Organic Electronics 34 (2016) 130–138

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

A benchmark study of commercially available copper nanoparticle inks for application in organic electronic devices

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ARTICLE INFO

Article history:
Received 21 January 2016
Received in revised form
24 March 2016
Accepted 9 April 2016
Available online 22 April 2016

Keywords:
Photonic flash sintering
Copper nanoparticle ink
Inkjet printing
Organic electronic devices

ABSTRACT

A set of three commercial copper nanoparticle based inkjet inks has been benchmarked with respect to their potential to form conducting printed structures for future applications in organic electronic devices. Significant differences were observed in terms of jetting properties, spreading behaviour and line formation on a number of relevant substrates. The inks' stabilities against oxidation were investigated, inkjet printed patterns were subjected to photonic flash sintering and their electrical properties characterized. As a result, optimized conditions for printing and post-deposition processing were determined. Photonic flash sintering, which is a roll-to-roll compatible manufacturing process, allowed a significant reduction in sintering time. Flash sintering was performed in the presence of air, thereby excluding the necessity for processing under inert atmosphere. One product was identified which showed satisfactory performances regarding all tested features: stable jet formation, well-defined definition of the printed structures and high electrical conductivity (20% of the value of bulk Cu). The obtained results can be considered as a promising step towards the future application of Cu inks in organic electronic devices.

1. Introduction

Printed electronics technologies are fundamental for the realisation of low cost and roll-to-roll (R2R) compatible organic electronic devices. High throughput production can be obtained by different process technologies [1]. Important elements of all electronic devices are highly conductive metal structures used as a circuit or electrodes. In the context of printed electronics, also these structures can be produced from solution by R2R printing and coating, as has been successfully demonstrated using inkjet [2], screen [3] or flexographic [4] printing. A number of printed electronics applications have been realized which contain conductive structures processed from metal based conductive inks, e.g. OPV [5], OLED [6], transistors [7], and integrated circuits [8]. A major challenge for the printed electronics industry, however, are the price and availability of suitable functional metal ink formulations.

Key requirements for the inks are good printability, acceptable printing resolution, and the possibility to process the inks at conditions which prevent damage to the plastic substrates [9], but at the same time achieve good electrical conductivities [10]. Currently, the most commonly used conductive inks are based on highly concentrated dispersions of silver flakes or nanoparticles [11]. The increasing price of silver, however, represents a limiting factor for industrial applications. Therefore less expensive metals are becoming more attractive alternatives [12]. The most promising candidates to replace silver inks are copper based conductive formulations. Indeed, the raw material is much more abundant (68 ppm vs. 0.08 ppm by weight in the earth's crust [13]) and cheaper than silver. Moreover, the bulk conductivity of copper is almost as high as that of silver ($5.96 \cdot 10^7$ S/m vs. $6.30 \cdot 10^7$ S/m). However, its main drawback is its tendency to oxidize easily under ambient conditions. The consequences of the presence of oxides on the nanoparticles' surfaces are a reduced electrical conductivity and increased sintering temperatures [14–16]. As a result, copper

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http://dx.doi.org/10.1016/j.orgel.2016.04.021
1566-1199/

nanoparticle inks typically need to be stored and processed in the absence of oxygen, unless additives or protective coatings are applied to prevent oxidation [17,18]. Furthermore, the sintering temperatures of copper inks are generally higher than 150 °C, which makes them incompatible with most plastic substrates, which, with only very few exceptions, lose their dimensional stability above 150 °C. Photonic sintering of copper based conductive inks has been recently introduced as a more selective and faster alternative to conventional oven sintering [19–21]. This approach results in a strong acceleration of the sintering process and shortens processing times by several orders of magnitude [22]. Moreover, it allows achieving high temperatures locally in the printed lines without affecting plastic substrates. Nevertheless, the majority of studies on flash sintering of Cu inks are still performed on glass substrates or special high temperature plastics [23,24].

In this work, three commercial conductive inkjet formulations based on copper nanoparticles were analysed for their potential as silver ink replacement in printed organic electronic devices. The interactions with different substrates (including PET and PEN), the printability and quality of the deposited films, stability in terms of oxidation, and finally photonic sintering behaviour and compatibility with PEDOT:PSS, were systematically evaluated, and based on these results, a promising candidate was identified for a number of applications.

2. Experimental section

Three commercially available copper nanoparticle inks purchased from industrial suppliers were evaluated in this study, namely, Ink 1: ANI IJ-070 from Applied Nanotechnologies, Inc. (Austin, U.S.A.), Ink 2: C2140723D1 from Gwent Electronic Materials Ltd. (Pontypool, U.K.), and Ink 3: CI-002 from Intrinsiq Materials Ltd. (Farnborough, U.K.). The inks were tested on different rigid and flexible substrates, namely: borosilicate glass Eagle 2000 and soda lime glass from Corning, polyethylene naphthalate (PEN) foil Teonex Q 65 HA (125 μm thick), and polyethylene terephthalate (PET) foil Melinex ST 504 (125 μm thick) from DuPont Teijin Films (Dumfries, U.K.). Surface modification upon different substrates was performed using a UV-ozone setup PR100 – Ultra Violet Products (UVP) for 5 min. Nitrogen plasma treatments were performed using a PVA TePla 300 Microwave Plasma System for 2 min at 600 W, 2.54 GHz and under reduced pressure (0.6 mbar). The inkjet printing performances of the three inks were tested using a DMP 2830 Materials Printer from Dimatix, using DMC-11610 cartridges, with a droplet volume of 10 pl. The exact waveforms used for each ink are reported in the Supporting Information. Sintering was performed in a two-step approach: The first step was a fast thermal pre-treatment in a Memmert hot air oven for 10 min at 80 °C or 5 min at 100 °C in air. Under these conditions, well dried samples were obtained, which were subjected to the second step, photonic flash sintering. This was performed with a PulseForge 1300 from Novacentrix using high power Xenon flash lamps. The flashing conditions like number of pulses, frequency, intensity, and pulse duration can be controlled via software provided by the supplier. The printed test structures were prepared via inkjet printing as described above. The resulting pre-dried and sintered test structures were inspected by an optical microscope (LEICA DFC 420), followed by measuring the electrical resistance (Keithley 2400 source meter). The cross section profiles of the printed lines were measured at different locations along the lines with a Veeco Dektak profilometer. For transmission electron microscopy (TEM) imaging, the samples were diluted by a factor 1000 with isopropanol containing 5 wt% of benzaldehyde and 2.5 μl of the resulting suspensions was placed on a copper grid supporting a Formvar carbon film. Subsequently, the grid was allowed to dry on paper, leaving the solid particles behind on the carbon film. The TEM studies were performed using a TECNAI F30ST TEM with a Field Emitter Gun operating at 300 kV.

Ink compositions were analysed using thermogravimetric analysis (TGA) under nitrogen atmosphere and in air at a heating rate of 20 °C/min. Then the compositions of the inks' volatile components were analysed using gas chromatography (GC-MS) coupled with mass spectrometry (GC-MS; split injection technique). For GC-MS analysis, the samples were diluted with acetone (Ink 1) or dichloromethane (Ink 2 and Ink 3), respectively, prior to the measurement with an Agilent 6890 GC, equipped with an Agilent 5973 mass selective detector.

Contact angle measurements were used to determine the surface energies of the substrates and were performed by vertically dispensing droplets of deionized water, diiodomethane and ethylene glycol (Sigma-Aldrich), which were used as received. Contact angles were calculated using the sessile drop method and recorded and analysed at room temperature with an EasyDrop Standard Krüss instrument.

In order to test the compatibility of the printed and sintered copper inks with organic materials commonly used in organic optoelectronic devices such as solar cells and light emitting diodes, high conductivity Orgacon PEDOT:PSS from Agfa was spin coated on the top of the printed structures. The structures covered with PEDOT:PSS were then optically inspected by a microscope (LEICA DFC 420). Scanning electron microscopy (SEM) images were acquired using a Nova 200 Nanolab Small Dual Beam.

3. Result and discussions

3.1. Contact angle measurements and surface energy determination

Advantageous wetting characteristics represent one of the most important prerequisites for a successful processing of functional inks for any printed electronics application. The wetting behaviour of an ink is determined by the surface properties of both the substrate and the ink itself. A number of different substrates relevant for printed organic electronic devices were tested, in particular borosilicate and sodalime glass, PEN and PET foils. To provide a good wetting of the ink onto the surface of the substrate, sometimes surface modification of the substrates was required. We have investigated UV-ozone and nitrogen plasma treatments of the substrates and the deposition of additional layers, e.g. silicon nitride (SiN). In order to determine the surface energies of the pristine and treated substrates, the contact angles of three test fluids (deionized water, diiodomethane, ethylene glycol [25,26]) were evaluated using the sessile-drop technique [27]. Using these test liquids on different substrates, it is possible to distinguish the polar and dispersive components of their surface free energy. The knowledge of these parameters represents the starting point to understand the liquid/solid interactions and to control the wetting of other fluids, like functional inks, on the substrates. Complete wetting occurs when the contact angle between liquid and surface (θ) is 0°. A contact angle below 90° indicates that wetting of the surface is favourable; if it is greater than 90° the wetting of the surface is unfavourable. Meanwhile complete de-wetting is observed when contact angles are greater than 150° [28]. Table 1 presents an overview of the measured contact angles of the three test solvents on the substrates used in this study, both in a pristine state and after two types of surface treatment.

The contact angle is related to the surface energy via Young's equation that considers the surface tensions between the three phases: solid, liquid and gas [29]. It predicts the contact angle of a liquid droplet on a solid surface from the knowledge of the three surface energies involved: