Coating Growth on Nanofibers: Multi-Scale Modeling, Simulations and Experiments

A. Buldum*, C.B. Clemons**, E.A. Evans***, K. Kreider**, G.W. Young**

* Dept. of Physics, Buldum@uakron.edu,
Dept. of Theoretical & Applied Mathematics, * Dept. of Chemical Engineering
The University of Akron, Akron, OH 44325

ABSTRACT

This investigation focuses on the coating of nanotubes and nanofibers with conductive materials using plasma enhanced physical vapor deposition. We examine experimental procedures for coating electrospun polymer nanofibers with metallic materials, then dissolve the inner polymer core to yield a nanotube of the coating material. The interrelationships among processing factors is investigated from a detailed modeling approach that describes the salient physical and chemical phenomena. Solution strategies that couple continuum and atomistic models are used. At the continuum scale we describe the reactor dynamics and deposition of the coatings on the nanofibers. At the atomic level, we use quantum mechanical (QM) and molecular dynamics (MD) simulations to study the deposition mechanisms and migration of atoms in the coating.

Keywords: nanofiber, coating, modeling

1 INTRODUCTION

Nanotubes have attracted great academic and industrial interest in recent years [4]–[6], [13], [14]. Improvement in the ability to synthesize nanotubes of different materials has resulted in the suggestion and development of novel devices based on the properties of the nanotubes [4]. Possible applications for nanotubes in the areas of filtration [3], composites [7], [9], biomedicine [2], [12], and electronics [5] have been suggested. However, several limitations to the widespread synthesis and use of nanotubes can be identified. First, the ability to produce large quantities of nanotubes with controlled electronic and structural properties is still undeveloped. Second, the nanoscale dimensions of these materials often lead to previously unobserved properties that need to be understood and ultimately controlled.

2 EXPERIMENTS

This work addresses some aspects of these issues through a coordinated experimental and modeling program. From the standpoint of nanotube synthesis, we examine physical vapor deposition techniques for applying conductive coatings to electrospun polymer nanofibers. We have successfully coated fibers with carbon, copper, and aluminum films by using a plasma enhanced physical vapor deposition (PEPVD) sputtering process (see Figure 4). The power supply drives a 2 inch diameter electrode which forms the target (or source) material. The nanofibers are placed on a holder that sits 8 cm above the target. A plasma is formed when electrons emitted from the target create ions in the gas phase. Once a plasma is formed, the ions sputter atoms from the target which are then transported to the nanofibers and deposited. The ions also strike the coated nanofibers and tend to make the deposited coating more uniform through a resputtering process. The coating growth rate depends on the rate at which atoms are supplied to the nanofiber surface, the nanofiber temperature, and the ion flux to the nanofiber. The morphology of the coating depends on the mobility of the atoms on the surface and how much time the atoms have to move around before the next atoms hit the surface. The rate at which atoms are supplied to the nanofiber is proportional to the rate at which atoms are sputtered from the target and how far away the nanofiber is from the target. The sputtering rate depends on the ion flux, which is determined by the power applied to the target, the pressure of the system, and the working gas used. The nanofiber temperature is controlled using a heater. The ion flux to the nanofiber is controlled by the potential drop between the plasma and the nanofiber, the working gas used and the pressure.

To determine the effects of these variables on the film growth rate and morphology we analyze the films using TEM. TEM analysis is used to determine the growth rate on the fibers. We compare average thicknesses of the fibers before and after the coating process to determine an average growth rate of the films. To determine coating morphology, TEM images and diffraction patterns are taken. Removing the nanofiber core leaves a polycrystalline nanotube of the coating material.

Figure 1 shows an aluminum-coated fiber. The cylindrical cross-section of a tube is shown in Figure 2, which indicates that the tube did not collapse after the polymer inside had been removed. The smallest inner diameter of the tubes was around 20 nm. The approximate thickness of the wall of the tubes was controlled by the sputtering process. A tube with different wall thickness

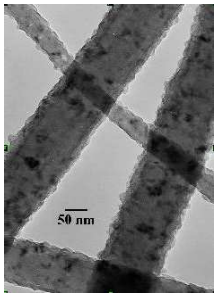

Figure 1: TEM images of aluminum-coated fibers.

Figure 2: TEM image of an aluminum nanotube.

is shown in Figure 3.

The above approach can be used to produce tubes of many materials including metals, semiconductors, ceramics and polymers with controlled diameters and a range of nanometer thickness walls.

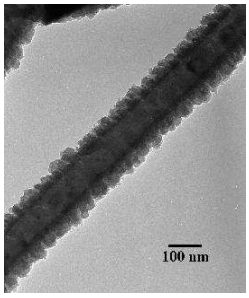

Figure 3: Aluminum nanotube of wall thickness 40 nm.

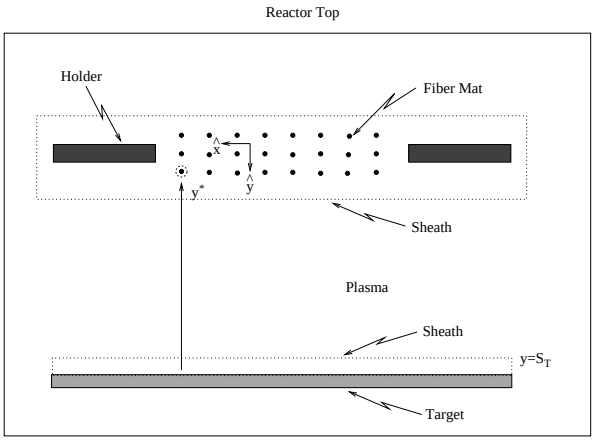

Figure 4: Global schematic of the reactor for neutral species transport within the reactor.

3 MODELING

The model for the coating of nanofibers is based upon deposition within our traditional PEPVD system. Our objective is to determine the influence of process conditions on the uniformity and morphology of the coating. Our system is characterized by a bulk gas phase dominated by neutral species, and sheath regions that separate the bulk gas phase from the substrate (nanofibers) and the target, as shown in Figure 4. There are several disparate geometrical length scales in the reactor system. The reactor size from target to the top is no more than 20 centimeters in length. The distance from the target to holder is centimeters in length. The sheath thicknesses are on the order of millimeters. The nanofibers are on average 100 nm in diameter. Further, the nanofiber mat is a sparse mesh of the fibers. Hence, we make the assumption that the holder region of nanofibers does not influence the electric field near the target and does not influence the global transport of neutral species within the reactor. Thus, the overall transport of neutral species will be separated into two components. The global or outer component will model the transport away from the target, as shown in Figure 4, without any influence from the sparse mesh of nanofibers and the holder. The local component will model the neutral species transport in the vicinity of a nanofiber as shown in Figure 5. The global information for neutral species concentration at a nanofiber location, $y = y^*$ from the target, will serve as the far field input to the local model of deposition on the nanofiber.

The mode of transport of the concentration of the deposition material is diffusion for both the global and local systems. Electromagnetic and ion fluid equations govern the transport of ions through sheath regions, and the interaction of the ions with the target and nanofibers. At the local nanofiber scale we examine polar and axisymmetric geometries. Coating deposition equations at the nanofiber include deposition rate parameters and desorption parameters due to ion bombardment. These parameters are functions of the fiber and coating curvature, ion flux to the surface, and ion kinetic energy. These parameters are passed to the continuum equations from molecular dynamics simulations that are described below.

Level set and evolution equation approaches are used to simulate the coating shape. Four basic coating mechanisms are included in these approaches. These are attachment kinetics, curvature effects, etching due to ion bombardment, and solid-state diffusion on the coating surface. These equations are solved numerically and an-

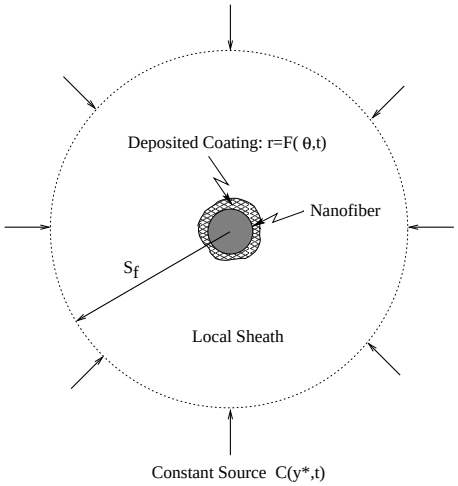

Figure 5: Local nanofiber coordinates for neutral species transport within the reactor.

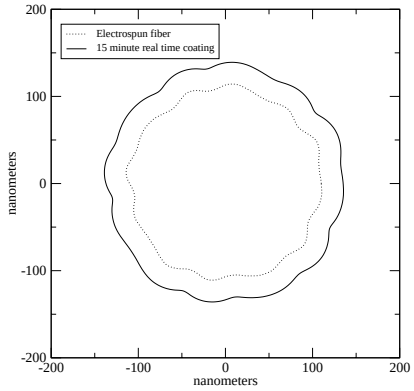

Figure 6: Level set model solution for nanofiber coating.

alyzed via boundary perturbation techniques. Results from these analyses verify basic experimental observations such as the wavelength and magnitude of the coating roughness is larger in both the axial and azimuthal directions for larger diameter fibers.

At the atomic level we use quantum mechanical (QM) (density functional theory (DFT) [8], [10], SCF-Pseudopotential electronic structure [11], and jellium model calculations) and molecular dynamics (MD) simulations to study the adsorption, reflection and sputtering mechanisms, and migration of atoms in the coating [1]. We input the ion kinetic energy, ion flux, and the thickness of the coating from the continuum models to the QM/MD simulations. This information serves as the initial conditions for the ion bombardment.

Because of the size of the fiber and the computational limitations of the QM/MD approach, it is not possible to simulate the entire circumference of the coating surface. Hence, we examine angular sectors of the nanofiber at various locations around the fiber, and at fixed discrete times, to develop a global picture of the coating growth.

Information from each of the sectors is input to a curve fit to form expressions for the deposition and desorption parameters that are valid around the circumference of the fiber and can be passed to the continuum model. The information obtained from the QM/MD simulations at each time snapshot is also curve fit to obtain expressions that are continuous in time, and for use by the continuum models. This creates a solution methodology that iterates between atomic and continuum length scales.

Putting all of the above pieces together, we present level set simulations of the coating front. The initial polymer nanofiber landscape is taken to be a superposition of Fourier modes, consistent with models of the electrospinning process. Predictions of the coating thickness are shown in Figure 6. These predictions agree well with our experimental observations.

4 SUMMARY

Polymer nanofibers are produced by electrospinning and then coated using rf magnetron sputtering. The resulting composite structure is then heated to remove the polymer core leaving a nanotube. We develop a comprehensive model integrating across atomic to continuum length scales for simulating the coating process. We investigate global and local models for transport of neutral species and ions within the reactor. We define, solve, and analyze a continuum evolution equation and level set formulation for the coating free surface. Further, we investigate QM/MD simulations of deposition and coating properties. We couple continuum models with atomic simulations. Information is passed between the various length scale models so that the simulations are integrated together. To keep the numerical simulations at a manageable level, asymptotic analyses are used to reduce the complex models to simpler, but still relevant, models.

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