Non-contact Laser Printing of Ag Nanowire-based Electrode with Photodegradable Polymers

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The roll-to-roll process is synonymous with newspaper production. If a similar high-throughput process is developed to fabricate electronics over large areas, it would revolutionize the printed electronics manufacturing process. Rapid fabrication of electrode, including patterning and nanoscale welding, is a necessary integration technique to reduce the duration of the process, but faces difficulties in being realized using conventional methods. This paper discusses material factors that affect printability, in the context of developing a promising fabrication technique called laser induced forward transfer (LIFT); LIFT is a non-contact printing technique applied previously to realize simultaneous pattern deposition and nanowelding of Ag nanowire (AgNW)-based electrodes. A photodegradable polymer, which is a key component in the printing process to render droplet acceleration, is investigated with regards to its mechanical and optical properties. Furthermore, the printing process of the AgNW-based electrode is visualized, resulting in deeper understanding of LIFT. Knowledge of these factors will contribute to rapid and precise patterning of AgNW-based electrodes with high stretchability and transparency toward flexible optoelectronics devices.

Keywords: Printable electronics, Metal nanowire, Transparent electrode

1. Introduction

Transparent electrodes, such as tin-doped indium oxide (ITO), are widely used in displays, touch screens, and solar cells. Alternative materials such as carbon nanotubes, graphene, conductive polymers, and metal nanowires have been studied toward flexible electronics owing to the limitation of brittleness in ITO-based transparent electrode [1–10]. Among these alternatives, Ag nanowire (AgNW) is highly suitable for transparent and flexible electrodes owing to its high conductivity (< 50 Ω/sq.), optical transparency (< 96%), and mechanical flexibility (< 100% strain) [5,11,12]. In addition, AgNW has high affinity to printable electronics with low environmental load by forming the required amount of materials locally at the required location, unlike the conventional manufacturing process of photolithography. Thus, for large area and high through put roll-to-roll processes, AgNW are excellent candidates toward flexible and transparent electronics.

However, networks of AgNW have low conductivity because small gaps exist at the wire–wire junctions. Thermal annealing or mechanical pressing usually improves the connection to achieve high mechanical and electrical properties. The strengthened nanowire networks retain their conductivity under mechanical deformations. There are concerns about the effect of thermal annealing (often over 150 °C) and high mechanical pressure (25 MPa) on delicate components in organic-based flexible electronics [1–3,13]. In addition, the
processes are time consuming from minutes to hours, which is unsuitable for a roll-to-roll fabrication process.

In this study, a one-step laser process of ‘laser induced forward transfer (LIFT)’ is investigated with respect to factors that affect electrode printability; LIFT was previously applied as a non-contact printing method to realize simultaneous pattern deposition and nanowelding on AgNW-based electrode [14]. The mechanical and optical properties of photodegradable polymers are important to discharge the AgNW and achieve optimal print condition. Subsequently, visualization techniques were employed to characterize the transfer process in order to achieve better process controls. This knowledge can be applied to achieve precise and rapid patterning of AgNW-based electrodes toward stretchable and transparent optical devices.

2. Experimental

Donor layers were prepared on quartz donor substrate by solution processes and placed upside down on a spacer separating the acceptor for LIFT (Fig. 1(a)) [14]. Triazen polymer (TP) layer [15] or polyethylene terephthalate (PET) was used as the dynamic release layer (DRL) and AgNWs/wet resin as the target material. TP layers with thicknesses of 100 nm, 150 nm, and 260 nm were fabricated using a solution prepared by diluting 2, 2.5, and 3 wt% TP in a mixture of cyclohexanone (Sigma-Aldrich Corp.) and chlorobenzene (Sigma-Aldrich Corp.) (1:1) before the solution was spin-coated at 600 rpm for 1 min on quartz glass and heated at 70 °C for 1 h. The AgNW solution was drop casted on the 150 nm thick TP layer by shedding the solution along the longitudinal/transverse of the substrate. The layer was air dried before wet resin with high optical transparency provided by Henkel was diluted with diethylene glycol monoethyl ether acetate and was spin coated onto the dried AgNW layer.

In order to fabricate the transparent electrode, the PET layer was prepared as the DRL and AgNW/poly(3,4-ethylenedioxythiophene)-poly(styrene-sulfonate) (PEDOT:PSS) was prepared as the target material. PET layers with thicknesses of 60 nm and 240 nm were fabricated using a solution prepared by diluting 0.3 wt% and 1 wt% PET (20080328-2, extruded by TenCate Nijverdal) in a mixture of trifluoroacetic acid (Sigma-Aldrich Corp.) and dichloromethane (Analytical Reagent grade, Stabl./Amylene, Biosolve Chemicals) (1:1) before the solution was spin-coated at 2000 rpm for 1 min on quartz glass and heated at 100 °C for 10 min. The AgNW solution was then drop casted on the 60 nm thick PET layer using the same approach employed for TP. After the layer was air dried, water-based PEDOT:PSS solution was spin coated onto the AgNW layer. The PEDOT:PSS provided by Agfa-Gevaert N.V. had been diluted with ethylene glycol and 2-propanol and filtered using PTFE membrane (Millex-SR, 0.5 µm of pore size, Millipore).

The optical properties of the target materials were determined as donor information. The absorption and transmittance were measured using a UV–VIS–NIR spectrophotometer (UV-3600, Shimadzu Corporation). To measure the optical properties of each material, the same technique of spin-coating or drop casting used in donor preparation was applied.

Fig. 1. LIFT with AgNW. (a) Schematic of preparation of donor and LIFT with flipped donor. (b) Microscopic image of printed AgNW from AgNW/wet resin. (c) UV spectrum for light absorption on triazen polymer (TP, thickness of 150 nm), polyethylene terephthalate (PET, thickness of 60 nm), and AgNW. Excimer laser wavelength is 248 nm. SEM image for (d) AgNW as deposited and (e) printed AgNW by LIFT. Sintered nanowires are in red-colored circles. Scale bars are 1 mm in (d) and (e). Data in (c) and (e) were referred from [14].
on the quartz glass. The real concentration of AgNW on the substrate could not be measured; however, it can be estimated from the absorption of AgNW—7% at 550 nm wavelength in this study. The sample was observed using optical microscopy (DFC420, Leica Microsystems) and scanning electron microscopy (SEM, XL40FEG, Philips).

3. Results and discussion

3.1. LIFT

Figure 1(b) shows the transferred droplet from the AgNW donor with wet resin using the DRL of TP. AgNW network with matrix (wet resin) in the target layer was consistently transferred. The laser beam (specification: excimer laser, 248 nm wavelength, and 10 ns pulse duration) was shaped with a square mask, which produced a laser spot with an area of approximately $5 \times 10^4 \mu m^2$. The diameter of the Gaussian beam was much larger than the square mask and was centered on the mask; thus, uniform laser energy was obtained in the mask, resulting in a 1:1 area transfer from the donor to the acceptor. More importantly, the intact AgNW network was transferred to the acceptor by tuning the energy fluence between 71 mJ/cm$^2$ and 77 mJ/cm$^2$. Laser light was utilized in the absorption by AgNW as well as ablation of DRL. The DRL of the 150-nm thick TP layer showed an absorption of 61%, whereas 39% of light was transmitted allowing light illumination to the AgNW (Fig. 1(c)). Surface plasmon resonance occurred in the AgNW under UV, resulting in heating of the nanowires under laser illumination. Figures 1(d) and 1(e) show the welded AgNW after LIFT. When the thickness of the TP layer was reduced to 100 nm, significant welding effects were detected because the DRL absorbed less light. Therefore, a printed AgNW with a clear square shape composed of intact and welded AgNWs was achieved at tuned laser energy fluence by varying the light intensity and DRL thickness [14].

Subsequently, AgNW/PEDOT:PSS was utilized to fabricate the transparent electrode. The sizes of the dots printed using LIFT were evaluated (Fig. 2). The blue band in the figure indicates the optimal size, which should be approximately $5 \times 10^4 \mu m^2$ owing to the size of the laser beam. The size of the dot significantly increased as the energy fluence increased. Desirable droplets were obtained with the same laser energy in the range of 70–80 mJ/cm$^2$ using donor TP and AgNW/wet resin. Desirable droplets were obtained with the same energy from different DRLs of TP and PET because they have essentially the same ablation threshold and absorption, as presented in Fig. 3 and Table 1. With a thicker spacer, the areas of the droplets were smaller, as shown in Figs. 2(a) and 2(b), which show a comparison of 125 μm and 250 μm spacers. We surmised that the droplet size changed with the difference in the thickness of the spacer due to the speed of the flyer. For example, the shape of the dots obtained around 77 mJ/cm$^2$ for AgNW/PEDOT:PSS with 125 μm spacer was clearly rectangular, resulting in consistent transfer and low electrical resistivity of $3–4 \times 10^2 \Omega$ cm (Fig. 2(c)). On the other hand, the desirable dot area was achieved with high energy fluence of approximately 81 mJ/cm$^2$ using 250 μm spacer. Furthermore, dot shrinkage was observed below 74 mJ/cm$^2$. The flyer speed must be reduced with increasing distance from the donor due to air resistance and collision with the occurrence of shockwave. Details of the mechanism is discussed in Section 3.3. The shrinkage is invariably due to the decreasing speed of the flyer. The ablated PET did not have enough energy to transfer. Therefore, clear rectangular droplets can be achieved by adjusting the spacer thickness and energy fluence.

3.2. Photodegradable polymers

High absorptivity and low ablation threshold are important criteria for a DRL in order to protect the sensitive target material. The optical and mechanical properties of DRL polymer films were measured at various thicknesses as presented in Fig. 3 and Table 1. Figure 1(c) shows a UV–VIS spectrum of TP and PET. TP has wider absorption regimes below the 400 nm wavelength than PET in the UV range. A dip in the absorption was observed for TP at 248 nm wavelength, with increase in the absorption as the thickness increased. Absorptions of 49%, 61%, and 78% were observed for thicknesses of 100 nm, 150 nm, and 260 nm, respectively. PET exhibited higher absorption even with a thinner thickness compared to TP. The absorptions of PET were 64% and 89% for thicknesses of 60 nm and 240 nm, respectively.

The absorption coefficient ($\alpha$) can be expressed by the Beer–Lambert law as [16]:

$$\alpha = \frac{-1}{x} \ln\left(\frac{I}{I_0}\right)$$  (1)

where $x$ is the thickness and $I/I_0$ is the transmittance of light from the initial intensity ($I_0$) to the pass intensity through a material ($I$). The absorption coefficient was calculated at 248 nm wavelength.
using equation (1), as summarized in Table 1. PET showed a higher absorption coefficient of approximately $2 \times 10^5$ cm$^{-1}$ compared to that of TP ($7 \times 10^4$ cm$^{-1}$). The result verified that PET had a higher absorption even with a smaller thickness owing to the higher absorption coefficient. More importantly, PET had a higher absorptivity than TP, which is traditionally used by numerous researchers as DRL to transfer sensitive materials.

The deposited TP and PET layers on quartz were illuminated directly by laser (Fig. 3(a)). Figures 3(b) and 3(c) show the ablation depth per laser pulse. Both TP and PET films were ablated from approximately 40 mJ/cm$^2$. The ablation threshold

![Fig. 2. LIFT for transparent electrode. (a) Optical microscope image of the printed electrodes with different laser energies and different gaps between donor and substrate. (b) Droplet size calculated from pictures in (a). (c) Demonstration of LIFT for large area patterning.](image)

![Fig. 3. Laser ablation. (a) Schematic diagram of experimental setup. Ablation depth per pulse for (b) TP and (c) PET for each thickness.](image)

| Materials / Thickness | TP / 100 nm | TP / 150 nm | TP / 260 nm | PET / 60 nm | PET / 240 nm |
|-----------------------|-------------|-------------|-------------|-------------|-------------|
| Absorption (%)        | 49          | 61          | 78          | 64          | 89          |
| Absorption coefficient (cm$^{-1}$) | $8.2 \times 10^4$ | $7.3 \times 10^4$ | $6.9 \times 10^4$ | $1.8 \times 10^5$ | $1.5 \times 10^5$ |
| Ablation threshold (mJ/cm$^2$) | 41          | 38          | 44          | 40          | 43          |
| Effective absorption coefficient (cm$^{-1}$) | $1.1 \times 10^5$ | $8.7 \times 10^4$ | $7.0 \times 10^4$ | $2.0 \times 10^5$ | $1.1 \times 10^5$ |
fluence ($F_{th}$) can be defined as given in the following equation [16,17],

$$\alpha_{eff} = \frac{1}{d \ln\left(\frac{F}{F_{th}}\right)} \quad (2)$$

where $\alpha_{eff}$ is the effective absorption coefficient, which influences the trend in ablation, $d$ represents the ablation depth per pulse, and $F$ is the irradiation fluence. The ablation threshold and effective absorption coefficient were calculated using the fitting lines of the plots in Figs. 3(b) and 3(c), as presented in Table 1. TP and PET showed comparable effective absorption coefficient of approximately $1 \times 10^5$ cm$^{-1}$ in some cases. The ablation thresholds were again calculated for TP and PET, with obviously a very low energy fluence of approximately 40 mJ/cm$^2$ compared to the other polymers [17–22].

3.3. Visualization

Visualization of the transfer process was performed using a schlieren system to study the optimal transfer parameters. It also provides insight into how the generated shockwave affects material transfer from donor to acceptor substrate. When part of the energy from the laser pulse interacts with the donor layer, it is converted into kinetic energy that propels the donor material. The speed of the ejection of the material due to the impact of kinetic energy causes a shockwave [23,24]. Shockwave and its collision to droplet is clearly observed when a thin metal as the target material is transferred (Fig. 4 a). Figures 4(b) and (c) depict that the flying target material collides with the shockwave, which travels faster than the flyer, and is reflected back after hitting the acceptor substrate. We also observed the influence of shockwave collision in the case of AgNW/wet PEDOT:PSS as the donor matrix. The speed was calculated without the acceptor (Fig. 4(d)). The shockwave was faster than the speed of sound, approximately $4 \times 10^2$ m/s, whereas the speed of the droplet was approximately $2 \times 10^2$ m/s. We surmised that the collision of the shockwave with the droplet reduced the speed of transfer. The speed of the droplets toward the acceptor was also calculated. The droplet was propelled at more than $3 \times 10^2$ m/s immediately after flying out from the donor. However, the velocity of the flyer was drastically reduced near the point where the collision occurred. Thus, interaction with the shockwave is a possible factor that can change the speed of the flyer and alter the size/shape of the transferred droplets considering that the size and shape of the transferred droplet changed as the distance between the donor and the acceptor varied. The results from visualization highlight one of the factors needed to obtain desirable droplets.

4. Conclusion

LIFT is a digital manufacturing technique that can print a wide range of high viscosity inks and even solid-state materials onto unconventional substrates. Various shapes can be achieved by changing the laser spot size from a few to hundreds of micrometers [15,25–27]. In this report, LIFT was utilized to pattern AgNW-based electrodes under...
operation in atmospheric conditions at room temperature. To facilitate simultaneous sintering and patterning, 150-nm thick TP was used as a DRL. Moreover, the optical and mechanical properties of PET were similar to those of TP; thus, PET as DRL can contribute to facilitate the fabrication process. In addition, the results of the visualization of the printing with PET as DRL showed a dramatic difference in the flyer speed with or without acceptor substrate. The result indicates that adjustment of the LIFT architecture is necessary. All the mentioned factors affect printability and when tuned appropriately, will contribute to the realization of a rapid and precise fabrication process of flexible and transparent AgNW-based electrode for next-generation optoelectronic devices.

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