Sintering Methods for Metal Nanoparticle Inks on Flexible Substrates

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Abstract

In this paper a number of selective sintering methods suitable for inkjet printed nanoparticles are demonstrated on two different coated papers. The selective methods demonstrated here are electric current heating, microwave sintering and photonic curing. As a reference, conventional heat chamber sintering is also included. Conductivity measurements and studies of sintered structures with optical and scanning electron microscopy are performed, as well as a qualitative evaluation of how the heat-sensitive substrates are affected. The purpose is to analyze characteristics of each method and gain insight in how different process parameters affect overall performance and reliability. With heat chamber sintering the best achievable conductivity without substrate deformation corresponded to less than 20% of pure silver. With some selective methods, conductivity reached well above 50% of pure silver.

Introduction

In functional printed applications where high conductivity of structures is needed, such as antennas for RFID tags, metal nanoparticle inks are commonly used. To meet conductivity requirements, sintering is typically necessary, in which the structures are heated in order to evaporate carrier solution and fuse individual particles together to form a continuous layer.

Metal nanoparticles have melting points much lower than the corresponding bulk metal because of thermodynamic implications of the very large curvature of the particle surface. Still, a common problem with traditional convection heating is that many substrates such as coated papers and plastic films have softening points below the required sintering temperatures, and therefore cannot be completely sintered without deforming the substrate. Therefore selective heating of the conducting layers with minimal heat transfer to the substrate is highly desirable.

Traditional sintering in an oven or heat chamber relies on heat transfer mainly by convection. Convection sintering gives a high degree of control and predictability and has been used extensively [1], [2]. Because the metal and substrate are equally exposed, this method has severe limitations for heat sensitive substrates such as coated papers and common plastic films.

Electrical sintering as a method in printed electronics developed quite recently [3]. The concept is to run electric current through the conducting structure, in which heat will develop because of resistive losses.

Heating by microwaves is an interesting alternative when the printed structures are thinner than the penetration depth of silver at the frequency of interest. Microwave heating is a rather unusual method but some investigations have been done [4], [5].

Photonic curing refers to the process of exposing the metal film to pulses of high power light [6]. With laser sintering, high power can be concentrated to a very small area, and the precise control of the beam location and power makes the method very flexible, although quite complicated and expensive [7], [8]. Other methods previously described is plasma sintering [9] and chemical sintering [10].

Experimental

Conducting lines of dimension 20 x 0.4mm were printed with the Dimatix 2831 piezoelectric inkjet system. A Dimatix 11610 10pL cartridge was used with a nozzle voltage of 24V and a suitable waveform supplied by the ink manufacturer. Drop spacing was set to 20µm with a nozzle and platen temperature of 28ºC. The polar silver nanoparticle ink DGP 40LT-15C from Advanced Nano Products was used on two coated papers; the photo paper 'Platinum PT-101' by Canon and the laser printer paper 'Silver Image Gloss' by M-real. The lines were dried in air for 2 hours before sintering. The thickness of the printed layer was measured to approximately 0.7µm with a d3100 atomic force microscope from Digital Instruments. This value was used in the resistivity calculations. All resistance measurements were averaged over 5 samples using a Keithley 2611 Sourcemeter in 4–point mode. Each sintering method was evaluated using both papers.

The convection sintering was made with a Pol-Eko SLW53 microprocessor controlled heat chamber with circulating fan. Samples were placed in the middle of the chamber.

Microwave sintering was done using a modified consumer microwave oven, Whirlpool AMW232 with a 2.46GHz magnetron. The modification was made by installing a variable transformer to control the anode voltage of the magnetron, giving the possibility of very low output power levels and fine tuning of the output power.

Electrical sintering was performed by programming a Keithley 2611 sourcemeter. On-off time, current limit and start voltage was selected for each experiment, and simultaneous measurement of voltage and current during sintering was made in 4-point mode. The start voltage was set to approximately half the initial resistance.

Photonic curing was conducted by Novacentrix using their PulseForge™ 3100 production model.

After sintering, all samples were visually inspected for substrate deformation. Fragility of substrate and conductor was examined by mechanically bending the substrate repeatedly, followed by electric checking for resistance increase or conductor break.

Results and discussion

With convection sintering it was found that the temperature to a large extent defines the result and is more important for the resulting resistivity than the time, as seen in figure 1-2. In most cases less than 10 minutes was sufficient to reach final resistivity of each tested temperature, longer times only degenerated the substrate. For example, heating for 30s at 180ºC resulted in slightly lower resistivity than 60 minutes at 150ºC.

As expected, substrate deformation was a limiting factor with the convection sintering. The photo paper was the most heat sensitive, showing mechanical deformation such as multi-directional curling and coating loosening from the substrate base. The coating also stiffened and became fragile, leading to break in the conductors (Fig.8F). The highest safe temperature was found to be 110 ºC, although 130ºC was acceptable up to 30s. This resulted in a resistivity of 10.7μΩcm, corresponding to 15% of the conductivity of pure silver.

The laser-printer paper proved to be much more heat resistant, only beginning to show a slight color change after 10 minutes at 180ºC. These conditions resulted in 8.9μΩcm or 18% of bulk silver.

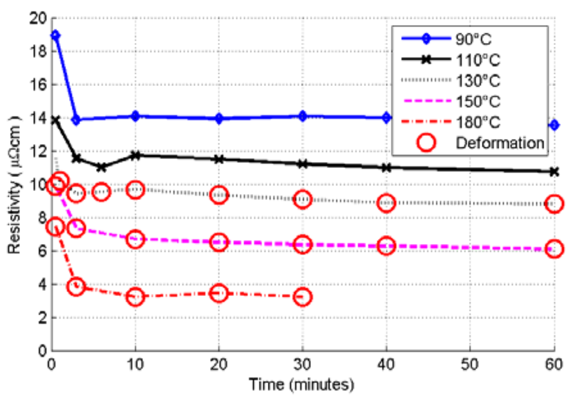

Figure 1. *Convection sintering with photo paper.*

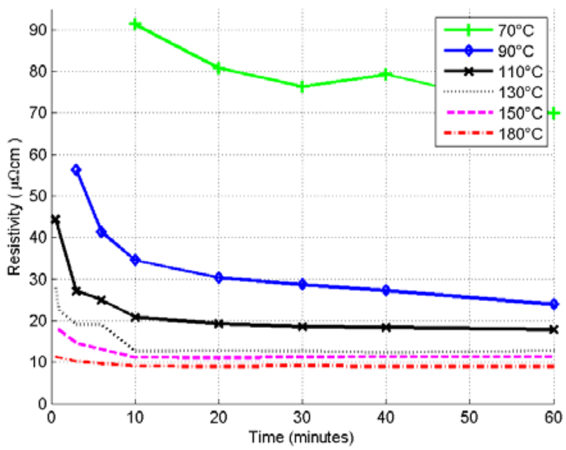

Figure 2. *Convection sintering with laser paper.*

Successful electrical sintering on the photo paper was found to have a current maximum of about 1.5A corresponding to over 5kA/mm^2 current density. At this current, the sintering process occurs very rapidly, leading to a narrow effective time window (Figure 4). Just a few milliseconds beyond the 115ms maximum, the conductors will overheat and deform. For a more controlled and predictable process a lower current is preferable. The most effective sintering conditions for these samples were found to be 0.9A and 1s where the resulting conductivity reached well above 50% of bulk silver without substrate deformation. Microscope inspection indicated a uniform change in color, suggesting that the current is evenly distributed in the conductor during sintering (Fig.8A).

With the laser paper, a higher initial voltage of 20V was used because of the higher initial resistance. The initial reaction was therefore quicker, with a peak power of 15W and a tenfold reduction in resistivity within 0.1s. Most effective sintering times were found to be shorter, about 0.5s with a current around 1A, which resulted in conductivities near 40% of bulk silver.

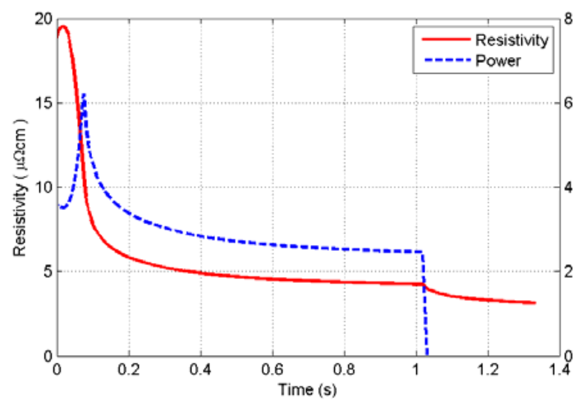

***Figure 3**. Dynamic measurement during electrical sintering on Canon paper. Current limit 1A and start voltage 7V. Note that resistivity drops further after current is stopped at 1s.*

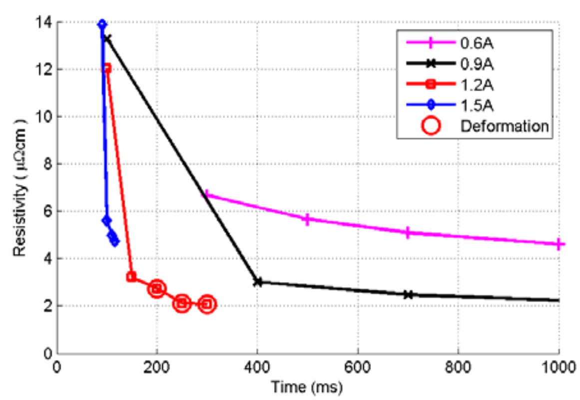

Figure 4. *Electrical sintering with photo paper.*

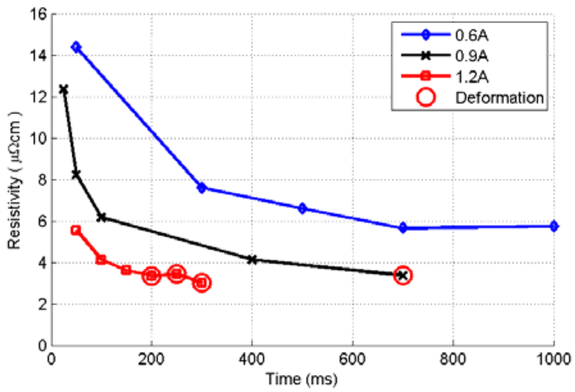

Figure 5. *Electrical sintering with laser paper.*

Photonic curing was carried out by using pulse lengths in the 0.1 – 10ms range. The most effective exposure resulted in a conductivity corresponding to 42% of bulk silver for the photo paper and 33% for the laser paper. There was no substrate- or ink degeneration detected for these exposure conditions (Fig.8E). The main factor limiting the exposure on the photo paper was delamination of the silver film, i.e. the film was separated from the paper above a certain power level (Fig.8G). With the laser printer paper the delamination occurred at a higher power, at the coating-paperbase interface, indicating a strong ink –substrate adhesion (Fig.8H).

Sintering with the microwave oven gave rise to a range of practical problems. First of all an examination of the field uniformity was made. It was found that the power is highly varying in space, in the X-Y plane parallel with the oven floor, but even more so along the Z axis perpendicular to it. A large power peak was found 30mm above the floor (corresponding to ¼ wavelength). Further, the physical direction of the sample was very important. The largest power was absorbed when the sample was placed along the X-axis (left-right direction). Almost no effect was observed in the Y-direction. Also the size and shape of the structure was found to be an important factor.

Note in the overexposure example (Fig.8D), that parts of the structure are subject to spectacular overheating where other parts are undamaged (right measurement pad). The conductor-field interaction is complex and difficult to predict and equalization of temperature by heat conduction is apparently not sufficient. The metal structure may be seen as an antenna, for which size, shape, location and direction will have influence on the coupling and energy transfer with respect to the electric- and magnetic field. In the experiments, each sample was placed in the same spot in the bottom middle of the oven, along the X-direction.

Effective time-power combination for these samples was found both in the lowest power range at 5-15s and at high power at 3s or below. Although very high conductivity was achieved at the longer exposure times or higher power levels on the photo paper, all of those samples were brittle and broke when bending the papers. With the criteria of acceptable physical reliability, approximately 40% of bulk silver conductivity was reached for the photo paper and 35% for the laser paper.

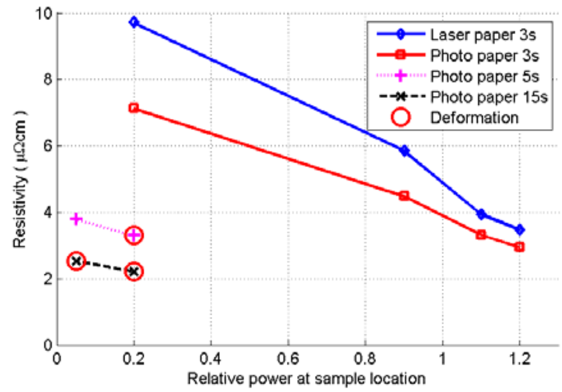

Figure 6. *Microwave Sintering. Relative power was calculated by measuring the temperature difference of 15ml of water heated in sample location.*

Fig.7 shows comparative SEM pictures of unsintered, convection heated and electrical sintered samples on both papers. With convection heating up to 150ºC, no physical change of the nanoparticle layer is apparent. This indicates that sintering is in an early stage and the increased conductivity is mainly due to evaporation of solvent and dispersants in the ink. After electrical sintering for 1s at 1A, the nanoparticles have evidently undergone a physical transition, aggregating into larger clusters and forming a continuous layer, explaining the large drop in resistivity.

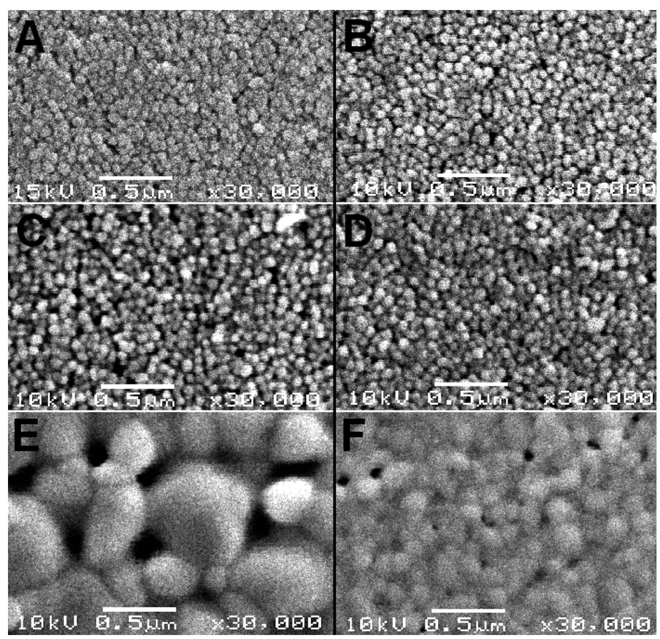

Figure 7. *SEM pictures.* ***A:*** *Photo paper, unsintered.* ***B:*** *Laser paper, unsintered.* ***C:*** *Photo paper, 110ºC 3min.* ***D:*** *laser paper, 150ºC, 20min.* ***E:*** *Photo paper electrically sintered at 1A, 1s.* ***F:*** *Laser paper electrically sintered at 1A, 1s.*

We note that these four types of sintering processes fall into three separate feedback mechanisms: Positive, negative, and neutral. Microwave and electrical sintering are positive feedback techniques in that as a portion of the film becomes more cured, the curing rate at that point increases which may lead to overheating or inhomogeneous curing of the film. The convection sintering method is neutral in its feedback in that the cure rate is only a function of the oven temperature. Photonic curing can be seen as a negative feedback process in that as the film becomes more cured, its reflectance increase, decreasing curing rate and limiting excessive curing.

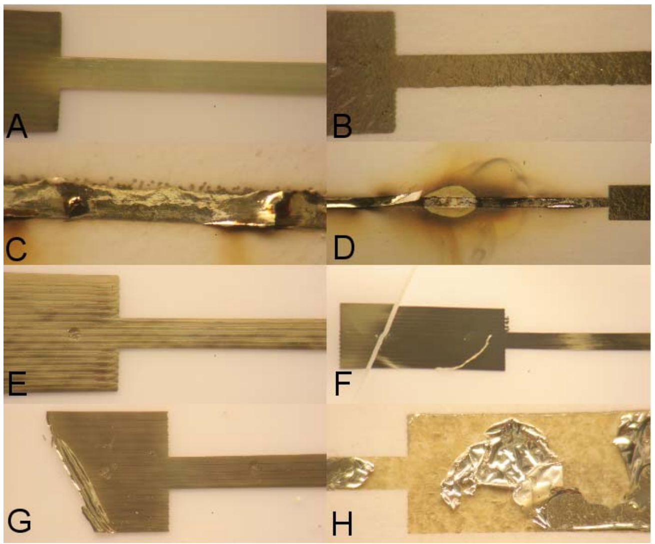

***Figure 8.** Sintered samples. **A:** Electrical sintering on photo paper at 1A, 1s. **B:** Microwave sintering on laser paper, 3s, rel.power 0.9. **C:** Electrical overheating on photo paper 1A, 1.2s. **D:** Microwave overheating on laser paper, 5s, rel.power 0.9 (note undamaged pad to the right) **E:** Photonic curing on photo paper at optimized exposure. **F:** Convection sintering, 130ºC, 1min. on photo paper (deformation in form of cracks in coating layer) **G:** Photonic overexposure on photo paper. **H:** Photonic overexposure on laser paper.*

Conclusion

When heat sensitive substrates are used, a selective sintering method with minimal heat transfer to the substrate is preferred. Each method has its application area and set of process parameters that needs to be optimized for the specific combination of ink and substrate. Not only is the resulting conductivity important but also the reliability and durability of the sintered metal-substrate combination, as well as the adaptability from a production point of view.

Convection sintering was limited to moderate temperatures due to substrate deformation, particularly on the photo paper where cracks in the coating layer appeared above 110ºC. Of the four methods tested, conductivity with convection sintering was the lowest.

With electrical sintering, the highest conductivity was achieved. However, as a contact method it may be complex and expensive to integrate in a production environment, and is further complicated if variations in conductor pattern or size is present.

With photonic curing, the conductivity on the laser paper was almost as high as on the photo paper. Delamination was the primary result of overexposure, indicating that sintering performance on the photo paper was limited by weaker ink adhesion.

Microwave sintering proved powerful, but was difficult to control, being sensitive to many parameters such as location, shape, and direction of the sample. Non-homogeneous sintering and fragility of the sintered metal was a problem. Using a more advanced microwave system with greater control over frequency, field distribution and short sintering times could be beneficial. Computer simulations would also be a valuable complement for looking further into microwave sintering.

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