Functional Materials for Printed Sensor Structures

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Summary: Today, printing technologies like Ink Jet - printing or Aerosol Jet® - printing are used not only for printing graphics. The printing of electronic structures using metallic nano-particulate dispersions as so called “functional inks” followed by a thermal consolidation process for full functionality is of special interest. For a customized packaging, also ceramic and organic materials are taken into account, requiring flexible technologies for deposition of different materials. For a further miniaturization, for many electronic and sensorial applications smaller structures are needed. Non-contact printing technologies are often a suitable solution to generate these functional structures of very different materials for various new applications. INKtelligent printing® combines the structuring possibilities of maskless printing technologies with the functionality of micro- and nano-scaled functional materials to generate functional structures like conductors, resistors and even sensors or sensor arrays, respectively. The functional structures are printed onto different flat or non-planar substrates like wafers, glass substrates, polymer foils or non-planar components. Typically, the structures have to be consolidated after printing, i.e. in a furnace, by use of laser treatment or high energy irradiation.

Keywords: Sensors, Alloy, Deposition.

1. Introduction

In recent years, digital printing has become more and more attractive. In contrast to conventional manufacturing methods which are mainly *subtractive*, new classes of manufacturing techniques have been established offering to manufacturers significant benefits regarding cost, time and quality across a broad spectrum of applications. These new techniques are collectively known as *additive manufacture*. During additive manufacture, material is deposited layer-by-layer to build, e.g., multilayer or three-dimensional parts or structures. Features of additive manufacturing processes include direct CAD-driven, “Art-to-Part” processing.

A much greater design flexibility offers the potential for revolutionary new end-products with improved performance based on novel size, geometries, materials and material combinations. The typical size for drops in Ink Jet - printing processes is about 50 µm in diameter, resulting in a drop volume of about 60 pl, restricting the viscosity to a few mPa s. The viscosity and the size of the generated drops in Ink Jet - printing limit the possibility of miniaturizing structures down to about 50 µm. Aerosol Jet® enables a further miniaturization of deposited structure below 20 µm, and allows a very flexible packaging with very different materials on a large variety of substrates [1]:

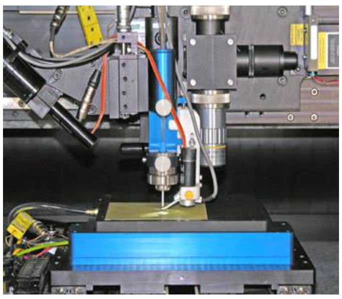

Figure 1. Aerosol Jet® technology (Optomec Inc.).

The Aerosol Jet® technology allows deposition of suspensions and material formulations covering a viscosity range from 0.7 to 1000mPas and a particle size up to 1µm for metal particles. An aerosol is produced from the suspension which is carried by a transport gas to a print head (fig 1). The aerosol is produced either with the help of an ultrasonic source (as seen in fig. 1) or with the help of a high velocity air stream. The aerosol droplet diameter is between 1 and 5 µm, which corresponds to a volume of some femtolitres. Inside the print head a sheath gas (e.g. nitrogen) focuses the aerosol beam and also prevents clogging of the nozzle. Besides, the focused aerosol beam allows printing on planar and non-planar surfaces with a minimum line width of about 10 µm. The printing process is followed by a thermal activation step to evaporate the fluid and to compact the printed structures. Oven sintering, laser- and UV-curing are possible solutions to ensure a best functionality and a high surface adhesion of the deposited structures. A laser or low-level oven sintering process guarantees faultlessness of the substrate and electrical conductivity of the printed sensor structure. Dielectric materials as well as high-viscosity globe-top materials, for example, can be deposited by aerosol-printing and consolidated by e.g. UV-curing, if necessary.

2. Material development for maskless printing

2.1. Deposition of conductive silver structures

To highlight the potential of maskless printing, a commercially available silver ink from Advanced Nano Products Co., Ltd., (ANP) can easily be deposited on different surfaces. The ANP material (ink) contains about 50–60 wt.% of silver with a mean particle diameter of about 20 nm. To prevent agglomeration of particles, the ink contains about 20-40 wt.% solvent as well as about 10–20 wt.% additives. Additives are necessary to avoid agglomeration and sedimentation of the silver particles as well as to lower the sintering temperature. The following figures show SEM images of the ink before printing (Fig. 2.a), after Aerosol Jet® deposition (Fig. 2.b) and after furnace sintering at 350°C (Fig. 2.c) under hydrogen atmosphere (60 min, heating rate 5 K/min). The ink has a homogeneous particle size distribution without agglomerates before printing. After deposition, the particles agglomerate to silver spheres with a diameter of around 1 µm and form a porous structure. After sintering at 350°C the silver particles are connected due to diffusion processes resulting in a condensed structure. Details are given in ref. [2]

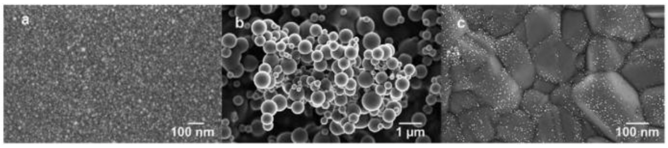

Figure 2. SEM images of (a) silver ink, (b) silver ink after aerosol printing and (c) silver ink after aerosol printing and furnace sintering @ 350°C, 60 min, heating rate 5 K/min [2].

Fig. 3 shows the dependence of the conductivity of printed silver structures on sintering time. For this purpose, test structures (van-der-Pauw-geometry) have been printed and sintered at T = 350°C and variation of sintering time from 60 to 600 min. There are no large differences in the measured conductivities which reach values of about 50–70% compared to bulk silver (6.25 x 10^7 Sm^{-1}).

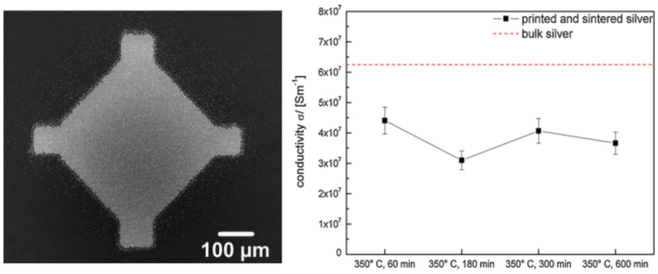

Figure 3. Left: Printed silver test structures, right: measured electrical conductivities.

Higher conductivities are difficult to achieve due to additives remaining in the structures even after a thermal post treatment.

2.2. Printable alloys

In addition to noble metals, certain alloys have unique conductive properties. The electrical resistivity of e.g. CuNi44 alloy is almost temperature independent and shows considerable strain sensitivity, which makes CuNi44 a very interesting material e.g. for strain gauges, but also for printed resistors. However, in contrast to the preparation of noble metal inks, the preparation of an alloy ink is much more complex. Various chemical methods such as hydrothermal reduction, solution combustion, sol-gel process, diol- and polyol reduction method, water-in-oil (w/o) microemulsion technique etc. have been used for the preparation of alloy or bimetallic nanoparticles.
Fig. 4 presents recent results of electrical characterization of printed CuNi van-der-Pauw – structures with various Cu:Ni ratios. Details of the preparation routes are given in reference. [3].

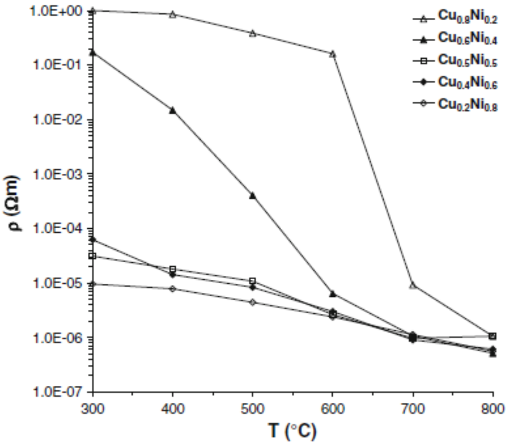

Figure 4. Resistivity change of printed alloy layers as a function of sintering temperature [3].

As seen in fig. 4, colloid chemical preparation of CuNi alloy inks leads to electrical conductivities in printed van-der-Pauw test structures suitable to facilitate sensor applications[3]. Similar studies focussing on the alloy composition Cu55Ni44Mn1 are discussed in reference [4].

3. Printed sensor structures

In the following chapter, strain gauges and thermocouple sensors deposited by use of Aerosol Jet® will be discussed:

3.1. Printed strain gauges

The printed strain gauges consist of three different material layers, all deposited with Aerosol Jet® technology. First, a polymer layer (Duraseal 1529H) with a thickness of about 5 µm is printed and cured to isolate the sensor from the metal substrate. In a second step the silver layer (ANP) with a thickness of about 1–3 µm in form of a meander structure is deposited. Finally the sensor is encapsulated again with a polymer (Duraseal 1529H). Fig. 5 shows an example of the three layer printed strain gauge package on an aluminum surface. Details are discussed in ref. [5].

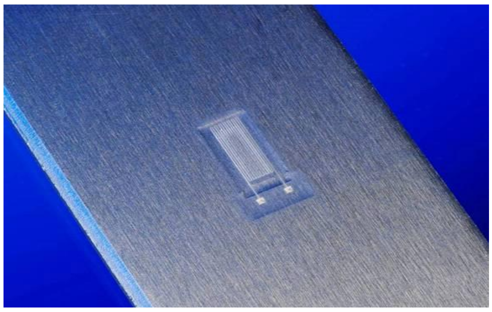

Figure 5. Printed silver strain gauges on aluminum surface.

For the characterization of printed silver strain gauges, a second strain gauge was printed on the metal surface in a 90° rotated position to avoid temperature influences caused by the high linear temperature coefficient of resistance of silver. In addition, a reference foil strain gauge (HBM Inc.) was glued on the substrate for comparison of the results. Fig. 6 shows the results of periodic stress (1000N tensile stress and 500N compressive stress) measurements of 1000 cycles with 0.5 Hz. Results show a constant peak to peak value of the printed strain gauge indicating reliable and reproducible signal and successful temperature compensation.

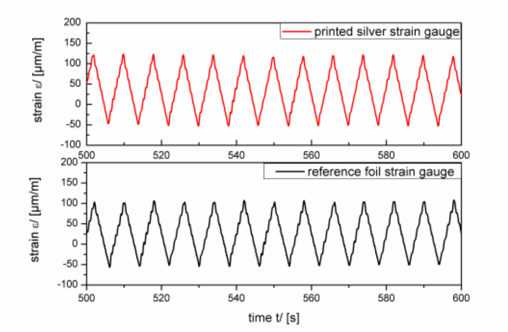

Figure 6. Characterization of printed strain gauges.

3.2. Printed thermocouples

INKtelligent printing® also allows the direct deposition of thermo couples on planar and non-planar surfaces and components. Thermocouples consist of two different materials, e.g. two different metals, and they produce an electrical voltage which is proportional to a temperature difference between a "hot" and a "cold" junction. A thermoelectric voltage results between the two junctions which is proportional to the temperature difference of the materials. Fig. 7.a presents a thermopile consisting of five silver-nickel thermocouples (details of the nickel dispersion preparation are given in [2]. The serial connection increases the voltage output compared to a single thermocouple. Figure 7.b indicates the measurement results of a thermally stressed thermopile. The sensor performance was characterized by using a hotplate to heat up the hot junctions while the output voltage was recorded in dependence of the temperature. The black curve shows the thermoelectric voltage while the red curve displays the temperature of the hot junction. The measurements show a good performance of the printed thermopile indicating that the thermoelectric voltage is proportional to the temperature difference between the hot and cold junctions. Experimental details are discussed in ref. [5].

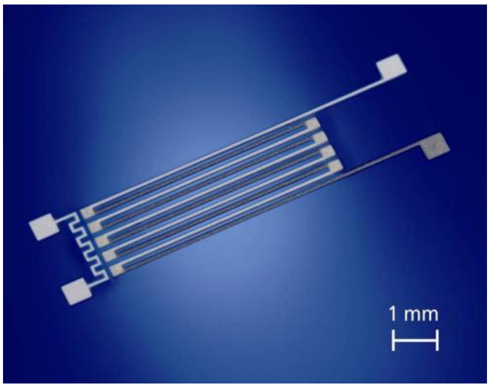

Figure 7. Printed thermocouple on glass surface.

4. Conclusion

Printing technologies like Ink Jet and Aerosol Jet®, which are employed for INKtelligent printing®, allow a digital, maskless deposition of a wide range of functional materials. Nano-particulate metallic and ceramic suspensions as well as polymer formulations can be used as so called "functional inks". The mask- and contact less printing processes are interesting for deposition of micro- or mesoscaled structures on planar and even non-planar surfaces. In this paper, several examples have been presented: Printed strain gauges applied on an aluminum surface, using a printed polymer as isolating and protective layer have been characterised. In addition, a printed thermopile was presented.

Acknowledgements

The authors acknowledge financial support given by the Innovation Cluster "Multifunctional Materials and Technologies" (MultiMaT) from the state of Bremen via the European Regional Development Fund ERDF, the Fraunhofer society and industry in equal parts. Work on colloid chemical synthesis of CuNi alloy nanoparticles has been supported by the State and University of Bremen in the framework of the ISIS (Integrated Solutions in Sensorial Structure Engineering) Sensorial Materials Scientific Centre (Fund Nr. 54 416 915 and 54 416 919).

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