

Transparent conducting films composed of graphene oxide/Ag nanowire/graphene oxide/PET

Katsuyuki Naito*, Riko Inuzuka¹, Norihiro Yoshinaga, Wu Mei

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

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ABSTRACT

Graphene oxide (GO) dispersed in ethanol, silver nanowire (AgNW) and GO are sequentially applied on PET films (5×6 cm) to prepare transparent conductive films with AgNW sandwiched by GO. A sheet resistance (R_s) value of one of the films was $10.4 \Omega/\text{sq}$, and the total transmittance (TT) was 82% (at 550 nm wavelength). By applying the diluted suspension of the GO twice to prepare the GO underlayer, the AgNW uniformity was improved, R_s values of the transparent conductive films decreased, and the relative standard deviation also decreased from 10–120% to 10–40%. R_s values were reduced by applying GO as an upper layer to form a sandwich structure GO/AgNW/GO. R_s values did not increase after bending the films 30 times with a 7 mm-diameter glass tube as a fulcrum.

1. Introduction

Application of graphene [1–6] and AgNW [2,7–9] as transparent electrodes replacing ITO has been expected. Graphene is flexible and flat, and it is possible to transport electrons through its plane, but there is a disadvantage in that electric resistance is high. AgNW films have low resistances, and they can be manufactured by coating. AgNW is flexible but unsuitable for exchanging electrons through a plane owing to the apertures of the AgNW network. We have developed hydrazine-reduced graphene oxide (h-rGO)/AgNW stacked layer transparent conducting films that can be prepared by coating. Transmittance and sheet resistance of the films were comparable to those of ITO glass. The films eliminated the disadvantages of the individual components. h-rGO prevented corrosion of AgNW [10]. By controlling the reduction condition, it is possible to change the work function of h-rGO [11]. The conductivity was improved by changing film forming conditions [12]. The stacked layer films are suitable for cathodes for electronic devices that exchange electrons at the interface such as OLED and OPV. Transparent electrode composed of AgNW sandwiched by reduced graphene oxide was recently applied to OPV [13]. The power generation efficiency of the cell was comparable to that using ITO.

Transparent electrodes in which GO and AgNW are laminated have also been investigated [14–17]. In these cases, GO layers are not reduced and, unlike reduced GO, they are unsuitable for the exchange of electrons at the interface. Transparency of GO, however, is higher than that of rGO. R_s values are also small because of the AgNW network.

Therefore, GO/AgNW systems are considered suitable for transparent electric wiring and for voltage application devices. A reduction process is unnecessary and they can be fabricated at low cost. GO and AgNW are generally dispersed in water or in alcohol. An aqueous dispersion system is preferable from the viewpoints of environmental considerations and cost. It is difficult to obtain uniform films because of high cohesiveness. In addition, hydrophilic treatment of the substrate is generally required.

Yun et al. [14] submerged a PET film in an aqueous dispersion of GO and gradually evaporated the water at 60 °C. The meniscus of the suspension retreated, resulting in GO layer preparation. AgNW layer was dip-coated from its aqueous suspension. Moon et al. [15] made a PET film hydrophilic with oxygen plasma treatment, applied a 2-propanol dispersion of AgNW with a bar coater, treated the film with further oxygen plasma, and sprayed an aqueous dispersion of GO. David et al. [16] spin-coated an ethanol dispersion of GO on a PEN film, transferred a mixed film of AgNW and CNT on to the GO, laminated an epoxy resin/PEN film and peeled off the underlying PEN to form a GO/AgNW-CNT/epoxy resin/PEN film. Wu et al. [17] prepared a GO film at the interface between water and pentane, transferred the film onto a PET film by dipping, and coated AgNW. These papers indicate the difficulties of preparing uniform films of GO/AgNW on PET or PEN film.

The authors dropped an ethanol dispersion of GO onto a PET film without making its surface hydrophilic, applied an aqueous dispersion of AgNW with an applicator, and dropped the ethanol dispersion of GO

* Corresponding author.

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

¹ Present address: Power and Industrial Systems Research and Development Center, Toshiba Corporation, 2-4 Suehiro-cho, Tsurumi-ku, Yokohama 230-0045, Japan.

again, resulting in a conducting film with high transmittance and low resistance.

2. Experimental

2.1. Materials

GO dispersed in ethanol (0.01 wt%, product name: RapGO pure), purchased from NiSiNa Materials (Okayama, Japan), was diluted to 0.005 wt%. GO (BF-1A) was synthesized from 1 μm -diameter graphite (product name: BF-1A) purchased from Fujikokuen (Tokyo, Japan) according to a previous paper [11]. An ethanol dispersion of GO (BF-1A) was prepared by dropping a 0.1–1 wt% aqueous dispersion of GO (BF-1A) into ultrasonicated ethanol to prepare 0.005 wt% dispersion. Supernatant suspensions of centrifugation of GO (NiSiNa) at 1000 rpm for 5 min and of GO (BF-1A) at 2000 rpm for 5 min were used. When GO (BF-1A) powder was directly dispersed in ethanol or in methanol, uniform dispersions were not obtained.

An aqueous dispersion of AgNW (TYP-989) with 85 nm diameter and 38.4 μm length and a binder polymer solution (TYP-186) were supplied by SEIKO PMC (Tokyo Japan). Ethanol dispersions of AgNW (LSV-NW35 and SLV-NW90) with 35 and 90 nm diameters respectively were purchased from Blue Nano (Charlotte, NC, USA). Optical PET films (188 μm thickness) purchased from Toyobo (Osaka, Japan) were used. The total transmittance (TT) at 550 nm of the PET film was measured to be 91%.

2.2. Preparation of transparent conducting films

After removing the charge on the PET film (5 \times 6 cm) by an ionizer, argon gas was flowed on the front and back sides of the film to remove dust. The surface of the film was rather hydrophobic (contact angle of water is 60–65°). The centrifuged GO suspension was diluted to a half concentration. 400 μL of the diluted suspension was applied, dried at room temperature, and heated in an oven at 60 °C for 10 min. The treatment was carried out twice. In other cases, the centrifuged GO suspension without dilution was applied once. The mixed aqueous suspension of AgNW and the binder polymer containing 6% 1-propanol was applied by using an applicator, and dried at 60 °C for 10 min. The gap of the applicator was changed from 0.5 to 10 mil. The AgNW concentration was 0.25 wt%. The weight ratio of AgNW to the binder polymer was 1: 0.75. Next, 400 μL of the centrifuged GO suspension was dropped, and dried at 60 °C for 10 min to prepare a transparent conducting film.

2.3. Characterization

Sheet resistance (R_s) was measured with the four-point probe method. The probe head, whose four probes were coated with rhodium, was purchased from BAS Corporation (Tokyo, Japan). Each probe has a 50 gf-spring for soft contact. 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 (R_s) [19]. The measurement was carried out at 9 points in a 3 \times 3 matrix on the film. A relative standard deviation (RSD) which was a value that a standard deviation was divided by a mean R_s value was a uniformity indicator of the film.

Sizes of GO particles were measured by AFM with an SII SPA400-SPM in dynamic force mode: GO(BF-1A) (< 500 nm) < 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 (BF-1A) (57%) < GO (NiSiNa) (116%). Optical properties were measured with a Shimadzu UV-3101PC spectrophotometer. Total transmittance (TT) at a wavelength of 550 nm was measured with the spectrophotometer with an integrating sphere mainly in the central part of

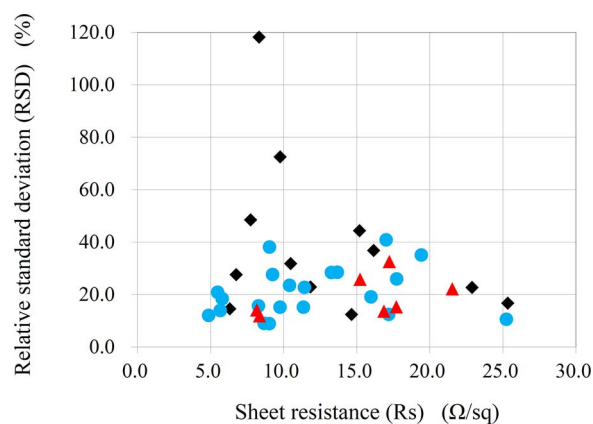


Fig. 1. Relative standard deviation (RSD) vs. sheet resistance (R_s) at the transmittance measurement point for GO/AgNW/GO/PET films.

◆ GO (NiSiNa) was undercoated once.
● GO (NiSiNa) was undercoated twice.
▲ GO (BF-1A) was undercoated twice.

the film, and the measuring part was recorded so as to correspond to R_s . The structure was observed with SEM (Carl Zeiss ULTRA55), AFM and digital optical microscope (KEYENCE VHX-2000). Flexibility was measured by bending a film with a length of 6 cm and a width of 2 cm with a 7 mm-diameter glass tube as a fulcrum until the film was overlapped by hand and the change in R_s due to the number of folds was measured.

In order to estimate GO thickness according to the graphene monolayer transmittance of 97.7% [18]. GO films were reduced by hydrazine monohydrate vapor at 90 °C for 60 min and at 110 °C for 30 min. The number of GO (NiSiNa) layers was estimated to be from 3 to 4. That of GO(BF-1A) was from 1–2.

3. Results and discussion

3.1. GO underlayer effects on the uniformity of transparent conducting films

Fig. 1 shows the relative standard deviation (RSD) vs. sheet resistance (R_s) at the transmittance measurement point. Applying the diluted suspension of GO (NiSiNa) twice decreased the RSD values from 10–120% to 10–40%. The small GO (BF-1A) further decreased the values.

GO has many hydroxyl and carboxyl groups and these functional groups are highly hydrophilic. GO also has hydrophobic nanographene structures [20], and it seems that the nanographene structure interacts with the hydrophobic PET benzene ring to form a stable coating film. It is also known that GO monolayers act as lubricants in water [21], and it is thought that the aqueous dispersion of AgNW can be spread on GO/PET.

Uniform films were not obtained without the GO underlayer or the binder polymer. Aggregations of AgNW were visually observed as shown in Fig. S1 (supplementary material). When PET films were treated with UV-ozone, the ethanol suspension of GO gathered around the edge of the films, resulting in very large R_s values. Changing the amount of the GO suspension had no effect. These results were probably attributable to the coffee-ring effect. The ethanol suspension was strongly absorbed on the hydrophilic PET surface treated by UV-ozone. The evaporation speed at the edge of the film is larger than that at the center. The suspension was continuously supplied from the center to the edge, resulting in the non-uniform films.

Fig. 2 shows the total transmittance (TT) vs. sheet resistance (R_s) at the transmittance measurement point. The TT values were increased by applying the diluted GO solution twice, and slightly increased when applying small-sized GO (BF-1A).

The R_s values tended to be smaller when increasing the gap of the

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