Proc. X National Conference with International Participation Conference "Electronica 2019", May 16 - 17, 2019, Sofia, Bulgaria

Sintering Temperature Impact on Sheet Resistance of Inkjet Printed Layers

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Abstract – **Printing technologies for the production of conductive layers and electronic devices are well developed because they use cheap materials and printers as well as fast methods for layer treatment. Still a major challenge for their application is that there is no information on the electrical parameters of the inks and substrates used, especially depending on the method of obtaining the structures. This paper explores the impact of sintering temperature on sheet resistance of three topologies on two types of substrates.**

Keywords – **Nano-silver conductive ink, Sintering, Resistivity, Sheet resistivity.**

I. Introduction

The continuous improvement of microelectronic and nanoelectronic technologies inevitably leads to new demands on the sensing elements and the materials from which they are manufactured. Some additional requirements are related to wider use of sensor components in process management, environmental monitoring and healthcare. Despite the fact that traditional silicon technologies are still dominant in the production of sensor elements, over the last ten years, designers and researchers have been increasingly interested in applying the unique properties of various innovative materials to the needs of sensor technology. Another stimulus for the development of this technology is the fact that R & D develops nanocomposite inks that are used with conventional inkjet printers. That allows for the development of prototype sensors in general research laboratories without the need for expensive and high-tech equipment. In this way, various design ideas can be applied with respect to the composition and form of the printed sensor elements and the analysis of their static and dynamic characteristics [1].

Printing electronics can be applied in various fields of electronics such as solar cells, electromagnetic shielding, displays, printed circuit boards, lightings, sensors, chemical sensors, biosensors, etc. The general requirement for all printing technologies is that the printing materials must be ink solutions which may consist of functional materials, such as metallic nanoparticles (Al, Ag, Au, Cu, etc.), single and multilayer carbon nanotubes, graphite, ceramic particles, conductive polymers (PEDOT, PPS, PANI) biomaterials, etc. In order to obtain the desired viscosity and surface tension, the composition of the inks may require additional materials such as solvents, primers and insulators [1].

A major problem in the design of printed sensor elements is that there is no information about the electrical parameters of the used inks and substrates. In previous papers, we reviewed the different types of inks [1] as well as the different properties of flexible substrates [2]. It is worth noting that the electrical characteristics of the ready printed structures also depend on the way they are produced. This paper focuses on the study of the impact of the sintering temperature and time on sheet metal impedance of printed electronic structures.

II. Sintering Process

The most commonly used conductive inorganic inks are based on nanoparticle technology. Metal nanocrystals (5 - 100 nm) are encapsulated in them by a process of sealing. These particles are then sprayed into a plain inkjet printing solution. After spraying on the substrate, a heating or pulse irradiation process is applied with ultraviolet light, evaporating the solvent, decapsulating and melting the nanoparticles to form a thin metallic layer. That type of metal nanoparticle ink such as gold, copper and silver has been available for several years on the market. Carbon nanoparticle inks for resistive ink are also being developed. Although silver and gold nanoparticle inks are much more expensive than those with copper particles, they are more often used. The reason for this is that the copper is oxidized in the air, which reduces its conductivity. The development of this type of ink is mainly in the direction of better printing of electronic elements (passive and active) and various sensors.

In order to reduce the ink to its corresponding metals, a sintering stage is required. Sintering is the atomic diffusion process of the material, depending on the reduction of energy between the metal particles. Figure 1 shows the process of sintering conductive nanoparticle inks. The required melting temperature for nanoparticles is determined by their size and the method of encapsulation. The melting point of the particles is much smaller due to the high surface to volume ratio. For example, gold nanoparticles encapsulated with butanethiol of 1,5 nm are melted at temperatures around 120°C (for comparison, gold melts at 1064°C). Due to their high conductivity and very low

978-1-7281-3622-6/19/$31.00 ©2019 IEEE

melting temperature, conductive inks are most commonly used with silver nanoparticles.

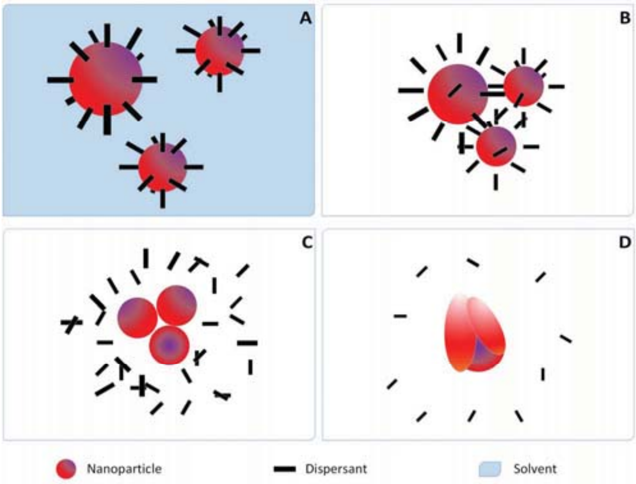


Fig. 1. Scheme of the sintering process of nanoparticle inks: A) before heating; (B) the solvent is evaporated and decomposition by heat begins; C) initiation of sintering; and D) a sintering coating

There are four possible ways of diffusion during sintering between the two particles shown in Figure 2. Variants 1 and 2 do not result in densification, whereas Variants 3 and 4 achieve this. Densification occurs only when the distance between the particle centres changes [3].

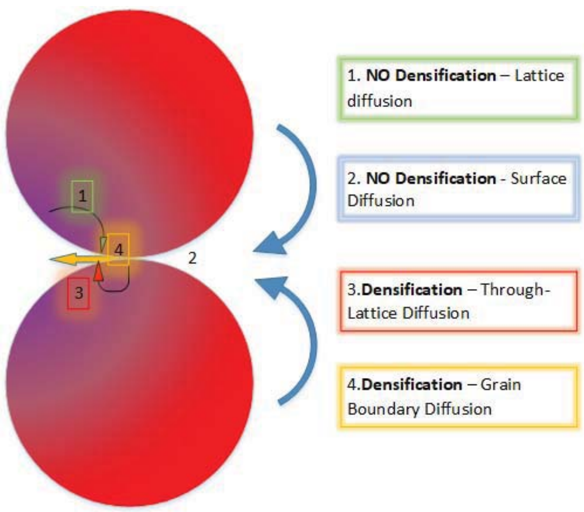


Fig. 2. Possible diffusion paths between two metal particles during sintering [3]

Sintering can be achieved at a low temperature due to the high ratio of surface volume to nano-particle volume [8]. Two different sintering techniques can be used. There is thermal sintering and sintering through ultraviolet impulses. The most commonly used method is thermal sintering. Sintering temperatures for this process are usually above 200ºC. That, however, limits the types of substrates that can be used, as most of them do not withstand these temperatures. Sintering with ultraviolet impulses follows the printed layer and processes it only without affecting the substrate. It is more effective from this point of view, but requires more expensive equipment.

Sintering not only makes the printed layers conductive, but also impacts the physical and electrical properties of the layers of metal nanoparticles themselves. A basic property associated with sintering is resistance. At lower sintering temperatures, the resistance of the printed nanoparticle layers can be up to 2 to 3 times lower than its calculated resistance [3].

The percolation theory of conductivity describes the statistical behaviour of the electrical conductivity in the silver nano-ink system. When electricity passes through that group of nano-silver structures, the particle energy is likely to interfere from one particle to another. This probability depends on the sintering density of silver particles in the structure where the probability of permeation is extremely low to reach a certain percentage. This percentage is called the percolation threshold. The permeation threshold can be determined experimentally for different systems. In order to obtain good conductivity in the printed ink layers, the degree of sintering is essential [3].

III. Experimental development

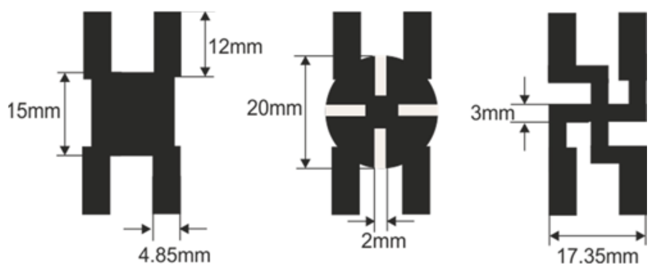
A. Materials

For the purpose of this study, Metalon JS-B25P nano-silver conductive ink from Novacentrix [4] has been used. The main parameters of the ink are: silver nanoparticles diameter 75 nm, Ag nanoparticles concentration 25%, coated with ethylene glycol, sintering temperature up to 100°C, submerged in polyethylene glycol 4 (tert-octylphenyl), sheet resistance imprinted on Novele IJ-220 pad about 60-70 mΩ /□.

The structures are printed using Epson C88 + Stylus printer on two substrates: Novely IJ-220 PET-based (poly-ethylene terephthalate) transparency film for printed electronics for low cost and low temperature applications from Novacentrix and bond uncoated paper

B. Test Structures Preparation

A modified version of the Van der Pauw method was used to measure sheet resistance. For this purpose, three different topologies are designed, shown in Figure 3. Their shapes and dimensions correspond to this method.



a) b) c)

Fig. 3. Different forms of printed structures

For the purpose of the study presented herein these forms are printed with three layers of conductive ink on two types of substrates: Novele PET and paper. Figure 4 shows photos of the three structures printed on Novele PET.

After printing, the printed layers were transferred to a hotplate to be cured. The sintering conditions selected for this study were 60ºC, 80ºC, 100ºC and 120ºC for 60 minutes. The resistances of each of the printed layers were measured after sintering and one was left at room temperature.

With each layer of three different forms for each pair of temperature and time curing condition, a total of 12 PET layers of samples and 12 paper layers were prepared.

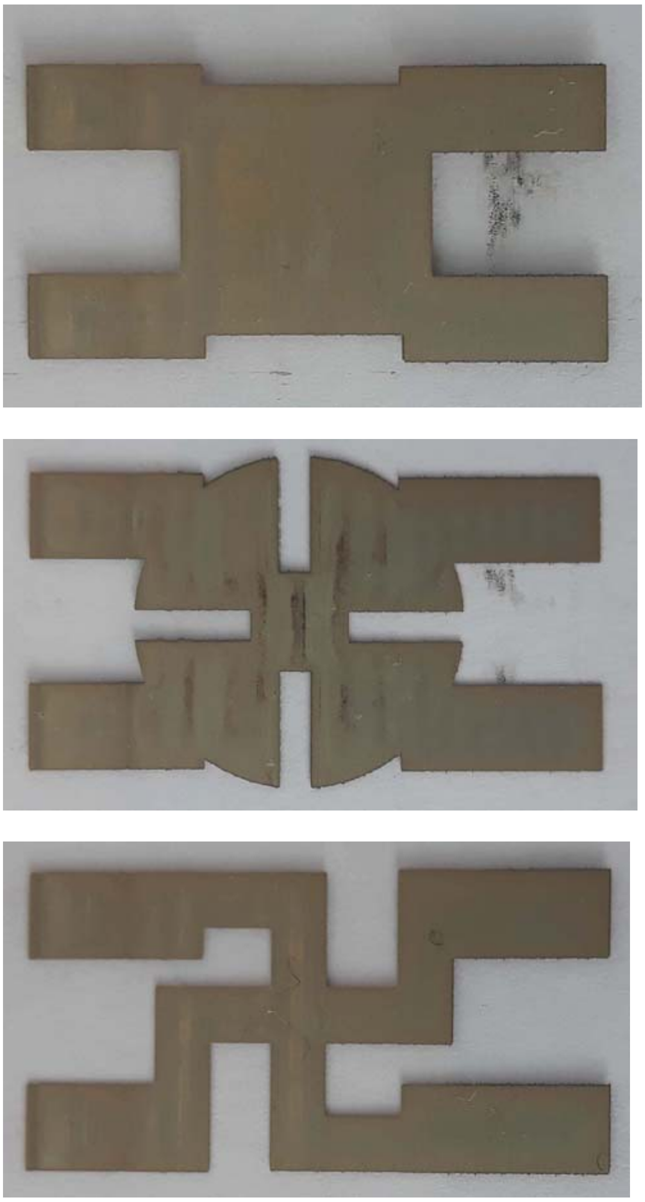


Fig. 4. The three different shapes, printed on PET

C. Measurement Method

To measure sheet resistance by the Van der Pauw method, in this study we use Keysight's U2722A USB Modular Source Measure (SMU) [7]. In this case, two of its modules, which operate in a power source mode, a voltage meter, are used.

After printing and sintering, the structures are cut and mounted in the designed and realized test fixture as can be seen in Figure 5.

Sheet resistance is calculated using the following equations [5, 6]:

$$R_S = \frac{\pi . R}{\ln(2)}, \quad R = \frac{R_{AC,DB} + R_{DB,AC} + R_{CA,BD} + R_{BD,CA}}{4}, \tag{1}$$

where:

$R_{AC,DB}$ is the topology resistance, when the current is driven into contact A and gets out from contact C, and the voltage is measured through contacts D-B (the denotions correspond to these in Fig. 5);

$R_{CA,BD}$ is the reciprocal resistance of $R_{AC,DB}$ i.e., when the current is driven into contact C and gets out from contact A, and the voltage is measured through contacts B-D;

$R_{DB,AC}$ is the structure resistance, when the current is driven into contact D and gets out from contact B, and the voltage is measured through contacts A-C;

$R_{BD,CA}$ is the reciprocal resistance of $R_{DB,AC}$ i.e., when the current is driven into contact B and gets out from contact D, and the voltage is measured through contacts C-A.

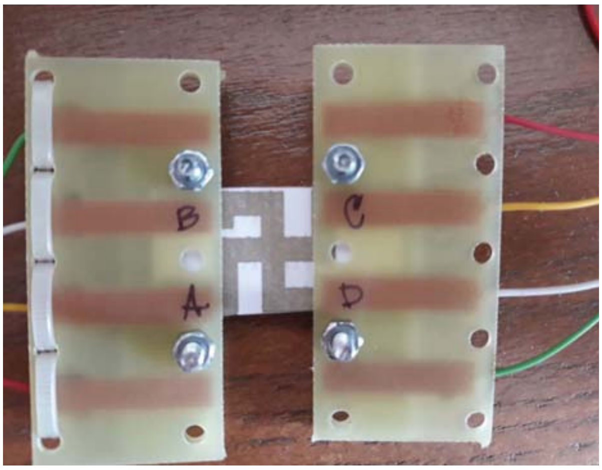


Fig. 5. The test fixture

The above resistances are calculated using Ohm's law at a DC current of 100 mA and the voltage measured at the corresponding coupling configuration.

IV. Results and Discussion

In Table 1 the defined values for the sheet resistance are given in mΩ/□ for the three structures printed on Novele PET and paper. The resistances are measured at four sintering temperatures (60°C, 80°C, 100°C и 120°C) for 60 min, and also structures which are not sintered.

Figure 6 shows the results for all three structures printed on Novele PET substrate. Generally, the resulting sheet resistance value corresponds to that given by Novacentrix, taking into account that three layers of ink have been printed. As can be seen the optimal sintering temperature on this substrate is 100°C because at 120°C or the resistance increases or tends to saturation. It should also be borne in mind that with the equipment used, resistances of the order of several milliohms are measured with a greater error as they reach the resolution of the measuring system.

TABLE 1. SHEET RESISTANCE IN mΩ/□ FOR THE DIFFERENT STRUCTURERS

Form, substrate	Without sintering	60°C	80°C	100°C	120°C
Cross, PET	5,89	9,29	9,40	4,08	5,33
Cross, paper	4050,48	5374,05	2876,12	578,74	3227,58
Disc, PET	5,55	15,18	15,18	6,80	36,14
Disc, paper	2531,80	8663,37	4856,04	1713,10	3453,38
Square, PET	143,55	53,82	50,76	30,82	25,72
Square, paper	2441,96	8317,01	12033,14	10705,72	2366,38

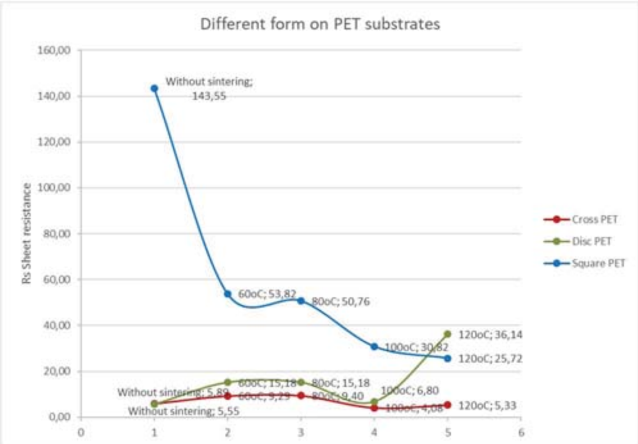


Fig. 6. Sheet Resistance in mΩ/□ for different form on Novele PET substrate

Similarly, Figure 7 shows the results obtained for the sheet resistance using the paper substrate. As can be seen the resulting resistances are much larger and heavily dependent on the sintering temperature, which means that the paper parameters also change significantly and its use as a substrate is not recommended. However, for not very dense layers (such as Square), the optimum sintering temperature is again 100°C.

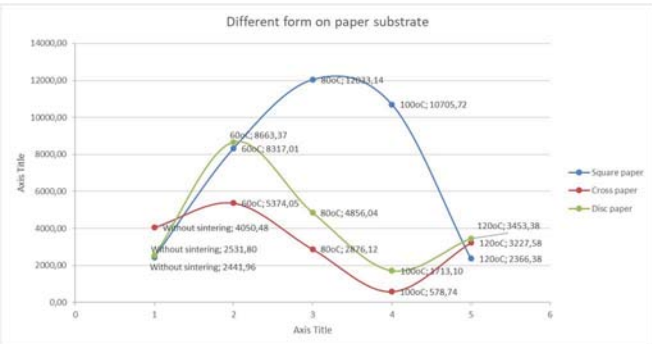


Fig. 7. Sheet Resistance in mΩ/□ for different form on paper substrate

From Figures 6 and 7 it can be seen that quite small resistances are also obtained when the structure is not sintered. It is worth noting that the layers thus obtained are quite unstable and their parameters will change with time and with change of ambient temperature and humidity. Also, if the structures are not sintered, their mechanical properties are not very good either.

V. CONCLUSION

The present paper presents research of the impact of sintering temperature on the sheet resistance of different printing structures. For this purpose, three different topologies were designed, printed by nano-silver ink on two types of substrates: Novele PET and paper. The measurements performed show that the electrical parameters of the printed structures, in addition to the ink and substrate used, depend heavily on the shape of the structure.

From the above study it can be seen that for most test structures the optimal sintering temperature is 100°C for a period of 60 minutes. The applied experimental results can be used in the design of various sensor elements using the described technology. Also, through the proposed approach, the impact of the conditions (temperature and time) of sintering and other electrical parameters of printed structures can be explored.

ACKNOWLEDGMENT

This work was supported by NIS project No 191PR0001-03 /02.2019.

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