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Lift-off patterning of Ag nanowire/PEDOT:PSS composite films for transparent electrodes using a fluoropolymer structure

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ABSTRACT

This paper describes a lift-off method of Ag nanowire (Ag NW) patterning using a poly(1H,1H,2H,2H-perfluorodecyl methacrylate) polymer (PFDMA) structure as a mask which is prepared by micro-contact printing. Unlike a conventional photoresist mask, the PFDMA polymer is inert to the dispersion solvent of Ag NW. In addition, the hydrofluoroether solvent used for removing the mask layer of patterned PFDMA films after Ag NW deposition does not chemically affect the polyethylene naphthalate (PEN) substrate or poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) coated on Ag NW layer. In this method, Ag NW/PEDOT:PSS composite films were patterned and the effects of the hot-press method were examined to further improve the electrical and optical properties of the composite films. Moreover, the hot-press method at 110 °C has an advantage of applying low pressure to make Ag NW/PEDOT:PSS embedded into PEN films compared to that of pressing samples without heating. The ratio of resistance change of patterned and hot-pressed composite film was only below 1% after repeated bending test.

1. Introduction

Recently, silver nanowire (Ag NW) has been studied extensively as an alternative to transparent doped metallic oxides, such as indium tin oxide (ITO) [1–20]. Ag NW offers higher electrical conductivity and mechanical flexibility than ITO [1–3]. The patterning method of Ag NW is crucial if they are to be used as a replacement for ITO films in many applications, such as touch screens [4,5], organic solar cells [6,7], organic light emitting diodes [8], or flexible electrodes [9,10]. On the other hand, the patterning of Ag NW has a limitation because Ag NW is dispersed in solution before forming thin films [3]. Generally, Ag NW is dispersed in organic solvents, such as methanol [7,10] or isopropyl alcohol (IPA) [5], and is coated on substrates using wire-wound rod [11], spray [12–14], brush [6,15], or spin coating [7,9,10] methods.

For Ag NW for transparent electrode preparation, etching technique is a common patterning method [16,17]. Etch mask patterns are formed on substrates coated with Ag NW films and then Ag NW films in the unmasked region are removed by a selective etching process [16,17]. However, the etching technique has problems such as contamination or undercuts. Ag NW films coated on patterned mold are, in some cases, transferred directly to the substrate by contact printing [18,19] or Ag NW patterns are prepared only on the dopamine-modified region of the substrate [20]. Both methods can cause protrusions of Ag NW at the edges of the patterns and have a limitation in pattern resolution.

An alternative method for the lift-off technique using a conventional organic photoresist also has a problem because the dispersion solvent of Ag NW can attack chemically the patterned photoresist mask. Another problem might be possible reaction of resist removing solvent with Ag NW films or organic substrates such as polyvinyl pyrrolidone. Therefore, a chemical reaction between the materials should be checked first in a lift-off process.

This paper reports a lift-off technique in which Ag NW film patterning can be processed by replacing the resist material and the resist removing solvent with poly(1H,1H,2H,2H-perfluorodecyl methacrylate) polymer (PFDMA) film and hydrofluoroethers, respectively. In order to improve the electrical and optical properties of Ag NW/poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) films have been added and effects of the spray-coated and hot-pressed composite films have been examined.

2. Experiment

The poly(dimethylsiloxane) (PDMS) mold, which was the master of the replica, was prepared by curing its prepolymer (Sylgard 184, Dow Corning) from the patterned photoresist (AZ 7220, Clariant) on a Si wafer. The PDMS mold had line/spacing patterns of 10/10 μm, 15/15 μm, 20/20 μm and 25/25 μm, and their line height was 1.6 μm. 1H,1H,2H,2H-perfluorodecyl methacrylate (FDMA) was solved at

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0040-6090/

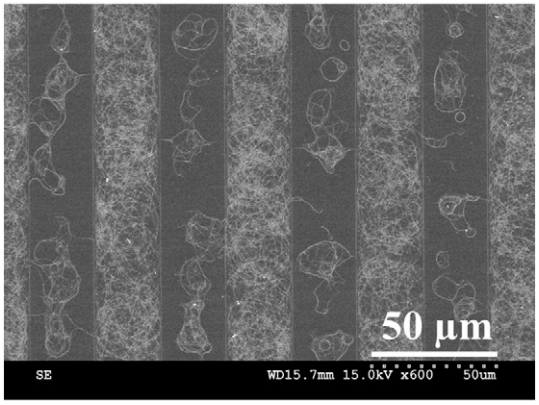

Fig. 1. SEM image of spray-coated Ag NW films. Some Ag NW films are observed on PFDMA lines.

11 wt.% in hydrofluoroether solvent (HFE-7500, 3 M). This solution was spin-coated on PDMS molds at 1000 rpm for 30 s and PFDMA films covered the PDMS mold surface after drying at room temperature. Micro-Contact Printing (μCP) was performed and parts of PFDMA films coated on lines of the PDMS mold were transferred onto substrates such as glass (Marienfeld) or polyethylene naphthalate (PEN, Teonex® Q65HA-125, Teijin DuPont Films) without any external pressure at room temperature [21]. 2 ml of Ag NW solution (NANOPYXIS), consisting of Ag nanowires with 25 ± 5 μm length dispersed in isopropyl alcohol (IPA) at 0.06 wt.%, was spray-coated on glass or PEN substrate, whose surface had PFDMA line and space patterns, using an airbrush (KP-HP-TH 0.5 mm, Iwata) at 70 °C. PEDOT:PSS (Sigma-Aldrich) with 1.3 wt.% was diluted in deionized water to have a concentration of 0.01 wt.% or 0.65 wt.%. Each solution was then mixed with IPA with a 1:4 ratio. Some of the samples were coated by this solution of PEDOT:PSS at 70 °C to form Ag nanowire/PEDOT:PSS composite films. The samples were positioned in the hydrofluoroether solvent (HFE-7300, 3 M) for 30 s in order to remove the PFDMA mask layers. The composite films were pressed without heating and hot-pressed at 110 °C for 2 min to 300 kPa, respectively.

The surface morphology of the patterned Ag NW films with various line and space sizes and patterned Ag NW/PEDOT:PSS composite films were examined by field emission scanning electron microscopy (FESEM, S-4300, Hitachi). The topography of the patterned films was analyzed by scanning probe microscopy (LEXT OLS4500, Olympus) in dynamic mode. A four-point probe (CMT-SR2000N, AIT) was used to measure the sheet resistance in auto contact mode. Optical transmittance was measured using a UV–vis spectrometer (Lambda 750, PerkinElmer). The same patterns of 25 μm width and 975 μm pitch and 1 × 5 cm size were prepared on the pressed and hot-pressed films, respectively. Durability of both samples were investigated by a bending test using semicircular polyethylene cylinders with different bending radii of 20 mm and 15 mm. It was a cyclic test with automated bending mode.

3. Results and discussion

A previous study reported that PFDMA films could be patterned by μCP on various substrates using a PDMS mold utilizing the very low adhesion force between PFDMA films and PDMS mold [21]. The PFDMA films could be dissolved in hydrofluoroethers without chemically attacking the organic substrates such as poly(methylmethacrylate) and poly(vinyl pyrrolidone), which opens the possibility of the orthogonal processing of diverse materials [21].

In this study, the patterned PFDMA films were used as the mask material for the lift-off process of Ag NW instead of a conventional photoresist. Fig. 1 shows the surface morphology of the Ag NW spray-coated on PEN substrates with patterned PFDMA films. The Ag NW films were formed on an un-patterned surface without damaging the PFDMA films because of the fluoropolymer as the PFDMA films was not dissolved in the dispersion organic solvent. The thickness of the transferred PFDMA films is an important parameter for the lift-off process and it determines the possible thickness range of the Ag NW films. The PFDMA films need to be thick enough to prevent a cross connection between lines. From the PDMS mold with a line height of 1.6 μm, the PFDMA films at 11 wt.% can have a maximum thickness of 480 nm. The highly fluorinated polymer has very limited adhesion to both non-fluorinated organic materials and hydrophilic surfaces [21].

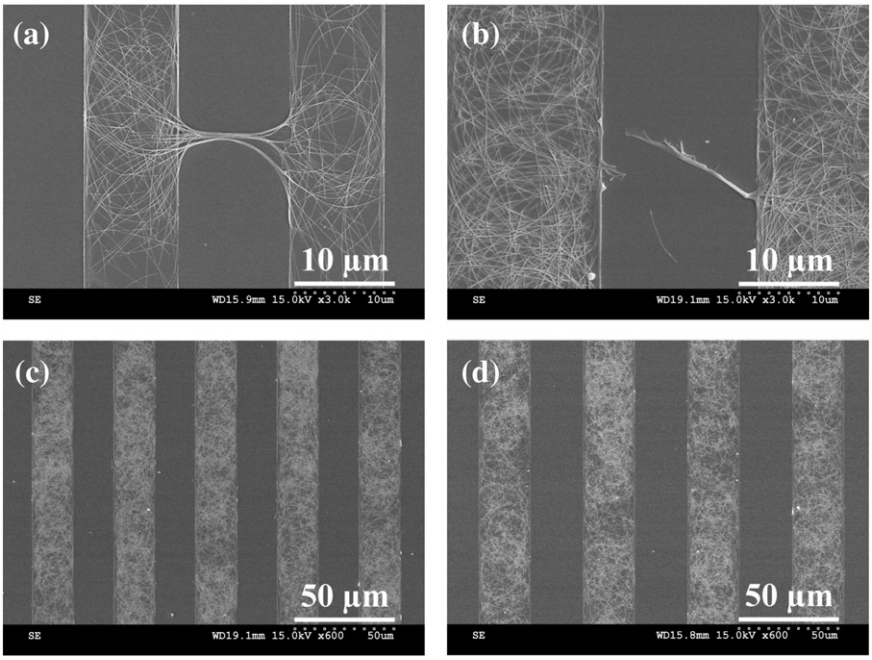

Fig. 2. SEM images of the patterned Ag NW films with a width of (a) 10 μm, (b) 15 μm, (c) 20 μm, and (d) 25 μm, respectively. When PFDMA pattern pitch is less than 20 μm, Ag NW is often cross-connected.