Thin Solid Films 562 (2014) 445–450

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Formation of electrically conducting, transparent films using silver nanoparticles connected by carbon nanotubes

Sunna Hwang [a], Sun Young Noh [a], Heesuk Kim [a], Min Park [a], Hyunjung Lee [b,*]

[a] Polymer Hybrid Materials Research Center, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
[b] School of Advanced Materials Engineering, Kookmin University, Jeongneung-dong, Seongbuk-gu, Seoul 136-702, Republic of Korea

ARTICLE INFO

Article history:
Received 11 November 2011
Received in revised form 13 March 2014
Accepted 18 March 2014
Available online 26 March 2014

Keywords:
Electrospinning
Carbon nanotubes
Bridging
Transparent conductive film
Silver fibrous microstructure

ABSTRACT

To achieve both optical transparency and electrical conductivity simultaneously, we fabricated a single-walled carbon nanotube (SWNT)/silver fiber-based transparent conductive film using silver fibers produced by the electrospinning method. Electrospun silver fibers provided a segregated structure with the silver nanoparticles within the fibrous microstructures as a framework. Additional deposition of SWNT/poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) layers resulted in a remarkable decrease in the surface resistance from very high value (>3000 kΩ/sq) for the films of electrospun silver fibers, without affecting the optical transmittance at 550 nm. The surface resistance of the SWNT/silver film after the deposition of three layers decreased to 17 Ω/sq with 80% transmittance. Successive depositions of SWNT/PEDOT:PSS layers reduced the surface resistance to 2 Ω/sq without severe loss in optical transmittance (ca. 65%). The transparent conductive films exhibited a performance comparable to that of commercial indium tin oxide films. The individual silver nanoparticles within the electrospun fibers on the substrate were interconnected with SWNTs, which resulted in the efficient activation of a conductive network by bridging the gaps among separate silver nanoparticles. Such a construction of microscopically conductive networks with the minimum use of electrically conductive nanomaterials produced superior electrical conductivity, while maintaining the optical transparency.

1. Introduction

Conventional transparent conductive thin films (TCFs) coated with metal oxides such as indium tin oxide (ITO) or zinc oxide are very brittle, and they easily form cracks. They are usually deposited by an uneconomical process, i.e., vacuum sputtering, while providing high electrical conductivity and high optical transparency in various optoelectric devices [1–5]. Thus, it is necessary to replace ITO with cost-effective materials that can easily form films over large area under practical conditions. Recent studies have shown the development of TCFs using carbonaceous materials (carbon nanotubes (CNTs), graphene, etc.), conducting polymers, and metal nanowires [6–13]. In particular, CNTs on glass or polymer substrates have been regarded as some of the most reliable candidates for TCF electrodes because of their extraordinary electrical, physical, and thermal properties [14–18]. Recently, promising results with considerably low sheet resistance (~100 Ω/sq) and high transmittance (>80% at 550 nm) have been reported for CNT-based TCFs [7,19–22]. However, the use of carbon materials cannot enable the simultaneous achievement of high electrical conductivity and high transparency because of the inverse relationship between the concentration of carbon materials and the sheet resistance. The current performance of carbon materials is still too poor for these materials to be used as substitutes for ITO.

A recent report states that the performance of a random mesh of metal nanowires exceeded that of a typical metal oxide; however, the mesh suffers from (a) inefficient transport paths of electrons and (b) substantial scattering of incident light when the nanowire density increases [23–25]. Interestingly, the researchers also observed that the transmittance of metal gratings was considerably superior to that of ITO at the same sheet resistance. Several research groups have attempted to demonstrate the use of metal gratings experimentally [26–28]. We addressed this issue by fabricating a silver fibrous microstructure using the electrospinning method. Recently, the combination of functional nanoparticles (metal or metal oxide) and polymer nanofibers has received considerable attention because alignment of these nanoparticles within nanofibers can have practical application for use as electrical conductive films [29–37].

In this study, we report a strategy to achieve optical transparency and sheet resistance comparable with those of ITO materials, by using electrospinning. Electrospun silver fibrous microstructure was used as

---

* Corresponding author. Tel.: +82 2 910 4662; fax: +82 2 910 4320.
E-mail address: hyunjung@kookmin.ac.kr (H. Lee).

http://dx.doi.org/10.1016/j.tsf.2014.03.066
0040-6090/

a conductive frame for the deposition of an ultra-thin film of single-walled carbon nanotubes (SWNTs)/poly-(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS). In order to reduce the scattering effect from a silver frame and enhance the optical transmittance, a minimum number of silver nanoparticles that formed a fibrous structure were produced, and a thin film of SWNT/PEDOT:PSS was linked with conductive silver domains on the substrate. These films exhibited a very low sheet resistance of ~17 Ω/sq with ~80% optical transparency. The resistance of these films increased up to 26 Ω/sq (~50%) in four months, which was staying still at the same order of the initial resistance in the air.

2. Experimental details

2.1. Materials

Silver nitrate ($AgNO_3$, 99 +%, ACS reagent) and polyvinylpyrrolidone (PVP, Mw = 1,300,000) were purchased from Sigma-Aldrich Co. SWNTs were purchased from Hanwha Nanotech Co., Ltd. (an Arc-discharge process), and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) solution was purchased from Baytron® Co.

In order to prepare electrospinning solutions of $AgNO_3$ and PVP, 2.5 g of $AgNO_3$ was dissolved in 2 ml of acetonitrile in a 10-ml vial by stirring for 30 min, and 0.5 g of PVP powder was dissolved in 5 ml of ethanol by stirring for 2 h. The $AgNO_3$ and PVP solutions were then mixed and stirred for 1 h. Thus, we prepared a homogeneous and viscous solution for electrospinning [34,38].

2.2. Electrospinning process

The setup for electrospinning comprised a high-voltage supply, a pressure gauge to measure nitrogen-gas pressure, a syringe with a metal tip, and a flat collector. Voltage of 20 to 25 kV was applied to this solution. The electrospinning solution was poured into a 30-ml syringe attached to a metal tip with a 22 gauge size (needle diameter: ca. 0. 64 mm) and was pushed at a nitrogen-gas pressure of 0.01 MPa. The tip-to-collector distance was 15 cm. The nanofibers formed on the quartz glass were calcined at 200 °C for 2 h and subsequently at 300 °C for 1 h in an air atmosphere at a heating rate of 10 °C/min.

2.3. Deposition of SWNT/PEDOT:PSS

In order to deposit the solution mixture of SWNT/PEDOT:PSS on an electrospun silver-fiber-coated quartz glass, SWNTs that were sonicated using a horn-type sonicator (330 W) were dispersed in dimethylformamide. Then, 3 ml of PEDOT:PSS solution was added to an SWNT-dispersed solution. The mixture was then sonicated for 30 min. A droplet of SWNT/PEDOT:PSS solution was placed on the silver-fiber-coated quartz glass and then was dried at room temperature. The deposition process of SWNT/PEDOT:PSS was repeated 3, 5, 7 and 9 times, respectively. A overall process for the fabrication of a transparent conductive film using a silver fibrous microstructure and SWNT/PEDOT:PSS layers is summarized in Fig. 1.

2.4. Characterization

The surface morphology of the films was observed by using field-emission scanning electron microscopes (FE-SEM, JSM-6701F, JEOL, Japan and FE-SEM, Hitachi S-4100, Hitachi, Japan). The operating voltage in SEM was 10–15 kV. The crystal structures of silver crystals were observed on an X-ray diffraction (XRD, D/MAX-2500, Rigaku International Co., Japan) with a graphite monochromator and Cu Kα radiation (λ = 0.154 nm) and focusing/parallel-beam configurations The scanning speed was 4°/min over the range from 20° to 100°. The film transmittance was measured with a UV/Vis/NIR spectrophotometer (V-670, Jasco International Co., Ltd., Japan). The electrical conductivity was measured using a Keithley Model 2182A nanovoltmeter and Keithley Model 6220 power source in a four-point probe set-up at room temperature. Atomic force microscopy (AFM) images of the LBL thin films were recorded under room temperature in a commercial AFM (Asylum Research MFP3D) in noncontact mode (alternating current (AC) mode) with 10 nm standard cantilevers (AC160TS, Olympus). cAFM imaging was performed using the ORCA module (Asylum Research MFP-3D) in noncontact mode with a doped Si tip, Electri-Lever (AC240TM, Olympus).

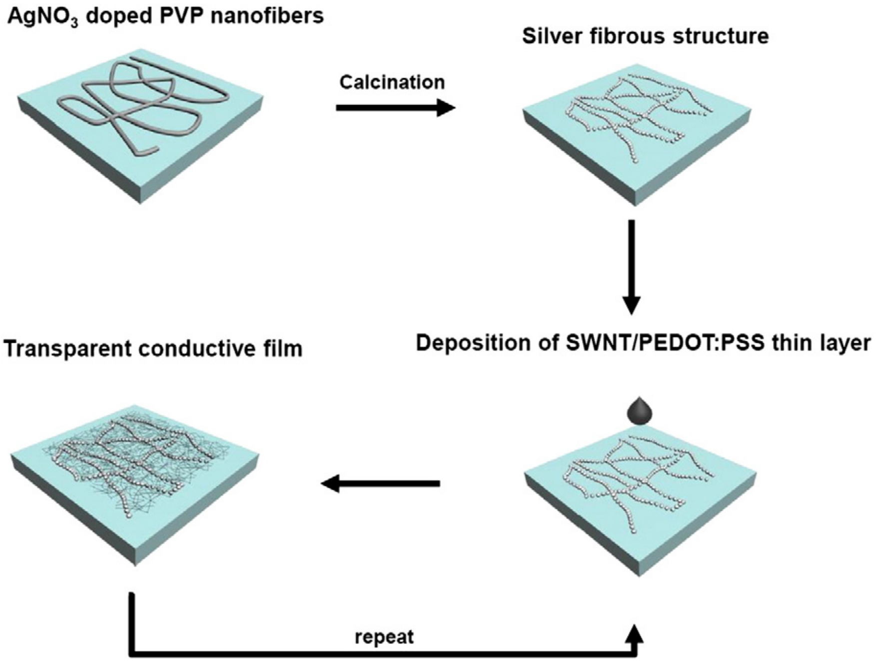

Fig. 1. Schematic representation of the fabrication of a transparent conductive film using a silver fibrous microstructure and a SWNT/PEDOT:PSS film. Detailed methods were described in the Experimental details section.