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Material- and process-effects on homogeneity and electric properties of transparent conducting films composed of hydrazine-reduced graphene oxide and/or silver nanowire

Katsuyuki Naito*, Norihiro Yoshinaga, Yoshihiro Akasaka

Corporate Research & Development Center, Toshiba Corporation, 1 Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 212-8582, Japan

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ABSTRACT

Photomicroscope observation of hydrazine-reduced graphene oxide (h-rGO) films indicates that the films prepared by spin-coating are more homogeneous than those prepared by dip-coating. Graphene oxide (GO) is apt to aggregate during the dipping process. Increasing rotation speed of the spin-coating decreased film thickness and increased surface resistant (Rs). Rs of small-sized h-rGO(BF1A) was smaller than that of large-sized h-rGO(NiSiNa). The h-rGO(NiSiNa) films prepared with a rotation number smaller than 2000 rpm had wrinkles about 5 nm in height and particles with about 15 nm height. The rotation number of 3000 rpm decreased the wrinkles and particles resulting in smaller Rs. Increasing the hydrazine-treatment temperature from 90 to 140 °C caused the Rs values to decrease. Work-function values of h-rGO(NiSiNa) were 3.6–3.8 eV; smaller than those of other h-rGOs. Larger ratio of pyrrolic nitrogen to oxygen-bound nitrogen gave smaller WF values. Silver nanowire (AgNW) films prepared by multiple spin-coating processes showed small Rs vales and small Rs deviations. Mechanical pressing at 100 °C made the thickness of AgNW films equal to the AgNW diameter and decreased the Rs values. Polymer (Cytop) was coated on the AgNW films and the h-rGO/AgNW/Cytop transparent conducting film was peeled off. The arithmetic average roughness of the h-rGO surface was 1.2 nm.

1. Introduction

Graphene films have been investigated with a view to their application as cheap and flexible transparent electrodes for organic photovoltaic cells (OPVs) [1,2] and organic-light-emitting diodes (OLEDs) [3,4]. Graphene films are light, flexible, transparent in a visible and near-infrared region, chemically stable and work-function(WF) controllable by modification. Large transparent graphene films were prepared on copper foil by thermal CVD and transferred onto a polymer sheet [5]. Their sheet resistance values, however, are rather large for such current-driving devices. The cost was also an issue because the copper foil was dissolved during the processes. The hydrazine-reduced graphene oxide (h-rGO) films were much cheaper but their Rs values were much higher [6].

In the case that graphene is used for the transparent current-driving electrode of large-size devices, small Rs values are required. ITO glass substrates with Rs of less than 10 Ω/sq are used for OLED and OPV devices. The authors have predicted that graphene will prove to be inapplicable without auxiliary electrodes.

Silver nanowires (AgNWs) can be expected to act as good auxiliary electrodes with Rs of less than 10 Ω/sq [2,7,8]. AgNWs have been used in touch panels. AgNW films are prepared by wet coating. They are flexible. Because of small amount of silver they are cheap. Compared with wire grid, the number concentration of AgNW per area is higher. This is preferable to decrease the effect of graphene defects and boundaries [9,10].

The authors have prepared a transparent conducting film composed of h-rGO/AgNW/polymer stacked layers with 4 Ω/sq sheet resistance (Rs) and 75% total transmittance at 550 nm [9]. The film is transparent at a wavelength ranging from 200 to 2600 nm. Its surface roughness is about 3–4 nm. It is stable against sulfur vapor owing to the h-rGO protective layer. The films were prepared by low-cost wet processes.

Energy levels of graphene are important for OPV and OLED electrodes, whereas that is not so in the LCD application [11]. For OPVs and OLEDs, indium–tin-oxide (ITO) electrodes with WF of about 5 eV are used as the anode. Aluminum with WF of 4.2 eV is

* Corresponding author.
E-mail address: katsuyuki.naito@toshiba.co.jp (K. Naito).

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typically applied as a cathode. The WF of graphene is 4.5 eV [12], which is small for the anode and large for the cathode. The authors reported that the WF values of the transparent conducting films composed of h-rGO/silver nanowire (AgNW)/polymer stacked layers were reduced by electrochemical or borohydride treatment [13].

Film homogeneity, flatness and energy level are important in applications for optoelectronic devices. The contact between h-rGO and AgNW should be tight. In this article the authors report material- and process-effects on homogeneity and electric properties of the transparent conducting films.

2. Experimental

2.1. Materials

GO(BF1A) was synthesized according to the literature [14]. 120 mL of 96% sulfuric acid was cooled at 4 °C. 2.74 g of $NaNO_3$ and 5.0 g of graphite with 1 μm diameter (product name: BF-1A) purchased from Fujikokuen (Tokyo, Japan) were added to the sulfuric acid. 5.2 g of potassium permanganate was slowly added into the vigorously stirred suspension for 45 min. The temperature of the reaction mixture rose to 10 °C. The mixture was stirred at room temperature for 3.5 h and left to stand for 15 h. 200 mL of water was slowly added while the mixture was stirred and cooled. The brown mixture was heated to105 °C and cooled to room temperature. 450 mL of hydrogen peroxide aqueous solution was slowly added for 13 min. The reaction mixture was centrifuged at 4000 rpm for 10 min. A precipitate was stirred in 1 N hydrochloric acid and centrifuged at 20000 rpm for 10 min. The precipitate was washed 4 times in the same manner. The resulting precipitate was dried at room temperature in vacuum for 1 h and then at 80 °C for 7 h. 7.19 g of black GO(BF1A) was obtained. GO(Z5F) was prepared from another graphite (Ito Graphite Z-5F, 4 μm diameter) by a similar method. GO(NiSiNa) (product name: dry GO) was purchased from NiSiNa Materials (Okayama, Japan). AgNW (NM) (product name: NM-SNW-40) was purchased from NanoMeet Technology (Beijing, China) (an average diameter of 40 nm and length of 20–80 μm according to Nano Meet). AgNW(SLV) (product name: SLV-NW35) was purchased from Blue Nano (Charlotte, USA) (an average diameter of 35 nm and average length of 10 μm according to Blue Nano). AgNW(SS) (product name: AgNW-115) was purchased from Seashell Technology (La Jolla, CA, USA) (average diameter of 111 nm and average length of 29.3 μm according to Seashell).

Hydrazine monohydrate was purchased from Tokyo Kasei Kogyo (Tokyo, Japan). Poly(perfluoro-4-vinyloxy-1-butene) with carboxylic acid end functional group (product name: CYTOP CTL-809A), was purchased from Asahi Glass (Tokyo, Japan)[15]. Poly (methyl methacrylate) (PMMA) of 75,000 molecular weight was purchased from Aldrich Japan (Tokyo, Japan). Block copolymer of methyl methacrylate and butyl acrylate (product name: KURARITY) was given by Kuraray (Tokyo, Japan)

2.2. Conducting film preparation

The GO film was dip- or spin-coated onto a hydrophilic quartz glass sheet and then reduced by hydrazine monohydrate vapor on a hot plate. AgNW suspension was drop- or spin-coated onto the reduced graphene oxide (h-rGO) films, and dried at 60 °C under an argon atmosphere for 30 min. Polymer solution was cast with an applicator or spin-coated onto the AgNW, and dried in vacuum and then at 60 °C under an argon atmosphere. The conducting film was peeled off from the quartz glass in water, and dried.

2.3. Characterization

Sheet resistance was measured with the four-point probe method. The distance between the probes was 1 mm. When a 1 mA DC current flowed between the outer two probes, the voltage between the inner two probes was observed. The obtained resistance value was multiplied with 4.5 (geometrical correction factor) to get the sheet resistance [16]. The measurement was carried out at 9 points on the film. Sizes of GO particles were measured by AFM with a SII SPA400-SPM in dynamic force mode: GO(BF1A) (<500 nm) < GO(Z5F) (<1 μm) < GO(NiSiNa) (1–5 μm). The oxygen to carbon atom ratio (O/C) was determined by XPS with a PHI Quantum-2000 X-ray photoelectron spectrometer: GO(Z5F)(37%) < GO(BF1A)(57%) < GO(NiSiNa)(116%). Optical properties were measured with a Shimadzu UV-3101PC spectrophotometer. Total transmittance was measured with an integrating sphere. X-ray photoelectron spectra (XPS) were observed with a PHI Quantum-2000 X-ray photoelectron spectrometer to measure the atom species.

The work functions were measured by ultra-violet photoelectron spectroscopy with HeI (UPS: PHI Versa Probe, $h\nu = 21.21$ eV). The WF values were determined using the secondary-electron cutoff of the UPS, employing gold as a reference. The position of the Fermi level was calibrated by measuring the Fermi edge of gold [17]. Negative bias (−10 V or −7 V) was applied to the stage. The gold surface was cleaned by argon ion etching. The carbon samples were not etched by argon ion.

3. Results and discussion

3.1. H-rGO film preparation by dip-coating

Table 1 shows transmittance at 550 nm, graphene layers, sheet resistance (Rs) and its standard deviation(SD) of the h-rGO (NiSiNa) films prepared by dip-coating at various dipping-speed (DS) and reduced by hydrazine monohydride at 90 °C. The thickness of graphene layers (layer number, LN) was determined from the specular transmittance values (ST). The transmittance of graphene monolayer is 97.7% [18]. The layer number (LN) increased and the resistance (Rs) decreased, as the dipping-speed (DS) increased. Fig. 1 shows photographs of the h-rGO films observed with an optical microscope. Some structures were observed. Aggregation of GO can be considered to take place either with or without centrifugal separation of the precipitate.

Table 1
Thickness and sheet resistance of h-rGO (NiSiNa) films prepared by dip-coating at various dipping speed and reduction with hydrazine monohydride.

Run	DS[a] mm/s	ST[b] %	LN[c]	Rs[d] 10^6 Ω/sq	SD[e]
1	0.4	98.1	0.8	Unstable	
2	0.6	97.2	1.2	Unstable	
3	0.8	96.7	1.4	4.8	1.3
4	1.0	96.2	1.7	2.9	0.81
5	1.2	95.6	2.0	2.7	0.75
6	1.2	95.5	2.0	2.9	1.5
7	1.4	95.3	2.1	1.6	0.81
8	1.4	94.6	2.4	1.8	0.51

[a] Dipping-speed.
[b] Specular transmittance at 550 nm.
[c] Graphene layer number.
[d] Average sheet resistance of 9 points.
[e] Standard deviation of Rs.