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Two-step flash light sintering of copper nanoparticle ink to remove substrate warping

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ABSTRACT

A two-step flash light sintering process was devised to reduce the warping of polymer substrates during the sintering of copper nanoparticle ink. To determine the optimum sintering conditions of the copper nanoparticle ink, the flash light irradiation conditions (pulse power, pulse number, on-time, and off-time) were varied and optimized. In order to monitor the flash light sintering process, in situ resistance and temperature monitoring of copper nanoink were conducted during the flash light sintering process. Also, a transient heat transfer analysis was performed by using the finite-element program ABAQUS to predict the temperature changes of copper nanoink and polymer substrate. The microstructures of the sintered copper nanoink films were analyzed by scanning electron microscopy. Additionally, an X-ray diffraction and Fourier transform infrared spectroscopy were used to characterize the crystal phase change of the sintered copper nanoparticles. The resulting two-step flash light sintered copper nanoink films exhibited a low resistivity (3.81 $\mu\Omega$ cm, 2.3 times of that of bulk copper) and 5B level of adhesion strength without warping of the polymer substrate.

1. Introduction

Recently, the flexible printed circuit board (FPCB) market has expanded as the use of smart devices, such as smart phones and tablet PCs, have gradually increased. FPCBs have been fabricated by photolithography processes. However, conventional photolithography has a high cost and is a time-consuming process because it has several process steps, such as exposure, developing, and etching [1]. For these reasons, the printing of electronics, which is a convenient and low-cost process, has been adopted as an advanced alternative [2–5].

Printed electronics on polymer substrates have various applications such as flexible displays, flexible solar cells, wearable electronics, organic light emitting diodes, radio frequency identification tags, and flexible touch pads [6–9]. The key component of printed electronics is the fabrication of conductive circuits. For conductive circuits, metal nanoparticle pastes, such as silver and gold, have been used because of their low melting point and oxidation stabilities [10–12]. However, silver and gold are too expensive for commercialization. For this reason, copper nanopastes have been developed as an alternative to silver and gold. However, most copper nanoparticles are easily oxidized or already covered with oxide shells [13]. Therefore, the flash light sintering process combined with poly(*N*-vinylpyrrolidone) (PVP) functionalization of copper nanoparticles was proposed to overcome this problem [14–17]. The flash light sintering method can immediately remove the oxide shells of copper nanoparticles and form pure copper films at room temperature in ambient conditions [16]. In our previous papers, we optimized the one-step flash light irradiation condition for sintering copper nanopastes on a polyimide (PI) substrate with a 225 μm thickness [14]. In the previous work, the copper nanopastes were fully sintered without any damage to the PI substrates. However, for thinner substrates, the flexible substrates were bent and easily damaged during the flash light sintering. These phenomena have been considered a critical problem to the reliability and productivity of electronic devices.

Therefore, in this study, a two-step flash light sintering method was employed to reduce substrate warping and enhance the electrical conductivity compared to the conventional one-step flash light sintering method (Fig. 1). In order to monitor the real time sintering process, in situ monitoring of the resistance and temperature of copper nanoink were performed using a Wheatstone bridge circuit and thermocouple based circuit, respectively. A heat transient transfer analysis was conducted by using ABAQUS to calculate temperature field of copper nanoink film and PI substrate during one-

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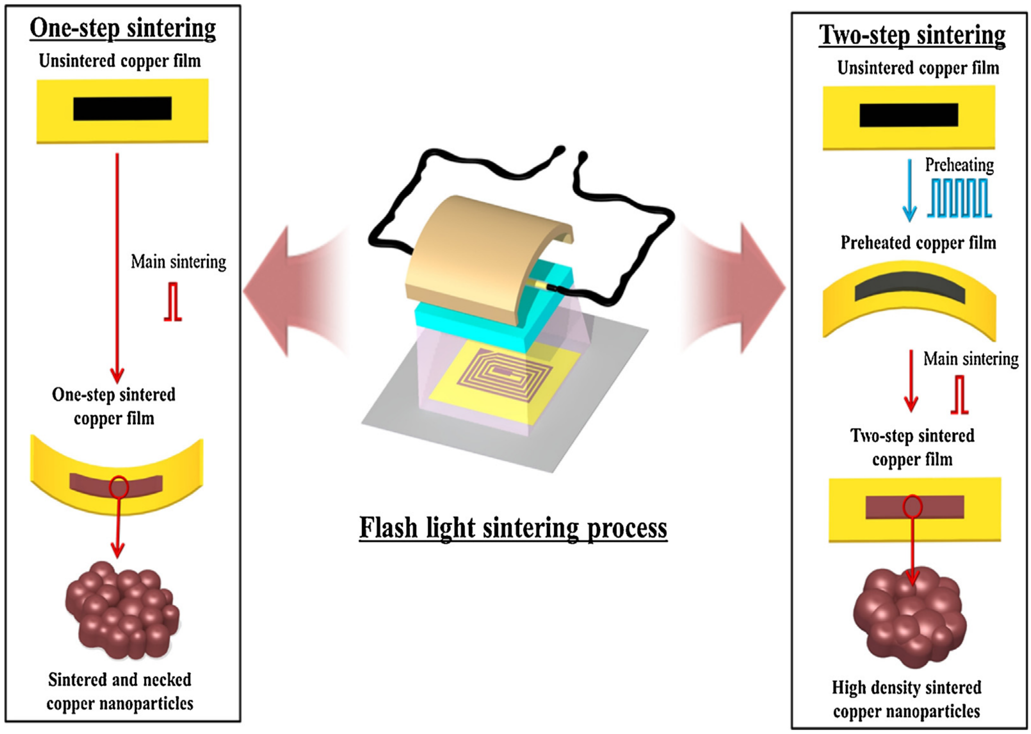

Fig. 1. Schematic diagram of one- and two-step flash light sintering processes.

and two-step flash light sintering processes. The sintered copper nanoink films were characterized using several microscopic and spectroscopic techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR).

2. Material and methods

2.1. Specimen preparation

To prepare the conductive copper nanoink films, copper nanoparticles with oxide shells (mean particle size: 40 nm, oxide shell thickness >2 nm, Quantum Sphere Inc.) were used [17]. First, 0.9 g of PVP (MW 55,000, Sigma Aldrich Co.) was dissolved in 3.0 g of diethylene glycol (DEG, Sigma Aldrich Co.). After that, 11.4 g of copper nanoparticles were dispersed in this mixed solvent with 3-roll milling for 30 min. The fabricated copper nanoinks (solid contents: 80%) were printed on PI substrates (PI, SKC KOLON) with a 50 μm thickness using a screen printer (Tiger SP2825-MT, Daeyoung High Tech Co., printing speed: 100 mm/s). The printed copper nanoink films were then dried using near infrared (NIR, wavelength range: 800–1500 nm, 500 W; Adphos L40) for 10 min at 100 °C.

2.2. Two-step flash light sintering

Flash light irradiation was used for the sintering of the printed copper nanoink films. This process was performed at room temperature in ambient conditions. The flash light sintering system is composed of a xenon lamp (PerkinElmer Co.), a simmer triggering pulse controller, a power supply, capacitors, and a water cooling system [14,15]. In this system, the xenon lamp generated white light over a wide range of wavelengths (from 380 to 950 nm). In this study, the flash light was applied at two steps; preheating sintering and main sintering. The preheating step was performed to reduce the substrate warping and decompose some of the organic binder in the copper nanoink films. In the preheating step, the flash light irradiation energy was varied from 6 to 12 J/cm^2, while the other flash light irradiation conditions, including the number of pulses (35), on-time (1 ms), and off-time (30 ms), were fixed. After the preheating step, the main sintering step was performed to sinter the copper nanoink films. The flash light irradiation energy was varied from 3 to 9 J/cm^2 with 3 ms on-time and single pulses. The energy of the irradiated flash light was measured by a power meter (Nove II, People Laser Tech.).

Table 1
Material constants of copper, PI, and aluminum.

	Copper	PI	Aluminum
Thermal conductivity (k, W/m °C)	401	0.52	170
Specific gravity (ρ, J/kg °C)	8940	1430	2700
Specific heat capacity (C_p, J/kg °C)	384.6	1150	950
Melting temperature (T_m, °C)	250[a]	–	–
Latent heat of fusion (H, J/kg)	2.05×10^5	–	–

[a] Mean-size of copper nanoparticles: 40 nm.

2.3. Transient heat transfer analysis

The commercial finite element software package ABAQUS 6.12 (Hibbitt, Karlsson and Sorensen, USA) was employed to perform transient heat transfer analysis about copper nanoink film and PI substrate. Fig. 2 shows the finite element model and mesh structure, the x- and y-dimensions are each 1 cm, and the thickness of each component (copper, PI film, and aluminum plate) is based on the real-size of specimen (Table 1). In this model, the 10 μm thick of copper nanoink film was positioned on the 50 μm thick of PI substrate. Also, aluminum plate which has 5 mm thickness was placed as floor beneath of the PI film. This model neglected the effect of PVP due to small amount and minimal influence of it [18]. The interfaces between each layer were perfectly attached by using the *TIE function in ABAQUS. The initial temperature of model is regarded as room temperature, 20 °C. In order to simulate the flash light irradiation, it is assumed that the irradiation energy is converted into