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Patterned silver nanowires using the gravure printing process for flexible applications

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ABSTRACT

Gravure printing is a promising electronics printing technology for fabricating flexible-large area devices at high speeds. Ag nanowire (Ag NW)-based transparent conductive electrodes are excellent candidates for replacing indium thin oxide in flexible electronics and optical devices, which require the preparation of patterned structures. Here, the gravure printing processing parameters for applying Ag NW ink were investigated to produce large-area patterned transparent and uniform Ag NW lines on polyethylene terephthalate substrates. The ink transfer properties changed with the printing speed and pressure, as discussed, and these parameters modulated the electrical properties of the printed Ag NWs annealed at various temperatures. The importance of the rheological behavior of the ink, the printing speed, and the pressure was confirmed to understand the mechanism underlying Ag NW ink transfer. The printed line resistance for a 450 μm of line width dried at 90 °C was 32 Ω mm^{-1} with a 95% of transmittance and a 100 μm gap between the printed lines. The line width and spacing of the printed patterned Ag NWs may be controlled using the parameters examined here to optimize the application-specific device performance.

1. Introduction

Roll-to-roll printing processes have been widely investigated for the use in printed electronics, such as radio frequency identification tags, sensors, and thin film transistors (TFTs) [1–3]. A variety of roll-to-roll printing systems have been developed, and the gravure printing technique has been investigated extensively for the use in both laboratory and industrial settings because its variables are readily controlled to yield high-speed production over large areas [4–7]. The use of this technique in printed electronics requires an understanding of the printing mechanisms that yield smooth and straight lines that are suitable (and often required) for many modern devices [8].

Gravure printing is a multistep process of filling, doctoring, and transferring [8,9]. The printed feature dimensions and quality depend strongly on the relationships between ink and the surface involved in each step. Sung et al. characterized the relationship between the cell configurations engraved in metal and the rheological properties of the nanoparticle ink during ink transfer [9]. Dodds et al. revealed the importance of the surface wettability of the ink for achieving a good transfer efficiency using a 2D Galerkin finite element method study [10]. In gravure printing applications using flat or curved surfaces, the transfer efficiency depends on the capillary number, which is a function of the ink viscosity, surface tensions and printing speed. Kitsomboonloha et al. showed that the printing performance (e.g., the filling, doctoring, and ink transferring) is governed by the ink wettability. The capillary number is strongly related to the printed volume [11]. Kang et al. demonstrated that the uniformity of the printed lines might be improved by using small nanoparticles that reduce the formation of pinholes in the printed lines [12]. Although gravure printing process are useful for preparing printed electronics using a variety materials [13,14], few systematic studies have examined the use of gravure printing on transparent conductive materials, which are critical to the fabrication of optoelectronic and other transparent devices [15].

Silver nanowires (Ag NWs) have emerged as transparent conductive materials with significant potential utility in printed electronics due to their high transparency, conductivity, and flexibility [16]. Several Ag NW deposition methods, including evaporation, template-guided synthesis, ultraviolet photoreduction, solid–liquid phase arc discharge, and electrochemical methods, have been developed for fabricating patterned on a variety of flexible substrates [17–19]. These methods are unfortunately unsuitable for the mass-production of patterned Ag NWs, because the methods are not conducted under ambient conditions, which is a requirement for the production of low-cost large-area electronics patterning methods. Recently, Lin et al. reported the fabrication of a Ag NW film using a gravure printing system and characterized the film's morphology and structure [20]. The printing

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parameters used to produce the specific patterns fabricated in that work were not reported.

In this study, we investigated the gravure printing of Ag NW inks using intaglio trench patterns with which fine printed Ag NW lines could be prepared on a flexible polyethylene terephthalate (PET) substrate. The printability of the Ag NWs in smooth and uniform lines was characterized by investigation the dominant ink transfer mechanisms under a range of printing speeds and printing pressures. The electrical properties of the resulting Ag NW lines after thermal annealing were characterized. The uniform printed Ag NWs lines may be used as transparent conductive electrodes in printed electronics.

2. Materials and methods

Fig. 1 presents a schematic diagram of the gravure printing process used to pattern Ag NW electrodes. The copper gravure pattern was fabricated using photolithography and chemical etching as follows. A designed pattern of 10 cm in length, 500 μm in width, 5 μm in depth, and with 70 μm line spacing was prepared on a transparent film. The patterned film was then exposed to a photolithography process and etched using $FeCl_2$ for 20 min. Next, the patterned copper plate was cleaned with a 40:60 mixture of NaOH:H_2O and dried at 25 °C for 30 min.

First, 10 ml of the Ag NW ink (1 wt.% in isopropyl alcohol; Nanopyxis) with average dimensions of 22 μm in length and 50 nm in diameter (aspect ratio: 440) was applied to a copper-based gravure plate to fill the trenches (Fig. 1a). The efficiency of the Ag NW patterning process was improved by passing a doctor blade over the pattern to fill the trenches with the dispersed liquid while removing the excess ink that remained on the elevated areas (Fig. 1b). The Ag NWs that filled in the trench pattern were then transferred onto a PET film wrapped around a silicon roller (Fig. 1c and d). The two processes were accomplished consecutively by mounting the blade ahead of a motorized draw down the roll. The effects of the printing speed and pressure on the pattern fidelity were investigated by applying printing speeds between 2 and 12 cm/s at a fixed doctor blade angle of 55°. Under each of the conditions tested, printing pressures of 174 and 24 kPa were applied to the 500 × 500 μm unit area to achieve ink transfer. The printed Ag NW patterns were then transferred onto the PET substrate and annealed at 60, 90, and 120 °C for 10 min.

To study the effects of annealing temperature for the Ag NW electrode, Ag NW electrodes were fabricated with spin coater (Spin coater—ACE 200, Korea). The sheet resistances were measured using 4 point probe method (Loresta EP MCP-T360). The rheological properties of the ink and the line resistance values were measured using a rheometer (AR 2000, TA Instruments, USA) and a two-point probe station (Keithley 2400, USA), respectively. To measure the contact angle, the ink dropped on PET was captured with high resolution camera and analyzed with image software (Photoshop CS4 (Adobe)). Optical images were obtained using scanning electron microscope (SEM) (S-4800, HITACHI, Ltd., Japan) and optical microscopy (Bx 51, Olympus, Japan).

3. Results and discussion

In general, gravure patterning is a superior printing method and is used to produce continues electrical conductive ink lines for the use in printed electronics [1,8,13]. The gravure printing of continuous lines may be achieved using one of the methods: gravure line printing, in which a series of separate cells is etched close together to form lines, or intaglio trenches, in which a continuous trench is etched into a gravure cylinder. The radius of the cells and the line spacings between the printed gravure lines must be optimized to from uniform lines with optimal drop spacings and drop radii. Intaglio trenches, however, avoid some of the problems with gravure line printing and may theoretically be scaled down to very small cell widths without emptying the cells. In view of these advantages, we designed a trench for fabricating continuous ink lines.

Fig. 2 shows that the Ag NW ink has a 0.2 Pa·s viscosity at a shear rate of 10 s^{-1}, and the viscosity of the Ag NW ink decreased with the shear rate in accordance with non-Newtonian fluid dynamics. These fluid properties are suitable for conventional gravure printing processes that require rapid ink filling and transfer to the gravure patterns and substrates at the applied printing speeds (2–12 cm/s with the trench width of 500 μm) [21]. The printed pattern morphology and pattern

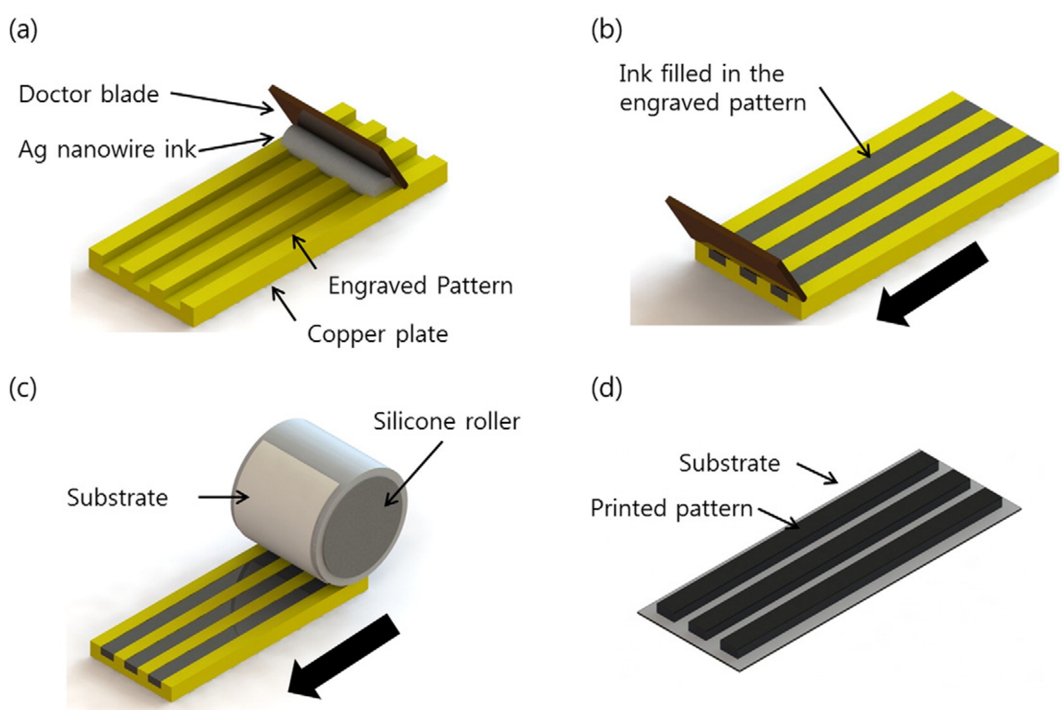

Fig. 1. A schematic diagram of the gravure printing process: (a) ink application, preparation for doctoring, (b) doctored plate, (c) printing by passing the filled pattern through nip of a plate roll set-up, and (d) printed pattern on the substrate.