Applied Surface Science 376 (2016) 69–73

Contents lists available at ScienceDirect

Applied Surface Science

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

High-transparency and low-resistivity poly (methylmethacrylate) films containing silver nanowires and graphene-oxide nanoplatelets

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ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form 4 March 2016
Accepted 9 March 2016
Available online 10 March 2016

Keywords:
Silver nanostructure
Carbon and graphite
Optical transmission
Nanocomposite
Nanowire

ABSTRACT

Nanocomposite films containing silver nanowires (Ag NWs) and graphene-oxide nanoplatelets (GONPs) were formed on glass, and the nanocomposite films were then transferred to poly(methylmethacrylate) (PMMA) films. Scanning electron microscopy images showed that Ag NWs with a length of 20 μm and a width of 80 nm, together with GONPs with a size of 15 μm, had been formed on the PMMA film and that the Ag NWs on the PMMA film were partially covered with the GONPs. While the transmittance of the PMMA film with the Ag NWs and the GONPs was almost the same as that of the PMMA film with the Ag NWs alone, the corresponding sheet resistance was decreased due to the generation of quaternary nitrogen in the GONPs, which the results of X-ray photoelectron spectroscopy and Raman spectroscopy confirmed. The transmittance and the sheet resistance of the PMMA film containing Ag NWs and GONPs were approximately 90% at 550 nm and 24 Ohm/sq, respectively.

1. Introduction

Recently, flexible devices have attracted a great deal of interest because of their potential applications in wearable portable devices [1,2]. Because an indium- tin-oxide (ITO) electrode, which has been extensively used as a transparent electrode in wearable electronic and optoelectronic devices, has an inherent problem of fragility, alternative transparent electrodes based on metallic nanowires, graphenes, and polymers have attracted a great deal of interest for potential applications in next-generation flexible devices [3]. Among the alternative candidates for flexible transparent electrodes in flexible displays, silver nanowire (Ag-NW) electrodes have emerged as excellent candidates due to their high transparency, high conductivity, and high flexibility [4–6]. A solution process for the formation of a Ag-NW electrode is much simpler than a vacuum-based process for the formation of the ITO electrodes, resulting in a low production cost for the formation of the transparent electrodes. Because the Young's modulus of the Ag-NW electrodes is larger than that of the ITO electrodes, the Ag-NW electrodes are more suitable for use as flexible electrodes. Even though Ag-NW electrodes have excellent advantages of high flexibility, high transparency, high conductivity, and low cost in comparison with the widely-used ITO, they have inherent problems of relatively high haze, high surface roughness, and high contact resistance [7–11]. Even though some investigations have been performed in attempts to decrease the surface roughness and the high contact resistance of Ag-NW electrodes and to improve their structural, electrical, and optical properties, studies concerning improved surface roughness and contact resistance for Ag-NW electrodes containing graphene-oxide nanoplatelets (GONPs) inserted into polymer films have not yet been conducted [12].

This paper presents data for high-transparency, low-resistivity poly(methylmethacrylate) (PMMA) nanocomposite films containing Ag NWs and GONPs. Scanning electron microscopy (SEM) measurements were performed to investigate the structural properties of the Ag NW/GONP nanocomposite films. X-ray photoelectron spectroscopy (XPS) and sheet resistance measurements were carried out to characterize the relationship between the chemical and the electrical properties of the PMMA films containing Ag NWs and GONPs. Raman and transmittance measurements were performed to investigate and clarify the optical properties of the Ag-NW/GONP nanocomposite films.

2. Experimental details

The Ag NWs used in this study were synthesized by using a modified polyol process, which reduced silver nitrate ($AgNO_3$) by using

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http://dx.doi.org/10.1016/j.apsusc.2016.03.074
0169-4332/

an ethylene glycol (EG) solution containing poly (vinylpyrrolidone) (PVP) [13,14]. After 5 mL of EG had been suspended in an oil bath at 151.5 °C for 1 h, 40 μL of a 4-mM $CuCl_2$ solution was mixed with the heated EG. After the solution had been heated for an additional 15 min, 1.5 mL of a 0.147-M PVP solution in EG was mixed with the heated EG, followed by the addition of 1.5 mL of a 0.094-M $AgNO_3$ solution in EG. After a reaction for 1 h in the oil bath, the synthesis of the Ag NW solution in EG was accomplished. When the obtained Ag-NW solution was sufficiently cooled in deionized water, the solution was diluted with acetone and centrifuged at 2500 rpm for 20 min. After the solution had been centrifuged, the supernatant EG and acetone were removed by using a syringe. The solution was repeatedly centrifuged with deionized water and methanol and was then dispersed in isopropyl alcohol or methanol. The glass or Si substrates used as auxiliary substrates were ultrasonicated in acetone and methanol at room temperature for 15 min and rinsed in deionized water thoroughly. After the auxiliary substrates had been dried, they were cleaned by using an ultraviolet/ozone cleaner for 20 min at room temperature under ambient conditions. The synthesized Ag-NW solution was repeatedly bar-coated, to increase its conductivity, onto the ultraviolet/ozone-treated auxiliary substrates [15]. After the Ag-NW-coated auxiliary substrates had been dried at room temperature for 10 min, they were heated on a hot plate at 85 °C for 15 min to remove the solvents completely. The GO solution with a concentration of 1 g/L was dispersed in ethyl alcohol by ultrasonication for 12 h. The Ag-NW-coated auxiliary substrates were dipped into the GO solution for 30 s and were then rinsed in ethyl alcohol. The GO-coated Ag-NW substrates were dried on a hot plate at 85 °C for 15 min.

The electrode patterning for device applications was done by removing the superfluous area with a swab. The surface of the patterned Ag-NW electrode was cleaned by using an ultraviolet/ozone cleaner to drop-cast the PMMA solution. After the 10-wt.% PMMA solution in dimethylformamide had been drop-casted to laminate the PMMA layer on the patterned Ag NW film, the substrate was placed in a vacuum oven. After thermal treatments in the vacuum oven at 120 °C for 2 h, the nanocomposite films were immersed in a dilute HF solution (H_2O: HF (49%) = 20: 1) for 10 min. The nanocomposite films were easily separated from the auxiliary substrate because of the etching reaction of SiO_2 in a dilute HF solution. After the isolated nanocomposite film had been rinsed in deionized water, the film was dried on a hotplate at 80 °C for 10 min. The detailed formation processes of the nanocomposite films are shown in Fig. 1.

SEM measurements were performed by using Nova Nano scanning electron microscope (FEI). Sheet resistance and transmittance measurements were performed by using the FPP-40K (DASOL) and the V-670 (JASCO) systems, respectively. XPS measurements were conducted by using a theta probe base system (Thermo Fisher Scientific Co.). All of the XPS spectra were calibrated by using the reference energy of the C1s peak at 284.8 eV from contamination to compensate for the charge effect. Raman spectra was measured by using a laser Raman spectrometer (NRS-3100, JASCO).

3. Results and discussion

Fig. 2 shows SEM images for the Ag NWs embedded in a PMMA film with and without the GONP treatments. The size and the width of the Ag NWs were approximately 20 μm and 40 nm, respectively. The Ag NWs with a large aspect ratio were synthesized by using slow injections of the $AgNO_3$ and the PVP solutions. The capping agent PVP not only prevented the Ag NWs from aggregating into bundles but also promoted their anisotropic growth. The faint lines shown in Fig. 2(a) were attributed to the immersed parts of the Ag NWs, and the bright lines were related to their exposed parts. The

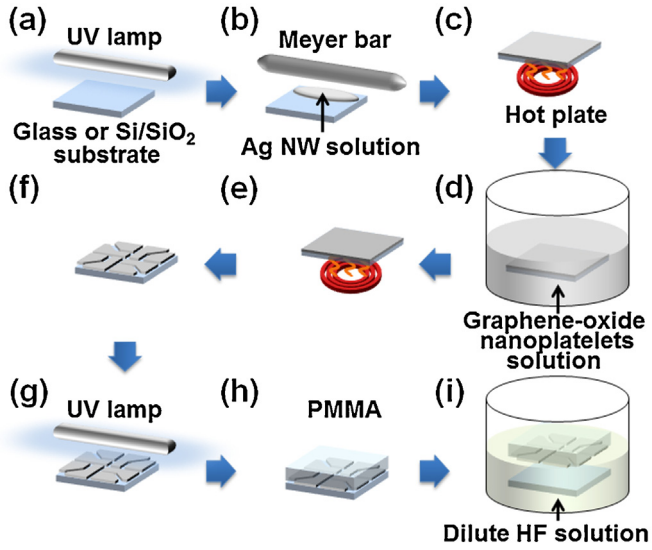

Fig. 1. Schematic diagrams of the formation process for the silver nanowire (Ag-NW)-graphene-oxide nanoplatelet (GONP) nanocomposite films: (a) ultraviolet/ozone treatment of glass or Si/SiO_2 substrates, (b) bar-coating of the Ag-NW solution, (c) drying, (d) dipping in GONP solution, (e) drying, (f) patterning nanocomposite layer, (g) ultraviolet/ozone treatment, (h) drop-casting of a PMMA solution, and (i) etching in a HF solution and isolation of PMMA and glass substrates.

GONPs with an average length of about 15 μm covered the Ag NWs and their intersections, as shown in Fig. 2(b). Even though some parts of the GONPs were wrinkled and overlapped each other, the GONPs maintained their typical shapes.

Fig. 3 shows the sheet resistances as functions of the amount of Ag-NW solution for the PMMA nanocomposite films. The average values of the sheet resistances were repeatedly measured at different regions. As the electrical network of the Ag NWs was increased, the mean sheet resistances of the nanocomposite films and their variances decreased with increasing amount of Ag-NW solution, as shown in Fig. 3. The density of the Ag-NW network increased with increasing amount of Ag NW solution, and the uniformity of the Ag NW network was improved, resulting in a decrease in the sheet resistances of the Ag-NW- embedded PMMA substrates and their variances. The GONP treatment significantly decreased the mean sheet resistances and their variances due to an increase in the conductivity of the GONPs. The mean sheet resistance of the Ag-NW-embedded PMMA substrate at 20 μL of the Ag NW solution decreased from 101.5 to 23.9 Ω/sq due to the GONP treatment, and the variance of the sheet resistances decreased from 138.8 to 8.9 Ω/sq. While the previous reports on GONP-treated Ag-NW electrodes showed that the sheet resistance and the transmittance of the GONP-treated Ag NWs after a hydrazine reduction process were approximately 27 Ω/sq and 70%, respectively [16], in this study, the corresponding values of the PMMA film containing GONP-treated Ag NWs were approximately 24 Ω/sq and 90%, respectively. The GONP treatment significantly improved not only the conductivity of the Ag-NW-embedded PMMA substrates but also the uniformity of their conductivities. Even though the GONP was an insulator, the surface of the GONP was partially reduced due to the oxidation of the Ag atoms at the contact areas of the GONP with a Ag-NW, and quaternary nitrogen was generated in the GONPs. The reduction and the nitrogen-doping processes for the GONPs took place only at the contact areas of the GONPs with the Ag NWs. Because the electrical conductivity of the GONPs was partially increased while the transmittance of the GONPs was not dramatically changed, the sheet resistance and the uniformity of the GONP-treated Ag-NW electrode were significantly improved.