The ink jet printing of high conductivity circuits on various substrates using polymer capped nano-particle silver

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Abstract

In this paper, we describe how specially developed polymer capped, nano-particle silver inks can be used to print circuitry for applications like displays, RFID antennas and "disposable electronics". The requirements of printing on temperature sensitive flexible substrates (such as polymer films and papers) that require low temperature curing is also discussed.

1. Introduction

Unlike inks developed using traditional metallic flake, nano-particle metals like silver demonstrate the ability to sinter into a contiguous layer at temperatures well below their melting point. In this paper we discuss >50nm silver particle inks that have been used to print conductive features on a variety of substrates. The intent is to provide a highly conductive electronic feature with maximum materials utilization in the IJ printing process. Several technical issues need to be addressed in the IJ printing and processing of these types of silver circuits. This paper discusses results obtained using the Spectra SE print head. Due to the cost of the material and the goal of many manufacturers to optimize material performance and device cost, the ability to IJ materials, specifically conductors, is becoming more of a viable option.

2. Nanoparticle Silver Inks

Nanoparticle inks are stable dispersions of nanoparticles in a liquid vehicle. Cabot inks contain surface modified ultra-fine particles that are engineered for a particular electronic application, making it possible to reliably inkjet print the nanoparticles and form high resolution electronic features on a variety of substrates.

Because metal nanoclusters have reduced melting and sintering temperatures as compared to their micron-sized counterparts, these inks can be processed at temperatures as low as 100 ºC. This enables printing of highly conductive metal features on low cost substrates such as paper, polymer, and glass. Figure 1 shows an example of IJ printing of Silver nanoparticle ink on medium density coated paperboard.

Figure 1. Example of Ink Jettable Silver nanoparticle ink capabilities. This image is an example of Cabot Corporation's Customer Demonstration coupon printed on medium density coated paperboard.

After low-temperature sintering, a continuous percolation metal conductor is formed, providing a very good channel for the conduction electrons to flow throughout the material without obstacles. Note that this is radically different from the traditional polymer thick film material approach, which uses metal flakes.

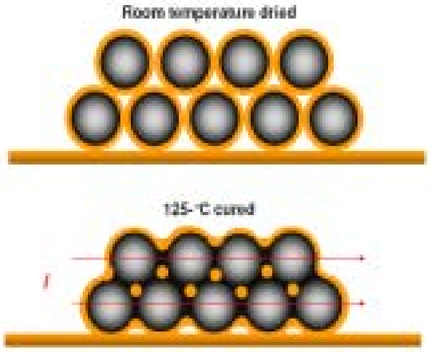


Figure 2. Schematic of structure and charge transport in a Low-T cured printed Ag layer.

Not only are these flakes hard to print, they are also inferior in terms of their electrical performance which suffers from an unreliable contact resistance between touching flakes.

3. Physical Properties of Printed and Cured Ink

The nanoparticle ink consists of two basic components: particles and a liquid vehicle. The liquid vehicle provides the liquid properties to the ink, enabling it to be printed and dispensed onto the substrate. The nanoparticles have two main components: a metal core and a polymeric shell. The polymer shell stabilizes the particles, preventing agglomeration in the liquid phase and providing surface functionality that enables stable dispersion in the liquid vehicle. After printing, the liquid vehicle is evaporated and the polymer shell no longer serves any of the two functions described above. In fact, the polymer is now an obstacle for sintering and for charge transport.

The polymer shell in Cabot Corporation's nanoparticle silver ink has been designed to allow for sintering at very low temperatures (100-150 ºC). This means that the polymer shell will not volatilize at these low temperatures, but rather move out of the way, allowing the metal cores of the particles to touch and sinter together. This mechanism is illustrated in the SEM images shown in Figure 3.

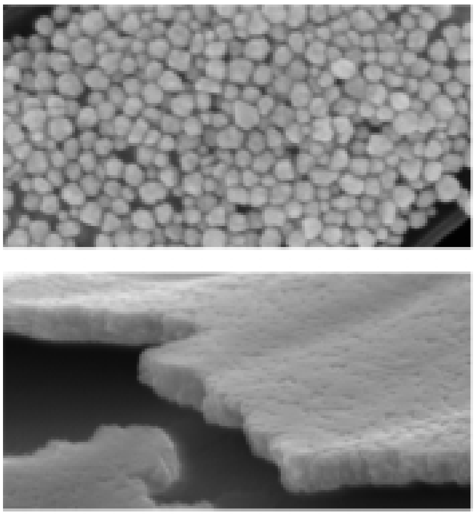


Figure 3. SEM images of a layer of printed ink, before and after a 10 minute cure at 180 °C

The polymer shell now provides a new function: it promotes adhesion of the printed film to a range of polymeric substrates such as FR4 or Mylar® (PET) and provides structural strength. As a result of the low-temperature sintering mechanism, a continuous percolation network is formed that provides continuous channels for the conduction electrons to flow throughout the material without obstacles. Note that this is radically different from the traditional polymer thick film approach, where electrical conductivity is established during thermal curing as a result of polymer matrix shrinkage, inducing compressive stress on the flake particles causing a reduction in their large contact resistance.

4. Electrical Performance and Resistivity of Cured Nanoparticle Ink Films

After the ink is printed on the substrate, it needs to be heated to yield the desired electrical performance, adhesion, and abrasion resistance. This heating can be accomplished in a variety of ways such as hot plate, convection oven, infrared radiation, laser radiation, UV exposure, etc. In general, the resistivity of a printed line will drop with curing temperature and curing time. The detailed time-temperature profile may also play a role: for example drying the ink at 80 ºC before heating it to 120 ºC may result in a line with a lower conductivity than a line that was printed and immediately heated to 120 ºC without allowing it to dry.

The electrical performance is often described in terms of the bulk resistivity of the cured lines. These values are obtained by measuring the resistance (R) of the printed line, the length (l), and the average cross sectional area (width times thickness: $w \cdot t$). The bulk resistivity (ρ) is calculated using the equation: $\rho(\Omega \cdot \mathrm{cm}) = R\,(\Omega) \cdot w \cdot t/l\,(\mathrm{cm})$. Figure 4. illustrates the change in resistivity with increasing temperature.

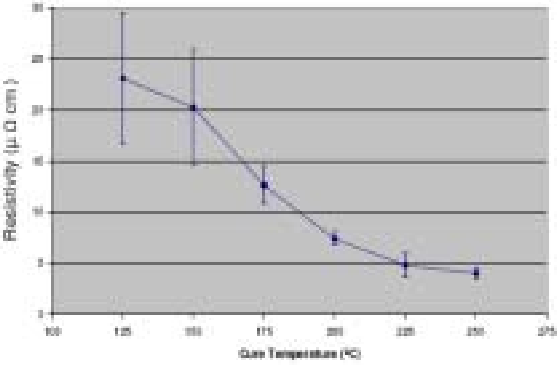


Figure 4. Resistivity versus temperature for constant cure durations

5. Sheet Resistance and Predictive Performance for Ink Jet Printed Features

Using the bulk resistivity value of the printed conductor and comparing it to the bulk performance of fully dense silver with the same geometry (length, width, and layer thickness) is somewhat misleading for inkjet printed Ag lines. This is especially true when a low curing temperate (below 150 ºC is used). In these cases, the final deposit has a significant amount of residual porosity and polymer content (the capping agent). For these layers the Ag content can be less than 50 % of the total volume. Conductivity in these materials is accomplished through necking of the Ag particles, creating an efficient percolation network. It is therefore more straightforward to compare the sheet resistivity (expressed in Ω/□) of a printed layer to the sheet resistivity of the equivalent solid Ag layer that has the same Ag content per unit area as the printed layer. The amount of Ag per unit area can easily be calculated from the dots per inch (dpi) data contained in the print file, inkjet drop volume, and the solid loading of the ink provided in the ink specification sheet. Figure 5 and Table 1 show the basic principle of continuous feature inkjet printing by adequate drop placement, taking into account ink drop volume and wetting behavior on the substrate.

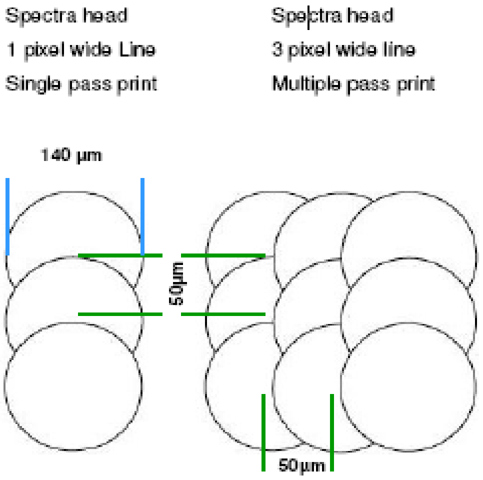
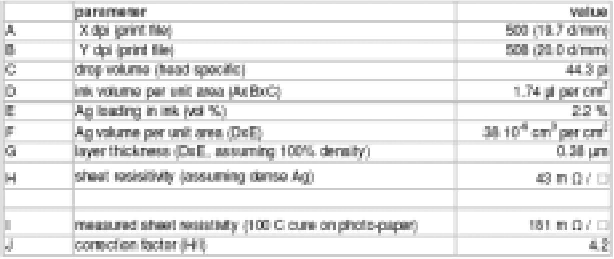


Figure 5. Ink Jet Drop Placement



	parameter	value
A	X dpi (print file)	500 (19.7 d/mm)
B	Y dpi (print file)	508 (20.0 d/mm)
C	drop volume (head specific)	44.3 pl
D	ink volume per unit area (AxBxC)	1.74 µl per cm^2
E	Ag loading in ink (vol %)	2.2 %
F	Ag volume per unit area (DxE)	38.10^{-6} cm^3 per cm^2
G	layer thickness (DxE, assuming 100% density)	0.38 µm
H	sheet resistivity (assuming dense Ag)	43 m Ω / □
I	measured sheet resistivity (100 C cure on photo-paper)	181 m Ω / □
J	correction factor (H/I)	4.2

Table 1. Ink Drop Characteristics and Resulting Sheet Resistivity

The worksheet in Table 1 provides an example of how to predict the performance of the Ag ink in an inkjet printed feature. In this specific example, lines were inkjet printing with a Spectra SE-128 head on a photo-paper substrate. The performance of the printed trace compared to the equivalent fully dense feature (optimum performance) yielding a correction factor for this particular application. Using this general approach, an application specific scaling factor can be calculated for any application by measuring the sheet resistivity value of a printed feature and correlating it to the other parameters. The application specific formula of the form (0.016 x 4.2 X µm x Ω/□) / (A x B x C x E) can then be used to accurately predict the performance of printed features for a specific ink (volume loading), a specific print file (dpi), print head parameters (drop volume), substrate, and curing process (correction factor).

6. Conclusion

Many advances in IJ printing of conductive circuits have been made over the past few years, enabling the technology to reach a point in the near future that will allow it to be a viable manufacturing alternative to present methods of conductor fabrication such as lithographic design and screen printing. Much of the advancement in IJ technology for purposes of electronic component fabrication is due to the development of Nanoparticle silver inks. This polymer capped nanoparticle silver ink allows for reliable ink jet deposition resulting in highly conductive features at that can be created using low sintering temperatures.