Gravure Printed Hydrophobic Templates onto PET Films for Guiding the Assembly of Nanowires: Towards the Ultralow-Cost Transparent Conductive Electrodes

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Abstract

We present our work of fabricating silver nanowires (Ag NWs) network with regularity and homogeneity as the transparent conductive electrodes for optoelectronic applications. Though patterning hydrophobic materials (e.g. PDMS) onto the substrate (polyethylene terephthalate (PET)) surface, we are able to adjust the surface energy level between the patterned and un-patterned area, which is crucial to the wetting/dewetting of the solution of the Ag NWs. This allows us to control the distribution of the percolated Ag NWs network evenly in the unprinted areas. In this way, we can fabricate transparent electrode very conveniently through a general printing method coupled with a deposition-drying process. The Ag NW network displays 2-D electrical conductivity and excellent optical transparency, which provides promising alternatives to ITO as transparent conductive electrodes.

Keywords

Silver nanowire, transparent electrode, flexible electronics, percolation network

I. Introduction

Optoelectronics devices are experiencing rapid development nowadays with huge numbers of different commercial products in the market such as light emitting diodes (LEDs), liquid crystal displays (LCDs), flexible displays and solar cells. As one of the key components, transparent conductive electrodes are currently under intensive studies, which are aimed for finding alternative materials for the indium-doped tin oxide (ITO) because of its high electrical conductivity and high optical transparency. However, there are many drawbacks in the case of Ito electrodes such as weak mechanical strength, high processing temperature and high fabrication cost [1]. The blooming nanotechnology facilitates scientists and engineers developing novel materials as the substitutes for the ITO. [2][3][4]

The next generation of the optoelectronics devices will be primarily based on the organic materials which are produced in very large quantity, low fabrication cost, flexible body and low processing temperature. Various materials have been investigated to replace ITO such as silver nanowires (Ag NWs) [2] and carbon nanotubes (CNTs) network [3], which display excellent electrical conductivity and a certain flexibility. However, CNTs have yet well prepared to match the properties of ITO (e.g. 90% of transmittance and below 100 Ω/sq) [14] while Ag NWs have been reported to have the potential to replace ITO [2][13]. Here in this paper we elucidate our work on assembling the Ag NWs based transparent electrode in a low-cost, scalable method using convenient printing method as a replacement for ITO.

Production of solution processable materials for conductive electrodes can be realized by adopting conventional printing technologies such as offset [5], gravure [6] and flexo-printing [7]. However those printing technologies require the fluid properties (i.e. surface energy and viscosity) of the solution processed materials within a limited range [8]. In this circumstance, the fluid properties of the solvents for Ag NWs have to be adjusted in order to conform to those printing technologies. We demonstrate a method of using polydimethylsiloxane (PDMS) as a hydrophobic template to assist assembly of Ag NWs to form transparent conductive electrodes. The advantages using this method to fabricate Ag NWs electrodes include scalable, easy transfer, low-cost processes.

To demonstrate the feasibility of fabricating Ag NWs transparent conductive electrode, a template prepared by a microcontact printing method was fabricated in order to achieve structural dimension down 50 μm. The technique uses the effect of wetting and dewetting of fluids onto surfaces with different surface energy levels. Similar principles were implemented by different research groups for the realization of source/drain electrodes by using poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) with the resolution down to 10 μm [9].

II. EXPERIEMENT

1. Materials

The silver nanowires were prepared in a modified polyol method which is briefly as follows: Silver nitrate (99%, Aldrich) and polyvinylpyrrolidone (PVP) (99%, Mw: 55,000, Aldrich) and sodium chloride (99%, Aldrich) were added into glycerol and the temperature is raised to 200 ^{o}C. The silver nanowires were collected by centrifugation and washed by ethanol for three times. Figure 1b shows the scanning electron microscopy (SEM) image of the Ag NWs, which suggests that the length is 10μm and the diameter is 60nm on average.

2. Fabrication of Silicon (Si) negative-patterned stamp

The negative patterns of 100 μm, 500 μm width (equal spacing) and 8mm length lines were transferred Si wafer by typical photolithography. Using the pattern as a mask, the wafer is etched in KOH solution so that groves with 100μm depth were fabricated.

3. Printing the PDMS patterns

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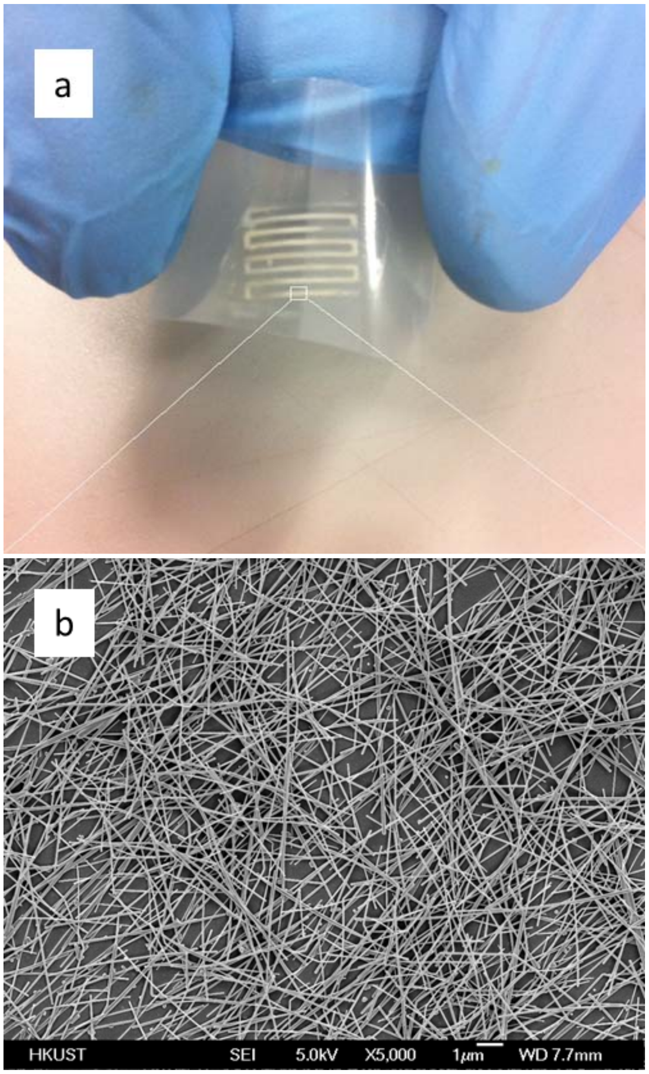


Fig. 1 a) Photography of patterned Ag NWs on the PET substrate b) An SEM image showing the Ag NWs.

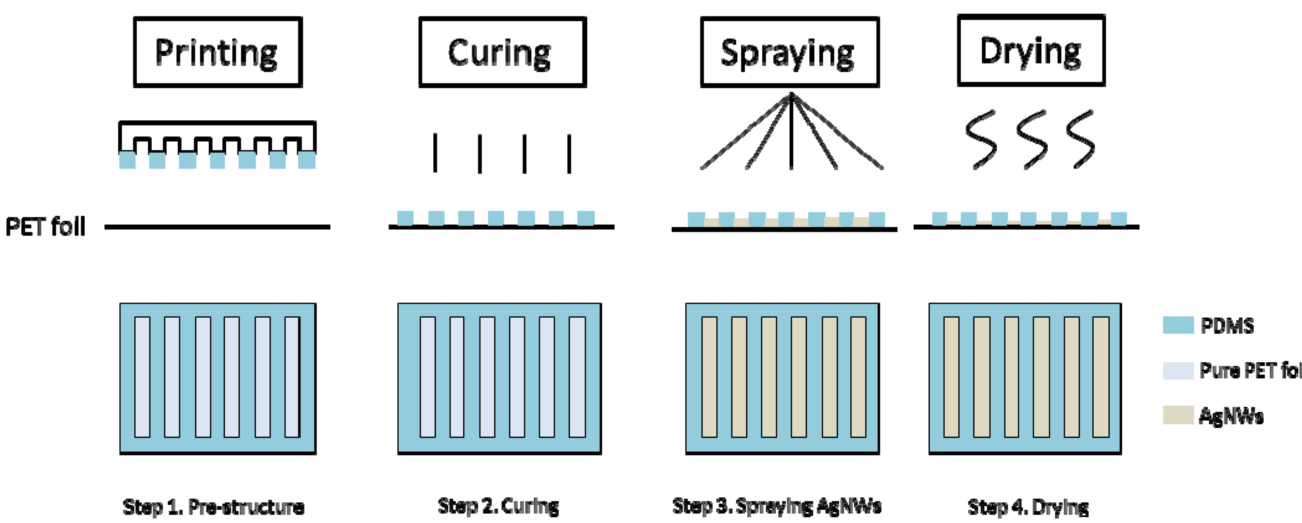
The printing method is based on microcontact printing method with the etched Si as the stamp, which is used to transferring the ink from the ink trough. The non-etched areas on the Si wafer can pick up the ink and transfer to the substrate. The procedures of printing negative patterns on the PET substrate by the Si stamp are shown on Scheme 1. The technique used the effect of hydrophobic and hydrophilic on the surface with different surface energy levels to the fluids [10][11]. The ink was made by polydimethylsiloxane (PDMS) (curing ratio 10:1) [12], using xylene as solvent (mixing ratio, 2:1 by volume) which was printed onto the substrate forming the negative patterns. Then, the printed patterns were cured on a hotplate at 120°C for 60mins.

Ag NWs were spray coated onto the substrate. After spray-coating the Ag NWs onto the substrate surface, the Ag NWs automatically fill in the patterns without leaving residue on the PDMS-stamped surface. Finally, the Ag NWs solution is dried by air-stream and transparent conductive electrodes were obtained.

III. RESULT AND DISCUSSION

1. Fabrication of the regular hydrophilic/hydrophobic template

The hydrophilic/hydrophobic template for the assembly of solution-processable Ag NWs was prepared by stamping method (the stamp material was silicon). For both of the different line width, e.g. 500 µm and 100 µm, the printed PDMS on the PET spread across the surface. The surface energies of the substrate and viscosity of the PDMS influence the spreading of the paste. So optimizations such as surface treatment of the substrate and adjustment of ink viscosity are both necessary to minimize these two effects. As demonstrations, here we tentatively pattern on the Si stamp of i) 500 µm and ii) 100 µm lines result in 680 µm and 150 µm in width respectively for the printed negative patterns on PET. In other words, the un-patterned areas are 320 µm (Fig. 2(a)) and 50 µm (Fig. 2(b)) respectively.



Scheme 1. A schematic of the fabrication process for the Ag NW-based transparent conductive electrdoe

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We used microcontact printing method to assembly Ag NWs and we used ethanol as the solution for Ag NWs. With regarding to the contrast on contact angle by Ag NWs in ethanol between PDMS-stamped and PET area, the Ag NWs was sprayed onto the top of the hydrophobic/hydrophilic template. As the surface energy of PDMS is lower than the unpatterned area on PET, there is a huge surface energy difference between them thus the negative patterned area can be used as a guide for the assembly of the solution-based Ag NWs. After that the assemblies of Ag NWs lines were formed on exact un-patterned/hydrophilic area on the PET (Figure 3) with sharp edges. The advantage of using this assembling method is that the hydrophobic/hydrophilic template can conveniently help to evenly distribute the surface tension of the Ag NW solution during its evaporation process, thus it automatically renders the Ag NWs distribute into a thin, regular, and adjustable film in large areas. This achievement can help to build up transparent conductive electrodes in a way which is more convenient and feasible in mass production.

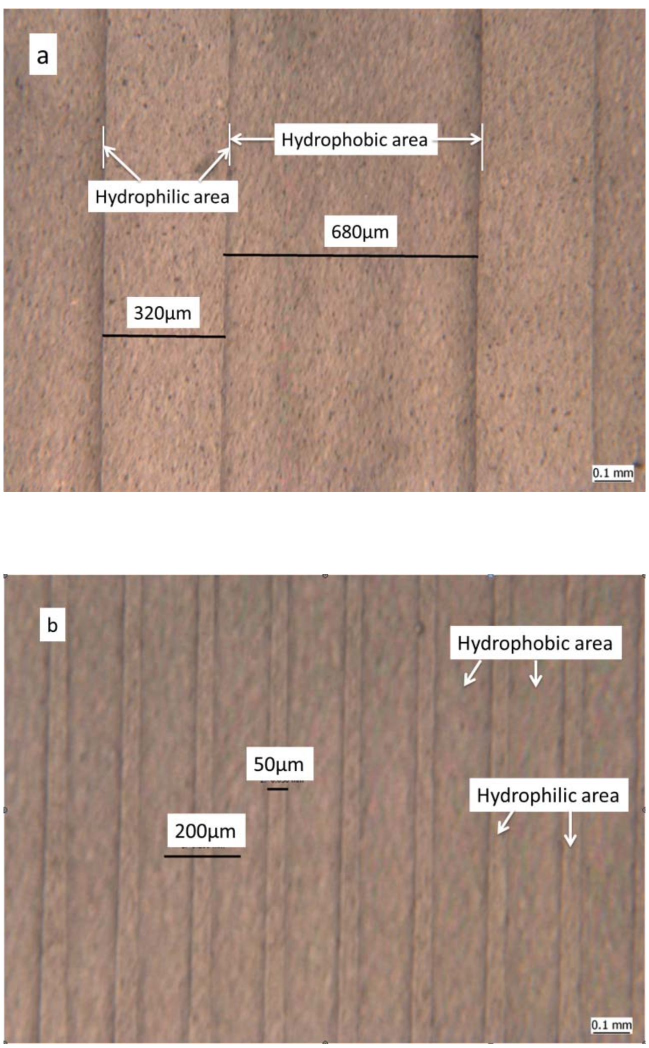

Fig. 2 Printed template by Si stamp on PET substrate (a) Patterns printed by 500μm width lines (b) Patterns printed by 100μm width lines

After demonstrating the feasibility of adopting the microcontact printing method for fabricating Ag NWs transparent conductive electrodes, a potential mass production printing technology, gravure printing can be used to fabricate the hydrophilic/hydrophobic template for the assembly of solution-processable Ag NWs. The gravure printing technology brings the advantages of high speed and large area production which makes ultra-low cost for printing conductive electrodes. Gravure printing technology provides high resolution for printed patterns, which is especially important for reducing the size of printed template in our case. The highest resolution reported for printing conductive electrodes were 10μm [9]. For a precise control of the gravure printing process it is essential to optimize the interplay between the properties of the hydrophobic materials (e.g. surface tension, viscosity) and the parameters of the printing process (e.g. cell volume, printing speed and pressure) together with the geometrical dimensions of the negative patterns. A gravure printer which is designed for the fabrication of hydrophilic/hydrophobic template is under manufacturing (Fig. 4).

2. Resistivity measurement results

The electrical resistivity of the Ag NWs based transparent conductive electrode is measured according to the equation,

$$R = \rho \frac{L}{A} \quad (1)$$

where ρ is the resistivity of Ag NWs, L and A are the length and cross sectional area of the Ag NWs electrode respectively. The samples have their line width of width of 320 μm, 500 nm in thickness and on average 8mm in length. According to (1), the measured resistance of the Ag NWs electrode was 49 Ω which suggests the resistivity of the Ag NWs is $9.8X10^{-7}$ Ωm and sheet resistance is 1.96 Ω/sq. By comparison, conductive electrodes fabricated by Ag NWs provide flexibility and are the potential replacement for ITO. However the Ag NWs electrodes need to remain transparent and highly conductive at the same time in order to replace ITO as an electrode. Thickness of the Ag NWs electrodes influences both transparency and sheet resistance. The transparency and the sheet resistance decrease with increasing thickness. The ratio of the patterned/unpatterned area is also a key point to the overall electrical conductance of the electrode. By adjusting these factors, we are able to achieve desirable property of the electrodes, with a balance among the transparency, electrical resistance, and mechanical strength. For example, a value of sheet resistance of 10 Ω/sq at transparency of 85% for Ag NWs is very comparable to the performance of ITO [2][13].

IV. Conclusion

In summary, we have successfully prototyped a method of fabricating the Ag NW-based transparent conductive electrodes by applying a pre-patterning step, the hydrophobic micro-patterns (PDMS) form on the hydrophilic PET substrates, which help to reduce the surface tension of the Ag NW solution in large areas. This helps the Ag NWs evenly distribute in the hydrophilic areas during the

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subsequent solvent evaporation step after applying the Ag NW solution. This simple printing step renders the Ag NWs form an evenly distributed percolated network rather than falling into agglomerations. When coupling this method with the low-cost gravure printing method, the Ag NW-based transparent conductive electrodes can be scaled up conveniently in mass production. As compared to the other method to fabricate the Ag NWs and CNTs ever reported, such as the Mayer rod method and the Bucky paper preparations, our method is especially effective in large areas with the feature resolution larger than 100 micron. The measurements of our prototypes suggests that the electrical resistivity of the Ag NWs thin film is $9.8X10^{-7}$ Ωm and sheet resistance is 1.96 Ω/sq which is comparable to ITO. Further investigation on the printing method is still undergoing, which is aimed to improve the printing resolution and the solvent evaporation condition etc.

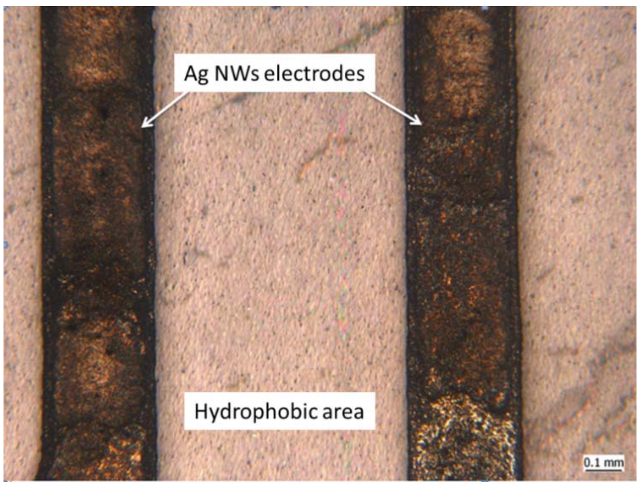

Fig. 3 Assembled AgNWs patterns

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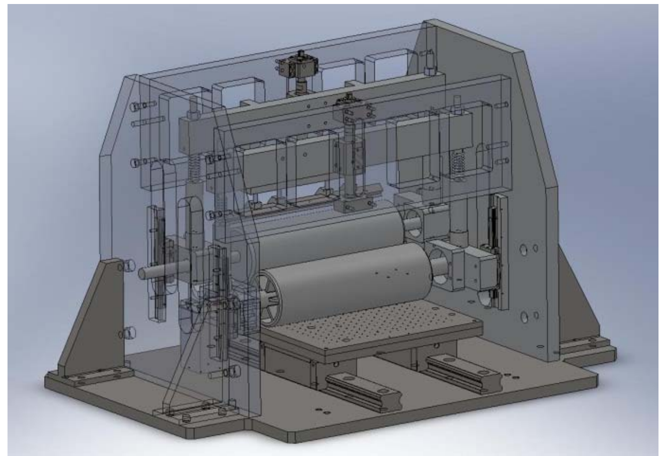

Fig. 4 3D drawing of gravure printing machine which was designed for this fabrication process

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