Surface Morphology and Conductivity Study of Inkjet Printed Traces from Ag Nanoparticle Inks

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Abstract

Non-contact printing of conductive traces for electronic device fabrication is attractive due to its low cost, high resolution and high throughput characteristics. Inkjet printing of Ag nanoparticle inks followed by thermal or photonic sintering has the greatest potential for commercialization. In this process, the chemical and physical properties of the ink formulation and post print processing have significant impacts on the performance of the printed traces. In this paper, the effects of sintering methods and process conditions on the surface morphology and conductivity of the fabricated Ag traces are discussed.

Introduction

In recent years, printed electronic technology has received a great deal of attention in its applications, such as flexible radio frequency identification (RFID) tags, flat panel displays, and circuit boards [1, 2]. Although conventional photolithographic technology has been widely applied to fabricate such devices, it is time consuming, complicated and expensive. Moreover, only limited substrates can be used for such process due to the nature of the technology. Therefore, direct printing techniques, such as inkjet printing, which are simpler and less expensive, are desired in the electronic industry. Compared with the photolithography, which involves multiple processes, inkjet printing is a one-step procedure and is able to make desired patterns on various substrates. In addition to the reduction in time, cost and waste, inkjet printing has the flexibility of changing patterns and the capability of printing on large areas [1, 3].

Silver nanoparticles are commonly used to formulate conductive inks based on different reasons: they have a lower melting point than bulk silver, do not easily form silver oxides in inks, and are highly conductive after sintering [4]. Silver nanoparticles can be sintered by heat, microwaves and photonic energy, for example. Among these sintering technologies, thermal sintering is commonly used. At elevated temperatures, individual silver nanoparticles fuse together and eventually form a continuous film. Therefore, the sintering temperature has a significant impact on the film morphology and conductivity. Thermal sintering has its limitation in cases where the substrates are susceptible to the heat treatment. Many widely used flexible substrates, such as polyethylene terephthalate (PET) or polyethylene naphthalate (PEN) film, are limited to process temperatures < 220 °C. Photonic sintering, due to its shallow penetration of the heat into the substrates, has found great potential to sinter Ag nanoparticles on flexible substrates. In addition, this technique can quickly remove the organic residues in the printed traces. In this study, we printed Ag inks on different substrates using a Dimatix inkjet printer, sintered the traces with thermal and photonic sintering methods at different conditions, and investigated the surface morphology and electrical properties of the printed traces.

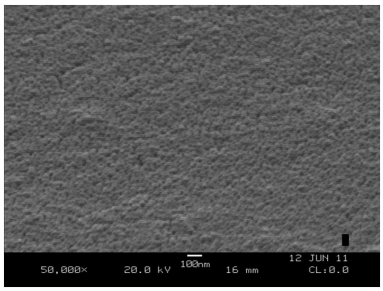
Experimental

The Ag ink containing 20 wt% of organic-capped Ag nanoparticles was printed with a Dimatix DMP-2800 Materials Printer from FUJIFILM Dimatix, Inc. The printhead temperature was varied between 30 °C and 45 °C. The platen temperature was maintained at 45 – 60 °C. Polished p-type Si wafers and PET were used as the substrates. After printing, all samples were prebaked at 80 °C on a hotplate for 10 minutes. For thermal sintering, the samples were then sintered for 150 sec at peak temperatures ranging from 160 °C to 400 °C using a Sierra Thermo belt furnace, For photonic sintering, the samples were sintered with a xenon lamp in a PulseForge® 3200 system from NovaCentrix. The morphologies of the samples after sintering were evaluated by scanning electron microscopy (SEM). The thickness of the trace was measured using a profilometer, and the sheet resistance was measured with a four point probe resistance meter.

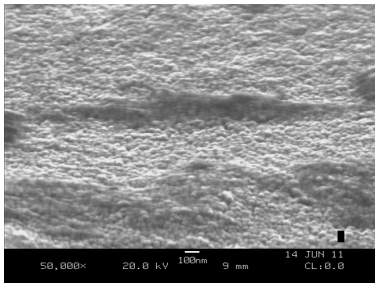
Results and discussion

Morphology of the silver nanoparticles sintered at different temperatures

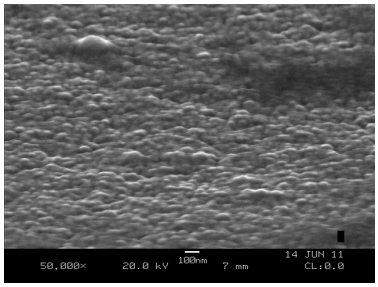
Figure 1 shows the SEM images of the printed samples thermally sintered in air at different temperatures, and Figure 2 displays the resistivity at different temperatures. Before sintering, sphere shaped Ag nanoparticles were observed with the particle size around 50 nm (Figure 1a), and the resistivity of the trace was in the MΩ range. When sintered at 160 °C and at 220 °C, the silver nanoparticles still showed similar morphologies to the unsintered ones. On the other hand, the particle size increased (Figure 1b and Figure 1c). Meanwhile the conductivity increased with increasing sintering temperature. At 300 °C, the original particle shape disappeared, indicating that the nanoparticles began to diffuse together and as a result, the resistivity of the film was only 2.1 times that of bulk Ag. After further increasing the temperature to 400 °C, many particles fused together to form large connected droplets with voids between the droplets. (Figure 1d). This phenomenon is likely due to poor wetting of the silicon substrate by Ag. As a result, the measured resistivity was higher than that of the film sintered at 300 °C.



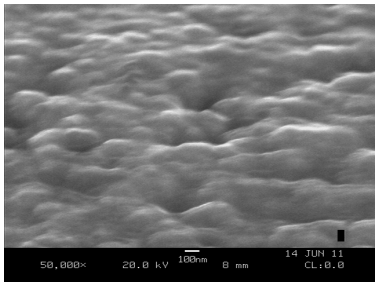
1a



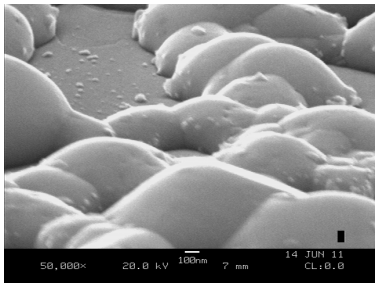
1b



1c



1d



1e

Figure 1*. SEM of the silver nanoparticle traces (a) before sintering and after sintering in air at different conditions: (b) at 160 °C, (c) at 220 °C, (d) at 300 °C and (e) 400 °C*

Atmosphere contribution on the morphology and conductivity

Silver nanoparticles were sintered in both air and nitrogen atmospheres, and the resultant conductivity of the silver traces depends on the sintering atmosphere (Figure 2). In a N_2 atmosphere, both the organic capping agent on the silver nanoparticles and the other organic additives present in the ink did not decompose completely upon sintering. The remaining organic materials prevented the individual Ag particles from fusing into a continuous film. Clearly, the nanoparticles sintered in N_2 did not fuse as completely as those sintered in air (Figure 3a and 3b). However, the presence of organics affected the de-wetting phenomenon of the silver metal on silicon, allowing better film formation and counteracting the poor particle fusing. These effects are seen in the resistivity measurement wherein the N_2 sintered particles are slightly lower than the air sintered particles over the 160°C to 230°C temperature range. The lowest resistivity seen was in N_2, at 1.8 times that of bulk Ag, which is much lower than the lowest resistivity of the air sintered particles.

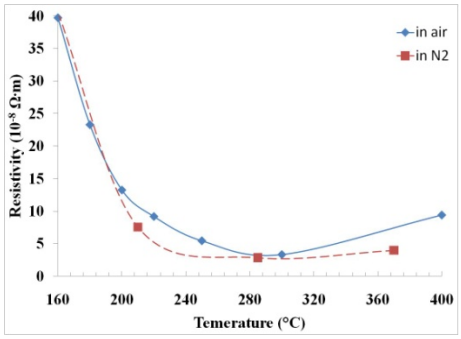
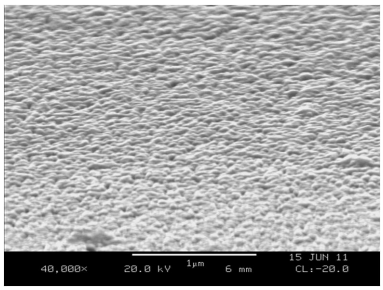


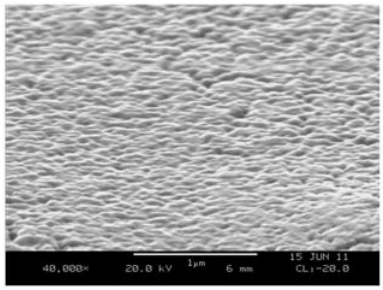
Figure 2.
Resistivity of the printed Ag traces sintered in different atmospheres and at different temperatures

Thermal and photonic sintering on PET substrate

Designs for thin film electronics often include materials such as plastic substrates or other materials that are vulnerable to high temperatures. For example, in cases where PET is used as the substrate, the process temperature is limited to 150°C to 200 °C. In this low temperature range, it is difficult to sinter metallic nanoparticles completely, as shown above. In order to achieve high conductivity without damaging the substrate, photonic energy was used to sinter silver nanoparticles printed on plastic substrates. Figure 4 shows the SEM images of the printed samples after thermal sintering at 200 °C and photonic sintering, respectively. The images clearly show that the photonically sintered silver sample is fused more thoroughly than that of the thermally treated sample. Measurements show that the resistivity of the photonically sintered sample is 6.7×10^{-8} Ω·m, which is lower than that of the sample thermally sintered at 200°C (15.1×10^{-8} Ω·m).

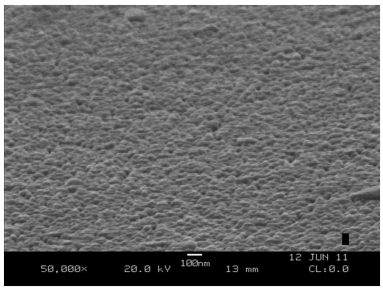


3a

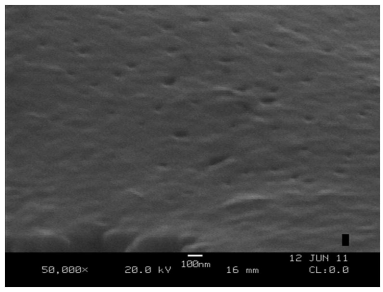


3b

***Figure 3**. SEM of the silver nanoparticle traces sintered in a N_2 atmosphere (a) at 300 °C and (b) at 400 °C*



4a



4b

***Figure 4.** SEM of the silver nanoparticle traces on PET substrate (a) with thermal sintering at 200 °C and (b) with photonic sintering*

Conclusion

A Ag ink has been printed on both polished p-type Si wafers and PET substrates. The printed traces were sintered both by thermal energy and photonic energy. When sintered in air, the degree of fusing increased with the increase of the temperature. Voids appeared when the temperature was at 400 °C when sintered in air, which were due to dewetting during the sintering process. The lowest resistivity achieved was about 2.1 times of bulk Ag when the sample was sintered at 300 °C in air. When sintered in N_2, the nanoparticles did not fuse as thoroughly as those sintered in air because the capping agent and other additives did not burn off completely. Voids were not observed in those films. The lowest resistivity achieved when sintered in N_2 was 1.8 times that of bulk Ag. On PET substrates, photonic sintering fuses the nanoparticles more thoroughly than the thermally treated samples, resulting in the resistivity of the photonically sintered sample of 6.7×10^{-8} Ω·m, which is lower than that of the lowest thermally sintered sample (15.1×10^{-8} Ω·m).

References

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Author Biography

Yanping Sun received her BS in Chemistry from University of Science and Technology of China (2001), her MS in Chemistry from Clemson University (2004) and her PhD in Chemistry from Purdue University (2010). Since then she has worked in Electronic Materials Division at the Dow Chemical Company in Marlborough, MA. Her work has focused on the development of conductive ink formulation for printed electronics and photovoltaic applications.