Electrodeposition of Metals onto Aligned Carbon Nanotube Microstructures

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Abstract and Introduction:

Nanocomposites offer a way to create materials with specific properties by ordering components on the nanometer scale. Carbon nanotubes (CNTs) are a particularly attractive choice for composites due to their small diameter and outstanding mechanical and electrical properties. Previous studies on CNT-metal composites codeposited the components, resulting in materials with a low concentration of randomly oriented CNTs.

We investigated electrodeposition directly onto vertically aligned CNTs as a means to realize nickel-CNT and copper-CNT composites, and attempted to optimize the procedure to produce uniform composite microstructures. The aligned nature of our structures could greatly enhance the composite's properties compared to randomly oriented CNT composites. Electrodeposition was performed at current densities ranging from approximately 2.5 to 500 mA/cm^2, with deposition occurring consistently at densities above 25 mA/cm^2 and composites becoming uniform above 100 mA/cm^2. Morphologies ranged from isolated nanoparticles on CNTs at low current density to thick coatings at high current densities. Infiltration of metal to the interior of the CNT forest was observed under some conditions, and is still under investigation. Future studies will characterize properties of the nickel (Ni) composites for mechanical applications and the copper (Cu) composites for electrical and thermal applications.

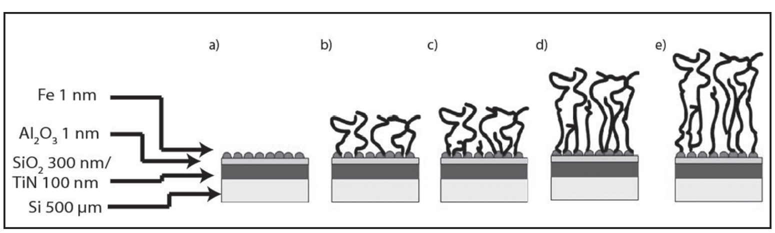

Figure 1: a) Wafer preparation. b) Crowding of CNTs results in c) organization and d) vertical growth until e) termination.

Methods:

The CNT structures were produced by thermal chemical vapor deposition on iron catalyst over an aluminum oxide layer (Al_2O_3). Figure 1 shows the process of growing CNTs. Unpatterned substrates resulted in thin, aligned CNT films called "forests." Patterned CNT structures would be produced by photolithographic patterning of the aluminum oxide and iron layers. Patterned structures would be densified by condensation and evaporation of acetone before metal deposition [2]. Some CNTs were plasma etched in argon before deposition. Electrochemical deposition of Ni and Cu occurred in proprietary electroplating solutions.

Results:

Ni-CNT composites were studied more extensively due to greater ability to control the deposition. Ni nanoparticles were found on CNTs at deposition current densities as low as 12.5 mA/cm^2, but consistent coating was only noticed at 25 mA/cm^2 or greater. Below 100 mA/cm^2, Ni nanoparticles could be found regularly on the surface of non-etched CNT structures, but the deposition was not a uniform thin film coating, as seen in Figure 2a.

The density of Ni nanoparticles was greater near the top of a bundle of CNTs than the bottom on non-etched structures. This is believed to be due to plating on the unorganized "crust" of horizontal CNTs at the top that remains from the crowding phase of growth. At equivalent low current densities and deposition run times, plasma etched CNTs showed less deposition or as Figure 2b shows, none at all, compared to non-etched structures. At current densities of 100 mA/cm^2 and greater, the external surfaces of etched and non-etched structures varied less. However, nickel was only found to penetrate

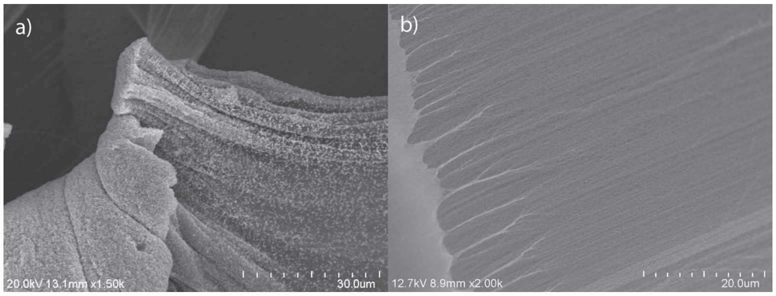

Figure 2: a) Non-etched and b) etched CNTs show different plating at low current density.

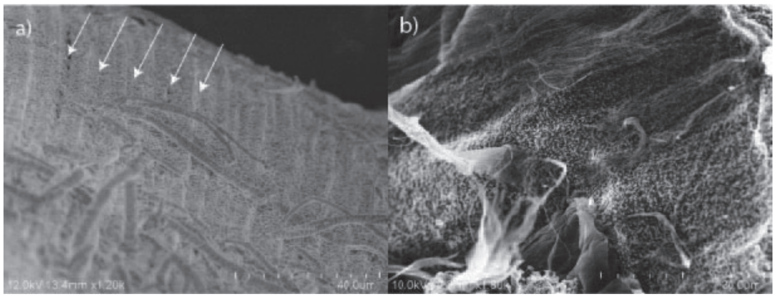

Figure 3: a) Exterior of etched CNT after 40 min deposition shows uniform coating. Arrows point out regular ridges, suggesting conformal coating. b) Interior of same structure.

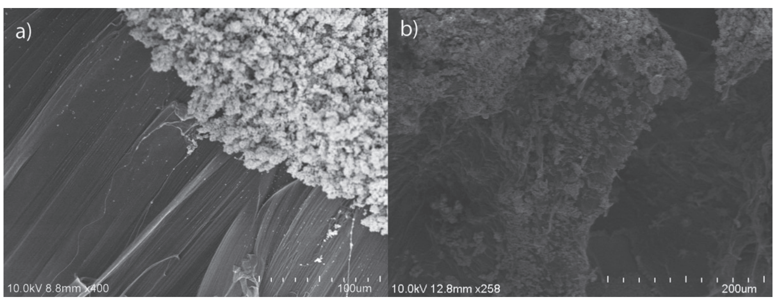

Figure 4: Cu plating of a) non-etched and b) etched structures.

the exterior surface of the structure and coat internal surfaces on the plasma etched CNTs. Running a 500 mA/cm^2 deposition current for 40 minutes resulted in a uniform Ni film on the CNTs, shown in Figure 3a, and also coated the interior, shown in Figure 3b. This interior nickel coating is less uniform than that on the exterior.

Copper was able to successfully plate the CNT structures, but yielded different morphologies. On non-etched "forest" samples, copper only deposited on the top of the structure, as shown in Figure 4a. No nanoparticles were observed on the side of the structures or the interior. On an etched sample, non-uniform depositions of Cu nanoparticles could be found on the side of CNT structures, as seen in Figure 4b, but not in the interior.

The growth of patterned structures did not occur as the use of a titanium nitride thin film instead of a silicon dioxide thin film underneath the aluminum oxide resulted in horizontal CNT carpets.

Conclusions and Future Work:

Our work has shown that electrodeposition is a feasible method of producing uniform metal CNT composites. Plasma etched CNTs were plated more uniformly and showed penetration of the plating metal, though only at higher current densities and deposition times. We suspect the uniformity may be related to the etching process destroying the top crust and also creating defect sites over the entirety of the surface, making it easier for ions to deposit uniformly over the surface. Similarly, the higher required current and deposition time might be a result of the defects and attachment of hydroxide groups from etching reducing the conductivity of the CNTs. The lack of interior Cu deposition might be from the Cu plating on the exterior occurring so fast as to prevent interior penetration.

The Cu electrodeposition needs further refinement. Future work will also look at depositing both metals onto patterned structures. Of particular interest is how metal penetration might be affected by the size of the structures. Characterization of the composites is also necessary to determine appropriate uses of these materials. The Ni-CNT composites are theorized to be useful in mechanical applications and the Cu-CNT composites could be useful for electronic or thermal applications.

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References:

[1] Y. Sun, et al. "Mechanical strength of carbon nanotube–nickel nanocomposites." Nanotechnology (2007).

[2] M. De Volder, et al. "Diverse 3D Microarchitectures Made by Capillary Forming of Carbon Nanotubes." Advanced Materials (2010): 4384-4389.