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Properties of electrophoretically deposited single wall carbon nanotube films

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ABSTRACT

This paper describes techniques for rapidly producing a carbon nanotube thin film by electrophoretic deposition at room temperature and determines the film mass density and electrical/mechanical properties of such films. The mechanism of electrophoretic deposition of thin layers is explained with experimental data. Also, film thickness is measured as a function of time, electrical field and suspension concentration. We use Rutherford backscattering spectroscopy to determine the film mass density. Films created in this manner have a resistivity of $2.14 \times 10^{-3}\ \Omega\cdot$cm, a mass density that varies with thickness from 0.12 to 0.54 g/cm^3, and a Young's modulus between 4.72 and 5.67 GPa. The latter was found to be independent of thickness from 77 to 134 nm. We also report on fabricating free-standing films by removing the metal seed layer under the CNT film, and selectively etching a sacrificial layer. This method could be extended to flexible photovoltaic devices or high frequency RF MEMS devices.

1. Introduction

Single wall carbon nanotubes (SWCNTs) have attracted many researchers because of their unique intrinsic properties. SWCNTs represent a nearly ideal material for enabling high-performance micro electromechanical (MEMS) and nano electromechanical (NEMS) devices because of their extraordinary mechanical and electrical properties [1,2]. These properties include a Young's modulus of 1 to 2 TPa, tensile strength over 60 GPa, and low mass density of 1.4 g/cm^3 [3,4]. Moreover, CNTs have superior electrical properties, exhibiting a mobility up to 100,000 cm^2/V-s at room temperature [5], and a current-carrying capacity of over 10^{10} A/cm^2 [6]. The mechanical properties of carbon nanotubes may allow one to make NEMS devices that operate at extremely high speed. We have demonstrated CNT-based switches operating at 1.6 GHz with a 3 V pull-in voltage [7]. Not only does this represent many orders of magnitude improvement compared to the MEMS literature, but it approaches the speed of heavily loaded transistors with the potential for far lower power dissipation. Other major applications of free-standing CNT films include sensors [8], energy storage [9], and photovoltaic devices [10].

Early device demonstrations used discrete CNTs placed randomly until one happened to bridge a pair of electrodes. More recently, techniques for depositing continuous films of CNTs have been investigated. This approach allows the use of standard lithography and etch processes to produce arbitrary patterns at any location on the wafer. If this could be done at low temperature (<300 °C), the film would be compatible with many substrates and so would be far more versatile than process such as selective CNT growth which requires high temperature. We previously demonstrated layer by layer processes for nonaligned and aligned films [11]. This used alternating layers of CNTs and polymers or alternating layers of positively charged and negatively charged CNTs [12]. Aligned films are required for polymer composites to achieve low resistivity. While successful, these processes are extremely slow, typically 4 to 8 h to deposit a 100 nm thick film. Aligned films that use electric fields have the additional problem of finding a way to produce uniform fields over a large area with enough amplitude to create an aligned film. Furthermore, we found the positively charged CNT suspensions extremely difficult to control and reproduce.

Electrophoretic deposition (EPD) is a simple and versatile processing method for room temperature deposition of carbon nanotubes [13]. EPD uses the motion of charged particles that are dispersed in an aqueous solution under an applied electric field [14]. This method can be used to deposit thin and thick films, as well as composite coatings with complex shapes and surface patterns [15]. Du et al. first applied this technique to CNTs, demonstrating that a post deposition anneal can be used to reduce the electrical resistivity of SWCNT films [16]. Kim and Lee used EPD to deposit SWCNTs on silica spheres, but no analysis was presented on the mechanical properties of the films [17]. Pei et al. studied similar films [18], but once again presented limited amount of material characterization. The characterization that has been done in this area has focused primarily on the electrical properties, and in a few cases, optical properties of these films. Rigueur et al. studied the mechanical properties of free-standing multi-walled carbon nanotube films which were fabricated by EPD, but no electrical properties or density data were presented [19]. The characterization that has been done

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in this area has focused primarily on the electrical properties, and in a few cases, optical properties of these films. Here we report on the electrical, optical and mechanical properties of electro-deposited SWCNT films. Also, we describe techniques to measure the film mass density and fabricate free-standing SWCNT films.

2. Experimental details

Commercial SWCNTs with an average diameter of 1.4 nm (Carbon Solution Inc.) were used for EPD processing. We treated SWCNTs with nitric acid to remove impurities such as amorphous carbon and catalyst contamination [13]. SWCNTs at a concentration of 1 mg/ml were used in deionized (DI) water with 1 wt.% of the sodium dodecyl sulfate (SDS) surfactant. Pristine SWCNTs form agglomerates in DI water due to their strong hydrophobic properties. Therefore, the preparation of a stable dispersion of SWCNTs in a liquid solution is a necessary prerequisite for using the EPD method. SDS, one of the most widely used surfactants, is used to promote a mutually repulsive force to stabilize the SWCNT dispersion [14]. The surfactant molecules consist of two parts: a hydrophobic tail and a hydrophilic head. While the ionized hydrophilic head reacts with water, the hydrophobic tail adsorbs physically on the hydrophobic surface of the SWCNT bundle. Then, the dispersed SWCNTs have negative surface charges in the DI water. These negative charges surrounding SWCNTs in suspension increase the repulsive double layer force to prevent SWCNT agglomeration [15,16].

The mixture was sonicated for 1 h. Then the solution was centrifuged at 3500 rpm for 1 h to remove any precipitates or agglomerates. Fig. 1a shows the mixture procedure to prepare the SWCNT suspension. The upper 90% of the solution was separated for the deposition. Sonication and centrifugation was done prior to each deposition. The deposition was carried out in room temperature. The finished SWCNT suspension along with the above process is shown in Fig. 1b. A schematic of the overall setup for electrophoretic deposition is presented in Fig. 1c.

Prior to SWCNT deposition, four inch silicon wafers were prepared as follows. A 300 nm thick layer of SiO_2 was grown thermally on the wafers by oxidizing at 1000 °C in a wet ambient for two hours. Next, a sacrificial layer of amorphous silicon (a-Si) was deposited by plasma enhanced chemical vapor deposition using a Plasmatherm 340. The process used 5%/95% of SiH_4/He at 10 mTorr. The plasma power was 200 W and the substrate temperature was 150 °C. Typical deposition rates with this recipe were about 5 nm/min. The film stress was typically about 1 GPa compressive. In some cases, anchor holes were etched in the film to later create free-standing CNT films.

A thin layer of nickel (Ni) was sputtered on the substrate to act as the anode during the CNT deposition. The Ni layer was deposited using an

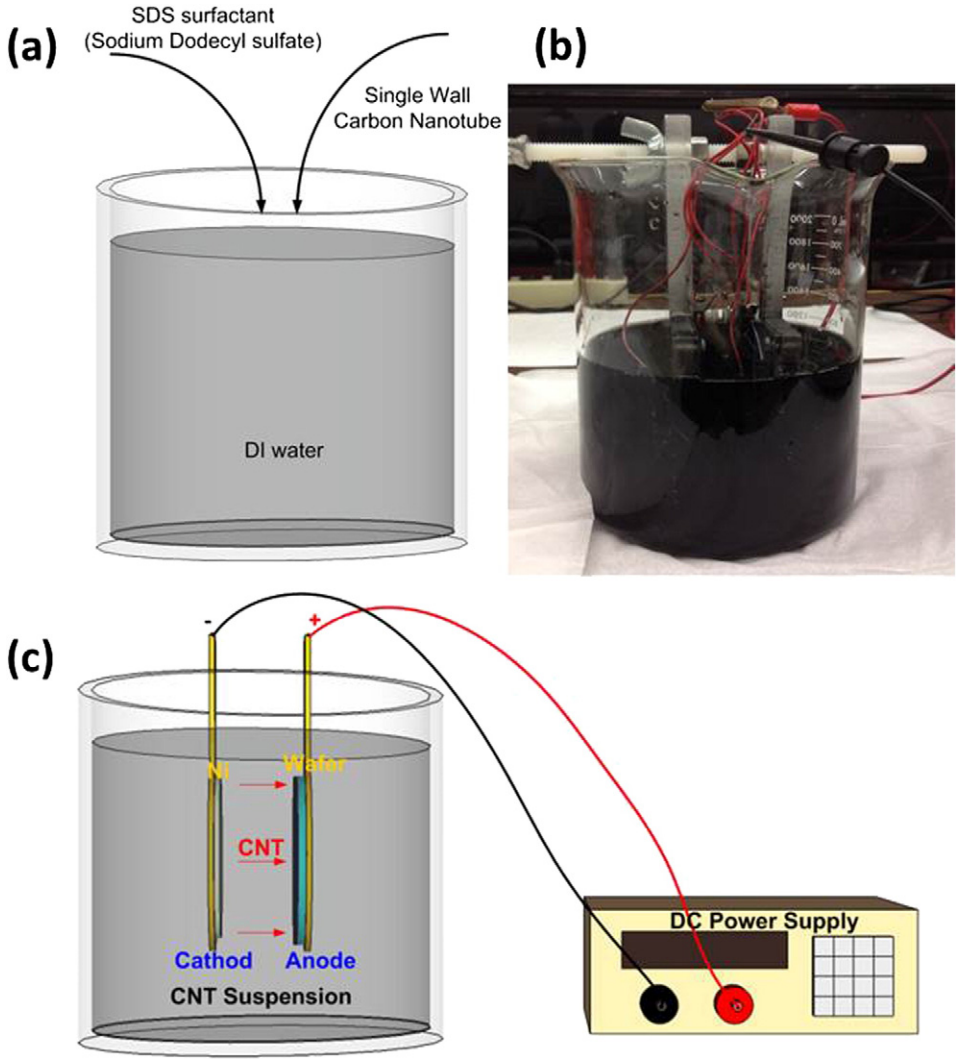

Fig. 1. Schematic of electrophoretic deposition of carbon nanotubes. (a) Prepare SWCNT suspension by adding SDS surfactants. (b) Experiment image of EPD: immersed wafer in SWCNT suspension. (c) Overall set up and deposition process.