

Imaging of Carbon Nanotubes Embedded in Polymer Composites via Low Energy Scanning Electron Microscopy and Scanning Lithium Ion Microscopy

Minhua Zhao^{1,2}, Kevin A. Twedt^{1,3}, Jabez J. McClelland¹, and J. Alexander Liddle¹

¹Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

²Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

³Maryland NanoCenter, University of Maryland, College Park, MD 20742, USA

Understanding the dispersion of carbon nanotubes (CNTs) embedded in a polymer matrix is critical for constructing the structure-property relationships that can be used to improve the performance of CNT composites. SEM imaging is, in principle, an effective way to determine the CNT dispersion. However, the limited conductivity of the polymer matrix can lead to excessive negative charge buildup in the polymer. To avoid this, we have developed approaches to create optimum imaging conditions by generating weak positive charging using both low-energy scanning electron microscopy (SEM) and scanning lithium ion microscopy (SLIM).¹ Positive charging on the polymer surface can be created in SEM in two ways, as shown in Figure 1. First, we use low-voltage SEM with electron landing energies between the first (E_1) and second (E_2) crossover energies (Fig 1. b). The contrast of embedded CNTs is bright relative to the polymer matrix at incident beam energy of 350 V, a typical case for positive charging². Second, if a conducting substrate is present, when the electron beam range is greater than the composite film thickness, we can use a penetrating beam to create a positive charging at region III with landing energy $E > E_3$, which is defined as a third crossover energy.^{2,3} The fact that we see similar contrast at both 3 kV and 350 V is consistent with the existence of E_3 for our samples, considering the electron beam range in epoxy at 3 kV accelerating voltage is comparable to the film thickness ($t=100$ nm). Although positive charging by a penetrating beam has been reported in both experiment⁴ and simulation⁵ before, the use of higher energy beams has been neglected by experimentalists and theorists. The advantages of a penetrating beam over a low-voltage beam in SEM imaging include improved spatial resolution due to reduced lens aberrations at higher accelerating voltages and deeper subsurface imaging depth due to the greater beam penetration.²

We also compare SEM imaging to SLIM imaging, where positive surface charging occurs for all ion beam energies. Figure 2 shows the same location of a 1 % CNT-epoxy film imaged by SLIM and SEM. Similar bright contrast for the embedded CNTs is observed by both techniques, which further suggests the existence of weak positive charging at the polymer surface. In addition, the application of these techniques is not limited to imaging of CNTs embedded in polymer composites. They are generally applicable to conducting nanostructures embedded in a dielectric matrix, such as graphene polymer composites or integrated circuit conductors covered by a dielectric layer.

References:

- [1] KA Twedt, L Chen, and J J McClelland, *Ultramicroscopy* 142 (2014), p. 24–31.
- [2] MH Zhao et al, *Nanotechnology* 26 (2015), 085703.
- [3] L Reimer et al, *Optik* 92 (1992), p. 14-22.
- [4] W Liu, J. Ingino and R.F. Pease, *Journal of Vacuum Science and Technology B*, 13 (1995), p. 1979.
- [5] WQ Li and HB Zhang, *Micron*, 41 (2010), p.416-422.

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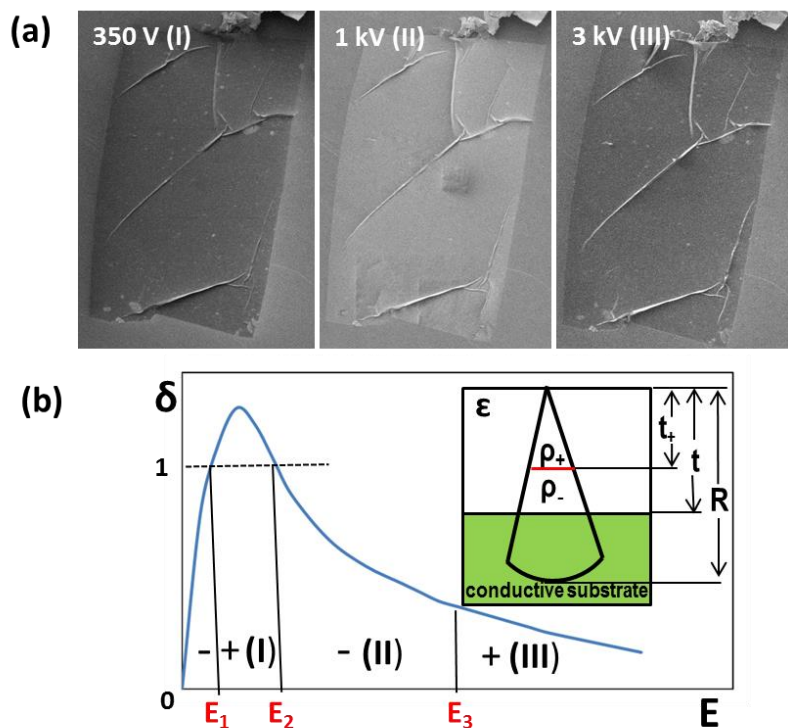


Figure 1 (a) SEM imaging of microtome-prepared 100 nm thick 1% CNT-epoxy film on conductive substrate by beam accelerating voltage of 350 V, 1 kV and 3 kV respectively. Horizontal field of view for all images is 270 μm . (b) Schematic curve of total secondary electron yield (σ) vs. electron landing energy (E). Inset: Schematic of a SEM beam interaction with a dielectric thin film attached to a conductive substrate.

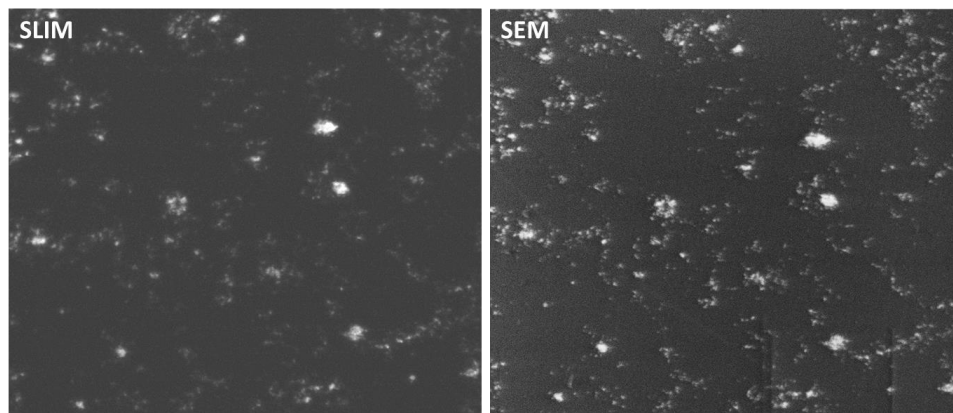


Figure 2: Same location imaging of microtome-prepared 100 nm thick 1% CNT-epoxy film on conductive substrate by SLIM (5 keV landing energy) and SEM (3 keV landing energy) respectively. Secondary electron signal is collected for both images. Horizontal field of view is 30.4 μm .