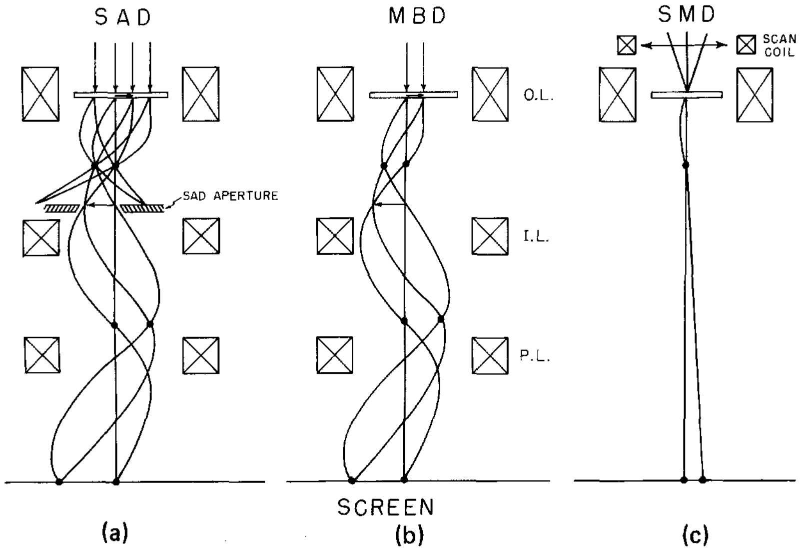

Figure 1 Schematic ray diagrams of various diffraction geometries. (a) CTEM – selected area diffraction. A large area of the specimen is illuminated with a paraxial beam of electrons. The SAD aperture in the first image plane of the intermediate lens limits the area on the specimen that contributes to the diffraction pattern. (b) CTEM – microbeam diffraction. A small static paraxial beam of electrons is incident on the specimen. The area contributing to the diffraction pattern is determined by the position and size of the microbeam. (c) STEM – convergent beam scanning microdiffraction. A fine convergent beam of about 20 nm diameter is scanned over the sample. The area contributing to the diffraction pattern is determined by the area scanned.

aperture) placed in the first image plane of the intermediate lens (see Fig. 1a). The minimum diffraction area is determined by the size of the SAD aperture and the spherical aberration of the objective lens (i.e. diffracted electrons from outside the area defined by the SAD aperture contribute to the diffraction pattern). Spherical aberration limits the minimum diffraction area to several hundred nanometers for 100 keV CTEM. Moreover the large incident beam size on the sample eliminates the possibility of recording successive patterns from adjacent areas for radiation sensitive materials.

Microbeam diffraction (MBD) is also possible with a CTEM by using a strongly excited first condenser lens and a very small second condenser lens aperture (typically 20 μm) to illuminate the sample with a fine parallel beam of electrons (see Fig. 1b). Since no field-limiting aperture is used, the spherical aberration of the objective lens does not play a role and the minimum diffraction area is the incident beam diameter (c. 250 nm). Because the incident beam only illuminates the area of interest, successive patterns may be obtained from adjacent areas. The only drawbacks are the 250 nm size limitation, the non-uniform intensity distribution across the illuminated area (approximately Gaussian), and lack of a precise means of repositioning the beam to an adjacent area of interest.

STEM microdiffraction uses the strongly excited objective lens in a STEM to focus a fine static electron probe on the sample (convergent beam diffraction). The diffraction pattern formed is then magnified by the lower half of the objective lens. The sample area producing the diffraction pattern is determined again by the incident beam diameter. The beam diameter is fixed by the objective and condenser lens settings and the technique is essentially the same as CTEM-MBD but with much smaller incident beam size due to the strong focusing action of the objective lens. Typical values for a tungsten hairpin filament source operated at 100 keV are 20 nm probe size with angular aperture of the convergent beam about 1×10^{-3} rad.

Recently, a second STEM microdiffraction method has been developed employing a rocking incident beam. The sample is positioned midway between the objective lens pole pieces such that a nearly parallel incident beam can be rocked about a point lying in the specimen plane. In this manner diffraction patterns have been obtained from 3 nm diameter metal crystals [5]. This is approximately the theoretical minimum crystal size for a meaningful diffraction pattern of about 5 times the unit cell size.

3. Results and discussion

The main obstacle to the sucessful application of microdiffraction to polymers is, of course, radiation damage. The minimum polymer sample size which can form a useful diffraction pattern is limited by the insufficient S/N statistics in the scattered peaks at low doses and destruction of the crystal by radiation damage at high doses. Experiments empolying the two standard STEM microdiffraction techniques using a JEOL 100 CX "TEMSCAN" with 20 nm electron probe and 12 nm thick polyethylene single crystals indicated severe radiation damage occurred before a diffraction pattern of the crystal could be obtained. To adopt STEM microdiffraction for radiation sensitive polymers the following procedure was developed (see Fig. 1c): the microdiffraction mode of the STEM is selected and the optics are adjusted for the normal convergent beam diffraction pattern at × 100 000 magnification. However, instead of operating in the spot scan mode (stationary beam) the selected-area frame scan mode is used. The selected-area scan is adjusted to scan a square area W cm × W cm on the CRT (corresponding to $W \times 10^2$ nm by $W \times 10^2$ nm on the sample). A *scanning* beam microarea diffraction pattern can thus be viewed on the fluorescent screen. By systematically varying the size of the scanned area and recording (using the normal electron image plates) diffraction patterns at fixed incident beam current, we determined that an area approximately 100 nm × 100 nm is the smallest area which yields a "useful" pattern (see Fig. 2). The usefulness of a particular diffraction pattern will, of course, depend on what information is required. There will be a sacrifice of signal to noise ratio for smaller diffraction volumes. The criteria for a useful pattern will also depend on the radiation damage characteristics of the particular reflections of interest. Some reflections simply weaken and disappear as the crystal damages whereas others weaken, shift and broaden, eventually forming an amorphous halo.

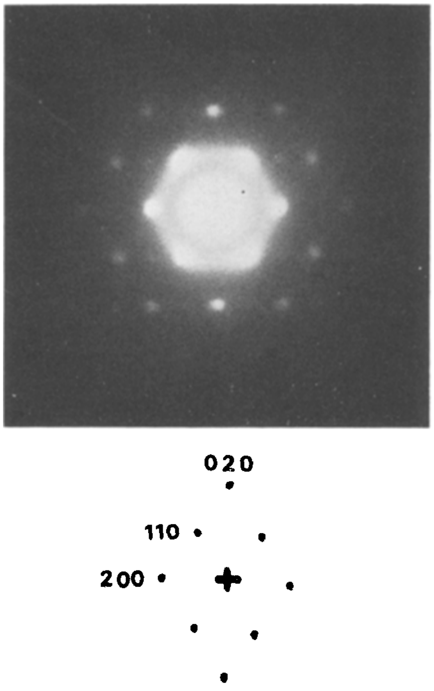

Figure 2 Scanning beam microarea diffraction pattern obtained from 100 nm × 100 nm area of a polyethylene crystal.

The essential differences between microbeam diffraction (MBD) and scanning microbeam diffraction (SMD) are incident beam diameter and beam divergence. To compare MBD and SMD, it is necessary to assess the effect of beam divergence and diameter on the scattered peak intensity and peak width. To resolve a given reflection in an electron diffraction pattern requires a sufficient signal/noise ratio and a sufficiently narrow peak breadth.

The effect of beam divergence will be to decrease the diffracted intensity and to broaden the reflections. Assuming kinematical scattering, the scattered intensity will vary as

$$I(s) \sim \frac{\sin^2 \pi s t}{\sin^2 \pi s}$$

where t is the crystal thickness parallel to the electron beam and s is the deviation of the incident beam from the Bragg condition ($s = 0$).

An overestimate of the decrease in the diffracted intensity due to beam divergence can be made by assuming all incident electrons to have a deviation from the Bragg condition equivalent to the beam divergence (e.g. 1×10^{-3} rad). For the 1 1 0 reflection of a 12 nm thick polyethylene crystal, this amounts to less than a 1% decrease in the scattered intensity.

Neglecting radiation damage and paracrystalline line-broadening contributions, the observed peak width will be:

$$\delta\beta^2 = \delta\beta_D^2 + \delta\beta^2\phi$$

where $\delta\beta_D$ is the broadening due to the beam diameter (effective crystal size) and $\delta\beta\phi$ is the broadening due to beam divergence.

Beam divergence and beam diameter are in general inversely related – for our conditions the beam divergence for a 100 nm beam is five times less than for the 20 nm beam. The contribution to the line broadening from beam size will usually be negligible in comparison to that from beam divergence.

Therefore, for a given total area illuminated and total incident beam intensity the MBD pattern will exhibit sharper reflections because of the inherently lower divergence of a larger incident beam.

The scanning beam diffraction patterns obtained exhibit broadened diffraction spots typical of the convergent (stationary) beam technique. High order reflections can be observed out to the available limit of 2θ. The strong 1 1 0 and 2 0 0 polyethylene reflections are superimposed on an amorphous halo which forms as the crystal becomes damaged during the diffraction pattern exposure. Since the selected scan area can (with the beam off) be electronically adjusted to any rectangular size and shape and as well accurately repositioned in two perpendicular directions on the sample, successive adjacent area scanning microdiffraction patterns can be obtained very routinely.

To demonstrate that such microarea diffraction patterns do, indeed, result from a 100 nm × 100 nm specimen area, we recorded STEM dark-field micrographs of a polyethylene crystal before and after obtaining scanning microdiffraction patterns (see Fig. 3). Initially a low dose 1 1 0 STEM dark-field micrograph was obtained of a single crystal, then a total of eight successive scanning microdiffraction patterns from adjacent areas of the same fold domain were obtained. The crystal was then re-imaged in 1 1 0 dark-field. As can be seen, eight small square regions are dark due to the loss of crystallinity from the local high dose required for each of the diffraction patterns. The dimensions of each region and their corresponding mutual orientation are consistent with that expected from the scanning diffraction geometry. Moreover, the remaining adjacent areas are still quite undamaged.

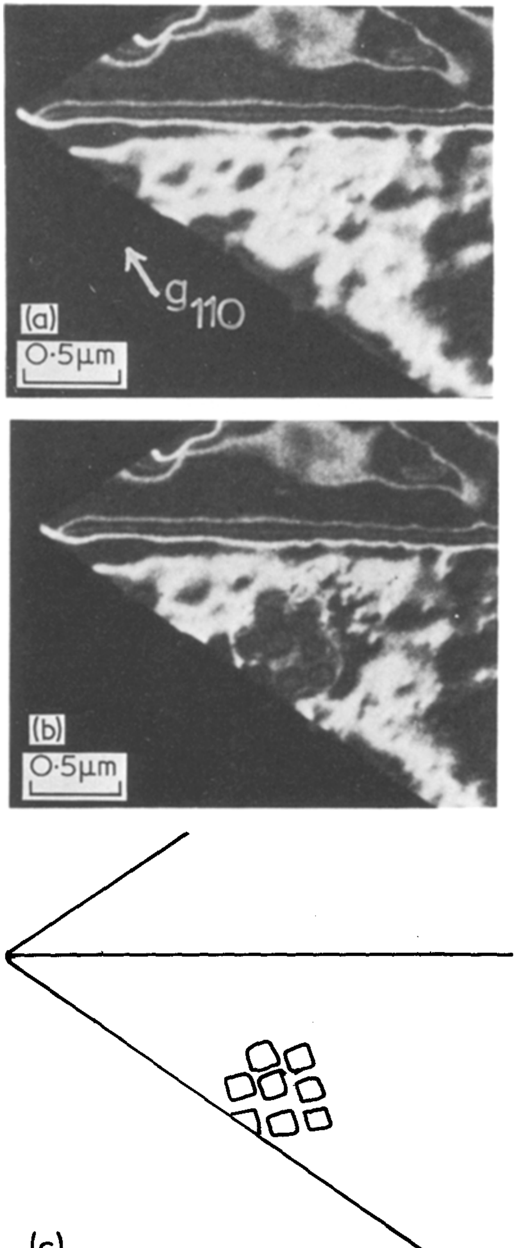

Figure 3 1 1 0 STEM dark-field micrographs of polyethylene single crystal. (a) Crystal before scanning microarea diffraction. (b) Crystal after eight successive scanning microarea diffraction patterns. Dark regions indicate loss of crystallinity in the regions used for diffraction patterns while the rest of crystal has remained undamaged. (c) Schematic drawing showing location of each 100 nm × 100 nm region used for forming each scanning microarea diffraction pattern.

The conditions we have used for the scanning microdiffraction are an incident beam diameter of 20 nm, incident beam current of approximately 5×10^{-13} A, beam divergence of approximately 1×10^{-3} rad (20 µm second condenser aperture), and the "rapid scan 2" mode which yields a beam velocity on the sample of 5×10^{-3} cm sec^{-1} horizontally and 1×10^{-5} cm sec^{-1} vertically (500 line scans/frame). The diffraction pattern fades in approximately 4 sec for these conditions. Assuming that the average current density can be approximated by the beam current divided by the area scanned, the total dose/cm^2 is then just the average current density times the exposure time. The calculated value of 2×10^{-2} coulomb cm^{-2} is in reasonable agreement with published values of the crystal lifetime dose for polyethylene at 100 keV at room temperature [2, 6]. Calculations also show that for the beam current density employed ($\sim 0.16\,A\,cm^{-2}$), sample temperature rise due to electron-beam heating should be negligible [7]. The only limitations of scanning microdiffraction are the maximum 2θ allowed by the inner bore of the microscope column (for our JEOL 100 CX $2\theta_{max} \simeq 3 \times 10^{-2}$ rad, e.g. reflections out to about 0.12 nm are obtainable, line broadening due to somewhat larger beam divergence than for MBD and the maximum scan distance along the sample due to inclination of the incident beam to the specimen surface as the beam scans across the sample.

The minimum sample volume for diffraction from polyethylene at 100 keV and room temperature is, therefore, approximately $10^5\,nm^3$ (e.g. 100 nm × 100 nm × 12 nm). This is diffraction from about 4 million carbon atoms. The ultimate spatial resolution would be set by using a single crystal sample of maximum thickness. For polyethylene at 100 keV this single scattering thickness is on the order of 100 nm. Thus the minimum area for a useful microdiffraction pattern from a 100 nm thick polyethylene film is $10^3\,nm^2$.

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