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# Temperature changes of copper nanoparticle ink during flash light sintering

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ABSTRACT

The copper nanoparticle ink was coated on polyimide substrates using a doctor blade method. The films thus formed were then sintered by flash light irradiation at room temperature under ambient conditions. The flash light energy was varied from 2 J/cm$^2$ to 12 J/cm$^2$. To measure the temperature change, a non-inverting amplifier circuit with an op-amp and a type-K thermocouple was devised. The sheet resistance change was simultaneously monitored using a Wheatstone bridge circuit. An analytical temperature calculation was conducted, considering the heat transfer phenomena during the flash light irradiation. As the results, the temperature of the copper nanoparticle films was reached to (318 °C) in 10 ms at the flash light irradiation energy higher than 12 J/cm$^2$ and they were melted and fully sintered. The analytical solutions of the temperature profile of copper nanoparticles film and polyimide substrate (maximum temperature of copper nanoparticles film and polyimide substrates are 279 °C and 140 °C, respectively) in which the latent heats for phase changes of the copper nanoparticles and the binder (PVP) were concerned, agrees well with the experimentally measured temperature profiles of them (maximum temperature of copper nanoparticles film and polyimide substrates are 318 °C and 135 °C, respectively). The analytical calculation method proposed, could be used to design the flash light sintering variables applicable to various low-temperature flexible substrates.



## 1. Introduction

Technologies for printing electronics on flexible substrates have emerged as alternatives to the conventional photolithography method, owing to their potential for mass production and low cost, as well as the additional applications enabled by physically flexible electronics. Electronic devices printed on flexible substrates using metal nanoparticle ink have been used in various flexible electronic applications including flexible displays, flexible solar cells, wearable electronics, organic thin-film transistors (Kim et al., 2007), and organic light emitting diodes (Dijksman et al., 2007). Metal nano-inks such as gold and silver nano-inks have been widely used due to their excellent electrical conductivity, thermodynamic stability, and sintering efficiency under conventional processing conditions (Kang et al., 2011). However, these noble metals are too expensive to be commercialized. Perelaer et al. (2010) represented that 1 ounce of gold and silver costs about $1100 and $17, whereas 1 ounce of copper and nickel are about 20 cents and 53 cents, respectively. Therefore, copper nanoparticle inks have attracted much attention as a low-cost alternative to gold and silver nano-inks for printed electronics. However, copper nanoparticles are easily oxidized upon contact with air and cannot be sintered by conventional thermal sintering under ambient conditions; sintering instead requires the supply of an inert gas to prevent oxidation, or a reducing gas to reduce the oxide layers to pure metal. Hence, several approaches have been developed for fabricating highly conductive sintered copper nanoparticle films without the oxidation of copper nanoparticles: Aslam et al. (2002) succeeded to sinter the copper nanoparticles using the reduction of aqueous copper precursor and Lee et al. (2008) used the polyol processes while Park et al. (2007) employed the use of metallic nanoparticle suspensions. Also, Yeh et al. (1999) change sintering method using laser irradiation to sinter the copper nanoparticles while Yung et al. (2010) use the camera flash light. These approaches have limitations for mass production or application on flexible substrates because of their low throughput, high complexity, and considerable environmental obstacles (e.g. requiring the use of high-temperature or vacuum conditions).

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Accordingly, a flash light sintering process was previously proposed to prevent the oxidation of copper nanoparticles and guarantee high-speed, room-temperature, and ambient-condition sintering; thereby preventing damage to flexible substrates such as polyimide (PI) (Han et al., 2011), polyethylene terephthalate (Chung et al., 2013), polyethylene naphthalate, and paper (Park and Kim, 2014). Also, Park et al. (2013) demonstrated the two-step sintering method was demonstrated to prevent the damage to flexible substrates. In addition, it is possible to sinter large areas of copper nanofilms using flash light from a xenon lamp. However, an in-depth study of the reducing and sintering mechanisms of copper nanoparticles combined with poly(N-vinylpyrrolidone) (PVP) functionalization and flash light irradiation has not yet been established. Chung et al. (2013) and Hwang et al. (2012) previously conducted in situ monitoring of the silver and copper nanoparticle sintering by millisecond flash light irradiation, respectively; however, the information provided by this monitoring included only the changes in electrical resistance with respect to flash light sintering conditions including pulse number, pulse width, pulse gap and energy. To further understand the flash light sintering mechanism of copper nanoparticles, the temperature change of the nanoparticle films should also be monitored and studied.

Therefore, the resulting temperature change in the copper nanoparticle film was measured and recorded by converting voltage changes in a non-inverting amplifier circuit including an op-amp and a thermocouple. The sheet resistance change was simultaneously monitored in real time using a Wheatstone bridge circuit. The copper nanoparticles 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. Experiments

### 2.1. Fabrication of copper nanoparticle films

Commercially available copper nanoparticles with oxide shells (10–70 nm in diameter, oxide thickness >2 nm; QSI-Nano Copper) were used. Copper nanoparticle inks were prepared as follows. First, 8.4 g of diethylene glycol (DEG, 99%; Sigma–Aldrich) and 0.8 g of PVP (MW 40,000; Sigma–Aldrich) were mixed together in an ultrasonic bath for 1 h. Second, 10.8 g of copper nanoparticles were added to this mixed solvent and dispersed for 3 h by simultaneous use of an ultrasonic bath and a mechanical stirrer. The ball milling was conducted for 12 h to further disperse the copper nanoparticles. A polyimide (PI) film of thickness 225 μm was used as the substrate material; it was prepared for use by ultrasonication in distilled water and ethanol for 10 min to remove surface contamination. After cleaning, a hole was drilled in the PI substrate using a pin; a thermocouple (type-K, 0.12 mm, Labfacility) was inserted into this hole and stuck it using adhesive polytetrafluoroetylene tape on the back of PI substrate to fix it. Then, the prepared copper nanoparticle ink was coated on the PI substrate by covering the thermocouple using a doctor blade method (Fig. 1(a)). The sample size of coated copper nanoparticle film was determined as 2 cm × 2 cm; the thickness of the film was 40 μm.

### 2.2. Flash light sintering process

The coated copper nanoparticle inks were sintered with the flash light irradiated area as 2 cm × 1 cm at room temperature under ambient conditions. The flash light sintering system consisted of a xenon flash lamp (PerkinElmer Co.), a power supply, capacitors, a simmer triggering controller, a pulse controller, and a water cooling system (Fig. 1(a)). The flash light from the xenon flash lamp has a broad wavelength range from 350 nm to 1.0 μm. The flash light sintering system was designed to supply 99 maximum shots and 100 J/cm$^2$ maximum energy on a millisecond scale with a minimum pulse interval of 1 ms by controlling the electrical current and voltage. The coated copper nanoparticle films were placed at a distance of 3 mm from the flash light lamp. The flash light irradiation energy was varied from 2 to 12 J/cm$^2$ as the experimental variable. The energy of the irradiated flash light was measured by a power meter (Nova II, People Laser Tech.).

### 2.3. In situ measurement of temperature&sheet resistance

The temperature measurement apparatus was devised combining a non-inverting amplifier circuit with an op-amp (LM 324 N, STMicroelectronics), a power supply (SDP 30-3DT, SM Techno) and a type-K thermocouple with a response time of about 1 ms (Labfacility, UK) (Fig. 1(a)). The power supply was used to apply a constant voltage (15 V) to the non-inverting amplifier circuit to operate the op-amp. In the non-inverting amplifier circuit, the values of the resistances $R_1$ and $R_3$ were fixed at 10 kΩ, while $R_2$ and $R_4$ were fixed at 100 kΩ (Fig. 1(b)). During sintering, the output voltage ($V_{out}$) was recorded using an oscilloscope (DL1740E; Yokogawa) at $20 \times 10^4$ samples per second (Fig. 1(a)). Based on the non-inverting amplifier circuit, the temperature changes of the copper nanofilms during sintering can be calculated from the output voltage ($V_{out}$) by using the following equations:

$$V_{out} = V_{in} \times \left[ \left(1 + \frac{R_2}{R_1}\right) \times \left(1 + \frac{R_4}{R_3}\right) \right] \quad (1)$$

$$V_{in} = \frac{\Delta T_{measured}}{\alpha} \quad (2)$$

$$\Delta T_{measured} = V_{out} \times \frac{\alpha}{(1 + R_2/R_1) \times (1 + R_4/R_3)} \quad (3)$$

where $V_{out}$ is the output voltage recorded by the oscilloscope, $V_{in}$ is the voltage differential converted by the temperature gradient of the copper nanoparticle film, $\Delta T_{measured}$ is the temperature change of the copper nanoparticle film, and $\alpha$ is a correction factor, which was measured to be 0.025 °C/μV.

The sheet resistances of the copper nanoparticle films were measured and recorded simultaneously using a Wheatstone bridge electrical circuit, a source meter (2611A; Keithley), and the oscilloscope (Fig. 1(a)). The source meter was used to apply a constant voltage (4 V) and current (1.2 A) to the Wheatstone bridge circuit. In the Wheatstone bridge circuit, the values of resistances $R_5$, $R_6$ and $R_7$ were fixed at 1 Ω (see Fig. 1(a)). The voltage difference ($V_D$) between the two middle points of the Wheatstone bridge was measured and recorded using an oscilloscope. From the voltage difference ($V_D$), the unknown resistance could be calculated using the following equation:

$$R_x(\Omega) = \frac{V_I + 2V_D}{V_I - 2V_D} \times 1 \quad (4)$$

where $R_x$ is the sheet resistance of the nanofilm, $V_I$ is the input voltage (4 V) of the Wheatstone bridge, and $V_D$ is the voltage difference across the Wheatstone bridge.

### 2.4. Transient heat transfer analysis

Transient heat transfer analysis was conducted to calculate the film temperature. As shown in Fig. 2, the modeled heat transfer system was composed of the film, the PI substrate, and the floor. To calculate the temperature changes in this model, several assumptions were employed. First, radiation of heat from the film was neglected. Second, convection between the air surroundings and the film was assumed to take place through the mechanism of