

# Deposition and patterning of conductive carbon black thin films

Matthew D. Walton, Yeon Seok Kim, C. Jason Jan, Ethan P. McConnel,  
W. Neil Everett, Jaime C. Grunlan\*

*Department of Mechanical Engineering & Polymer Technology Center, Texas A&M University, College Station, TX 77843-3123, United States*

Received 28 January 2007; received in revised form 30 June 2007; accepted 2 July 2007

Available online 27 August 2007

## Abstract

Highly conductive carbon black-filled composite thin films were prepared using layer-by-layer assembly. Films were grown by alternately dipping a PET substrate into aqueous suspensions containing carbon black and polyethylenimine (PEI) or poly(acrylic acid) (PAA). Growth rate and sheet resistance of these films were tailored by varying the polymer concentration in the suspensions and completely removing carbon black from one solution or the other. Films made from an aqueous mixture containing 0.25 wt.% carbon black and 0.05 wt.% PAA and another solution containing 0.1 wt.% PEI grew at a rate of 735 nm per bilayer (BL) deposited and achieved the lowest sheet resistance at 10-BL (~500  $\Omega$ /sq), with a thickness of 5.4  $\mu$ m, making its bulk resistivity below 0.3  $\Omega$  cm. These composite thin films were patterned using a traditional photolithographic lift-off process that could be used to process them for a variety of electronics applications.

© 2007 Elsevier B.V. All rights reserved.

*Keywords:* Carbon black; Carbon composites; Electron microscopy; Electrical properties; Patterning

## 1. Introduction

Layer-by-layer (LbL) assembly is a process that can utilize a variety of attractions between deposited species to create thin films of varying thickness and behavior [1,2]. These thin films are most often created by alternately exposing positively and negatively charged particles or polymers, in a dilute aqueous mixture or solution, to a charged or polar substrate. Each pair of deposited species (consisting of two individual ingredients) is referred to as a bilayer (BL) and can range in thickness from one to more than 100 nm thick depending on chemistry [3], molecular weight [4], temperature [5], counterion [6], ionic strength [7], and pH [8]. This process can be used to create functional thin films with a wide range of applications including optical-to-electric power conversion [9], antimicrobial coatings [10,11], magnetic sensing [12], battery electrolytes [13], and controlling cell growth [14]. The LbL process has many advantages over other coating methods, including ease of processing and the ability to control thickness and composition at the nanometer level. The present study is focused on the growth and electrical

resistance of carbon black-filled thin films produced using this deposition method.

The most common techniques used to produce electrically conductive composites with carbon black are melt mixing [15–17] and solution processing [18,19]. Polymer composites have been studied for use as temperature [20] and chemical sensors [21], electrostatic dissipation layers [22], and electromagnetic interference shielding [23]. Traditional carbon black-filled composites require a significant concentration of filler to achieve reasonable conductivity. High carbon black concentrations produce films with increased porosity due to aggregated filler, increased brittleness, poor mechanical properties, and high mixing viscosity [24,25]. LbL processing avoids these problems by using low viscosity (<5 cP), dilute mixtures (<1 wt.% solids) to generate thin composite films with high carbon black concentration (>40 wt.%). In this case, carbon black is combined with polyethylenimine (PEI) and/or poly(acrylic acid) (PAA) to impart charge prior to deposition. Each individual layer is thin ( $\ll$ 1  $\mu$ m), allowing for tailored thickness while retaining flexibility and relative density. Previous work demonstrated the ability to tailor sheet resistance ( $R_S$ ) by modifying processing parameters such as sonication and post-deposition oven treatment [26]. In the present work an even greater level of control is achieved by altering the composition of the aqueous deposition

\* Corresponding author. Tel.: +1 979 845 3027; fax: +1 979 862 3989.

E-mail address: [jgrunlan@tamu.edu](mailto:jgrunlan@tamu.edu) (J.C. Grunlan).

mixtures. With the appropriate recipe, it is possible to produce films with a thickness of 5.4  $\mu\text{m}$  and sheet resistance of 500  $\Omega/\text{sq}$  with just 10-BL. All of the films achieve a bulk resistivity below 1  $\Omega\text{ cm}$  after 10-BL of deposition, regardless of the recipe, making these among the most conductive carbon black-filled composites ever reported. It is also shown that this deposition can be used in conjunction with traditional photolithography to generate patterned features with lateral dimensions of less than 5  $\mu\text{m}$ .

## 2. Experimental

### 2.1. Materials

Poly(acrylic acid) (PAA), with a molecular weight of 100,000 g/mol, and polyethylenimine (PEI), with a molecular weight of 25,000 g/mol, were purchased from Aldrich (Milwaukee, WI). It should be noted that Aldrich PEI is a branched polymer whose intrinsic properties ( $T_g$ , crystallinity, etc.) and layer-by-layer assembly behavior is significantly different than linear PEI [27]. PEI is a basic polymer and PAA is acidic, which is the source of their mutual attraction. Poly(ethylene terephthalate) (PET) film (trade name Melinex ST505), with a thickness of 175  $\mu\text{m}$ , was purchased from Tekra (New Berlin, WI). Carbon black (tradename Conductex 975 Ultra) was provided by Columbian Chemicals (Marietta, GA). This grade of conductive CB has a nitrogen surface area (NSA) of 242  $\text{m}^2/\text{g}$  and a primary particle size of 21 nm. Conductex is a high structure carbon black that exists as elongated, covalently fused aggregates of numerous primary particles [28,29], which can make the smallest dispersible particle size hundreds of nanometers in length [30]. Furthermore, as with most carbon blacks [31], the surface of these agglomerates is decorated with hydroxyl, carboxylate and nitrogen-containing species that generate polarity and promote interaction with water-soluble polymers [29,32].

PEI and PAA solutions were added to deionized water and rolled slowly ( $\sim 4$  rpm) for at least 12 h on a Cell-Production Roller Apparatus by BELCO Biotechnology (Vineland, NJ) to produce solutions of varying concentration (0.025–0.5 wt.%). Carbon black was then added (when applicable) at a concentration of 0.25 wt.% with a high speed impeller for 15 min at 3600 rpm, followed by rolling for 12 h under ambient conditions to achieve equilibrium. The mixtures were always sonicated just prior to use for 15 min in a Branson Tabletop Ultrasonic Cleanser by Branson (Danbury, CT). Microposit S1813 photoresist and MF 319 developer (Rohm and Haas Electronic Materials, Marlborough, MA) were used for photolithographic patterning on standard microscope slides (Corning, Inc., Corning, NY). Prior to patterning, microscope slides were immersed in piranha solution (3:1 mixture of 99%  $\text{H}_2\text{SO}_4$  and 35%  $\text{H}_2\text{O}_2$ ; caution: dangerous oxidizing agent) for 1 h to remove organic contaminants.

### 2.2. Layer-by-layer deposition

Prior to use, PET substrates were cut to size (5 cm  $\times$  10 cm) and rinsed with methanol and deionized water to remove grease

and other impurities. Cleaned substrates were then corona treated using a BD-20C Corona treater (Electro-Technic Products Inc., Chicago, IL) to oxidize the surface [33]. The fully prepared substrate was initially dipped in the cationic (PEI-stabilized) aqueous mixture for 5 min, followed by rinsing with deionized water and blow drying with nitrogen or dry air. The same procedure was followed with the anionic (PAA-stabilized) aqueous mixture to complete the first bilayer. Subsequent layers were deposited by dipping for 1 min in each mixture. Films were heated for 15 min at 70  $^\circ\text{C}$  following deposition. All samples were stored in ambient conditions for at least 12 h prior to testing.

### 2.3. Thin film characterization

Sheet resistance of the deposited films was measured with a home-built four-point probe (FPP) [26]. Thermogravimetric analysis (TGA) of the composite films provided compositional information. TGA measurements were obtained with a TA instruments Q600 TGA (New Castle, DE) operated from 25 to 900  $^\circ\text{C}$  at a rate of 10  $^\circ\text{C}/\text{min}$ . Film thicknesses were obtained using a Daktek 3 profilometer (Veeco Instruments Inc., Woodbury, NY). Surface images were obtained using a Zeiss 1530 VP FE-SEM (Carl Zeiss, Inc., Thornwood, NY) and a Vega II SEM (Tescan, Czech Republic). All films were sputtered with 4 nm of platinum prior to imaging. An optical microscope (Axioplan 2, Zeiss, Germany) was used to image patterned films.

## 3. Results and discussion

Previous work has shown that sonication of carbon black–polyelectrolyte mixtures prior to film deposition, and heating at 70  $^\circ\text{C}$  for 15 min following deposition, resulted in the lowest values of sheet resistance for a given deposition mixture

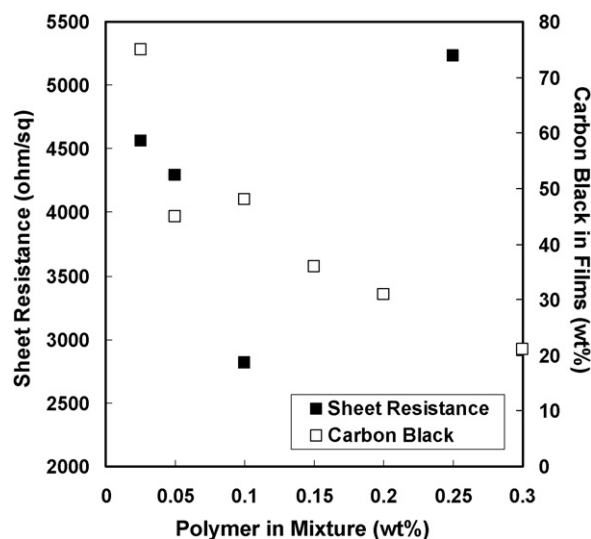


Fig. 1. Comparison of sheet resistance and carbon black concentration in films made with different polymer concentrations in the deposition mixtures. Carbon black is 0.25 wt.% for all of the systems shown here.

Download English Version:

<https://daneshyari.com/en/article/1443146>

Download Persian Version:

<https://daneshyari.com/article/1443146>

[Daneshyari.com](https://daneshyari.com)