Photonic Sintering of Inkjet Printed Copper Oxide Layer

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Abstract

Recently, printing technologies have been adapted for the manufacturing of flexible electronic devices such as RFID antennas, capacitors, rectifiers, organic thin film transistors, photovoltaics, etc. In contrast to traditional production of electronics, printing technologies can enable low cost, high throughput, and large-area processing on flexible polymer materials. Photolithographical processes can be substituted by direct printing, e.g. of metal nanoparticles (NPs) or organic inks on flexible polymer foils. After the deposition of the materials by printing, curing, drying and/or sintering is required to remove solvents and additives, and to develop a functional layer. The operating temperatures of these post-printing processes are usually higher than the tolerable temperature of the polymer foils, which results in plastic thermal deformations of the foils. Photonic sintering is considered as one of the promising technology, especially for R2R processing, to prevent the thermal deformation of the substrate. It allows processing in ambient conditions without damaging the polymer foils due to energy exposure in microseconds-scale.

In this paper, the effect of photonic sintering conditions on inkjet printed copper oxide (CuO) layers was investigated. We found that the conductivity is proportional to the exposure energy. However, excessive energy will lead to "over-sintering" and thus destroys the copper layer. Optimized photonic sintering parameters were proposed to obtain inkjet-printed copper layers with high conductivity and no layer ablation.

Introduction

Photonic sintering by using intense pulsed light (IPL) has been introduced a couple of years ago as promising tool for printed electronics [1]. This technology was formerly developed for the sintering of silver (Ag) NPs, copper oxide (CuO) NPs, and composite materials in ambient conditions [2, 3]. Especially in printed electronics, IPL sintering technology has many benefits in comparison to traditional curing processes. Most of the traditional sintering processes such as simple thermal heating on a hot plate or in an oven apply heat to the entire materials including the substrate. However, in most cases of printed electronics the substrates are polymer foils, which are temperature sensitive [4]. In contrast, IPL sintering is a more selective sintering method as it heats mainly the deposited materials by exposure of broadband light in microsecond scale. Therefore, it is possible to prevent thermal defects on the substrate and reduce the very long and sophisticated paths of post-treatment processes usually employed in traditional heating concepts for R2R printing systems.

Recently, CuO ink is considered as a promising material for conductive layers, which is an alternative for the commonly used copper (Cu), silver (Ag) NPs and gold (Au) NPs. In case of CuO inks it was shown, that the photonic sintering method can eliminate the oxide shell of Cu without damaging the polymer substrate. Kim et al. published one of the first research work about IPL sintering of nanoparticles painted on polymer substrates [1]. They already predicted the promising potential of this technology for printed electronics. Starting from the year 2010, several articles were published focusing on IPL sintering of printed layers, e.g. based on inkjet, flexography or gravure printing. In most cases, the research works demonstrate the feasibility of IPL sintering for copper and silver in the field of printed electronics. They focus on the investigation of the layer conductivity as function of energy irradiation [1, 5]. Ryu et al. suggested the equation for chemical reduction of copper oxide photonic sintering process [6]. The effect of multi-pulse irradiation on the spin coated copper oxide layer was studied as well as the re-oxidization effect during the pulse irradiation [7]. However, there are barely scientific studies regarding the relations among irradiation energy, pulse number, and topography of sintered copper layers. Detailed investigations of parameters for photonic sintering and its influences on the printed layer are prerequisite to evaluate the applicability of photonic sintering for R2R-printed electronics.

In the current study, the correlations were analyzed between photonic sintering parameters such as energy exposure, pulse length and number of pulses, and the conductivity of sintered Cu layer. Morphological properties of the layers (e.g. thickness, roughness, and structure of the layer) were determined by means of scanning electron microscopy (SEM) and surface profiler. Electrical properties of the layers were measured by four-point probe station. We found that in general the conductivity is proportional to the exposure energy. However, excessive energy will lead to "over-sintering" and thus destroys the copper layer by removing it from the substrate. Optimized photonic sintering parameters were proposed to obtain inkjet printed Cu layers with high conductivity.

Experiments

For the Cu layers on PET substrate, a commercially available water-based CuO ink (ICI-002HV, NovaCentrix) with 16wt% CuO was used. The CuO ink was percolated by a polytetrafluoroethylene filter with a pore size of 1 µm before printing. One side primer-coated PET foil (IJ-220, NovaCentrix) was applied as substrates. An Autodrop deposition system from Microdrop Technologies was employed to print the prepared CuO ink in squares of 5 x 5 mm² (Fig. 1). The system was equipped with a piezoelectric inkjet single nozzle having a nozzle orifice diameter of 69 µm. The IPL sintering system PulseForge 3200 (NovaCentrix, Fig. 2) was used to sinter the inkjet-printed CuO layers. The IPL system consists of four xenon lamps, a reflector system, a water-cooled metal plate for the samples (see scheme of the sintering system in Fig. 2.) The exposure energy of a single pulse can be adjusted from 0.01 J/cm^2 to 15 J/cm^2 by two parameters, voltage and pulse duration. Voltage and pulse duration were adjusted between 150 V to 390 V, and 30 µs to 10 ms, respectively. Also multi-pulses with a frequency range of 0.01Hz to 50 kHz are possible.

The layer surface was characterized by scanning electron microscopy (SEM). For the measurement of sheet resistance, a 4-point probe station (PM5, Suss Microtec) with source meter (2636A, KEITHLEY) was employed. The layer morphology of the sintered Cu was measured using a surface profiler (Dektak 150, Veeco).

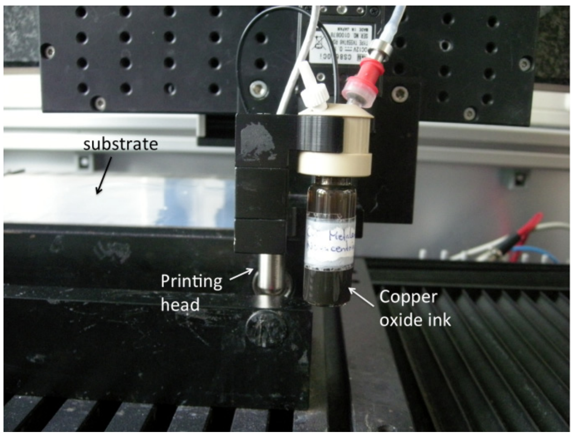


***Figure 1**. Autodrop inkjet printing system*

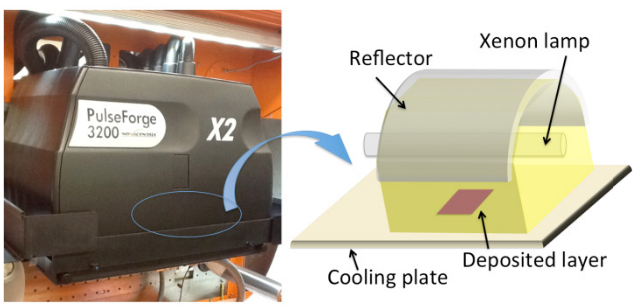


***Figure 2**. Photonic sintering system (left) and its conceptual drawing with a printed sample (right)*

Results

In this experiment, photonic sintering with multiple repetition of IPL irradiation was performed to evaluate the effect of pulse number and energy on the conductivity and topography of sintered Cu layers on the PET substrate. The productivity of the R2R IPL sintering system depends on the number of pulses and the frequency. For the experiment, the number of pulses was set to 1, 2 and 3 with a constant total duration of 6 ms and a fixed frequency of 10 Hz. Figure 3 shows the obtained sheet resistances of IPL sintered Cu as a function of energy exposure. The sheet resistance of Cu is reversely proportional to the energy exposure. When the exposed energy is less than 3.98 J/cm^2, the CuO layer is not sintered and no conductivity can be measured. The energy is too small for the chemical reduction of CuO and elimination of organic stabilizers [6]. Using a single pulse of 3.98 J/cm^2 ~ 5.01 J /cm^2, the sheet resistance was measured as 0.389 Ω/□ ~ 2.861 Ω/□. Energies higher than 5 J/cm^2 decrease dramatically the sheet resistance. The sheet resistance was measured to 0.142 Ω/□ ~ 0.28 Ω/□ for double pulses in the range of 5.01 J/cm^2 ~ 7.03 J/cm^2. And for triple pulses of 7.48 J/cm^2 ~ 9 J/cm^2, the sheet resistance was measured as 0.121 Ω/□ ~ 0.134 Ω/□.

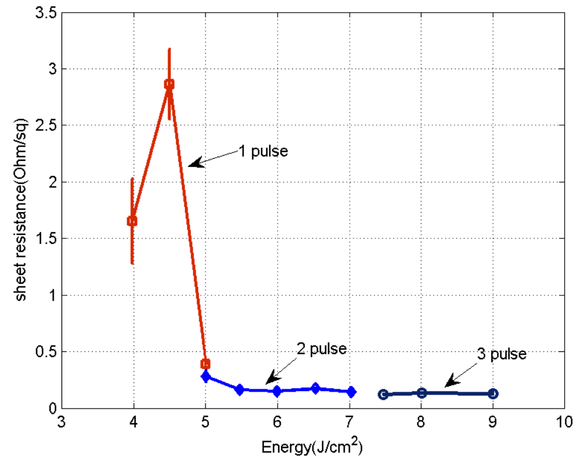


***Figure 3**. Sheet resistance of sintered Cu layers according to energy exposure and number of pulses*

It is noteworthy that excessive energy with relatively short pulse duration causes a (partial) delamination of the Cu layer from the substrate. The delamination follows the deposition path of the inkjet printhead and thus depends strongly on the conditions of deposition. Normally, the deposited droplets coalescence and accumulate as a wet film when using non-absorbent substrates and certain printing conditions. We call this 'wet-in-wet printing'. The topography of the deposited layer is mainly determined by the conditions of evaporation (e.g. convection flows and therefore fluidic circulation). In contrast, a droplet deposited on porous substrate, which used in this study (primer-coated PET) is pinned immediately after the contact with the substrate due to the liquid absorption, which also initiates the drying of the droplet.

When printing another droplet of CuO next to the deposited one ("in printing direction"), the drop will coalesce with the former one because pinning and drying has not been advancing much. Droplets printing in one line in printing direction will thus coalescence. The droplets deposited in the second line will thus not coalescence with the droplets printed before leading to clearly visible lines in the printed pattern as shown in Fig. 4. The delamination during IPL sintering of the printed layers occurred due to the inhomogeneous distribution of CuO caused by the deposition process. We assume that the inhomogeneous and especially rapid evaporation of the liquids (liquid in the droplet and already absorbed by the substrate) and binders of the CuO ink initiate the delamination. Former research on IPL sintering of Cu and Ag demonstrated that the delamination of sintered layers can be prevented by multi-step sintering with 8 ~ 16 pulses [7]. However, this strategy is not qualified for R2R IPL sintering where usually high productivity is necessary. As the required number of pulses increase, the operating velocity of the system should be decreased in constant frequency of IPL (which is physically limited due to capacitor charging period in continuous irradiations). Therefore, we investigated the effects of number of pulses for high productivity as well as prevention of delamination by fine-tuning of process parameters.

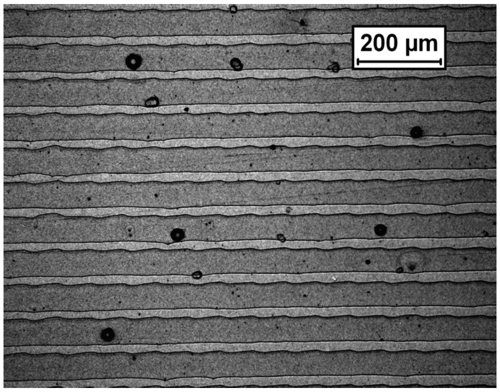
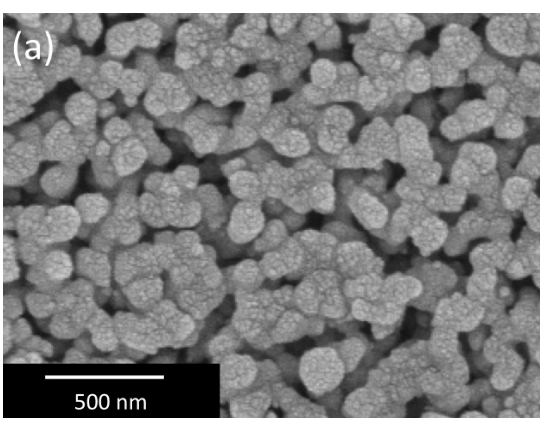
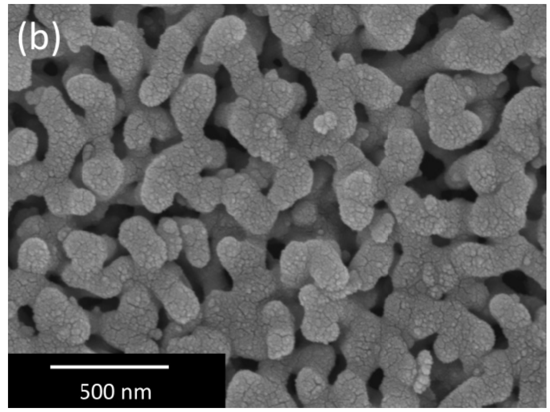


***Figure 4**. Microscopy image of as printed CuO layer on porous substrate*

Figures 5(a) to 5(c) show the SEM images of sintered Cu at different energy of IPL exposure. The SEM images clearly verify that the Cu NPs are agglomerated and a conductive networked is established. The increasing irradiation energy applied results to grain size growth and to fewer pores, which finally improves the conductivity as already shown in Fig. 3. Figure 5(a) shows fewer pores than Fig. 5(b) because probably a few organic binders remained caused by the low energy of IPL exposure. These residues in Fig 5(a) could interrupt the electron transfer and thus decrease the conductivity. In Fig. 5(b) the residues were eliminated and formed branches between Cu NPs by higher energy irradiation at 6.35 J/cm^2. Figure 5(c) shows that the Cu NPs have created complex thickets with fewer pores. The porosity, however, can not be decreased to the porosity of a Cu bulk material due to the short time of IPL irradiation. It was found that higher energies of IPL sintering lead to higher conductivity. However, the number of IPL should be controlled to prevent delamination initiated by rapid evaporation. In addition, the IPL technology can not generate sintered Cu layer without porousness because microseconds period of IPL is not sufficient for a proper melting and aggregation of the Cu NPs.





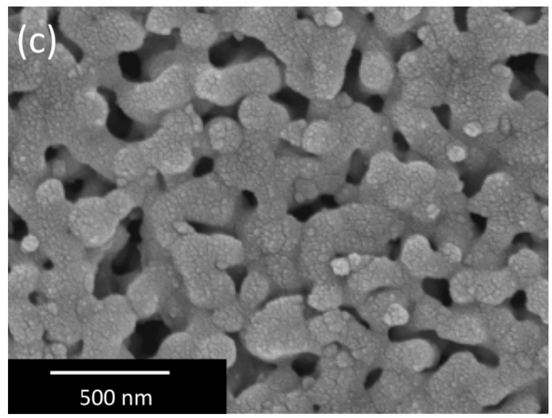


***Figure 5**. Scanning electron microscopy (SEM) images of Cu layers after IPL sintering of (a) 5.01 J/cm^2- one pulse, (b) 6.35 J/cm^2- two pulses, (c) 8.02 J/cm^2 – three pulses*

The topography of sintered Cu layers as a function of the IPL energy is illustrated in Figs. 6 and 7. The thickness of inkjet printed CuO without any treatments was measured to about 1020 ± 70 nm.

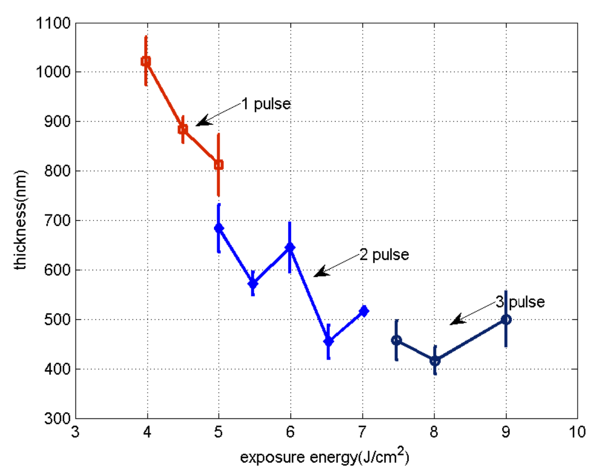


***Figure 6**. Thickness of sintered Cu layers according to energy exposure and number of pulse*

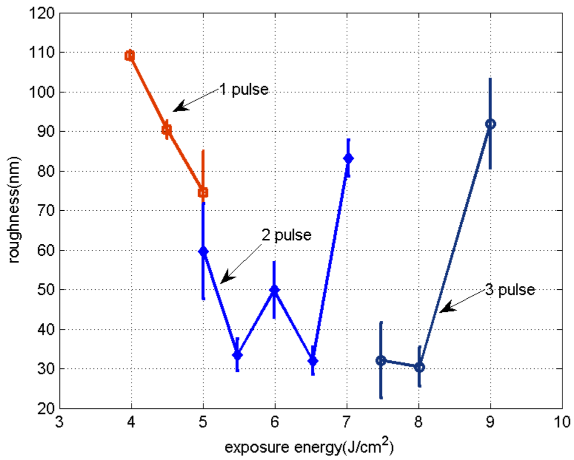


***Figure 7**. Roughness of sintered Cu layer according to energy exposure and number of pulse*

The thickness of sintered Cu layer decrease as the exposure energy increase. With a single pulse of 3.98 J/cm^2 ~ 5.01 J/cm^2, the thickness was reduced to about 1000 nm ~ 800 nm. In case of double pulses of 5.01 J/cm^2 ~ 7.03 J/cm^2, the thickness decreased to 680 nm ~ 450 nm. However, for the highest energy used in the triple pulse with 9 J/cm^2, the thickness increased again up to 500 nm because of generation of huge grains in the Cu layer, which induced shear force for delamination from the substrate. The trend of roughness of sintered Cu layer also follows that of the thickness. As the irradiation energy increases, the roughness decreases because grain size increased except for the cases of high energies from 6.53 J/cm^2 ~ 7.03 J/cm^2 as well as 8.02 J/cm^2 ~ 9.98 J/cm^2.

Conclusion

We investigated the photonic sintering of inkjet printed CuO layers on primer-coated PET substrates. The resistance of Cu decreased as the irradiation energy increased. Excessive IPL energies lead to delamination of the Cu layer. The delamination occurred along the deposition path of the inkjet droplets and is caused by an irregular distribution of materials within the layer. Multiple pulses of IPL were proposed to avoid delamination of the layer and enabling at the same time high conductivity. In contrast to literature, less number of pulses were required which is beneficial for higher productivity, e.g. in R2R processing. Therefore, these results can be easily adapted for continuous R2R IPL sintering of CuO layers.

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Reinhard R. Baumann graduated from the Leipzig University in Physics and holds a PhD in Chemical Physics. Primarily his research interests focused on areas of Physical Chemistry and Electrical Engineering of organic materials for polymer electronics. He is a professor for Digital Printing and Imaging Technology at the Institute for Print and Media Technology of the Chemnitz University of Technology since 2006 and since 2007 he is the head of the Printed Functionalities department of the Fraunhofer Institute for Electronic Nanosystems ENAS in Chemnitz, Germany.