3D Characterization of carbon nanotube polymer composites using Scanning Electron Microscopy and Confocal Raman Microscopy

Minhua Zhao,^{*****} Andras E. Vladar,^{**} Rachel J. Cannara,^{*} and J. Alexander Liddle^{*}

^{*}Center of Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD, USA. Email: <u>mzhao@nist.gov</u>

Physical Measurement Lab, National Institute of Standards and Technology, Gaithersburg, MD, USA. *Department of Materials Science & Engineering, University of Maryland, College Park, MD, USA.

ABSTRACT

Scanning Electron Microscopy (SEM) and Confocal Raman Microscopy (CRM) were employed to characterize the 3D state of carbon nanotube (CNT) dispersion in a polymer matrix. First, non-destructive subsurface imaging on CNT-polymer was conducted by charge-contrast SEM imaging. 3D reconstruction on stereo-pair of SEM images was demonstrated to a depth of up to 1 µm. Second, highthroughput and good depth-resolution 3-D characterization of CNT polymer composites to a depth of 30 µm was demonstrated by optimizing CRM parameters and the use of high-numerical aperture immersion lenses. While this is about two orders of magnitude deeper than possible with SEM, the spatial resolution of charge-contrast SEM is about an order of magnitude greater than that of CRM, making the two techniques complementary. Finally, these techniques can be applied broadly in nanotechnology, such as through-die overlay measurements in semiconductor manufacturing and the measurement of nanoparticles endocytosed by cells.

Keywords: confocal Raman microscopy, scanning electron microscopy, 3D, carbon nanotube, polymer composites.

1 INTRODUCTION

Three-dimensional (3D) characterization of carbon nanotube (CNT) dispersions in nanocomposites [1-2] is a critical step in enabling structure-property relationships to be determined. In this study, Scanning Electron Microscopy (SEM) and Confocal Raman Microscopy (CRM) were employed for this purpose. In general, the ability of SEM to provide sub-surface images of CNTs in polymer composites is still a controversial topic, with reported values ranging from less than 50 nm [3], to hundreds of nanometers [4] to several micrometers [5]. One of the objectives of the present work is to clarify this issue using 3D reconstructions generated by stereo-pair images captured by charge contrast SEM imaging. In addition, CRM, a combination of confocal microscopy and Raman spectroscopy, is demonstrated to be a promising technique for noninvasive 3D chemical imaging with sub-micrometer lateral resolution. The main obstacles to using CRM as a

3D-imaging technique are low-throughput [6] and poor depth resolution [7]. Here we will demonstrate progress made toward high-throughput 3D CRM imaging with good depth resolution.

2 EXPERIMENTAL

2.1 3D SEM imaging

Purified laser ablated (LA) and high-pressure carbon monoxide decomposition (HiPco) SWCNTs were used as CNT source. The polymer matrix was an electroactive polyimide. Single-wall carbon nanotube (SWCNT)polyimide nanocomposite films having a thickness between $25 \ \mu m$ and $65 \ \mu m$ were prepared by *in situ* polymerization as described previously [8].

The SEM study was conducted using a dual-beam system. The composite film was attached to an aluminum sample stub using conductive carbon tape. No additional sample treatment, such as coating with a conductive layer, was used. The beam accelerating voltage was varied between 0.3 kV and 30 kV, while the beam current was maintained at 43 pA. 3D SEM imaging was achieved by reconstructing images captured at tilt angles of -5° and $+5^{\circ}$ using 3D reconstruction software, when the sample was kept at eucentric tilting position at a 4 mm working distance. A through-the-lens detector was used to collect the secondary electrons. A beam dwell time of 40 µs was used for each image pixel.

2.2 3D CRM imaging

MWCNTs were synthesized using a method described by Singh et al. [9] based on a chemical vapor deposition technique. Polystyrene (PS)/multi-wall carbon nanotube (MWCNT) composite was prepared using a solution mixing method. The composite was further processed in a heated parallel-plate rotating-disk shear-cell to form a film with typical thickness around 70 μ m.

3D CRM imaging was conducted using a commercial confocal Raman microscope equipped with 514.5 nm Argon-ion laser and a grating with a groove pitch of 600

 mm^{-1} . Both an 100× dry objective (NA=0.8) and oil immersion objective (NA=1.4) were used at the same location of the sample for comparison. The laser power on the sample was kept below 1 mW to avoid the damage to the polymer composite film.

3 RESULTS AND DISCUSSIONS

3.1 3D SEM imaging

The maximum depth that embedded CNTs can be distinguished from the surrounding polymer matrix, referred to as the imaging depth, depends on the sample properties and imaging conditions such as beam accelerating voltage. The previously reported imaging depth was derived indirectly by coating a known depth of polymer onto the surface of a CNT polymer composite [10].



Figure 1: (Top) Stereo image pairs of 0.5% SWCNT(LA)-PI film captured by 28 kV SEM at tilting angles of -5^0 and $+5^0$ respectively. The horizontal fields of view are 10.6 μ m. (Bottom) 3D SEM image of 0.5% SWCNT(LA)-PI film by reconstruction of stereo image pairs.

In this study, the SEM imaging depth of SWCNTs embedded in a polyimide matrix is presented through 3D graphs by reconstructing SEM images captured at different tilt angles. Figures 1 and 2 show 3D images of SWCNTs prepared by laser-ablation (LA) and HiPco CVD processes respectively embedded in a polyimide matrix, which are reconstructed from stereo image pairs captured at 28 kV accelerating voltages. The red arrows point to CNTs that have a very intense contrast and were used as references for the film surfaces. The depth of LA-CNT marked by the blue arrow was measured to be (258 ± 28) nm in Figure 1, while it was (728 ± 56) nm for the HiPco CNT in Figure 2 (Unless otherwise noted, all uncertainties are \pm one standard deviation).



Figure 2: (Top) Stereo image pairs of 0.5% SWCNT (Hipco)-PI film captured by 28 kV SEM at tilting angles of -5^{0} and $+5^{0}$ respectively. The horizontal fields of view are 15 µm. (Bottom) 3D SEM image by reconstruction of stereo image pairs.

Therefore, the subsurface imaging depth of SWCNTs embedded in polyimide matrix is confirmed to be at least hundreds of nanometers, which is consistent with the previous results based on geometrical relations [11]. It was also revealed that the bundle size of LA-SWCNTs was much smaller than that of HiPco-SWCNTs, indicating a better dispersion of LA-SWCNTs in the polyimide matrix. The reason that a poorly-dispersed sample will have a deeper imaging depth than a better-dispersed sample can be accounted for in terms of the variance of the near surface charge density. As shown in Figures 1, well dispersed SWCNTs sample implies a more dense and uniform near surface charge density, which prevents imaging of the more deeply embedded CNTs.

3.2 3D CRM imaging

Figure 3 is a comparison of Raman spectra taken at the same location of a 0.1 % (mass fraction) CNT-PS film using $100 \times$ oil immersion lens (NA=1.4) and $100 \times$ dry lens (NA=0.8) respectively. We were able to capture each spectrum at a throughput of 100 ms integration time after the optimization of CRM, which was several seconds initially. Since the Raman images (inset) are displayed on the same intensity scale, it is clear that a higher signal to noise ratio was achieved with the oil immersion lens, suggesting further improvement of throughput is possible in the future.



Figure 3: Comparison of Raman spectra at the same location of 0.1% CNT-PS film (red arrow) using 100× oil immersion lens (NA=1.4, black) and 100× dry lens (NA=0.8, red). The inset Raman image is a map of the CNT 2D band (2660-2690 cm⁻¹), which consists of 101×101 pixels at a pixel size of 300 nm × 300 nm.

Figure 4 shows some representative 2D slices of CRM images. The CNT Raman signal is still strong and sharp at a focus depth of 28 μ m below the surface using the 100× oil immersion lens, while this is not true for dry lens (not shown). 3D CRM image (30 μ m × 30 μ m × 30 μ m) was shown in Figure 5, which was reconstructed by 61 slices of 2D images from z= 0 μ m to 30 μ m at a z step of 500 nm using ImageJ [12]. Another reason for CRM to use an oil immersion lens is great improvement of depth resolution, as illustrated in Figure 6. For instance, the CRM image by 100x dry lens at focus depth of 3 μ m matches well with that by 100x oil immersion at focus depth of 6 μ m. This discrepency can be accounted for in terms of the refractive index mismatch between air (n=1) and the polymer matrix (n_s≈1.5).



Figure 4: CNT 2D band mapping of 0.1% CNT-PS film at various focus depth using 100x oil immersion lens.



Figure 5: 3D CRM image (30x30x30 μm) of 0.1% CNT-PS film by reconstruction of captured 2D sliced images from depth z=0 μm to 30 μm using ImageJ.

Figure 7 illustates the depth-inaccuracy of dry lens using Snell's law:

$z/\Delta = tan\theta_i/tan\theta_t \approx n_s$ (1)

where z is real focal depth due to refraction, Δ is nominal focal depth without refraction and n_s is the refraction index of sample. Hence, the focus shift (z- Δ) by dry lens can be estimated as:

(2)

z-∆≈(n_s-1)∆

Hence the deeper the focus, the more focus shift by dry lens. In contrast, the refractive index of immersion oil matches that of polysterene sample, which is critical to ensure a good depth resolution in 3D CRM imaging.



Figure 6: Comparison of confocal Raman mapping of CNT 2D band at various focusing depth using 100x oil immersion lens (NA=1.4) and 100x air lens (NA=0.8).



Figure 7: Illustration of depth-inaccuarcy of CRM imaging by dry lens.

4 CONCLUSION

Both SEM and CRM are suitable for 3D characterization of CNT-polymer composites. While the imaging depth by CRM is about two orders of magnitude greater than that possible with SEM, the spatial resolution of charge-contrast SEM (tens of nanometers) is about an order of magnitude greater than that of CRM (hundreds of nanometers). SEM throughput is also several orders of magnitude higher than that of CRM, making the two techniques complementary. Finally, these techniques can be applied broadly in nanotechnology, and can potentially be used for overlay imaging in semiconductor fabrication and to monitor nanoparticles endocytosed by cells. Instrumenation development on a higher throughput 3D CRM is ongoing.

ACKNOWLEDGEMENTS

Financial supports from NIST-ARRA senior awards and NIST SERI projects are acknowledged. SWCNT-PI films and MWCNT-PS films are courtesy of Dr. Cheol Park (National Institute of Aerospace) and Dr. Kalman Migler, (NIST), respectively.

REFERENCES

[1] Zhao MH, Gu XH, Park C, Nguyen T et al, Nanotechnology, 21, 225702, (2010).

[2] Zhao MH et al, NanoTech 2010, paper #884, Anaheim, (2010).

[3] Kovacs JZ et al, Carbon, 45, 1279-1288, (2007).

[4] Li WJ et al, Carbon, 49, 1955-1964, (2011).

[5] Loos J et al, Ultramicroscopy, 104,160-167, (2005).

[6] Govil A, Pallister DM and Morris MD, Applied Spectroscopy, 47, 75-79, (1993).

[7] Everall NJ, Analyst, 135, 2512-2522, (2010).

[8] Park C et al, Harrison JS and Clair TLS, Chemical Physics Letters, 364, 303, (2002).

[9] Singh C et al, Chem. Phys. Lett., 372, 860–865, (2003).

[10] Li WJ, Buschhorn ST, Schulte K and Bauhofer W, Carbon, 49, 1955-1964, (2011).

[11] Lillehei PT et al, Nanotechnology, 20, 325708, (2009).[12] Philippe A and Thomas B, "3d Image Processing and

Analysis with ImageJ [ImageJ Documentation Wiki]," Oct-2010.