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Porosity reduction in inkjet-printed copper film by progressive sintering on nanoparticles

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ABSTRACT

This work demonstrates a progressive three-step sintering for inkjet-printed copper (Cu) nanoparticles. For the inkjet-printed Cu thin films, the proposed processes of sequential low-pressure drying, near-infrared sintering, and intense pulsed light (IPL) reduction ensure high nanoparticle compactness, complete Cu sintering, and low oxygen content, respectively. Experiments showed that the highest Cu conductivity resulted from a combination of 65.7% improvement on surface roughness, 37.3% porosity reduction, and 91.7% oxygen elimination provided by the proposed method. Enhanced adhesion between the Cu and the substrate confirmed by mechanical examinations indicated other benefits of this progressive sintering. In addition, the cracks that resulted from different thermal expansions in the Cu thin film and the substrate during IPL reduction were quantified, and the results explained the degraded electrical performance of the Cu thin films that had been processed beyond the optimal condition.

1. Introduction

Inkjet printing for flexible and organic electronic devices has been widely proposed and demonstrated for its high production efficiency, operational simplicity, low material waste, and high compatibility with roll-to-roll and continuous manufacturing systems. Inkjet printing methods have been developed for inks based on metals such as silver (Ag), gold (Au), and copper (Cu) to support circuit patterning. Although inks based on other metals, such as nickel [1], iron [2], and aluminum [3] have been also proposed as alternatives and are available on the market, only Ag [4–6] and Au [7–9] are practical for electrical connections because of their stability during preservation and manufacturing. Because Ag and Au are precious metals, they are too costly for mass production, and inexpensive Cu is always expected to replace Ag and Au, not only in printed circuits, but also in conventional electronics.

Although cost reduction is highly desirable, typical Cu nanoparticles are not suitable for inkjet printing because Cu nanoparticles react more easily with oxygen than bulk Cu, forming insulative Cu oxide (Cu-O). To alleviate this, inks with Cu nanoparticles usually contain crucial functional chemicals that prevent intensive Cu oxidation. Consequently, consecutive sintering after inkjet printing must remove these functional chemicals and also connect the Cu nanoparticles to form a continuous thin film. In practice, heat [10], microwave [11–12], plasma [13] near-infrared (NIR) [14], electric current [15], and laser [16] sintering methods have been proposed for various nanoparticles but all of them are conducted in ambient air at atmospheric pressure; these methods are not desirable because they tend to leave potentially resistive Cu-O in the Cu thin films.

Intense pulsed light (IPL) [17–20] has been proposed for low-temperature and short-duration Cu sintering, but incomplete IPL sintering often produces cracks and delaminations in Cu thin films that limit maximal achievable conductivity [19–21]. The cracks and delaminations occur at points on the solidified Cu surfaces where the remaining solvents cannot evaporate. Even though the cracks and delaminations may be alleviated by series of multiple IPL exposures [21], in which small amounts of IPL energy are applied for preheating before more IPL energy is applied for sintering, the relationship between IPL intensity and the requirement for preheating or sintering in various Cu inks is unclear. IPL-only sintering inevitably limits the applications of Cu nanoparticles if the contributions of IPL to preheating, sintering, and reduction are not quantified.

Low resistivity can reportedly be achieved if the porosity of the Cu thin film is suppressed below 15% [22], and studies have implied that Cu resistivity involves bulk resistivity and nanoparticle porosity [22–23]. However, these studies did not consider oxygen content and cracks in thin films; the conclusions were only applicable to oxygen- and crack-free conditions. To clarify the aforementioned ambiguities, we separated the process of Cu nanoparticle sintering into three phases. Although numerous studies have used IPL for all phases, the present study uses a sequential three-step procedure of ink drying, nanoparticle

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sintering, and Cu-O reduction by low-pressure ambient air, NIR exposure, and IPL exposure, respectively. During the three steps of the proposed sintering procedure, the roles of oxygen and cracks in the Cu thin film were examined in detail.

2. Experimental

2.1. Sample preparation

Cu nanoparticles (Intrinsiq Materials, CI-003) together with polyvinylpyrrolidone-, polyvinyl alcohol-, and polyethylene glycol-based protection and surfactant in the formulation (viscosity of 12–14 cP, metal loading of 20%, average particle size of 70 nm, and surface tension of 30–32 dyne/cm) were inkjet printed (FujiFilm, Dimatix DMP-2831) on a 75 μm-thick polyimide (PI; UBE America Inc., UPILEX-75S) substrate at 25 °C in atmospheric air under 101 kPa. The contact angle of the Cu ink on the PI was 38° and a single drop (10 pl) was measured to have a diameter of 43 μm on the PI. To measure electrical conductivity, multiple drops were printed with a drop space (the distance between the centers of two consecutive drops) of 25 μm to generate overlaps between individual drops. In addition to the drop space, the piezoelectric voltage, nozzle temperature, substrate temperature, distance between the nozzle and the substrate was set to 25 V, 28 °C, 28 °C, and 500 μm, respectively.

2.2. Low-pressure drying

Because the continuity between and the density of the nanoparticles seriously influence the electrical performance of Cu, the inkjet-printed sample was put in a customized low-pressure chamber for drying at 25 °C for 6.5 min to increase the compactness of the Cu nanoparticles. Although the drying process took 6.5 min to reach 10 kPa in this work, it was limited by the current facility. An efficient drying system, such as a connection of a vacuum chamber and a two-stage pump, would facilitate the drying procedure.

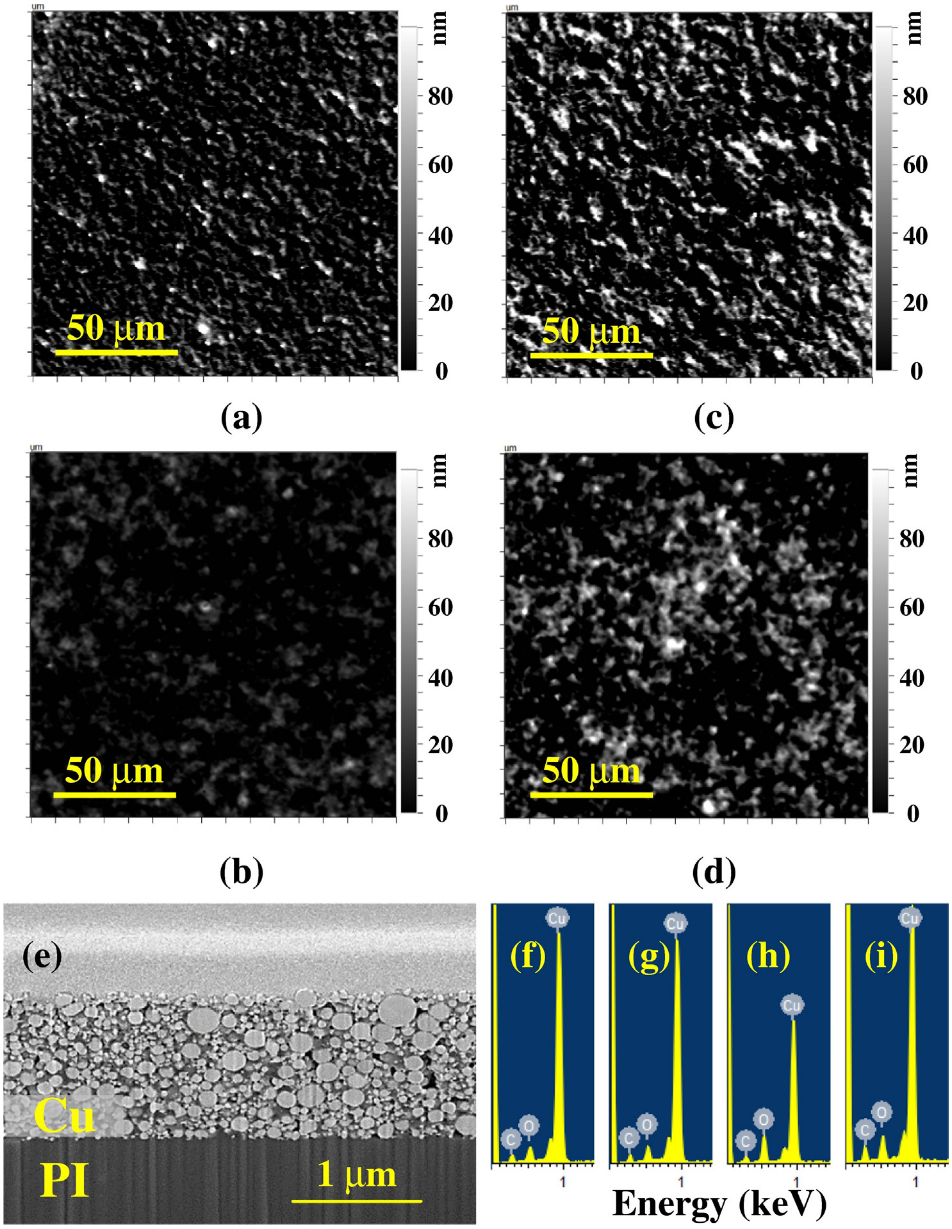

Fig. 1. Surface profilometry images for samples dried at 25 °C under (a) 101 kPa and (b) 10 kPa, and at 50 °C under (c) 101 kPa and (d) 10 kPa, (e) Cross-section SEM image of as-dried inkjet-printed Cu thin film on PI with 38.3% porosity and EDS spectra (f, g, h, i) of samples dried conditions used in (a), (b), (c), and (d), respectively.