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Photoresist-assisted fabrication of thermally and mechanically stable silver nanowire-based transparent heaters

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ABSTRACT

Networked structures of percolated silver nanowires (AgNWs) are an important substitute for brittle indium tin oxide (ITO)-based transparent electrodes, owing to their high ductility and tunable optical and electrical conductivities. Recently, AgNWs have been used in the fabrication of flexible transparent heaters, but only when firmly adhered to the underlying polymer substrate so that the electrodes are reliably flexible. Another requirement is that these electrodes must be passivated from the atmosphere, preserving them even when the fabricated heaters are biased at high voltages or exposed to harsh environments. Here, we used conventional photolithography with a coating of commercial photoresist, UV exposure and development, in order to make protected AgNW networks. For this, AgNW networks preformed on a transparent polymer were used as a photomask layer, so that the photoresist could be developed to be selectively present on the AgNWs. As a result of this simple approach, the mechanical/thermal stability and heating performance of our AgNWs-based transparent heaters were successfully enhanced. It displays an increase of <2% in R_s when bent to a radius of 500 μm for 10,000 cycles, and a biasing voltage to the heater rapidly increased its temperature above 160 °C within a very short time period.

1. Introduction

Silver nanowires (AgNWs) are a promising material for flexible and transparent electrodes by virtue of their high electrical conductivity, high aspect ratio (resulting in low-density percolation), and their intrinsic high ductility [1–10]. A number of different approaches have been suggested for using AgNWs to achieve diverse structural configurations that could be employed in the fabrication of organic light emitting diodes [11,12], organic photovoltaics [13–15], touch sensors [16,17] and pressure sensitive devices [18,19]. Recently, AgNW-based structures have also been used to produce transparent heaters, made possible by their low surface resistivity and high chemical stability. For instance, Kim et al. reported that uniformly interconnected AgNW networks could be successfully employed in the fabrication of transparent film heaters, and the fabricated heaters simultaneously possess high transparency and good heating capability; these could be heated above 100 °C within 50 s [20]. According to Ji et al., the thermal response of AgNW-based transparent heaters could be enhanced by hybridization with poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) [21]. Other materials such as graphene [22] and metal oxides [23] have also been used to enhance the heating performance of AgNW-based heaters.

Meanwhile, enhancing the mechanical stability of AgNW electrodes has been extensively studied, focusing primarily on increasing AgNW adhesion to the underlying polymer [24,25]. Using a transparent adhesive between the nanowire network and the polymer is an effective and intuitive method to firmly attach AgNW networks onto polymers [24,25]. However, increased film thickness, decreased transparency (due to the addition of an interlayer), and deteriorated processibility (by the sticky properties of the adhesive) are relevant issues with this method. Moreover, most of the nanowires in this case would be exposed to air, which can promote melting or oxidation when heated. Inverted layer processing was developed to fully bury these AgNW networks into the surface of the transparent polymers [11,26]. Highly enhanced mechanical stability and thermal stability can be achieved by employing this method, but a peeling-off procedure is required after curing the polymer to flip over the fabricated film. This causes the surface of the electrode to be exposed such that a device can be fabricated or power sources can be connected. However, inverted

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layer processing can sometimes be time-consuming and result in defects, such as extruded AgNWs from the surface of the polymer. Furthermore, the procedure is typically not compatible with the work flow of commonly used fabrication procedures (deposition of electrode materials on a transparent polymer and subsequent patterning). This implies that a simpler and well-established method is still needed to fabricate mechanically and thermally stable electrodes that can be used as flexible transparent heaters, without employing any additional materials or peeling-off procedures.

Herein, we used a photoresist (PR)-assisted approach to make mechanically and thermally stable AgNW-based transparent heaters. A positive-type PR was employed to selectively preserve the AgNWs coated on a transparent polymer. A regular photolithography (PL) procedure was employed to develop the PR layer and preserve the nanowire network. The amount of PR coverage on the nanowires and their adhesion to the underlying polymer were determined, as were the effects of PR coverage on the heating performance and optical transparency.

2. Materials & methods

A schematic of the surface modification with AgNWs is shown in Fig. 1. Here, a glass substrate was first cleaned sequentially with detergent, de-ionized water and isopropanol, and then a varnish of colorless polyimide (cPI: Kolon Industries INC., Korea) was spin coated onto it. The sample was annealed at 200 °C for 1 h to form a cPI film 20 μm in thickness on the glass. Several drops (0.3 mL) of an AgNW-containing ink (Nanopyxis Ltd., Korea) (average wire diameter and length of 30 nm and 20 μm, respectively) were then applied, and a #8 Mayer rod (R.D. Specialties, Inc., USA) was immediately rolled over the surface to evenly spread the ink across the glass surface. A commercial positive-type PR (AZ GXR-601, AZ-EM, USA) was spin coated onto the AgNW electrode at a rotation speed of 3000 rpm for 30 s, followed by baking at 90 °C for 3 min. The sample was exposed to UV light (MA6/BA6, SUSS MicroTec, Germany) from the glass side as described in the 5th sequence of Fig. 1, and then developed by dipping in a positive-type developer (DPD-200, Dongjin Semichem, Korea). Once the cover material (developed PR) was selectively formed on the AgNW network, the sample was soaked in water (25 °C) to help safely peel the film from the supporting glass through hygroscopic swelling of the cPI film.

The optical transmittance of the films was measured using a UV–vis spectrophotometer (Jasco V-560, Japan), while the sheet resistance (R_s) was measured with a non-contact measurement system (EC-80P, Napson Corp., Japan). The surface morphology was measured by atomic force microscopy (AFM; XE-100TM, Park Systems, USA). A field-emission scanning electron microscope (FESEM; JSM6700F, JEOL Ltd., Japan) was used to investigate the microstructures of the AgNW networks. The mechanical stability of the film was evaluated using an automatic bend-testing machine (Bending tester, Jaeil Optical Systems, Korea), whereby bending radiuses of 0.5 mm and 0.1 mm were used to induce ~2% and ~10% strain, respectively. The films were bent at a cycle rate of 0.3 Hz, with their resistance being measured during the outward bending cycles. For applying voltage to the fabricated heaters, a source meter (KEITHLEY, 2430 1KW Pulse Source Meter, USA) was used. A thermocouple incorporated in a multimeter (KEITHLEY, 7700 20 Chan Multiplex, USA) and IR camera (FLIR, T335, USA) was employed to measure the temperature of the heaters during voltage application.

3. Results and discussion

Here, we selected cPI as a substrate for flexible transparent heaters because of its high glass transition temperature (>350 °C), high modulus of elasticity, and high transparency [11]. First, we investigated the effects of the PL on the microstructure of the AgNW-based electrodes formed on the cPI film. Fig. 2a and c respectively shows FESEM and AFM images of AgNWs deposited on cPI, while those after PL application are shown in Fig. 2b and d. The pristine AgNWs in Fig. 2a demonstrate that the edges of the as-deposited AgNWs are quite clear, and there is no discernible material covering the AgNWs. In this case, the individual nanowires are irregularly stacked, resulting in a porous networked structure as can be seen in Fig. 2c as well. High peak to valley roughness (R_{pv}) indicates that the contact areas and adhesion between the nanowires and cPI are largely limited, originating primarily from the low surface energy of the cPI. The poor adhesion makes it difficult to achieve high mechanical stability, implying that a simple and post-processible method is necessary at this stage for further enhancement. The AgNW network preformed on a transparent substrate could be used as a photomask layer to shield from UV light when irradiated from the substrate side [27]. After development, the non-irradiated PR selectively remains on the AgNWs as shown in Fig. 2b, while the irradiated PR was removed from the vacant areas between the nanowires. Fig. 2d shows that the roughness values were increased by this procedure. This revealed that the self-masking concept was successful, in that the PR residues elevated only the highest areas (top of the PR on AgNWs) without increasing the lowest areas (valleys on the surface of cPI).

A powerful benefit that could be obtained by this approach is that the transmittance is not noticeably affected by whole layer deposition. In Fig. 3, the transmittance and haziness of the cPI, AgNWs/cPI, PR/AgNWs/cPI and developed PR/AgNWs/cPI are compared. Over a very broad spectral range of 420–750 nm, all samples except the PR/AgNWs/cPI exhibit high transmittance (>80%). A steep decrease in transmittance near 400 nm originates from the high light absorption of aromatic compounds in cPI and the formation of charge transfer complexes in their highly conjugated molecular structures. A deposition of PR onto the AgNWs/cPI resulted in a large decrease in transmittance and increase in haziness due to the poor transparency of the PR. Of note, excess PR on the vacant sites could be successfully removed by subsequent development, and the overall optical performance of the electrode recovered to that of the AgNWs/cPI. Considering that the R_s of the fabricated electrode was approximately 35 ohm/sq, this performance is comparable to that of commercially available ITO films (R_s: 100 ohm/sq and transmittance: 88%). R_s was not affected by the PL procedures.

In order to investigate the heating performance of the fabricated transparent heaters (30 mm by 30 mm in dimension), input voltages were supplied to the heating films through two-terminal side Ag electrodes, forming stable contacts with the heaters along opposite edges. Fig. 4a and b respectively shows the heating profiles of the AgNWs/cPI and the developed PR/AgNWs/cPI heaters as a function of time. The temperatures of both heaters were exponentially increased from room temperature to 80% of their steady-state temperatures in less than 50 s. The high lateral conductivity of the percolated AgNW networks caused the rapid and efficient heating performances of these heaters. The increase in the bias voltage from 3 V to 8 V elevated the steady-state temperature from 27 °C to 73 °C. Applying a bias voltage of 9 V damaged the heaters before they could reach a steady-state temperature. This indicates that pure AgNWs deposited on a polymer film are not suitable for high-performance heaters, since the fully exposed nanowires are not resistant to biasing. When biased with higher voltages, the unstable nanowire junctions exert a detrimental effect on the network stability, resulting in oxidation, melting or breaking of the AgNWs. Surprisingly, the developed PR selectively formed on the AgNW networks enhanced the thermal stability of the heaters as shown in Fig. 4b. The heaters with developed PR could sustain much higher voltages, reaching 14 V without showing any signs of