Gravure Printed Network Based on Silver Nanowire for Transparent Electrode

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ABSTRACT

Silver nanowires were gravure printed on flexbile Poly(ethylene terephthalate) film to form conductive transparent patterns. Suspensions containing silver nanowires with different concentrations were formulated and various cell parameters in grauvre plate were investigated in the printing experiments. Printed samples were characterized by microscope and probes for their optical and electrical properties. It was found that concentration and uniformity of the Ag NW network play key roles in the optical transmission and electrical conductivity of printed films. Experimental result showed that with optimized parameters the transmission of 89% at sheet resistance of 200 Ω/sq have been achieved in the gravure printed transparent conductive films.

Keywords: conductive, flexible, gravure printing, silver nanowire, transparent

1 INTRODUCTION

Transparent electrodes are critical components of optoelectronic devices such as solar cells, organic light-emitting diodes, displays, and touch sensitive screens. Most high-performance transparent conducting films at present are composed of sputtered metal oxides, [1] which have limited flexibility because of its brittleness. Vacuum sputtering is also an expensive and high energy consumption process. Various new methods have been attempted for making flexible transparent conductive films in recent years. [2-4] Conductive network based on solution-processed silver nanowire (Ag NW) has received substantial attentions because of its high conductivity, low-cost and easy-processing, and have been studied in details and used in optoelectronic devices. [4, 5] However, most of reported conductive Ag NW networks were deposited without pattern, which need additional patterning procedures for practical applications.

As a fast and simple printing technique, gravure is traditionally used for high-quality and long-run printing of currency, postage stamps, magazines, and packaging. [6] During gravure printing, the cells are filled with ink, and transferred reproducibly to the substrate, while the excess ink is removed by a doctor blade (Shown in Figure 1). The printed pattern containing solvent was dried during this process. Different from inkjet pringing, gravure has the highest throughput in comparison to other mass printing techniques, and can use inks with viscosity of 40-2000 cP. [6, 7] More importantly, gravure printing can deposit suspensions containing micron-size paticles or very long nanowires very fast and effectively. As a result, the use of gravure for printing organic electronics or flexible electronics has received substantial attentions in both research community and industrial sectors. [8, 9]

Here we report gravure printing of suspension containing 20-60 micron Ag NWs on flexible PET film to form patterned conductive transparent electrodes.

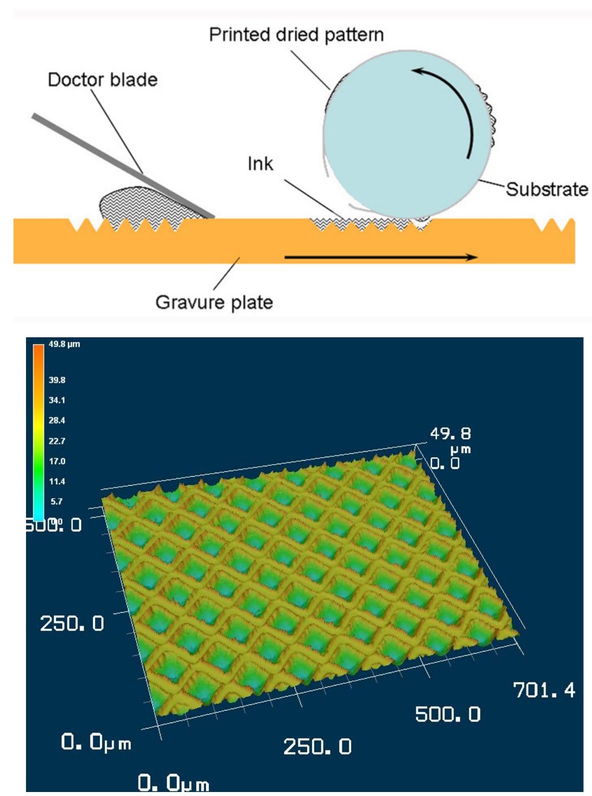

Figure 1: Schematic image of gravure printing Ag NWs suspension (top), and the structure of gravure plate (bottom).

2 EXPERIMENTAL

Ag NW (AW015, diameter 75-105 nm, length 20-60 micron, 50 mg/mL in alcohol) suspension was purchased from Zhejiang Kechuang Advanced Materials Technology Co., Ltd.. The suspension was then diluted into 10 mg/mL, 4 mg/mL, and 1 mg/mL respectively using alcohol for gravure printing. The suspensions were ultrasonic dispersed for 30 min before gravure printing. All of the Ag NW suspensions were gravure printed using a Labratester Laboratory gravure printing machine from Norbert Schlaefli Maschinen, with a standard printing speed of 36 m/min. A gravure plate contains 8 fields of different engraving parameters from 70 to 210 line/cm was also provided by Norbert Schlaefli Maschinen. Poly(ethylene terephthalate) (PET) film was purchased from Bayer Material Science. The printed samples on PET films were baked at 150 ℃ for 10 minutes.

Transmission measurements of the samples were performed by a LAMBDA7500 spectrometer. The sheet resistances were measured by four-probe method using a Keithley 4200 semiconductor characterization system and a probe station. The structure of the cells on gravure plate were observed by a VK9700 violet laser scanning microscope. The viscosity were measured by a SNB-2 viscometer from Shanghai Nirun Intelligent Technology Co., Ltd.

3 RESULTS AND DISCUSSION

Different from the traditional gravure inks containing polymer, the viscosity of the Ag NW suspensions we used is lower than 5 cP, the gravure speed should be high enough for well printed pattern [9] . As a result, all of the samples was gravure printed with a high speed of 36 m/min. On the other hand, alcohol was choosed to be solvent because it has smaller contact angle and easy to evaporate during the printing, which can make the gravure printed Ag NWs pattern more homogeneous.

3.1 Gravure printing with different plate parameters

A gravure plate containing 8 fields of different engraving parameters was used to research the role of cell parameters in Ag NW suspension gravure printing. Figure 2 shows the patterns on a PET film printed by such a plate. These patterns were found to have different thickness and uniformity, though they were printed in the same gravure process.

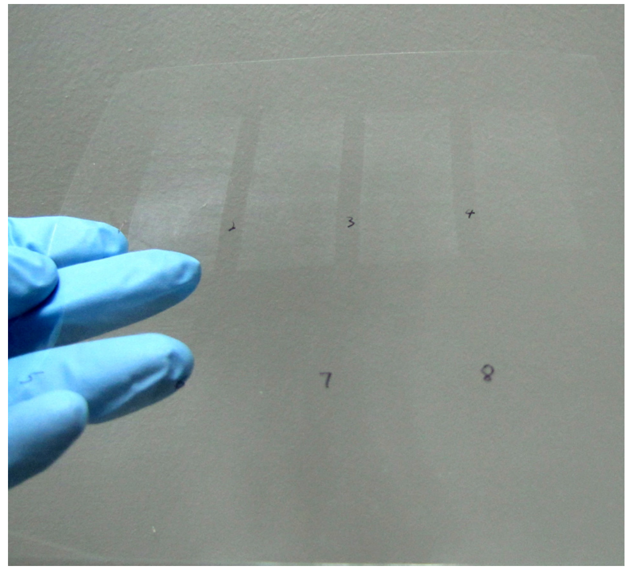

Figure 2: A PET film gravure printed by a plate with 8 fields of different engraving parameters.

The most important parameter of the engraved gravure cells is the number of lines per cm. As all the cells were engraved using the same graver angle, the cell with less lines means larger cell width and depth. For example, 70 lines/cm cells were much wider and deeper than the cells of 160 lines/cm, as shown in the inserts of Figure 3.

The Ag NWs patterns printed by cells with four different plate parameters (70, 100, 140, and 160 lines/cm, respectively) were observed and compared, as shown in Figure 3. It is found that the amount of Ag NWs transferred by 70 lines/cm cells were much more than others, and the more the lines the less the amount of Ag NWs. 160 lines/cm cells trasfer the least amount of Ag NWs. The results can be explained that the volume of ink transferred by the 70 lines/cm cells was larger than others because of it has the largest width and depth.[10] At the same time, the cells with smaller width and depth transferred less ink to the PET substrate, and 160 lines/cm cells trasfer the least materials.

However, the pattern printed by 70 lines/cm cells was found to be heterogeneous, as shown in Figure 3. There are two reasons explaining this result. Firstly, the pattern printed by larger cells contains more solvent, which also means longer time is needed for the pattern to dry. The printed Ag NWs can move spontaneously before the solvent completely evaporates. Secondly, the cells are designed for restraining the movements of ink on the grauvre plate during the printing process. It’s possible that the very low viscous ink in a large cell flows and makes the printed pattern heterogeneous, while patterns printed by smaller cells are more uniform.

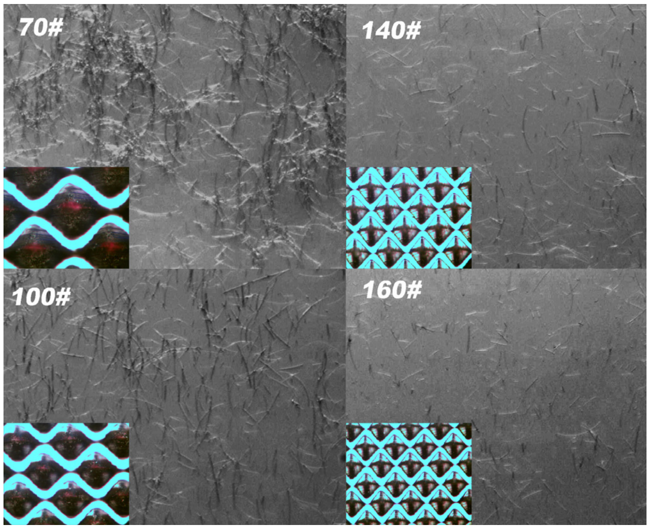

Figure 3: Optical microscope images of Ag NWs printed by different plate parameters, # stands for line/cm. Insert images show the cell structures.

3.2 Gravure printing using suspension with different concentrations

To achieve good uniformity and avoid agglomeration in the printed pattern, the Ag NWs in suspension used for printing should be well dispersed. It is noted that the suspension containing Ag NWs longer than 20 micron is not stable. Decreasing the concentration of nanowires can improve the stability of the dispersion system. However, the gravure printed film using low viscosity ink becomes too thin. There are very few Ag NWs in the printed film if the concentration is not high enough.

Ag NWs suspensions with 3 different concentrations (10 mg/mL, 4 mg/mL, and 1 mg/mL) were prepared, and gravure printed using 100 lines/cm gravure plate. as shown in Figure 4. It can be found that Ag NWs were deposited not uniformly when it was gravure printed using 10 mg/mL suspension, and the uniformity of patterns printed using lower concentration suspensions were much better.

On the other hand, there were too few Ag NWs to form a network in the sample printed using 1 mg/mL suspension, which means the pattern may not be conductive. This result show that the concentration of Ag NW suspension used for gravure printing should be more than 1 mg/mL, which is much high than the Ag NW dispersion systems reported before.[7, 8]

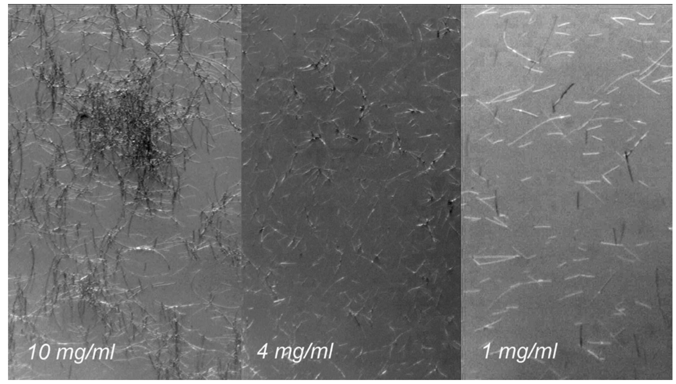

Figure 4: Optical microscope images of Ag NWs printed using Ag NWs suspensions with different concentrations

3.3 Gravure printing for multilayers

As mentioned before, the sample printed using 1 mg/mL suspension contains too few Ag NWs to be conductive, though the wires can be very homogeneous in the printed pattern. To get a uniform conductive electrode by printing 1 mg/mL Ag NWs suspension, multilayer were gravure printed by 100 lines/cm gravure plate. The printed samples are proved to be conductive and uniform, which can be observed in Figure 5.

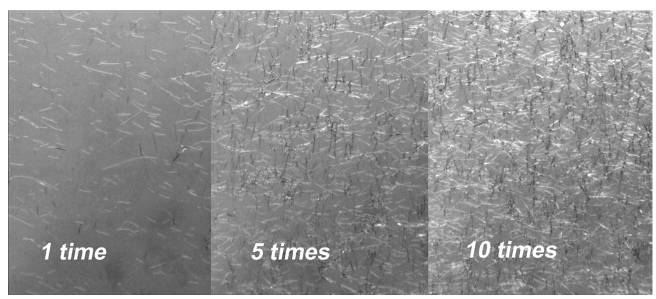

Figure 5: Optical microscope images of Ag NWs gravure printed for different times.

Figure 5 shows that the Ag NWs can form a network after printed for five times, and the Ag NWs network in 10-layer pattern has a quite high density. The uniformity of the 10-layer pattern printed with 1 mg/mL suspension is much better than single layer printed pattern using 10 mg/mL suspension, though they contain similar amount of Ag NWs.

3.4 Characterization of gravure printed sample

Transmission of the 5-layer and 10-layer Ag NWs network samples on PET films was measured, as show in Figure 6. We observed that the transmission of the two smaples are quite similar, though 5-layer sample has a better transparency than the 10-layer sample. Both of the samples have a transmission more than 85% in the range of 380–500 nm wavelengths, and more than 89% in the 500–800 nm area. Considering the transmission of the 10-layer sample can increase to more than 95% in 440-800 nm after deducting the transmission loss from the PET substrate, it can be concluded that the transmittance of the conductive Ag NWs network is good enough for fabricating transparent electrodes.

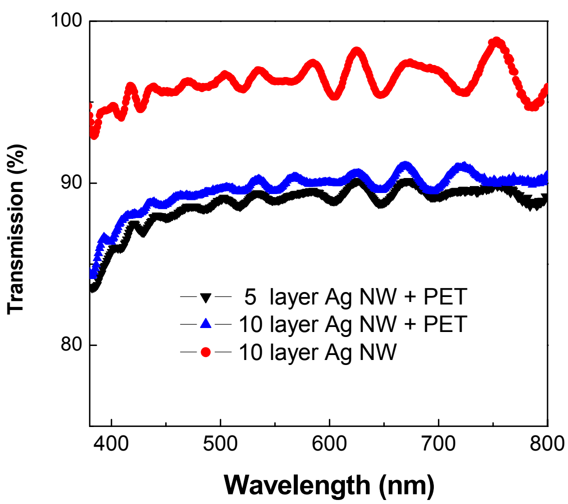

Figure 6: Transmission of printed Ag NWs on PET substrate over the wavelengths 380–800 nm.

The sheet resistance measurements of the samples were also performed. The single layer printed using 1 mg/mL Ag NWs suspension is not conductive. The 5-layer printed samples have an average sheet resistant from 1000-5000 Ω/sq, and the an average sheet resistant of 10-layer printed Ag NWs samples can be 80-200 Ω/sq. It is found that the sheet resistance drops rapidly from the 5-layer pattern to 10-layer pattern.

More importantly, the sheet resistance of single layer printed pattern using 10 mg/mL suspension is either larger than 5000Ω/sq or not conductive, though its amount of Ag NWs is similar as 10-layer pattern using 1 mg/mL ink. It can be concluded that the uniformity plays a key role in the network conductivity, and the multilayer pattern can increase the conductivity significantly by reducing the defects in the printed network.

4 CONCLUSION

In summary, Ag NWs were gravure printed on flexible PET film to form conductive transparent patterns. A series of Ag NW suspensions with different concentration were formulated and various grauvre plate cell parameters were investigated in our printing experiments. The results show that gravure printed sample using low concentration suspension can achieve better uniformity. It was found that with optimized parameters the transmission of 89% at sheet resistance of 200 Ω /sq have been achieved with the gravure printed transparent conductive films. These preliminary results indicate that it is possible to fabricate conductive transparent network pattern by gravure printing.

5 ACKNOWLEDGMENT

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