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Electromechanical properties of printed copper ink film using a white flash light annealing process for flexible electronics

Kyoungtae Eun [a], Min-Woo Chon [b], Tae-Hee Yoo [c], Yong-Won Song [c], Sung-Hoon Choa [a,*]

[a] Graduate School of NID Fusion Technology, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea
[b] Department of Mechanics & Design, Kookmin University, Jeongneung-Ro 77, Seongbuk-Gu, Seoul 136-702, Republic of Korea
[c] Future Convergence Research Division, Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea

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ABSTRACT

We report on a systematic study of the electromechanical properties of flexible copper (Cu) thin film for flexible electronics. Cu ink is synthesized with chemical reduction process. Cu ink film spin-coated on a polyimide substrate is annealed with white flash light, also known as intense pulsed light (IPL), which guarantees a room temperature and sub-second process in ambient conditions. IPL annealed Cu film shows the electrical resistivity of 4.8 μΩ cm and thickness of 200 nm. The electromechanical properties of IPL annealed Cu film are investigated via outer/inner bending, stretching, and adhesion tests, and it is compared with conventional electron-beam evaporated Cu film. IPL annealed Cu film shows a constant electrical resistance within a bending radius of 6 mm. The bending fatigue test shows that the Cu film can withstand 10,000 bending cycles. In the stretching test, the Cu film shows a 50% increase in resistance when a strain of 2.4% was induced. At 4% strain, the resistance increases more than 200%. Meanwhile, the electron-beam evaporated film shows a constant resistance up to a strain of 4%. Lower stretchability of IPL annealed Cu film is attributed to its inherent cracks and porous film morphologies. IPL annealing induces the local melting at the interface between the substrate and Cu film, which increases the adhesion strength of the Cu film. These results provide useful information regarding the mechanical flexibility and durability of the nanoparticle films for the development of flexible electronics.

1. Introduction

Recently, a variety of printing technologies, including ink jet [1], offset [2], gravure [3], and roll-to-roll [4] printing, has generated intensive interest in the application of flexible electronic devices, such as solar cells, displays, thin-film transistors, and printed circuit boards [5–7]. Flexible electronics will be evolved into stretchable and wearable electronics using printing technologies in the near future. Printing technologies inevitably require a selection of proper inks. Gold (Au) or silver (Ag) nanoparticles (NPs) or inks are widely used for fabricating the conducting lines or electrodes due to high conductivity and efficient annealing processing [8,9]. However, Au and Ag are noble metals, which are too expensive to be used in large quantity. In order to resolve this disadvantage, copper (Cu) is an alternative, as it is much cheaper but exhibits fairly high conductivity. Much research has focused on the development of the Cu inks that mainly consist of Cu NPs [10,11]. Various methods have been utilized to synthesize Cu nanoparticles for printing technologies including thermal reduction, chemical reduction, modified electrolysis, and electrodeposition method [12–15]. The formation of Cu NPs in non-aqueous environment using poly(vinyl pyrrolidone) (PVP) polymer as a capping agent has also been suggested [16]. However, a fundamental problem with Cu ink is its high susceptibility to oxidation in air. The Cu inks are typically synthesized using a suspension of Cu NPs, which are easily oxidized in air. The presence of Cu oxides drastically deteriorates the conductivity and increases the annealing temperature [12]. Recently, atmospherically stable and large-scale synthesizable Cu inks, based on organometallic precursors, have been reported [13,14]. Copper complex inks using electrolysis have also been demonstrated [15]. However, electrolysis is a complicated process that is limited in terms of the ion concentration adjustment; the resulting pattern thickness is very thin after drying and calcination. In a previous study, therefore, we had developed Cu ion ink with a chemical reduction using additives rather than an electrolysis method [17]. Developed Cu ion ink did not require dispersion stability, so it could be fabricated at low temperatures.

The actual use of printing technique is, however, much limited because the annealing process step remains as a huge practical

* Corresponding author.
E-mail address: shchoa@seoultech.ac.kr (S.-H. Choa).

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drawback. In the fabrication of the electrode layers, a post-annealing process is required to achieve high conductivity of the printed Cu film. However, the presence of Cu oxides results in an increase in the annealing temperature and leads to cracks on the surface of the annealed Cu film [18]. The conventional thermal annealing process using a furnace takes considerable annealing times, and requires high temperatures (150–350 °C). For application to flexible devices, the annealing temperature should be as low as possible to minimize the damage of flexible polymer substrate. Additionally, the thermal annealing process is a batch process, and it is difficult to implement in roll-to-roll processes. Thus, a high-speed and atmospheric annealing method for Cu inks printed on flexible substrates that guarantees minimal oxidation is in high demand. Recently several alternative methods for an annealing technique were suggested, such as laser [19,20], halogen lamp [21], infrared [22], plasma [23], ohmic [24], and microwave annealing [25]. Since these techniques are less practical for the fast and large-area annealing of metal NPs, the intense pulsed light (IPL) process using a xenon lamp was recently demonstrated as an alternative annealing process [26,27]. IPL annealing has various advantages, such as high speed annealing within few seconds, reduction of the CuO by reaction with a polymer material, and lowering the damage of flexible substrates in room temperature processes under ambient conditions.

Despite the successful demonstration of several inks and annealing methods, research on the flexibility and electromechanical properties of Cu ink film on flexible substrates is still lacking. Previous studies regarding Cu inks primarily focused on the influence of processing parameters on the microstructure and resistivity of NP inks [28,29]. Flexible electronic devices will be subjected to various mechanical deformations, such as bending, compression, and stretching, depending on their application and fabrication processes. Now it is a primary concern whether printed ink film will maintain good performances under these severe deformations. Therefore, a more detailed understanding of the deformation durability of the metal ink films under various types of mechanical deformation is important for commercialization and mass production. In particular, a comparison with metal thin films fabricated with conventional vacuum deposition processes should provide important information for the printed electronic industries. Kim et al. [30] conducted tensile tests, and found that thermal annealed Ag NP film has lower failure strain than those of e-beam film due to highly porous film morphologies. Wu et al. [31] investigated the characteristics of thick Cu-plated patterns on polyimide substrate. To the best of our knowledge, the flexibility and the electromechanical properties of Cu ink film on a flexible substrate after IPL annealing have not yet been studied in detail.

To address these issues, we synthesized Cu ion ink using a simple chemical reduction process without any Cu nanoparticles. IPL was used to anneal Cu ink films on polyimide (PI) substrate instantaneously for calcination under room temperature conditions. Then we investigated the electromechanical properties of Cu films annealed with IPL via outer/inner bending, cyclic bending fatigue, and stretching tests. The adhesion strength of the Cu films on the PI substrate was evaluated by a peel-off test and a nano-scratch test, respectively. The electromechanical properties of Cu film annealed with IPL were compared with Cu film fabricated with an electron beam (e-beam) evaporation method.

2. Experimental methods

We fabricated copper ion inks using chemical reduction method. To synthesize copper ion inks, all reagents were purchased from commercial suppliers and used without further purification. Copper ion inks were formulated with copper (II) hydroxide [($Cu(OH)_2$), Sigma–Aldrich] as a metal precursor. Ammonium hydroxide (NH_4OH, Sigma–Aldrich) and deionized water were used as a complexing agent and solvent, respectively. To increase Cu ion solubility, the formic acid (HCOOH, 99.5% purity; Sigma–Aldrich) and citric acid ($C_6H_8O_7$, 99.5% purity; Yakuri Chemical) were added as a complexing agent for Cu ion reduction and stabilization. The fabricated Cu ion ink has pH 8. Finally, in order to achieve a proper level of viscosity and surface tension, 2-methoxyethanol ($CH_3OCH_2CH_2OH$, 99.8% purity; Sigma–Aldrich) and ethylene glycol ($HO(CH_2)_2OH$, 99.5% purity; Junsei Chemical) were mixed at a ratio of 9:1, after which poly (N-vinylpyrrolidone) (M_W = 4000 g mol^{-1}; Sigma–Aldrich) was added to fabricate the final Cu ion ink. The chemical reaction process for fabrication of the Cu film can be understood as follows:

$$Cu(OH)_2 + 4NH_4OH \rightarrow [Cu(NH_3)_4](OH)_2 + 4H_2O \quad (1)$$

$$3[Cu(NH_3)_4](OH)_2 + C_6H_8O_7 \rightarrow Cu + Cu_2O + 12NH_3 + 6CO + 6H_2O + H_2 \quad (2)$$

$$Cu_2O + HCOOH \rightarrow 2Cu + H_2O + CO_2 \quad (3)$$

To fabricate the Cu ion ink, copper (II) hydroxide and ammonium hydroxide (NH_4OH) were mixed (1). Then, we added the citric acid ($C_6H_8O_7$) in mixed solution for Cu reduction (2). At this time, the copper oxide (Cu_2O) is also reduced. Thus, we added the formic acid (HCOOH) to fabricate only copper (3). The chemical reaction needs energy to form Cu (3). In this study, IPL was used to induce the intense pulsed energy to form the Cu film. The more detailed fabrication procedures are explained in Ref. [18]. PI substrate (Isoflex Co.) with a thickness of 200 μm was used as the substrate material. PI was ultrasonicated in deionized water for 10 min to remove surface contamination. Then the prepared Cu ion inks were spin-coated onto a PI substrate at 2000 rpm for 20 s under ambient condition. The prepared Cu ink films were irradiated by the pulsed xenon flash light.

The lab-made IPL system was composed by a xenon flash lamp (Excelitas Technologies, L6755), power supply, capacitors, pulse controller, and a water cooling system. The lamp produces instant white light with a continuous light spectrum for a wide range of wavelengths from 200 nm to 2 μm. Once the Cu ink films were placed underneath the flash lamp at a distance of 3 mm, high-intensity lights were emitted onto them with the projection area of 150×10 mm^2. The light intensity of the IPL system can be adjusted by controlling the applied voltage ranging from 1 to 430 V. Additionally, number of pulses, pulse duration and time interval between each pulse were controlled, respectively. The conversion efficiency of a xenon flash lamp from electrical input power into radiated optical power is approximately 50% in the spectrum between 200 and 1100 nm [32]. Our IPL system was designed to provide up to 99 shots within the millisecond scale with a minimum pulse interval of 2 ms. Based on the preliminary experiments, the IPL annealing conditions were optimized. In this study, we applied 70 rectangular pulses with a 30 ms gap between pulses. The applied voltage to the xenon flash lamp was 310 V. The energy of one pulse was measured for 0.77 J/cm^2 and the total energy of irradiated pulses was 70 ± 5 J/cm^2. Total process time is just 2170 ms. An average thickness of Cu films after IPL annealing was ~200 nm. For the comparison with the Cu ink film, the Cu films of 200 nm thickness deposited on a PI substrate by e-beam evaporator (MEP 5000; SNTEC) were separately prepared.

Fig. 1 shows the schematic drawing, and the optical microscope (OM) images of the IPL annealed Cu film and the e-beam evaporated Cu film, respectively. The resistance of the films was measured using a digital multimeter (34401A; Agilent), and the four-point probe method was also used to cross-check the resistivity