Rapid Electrical Sintering of Nanoparticle Structures


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ABSTRACT

A method for rapid electrical sintering (RES) of nanoparticle structures on temperature-sensitive substrates is presented. For an inkjetted silver nanoparticle conductor, a conductance increase of five orders of magnitude is demonstrated to occur in a timescale that typically varies between a few and one hundred milliseconds depending on process parameters. Furthermore, most of the conductance change takes only a few microseconds. The achievable final conductivities are within a factor of two from the bulk silver conductivity, as calculated using the external geometric dimensions of the structure ignoring porosity. The method is also applicable to other inorganic conductors such as indium-tin-oxide (ITO). More generally, the method offers a versatile tool in nanotechnology for electrical functionalization of nanoparticle structures. The method is also potentially suited for mass production.

INTRODUCTION

Inorganic materials are gaining a significant role in printed electronics. Silver nanoparticle- and flake-based inks for realizing conductor structures are widely available from companies such as Acheson, Parelec, Cabot, Advanced Nano Products (ANP), InkTec, and NanoMas. Conducting and semiconducting metal oxide dispersions have been increasingly studied for transparent-conductor (ITO), solar-cell (CIGS) [1] and transistor applications (Si, ZnO) [2,3,4] with many advantageous properties such as electrical performance and environmental stability over the organic counterparts [5].

Curing at elevated temperatures is a necessary step to form a functional, continuous structure of the deposited inorganic particles, especially for nanoparticle-based inks. Although the typical required sintering temperatures (150°C...250°C) for the silver inks are only a fraction of the bulk material melting point (960°C) [6], they still limit the choice of the compatible paper or plastic substrates. Furthermore, the curing becomes even more challenging for metal oxide systems with higher melting points.

To overcome the challenges of high-temperature curing, we present the rapid electrical sintering method (RES) for nanoparticle structures [7,8]. One of the key merits of the method is that the sintering process is induced locally in the nanoparticle structure, thus significantly reducing the thermal loading of the substrate [7]. The electrical sintering method is an alternative to conventional thermal (oven) sintering, as well as to laser sintering [9], photonic sintering [10] and microwave sintering [11].
An example of the electrical sintering process is schematically shown in Figure 1. Here a conductor track with resistance $R_{tr}$ is first printed on a substrate. Next, a voltage $U$ is coupled between the contacting electrodes. A sufficient initial current flow and power dissipation in the nanoparticle structure is enabled by inter-particle tunneling and/or leaky particle encapsulant. As the temperature of the printed structure is increased, the resistance $R_{tr}$ decreases due to the reduced particle-particle separation which results in an increase of dissipated power $P_{tr}$ as given in Eq. (1), where $Z_s$ is the impedance of the voltage source including the contact resistance or reactance. Thus the voltage boundary-condition causes a strong positive feedback facilitating an extremely fast sintering. We have demonstrated a five orders of magnitude resistance drop in a few milliseconds (with the majority of the transition occurring in microseconds) [7].

$$P_{tr}(t) \sim U^2 \frac{R_{tr}(t)}{|Z_s + R_{tr}(t)|^2}.$$  

Figure 1: Schematic of the electrical-sintering setup. The series resistor ($|Z_s|=R_s$) is used to limit the maximum current in order to prevent overheating and damaging the conductor.

Further benefits of the method include, (i) control of the final conductivity by adjusting the process parameters such as the value of the bias resistor, (ii) area-specific sintering (direct writing), and (iii) suitability for non-contact processing. [7,12]

EXPERIMENT

The electrical sintering method was applied to rectangular test tracks printed using the Silverjet DGP-30LT-15C ink of ANP. The ink contains 34.5 wt% of silver nanoparticles, with particle diameters of 40–60 nm, dispersed in triethylene glycol monoethyl ether solvent. The structures were printed at room temperature onto a Siena 250G photopaper using a Microdrop Autodrop inkjet printer with a 40-µm head. The sintering experiments were performed using a standard computer-controlled DC power supply and data were recorded using a Tektronix DPO 4034 oscilloscope at 10^7 samples/s. In order to obtain information on the track temperature during the process, thermal images were acquired with a Cedip Titanium 560M infrared ($\lambda = 1.5 – 5.1 \mu m$) camera having a frame rate of 870 fps at 160 × 128 pixels. The IR camera was equipped with a microscope lens providing a pixel size of 5 µm. The SEM images of the nanoparticle structure were taken with a LEO Supra 35 microscope.

Figures 2 and 3 illustrate the behavior of the electrical sintering process by showing the data of sintering a track with size of 200 µm × 1500 µm using a total voltage of $U_{dc} = 90$ V and a series resistance of $R_s = 198 \Omega$. Tungsten probes with $d = 200 \mu m$ tips were used to make wide-area contacts to the track ends.
Figure 2 shows that approximately 30 ms after switching on the voltage, the resistance decreased suddenly by nearly five orders of magnitude, associated with a sharp peak in the dissipated power. The inset in Figure 2 (b) reveals the timescale of this transition to be only a few microseconds. This rapid behavior results from the positive feedback in the dissipated power (Eq. (1)). The power maximum occurs at the matched condition $R_{\text{tr}} = R_s$, after which power is mostly dissipated in the series resistor $R_s$ that limits the maximum current to 0.45 A.

Figure 3 shows IR images of the track during sintering. When converting the IR intensity into temperature, the surface emissivity ($\varepsilon$) has to be taken into account. The emissivity was determined by placing a similar sample on a hotplate and varying its temperature. It was observed that the electrical sintering decreases the emissivity of the nanoparticle ink from 0.64 to 0.17. For the photopaper, an emissivity of 1.0 was used. The three temperature values assigned to the palette in Figure 3 thus correspond to unsintered ink, sintered ink, and photopaper, respectively. The track geometry and the imaged area are shown in Figure 3 (a).

Figure 3 (b) shows the last recorded frame before the transition. The hottest path in the track has heated above 90 °C but the edges are clearly cooler. In the next frame (c) the transition has taken place resulting in a sintered path with decreased emissivity and higher temperature (about 130 °C). It should be noted, however, that the emissivity change is probably not step-like and therefore the temperature conversion may be inaccurate especially at the edges of the sintered area. Finally in (d), the sintered region has widened and reached the edges of the track and the temperature is around 100 °C. The formation of the sintered path followed by its widening can be caused by nonuniform sample thickness as revealed by AFM measurements. The thickness variation is largely due to the track being printed in four consecutive passes with an ink that wets more the previously printed areas than the bare substrate.

The emissivity-corrected temperature at the track and paper locations is plotted as a function of time in Figure 2 (c). While the track reaches 130 °C, the substrate temperature stays below 60 °C. The maximum track temperature coincides with the electrical transition, but the 1.15 ms time step between the IR frames was presumably too long to detect the true maximum temperature. A value of 180 °C – 250 °C for the peak temperature was estimated (assuming thermodynamic equilibrium) using the measured power dissipation data and modelling the heat-conduction dynamics either with finite elements (FEM) or with a one-dimensional analytical continuous model. The free parameters in the models were obtained by fitting to the constant-power heating of the pre-sintering phase. We note, however, that during the rapid transition, the electron and phonon gases in the system can locally deviate from thermodynamic equilibrium. Furthermore, heat release or capture in endothermic or exothermic phase transitions such as solvent evaporation are not taken into account in the modeling and due to the 10 MHz sampling rate of the oscilloscope, any processes faster than 0.1 µs are not correctly recorded.

The pre-sintering phase can be shortened by using a higher voltage. In [7], we reported sintering of a 60 µm × 500 µm track in 3 ms. For the present paper, a longer pre-sintering phase was used simply to better comply with the maximum frame rate of the IR camera. The measured final resistance between the two probes was about 2.5 Ω. However, due to a significant contact resistance between the tungsten probes and the printed structure, the true final material resistivity is significantly smaller. Using four-point resistance measurement, and an AFM-determined layer thickness of 1 µm, the typical final conductivities approach the bulk silver conductivity of $6.3 \times 10^7$ S/m. The maximum conductivity obtained so far with electrical sintering is $3.7 \times 10^7$ S/m [7] as calculated for the external geometric dimensions of the structure which ignores porosity and thus overestimates the particulate structure volume and underestimates the material conductivity.
Figure 2: Electrical sintering process as a function of time. t = 0 is the moment when the voltage source was switched on. (a) Total voltage $U_{dc}$ applied over the circuit and the measured current $I$ ($R_s = 198 \, \Omega$). (b) Track resistance $R_{tr}$ and the power $P_{tr}$ dissipated in the track. The inset shows the transition region. (c) Temperature $T$ of the track (1) and the paper substrate (2) based on IR imaging. The temperature measurement locations are indicated in Figure 3 below, and the temperature values are corrected for the variable emissivity. The temperature behavior over a longer period is plotted in the inset with the dashed line showing the moment when the voltage was switched off.

Figure 3: IR images of the track at different phases of the sintering process. (a) Sample geometry, (b) the last frame before the transition, (c) the first frame after the transition, and (d) a frame 18.7 ms after the transition. The temperature measurement locations for Figure 2(c) are indicated with the white lines (1) and (2) and the edges of the track with brown dashed lines. Three temperature values are assigned to the palette corresponding to emissivities of 0.64 (unsintered ink), 0.17 (sintered ink), and 1.0 (paper).
Figure 4 shows the effect of the sintering on the nanoparticle layer structure. A key parameter, strongly correlating with the particle growth and neck formation, is the peak power $P_{tr,max}$ which is determined by the applied voltage $U_{dc}$ and the series resistance $R_s$ (Eq. (1)).

Figure 4: SEM images of the nanoparticle structures obtained using different sintering powers.

For wide conductors, the process in Figure 1 becomes problematic because the widening of the sintered area, as discussed above, slows down and can stop before reaching the conductor edges. Therefore, for wide conductors such as antenna structures, we have used the non-contact AC sintering as schematically illustrated in Figure 5. The lateral sintering current is here capacitively coupled to the ink layer. A high frequency of 1.8 GHz was used to minimize the reactive load-impedance component. Figure 6 shows a resulting position-dependent conductivity of a 3-mm-wide track printed with ANP DGP-45-LT ink on the Siena photopaper, as measured using a scanning surface-impedance measurement similar to the writing setup in Figure 5 but at 50 MHz. The sintering was done in three consecutive passes of the probe tip over the track as indicated by the arrows in Figure 6(b). With 40 V sintering voltage and 10 mm/s scanning speed, the four-point-measured DC sheet resistance of the printed track decreased from more than 60 k$\Omega$/□ to 1 $\Omega$/□. The layer thickness of the conductor was approximately 1 $\mu$m.

Figure 5: Vertical AC sintering setup.

Figure 6: Measured sheet resistance of a 3-mm-wide track before (a) and after (b) AC sintering. The arrows in (b) indicate the movement of the non-contact AC sintering head.
CONCLUSIONS

A rapid electrical sintering method for printed nanoparticle structures is described. The method is based on electrical power transfer into the printed structure significantly reducing the temperature loading of the substrate compared, for example, to oven sintering. The sintering can be done very rapidly. Namely, relative resistance changes of $\sim 10^5$ has been demonstrated in milliseconds for silver nanoparticle structures. The final sintering degree (conductivity, grain growth) can be controlled, e.g., by adjusting the delivered maximum power. Full-width DC sintering has been achieved for 300 µm wide tracks. For wider conductors, the non-contact AC sintering can be applied. Critical for the method is a sufficient initial conductivity of the material, which for the studied silver nanoparticle systems, has been found to be provided by inter-particle tunneling and/or leaky surfactant. The intra-particle conductivity becomes crucial for non-metallic systems such as semiconductors. For ITO, our preliminary experiments have revealed successful sintering. In general, the demonstrated method offers a significant promise for a versatile electrical functionalization of nanoparticle systems.

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REFERENCES