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Flash light sintered copper precursor/nanoparticle pattern with high electrical conductivity and low porosity for printed electronics

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ABSTRACT

In this work, the hybrid copper inks with precursor and nanoparticles were fabricated and sintered via flash light irradiation to achieve highly conductive electrode pattern with low porosity. The hybrid copper ink was made of copper nanoparticles and various copper precursors (e.g., copper(II) chloride, copper(II) nitrate trihydrate, copper(II) sulfate pentahydrate and copper(II) trifluoroacetylacetonate). The printed hybrid copper inks were sintered at room temperature and under ambient conditions using an in-house flash light sintering system. The effects of copper precursor weight fraction and the flash light irradiation conditions (light energy and pulse duration) were investigated. Surfaces of the sintered hybrid copper patterns were analyzed using a scanning electron microscope. Also, spectroscopic characterization techniques such as Fourier transform infrared spectroscopy and X-ray diffraction were used to investigate the crystal phases of the flash light sintered copper precursors. High conductivity hybrid copper patterns (27.3 μΩ cm), which is comparable to the resistivity of bulk copper (1.68 μΩ cm) were obtained through flash light sintering at room temperature and under ambient conditions.

1. Introduction

Printed electronics have received attention because they represent a low-cost solution to the production of electronic devices. Printed electronics using metal nano-ink have potential applications in flexible radio frequency identification (RFID) tags, active-matrix LCDs, e-paper, flexible organic light emitting diodes (OLEDs), and wearable electronics [1–11]. Currently, noble metal nanoparticles such as gold and silver are widely employed because of their excellent conductivity, stability and sintering efficiency under conventional process conditions [2,12]. However, the price of these noble metals is too high for mass production. For this reason, copper nanoparticles have received considerable attention due to their lower cost; however, copper nanoparticles can be easily oxidized and cannot be sintered by thermal sintering under ambient conditions. To solve these problems, various sintering methods such as laser irradiation [2], microwave [13] and precursor processes [14–16] were studied by several researchers. These approaches have limitations in mass production because of their low throughput, high complexity, and considerable environmental obstacles (e.g., high temperature or vacuum conditions). In addition, the sintering of copper nanoparticles requires a very sophisticated process that includes an inert or reducing gas (e.g., hydrogen) chamber to prevent copper oxide formation during the sintering process.

For these reasons, we previously developed an intense pulsed light (flash light) sintering method using poly(*N*-vinylpyrrolidone) (PVP) functionalization of copper nanoparticles [8]. The flash light sintering method can sinter faster (a few milliseconds) than any other sintering methods and can simply remove the oxide shells of copper nanoparticles at room temperature and under ambient conditions without damaging the substrate [3–9]. However, in a previous study, the flash light sintered copper patterns using only copper nanoparticles still had high resistivity compared with bulk copper because of high porosity in the sintered copper nanopatterns [15,16].

In this study, to decrease pores between copper nanoparticles, the copper precursor was used with copper nanoparticles simultaneously. The various precursors (e.g., copper(II) chloride, copper(II) nitrate trihydrate, copper(II) sulfate pentahydrate and copper(II) trifluoroacetylacetonate) were used in hybrid copper ink. Several flash light irradiation conditions (irradiation energy and pulse duration) for sintering hybrid copper ink were optimized for high conductivity of the hybrid copper patterns printed on PI substrates. The flash light sintered hybrid copper patterns were characterized using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy

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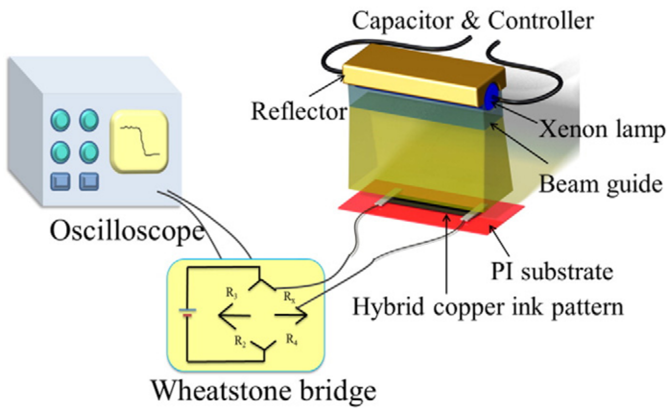

Fig. 1. Schematic diagram of the flash light sintering and in-situ monitoring of the sintering process hybrid copper ink.

(FT-IR) and X-ray diffraction (XRD). Also, the sheet resistance of the hybrid copper patterns was measured by using a four-probe method.

2. Experiment details

2.1. Hybrid copper precursor/nanoparticle ink formulation

For synthesized hybrid copper ink, copper precursors and copper nanoparticles (10–70 nm in diameter, oxide thickness > 2 nm; QSI-Nano Copper) were used in this study. The precursors used were copper(II) chloride ($CuCl_2$, 99.9%; Sigma Aldrich), copper(II) nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%; Sigma Aldrich), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 99.9%; Sigma Aldrich), and copper(II) trifluoroacetylacetonate ($Cu(C_5H_4F_3O_2)_2$, 97%; Sigma Aldrich). For ink formulation, poly(*N*-vinylpyrrolidone) (PVP, MW 40,000; Sigma Aldrich) (0.8 g) was dissolved in diethylene glycol (DEG, 99%; Samchun Chemical) (7.2 g) in an ultra-sonicator for 1 h. Copper precursors (from 1.08 g with 0 wt.% copper nanoparticles to 10.8 g with 100 wt.% copper nanoparticles) were dispersed in a prepared solvent using an ultra-sonicator for 1 h. Copper nanoparticles (10.8 g), diethylene glycol butyl ether (99%; Samchun Chemical) (5 ml), and the complex solvent

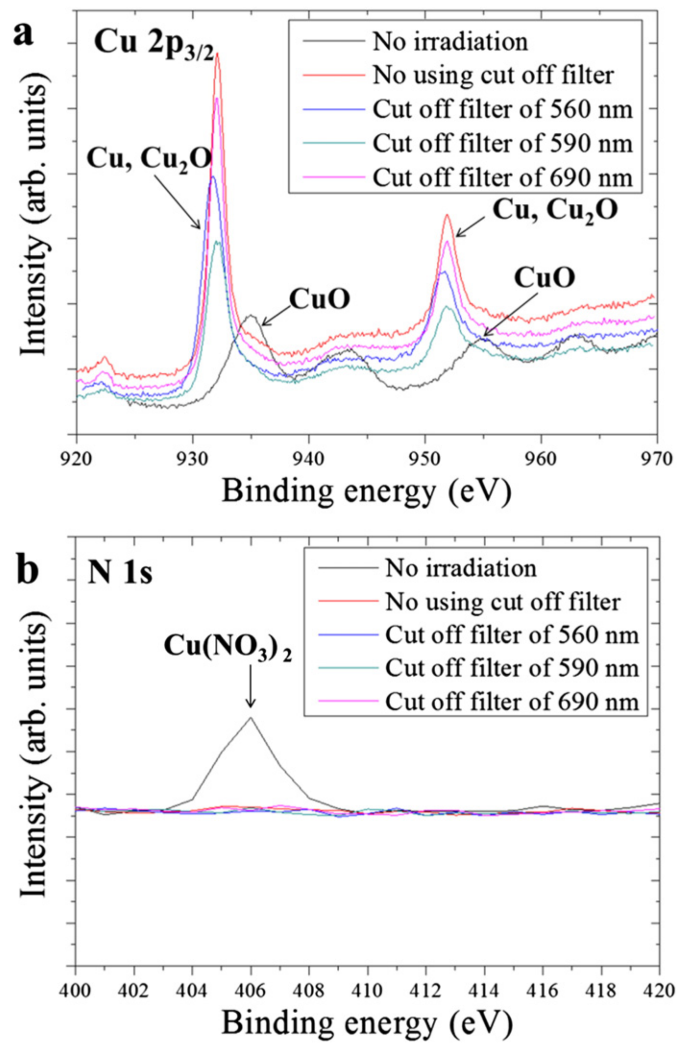

Fig. 3. The XPS spectra of unsintered and sintered hybrid copper films for (a) Cu $2p_{3/2}$ and (b) N 1s.

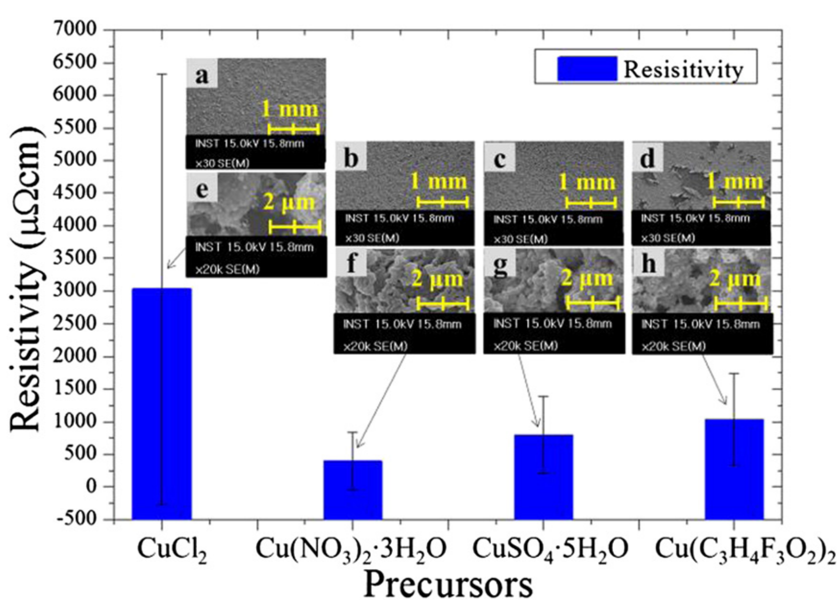

Fig. 2. The resistivity of the flash light sintered hybrid copper patterns (the weight fraction of the copper precursors: 10 wt.%, irradiation energy: 10 J/cm^2, pulse duration: 10 ms, pulse number: 1).