Annular bright and dark field imaging of soft materials

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Abstract. Here polyethylene, as an example of an important soft material, was studied by STEM annular bright and dark field. The contrast as function of the probe size/shape and the detector collection angle are discussed. The results are compared to conventional bright field transmission electron microscopy, electron energy filtered imaging and energy dispersive spectroscopy mapping. Annular bright and dark field gave a higher contrast than conventional transmission and analytical mapping techniques.

1. Introduction

The properties of soft materials are determined by their microstructure. To control, design and optimise these properties, it is necessary to observe the morphology at different size scales. Transmission electron microscopy (TEM) techniques can offer the nm-scale spatial resolution. However, the beam sensitivity and the relatively poor contrast due to the weak scattering are limiting factors for studying soft materials. The contrast \( C \) is the relative change in image brightness \([1]\):

\[
C = \frac{I_1 - I_2}{I_2}
\]

The contrast improves when the average intensity of an image decreases. However, lowering the average intensity will lead to a poor signal-to-noise ratio (S/N) and hence a noisier image. The low contrast could also influence the resolution, defined as the minimum distance between two features, which still can be distinguished from each other. If the contrast is particularly low (< 5%), interesting structural features could be missed, despite having a sufficient instrumental resolution. This is commonly the case for soft materials. Staining with heavy elements is often applied to enhance the mass-thickness contrast \([2]\).

Annular bright field (ABF) and annular dark field (ADF) scanning transmission electron microscopy (STEM) have some advantages over conventional TEM techniques, e.g. a lower electron dose, and a better control over the signal’s and image’s contrast/brightness. In addition, ADF is more integrated with analytical techniques and has a higher signal collection efficiency \([1,2]\). A Z-dependent high angle ADF image is formed by incoherently scattered electrons. Hence, it can take advantage from the Z difference introduced by the staining procedure. However, this Z-contrast has, despite the apparent advantages, not yet been systematically studied for soft materials.
In this work, the contrast of negatively stained polyethylene (PE), an important soft material, is studied in ABF and ADF-STEM as a function of the probe size/shape and collection angle. The contrast is compared to that of conventional bright field TEM (BF TEM), electron energy filtered imaging (zero loss and core edge loss EFTEM) and energy dispersive spectroscopy (EDS).

2. Experimental

Ultramicrotomed thin PE foils were studied using a 200 kV field emission TEM/STEM (Jeol 2010F, Cs= 1 mm). The foils were stained with chlorosulphonic acid. The contrast was further increased by uranyl acetate. To reduce beam damage, the sample was cooled down to -160°C. Additional ABF and ADF images were taken at 25°C. A 2k CCD (Gatan Multiscan) was used for BF TEM, zero loss filtered BF TEM and EFTEM. STEM images were recorded with a Jeol bright field and a high angle ADF detector (9-170 mrad). Two types of probe were used: a broad 1.0 nm analytical (ANA) probe (convergence angle 24 mrad) for maximum signal and a sharp high resolution (HR) probe of 0.2 nm diameter (convergence angle 10 mrad). The point resolution was 2.3 Å in BF TEM, 2 Å for HR ABF/ADF and ~ 1 nm for ANA ABF/ADF and EFTEM. Here, the resolution was not systematically studied nor was it necessary to approach these instrumental resolutions limits.

For the STEM imaging, the signal brightness was minimised. The average signal intensity was controlled only with the signal’s contrast. The histograms of all images were inspected to assure that no artifacts were introduced by black-level clipping [3]. No additional post acquisition image processing routines were applied. By using the 1.0 nm probe, EDS and EELS maps and line scans were recorded using an Oxford INCA system and a post column energy filter (Gatan GIF 2000).

3. Results and discussion

The crystalline regions appeared bright in ABF and dark in ADF (Figures 1(a-b)). ADF gave a 3 to 4 times higher contrast than ABF when the ANA probe was used. The degree of staining was higher adjacent to the crystalline regions. The chlorosulphonic acid diffuses into the amorphous regions. The uranyl acetate enhances and stabilises the contrast further, because U deposits at the lamella surface (unsaturated C=C) [1,2]. Additionally to the high contrast, the ADF suggested a finer texture between the crystalline lamellae (Figure 1(c)). This texture could not be resolved in the ABF images or any of the imaging conditions discussed below. The contrast values as determined by (1) from a line scan (box in Figure 1(a)) strongly depended on the local staining efficiency and the defocusing value.

Increasing the collection angle of the ABF detector hardly affected the image contrast, brightness and total appearance. This was due to the fact that most electrons, which formed the ABF image, are scattered within the first 5 mrad. It was important that the ABF detector was symmetrically aligned with respect to the scattering pattern. The ADF signal depended slightly on the collection angle range. Increasing the collection angle led to a slight decrease in contrast and S/N. The smallest collection angle range gave the highest contrast, but the image was less incoherent. An inner collection angle of around 25 mrad gave the best overall results.

The contrast of both ABF and ADF decreased dramatically with the 0.2 nm HR probe (Figure 1(d-e)). The importance of a strong signal for STEM has also been suggested on the basis of theoretical considerations [4]. The resolution in ABF and ADF deteriorated, because of this reduced contrast. In ABF, the contrast was collection angle independent, while in ADF it decreased with increasing collection angle. At low collection angles the image quality was governed by the poorer S/N. An advantage of the 0.2 nm HR probe compared to the 1 nm ANA probe is the lower electron dose on the sample. The HR probe could therefore be used at room temperature without damaging the TEM foil (Figure 1(f)). The contrast of ABF at room temperature and -160°C was comparable. However, the contrast of ADF was roughly four times weaker at room temperature than at -160°C. The contrast of ADF was always higher than that of ABF under comparable conditions.
In conventional BF TEM the crystalline regions appeared bright on a gray background as can be seen in Figure 2(a). The contrast for BF TEM was strongly reduced, 2-100 times, compared to the ABF and ADF. For the human eye the BF TEM images might be more aesthetic, because the contrast is less hard ("black and white") than in the ABF and ADF images. By using a smaller objective aperture, the apparent mass-thickness contrast increased, however the S/N ratio decreased. The sum of 10 exposures at half the saturation value for the CCD increased the total image signal, but did not improve the contrast. Zero loss filtering made the images crispier, but also noisier. The contrast as defined in (1) for an averaged line scan did not change. It appeared that zero loss enhanced more the contrast of the foil surface, not the contrast between the amorphous and crystalline regions. Mainly the unstained regions with the lower Z and hence higher inelastic scattering, benefited from zero loss filtering [5].

The staining introduced compositional differences between the amorphous and crystalline regions. These differences could in principle be visualised by EDS mapping. However, after 20 minutes mapping (with active drift composition) only the Cl and U maps showed a very weak contrast between amorphous and crystalline regions. These maps were noisy due to the low detected signal. EDS line scans turned out to be a more efficient way to detect the crystalline regions. The contrast from the EDS line scans was comparable to ADF with HR probe at -160°C. The U signal suggested an increased U content in the amorphous regions adjacent to the crystalline regions (EDS not shown here).

The EELS spectrum exhibited a strong C K and a weak O K edge with no apparent difference in the fine edge structure between the amorphous and crystalline regions. Strong edges from U O4,5 at 90-120
eV and $U_{\text{rel}}$ at 755-795 eV were present. The low loss spectra showed that the thickness relative to the electron mean free path was 0.31 and constant over the scanned interface. The clear difference in the EELS edges between the amorphous and crystalline regions, was used to map the two different phases using EFTEM (Figure 2(c)). EFTEM mapping depicted the morphology, but the images were noisy due to low counts. The contrast in EFTEM was comparable to BF TEM.

![Figure 2](image)

**Figure 2.** (a) Bright field TEM image with 20 µm (4 mrad) objective aperture. (b) Zero loss filtered using a 10 eV slit. (c) EFTEM image (113-123 eV, $U_{\text{rel}}$).

### 4. Conclusions

ADF gave the highest contrast between amorphous and crystalline regions in stained PE. ABF images also had a higher contrast than the conventional TEM imaging and the analytical techniques used here. ADF with the bright probe was able to resolve a fine texture within the amorphous region, which was not visible using any of the other imaging techniques. Both ABF and ADF were relatively insensitive to the collection angle range when a bright scanning probe was used. The signal from the weaker HR probe resulted in noisier and less contrast-rich images, but this probe can be used at room temperature and still have a better contrast than the conventional TEM imaging techniques. The signal of the HR probe was too low to do simultaneous EDS or core loss EELS mapping. For this less intense probe, the inner collection angle for ADF should be small enough (~25 mrad) to obtain a high enough signal. This comparative study showed that ADF is the preferred technique for imaging stained soft materials.

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