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Cu-based composite inks of a self-reductive Cu complex with Cu flakes for the production of conductive Cu films on cellulose paper

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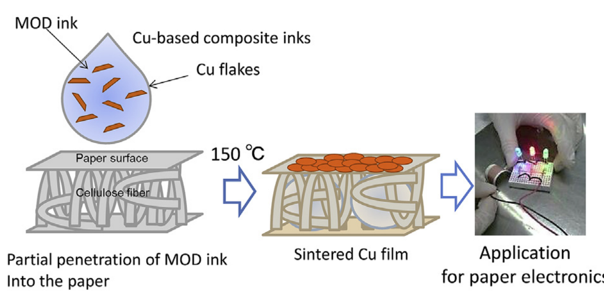
HIGHLIGHTS

- Cu-based composite inks of self-reductive Cu complex with Cu flakes were prepared.
- Cu film resistivity on paper was ~10 times lower than that on polyimide or glass.
- Higher bending stability of Cu film on paper than that on polyimide.

GRAPHICAL ABSTRACT



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ABSTRACT

Paper-based electronics have been attracting significant attention because of their inexpensive, renewable, and eco-friendly substrates. In this study, Cu-based composite inks composed of a copper-based metal-organic decomposition (MOD) ink and Cu flakes were prepared as precursors to obtain conductive Cu films on untreated cellulose paper. Copper-based MOD inks have not been explored for the production of conductive Cu films on cellulose paper because the properties of the paper, such as high porosity, high permeability, and surface roughness, are not favorable to obtain continuous conductive Cu films. However, using our method, we have obtained Cu films on paper with resistivities that are ~10 times lower than those of films on polyimide or glass substrates. Importantly, the Cu films on paper exhibited better mechanical resistance than those on a polyimide substrate, without any pre-treatment of the paper surface.

1. Introduction

Paper-based electronics have been drawing intense attention because of their inexpensive, renewable, and eco-friendly substrates [1,2]. Using attractive characteristics of the cellulose paper, such as chemical stability, mechanical strength, biodegradability, functionality, and permeability, a variety of paper-based flexible devices has been proposed [1,2]. Several methods have been demonstrated to produce highly conductive metallic tracks (or films) on paper, such as metal sputtering [3], direct-writing of conductive inks [4–6], printing of liquid metal [7,8], and printing of conductive inks (*e.g.*, metal nanoparticles and metal nanowires) [9–15]. A high electrical conductivity, good adhesion of the metallic film to the paper substrate, and good bending stability are desirable to produce flexible, paper-based electronics. Papers are complex porous materials with non-uniform physical and chemical properties. Therefore, untreated paper is not considered as a suitable

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substrate for printed electronics. Various coating materials such as wax, organic/inorganic polymers, and ceramics have been utilized to modify the surface properties of paper, such as wettability, roughness, and functionality [12,13,16].

Metal-based inks offer a viable route to fabricate continuous metal films, with high conductivities after heat treatment. Silver nanoparticle-based inks, including Ag nanoparticles and Ag nanowires, are common choices as metal-based inks because of their high conductivities and good stabilities under ambient conditions [9–11,13–15]. However, the high cost of silver is a deterrent for cost-sensitive applications. Copper nanoparticle-based inks are potentially more cost-effective, but a major challenge in using copper-based inks is their propensity to undergo oxidation in air, during storage and sintering [12,17–23]. Copper-based metal-organic decomposition (MOD) inks enable us to overcome the problem of copper oxidation, because the metal is already present in its oxidized form (*i.e.,* Cu(II)) [24–30]. Some recent studies have demonstrated that composite MOD inks made of micron-sized Cu particles and self-reductive Cu complex can produce highly conductive Cu films on smooth plastic substrates at temperatures lower than 150 °C [31–34]. However, there are no reports on the application of composite MOD inks on paper substrates. Although MOD inks have been investigated for printed electronics for years, to date, they have not been explored for the production of conductive Cu films on cellulose paper. This is probably due to the high porosity, high permeability, and surface roughness of paper, which limit the formation of continuous Cu films on paper, in contrast with smooth plastic substrates (*e.g.,* polyethylene terephthalate (PET) and polyimide (PI)). The MOD ink is a particle-free solution, so it tends to penetrate paper due to capillary action. In addition, it is partially segmented, which is unfavorable to build continuous Cu films with a stable connectivity on paper. Only cellulose nanopapers composed of densely packed 15–60 nm wide cellulose nanofibers have been reported to be suitable for the fabrication of conductive silver films from a particle-free MOD ink, because of their nano-sized pores [10].

In this study, we have developed composite MOD inks of micron-sized Cu flakes and a self-reductive Cu complex as precursors to produce conductive Cu films on commercial cellulose paper substrates at low temperature, without the need for chemical pre-treatment or post-treatment of the paper. The resistivities of obtained Cu films on paper were approximately 10 times lower than those of films on PI or glass substrates. Importantly, the Cu films on paper exhibited better mechanical resistance than those on PI substrates, without any pre-treatment of the paper surface. Finally, the reason for the superior properties of Cu films on paper from composite MOD inks is discussed in terms of the different MOD ink properties.

2. Experimental

2.1. Chemicals and materials

Polyimide (PI) substrate with a thickness of 77 μm (DU PONT-TORAY CO., LTD., Japan), glass slide (MICRO SLIDE 1102, Az-one, Japan), and commercial filter paper (Whatman™ 1450–125 Hardened Low Ash Grade 50 Quantitative Filter Paper with average pore size: 2.7 μm) were used as substrates for the Cu films. All the chemicals were used as received without further purification. 1-amino-2-propanol (AmIP, 98%), ethylene glycol (99.5%), glycerol (97%), and methanol (99.5%) were purchased from Wako Chemicals, Japan. Micron-sized Cu flakes (MA-C025-KP) with sizes of 1–2 μm were purchased from Mitsui Mining & Smelting Co. Ltd., Japan.

2.2. Preparation of copper inks

A Cu(II)-AmIP complex was prepared by mixing Cu(II) acetate (3 g) and AmIP (2.6 mL) in methanol (7 mL) [33]. The resulting solution was stirred magnetically for 2 h. Free acetic acid and residual methanol were removed in vacuum for 1 h at 50 °C and then for 24 h at room temperature (~23 °C), to obtain a solid complex. A composite MOD ink was prepared by grinding the solid complex with a given amount of copper flakes and ink solvent (mixture of 30 μL ethylene glycol, 30 μL glycerol, and 150 μL AmIP) in a mortar under air, until the mixture turned into a paste. The composite MOD inks were prepared with different weight ratios of the Cu flakes to the Cu(II)-AmIP complex: 5:1 (0.33 g: 0.07 g), 4:1 (0.32 g: 0.08 g), 3:1 (0.30 g: 0.10 g), 2:1 (0.27 g: 0.13 g), 1:1 (0.20 g: 0.20 g), and 1:2 (0.13 g: 0.27 g). Before mixing, the copper flakes were immersed in *N,N*-diethylhydroxylamine to remove the surface copper oxide layers of copper flakes, and washed with AmIP to obtain AmIP-protected Cu flakes.

2.3. Characterization methods

The composite MOD ink was deposited into wiring gutters on PI, glass, or paper substrates using a doctor blade method. The resulting Cu films were then annealed at various temperatures for 60 min in an electric furnace (FT-6000, FuLL-TECH, Osaka, Japan) under a N_2 gas flow at 1.1 L/min. The thickness of each Cu film after annealing was determined using a digital micrometer (MDH-25M, Mitutoyo Co., Japan). The electrical resistivity of each Cu film after sintering was determined from its thickness and the measured sheet resistance values, by using a four-point probe instrument (Loresta AX MCP-T370, Mitsubishi Chemical Analytech Co., Japan). Field-emission scanning electron microscopy (FE-SEM; JSM-6700, JEOL, Japan) images were collected at an acceleration voltage of 5.0 kV. X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (D2 Phaser, Bruker, Germany) with a Cu-K_α radiation source (λ = 1.5406 Å). Thermo-gravimetric analysis (TGA) was performed using a TG analyzer (Thermo plus EVO, Rigaku, Japan) at a heating rate of 10 °C/min under a nitrogen flow. Atomic force microscopy (AFM) images of paper, PI, and glass substrates were obtained using an SPA-400 (Seiko, Japan) multiple function unit together with an SPI-3800N control station, in tapping mode in air.

2.4. Bending test

Bending tests on the sintered Cu films were conducted under repeated tensile and compressive loading on a custom-made bending tester. The bending tester consisted of a gripping part to hold the Cu films on the substrates in position and a moving part to bend the Cu films using an electronic motor. The bending tests were conducted at a frequency of 1 Hz, and a four-point probe was used to measure the changes in sheet resistance after 1000 cycles.

3. Results and discussion

3.1. Cu films on glass substrate

In a previous study, we reported on the use of composite MOD inks consisting of a formate-free Cu(II)-AmIP complex and micron-sized spherical Cu particles for the fabrication of conductive copper films on PI substrates [33]. Here, we use Cu flakes in the composite MOD inks in place of spherical Cu particles to increase the packing density of Cu on the paper surface and to enable a good metallic contact. The mixing ratio of the Cu(II)-AmIP complex and Cu flakes in the composite MOD ink was optimized to produce the lowest