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Image formation mechanisms in scanning electron microscopy of carbon nanotubes, and retrieval of their intrinsic dimensions.

H. Jackman^{a,*}, P. Krakhmalev^b, K. Svensson^a

^a*Department of Physics and Electrical Engineering, Karlstad University, SE-651 88 Karlstad, Sweden*

^b*Department of Mechanical and Materials Engineering, Karlstad University, SE-651 88 Karlstad, Sweden*

Abstract

We present a detailed analysis of the image formation mechanisms that are involved in the imaging of carbon nanotubes with scanning electron microscopy (SEM). We show how SEM images can be modelled by accounting for surface enhancement effects together with the absorption coefficient for secondary electrons, and the electron-probe shape. Images can then be deconvoluted, enabling retrieval of the intrinsic nanotube dimensions. Accurate estimates of their dimensions can thereby be obtained even for structures that are comparable to the electron-probe size (on the order of 2 nm). We also present a simple and robust model for obtaining the outer diameter of nanotubes without any detailed knowledge about the electron-probe shape.

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1. Introduction

The development of scanning probe microscopy (SPM) instruments combined with scanning electron microscopy (SEM) and transmission electron microscopy (TEM) enables free standing nanostructures (such as carbon nanotubes) to be studied in terms of their mechanical and electrical properties. The microscope is mainly used to obtain structural information while the SPM instruments are used to perform the material analysis by applying forces or electrical currents [1]. The space available inside SEM instruments is comparatively large and several probes can be used [2]. In TEM the space is much more limited and usually only one SPM probe is fitted [1], while two probes have also recently been demonstrated [3]. One major drawback with the SEM is that the resolution is limited by the electron-probe shape and the imaging mechanisms. Nanoscale structures are thereby substantially broadened in SEM-images.

An accurate measure of the nanotube dimensions is crucial for the analysis of mechanical, and electrical, properties. One route is then to combine the SEM in-situ analysis with regular TEM imaging [4, 5]. The material testing would then first be performed inside an SEM, and the sample of interest subsequently transferred into a TEM to obtain the detailed structural information. Apart from providing only post-mortem information, the method is also difficult, as the exact sample location and orientation should preferably be analyzed inside both the SEM and TEM. This requires a transfer of the whole sample, or SPM probe, with remnant carbon nanotubes on it [4].

Alternatively one can also transfer parts of the analyzed carbon nanotube onto a regular TEM-grid for subsequent TEM analysis [5]. It would instead be preferable to do all of the analysis inside an SEM instrument [6].

The smallest electron-probe size in a modern, field emission gun (FEG) SEM can be of the order of 1 nm at optimum settings [7], and individual carbon nanotubes can thereby fairly easily be imaged, but the SEM shows a much broader structure than the true one (as obtained from TEM imaging). The problem is illustrated in Fig. 1 where the same carbon nanotube has been imaged both in an SEM (Fig. 1 (a)) and a TEM (Fig. 1 (b)). If the broadening in the SEM image can be taken account for, then the whole analysis could be done from only in-situ SEM experiments.

In this work we show how the SEM image formation can be fully modelled for nanofibres, such as carbon nanotubes, by a convolution of the secondary electron yield with the electron-probe shape. With a known electron-probe shape the SEM image can then be deconvoluted and reveal more details. We also present an easy way to obtain the outer diameter of carbon nanotubes imaged in SEM, without doing the full deconvolution. The simple model is fairly robust with respect to the detailed electron-probe shape and enables an accurate estimation of the nanotube outer diameter. A full investigation can thereby be performed inside the SEM without the need for complementary TEM imaging.

2. Materials and Methods

2.1. Sample preparation

Two types of commercial CNTs have been studied: NC2100 and NC2101, obtained from Nanocyl. Both types

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*Corresponding author

Email address: henrik.jackman@kau.se (H. Jackman)

Figure 1: Images of the same CNT acquired by (a) SEM and (b) TEM. (c) Shows the integrated intensity profiles from the two rectangles in (a) and (b), and the diameter estimated from the TEM profile is indicated.

were produced by catalytic chemical vapor deposition (CCVD) with the difference being that NC2101 was functionalized with a carboxyl group (-COOH) to reduce bundling. The CNTs are marketed as double-walled with an average diameter of 3.5 nm and lengths varying between 1-10 μm . As received CNTs were first dispersed in ethanol and then sonicated for 15 minutes to reduce bundling. Sonication for longer periods of time can introduce defects so that the concentric cylinder structure is broken [8]. No damages could be seen in TEM images of the CNTs due to the sonication.

The solution containing the CNTs was drop-casted onto a holey carbon support film for TEM (R 2/1 produced by Quantifoil) and then allowed to dry. CNTs were in this way distributed uniformly over the film enabling imaging of single CNTs without any underlying substrate.

2.2. Microscopy

The samples were first studied in a JEOL (JEM 2100) TEM equipped with a LaB₆ cathode and a digital camera from Gatan (SC1000 Orius). Single CNTs, with well defined concentric cylinder structure and with no amorphous carbon deposits, were chosen and imaged. The acceleration voltage used was 100 kV, since imaging at higher voltages can cause damage to the CNTs even if they are imaged for short periods of time [9]. Even at 100 kV the CNTs can become damaged if subjected to a high current

density beam for longer times. Therefore the current density of the beam and the time of exposure to the beam were minimized so that the CNTs did not get damaged.

The best performance of the TEM is obtained at the Scherzer defocus [10]. One result of this defocus is that bright Fresnel fringes appear at the edges of the CNT, as shown in Fig. 1 (b) and (c). From intensity profiles, obtained from TEM images, the diameter, d_{TEM} , was estimated by taking the distance between the points where the bright Fresnel contrast returns to background intensity, as shown in Fig. 1 (c). The width of the dark regions varies with focus, but for small deviations from the Scherzer defocus they stay approximately constant [11]. Estimating the diameter this way yields the width of the CNT that interacts with the electron beam, both in SEM and TEM, i.e the outer diameter. The error when estimating the diameter of a CNT from TEM images is less than 10% for diameters larger than 1 nm [11]. Since all CNTs used in this study had $d > 1$ nm, the diameters measured in the TEM should deviate less than 10% from the true diameter.

After the CNTs had been imaged in the TEM they were imaged in a LEO 1530 FEG-SEM. The samples were mounted in a custom made scanning transmission electron microscopy holder enabling imaging of the CNTs without any contribution from an underlying substrate. The electron-probe size and the secondary electron yield both decrease with increasing acceleration voltage [7]. A higher acceleration voltage thereby improves the resolution but decreases the signal-to-noise ratio in the SEM image. An acceleration voltage of 12 kV was found to be a good trade-off between resolution and signal-to-noise ratio and was used when acquiring all images in this study.

Electron beam-induced deposition (EBID) can be a problem during SEM analysis and it will increase the diameter of the CNTs [12]. Such effects were minimized here by leaving the samples in the SEM chamber for at least 10 hours, resulting in a chamber pressure down to 5×10^{-7} mbar, before exposing them to the electron beam. To check if EBID had occurred in the SEM, all CNTs were imaged one more time in the TEM and the EBID was found to be negligible.

2.3. Modelling

An SEM image can be thought of as the detected secondary electron (SE) intensity as a function of the lateral coordinates, $I(r)$. This can be described as a convolution of the SE yield at each sample position, $\delta(r)$, with the electron-probe shape, $i(r)$:

$$I(r) = [\delta * i](r) = \int \delta(r') i(r - r') dr' \quad (1)$$

At low magnifications, the influence of $i(r)$ on the recorded image can be neglected, while at higher magnifications $i(r)$ will smooth out any sharp sample details. The exact shape of $i(r)$ is generally unknown and depends on a number of parameters in the microscope. Estimation of CNT diameters can be done on integrated intensity profiles, as shown

in Fig. 1 (c). In these intensity profiles, a radial symmetric $i(r)$ can be described as one dimensional and Gaussian and Lorentzian functions can be used to describe $i(r)$. An area normalised Gaussian function is given by:

$$i_G(r) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{r^2}{2\sigma^2}\right) \quad (2)$$

where the full width at half maximum (Γ) is equal to $\Gamma_G = 2\sqrt{2\ln 2}\sigma$, while an area normalised Lorentzian function is given by:

$$i_L(r) = \frac{1}{\pi} \frac{\frac{1}{2}\Gamma_L}{r^2 + (\frac{1}{2}\Gamma_L)^2} \quad (3)$$

where Γ_L is the full width at half maximum.

The SE yield from a homogeneous material depends on the generation and scattering of SE. Three types of SE are generated inside an SEM: SE1, SE2 and SE3 [7]. Electrons labelled SE1 are excited directly by the primary beam, SE2 are excited by backscattered electrons (BSE) near the specimen surface, and SE3 are excited by backscattered electrons outside the specimen. When the experimental SEM images were obtained in this study an in-lens detector was used which effectively excludes SE3 [13], and the contribution from SE3 was neglected when modelling $I(r)$. In order for SE2 to be emitted, there must be a considerable amount of backscattered electrons from the incoming beam. Considering CNTs with a diameter up to about 10 nm, an insignificant fraction of the incident beam will be backscattered, and the SE2 contribution was also neglected here. The generation of SE1 is assumed to be proportional to the energy loss of the incoming electrons [14, 7]. Having a thin specimen with a low average atomic number, such as a CNT, the incident electrons will lose a negligible amount of energy travelling through the specimen. This makes the probability of generating SE approximately constant throughout the thickness of the sample.

For SE to be detected they need to escape the specimen and reach the detector. Because of their low energy, the SE are more easily absorbed than the incoming high-energy electrons. The probability of escaping a specimen decreases exponentially with the distance travelled in the solid, z :

$$P_{escape} \propto e^{-\alpha z} \quad (4)$$

with α being the absorption coefficient for SE of the specimen material. Combining the relations for generation and escape of the SE an expression for the SE yield, as a function of the thickness t , was derived in [14]:

$$\delta_t \propto \frac{1}{2\alpha} \left(1 - e^{-\alpha t} (1 - \alpha t) - (\alpha t)^2 \int_{\alpha t}^{\infty} \frac{e^{-\xi}}{\xi} d\xi \right) \quad (5)$$

where the thickness can be a function of the lateral coordinates, $t = t(r)$.

For a flat specimen of constant tilt angle, ϕ , Eq. 5 describe the SE yield. However for a CNT, ϕ will vary across its surface and δ increases with increasing ϕ . The relation between δ and ϕ is given approximately by [16]:

$$\delta_\phi \propto \sec \phi \quad (6)$$

where the tilt angle can be a function of the lateral coordinates, $\phi = \phi(r)$. For a specimens with low average atomic number, Z , the dependence on ϕ becomes more rapid than $\sec \phi$ [16]. On the other hand, the dependence also becomes slower with lower V_{SEM} , so although carbon has a low Z , Eq. 6 is a reasonable approximation of the dependence of δ on ϕ since we used $V_{SEM} = 12$ kV in this study.

By combining Eq. 5 and 6, the total SE yield is given by:

$$\delta_{sim}(r) = \delta_t(r)\delta_\phi(r) \quad (7)$$

Figure 2: (a) The total SE yield, δ_{sim} , for two different α -values (solid lines), calculated for the CNT dimensions indicated by the dashed lines. (b) Two simulated intensity profiles, I_{sim} , for the CNT dimensions in (a) using $i_{sim} = i_G$ and $i_{sim} = i_L$ with $\Gamma_G = \Gamma_L = 2.1$ nm (for $\alpha = 1/20$ nm $^{-1}$).

To obtain $\delta_{sim}(r)$ for a carbon nanotube we need a value for the absorption coefficient α . Experimental data is scarce, but α may be as low as $1/20$ nm $^{-1}$ for carbon and around $1/10$ nm $^{-1}$ for polymers [15]. In Fig. 2 (a) we show the obtained δ_{sim} for both values of α . The influence of α on δ_{sim} is small and we have used the value for carbon ($1/20$ nm $^{-1}$) for the remaining analysis.

Simulated intensity profiles, $I_{sim}(r)$, were obtained through a convolution of δ_{sim} and i_{sim} , where linear combinations of i_G and i_L were used to describe the probe shape i_{sim} . The convolution was done by sweeping a function of the probe shape, $i_{sim}(r - r')$, over the total SE yield, $\delta_{sim}(r')$,

and taking the integral of the product of these two functions:

$$I_{sim}(r) = [\delta_{sim} * i_{sim}](r) = \int_{r-5\Gamma}^{r+5\Gamma} \delta_{sim}(r') i_{sim}(r-r') dr' \quad (8)$$

Ultimately the integration above should be performed in the interval $[-\infty, \infty]$, but since the equations describing $i(r)$ rapidly goes to zero we used the interval $[r-5\Gamma, r+5\Gamma]$ to reduce the computational intensity. The integration in Eq. 8 was performed numerically in MATLAB, where both $i_{sim}(r-r')$ and $\delta_{sim}(r')$ were divided into small elements. Pair of elements were multiplied and the products summed together in each step. An example of two simulated intensity profiles is shown in Fig. 2 (b), for purely Gaussian and Lorentzian probe shapes.

This method is not limited to CNTs, as it can be applied on any homogeneous nanofiber structure. In the case of filled nanotubes it can easily be used by adding the δ contribution of the filler to Eq. 7.

3. Results and Discussion

The inner and outer diameter of the CNTs obtained from the TEM images was used as parameters when simulating intensity profiles, I_{sim} . Good agreement between I_{sim} and experimental SEM intensity profiles (I_{SEM}) was obtained when using a combination of i_G and i_L to model the probe shape (with $\Gamma_G = \Gamma_L = \Gamma$). On average a good agreement was found when:

$$i_{sim} = \frac{1}{2}i_L + \frac{1}{2}i_G \quad (9)$$

A result of such a simulation is shown in Fig. 3 (c), where the SEM profile of the CNT seen in Fig. 3 (b) was simulated. The average Γ from all analysed profiles was found to be 2.05 ± 0.05 nm.

The probe shape that worked best for reproducing I_{SEM} should not be seen as an instrumental constant, since $i(r)$ depend on a number of SEM parameters. Therefore $i(r)$ likely varies between different SEM instruments and even for a certain SEM as the experimental conditions are altered, by changes in focus and astigmatic corrections. Knowing the exact probe shape, one can deconvolute a full SEM image to obtain the SE yield, and in turn from that retrieve the intrinsic nanotube dimensions. We have used the two dimensional version of Eq. 9 as the input point spread function in the MATLAB-function `deconvblind` to deconvolute SEM images. The result of one such deconvolution is shown in Fig. 4, where Fig. 1 (a) was used as the raw SEM-image.

Even though the deconvoluted image in Fig. 4 (b) contains more detail, it is still quite far from the sharp function describing δ in Eq. 7 (as can be seen in Fig. 4 (c)). One reason that the deconvolution cannot fully retrieve the underlying structures, is the image noise in the shape

Figure 3: Images of the same CNT acquired by (a) TEM and (b) SEM. In (c) the SEM profile, $I_{SEM}(\cdot)$, is plotted along with three simulated intensity profiles, obtained by using different probe shapes (with $\Gamma_G = \Gamma_L = 2.0$ nm).

of streaks. This may be the result of vibrations or other sources of instabilities, such as external electromagnetic fields. Another reason is that Eq. 9 is an approximation of the exact probe shape $i(r)$. Other attempts to describe the probe shape assumes a Gaussian probe shape and fails to determine probe sizes below than 2 nm [17].

Instead of having to rely on the exact shape of $i(r)$, we have looked for an easier way to extract the outer diameter of the nanotubes which is an important parameter when studying the mechanical properties. We have previously shown, from empirical studies, that the width of the SEM profile can be used to estimate the outer diameter of the nanotubes [6]. Here we investigate this further by using our knowledge of the image formation mechanisms. The electron-yield from a nanotube has a sharp step at the positions of the outer edges (see Fig. 2 (a)) which are the positions that will give us the outer diameter. If we look at the convolution of a step function, $H(r-r_0)$, and an arbitrary symmetric probe shape with a distinct maximum, $I_H(r) = [H * i](r)$, the second derivative, $\frac{d^2}{dr^2} I_H(r)$, becomes zero when the maximum of $i(r)$ meets the edge of the step function at r_0 . If the SE yield of a CNT would be constant across the width, then the diameter would

Figure 4: SEM images of a CNT showing (a) a raw-image and (b) a deconvoluted image. The integrated intensity profiles from the boxes in (a) and (b) are plotted in (c).

be given by the distance between the two zero points of $\frac{d^2}{dr^2} I_{SEM}(r)$, given that the width of $i(r)$ is smaller than the diameter of the CNT. Having a negative slope after the step will shift the zero points away from the step resulting in an overestimate of the diameter. However, δ only has a slow decrease after the step, and the second derivative should still give a good measure of the diameter.

One difficulty in obtaining the second derivative of $I_{SEM}(r)$ is the random noise present in SEM images. To get a smooth intensity profile a 10th order polynomial was fitted to the experimentally obtained data. The second derivative of this fit became smooth enough to find the two zero points. In Fig. 5 (a) experimental data, a polynomial fit to the data, and the second derivative of this fit is plotted along with the TEM intensity profile of the same triple-walled CNT.

The zero points of the second derivative were used to estimate the diameter, d_{SEM} , for seven different CNTs and the results is shown in Fig. 5 (b), where d_{SEM} is plotted against the diameter obtained from TEM images. We have calculated the mean value of d_{SEM} from 3-5 images for each nanotube and from the deviations between the images 90% confidence intervals was obtained, indicated as error bars in Fig. 5 (b). Using our model for the image formation we can also calculate the diameter that one would expect to obtain (with the second derivative method) for a certain size of the probe shape, indicated by a solid line in Fig. 5 (b) for a probe with $i(r)$ given by Eq. 9 and

Figure 5: (a) TEM and SEM profiles, from images in Fig. 3 (a) and (b), together with a polynomial fit of $I_{SEM}(r)$, and the second derivative of this fit (the zero points are indicated). (b) Diameters estimated from SEM images using the second derivative versus the diameter measured in TEM. The predicted diameter from simulations (using $\Gamma_G = \Gamma_L = 2.0$ nm) is shown as a grey line. (c) The robustness is tested with five prediction curves (obtained using $i_{sim} = \frac{1}{2}i_L + \frac{1}{2}i_G$ and $\Gamma_G = \Gamma_L$).

$\Gamma = 2$ nm.

In order to study the influence of the probe shape on the outcome of the second derivative method, we have calculated the diameter that one would obtain for different Γ ranging from 1.0 - 3.0 nm (shown in Fig. 5 (c)), again with $i(r)$ given by Eq. 9. This indicates that for nanotubes having diameters larger or similar to the probe width, the method will give an adequate result without having to know the detailed probe shape. If the detailed shape of $i(r)$ is unknown, this method still estimates the diameter well as long as $i(r)$ has a distinct maximum. When fitting the experimentally obtained SEM intensity profiles by simulations, the best results were obtained in our case when

using $i(r)$ in Eq. 9 with $\Gamma = 2.05$ nm. Widths of this size and smaller are routinely obtained using FEG-SEM [7, 17], thus enabling accurate estimates of CNTs with $d \gtrsim 2$ nm.

Modelling the intensity profile using Eq. 7 and 8 ignores the contribution from SE2 to δ . This is only valid for thin specimens with a low atomic number, because of the increase in backscattered electrons with t and Z . Using this theory to model larger diameter tubular specimens with larger Z may therefore not reproduce experimental SEM intensity profiles as accurate. Estimating the diameter using the zero points of the second derivative should however still be valid since the thickness close to the edge of the tube is still fairly small.

4. Conclusions

A method for reproducing SEM intensity profiles of CNTs has been presented. The intensity profile is modelled as the convolution of the electron-probe shape and the secondary electron yield, $[\delta * i](r)$. The model reproduced experimental intensity profiles well when a combination of a Gaussian and a Lorentzian function for the probe shape was used. Information regarding the true sample structure can thus be obtained and SEM-images can be deconvoluted to improve the resolution.

A simple method for estimating the outer diameter is also proposed, where the distance between the two zero points of the intensity profile's second derivative is used. This method was tested on CNTs with $d = 2.5 - 4.5$ nm where it estimated the diameters accurately. The robustness of this method to different probe shapes was also tested, and we found that the diameter is accurately estimated when $d \gtrsim \Gamma$. The theory described should also be applicable to other homogeneous nanofibers and can aid the analysis of in situ SEM experiments.

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6. References

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