doi:10.1017/S1431927620017353
Microsc. Microanal. 26 (Suppl 2), 2020
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Measuring the Thickness of 2D Materials Using EDS

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dD materials, such as graphene, have been hailed as wonder materials due to their enhanced mechanical and electrical properties [1]. These properties change as a function of the sample thickness, specifically with respect to the number of stacked 2D layers. With graphene for example, once a multilayer structure is approximately > 10 layers thick it is no longer referred to as graphene and will exhibit the same properties as bulk graphite [2]. As monolayer graphene has a sample thickness of 0.335 nm and is a repeating lattice of Z=6 carbon atoms, it is challenging to observe and is typically imaged using advanced light microscopy, electron microscopy or AFM. Light microscopy utilises image contrast to calculate the number of 2D layers observed in a sample while AFM can measure the difference in step heights between 2 overlapping layers to determine the number of layers in a stack. Electron microscopy is a powerful tool for imaging 2D materials as it has the ability to resolve 2D materials atomically and gains enhanced contrast from atomic number contrast detectors. Currently the only method to differentiate the number of layers in a transmission electron microscope (TEM) is through the acquisition of selected area electron diffraction (SAED). This does not generate a direct thickness measurement resulting in a calculation of the number of 2D monolayers within an isolated stack. An estimation of the thickness can then be calculated by multiplying the number of monolayers with the reported thickness value of a single layer. This technique can be complicated as it does not directly report any chemical information so the user can not easily differentiate between different 2D materials and contaminants. The ability to chemically characterise 2D materials while imaging them can only be achieved through the combination of electron microscopy and energy dispersive x-ray spectroscopy (EDS).

EDS allows for the quantitative analysis of 2D materials to determine their elemental composition. For quantitative EDS within the TEM, the Cliff-Lorimer method [3] is the most widely used. This is due to its simple concept of relating the ratio of the element intensities with the ratio of element concentration. The classical Cliff-Lorimer method assumes a thin film criterion in which the sample is sufficiently thin enough that no X-ray fluorescence or absorption will occur within the sample. However, ignoring X-ray absorption can induce errors in the quantification results, when examining thick samples, light elements or combinations of elements with strong absorption. While the Cliff-Lorimer expression can be expanded to include an absorption corrector factor, it requires the mass thickness of the sample (sample thickness times its density) to be known. The ζ-factor method [4] was developed to solve this conundrum by solving for both the unknown composition and mass thickness of the sample but requires multiple thin film standards and an accurate beam current measurement. Besides the difficulty to produce, maintain and measure multiple thin film standards, very few TEMs are equipped with an integrated Faraday cup to measure the beam current. An alternative method is M^2T, an expanded Cliff-Lorimer approach that has been developed to utilise a single calibration standard [5]. The use of a single calibration standard removes the need for a beam current measurement. In addition to correcting for X-ray absorption and making the approach more accessible, the thickness of a sample can now be measured directly from an EDS spectrum.

We present the application of M^2T to measure the mass-thickness of 2D materials as a method to differentiate between mono and multilayer structures. A Si_3N_4 mass-thickness standard was used as the

https://doi.org/10.1017/S1431927620017353 Published online by Cambridge University Press

single calibration standard. The data was collected with an accelerating voltage of 200 kV on a JEOL 2100 using an Oxford Instruments X-max 80T EDS detector. Selected area electron diffraction was acquired to verify the number of layers of 2D material in each measurement. Figure 1 shows a TEM micrograph of the lacy carbon support film containing flakes of both monolayer and multilayer graphene. A SAED pattern, used to identify the number of graphene flakes in a layer, is included for monolayer graphene. Care was taken during EDS measurements to locate regions of sample that were free from detector occlusions and to minimise background signal originating from the Cu support grid. To ensure accurate thickness measurements the Cu EDS signal was deconvoluted from the spectrum before quantification. A range of different layer thicknesses were identified using SAED before being measured using the M^2T technique. Figure 2 shows a graphical representation of the thickness measurements against the number of layers of graphene. This result shows the expected linear relationship between the number of layers and layer thickness, with the thickness of a single layer of graphene being measured as **0.338 ± 0.02 nm**. This result agrees with the established thickness value of 0.335 nm. This demonstrates the accuracy of the M^2T down to layer thicknesses of less than 0.5 nm.

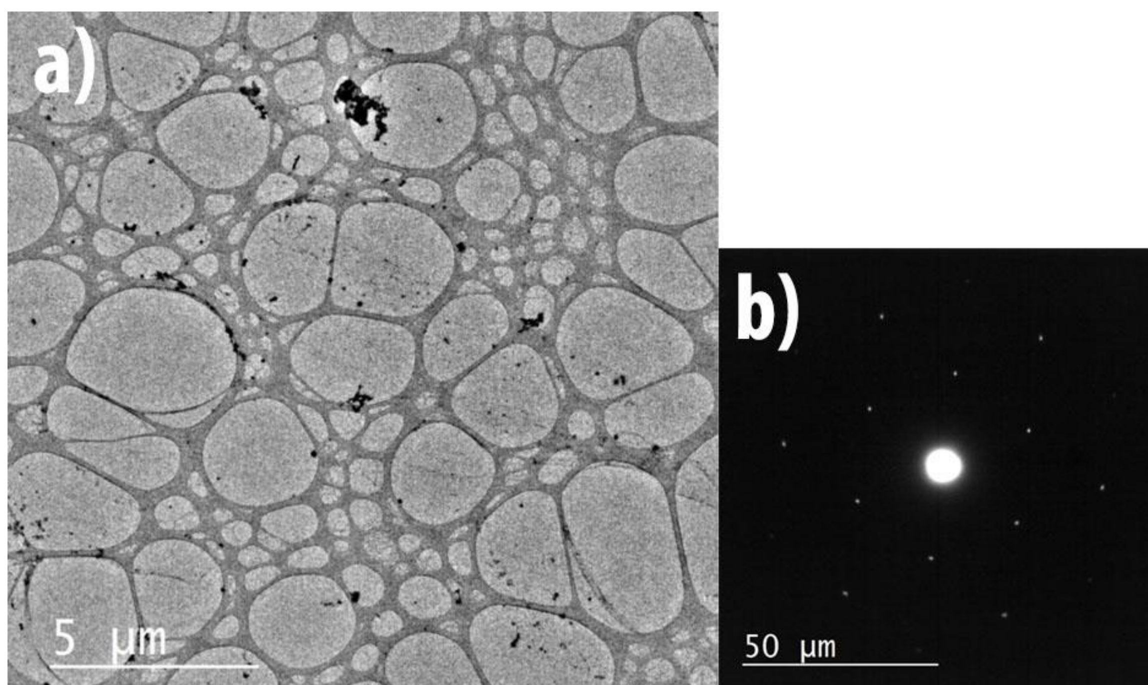

Figure 1. a) TEM image of graphene flakes distributed on a lacey carbon support film on a Cu grid. Care was taken to acquire EDS data from within the central regions of the Cu grids, on flakes over the vacuum to minimise erroneous spectra from the supporting grid and film. b) Inset SAED of a monolayer of graphene, used to identify the number of graphene layers being analysed.

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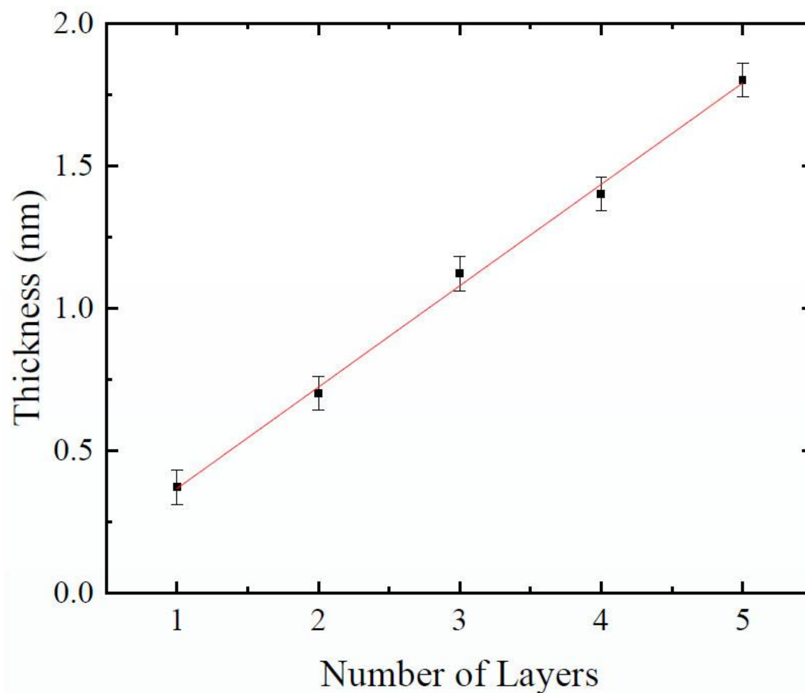

Figure 2. A plot of the measured graphene thickness, from the EDS data, against the calculated number of graphene layers.

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https://doi.org/10.1017/S1431927620017353 Published online by Cambridge University Press