Composites Science and Technology 143 (2017) 98–105

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Large reduction in electrical contact resistance of flexible carbon nanotube/silicone rubber composites by trifluoroacetic acid treatment

Sang-Eui Lee [a], Sang Soo Jee [a], Hyokeun Park [a], Sung-Hoon Park [b], Intaek Han [a, *], Soichiro Mizusaki [a, *]

[a] Materials Research Center, Samsung Advanced Institute of Technology, Samsung Electronics, 130 Samsung-ro, Suwon, 446-712, South Korea
[b] Department of Mechanical Engineering, Soongsil University, 369 Sangdo-ro, Donjak-gu, Seoul, 156-743, South Korea

ARTICLE INFO

Article history:
Received 24 May 2016
Received in revised form
2 March 2017
Accepted 4 March 2017
Available online 7 March 2017

Keywords:
Electrical contact resistance
Carbon nanotube
Trifluoroacetic acid
Stretchable composite
Flexible composite

ABSTRACT

We report a large reduction in contact resistance between stretchable carbon nanotube/silicone rubber composites and silver electrodes by a chemical surface treatment, accompanied by an enhancement in the electrical conductivity of the composites. The reactive solvent, trifluoroacetic acid, works for the purpose. In addition, the treatment makes a uniform etching in a micro level with little sacrifice in surface roughness of the nanocomposites. The electrical conductivity of 1.0 wt% nanotube composite was enhanced approximately two-fold and three-fold by ten- and thirty-second treatment, which was induced by the reduction in the contact resistance to one half of an original value. It is meaningful that our finding can be an approach to reduce the nanoparticle loading while keeping electrical conductivity in a high level, which can be crucial for securing flexibility or stretchability in a viewpoint that the elongation is inversely proportional to the conductive particle loading.

1. Introduction

Carbon nanotubes (CNT)/elastomer-based composites have attracted much attention in a variety of electroactive applications, such as piezoresistive or strain sensors [1–3], electroactive or electrothermal actuators [4,5], and heaters [6,7] due to their flexibility and deformability. In recent years, the composites have extended tremendous attention in the field of electronics, in particular, in stretchable and deformable electrodes [8–11]. In all above-mentioned applications, there exist contact regions between the elastomeric composites and electrodes indispensable for electron migration. However, electrical contact resistance at the interface causes unnecessary power losses, and thus it is essential that the contact resistance should be in a minimum level.

The contact resistance in CNT-reinforced polymer composites can be reduced by increasing effective contact areas between an electrode and CNTs by exposing the nano fillers from the contact surface, leading to electrical links between the two contact media. Mechanical polishing [12,13] and plasma treatment [14] have been widely used for the decrease in the electrical contact resistance. However, the mechanical approach has a drawback to be applied to stretchable/flexible composite devices, especially to ones having micro/nano-scale patterns or features [8–10]. The plasma treatment can cause damages on the surface of the carbon structure, leading to deterioration in the electrical conductivity of CNT by introducing functional groups, such as carboxyl, and hydroxyl groups, which are undesirable to electrically conductive networks, and even by burning out the particles in a long plasma exposure [15]. From the above-mentioned issues, wet chemical treatment can be an optimal consideration for stretchable/flexible conductive devices, especially in cases with patterns or curvatures [8,9]. In addition, the chemical approach makes it possible to do uniform etching over all the areas by a sequence of simple dipping, washing, and drying.

Among a variety of etchants, we found that trifluoroacetic acid (TFA) can be an appropriate candidate for the purpose. TFA is volatile (boiling point 72 °C) and can be easily washed out by high miscibility with water and other common organic solvents. It was revealed that concentrated TFA dissolved polydimethylsiloxane (PDMS) [16,17]. It was also reported that hydrophilic nanoporous poly(acrylic acid)-b-polystyrene (PAA-b-PS) was developed from a triblock copolymer, PDMS-b-poly(tert-butyl acrylate)-b-PS (PDMS-b-PtBA-b-PS), by removing PDMS with TFA through three-hour

* Corresponding authors.
E-mail addresses: intaek.han@samsung.com (I. Han), s.mizusaki@samsung.com (S. Mizusaki).

http://dx.doi.org/10.1016/j.compscitech.2017.03.004
0266-3538/

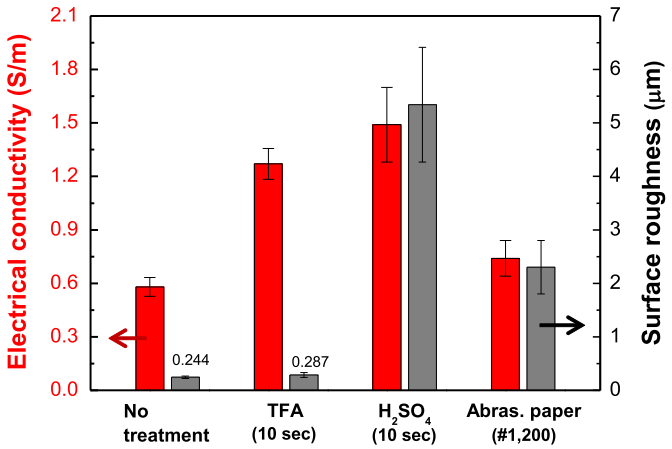

Fig. 1. Electrical conductivity and surface roughness of 1.0 wt% SWNT/PDMS composite with TFA, H_2SO_4, and abrasive paper (mechanical polishing).

stirring [17]. On one hand, an additional positive effect can be expected to help purify multiwalled carbon nanotubes (MWNTs) and remove carbonaceous impurities and metal catalysts on them [18].

We here demonstrated short-time TFA treatment can be an efficient method for contact resistance reduction and conductivity enhancement of stretchable CNT/PDMS composites. We investigated relationships between microstructures, surface roughness, and electrical conductivity of the carbon nanotube/silicone rubber composites according to TFA treatment time. In addition, the contact resistance between the composite and a silver electrode was measured by transfer length method (TLM).

2. Experimentals

2.1. Nanocomposite preparation and surface treatment

Purified single-walled carbon nanotube (SWNT) and PDMS (Sylgard 184), were purchased in Unidym and Dow Corning, respectively. The SWNTs were 1.1 nm in average diameter and a few microns in length due to bundling in ropes [19]. PDMS was selected as it has been widely used for stretchable or deformable materials and devices in recent years [5,8–11]. In order to disperse the carbon nanotube into the silicone rubber, two-step shearing process was adopted: first, a planetary milling as a preliminary step, and then three roll milling as primary one. A planetary mixer (PDM-1kv, Dae Hwa Tech) and a ceramic three roll mill (TRM, type C-43/4 × 10, Inoue Co) were used. After the planetary mixing with rotational and revolutional speeds of 700 and 600 rpm for 5 min, the SWNT/PDMS paste was three-roll-milled four times at 0.5 MPa of the setting pressure between the rolls, and then six times at 1.0 MPa, with the rotational frequency of the final roll at 40 Hz. The paste was then hot pressed between release Teflon films at 120 °C for 1 h. The rectangular specimens were cut out with the dimension of 30 mm long, 10 mm wide, and 500 μm thick. Electrodes were formed on the treated composite surfaces with a silver paste (ACH35001, Protavic), which was cured at 90 °C for 30 min and then 175 °C for 2 h.

Trifluoroacetic acid (assay ≥ 99%), and sulfuric acid (assay 95–98%) were purchased from Sigma Aldrich Co. They were used as provided for etching. The area of electrodes was etched by simple dipping into the acids, and then washed in acetone and distilled water in order for 1 min, respectively. The mechanically-polished sample was also prepared with an abrasive paper in grade 1200 grit for comparison.

2.2. Characterization

DC electrical conductivity was measured by a four-point probe technique at room temperature with a low resistivity meter (MCP-T610, Mitsubishi Chemical Analytech) and by a two-probe method with an electrometer (6517A, Keithley Instruments, Inc.). The morphology of SWNT/PDMS composite was observed by using scanning electron microscopy (FE-SEM, S-4500). The composite specimen was fractured out in liquid nitrogen to observe the cross section, and sputtered with palladium. The surface roughness was

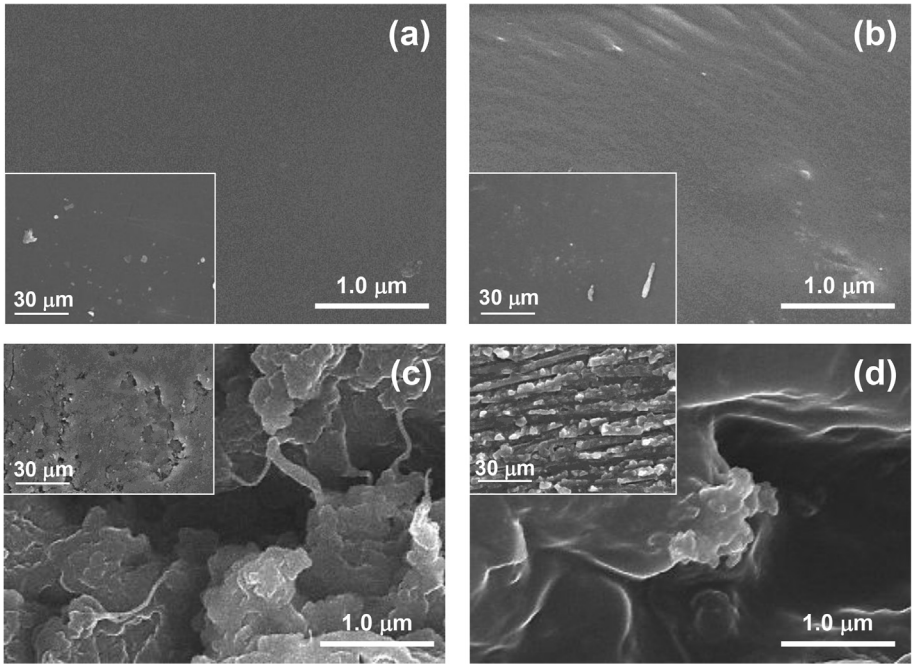

Fig. 2. Surface treatment effect on microstructures of 1.0 wt% SWNT/PDMS composite with (a) no treatment, (b) TFA, (c) H_2SO_4, and (d) mechanical polishing.