Ink-jet printed high conductive silver traces on polymer substrates sintered at room temperature by a camera flash lamp

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Abstract
A simple and facile camera flash sintering method has been developed to sinter the ink-jet printed silver nanoparticle traces at room temperature to form conductive circuit on flexible polymer substrates. The electrical resistivity of silver traces sintered by two times of camera flash can be decreased to 8.4 μΩ cm, which is only about 1/3 that of the silver tracks thermally sintered at 150 °C for 80 min. As camera flash sintering is fast, simple and cost-effective, it is promising to be widely used for nanoink-jet printed electronics. Furthermore, this method is expected be readily generalized to prepare other types of metal lines on various substrates such as glass and polymer owing to the room temperature process. The sintering mechanism is also investigated via in-situ recording temperature of the Ag nanoparticles based track during the flash sintering, which confirms the enhanced photothermal effect of nanostructures.

Keywords—ink-jet printing, flexible substrate, conductive circuits, silver nanoparticles, camera flash sintering.

I. INTRODUCTION

Ink-jet printing has been widely used in electronic industry to fabricate nanoparticles based conductive tracks (circuits) [1-5]. To fabricate conductive tracks, sintering is a crucial step to obtain high conductive circuits. Some methods have been developed to sinter the printed tracks. The most popular one is thermal oven sintering process, wherein the printed lines are typically treated at 150-260 °C for 30-60 min [1, 4, 5] and the resistivity of the sintered lines approaching 3 to 10 times than the value of the bulk material. However, it is time consuming and the conductivity of the lines depended on sintering temperature and time. It is also limited for the application in substrates which cannot endure the high temperature aging. Another one is laser sintering [6, 7] which can follow the conductive tracks and sinters selectively, without affecting the substrate. However, this method is costly and complex for the wide application in industry. Microwave heating was also reported which was similar to thermal oven sintering process except using microwave as heating source and the time for sintering can be reduced to about 2 min [8]. However, the applications would be limited as the temperature of the microwave reactor vessel reaches to 200 °C during the sintering. Recently, electrical sintering was also presented [9], but it is a low throughput method. Thus, it is very necessary to develop a low sintering temperature, low cost and high throughput technique for sintering of ink-jet printed nanoparticles-based tracks.

Herein, we present a facile method to sinter ink-jet printed lines containing silver nanoparticles on polymer substrate at room temperature by using camera flash. The camera flash sintered silver lines demonstrate a low resistivity of ~8.4 μΩ cm.

II. EXPERIMENTAL

The silver nanoparticles were synthesized by the chemical reduction method using formaldehyde as the reducing agent and polyvinyl pyrrolidone (PVP) (molecular weight = 10 000) as protective agent according to the previous report [10]. About 1.43 g PVP/gAg was used for this work. AgNO3 (0.07 mol/L) was the source of silver ions which were reduced by a reducing agent, formaldehyde (0.35 mol/L). During the reaction, a stoichiometric ([Na2CO3]/[Ag+] = 0.06) amount of Na2CO3 was added drop by drop, which can enhance the reducing power of formaldehyde, to speed up the sintering process. After completion of chemical reduction, the suspension was centrifuged and washed 5 times with ethanol. Silver nanoparticles were dispersed uniformly in ethanol for jet printing. The as-prepared silver ink contained 14 wt% Ag nanoparticles was printed on polyimide substrate and mylar substrate by a piezoelectric ink-jet printer (Microdrop MD-E-201H). Scanning electron microscopy (SEM, JEOL 6335) and atomic force microscopy (AFM) was used to characterize the microstructure of printed lines.

III. RESULTS AND DISCUSSION

Figure 1 XRD pattern of as-prepared silver nanoparticles.

Figure 1 shows the XRD patterns of as-prepared silver nanoparticles. The diffraction peaks are indexed to the (111), (200), (220), (311) planes of silver face-centered cubic (fcc) crystalline (JCPDS card no. 04-0783), respectively. The shape
of broad peaks suggests that the nanoparticles of the as-prepared silver samples. The TEM results (Figure 2) displays that the diameters of as-prepared silver nanoparticles is almost smaller than 10 nm.

Figure 2 TEM image of the as-prepared silver nanoparticles.

The morphology and particle packing within the line before and after sintering are shown in Figure 3. Before camera flash sintering, it could be observed many voids between the aggregated silver particles with a typical diameter of 30–40 nm on the substrate (Figure 3a). Upon drying, most of the solvent evaporated, which caused the particles to agglomerate together loosely, so there were lots of voids between the particles. Figure 3b indicated that most of the boundaries between the silver particles disappeared after camera flash exposure for 2 times. Figure 4 showed the AFM micrograph of the silver track on the PI substrate after 2 time flash sintering. The thickness of the silver was about 420 nm. It is clear that the silver coating was uniform and dense packing. The interface between the coating and PI was dense packing and no obvious cracks or delamination were detected. The AFM result also confirmed that the silver nanoparticles were well sintered together after the camera flash exposure. It is well known that the absorption of light by a material can generate heat through nonradiative energy dissipation and exothermic photochemical reactions. In nanostructure materials, the heat generated through photothermal processes would be confined within the individual nanostructure when heat transfer to adjacent nanostructures and environment is slow, which leads to the local temperature of the nanostructures can be quickly increased [11, 12]. During the camera flash, the local temperatures of the silver nanoparticles increased due to the enhanced photothermal effect of nanostructures, and the nanoparticles would melt and sinter then consequently the electrical resistivity of the track might decrease. As the flash duration is only 1-2 ms, thus this camera flash method is high efficient for sintering nanoparticles-based tracks.

Figure 3. SEM images of an ink-jet printed silver line. (a) Before sintering and (b) after two times of flash sintering.

Figure 4. AFM micrograph of an ink-jet printed silver track after two times of flash sintering.

The electrical resistivity $p$ of an ink-jet printed tracks was calculated from the resistance $R$, the length $l$, the cross sectional area $A$ of the line, using $p = R \cdot A / l$. In order to obtain a track with uniform thickness, a printed silver band with width of about 4 mm and length of 60 mm was printed on the PI substrate. Then only the center part of the wide band with 1.5 mm width and 30 mm length was cut to study the resistivity. The electrical resistivity change of one typical line after the camera flashing with the flashing time is shown in Figure 5. After the first flashing, the printed non-conductive track turned into conductive and resistivity dramatically decreased to 9.84 $\mu\Omega$ cm. After the second flash sintering, the resistivity further decreased to 8.4 $\mu\Omega$ cm. Then the change of the resistivity was relatively small, and it nearly remained constant after the third and forth flashing. This phenomenon was ascribed to the enhanced photothermal effect of the nanoparticle based track decreased as the result from most of the small nanoparticles melted into larger agglomerates and sintered together after two times of flashing sintering. Thus 2 times of flashing was reasonable choice with this camera flash lamp. For comparison, the silver tracks sintered by conventional thermal oven sintering process (150 °C, 80min) were also prepared, and their resistivity was measured to be about 3 times that of siver tracks by camera flash sintering method. Therefore, the camera flash sintering can obtain lower resistivity of silver nanoparticles much fast and easily compared to traditional heat sintering.
Figure 5. Electrical resistivity as a function of the number of flash sintering.

Figure 6. Temperature map of the surface of one line during the flash sintering. The inset shows the optical microscopy image of the line before the flash sintering.

In order to understand the sintering mechanism of nanoparticles based tracks using camera flash, an IR camera (NEC TH9100PWV) was used to record the temperature on the surface of the track printed on a mylar film during the flash sintering. The IR camera was put on the side of silver tack while the camera flash was put on the side of mylar film to sinter the track. The thickness of the mylar film was 20 μm and that of silver nanoparticles coating was about 200 nm. As the mylar film was transparent, the absorption of the light was ignored. Figure 6 showed the highest temperature map was recorded during the flashing. It was clear that the maximum temperature on the surface of the line was 109.9 °C, while that on the mylar surface was below 30 °C, which identified the temperature increasing of the silver track was induced by the enhanced photothermal effect in nanostructures. However, the recorded maximum temperature on the metal tracks was much lower than the assumed temperature of 1500 °C within the carbon nanotubes [11]. It might be responsible for the reasons: 1) the recorded temperature was not the surface that was sintered. 2) IR camera cannot record the temperature on individual nanoparticle due to the low resolution. 3) the thermal conductivity of silver is very high. Thus, it should be to believe that the local temperature might be several hundred degrees as we could clearly observe that some nanoparticles melted into large particles and sintered together in the tracks.

In a conclusion, we have demonstrated a facile camera flash method to sinter the nanoink-jet printed silver tracks at room temperature with high throughput. The electrical resistivity of the camera flash sintered silver tracks was 8.4 μΩ cm which was only 1/3 that of thermally sintered Ag nano-ink. The method is fast, simple and cost-effective and promising to be widely used for nanoink-jet printed electronics.

REFERENCES