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Thermal conductivity estimation of inkjet-printed silver nanoparticle ink during continuous wave laser sintering

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ABSTRACT

We determined the thermal conductivity of silver nanoparticle ink during laser sintering by applying the Wiedemann–Franz law to two-dimensional heat conduction equations. Ink with 34 wt% silver (Ag) nanoparticles with an average size of approximately 50 nm was printed on Eagle-XG (Samsung–Corning) glass substrate by inkjet printing. Inkjet-printed patterns were irradiated with a 532 nm continuous wave laser at various laser intensities. To obtain a transient thermal conductivity trace of the ink during the laser sintering process, *in-situ* electrical resistance data were measured to estimate the thermal conductivity of the inkjet-printed ink using the Wiedemann–Franz law. Two-dimensional heat conduction equations were iteratively solved to obtain transient temperature information about the sintered ink. As the laser sintering temperature increased, the surface morphology of the sintered ink affected the thermal conductivity of the laser-sintered ink. Thermal conductivity of the laser-sintered Ag nanoparticle ink was estimated by considering the thermal conductivity of the air confined in pores.

1. Introduction

Inkjet printing technology to support a variety of fields such as displays, solar cells, optics, and electronics has been developed due to the simplicity of the process and minimization of the loss of materials. Metal nanoparticle inks are considered good solutions for inkjet-printing processes because these inks potentially have excellent electrical properties [1]. However, the surfactant surrounding the metal nanoparticles in inkjet-printed ink isolates the metal nanoparticles from one another, preventing electrical functioning [2]. Inkjet-printed metal nanoparticle inks must be sintered at temperatures ranging from 373 to 573 K to remove the surfactant and allow nanoparticles to connect to allow for the establishment of electron paths or networks. After sintering, which can be performed by furnace [3], electrical field [4], microwave [5], xenon flash [6], or continuous wave laser [7], the metal nanoparticles can coalesce to form continuous electrical contacts for free electron flow [8]. Sintering temperature in particular plays an important role in controlling the morphology of the metal nanoparticle ink, which is a crucial determinant of the electrical performance of the printed circuits.

Continuous wave laser sintering is ideal for ink printed on temperature-sensitive substrates; damage to the substrate can be minimized because most of the laser energy is absorbed by the printed ink. As mentioned above, temperature is known to be an important parameter in the sintering of metal nanoparticles as it determines the surface morphology established by necks, networks, and grain growth. However, it is difficult to perform *in situ* monitoring of continuous wave laser irradiation of printed ink. Numerical temperature estimation is an alternative to measuring the sintering temperature, but the calculation accuracy needs to be improved. Knowledge of the transient thermal conductivity of the ink sintered by a laser can increase the accuracy of temperature estimation. Surface morphology resulting from neck formation, percolation networks, and grain growth will affect the value of the thermal conductivity of printed Ag ink during laser irradiation. However, it is difficult to use conventional methods to obtain the transient thermal conductivity of printed ink samples during laser sintering. The fact that heat transfer in pure metal is mainly due to electron flow can be utilized to estimate the thermal conductivity of printed ink samples.

In this work, we estimated the thermal conductivity of printed ink lines by measuring the *in-situ* electrical resistance during a 532-nm continuous laser sintering process. Transient electrical conductance was obtained from the experimentally measured resistances of the samples. Specific electrical conductance was

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utilized to estimate the thermal conductivity of the sintered ink by calculating heat conduction equations coupled with the Wiedemann–Franz law [9]. To improve the accuracy of the transient behavior, the adoption of this method looks reasonable instead of using the bulk Ag thermal conductivity in the initial stage of the sintering process. To determine the effect of the surface morphology of the laser-sintered ink, we performed scanning electron microscopy. The effect of surface morphology was modeled to estimate the thermal conductivity.

2. Experiments

Silver nanoparticle ink was printed on Eagle-XG (Samsung–Corning) glass using a DMP-2831 inkjet printer (Dimatix). The conductive ink had 34 wt% silver nanoparticles with an average size of 50 nm. Eagle-XG (Samsung–Corning) glass substrate was used to minimize the spurious diffusion of alkali metals into the ink during the sintering process. Before printing the ink on the glass substrate, the glass substrate was cleaned in an ultrasonic cleaner for 5 min. The substrate was then baked in a furnace at 423 K for 900 s to remove extra moisture on the substrate. As shown in Fig. 1, the patterned line size of the printed ink was $3000 \times 130 \times 0.36\ \mu m^3$ (length × width × thickness) and the pad size was $1000 \times 1000\ \mu m^2$. To reduce pad resistance, printed pads were sintered in a furnace at 323 K for 30 min and sintered continually in a furnace at 523 K for an additional 30 min. The patterned line was printed after pad sintering to minimize pad resistance and improve the accuracy of transient electrical resistance measurements.

A schematic diagram of the laser sintering system employed is shown in Fig. 2. Laser sintering of printed ink was carried out using a 532 nm continuous wave laser. The laser beam was designed to have an elliptical shape by using one concave cylindrical lens and two convex cylindrical lenses. The first cylindrical lens, with a focal length of −50 mm, was used to expand the laser source beam of a diameter of 2.25 mm. The second convex cylindrical lens with a focal length of 50 mm reduced the minor axis of the ellipse to 360 μm. The third convex cylindrical lens with a focal length of 200 mm was rotated by 90° to downsize the major axis of the ellipse to 4200 μm. To adjust laser irradiation times and to place the irradiated laser beam on the printed sample, a shutter and automatic *xy*-translation stages were used. To control the delay time between the multimeter and the shutter, a DG535 delay/pulse generator (Stanford Research Systems) was used. The power of the laser beam was measured using a FieldMax-II power meter (Coherent).

Printed ink was irradiated at laser intensities of 121, 222, 348, and 467 W/cm^2. Irradiation was performed for 60 s at room temperature. The *in-situ* electrical resistance of the conductive ink during the laser sintering process was measured using a L4411A multimeter (Agilent) connected to two S-725 micro positioners (Signatone) and probe tips (Signatone). The probe tips were connected to the previously furnace-sintered pad of the pattern. After continuous wave laser sintering, the cross-sectional area of the sintered ink was measured using an Alpha step IQ surface profiler (Kla-Tencor) to obtain the electrical conductance of the sintered ink by *in-situ* electrical resistance measurements. This transient conductance information was used to estimate the thermal conductivity of the laser-sintered ink. To investigate the surface morphology of the sintered ink to improve thermal conductivity estimation after sintering, field-emission scanning electron microscopy (FESEM, Hitachi S-4800) was performed to determine the porosity of the laser-sintered ink. Image analysis (Image Xpert) was conducted to determine the porosity of the sintered ink.

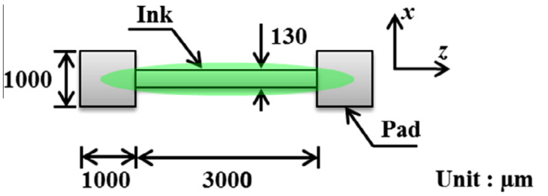

Fig. 1. Pattern of conductive ink for continuous wave laser sintering.

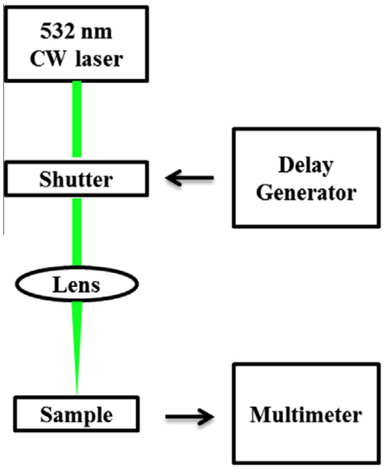

Fig. 2. Schematic diagram of the laser sintering system employed.

To determine the normal reflectivity of the sintered ink according to temperature variation at a wavelength of 532 nm, which was the wavelength of the laser beam the ink was irradiated with, samples were spin-coated on glass substrates using a spin coater, because the sample width of 130 μm was not wide enough for ellipsometry measurement of the optical properties of the ink. The sample thickness was controlled to be 10 μm by setting the revolution rate of the spin-coater to 250 rpm. Samples were then sintered in a furnace at temperatures of 323, 373, 423, 473, and 523 K for 30 min. Refractive index, n, and the extinction coefficient, κ, of the samples were measured by ellipsometry at room temperature. These optical properties were included in the source term of temperature calculations to evaluate the absorbed laser energy.

3. Calculations

The Wiedemann–Franz law was applied to obtain the transient thermal conductivity of the sintered ink during continuous-wave laser sintering. The Wiedemann Franz law is as follows:

$$k_{\text{ink}}(t) = L_{\text{silver}} \cdot \sigma(t) \cdot T_{\text{ink}}(t) \tag{1}$$

where k_{ink}, $T_{\text{ink}}(t)$, and $\sigma(t)$ are the thermal conductivity, transient temperature, and transient electrical conductance, respectively. Transient electrical conductance was experimentally determined by inverting the experimentally obtained specific resistance of the ink. The Wiedemann–Franz law states that the ratio of the thermal conductivity to the electrical conductance of a metal is directly proportional to the temperature above a specified lower temperature limit. The value of the constant of proportionality, the Lorentz number, is considered independent of the choice of metal. However, the Lorentz number has been found to be dependent on the type of metal and temperature within a difference of 5%. Therefore, we used the experimentally measured Lorentz number for silver at 100 °C, $L_{\text{silver}} = 2.37 \times 10^{-8}\ \text{W}\,\Omega/\text{K}^2$, for this work [9].