doi:10.1017/S1431927619004690
Microsc. Microanal. 25 (Suppl 2), 2019

In-Situ Mass Thickness Calibrations Using MWCNTs

M. Malac[1,2], D. Homeniuk[1], M. Hayashida[1], T. Fujii[3], T. Yaguchi[3], R.F. Egerton[2]

1. NRC-NANO, Edmonton, Canada.
2. Department of Physics, University of Alberta, Edmonton, Canada.
3. Hitachi High-Technologies Corp., Hitachinaka-shi, Ibaraki-ken, Japan.

Bright field transmission electron microscope (BFTEM) images are often used to measure sample size in two dimensions (2D). Mass thickness (ρt) maps of the sample along the electron beam direction, although measurable with a monolayer precision [1,2], are seldom obtained. To measure ρt, a calibration sample is needed. We show that calibration can be obtained *in-situ* using multi wall carbon nanotubes (MWCNTs).

BFTEM contrast C for the purpose of ρt measurement is defined as $C = \log(I_0 / I_{tr})$ and is proportional to (ρt).

$$C = \log(I_0 / I_{tr}) = N_a A^{-1} \sigma \rho t \qquad (1)$$

Here I_{tr} is the intensity transmitted through a sample and the subsequent angle-limiting aperture. I_0 is the corresponding incident intensity in vacuum, N_a is the Avogadro number, A is their atomic weight and σ is the scattering cross section to angles larger than the collection angle [1-3]. To relate C to ρt in units of [μg/cm^2], the contrast C of objects with known ρt must be measured. MWCNTs have wall density of graphite (ρ =2.266 g/cm^3) and a core that is either hollow or contains other materials. The projected thickness of the MWCNT *wall* can be calculated, see Fig. 1, as function of distance x from its center in the specimen plane. The projected ρt of MWCNT can be written as:

$$\rho t = 2\rho\sqrt{R_1^2 - x^2} \qquad \text{for } R_2 < x < R_1 \qquad (2)$$

Here R_1 and R_2 are the external and internal radii of the MWCNT. Eq. (1) and (2) lead to

$$C^2 = (N_a A^{-1} \sigma)^2 4\rho^2 R_1^2 - (N_a A^{-1} \sigma)^2 4 \rho^2 x^2 \qquad (3)$$

that is in the form $y^2 = b - a x^2$. A linear fit to a plot of measured C squared as function of x^2 for a MWCNT, see Fig 2, yields $a = (N_a A^{-1}\sigma)^2 4\rho^2$ that relates measured C to ρt, as $\rho t = 2*\log(I_0 / I_{tr}) / \text{sqrt}(a)$, that can be evaluated at every pixel of an image, resulting in a ρt map. A fitted radius can be obtained as $R_1 = \text{sqrt}(b/a)$.

Experiments were performed in a Hitachi HT7700 equipped with a Gatan Orius SC200W camera and W hairpin filament, operated at 100 kV. A 12.4 mrad collection angle was defined by the objective aperture. A 19 nm-wide contrast profile of a clean segment of a MWCNT was extracted and fitted in Fig 2 for the x>0 (red) and x<0 (blue) sections of the MWCNT. The slope $a = 4.7\text{x}10^{-4}$ nm^{-1} (blue) and $3.7\text{x}10^{-4}$ nm^{-1}(red) for the respective sections of the MWCNT fit.

Fig. 3 shows ρt profile obtained from $2\log(I_0 / I_{tr}) / \text{sqrt}(a)$ in blue and red, simulation using Eq.1 and 2, and fitted R_1 and $N_a A^{-1} \sigma$ (R_1 = 11.2 nm in purple for the $x > 0$ region and R_1 = 11.4 nm in yellow for x<0 region). Fig.3 also shows simulated ρt using visually measured R_1 = 14 nm and fitted $N_a A^{-1} \sigma$(green). The fitted values of R_1 are an underestimate as compared to visual measurement of a BFTEM image, possibly due to presence of a Fresnel fringe at the edge of the MWCNT. The ρt obtained using fitted $N_a A^{-1} \sigma$ and experimental $C(x)$ in red and blue yields a good agreement with the expected ρt for visually measured R_1 (green). The mean difference of ρt over the MWCNT, indicated by an arrow in Fig. 3, is (-

0.2 ± 0.3) μg/cm². It indicates that the slope *a* yields a reasonable estimate of $N_aA^{-1}\sigma$, but the intercept *b* underestimates R_1.

Fig. 4 shows an example 2D ρt obtained by the above method. Part of the MWCNT area marked by a green rectangle was fitted to obtain the calibration constants *a* and *b*. Fig. 4. also illustrates the effect of diffraction contrast. To reduce the effect of diffraction contrast, a large collection angle should be used, although the large collection aperture reduces the slope *a* and thus sensitivity of the method [1, 2, 4].

References:

[1] T Fujii et al., Microscopy and Microanalysis **24**, p. 1612.
[2] H-R Zhang et al., Micron **43**, p. 8.
[3] L Reimer, H Kohl, Transmission Electron Microscopy 5th ed., Springer, 2008.

[4] We acknowledge Dr. Francisco Paraguay Delgado, CIMAV, Mexico, for kindly providing the MWCNT sample.

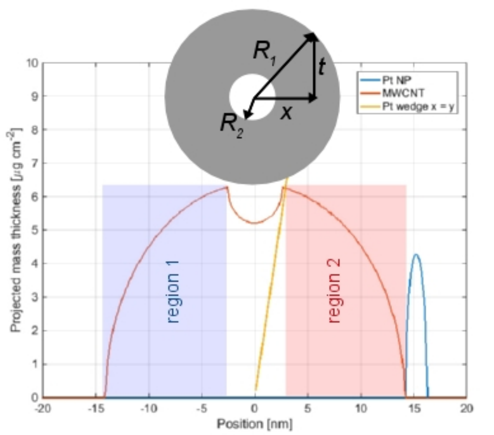

Fig 1. Simulated ρt of MWCNT (red) Pt NP (blue) and a 45° Pt wedge (yellow). The contrast is fitted over regions 1 and 2 separately. The blue region is flipped to the positive quadrant for the purpose of the fit. A schematic drawing of MWCNT cross section with outer radius R_1 projected thickness *t* is shown in grey. The yellow line can be used to interpret contrast of Pt NPs.

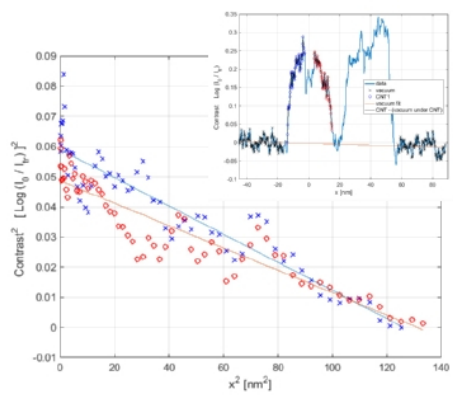

Fig 2. Contrast squared, C^2, plotted as function of square distance x^2 from the centre of the MWCNT. A linear fit for region 1 and 2, as indicated in Fig 1, allows to relate image contrast and known mass thickness of the MWCNT. Inset: raw contrast profile (see Fig. 4) and background removal.

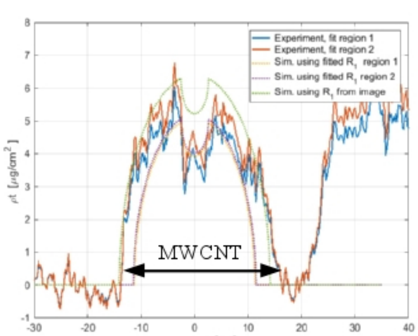

Fig 3. ρt of MWCNT using fitted $N_a A^{-1} \sigma$ and experimental *C* (red, blue) and simulations using Eq. 1 with R_1 from fit (yellow, purple) and $N_a A^{-1} \sigma$ from fit and R1 obtained from visual measurement of inset in Fig. 2.

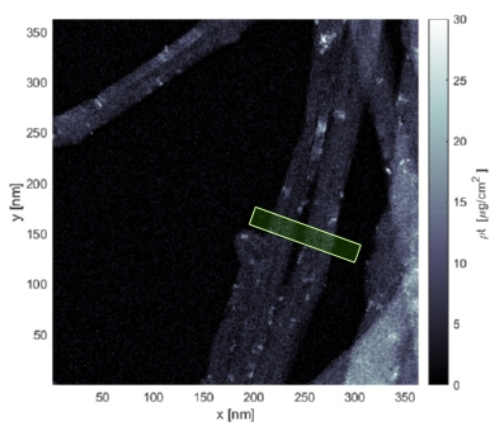

Fig 4. Mass thickness map obtained from a single BFTEM image complemented by a vacuum image as $\rho t = \log(I_0 / I_{tr}) * (N_a A^{-1} \sigma)^1$. The calibration was obtained using the NP-free region of the MWCNT marked with a green rectangle.

https://doi.org/10.1017/S1431927619004690 Published online by Cambridge University Press