Ink-Jet Printed Copper Complex MOD Ink for Plastic Electronics

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Abstract

The development of highly conductive copper patterns on low-cost flexible substrates (PET, PEN, etc.) by inkjet printing is reported. Copper films were obtained from a metallo-organic decomposition (MOD) ink composed of a copper complex and suitable low-viscosity solvents. Upon heating the ink decomposed and was converted into metallic copper under nitrogen as inert atmosphere.

Additionally samples were prepared using inkjet technology on various substrates. The required layer thickness for current conduction was assessed by printing on PET and sintering at 150 °C in a vacuum oven.

Introduction

In the past decade, a great interest in printed electronics had become evident [1-3]. Printed electronics refers to the application of printing technologies for the fabrication of electronic circuits and devices. Especially important is the manufacturing of such devices on flexible substrates. Traditionally, electronic devices are mainly manufactured by photolithography, vacuum deposition, and electroless plating processes. All these methods are multi-staged, require high-cost equipment and the use of environmentally, undesirable chemicals, which result usually in the formation large amounts of waste. However, the market of printed electronics, which is estimated to exceed $300 billion over the next 20 years [4], requires manufacturing techniques that are faster, cheaper and more environmentally compared to traditional production methods. In this regard, additive inkjet printing, which is a non-impact, dot-matrix digital patterning technique, is a very attractive technology for direct metallization. This is important for manufacturing printed circuit boards, RFID tags, thin film transistors, light emitting devices, solar cells, transparent electrodes, touch screens, and flexible displays. Inkjet printing [1,3-5] is favorable for automation and enables patterning with high resolution: line and space dimensions can be as small as 20 µm [3]. In addition, inkjet printing is very suitable for manufacturing large area plastic electronics by the roll-to-roll (R2R) technique.

The field of fabricating conductive structures using metallic inks is receiving wide-spread attention [1]. Usually, two main types of ink are being used; metal nanoparticles based ink and metallo-organic decomposition (MOD) ink. The most commercial metal used is silver [6] because of its low resistivity (1.59 µΩ cm) and high stability in air that ease the ink processing. However, the high cost of these silver based nano-inks limits the fabrication of low cost plastic electronic devices. Therefore, there is a need for ink formulations based on low cost, ease for processing and highly conductive metal. Copper is a desirable candidate because it possesses low resistivity (1.72 µΩ cm) as well as a low price compared to silver. Since in the case of copper NPs [7], it is hard to prevent their oxidation and a sintering step is required to maintain their high conductivity, a MOD copper ink seems to be the optimal solution.

Here we present an MOD ink based on copper complexes that undergoes decomposition to generate copper metallic patterns at low temperatures, and therefore enables printing conductors on heat sensitive plastic substrates (PET, PEN, etc.). The high stability of the ink is first due to the absence of copper NPs (the ink is based on soluble copper complexes) and secondly the direct formation of large copper grains without the need of particles sintering. The ink is stable in air for prolonged periods, without problems which are usually encountered in copper nanoparticles inks, such as aggregation and creation of metal oxides.

Experimental

DSC-TGA was performed using a DSC-TGA 1 (Mettler Toledo, Switzerland). X-Ray diffractograms (XRD) were obtained for the dried samples using a D8 Advance (Bruker AXS) diffractometer.

Printing was performed using a Xaar126 printhead with a nominal droplet volume of 50 pL with a dedicated waveform. The whole printhead was heated to 50 °C in order to match the ink viscosity (13 mPa s) to the operating window of the printhead. The printhead was mounted at an angle of 59.04° in order to achieve a square grid of 360 x 360 dpi^2. Printing was performed on microscope slides, polyethylene-terephthalate, polycarbonate (Makrofol) as well as polyethylene-naphthalate using a custom built x-y printer. Substrate temperatures were altered in order to optimize wetting behavior of the ink on the respective substrate. Sintering was performed in a vacuum oven (Thelco 19, Scientific Products, US) at 150 °C.

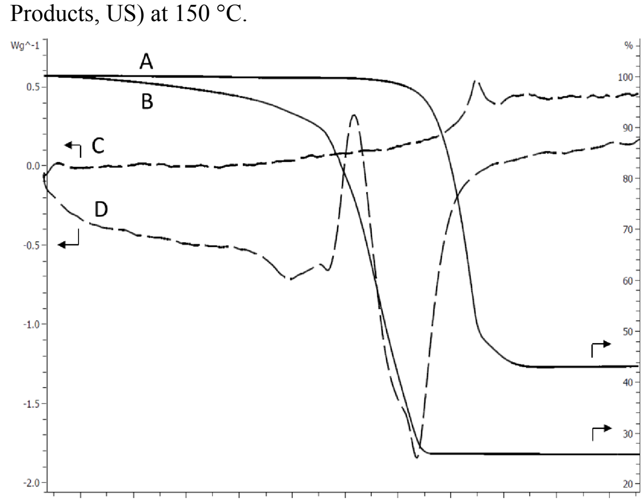

Figure 1: TGA-DSC plot of copper salt (A and C respectively) and copper complex (B and D respectively).

Ink Preparation

The fabrication of the MOD ink was done by evaluating various copper salts and complexing agents. The selection of the copper salt was aimed at finding the salt with the lowest organic content in order to prevent undesired residues in the final obtained copper film. Furthermore, a low enough decomposition temperature was required to enable the use of temperature sensitive plastic substrates. Since conductive patterns are the final goal of the present work, the effect of the ligand on the obtained conductivity was evaluated as well. It was found that most of the tested ligands led to significant decrease of the decomposition temperature relative to pure copper salt, but only one ligand led to good copper films morphology as well as high conductivity.

Figure 1 presents the differential scanning calorimetric (DSC) and thermo gravimetric analysis (TGA) plots of the copper salt as received from manufacturer, as well as the copper complex. It can be clearly seen that the complex had a lower decomposition temperature relative to the copper salt (150 °C vs. 185 °C, respectively). For the copper salt the decomposition was accompanied by a small exothermic peak, while for the copper complex a clear exothermic peak was followed by a large endothermic peak. XRD analysis of a film after complex decomposition indicates the formation of pure crystalline copper, free of any copper oxides (cf. Figure 2).

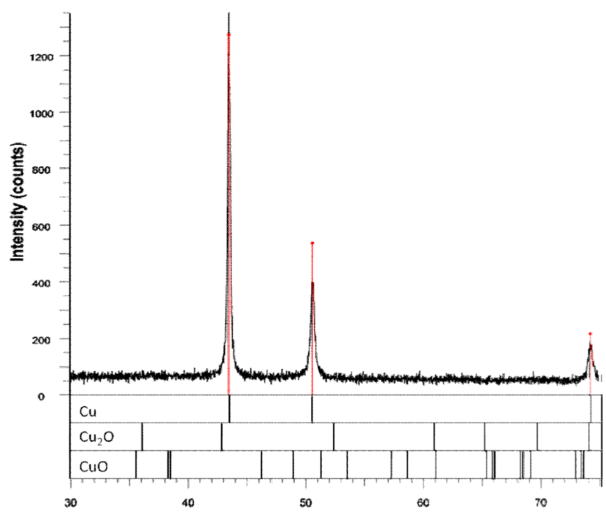

Figure 2: XRD pattern of the obtained copper nanoparticles with peak positions of copper(I) oxide and copper(II) oxide for comparison.

Inkjet Printing

Initial studies focused on the assessment of the track formation as a function of applied material. As the amount of the copper salt-complex was about 7 wt%, deposition of higher amounts of material was desired to relieve the influences of surface scattering on the conductivity in very thin films.

Figure 3 summarizes the print results of the investigated ink on different substrates with the substrate temperature set to 80 °C. The printed samples were removed from the heated chuck used for printing and left to dry at room temperature in ambient air. The influence of the different surface energies can be clearly distinguished from the results. Optimal line formation was found on Makrofol and PEN (cf. Figure 3 a and b), whereas PET and microscope slides (cf. Figure 3 c and d) needed specific cleaning techniques in order to achieve good line formation. The images furthermore reveal in interesting phenomenon. During the evaporation of the organic solvent, crystals where formed whose shape and size depended on the line morphology and on the substrate type. As the volume of the deposit was comparable for the different lines, crystallization changed for the different line morphologies. The high aspect-ratio line on Makrofol exhibited no crystallization after an extended period of drying. The rather broad and consequently shallow track on PEN produced rather small crystallites, whereas PET and glass substrates resulted in large aspect ratios seeming to favor the formation of larger crystals. This extend of drying, however, is not present in the final application of the developed ink, where a short heating step at 130 °C is included in the process in order to remove the solvent.

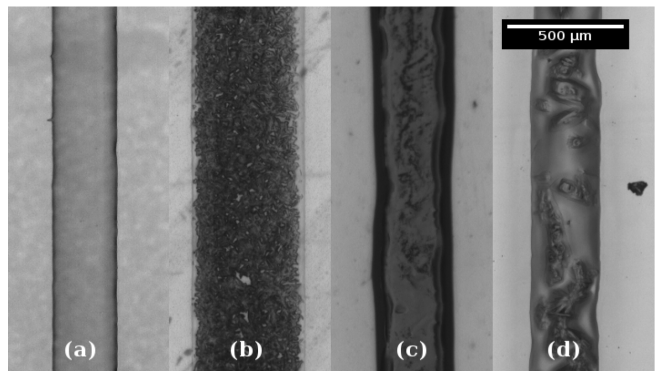

Figure 3: Line formation using seven layers of ink on different substrates and respective cleaning techniques: (a) Makrofol – as received (b) PEN – as received, (c) PET – pre-cleaned with isopropyl alcohol and (d) glass – pre-cleaned with DI water.

Sintering experiments where performed using PET in order to demonstrate the application of the ink to substrates with glass transition temperatures below 200 °C. Figure 4 depicts the dependence of the measured resistance on the numbers of layers printed. For this experiment structures were dried at 110 °C for five minutes on a hot plate. Subsequently, sintering was performed for 30 minutes at 150 °C in a vacuum oven.

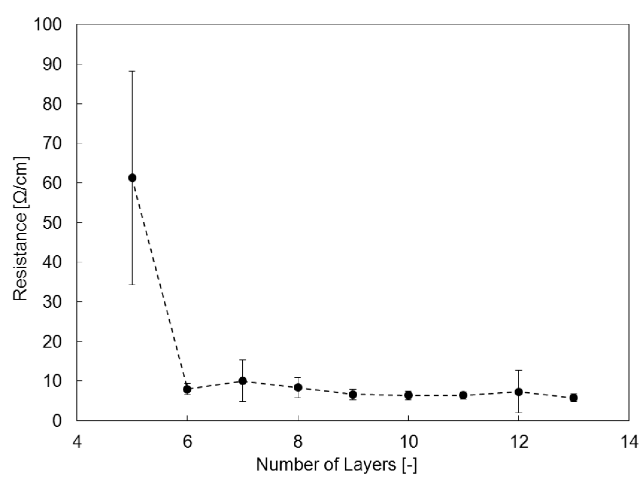

Figure 4: Resulting resistance of inkjet printed microstrips (four pixel width) as a function of printed layers [PET, substrate thickness 125 µm, sintered using a vacuum oven at 150°C for 30 minutes].

The tracks exhibited conductivity when more than 4 layers were printed. Below this the amount of copper contained in the tracks seemed to be insufficient to create a percolation path for electron conduction. A rather strong standard deviation of the resulting conductivity was observed for five printed layers, which may relate to the percolation threshold. Above this layer number consistent resistances were found, however, with no distinctive reduction in resistance with increasing layer count. One possible explanation is the remaining solvent due to low temperatures applied. Hence, these residues may have interfered with the merging of copper particles and also showed some voids in when tracks were examined under a microscope. An additional influence may originate from the resulting aspect ratio of the track, where the additionally deposited material mainly increases the width while leaving the thickness at a comparable value. This may impede the development of sufficiently conductive percolation paths and thereby explain the observations.

Conclusions

The paper showed the possibility to use copper salt complexes for the generation of printed structures using inkjet technology. Screening of copper salts, complexing agents as well as ligand enabled the formulation of a copper salt complex with a reduced decomposition temperature compared to the pure copper salt and hence enables sintering at low temperatures. An XRD analysis of the complex sintered in nitrogen atmosphere exhibited no peaks characteristic for oxides.

Inkjet printing was evaluated on various substrates. Makrofol and PEN substrates showed uncritical behavior for line formation, whereas PET and glass substrates needed special pre-treatment. The sintering in a vacuum oven revealed conductive structures from a minimum layer count of five, using a track of four pixels in width at a resolution 360 x 360 dpi^2. Further increase showed no clear trend for resistance reduction. This may be due to a high amount of residual solvent or the increased spreading with increased layer count at an almost constant low thickness.

Further investigations will focus on the optimization of the sintering process alongside with first functional applications.

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Yousef Farraj holds a bachelor in chemistry, and is currently finishing his master thesis at the Hebrew University of Jerusalem. Thereafter he will pursue a PhD degree at the Institute of Chemistry at the Hebrew University of Jerusalem, Israel. His master's thesis focused on the fabrication of conductive copper complex inks for obtaining highly conductive structures on cost-effective transparent substrates