High Performance Silver Nanowire based Transparent Electrodes Reinforced by EVA Resin Adhesive

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***Abstract*—Transparent conducting films (TCFs) based electrodes are indispensable for most optoelectronic devices e.g. liquid crystal displayers, transparent touch panels, organic light-emitting diodes, and solar cells. Traditional TCF materials, such as indium tin oxide (ITO), have some inherent shortcomings, such as high-vacuum deposition process, high deposition temperature, relatively high cost, and brittleness. With the bloom of flexible and wearable electronics, flexible TCFs become more important than ever. Among various candidates, silver nanowires (AgNWs) based TCF draws more attentions than others for its superior electrical and optical properties. However there are still some challenges to be overcome, such as the poor electrical contact among the AgNWs and the weak mechanical contact between the AgNWs conducting networks and transparent substrate. In this work, combining the electrostatic spraying and Mayer rod coating processes, we have fabricated a high performance AgNWs based TCF with over 85% optical transmittance, less than 50 Ω/sq sheet resistance, and excellent adhesion to the substrate with the involvement of ethylene viny acetate (EVA) resin as the interlayer. This simple two steps process is also compatible with the roll-to-roll coating process, which can well address the challenges of low cost, high performance, flexibility and robustness.**

Keywords—transparent electrodes, silver nanowires (Ag NWs); ethylene viny acetate (EVA); electrostatic spraying; adhesion

Introduction

Transparent conducting electrodes (TCFs) are a core component for many optoelectronic devices such as liquid crystal displayers, transparent touch panels, organic light-emitting diodes, and solar cells which have been showing tremendously rapid growth recently [1]. As the core material, indium tin oxide (ITO) has been the most dominant transparent conductor.

However, for its high cost and brittleness, ITO can't meet the key demands of the next generation flexible and wearable electronics. At the same time, many candidates have been explored recently, such as super-aligned carbon nanotubes, graphenes, conducting polymers, metal nanowires and so on [2-5]. Among the various candidates, silver nanowires (AgNWs) are a promising alternative due to its superior electrical and optical properties [6-11]. While the poor mechanical interconnection between the AgNWs conducting networks and transparent substrate is yet to be improved, which limits wider applications.

In this paper, in order to address the above problem, commercial ethyl vinyl acetate (EVA) was chosen to coat on the transparent substrate as the interlayer, so that the mechanical interconnection between the AgNWs conducting networks and the transparent substrate can be enhanced. In this way, AgNWs based TCFs with optical transmittance and sheet resistance of 85% and 50 Ω/sq were obtained.

I. EXPERIMENTAL PROCEDURE

A. Materials

20 mg/mL AgNWs suspension (purchased from Suzhou kechuang Materials Tech Co. Ltd.; diameter: 20-30 nm; length: 10-20 μm) was diluted into 1 mg/mL with ethanol. Commercial EVA resin was purchased from Shenzhen Nanlin Chemical Engineering Co. Ltd. The PET substrates were obtained from Ningbo Hughstar Advanced Material Technology Co.Ltd.

B. Measurements

The sheet resistances of the TCEs were measured by a 4-point probe system (Mitsubishi MCP-T610). All the field emission scanning electron microscopy (FE-SEM) images were taken on a ZEISS SUPRA®55 (Germany). Optical transmission spectra of the Ag NWs films were recorded using a UV/VIS/NIR spectrophotometer (cary5000), and the reference spectra were evaluated from the bare PET substrates. The mechanical adhesion property was evaluated by cross-cut testing (the tape was from 3M Company). The plasma treatment experiment was carried out in a plasma chamber(PDC-MC, Chengdu Mingheng Science & Technology Development Co. Ltd. ,13.56 MHz, 150 W).

C. Transparent electrodes fabrication

The polymer interlayer was coated on a piece of polyethylene terephthalate (PET) film by a Mayer rod and the PET substrate had been cleaned by plasma before use. Then the

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coated PET was dried in air at room temperature. After the solvent in EVA resin had been evaporated, The AgNWs layer was coated onto the EVA/PET substrate using the electrostatic spraying technique. The electrostatic spraying process contains three parts: the feeding system, the highly electrostatic field generation system and a temperature-humidity controlling system [12]. By using the feeding system and electrostatic field system, we could adjust the liquid flow rate and the electric potential to obtain a suitable droplet size. By controlling the temperature-humidity controlling system, we could adjust both temperature and humidity so as to let the solvent in the AgNWs droplets evaporate as soon as possible when they dropped onto the substrate. In this way, we got a uniform layer of random distribution of the AgNWs on the substrate. The final step was the heating process, as the AgNWs/ EVA/PET film was placed in a vacuum dryer, and the thermal energy could soften the EVA layer at elevated temperature; besides, the AgNWs could sink in the EVA layer and be fixed by the EVA resin when the temperature cooled down. Similar with our studies about plasma-treatment before [13], we used the plasma chamber to improve the electrical conductivity (treatment atmosphere: air, treatment time: 5 min) of the films.

For obtaining a uniform AgNWs layer, some form factors are crucial. The concentration of the AgNWs suspension was 1 mg/mL and the liquid flow rate was maintained at 1 mm/min. The temperature and humidity of the experiment room were kept at 35℃ and lower than 50%. The nozzle of the feeding system was a stainless steel noozle (inner diameter: 0.6 mm, outer diameter: 0.8 mm), which was 4 cm height above the substrate. The electrical potential applied to the nozzle was +14 kV, and in the meantime, the electrical potential applied to the cathode on the substrate was -3 kV.

II. Results and Discussions

A. Characterization of TCEs

SEM images (Fig. 1a, b) indicate that the AgNWs on the substrates were uniformly distributed on the substrate, which formed an effective conducting network. Various electrical and optical properties of the AgNWs/EVA composite TCEs with different AgNWs weight densities are shown in Table 1. In this work, the TCE films showed 91.3% transparency and 43.3 Ω/sq sheet resistances. And more importantly, we obtained excellent adhesion between the AgNWs layer and the substrate.

B. EVA resin adhesive

After coating the EVA layer, the optical transmittance of the sample film changed from 84.3 to 84.2, which was negligible. Then, the AgNWs was sprayed on top of the coated polymer layer. After heating the AgNWs/EVA composite film, the AgNWs sank in the polymer, which resulted in an improvement in the interfacial adhesion. By controlling the heat treatment condition, the depth of the AgNWs sank in polymer can be adjusted; besides, the adhesion strength, optical transmittance, and electrical conductivity were all controllable.

TABLE I. Comparison of the Electrical and Optical Properties of Silver Nanowires based TCEs with Different Silver Nanowire concentrations Deposited on the PET Substrate

AgNWs concentration (mg/m²)	*T_{550} nm(%)*	*Sheet resistance(Ω/sq)*
52	91.3	43.3
77	87.0	25.1
102	83.9	11.8
129	78.4	6.3
153	71.2	4.9

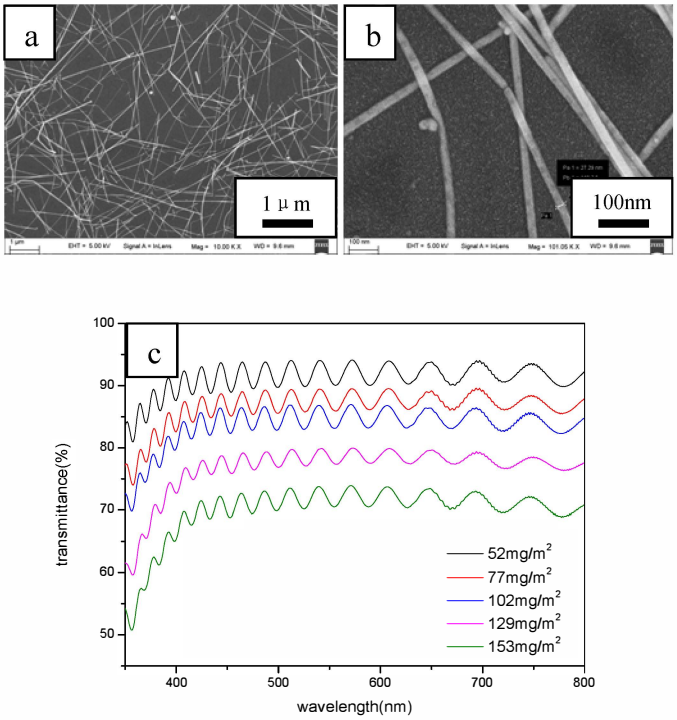


Fig. 1 (a) SEM image of the AgNWs/EVA composite film on a PET substrate; (b) Magnified SEM image of the AgNWs/EVA composite film, showing the diameter of the Ag NWs (diameter ~25nm); (c) The optical transmittance spectra of the transparent film samples with different AgNWs concentrations. With the increase of AgNWs concentration, there was a decrease of the transmittance. The unusual wavy curves are related to the PET films that we used, which is an interesting phenomenon yet to be explored .

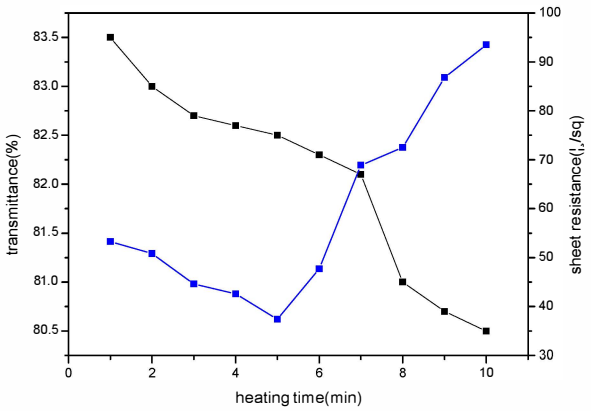


Fig. 2 Variation of transmittance and conductivity over diffferent heating time.

Fig. 2 shows the change of optical transmittance and electrical conductivity of the transparent film samples over different heating time. The softening temperature of this EVA resin was 110℃, and thus we heated the TCEs to 110℃ and kept for different periods of time. We found that the optical transmittance was reduced slowly as the AgNWs sank into the resin. The electrical conductivity gradually increased in the first 5 minutes, and then decreased. Such phenomenon could be explained that, in the first 5 minutes of the heating process, the PVP on the surface of AgNWs was partially removed by the high temperature [14], and the conductivity could be increased as a result. In the subsequent 5 minutes, some AgNWs were gradually embedded in the EVA layer, and thus the conductivity was gradually decreased. As shown in Fig. 3, the AgNWs was partially embedded in the resin after heating, and became deeper over time.

In order to evaluate the adhesion strength between the AgNWs layer and the substrate, a peeling test was employed. As Fig. 4 shows, with the help of the EVA interlayer, the transparent film samples obtained a good mechanical adhesion performance. When the AgNWs/EVA composite film was heated for 5 minutes, the sheet resistence only increased from 60 Ω/sq to 120 Ω/sq after ten times of tape peeling. On the contrary, without the existence of EVA interlayer, the sheet resistence increased from 60 Ω/sq to ∞ Ω/sq after only one times of tape peeling.

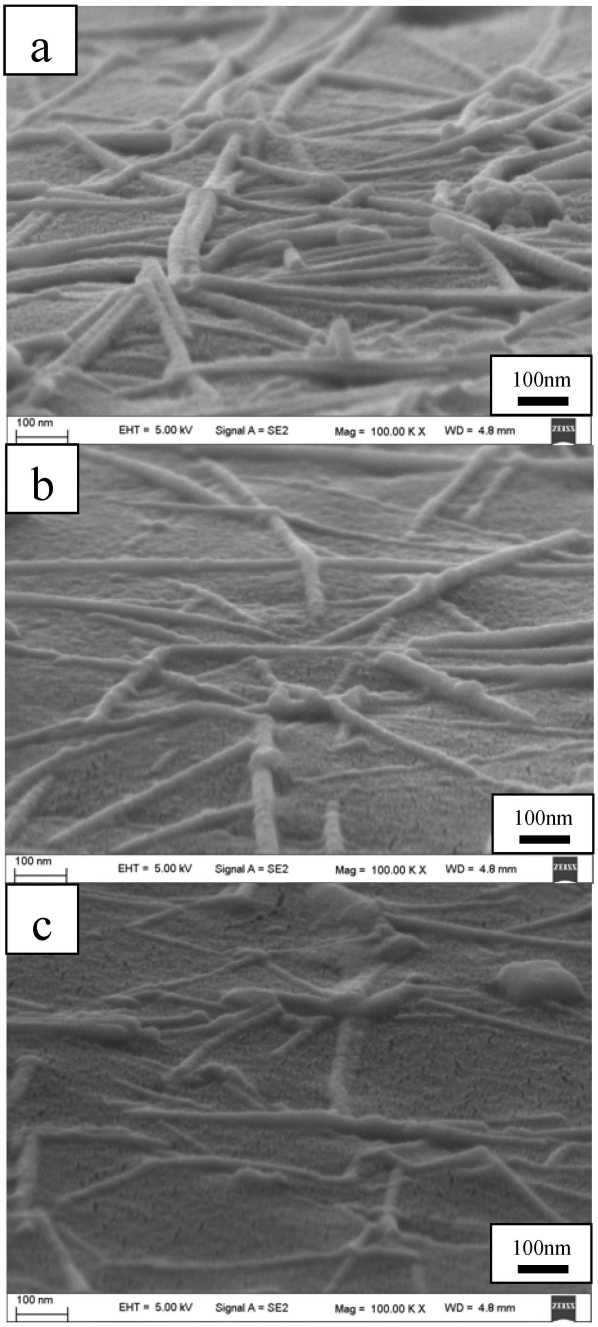


Fig. 3 With different heating time, the AgNWs on the EVA shows different morphologies; AgNWs was grdually embedded in the resin as the time went on for (a) 1 min; (b) 5 min; (c) 10 min.

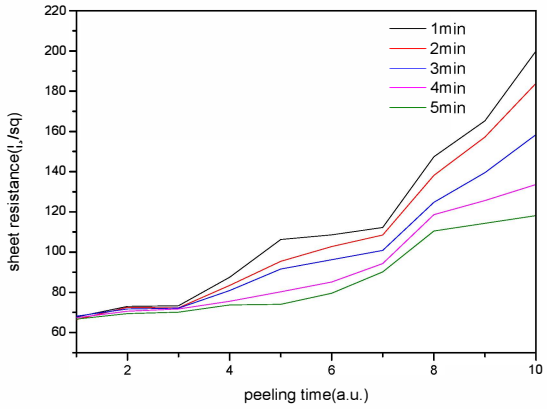


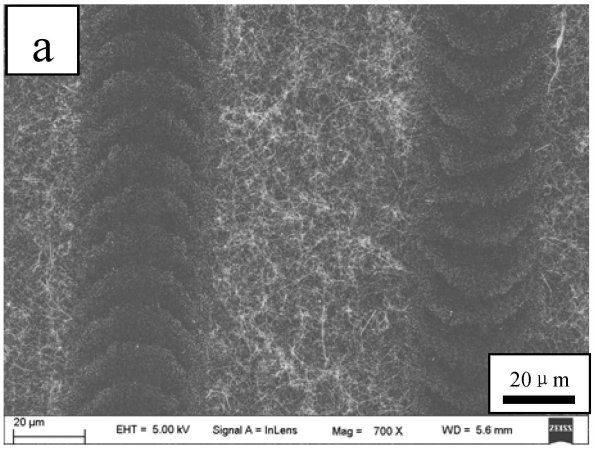
Fig. 4 The peeling test of AgNW/EVA/PET films with different heating times.

C. *Laser patterning*

Patterning is a very important processing step to achieve the functionality of a touch module. Traditional ITO films were patterned by developing and etching. Here we demonstrate the laser patterning feasibility of the AgNWs/EVA composite film.

By applying the laser beam (wavelength: 355 nm, model: Han's Laser EP-15-DW, nanosecond frequency, scanning line speed 5m/s) to the sample film, the AgNWs broke and melted into tiny beads, resulting in non-conductive regions along the otherwise conductive paths without damaging the underlying EVA/PET film [15-16]. As Fig. 5 shows, a conductive path which was about 40 μm in width and 30 μm in distance was formed by laser. AgNWs still kept a good connection between each other and insured a good conductivity. In non-conductive regions, AgNWs was totally broken and melted into tiny beads, leaving a corrugated trail showing the moving direction of laser beam.

As compared with developing and etching processes for ITO patterning, laser patterning is much convenient for rapid sampling, it is also a dry and green process. Patterning resolution could be adjusted by changing the space between two adjacent laser scanning lines and we got an excellent patterning resolution down to 20 micron by this way.



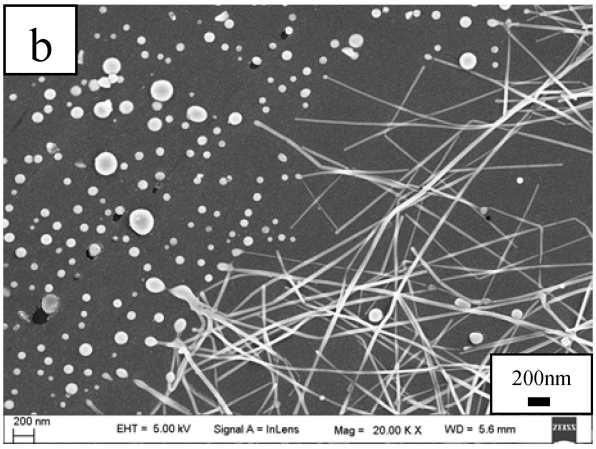


Fig. 5 (a) SEM image of the AgNWs/EVA composite film after the laser patterning process. (b) Magnified side-view SEM image of the edge of the conductive road, showing that the AgNWs were melted into small silver balls. We could clearly see the laser path where the AgNWs were melted into small silver balls to cause the open circuit and form a conductive road.

III. CONCLUSIONS

In summary, by combining the electrostatic spraying and Mayer rod coating processes, we developed a high performance AgNWs TCE fabrication technology with over 85% optical transmittance, less than 50 Ω/sq sheet resistance, and excellent mechanical property. In order to improve the performance characteristics of the samples, we optimized the spraying processing window, and thus enhanced the electrical conductivity of the film. By introducing a heat treatment process, the AgNWs was gradually embedded in the resin over time. With the help of EVA interlayer, we got a good adhesion performance that the sheet resistence only increased from 60 Ω/sq to 120 Ω/sq after ten times of tape peeling. In order to balance between conductivity and optical performance, we discussed the effect under different heating times. Besides we also tried to pattern the AgNWs/EVA composite film through laser process and got excellent patterning resolution down to 20 micron.

After all, this work addresses some challenges of low cost, high performance, flexibility and robustness property requirements for flexible TCEs and is promising in mass production.

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