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Hydrazine vapor-based rapid and low temperature post-processing for inkjet printed conductive copper patterns

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ABSTRACT

We present a useful and effective conversion process for inkjet-printed conductive copper features on common polymer substrates. The process is based on causing burst nucleation from an as-printed copper complex ion pattern by an exposure to hydrazine vapor. This hydrazine based treatment at 150 °C for 1 min leads to copper patterns with a well-sintered microstructure and resistivity of 15.18 μΩ cm. This new approach could be an alternative to a conventional hydrogen gas treatment and is suitable for organometallic or metal complex based inks as well as most commercial plastic and paper substrates for flexible and disposable electronics.

1. Introduction

In recent years, there has been increased interest in manufacturing flexible printed electronics by means of an inkjet printing process because of its simplicity, productivity and availability of low cost flexible polymer substrates compared to traditional photolithography techniques. The inkjet printing process is frequently utilized as a fabrication method for conductive features on flexible polymer and paper substrates for electrodes, contacts or interconnects, and antennas of flexible electronic devices [1–3]. Due to its low resistivity (1.72 μΩ cm) and significantly lower cost compared to silver, copper is the most suitable material for inkjet-printed conductive features. There are two main types of copper inks based on copper nanoparticles and copper–organic compounds [4–8]. The latter is the solution form of metal–organic copper (I) and copper (II) compounds without any particles, which have the advantage of being easy to prepare with mass production and being free from oxidation and nozzle clogging during storage and printing compared to ink with copper nanoparticles. In addition, in the case of ink based on metal nanoparticles, it is necessary to use dispersion agents that could inhibit the decrease in its stability by coating a dispersion agent on the surfaces of the nanoparticles [9–11]. However, these dispersion agents generally have high molecular weights, thus, a high temperature was demanded to decompose such heavy molecular materials, which hinder the application of metal nanoparticle based ink on flexible substrates, such as polyimide and epoxy. If the annealing temperature is lowered to enable the use of flexible substrates, electrical conductivity will be degraded by residual organic materials and porous microstructures of patterns.

All kinds of inks are necessary for calcination or reduction and sintering steps after the inkjet printing process to remove organic compounds into inks, to convert metal-organic compounds to pure metals and/or to chemically combine all particles into a bulk counterpart. The process temperature of the step should clearly be lowered to use low-cost plastic substrates with low thermal stabilities such as polyethylene terephthalate films and conventional papers. Recently, alternative post-printing techniques using high-energy sources including a laser, microwave, pulsed light and plasma have been reported. They are able to directly convert surface-oxidized nanoparticles to a bulk film and to easily decompose organic dispersion agents for short time and low temperature processing [12–16]. However, it is difficult to apply these techniques to metal-organic compound inks because they need to be simultaneously decomposed into organic substances and reduced to a zerovalent metal in the middle of the post treatment. Especially in the case of copper-organic compound inks, the decomposition and conversion reaction should be completed without any oxidation reaction, unlike other noble metals such as silver and gold. Thus, it is necessary to maintain a reducing atmosphere throughout the post treatment process. Current alternative post-processing technologies for copper-organic compound inks are indispensable to generate electrically copper conductive patterns on flexible substrates using copper-organic compound inks.

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In this study, we present a fast, low temperature post-processing technique for copper-organic compound inks using a hydrazine vapor as a chemical sintering agent. The hydrazine is selected because it is a strong reducing agent used as a rocket fuel and is a very convenient reductant that typically generates nitrogen gas and water as by-products. As a proof of concept, a copper complex ion ink is synthesized by a modified electrolysis method and inkjet-printed on a polyethylene terephthalate (PET) substrate. The patterns are post-treated by hydrazine vapor processing and the microstructure and electrical resistivity of the patterns are examined as a function of the sintering temperature.

2. Experimental details

The copper complex ion ink was synthesized using a modified electrolysis process, which we developed and reported in our previous research [17]. Two copper plates ($2.5 \times 5 \times 0.1$ cm^3, Aldrich, 99.9%) were used as electrodes in the electrolysis process. The electrolyte was prepared by dissolving 20 mM formic acid (HCOOH, Junsei Chemical, 99.5%) and acetic acid (CH_3COOH, Showa Chemical, 99.7%) into ammonium hydroxide solution (25.0–28.0% NH_3, Dae-Jung Chemical). After the copper electrodes were dipped in the electrolyte solution, 40 V of direct voltage were applied between the electrodes to generate copper complex ions through a complexing action of copper cations with carboxyl and amine functional groups. The copper concentration of the ink was 15 wt%, which was calculated based on the weight loss of the copper. The inkjet printing of the ink was performed using a multi-nozzle piezoelectric inkjet printer (Dimatix, Fujifilm, Japan; nozzle diameter of 50 μm) on PET substrates. Before ink-jet printing, the PET film was treated with oxygen plasma for 3 s using plasma surface modification equipment (ICP-PIE, SNTEK, Korea) to control the inkjet-printed pattern shape by introducing hydrophilic groups on the PET surface.

The chemical conversion of the as-prepared patterns into zerovalent-copper patterns was achieved by hydrazine vapor during post-processing. Fig. 1 shows the system configuration for the chemical conversion treatment. It consists of two chambers. The first one is used to generate a hydrazine vapor and the other one is used for the chemical conversion of inkjet-printed copper complex ion patterns with the vapor. A hydrazine monohydrate solution (64–65% N_2H_4 in H_2O, Sigma-Aldrich) was injected into the first chamber. Hydrazine is highly toxic and dangerously unstable unless handled in solution, so it is important to keep the hydrazine to liquid state outside the reaction chamber. It was vaporized by heating the chamber to 80 °C. The vapor moved into the reaction chamber with the inkjet-printed copper complex ion pattern and a chemical conversion was conducted. The temperature of the chamber was varied from 100 °C to 175 °C and the reaction was carried out for 60 s. After the reaction has finished, the residual hydrazine vapor is expired from the reaction chamber to a liquefier which is full of water by an aspirator to transform the hydrazine vapor to the liquid state. The fabricated copper patterns were characterized using an X-ray diffractometer (XRD; Ultima IV CuKα, Rigaku, Japan), field emission scanning electron microscope (FE-SEM; S-4800, Hitachi, Japan) and focus ion beam equipped SEM (FIB; LYRA1, Tescan, Czech Republic). The sheet resistance was measured by a four-point probe (CMT-SR2000N, AIT, Korea) and the resistivity of the patterns was calculated from the sheet resistance and the pattern thickness.

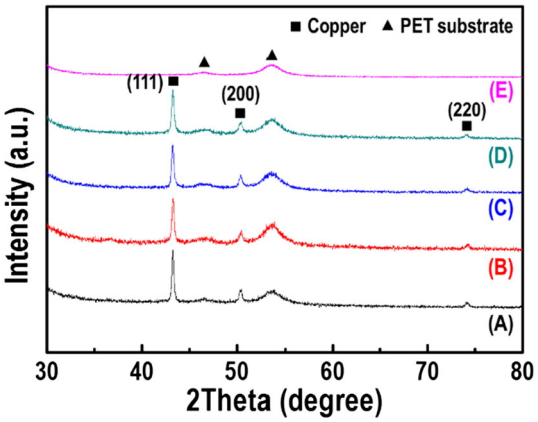

Fig. 2. X-ray diffraction patterns of ink-jet printed Cu patterns treated for 1 min in hydrazine vapor at (A) 100 °C, (B) 125 °C, (C) 150 °C and (D) 175 °C. (E) is the diffraction pattern of the bare PET substrate.

3. Results and discussion

Fig. 2(A–D) show the X-ray diffraction patterns of the ink-jet patterns printed using copper complex ion inks and thermally treated at different temperatures for 1 min in hydrazine vapor. All samples have three diffraction peaks at 43.3°, 50.4° and 74.1° which can be indexed to the (111), (200) and (220) faces of face-centered cubic copper structures, respectively, as shown in the Joint Committee on Powder Diffraction Standards (JCPDS) file for pure copper products (JCPDS File Card No. 04-0836). Two other peaks at 46.5° and 53.9° correspond with the

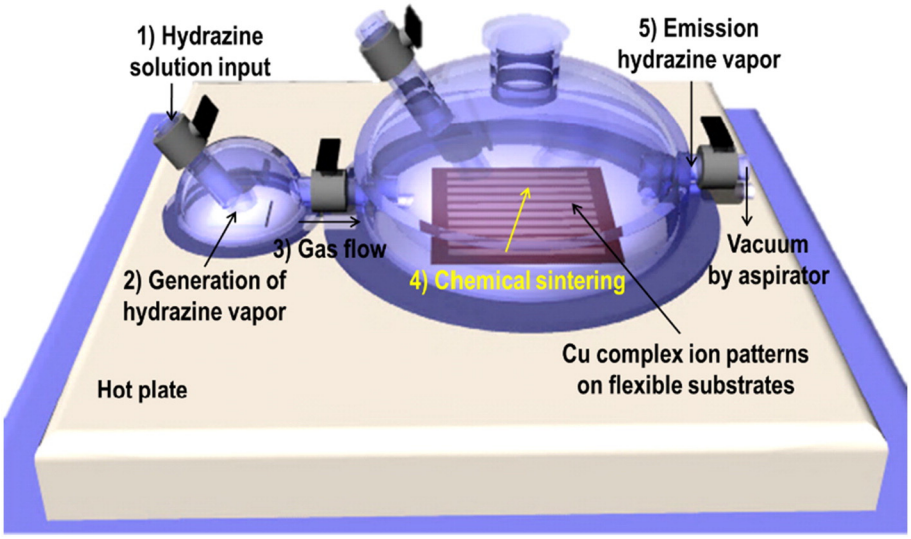

Fig. 1. An illustration showing a system configuration for a chemical conversion treatment based on a hydrazine vapor.