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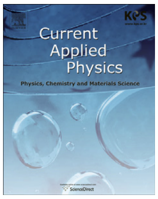

Thermally stable and flexible transparent heaters based on silver nanowire-colorless polyimide composite electrode

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ABSTRACT

Transparent and flexible heaters are promising as flexible display components for their protection against adverse ambient conditions by defrosting or demisting the displays. Herein, we employ inverted layer processing to bury silver nanowires (AgNWs) at the surface of colorless polyimide (cPI), resulting in thermally stable and flexible transparent heaters. In comparison with conventional heaters with AgNWs surface-coated on cPI heaters, the embedded electrodes show enhanced optical performance, heating capability, and mechanical and thermal stability. All these enhancements were mainly ascribed to its unique structural configuration of nanowires fully embedded at the surface of heat-resistant cPI. This approach is therefore considered readily applicable to the fabrication of stable transparent heaters with high flexibility.

1. Introduction

Transparent heaters are of great importance to enable continued use of flat panel displays in adverse ambient conditions by defrosting or demisting the displays [1]. Indium tin oxide (ITO) has been a commonly used material for transparent heaters, mainly due to its high chemical stability and high figure-of-merit (defined as σ_{DC}/σ_{Op} where σ_{DC} is the direct current conductivity and σ_{Op} is the optical conductivity of the electrode) [2,3]. However, its use has several drawbacks, mainly centered on its scarcity, which leads to a steep increase in material cost [4], and its ceramic nature, which causes ITO films to be brittle and easily damaged [5–8]. ITO's brittle nature has inspired the development of novel transparent conductive materials that can be mechanically deformed without losing conductivity. For the fabrication of transparent electrodes, silver nanowires (AgNWs) have been considered as one of the most promising alternatives to the brittle ITO; they possess high flexibility due to their ductility, high conductivity, and a low percolation threshold, with only a small fraction of the percolated AgNW network required to form a highly conductive electrode [9–15]. This implies that mechanically stable and transparent electrodes could be made with AgNWs, but only if they can be suitably formed on a flexible and transparent substrate [16].

One of the most intuitive methods to attain AgNWs-based heaters involves direct deposition of AgNWs onto a free-standing transparent films such as those from poly (ethylene terephthalate) (PET) or poly (ethylene naphthalate) (PEN). Using this simple approach, highly conductive and transparent electrodes can be very easily fabricated, which can also be used as heaters. However, two major issues still remain, i.e., poor AgNW adhesion to the film [17,18] and its low heat resistance [19,20]. The low adhesion between AgNWs and polymer typically causes mechanical instability of the electrodes, especially when they are mechanically stressed by severe bending or folding. Several approaches have been suggested to resolve this, such as the transfer of AgNW networks formed on a preliminary substrate to an adhesive-coated polymer [21,22], or photo-enhanced sintering of AgNWs preformed on a thermoplastic polymer [23,24]. However, it has been reported that buckles or wrinkles can form on the surface of transferred AgNWs networks, which makes the first method unsuitable for the fabrication of optically clear heaters. The addition of an adhesive layer could degrade the resulting electrode's transparency even further, if the adhesive has poor optical characteristics such as a low transmittance and high haziness. The photo-enhanced sintering approach, on the other hand, has been reported to be a powerful tool to enhance adhesion [23,24], but costly equipment is essential to irradiate the electrodes with high energy pulsed light. Moreover, both approaches do not resolve the low

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heat resistance issue, indicating that a simple process using well-established methods is still needed to fabricate a mechanically stable and heat-resistant heater.

Here, we report employing inverted layer processing to bury AgNWs at the surface of a polymer, so that the mechanical stability of the heaters could be significantly enhanced. There have been some previous studies reporting similar methods to embed the nanowires at the surface of polymers [10,25,26]. In terms of heat resistance, colorless polyimide (cPI) was used as a transparent and flexible substrate, because of its high glass transition temperature of more than 350 °C. For comparison, AgNWs-based heaters were also fabricated by directly depositing a AgNW dispersion onto cPI.

2. Materials and methods

2.1. Fabrication of AgNW/cPI heaters

The procedure for fabricating AgNW-embedded cPI (AgNW/cPI) is schematically illustrated in Fig. 1a. A glass substrate was first cleaned with detergent, de-ionized water, acetone, and isopropanol. Then, several drops (0.5 mL) of a AgNW solution (Nanopyxis Ltd., Korea) were deposited onto the glass. A Mayer rod #8 (R.D. Specialties, Inc., USA) was immediately rolled over the glass surface to evenly spread the AgNW solution. The solution was then carefully dried under infrared (IR) illumination for 10 min. To collapse the AgNWs, they were irradiated with intense-pulsed-light (IPL, pulse: 500 μs) by employing a photonic sintering system (Polytec Ltd., Sinteron 2000, USA) operating at a voltage input of 1.8 kV. This made the AgNWs adhere to the glass, so that patterning could be performed without damaging them. To create the desired heating patterns, a barrier layer was formed using photolithography and the electrodes were etched with a dilute acidic solution (Chromium Etchant, Sigma-Aldrich). Subsequently, a cPI varnish (Kolon, Korea) was spin-coated onto the electrodes and cured at 200 °C for 1 h. Because of the high modulus of cured cPI, the thickness of the films could be reduced to 20 μm without losing structural reliability. Once the cPI films had formed on the electrodes, they were hygroscopically swollen by soaking the samples in water, which assisted in safely peeling the films from the supporting glass substrates. To enlarge the surface coverage of the conducting electrodes, selective plasma etching for 120 s at a power of 300 W was performed to remove the cPI layers and expose the AgNWs. Considering that the AgNWs can be easily oxidized, Ar was selected for this treatment, without employing O_2. The gas flow rate and gas pressure were controlled to be 50 mL/min and 30 Pa, respectively. For comparison, films were also prepared by directly coating the AgNWs onto a cPI film, followed by drying under IR illumination for 10 min.

2.2. Evaluation of the fabricated heaters

Scanning electron microscopy (SEM, JEOL Ltd., JSM6700F, Japan) was used to investigate the AgNW network microstructures. The optical transmittance and haziness of the films were measured using a UV-visible spectrophotometer (Jasco, V-560, Japan). The sheet resistance (R_s) was measured using a non-contact measurement system (Napson Corporation, EC-80P, Japan). The surface roughness of films was determined by atomic force microscopy (AFM, Park Systems, XE-100TM, USA). The mechanical stability of electrodes after being peeled from the glass support was evaluated by cyclic bending endurance testing. An automatic bend-testing machine (Toyoseiki Ltd., MIT-DA, Japan) was used to measure the long-term reliability of the devices under repeated bending cycles. This device subjected the electrodes to alternating outward and inward bending (or tensile and compressive stresses, respectively) with a bending radius of 500 μm. The electrodes were bent at a cycle rate of 1 Hz, and the resistance of the tested device was measured throughout the inward and outward bending cycles. For the application of voltages to the fabricated heaters, a source meter (KEITHLEY, 2430 1 KW Pulse Source Meter, USA) was used. A thermocouple incorporated in a multimeter (KEITHLEY, 7700 20 Chan Multiplex, USA) and IR camera (FLIR, T335, USA) were employed to measure the temperature of the heaters during voltage application.

3. Results and discussion

Inverted layer processing fully embedded the AgNWs at the surface of the cPI, so only very limited parts of them would be exposed to air. Comparing Fig. 1b and c, AgNWs coated on cPI (Fig. 1b) are more distinctly observed in high contrast ratio, while those embedded (Fig. 1c) are gray, which means that a thin cPI layer covers the buried AgNWs. To investigate their effects on the heaters' characteristics, we compared various properties of the AgNWs-based heaters fabricated by the two methods. Here we also partially removed the thin cPI layer covering the AgNWs using Ar gas plasma treatment, so that the wires would be partially exposed (but note that the wire bodies are still mostly buried at the surface of the cPI). Fig. 2a and b shows the transmittance and haziness (i.e. the ratio of diffused to total transmission) of the heaters, which were optimized to have an identical R_s of approximately 23 Ω/sq. Over a very broad spectral range of 420–700 nm, all heaters

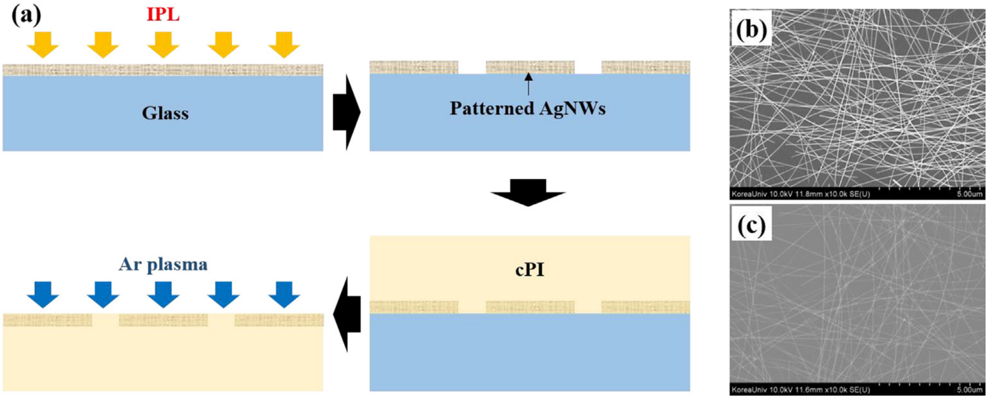

Fig. 1. Schematic showing the fabrication of transparent heaters by inverted layer processing (a) (IPL: intense-pulsed-light), a scanning electron microscope (SEM) micrograph for silver nanowires (AgNWs) deposited on a colorless polyimide (cPI) (b), and an SEM micrograph for the AgNWs at the surface of cPI (c), embedded by the procedure shown in (a).