Quantification of ADF STEM images of molybdenum chalcogenide nanowires

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Abstract. Molybdenum chalcogenide nanowires have potential applications in some of the same areas as carbon nanotubes but are, as yet, not as well understood structurally. Previous investigations to determine atomic structure using x-ray diffraction and high-resolution transmission electron microscopy have been inconclusive. Images obtained using an annular dark field detector in an aberration corrected scanning transmission electron microscope have provided an additional means of structure determination. Simulations of the electron scattering within the sample were performed by including thermal diffuse scattering into a multislice routine. Such simulations allow insight into the location of certain atomic species and the nature of the packing into bundles of the wires. It is also shown that for structure refinement, a simple object function approach is sufficient, rather than a full dynamical calculation.

1. Introduction

Nanotubes have become highly sought after items in the nanotechnology sector due to their impressive electronic and mechanical properties. One of their possible uses would be as nanowire interconnectors for the fabrication of nanoscale devices, potentially revolutionising the electronics industry. Molybdenum chalcogenide based systems that form 1-D molecular chains may have many of the potential applications of carbon nanotubes but without some of their disadvantages [1]. A particular example of these types of systems is the group of nanomaterials having the stoichiometric form Mo$_{6}$S$_{9}$$_{-x}$I$_{x}$. These nanowires typically form bundles with diameters as small as 4 nm.

While the stoichiometry is usually known, the exact atomic structure remains difficult to determine. The small size of the nanowire bundles is a significant setback for some of the techniques traditionally employed for structure determination. Efforts using X-ray diffraction have been inconclusive due to packing anomalies such as shearing, defects and kinks. The nanowire bundles are often supported on a substrate which makes phase contrast high resolution transmission electron microscope (HRTEM) imaging difficult for very narrow bundles.

Using an annular dark field (ADF) detector in the scanning transmission electron microscope (STEM), it is possible to directly image the atomic configuration of the nanowire bundles. In addition, not only is direct imaging possible but it is also possible to examine and characterise the anomalies mentioned above as they are no longer a hindrance for this local imaging technique. Atomic resolution ADF STEM provides images with what is known as Z contrast, the intensity varies approximately as the square of the atomic number ($Z^2$). Thus, sample sizes can be significantly smaller than those used in HRTEM, as the sample can always be differentiated from...
the support film. The major advantage ADF STEM has over HRTEM is that it is not a phase contrast image, and does not show the contrast reversals often seen in HRTEM [2]. However, due to the complicated structure and packing irregularities, a full compositional interpretation of ADF images can only be performed alongside simulations of the electron scattering within the bundles.

2. Annular Dark Field Simulation
Dynamical scattering calculations were performed by incorporating the effects of thermal diffuse scattering (TDS) into a multislice approach. The multislice technique involves dividing the sample into a series of thin slices and calculating the contribution to the cross-section at each slice. Images resulting from high-angle scattering out to the ADF detector are formed via predominantly incoherent scattering processes. We have assumed that the incoherence is dominated by scattering from phonons, the mechanism behind TDS. The Einstein approximation is invoked by assuming all phonons within the sample oscillate at the same frequency, independent of the wavelength. As there are no correlated phonons, the vibration of an atom is independent of its neighbours. Thermal smearing of the atomic potential is obtained through the introduction of a Debye-Waller factor.

The essentials of the incoherent scattering are included into a multislice routine via the use of the mixed dynamic form factor (MDFF) [3]. The MDFF for ADF contrast is a quantity which depends upon two reciprocal space vectors and is often referred to as defining a ‘non-local’ potential. For both ease of application and visualisation, a ‘local’ approximation is often made and the MDFF then only depends upon the difference of these two reciprocal space vectors. Making the local approximation allows for the definition of an incoherent scattering potential. Two local scattering potentials are defined: The total inelastic scattering is included through the use of the usual absorption potential, $V'_{\text{abs}}$. Only a fraction of this scattering will reach the annular dark field and so a second potential, $V'_{\text{ADF}}$, is used to compute this fraction. The total absorption is calculated at each slice by evaluating the integral of the product of the electron intensity and the incoherent scattering $V'_{\text{abs}}$. The scattering from each slice to the detector is computed using only $V'_{\text{ADF}}$, and is then summed over all the slices.

Typically, calculations of this type require a ‘unit cell’ to be tiled, creating a supercell. The large real space supercell increases the sampling in reciprocal space, which needs to be sufficiently fine in order to sample both the probe aberrations, the Fresnel propagator and the scattering potential accurately. The equivalent real space picture is that the specimen size must be large enough to contain the probe spreading which occurs during propagation and the electron scattering. A single unit cell is usually not adequate.

We have assumed an 100 keV, aberration-free probe with a 22 mrad probe forming aperture. The ADF detector spanned a range of 70-210 mrad. The size of the unit cell is 35 Å x 35 Å distributed over 512 x 512 pixels. The nanowire bundle contains seven nanowires and is approximately 28 Å thick. Thus the maximum scattering angle contained within this cell is 560 mrad, which is much greater than the convergence angle of the probe and well beyond any scattering likely to occur within the bundle. Therefore, there is sufficient reciprocal space sampling without additional tiling. The simulations were performed using the Melbourne STEM program developed by L J Allen, S D Findlay and M P Oxley [3]. It should be noted that the calculation considers single channelling only. Inelastically scattered electrons are assumed to not undergo any further scattering events. Higher-order Laue zone (HOLZ) effects are also ignored.

3. Results from the Full Dynamical Scattering Calculation
Electron microscope images of molybdenum chalcogenide based nanowires (of stoichiometric form Mo$_6$S$_3$I$_6$) were taken using the aberration-corrected 100 keV electron microscope at the SuperSTEM facility in Daresbury. One such ADF STEM contrast image is shown in Figure 1.
The sulphur atoms are unlikely to be imaged in this situation due to their low atomic number with respect to the molybdenum and iodine. However, the individual wires in the bundle are clearly resolved and the location of atoms along the wire can also be seen. A simulated ADF STEM image of a seven wire bundle is shown in Figure 2.

Figure 1. ADF STEM image of a molybdenum chalcogenide nanowire bundle. The data was taken using the 100 keV electron microscope at the SuperSTEM facility in Daresbury. The microscope is fitted with a NION aberration corrector.

Figure 2. ADF STEM image simulation for a seven wire bundle. The incident energy of the aberration-free probe is 100 keV with a probe forming aperture of 22 mrad. The ADF detector is 70-210 mrad. Inset: Schematic of the bundle in cross section

A ‘backbone’ can be seen through the middle of the simulated bundle, a result of a number of molybdenum and iodine atoms being in projection. There is an apparent zig-zag pattern through this backbone which is repeated in the peripheral regions of the bundle, albeit to a less obvious extent. A minimum of three nanowires in projection was necessary to obtain this pattern. The same zig-zag pattern, while not as clearly resolved in the experimental images, is visible in the top right region of the image. We have, however, noted a discrepancy between simulation and image in the configurational relationship between neighbouring wires in a bundle. Structure refinement is currently underway and will be presented in a future publication.

4. Object Function Approximation
The object function approximation is, in this case, a reasonable approximation to make as both the wires and bundles are thin and strong channelling conditions do not exist. Supplementary investigations have shown that the contribution from HOLZ scattering is small and ignoring this in the full simulation was justified. If the effects of dynamical scattering are also ignored, then the ADF image may then be simply regarded as a convolution of some object function with the probe intensity function. The object function is taken to be the projected potential raised to a power $\gamma$. Rutherford scattering from a pure Coulombic potential would give $\gamma = 2$ but scattering from a screened potential would be expected to yield a dependence of $\gamma < 2$. Shown in Figure 3, is an image calculated by raising the projected potential to the power of 1.7 and convolving it with the probe intensity function formed assuming a 22 mrad aperture with negligible aberrations. In order to compare this calculation with the full simulation shown in Figure 2, line profiles were taken from both the full simulation and the approximation along the
Figure 3. Simulated image calculated assuming an object function approximation. The projected potential was raised to the power of 1.7 and convolved with the probe intensity assuming a 22 mrad probe forming aperture.

Figure 4. (a) Line profile from the full simulation. (b) Line profile from the object function approximation.

lines (A) to (B) as indicated on the respective figures. The line profiles are shown in Figure 4. The relative peak heights compare extremely well and it is interesting to note how well this approximation performs. We conclude from this that interpretation of the ADF image in terms of the atomic structure may be made directly from the projected potential.

5. Conclusions
We have shown that ADF STEM imaging is capable of delivering results and providing insight into structure determination problems where other traditional techniques have faced difficulty. The simulations, in combination with the experimental images, are able to help determine the location of different atomic species within individual chain molecules and the packing structure of the nanowires into bundles. Dynamical calculations have been performed, but for nanowire bundles of the type presented here, a simple object function approximation based on the projected potential suffices.

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