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Involving Low-Pressure Plasma for Surface Pre-Treatment and Post Print Sintering of Silver Tracks on Polymer Substrates

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A method of production conductive silver tracks on thermally sensitive polymer (BOPP) was offered, involving plasma for preprint polymer surface activation to enable better adhesion properties and post-print selective etching to reduce amounts of polymer and raise electroconductivity. Inkjet, spin coating, and roll-blade coating were the methods of application of silver nanoparticle inks. We report to achieve two magnitudes lower sheet resistance of silver thin film with no effect on polymer substrate. This method with little modification could be adopted for production of flexible electronics on highly thermally sensitive polymers.

Keywords: Plasma treatment, Polypropylene surface activation, Inkjet printing, Roll-blade deposition, Nanosilver ink, PVP etching.

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1. INTRODUCTION

Flexible electronics is the electrics built on flexible substrate, for example plastic [PET, PP], fabric, paper and metal foil. The beauty of this technology is the flexibility, lightweight and durability. Recently, it attracts a growing research interest, due to its big potential of substantial cost reduction through maskless processing or Roll-to-Roll production of low-cost, and disposable electronics applications. To date, it mainly relies on two fabrication strategies: one in which substrates bearing thousands of Field-effect Transistors (FETs) are bonded to plastic by transfer printing or pick-and place methods [1]; another in which FETs are prepared directly on the target substrate by several coating, curing and lithographic steps [2,3]. Rubber stamping, embossing and ink-jet printing reduce the number of such fabrication steps. Feasible products based on printable electronics might include ultra cheap radio-frequency identification tags, inexpensive and disposable displays/electronic paper, interior interconnections, parts of an electronics assembly (e.g PWB, phone chassis etc.), sensors, memories, and wearable user interfaces. The main challenge of such opportunity is to provide sufficient quality of interconnecting traces by appropriate materials manipulation and sintering, more precisely appropriate material deposition, process control and sufficient electric conductivity of printed interconnections.

Metal nano-inks are currently involved in every printing method for production of printable electronics, e.g. flexography, offset, gravure, inkjet and screen printing [4]. They consist of a colloidal suspension of nanometer-sized metal particles coated with a thin stabilizer shell. Very small particle sizes result in their ability to sinter at exceptionally low temperatures of ~10 % of the melting temperature compared to their bulk counterparts, due to their high surface area to volume ratio. Nanogold and silver are dispersed in the presence of organic stabilizers such as PVP which also happens to be a reducing agent. The molecular weight of this organic chemical ranges between 10 000 and 60 000, and it serves as a dispersing agent to separate metal ions from each other [5]. PVP is dielectric. Therefore, if its amount in the ink is too significant, it can decrease electro conductivity of printed nanometal layers. Generally, after a nano-ink has been printed and cured, upon solvent evaporation, it forms a continuous conductive thin film comprising the printed feature. Cure is a necessary step in establishing electrical contact in the feature, since the ink is essentially an insulator in its as-dried state. Raising the temperature above that required for solvent evaporation initiates polymer flow, allowing the stabilizer shell to move away from the interparticle regions, establishing contact between metal particles. As the temperature is raised above 100 °C, the conductivity increases and the film becomes mechanically robust. Particulate materials have been shown to coalesce and form continuous features using, for instance, conventional heating [6], LASER sintering [7], exposure to microwaves or UV [8], and high temperature plasma sintering [9,10]. Isothermal sintering is the most common way these days, to the best of our knowledge. However, these techniques are not suitable for common polymer substrate materials due to the large overall thermal energy impact. Besides thermal sintering, plasmas have been shown to densify particulate materials, but also process thermally vulnerable materials in etching and sintering [10]. PVP with added acidic dye has been successfully etched by plasma before. Reinhold [11] *et al.* offered low pressure plasma sintering of inkjet printed silver tracks. This process was intended for thermally sensitive polymers. They reported one magnitude higher resistance of applied

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silver layer then that of a bulk silver. But this method is not suitable for PP/BOPP printable electronics, as during inkjet printing process the substrate was heated to 120 °C to stimulate solvent evaporation. In our case it's impossible since PP decomposition temperature is below 90 °C. Consequently, PP-based electronics requires solvents with lower evaporation temperatures as well.

Additional problem while printing on polymer substrates has always been lack of adhesion on the border ink composition – polymer film. Low-pressure plasma is known to be one of the methods for preprint polymer surface activation to achieve better adhesion properties. However, to our knowledge little research was conducted on whether this method is applicable for printable electronics and conductive ink compositions, in particular.

In this contribution we evaluate low-pressure argon and oxygen plasma exposure polymer surface activation method before applying silver nanoparticle inks with PVP as stabilizer by roll-blade, spin-coating and inkjet printing methods on BOPP substrate; plasma is then used as post print method for selective sintering of silver nanoparticles and simultaneous PVP etching to increase layer's electro conductivity.

2. EXPERIMENTAL

Bi-axially oriented polypropylene (BOPP), polyethylene (PE) (both 40 μm thick), and microscopy slides were used as substrates, all cleaned prior to experiment ultrasonically in ethanol, following deionized water. Preliminary plasma treatment was conducted on polymer substrates in a stainless-steel vacuum chamber as Figure 1 shows. The dimension of the vacuum chamber is 500 × 9 550 × 9 350 mm. A unipolar pulsed mid-frequency (40 kHz) generator was employed as the power source, where the 20 % duty cycle was set up on the whole process. The diameter of upper and bottom electrodes is 250 mm, and the distance between them is 50 mm. Argon (Ar, 99.99 %) and oxygen (99.999 %) were two activation gases. In all experiments the base pressure and averaged discharge power were kept constant at 8.0 Pa and 75 W, respectively. Time was varied between 30 and 300 sec. Water contact angle (and simultaneous inkjet printing) was measured 20 min., 2 hours and 24 hours after treatment. Next to subsequent drying 15 hours in 45 °C adhesion was evaluated utilizing 3M tape for splitting method. Applied scale was from 1 to 5 (1 = poor, 5 = excellent).

Nano-silver solvent-based ink for inkjet printing process was prepared, containing 17 wt% of silver, with a particle diameter between 80 and 100 nm. PVP (1.1 wt%) was used as a stabilizer; and mixture of ethanol (24.6 wt%), propanol (24.6 wt%) and ethylenglycol (32.7 wt%) created ink solution. Inkjet printing was performed using Epson ME office 70 printer. Roll-blade coating was done manually by roll-blade with diameter 10 mm and line frequency 2 lines/mm. Estimated layer thickness was 20 μm. Ink was also spincoated between 800 and 1000 rpm, and after drying ink layer was on the order of ~500 nm.

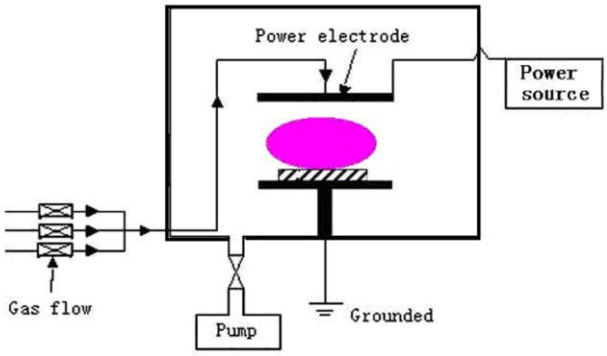


Fig. 1 – Schematic diagram of plasma setup

Best parameters of plasma surface pretreatment were applied on BOPP substrate for plasma etching and sintering experiment together with microscopy slides (roll-blade coating). Weight of ink was measured by Sartorius BT 125D (Shanghai Liangheng IM & EX Co., Ltd.) before and after plasma treatment. Same plasma set-up was used for etching PVP and sintering silver nanoparticles. We varied pressure and discharge power from 3.0 Pa to 10 Pa and from 30 W to 200 W, respectively. Sheet resistance was measured by four-point probe measurement (Guangzhou Four-point Tech Co, Ltd). Surface topographies of silver layers were imaged by a scanning electronic microscope (SEM), Shimadzu SS-550 (Japan), before and after plasma treatment. X-Ray diffraction (XRD) data were recorded using a Rigaku D/Max-gB diffractometer at room temperature. Step scans were conducted from 2° to 80° with a step size of 0.02°.

3. RESULTS AND DISCUSSION

3.1 Preprint plasma treatment

Polymer lines 15 × 5 cm were placed in the middle of grounded electrode. After air was pumped out of vacuum chamber, and pressure reached 4 Pa, argon or oxygen were fed with flow rate 5 sccm. We experimented with both gases. Inert gases normally do not result in the deformation of the polymer substrates, in contrast to oxygen. But adhesive properties strongly depend on how well substrate's surface is modified. Consequently, research of how feeding gas for plasma generation influences polymer's printability was advisable.

A pattern was designed that contained both lines for conductivity checks (see Fig. 2a) and solid printed 100% black area for adhesion evaluation (see Fig. 2b). We have observed that the more time has passed after plasma surface pretreatment, the worse was the quality of printed images. After 24 hours there were ink flows on the substrate immediately in the printer. Adhesion strength decreased in the same manner as printing quality. Best adhesion results were received after oxygen plasma treatment for 5 min (see Fig. 3). These results homologate with the common view in packaging industry that printing should be conducted right after surface pretreatment for better results. Therefore, machines for printing on polymer substrates are always equipped with surface activator, placed before the first printing section.

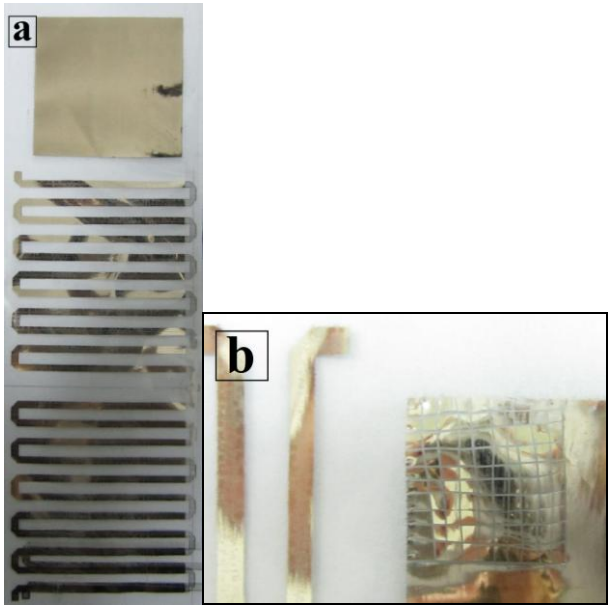


Fig. 2 – Inkjet printed nanosilver ink pattern ready for adhesion measurement (a), and after splitting evaluation method (b)

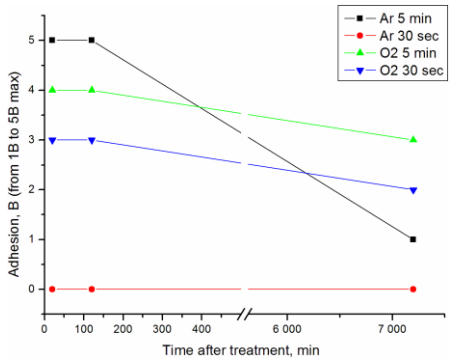
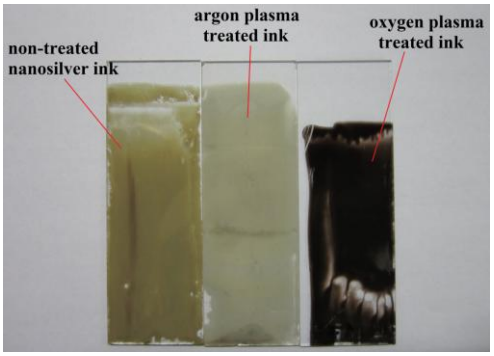


Fig. 3 – Influence of the time after treatment on PE adhesive properties

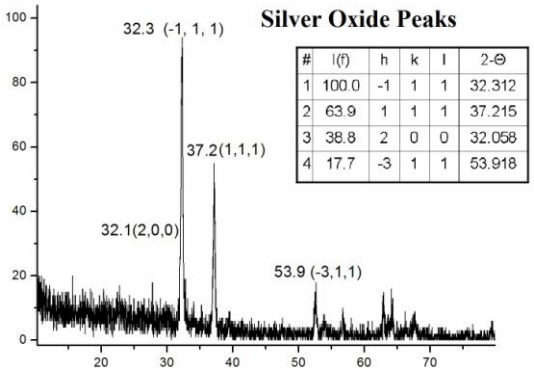
None of the printed or coated features showed conductivity. It was due to the low concentration of silver nanoparticles in solution. Another reason was presence of PVP on the substrates. As a stabilizer with dielectrical properties it prevented nanoparticles from forming homogenous conductive layer. So in order to receive features with lower resistivity post print treatment was necessary.

3.2 Post print Plasma Etching and Sintering

For research on whether low-pressure plasma can successfully etch thin PVP film we prepared water dispersion of app. 5 wt%. It was applied on microscope slides and treated in plasma (O_2 and Ar; 30 sccm; 30 W; 16 Pa). Weight of samples was measured after cleaning, after drying of PVP dispersion (7 min in 45 °C) and after plasma treatment to calculate the etching rate. Oxygen plasma showed higher etching speeds (65 μg/h) than argon (36 μg/h) plasma. However, although for this reason oxygen seemed like a natural choice for the purposes of nanosilver layer etching, first experiments with ink (see Fig. 4a) proved that oxygen plasma oxidizes silver on the surface. Color of treated in oxygen plasma samples became dark brown. On the other hand, samples treated in argon plasma attained light silver color instead of initial gold. To make sure of our hypothesis we did X-ray diffraction (XRD) crystallography analysis (see Fig. 4b). Results fully corresponded with reported before data for oxidized silver. These samples also showed no conductivity, so final decision was made to use only argon as feeding gas for plasma generation.



a



b

Fig. 4 – Oxygen plasma treated nanosilver ink – visual effect (a), and its X-ray diffraction pattern (b)

Our purpose was to discover the most suitable plasma treatment characteristics to achieve highest possible electro conductivity. We experimented with discharge power and pressure (see Fig. 5) during etching and sintering in vacuum chamber. Results suggest treating printed samples in pressure of 9.5 Pa (20 sccm Ar flow rate) at 75 W discharge power. With higher discharge powers total energy impact on substrates was too high for PVP; with lower discharge powers plasma sintering produced little effect on applied layer's resistivity. However, even under these conditions inkjet printed features showed no conductivity. We have printed up to three layers and did plasma sintering after each print based on previous reports [11], but it has proved to be insufficient. We expect though that this is mainly due to low concentrations of silver in the ink. Resistance was measured on the whole surface of samples coated by roll-blade and spin coating.

To make sure of conductive contents on the surface after plasma sintering we have analyzed it with XRD. The results are depicted in Fig. 6, showing a clear face-centered cubic (fcc) crystal structure of bulk silver with good agreement to theoretical lattice parameters. Broadening can be also seen in the bottom of the (100)

peak as an indication of the presence of residual unsintered nanoparticle material, PVP.

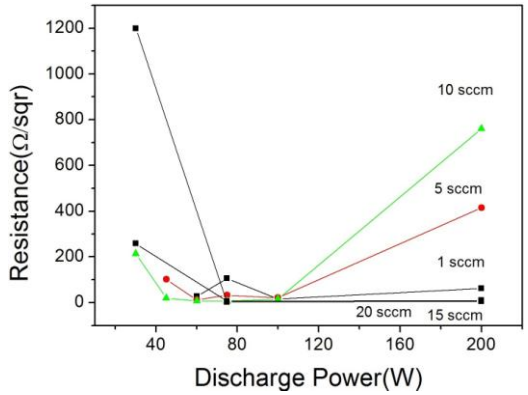


Fig. 5 – Influence of discharge power of plasma on resistivity of ink layer under various pressure conditions

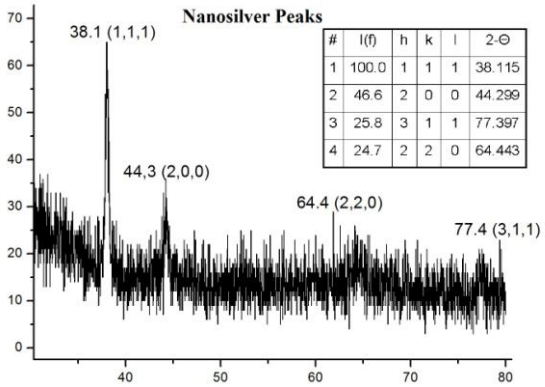


Fig. 6 – X-ray diffraction pattern of Argon plasma treated nanosilver ink

SEM images in Fig. 7 depict the effect of plasma sintering on silver nanoparticle layers deposited by inkjet process two times and sintered after each print. It can be observed that plasma etches PVP and slightly melts silver that tend to form homogeneous layer. However, the concentration is not enough to form such layer on entire surface of ink application. We report that adhesion after second plasma sintering on polymer substrates is improved and evaluated as "excellent" in every case.

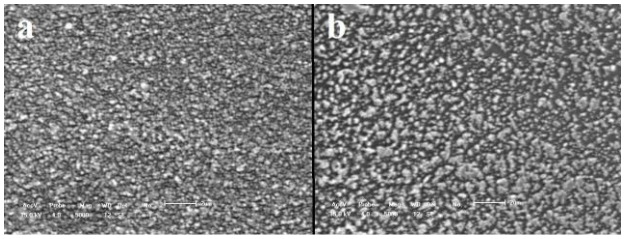


Fig. 7 – Ink-jet printed (2 layers) of silver nanoparticle ink with no plasma treatment (a), and Ar plasma treatments after each print (b)

4. CONCLUSIONS

We have evaluated an alternative and selective low pressure polymer surface activation and sintering method for inkjet printed colloidal silver inks on thermally sensitive polymer substrates, without affecting it. The process yields comparable conductivities to conventional heating methods. The application of the process presented here may be employed in printed electronics, where conductive features are manufactured onto common polymer substrates that have a relatively low Tg.

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