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Application of flash-light sintering method to flexible inkjet printing using anti-oxidant copper nanoparticles

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ABSTRACT

Copper nanoparticles were protected against oxidation by coating with 1-octanethiol. The copper nano-ink was synthesized by dispersing the coated copper powder in 1-octanol solvent at a concentration of 18 wt%. Inkjet patterns printed on a flexible polyimide film and subjected to flash-light sintering displayed excellent anti-oxidation behavior over 2 months. The optimal light-sintering condition was 24.7 J/cm^2 of energy density from a 5-ms pulse, which resulted in a resistivity of 2.4×10^{-7} Ω·m. After bending more than 1000 times, the resistivity of the light-sintered pattern was 1.45-times higher than that of the unbent pattern. The light-sintered pattern printed with the anti-oxidative copper nano-ink shows great promise for flexible device applications.

1. Introduction

Printed electronics are widely used in flexible devices such as radio frequency identification (RFID) tags, smart cards and disposable electronic devices [1–4]. Printing can replace conventional photolithography because of its low fabrication cost and waste reduction. Printing technologies, such as inkjet printing, use the drop-on-demand (DOD) system and do not require contact with the substrate. Inkjet printing has been proposed for flexible substrates [5], which are required for the roll-to-roll printing process [6,7]. Many studies on metal nano-ink to be applied to Inkjet printing process, was studied to form line pattern. Since metal nano particles were used for the pattern, sintering process such as heat furnace sintering, is required. Also, conventional heat sintering process typically requires high temperature heating to enhance the particle diffusion, resulting in densifying structure among nano-particles. However, this temperature is higher than the glass transition temperature (T_g) of many flexible polymeric substrates [8,9]. Recently, flash-light sintering has been developed because of its rapid sintering time under atmospheric conditions [10,11]. Flash-light sintering uses photon energy, which is related to the photothermal effect [12]. Flash-light sintering technology solves the conventional heat sintering problem by irradiating a sample with white light at a specific frequency for only milliseconds using a short momentary pulse [13,14]. There is great interest in silver-based nano-inks because of their high conductivity and oxidative stability under ambient conditions [15]. However, they are expensive to use at the large volumes required for commercial roll-to-roll printing. To overcome this problem, copper has been studied because of its low cost and high conductivity [16–21]. However, copper is easily oxidized [22]. To solve this issue, the vapor self-assembled multilayers (VSAMs) method was developed, in which 1-octanethiol vapor is coated on a pure copper surface (Fig. 1(a)). Alkanethiols, such as 1-octanethiol, can form strong covalent sulfur bonds with a non-oxidized metal surface (Fig. 1(b)) [23–27]. Previous studies have shown that 1-octanethiol-coated copper nanoparticles are resistant to oxidation over 40 days [24]. In this work, a copper pattern was formed by inkjet printing of a nano-ink made with 1-octanethiol-coated copper nanoparticles on a polyimide substrate. The printed pattern was sintered using flash-light from a xenon flash lamp (Fig. 2). The stability of the flash-light sintered copper patterns was evaluated by monitoring the resistivity as the sample was bent over 1000 times. An LED circuit was designed using the pattern to demonstrate potential future applications.

2. Experimental details

2.1. Synthesis of the 1-octanethiol-coated copper nano-ink

Copper nanoparticles were synthesized using the polyol method, as reported previously [23]. They were then coated with 1-octanethiol using the VSAMs method, under the conditions of 5 min and six cycles at 4.0×10^{-6} Torr [24,26]. Fig. 1 shows schematic diagrams of the VSAMs system and a 1-octanethiol-coated copper nanoparticle. To fabricate the 18 wt% copper nano-ink, 0.7 g of 1-octanethiol-coated copper nanoparticles were mixed with 1.6 mL of 1-octanol solvent. The

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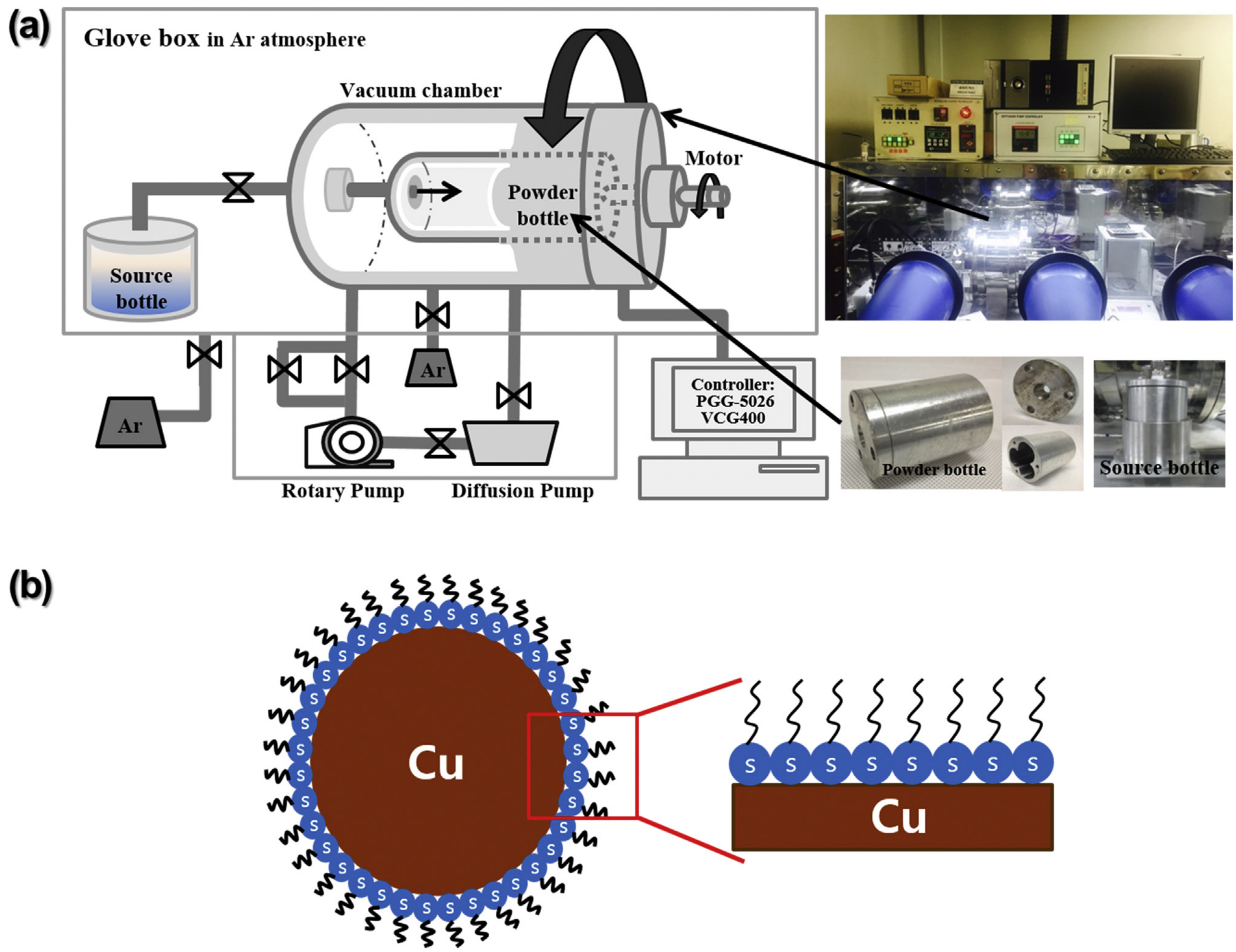

Fig. 1. Schematic diagrams of (a) the vapor self-assembled multilayers (VSAMs) technique [27] and (b) an 1-octanethiol-coated copper nanoparticle.

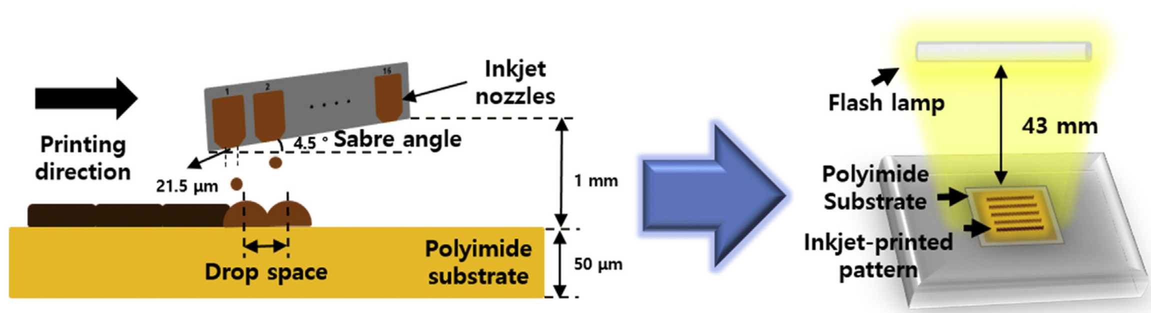

Fig. 2. Inkjet printing using flash-light sintering.

suspension was then ultrasonicated for 30 min at room temperature.

2.2. Inkjet printing and flash-light sintering conditions

A 50-µm thick flexible polyimide substrate (SKC KOLON PI) was cleaned with ethanol for 10 min. The hydrophobicity of the substrate was enhanced by treatment with a Plasma Enhanced Chemical Vapor Deposition System (PECVD at 50-watt power in Argon atmosphere at 3.0×10^{-1} Torr for 1 min. The copper nano-ink was printed using an inkjet printer (Dimatrix Materials Printer DMP-2831; Fujifilm) on the plasma-treated polyimide substrate. The number of nozzles was 16, with the drop spacing varying from 20 µm (1270 dpi) to 30 µm (846.67 dpi) and 40 µm (635 dpi). The printing voltage ranged from 26 to 32 V. The pattern size was $0.8 \times 10\ mm^2$ for the bending test. After patterning, the ink solvent was vaporized at room temperature. Sintering was accomplished in two ways. First, heat sintering was done in a furnace at 200 °C for 1 h for de-binding to remove 1-octanethiol coating (its boiling point is 196 °C), followed by 250 °C for 4 h for main sintering under a hydrogen atmosphere (100%, H_2) (Table 1) [26]. The main sintering temperature is 250 °C to minimize the substrate damage. Second, flash-light sintering was done, at its peak power of 1.5 MW, for 2–5 ms per pulse, using flash-light sintering equipment (model IPL-45kW_2100; PS Teck). Usually, the power reached a maximum value during one flash of light of the xenon lamp. The distance between the