Nanomaterials for Printed Electronics

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Abstract

We will address two major issues in the field of printed electronics: printing metallic conductive patterns on heat sensitive substrates, and obtaining transparent patterns and coatings for opto-electronic devices. New concepts for obtaining conductive patterns at low temperature will be presented, all based on spontaneous sintering of metallic nanoparticles caused due to removal of the ink stabilizer. The process can be performed with inks containing built-in sintering agent, or by sequential printing of the metallic ink and the sintering agent. A new method for fabrication of conductive transparent electrodes will be also described, based on spontaneous self-assembly of metallic nanoparticles into a grid pattern on plastic substrate, and on thin films of CNTs. Combining the printing with transparent patterns will be demonstrated in fabrication of a plastic electroluminescent device.

Introduction

Fabrication of various electronic devices requires formation of a conductive structure (electrical circuit), which connects various components of a device. Inkjet printing provides facile technology for fabrication of high quality and low cost conductive circuits. Nowadays most of conductive inkjet inks are based on metal nanoparticles, mainly silver, and to some extent on inks containing soluble metal precursor, e.g. metallo-organic decomposition inks, which transform to metal after post-printing treatment [1-3]. Recently dispersions of carbon nanotubes (CNT) were also used as functional materials for inkjet printing of conductive patterns [4, 5].

In the electronic industry, manufacturing electronic devices such as flexible displays, RFID tags, sensors, OLEDs, PV devices including solar cells, batteries, and printed circuit boards (PCB) by inkjet printing of conductive inks can provide low-cost technology for manufacturing large-area electronics with high resolution. The main advantages of inkjet printing compared to other deposition methods, such as electroless plating, photolithography, and screen printing, are one-step processing, low cost and compact equipment, usually lack of hazardous wastes, and applicability to various substrates [1]. An important advantage of inkjet printing is also the wide range of materials, which can be used as substrates: paper, glass, metals, ceramic, polymeric films. The last are especially important for industrial fabrication of flexible plastic electronic devices by R2R printing.

While using nanoparticulate inks, two important challenges arise. First is obtaining high electrical conductivity after printing. Since inkjet ink is a dispersion of conductive nanomaterial, e.g. metal in a solvent which contains mainly organic additives (stabilizer, binder, wetting agent etc.), the post-printing sintering of nanoparticles in order to remove the insulating organic components is usually required. The routine method for sintering is the heating of the printed pattern to temperatures above 200 ºC, to cause decomposition of the organic materials [1, 6, 7]. However, heating to high temperature is inapplicable in the case of paper or plastic substrates, such as, for example, polyethyleneterephthalate and polycarbonate, which are widely used in plastic electronics. Therefore, development of new low-temperature methods for sintering is required. To avoid destructive heating of polymeric substrates, other sintering methods are now under development: photonic, microwave, plasma, and electrical [1]. All these methods enable obtaining printed patterns with rather high conductivity, but their common disadvantages are the high-cost equipment and high energy consumption. Therefore, there exists a need for ink formulations and methods of substrate tailoring, which would enable obtaining high conductivity at low temperatures.

The second challenge in this field is obtaining transparent conductive coatings, which can be utilized in displays, touch screens, electroluminescent devices and solar cells. Conductive oxides, such as tin-doped indium oxide (ITO), which are traditionally used for fabrication of transparent electrodes, have a number of disadvantages, such as high cost and low conductivity. Therefore, much efforts is devoted nowadays to finding alternatives, which will bring high conductivity and yet high transparency.

Here we report on a new concept for obtaining conductive patterns on various substrates by spontaneous sintering of printed metallic nanoparticles (3D coalescence) at low temperatures by modification of inkjet formulation with built-in sintering agent (SA) and by sequential printing of ink and SA. We also show how this process can be utilized for fabrication of electroluminescent (EL) plastic devices. In the second part we present a new method for fabricating conductive transparent electrodes based on spontaneous self-assembly of metallic nanoparticles into a grid pattern on plastic substrate. In the third part we describe an effective route for fabrication of flexible EL devices with inkjet inks composed of aqueous dispersions of CNTs.

Results and Discussion

Metallic inks and sintering at room temperature

For printing experiments we used water- and solvent-based polymer-stabilized dispersions of silver nanoparticles with an average size of 10-15 nm and metal content of 20-40 % that were synthesized in our lab by wet chemistry methods [8]. The printing was performed by an Omnijet100 inkjet printer (Unijet, Korea) equipped with Samsung piezoelectric printhead of 30 picoliters. The sintering of printed patterns was performed with the use of conductive silver inks that contain a built-in SA, NaCl, or by sequential printing of silver nanoparticles and electrolyte sintering solution ("double printing") [9] as presented in Figure 1. The

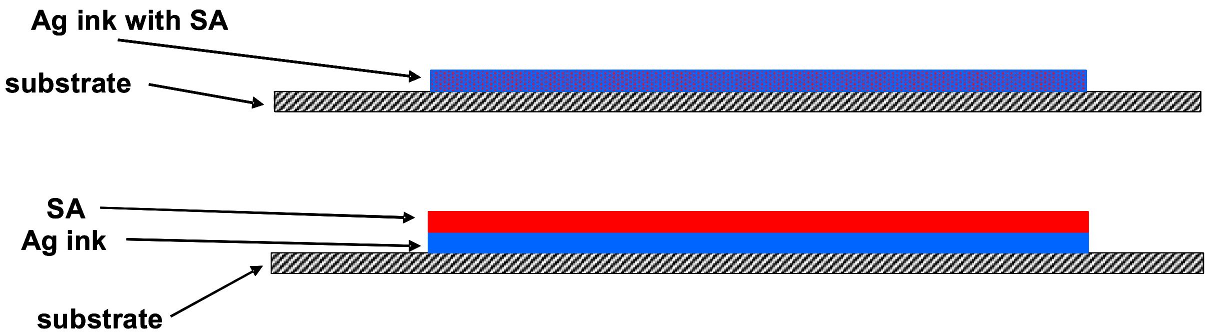

Figure 1. Schemes of obtaining sintered printed patterns with the use of built-in SA (top) and by sequential printing of ink and SA (bottom).

ability to decrease the resistivity of printed silver nanoparticles by chemical means was reported by Zapka et al. [10].

The mechanism of sintering with built-in SA is based on replacement of the stabilizing polymer molecules which are present on the surface of silver nanoparticles, by chloride ions. This sintering approach enables obtaining printed pattern with conductivities up to 41% of that for bulk silver without any post-printing treatment [8]. Similar mechanism operates also at sequential printing – replacing the polymer molecules thus diminishing their electrosteric stabilizing effect that results in formation of metallic patterns with conductivities above 30% of bulk silver. Figure 2A presents a flexible transparent four layer EL device (PET:ITO:ZnS:$BaTiO_3$) with electrodes printed with the use of silver ink containing built-in SA, and Figure 2B shows printed silver tracks sintered by a "sequential printing" method.

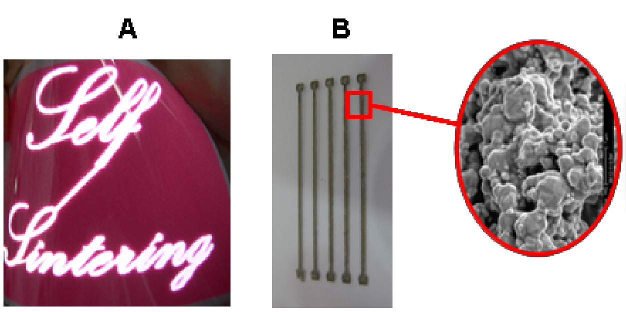

Figure 2. EL device with silver electrodes printed with ink containing built-in SA (A) and silver tracks printed by "sequential printing" (B).

Conductive transparent electrodes (grids) composed of metallic nanoparticles

In addition to the required high electrical conductivity, in a number of applications, such as displays (LCDs, touch screens, e-paper, etc.), lighting devices (EL, OLEDs), and solar cells, transparent conductive coatings are required. An alternative to the widely used ITO coatings is transparent coatings (transparency up to 95%) based on self-assembly of metallic nanoparticles in the form of 2D arrays of interconnected micrometric rings obtained by inkjet printing of picoliter droplets of silver dispersion [11]. Another approach is based on evaporative lithography process [12], which is performed directly on plastic substrates by placing a droplet containing silver nanoparticles on the top of metallic mesh followed by instantaneous spreading over the mesh and the plastic substrate [13]. After drying, a transparent grid composed of the nanoparticles is formed. The immediate sintering of silver nanoparticles stabilized by polyacrylate in the thin lines of the grid occurs even at room temperature upon short exposure to HCl vapors enabling formation of transparent patterns (transparency above 75%). Figure 3 shows a HR-SEM image of such a grid formed by placing a droplet of silver nanoparticles on top of a stainless steel mesh. After complete evaporation of the liquid, the mesh is removed and a transparent grid pattern is formed (Figure 3). The line width is only a few micrometers in average, which makes the grid transparent, and the height can be of up to 1.5 um, which is important in applications such as solar cells and OLED devices. Typically the whole process takes no more than a few minutes and does not require any complicated equipment, yielding a transparent grid with a resistivity of about 10^{-5} Ω·cm.

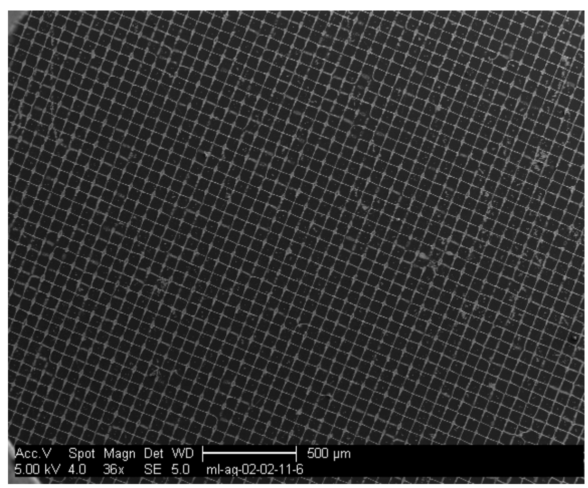

Figure 3. Transparent silver grid obtained by evaporative lithography process.

EL devices with CNT-printed electrodes

Patterned electrodes with high transparency, which are suitable for fabrication of EL devices, can also be obtained by inkjet printing combined with wet coating of CNT-based inks. The conductivity of a CNT film is mainly determined by its thickness - the thicker films result in lower sheet resistance, but obviously less transparent.

Here we demonstrate the formation of flexible EL devices using a low cost ink based on Multi-Walled Carbon Nanotubes (MWCNT). The electrodes were formed by two deposition methods: the transparent electrode (back electrode) was a thin MWCNT film prepared by bar coating, and the counter electrode (grid) was formed by inkjet printing.

The thickness of transparent (back) electrode was in the range of 6 - 80 µm (wet film thickness). The counter electrode was formed by inkjet printing of the same MWCNT dispersion. The performance of the devices was compared by luminance measurements after applying a voltage of 200 V. A scheme of an EL device with MWCNT electrodes and a photo of a working device are shown in Figure 4.

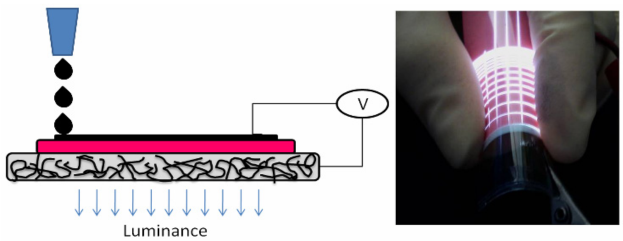

Figure 4. Scheme of EL device with MWCNT electrodes (left) and a working EL flexible device (right).

It was found that increase in wet thickness of the back electrode results in a decrease in sheet resistance, but as could be expected, is accompanied by a decrease in transmittance. The thinnest film (wet thickness of 6 µm) has R = 16.3 ±2.9 KΩ/□ and T = 66.3 ±0.4%. For the thickest film (wet coating of 80 µm), the resistance was 0.7 ±0.2 KΩ/□ but the obtained film was not transparent (T = 0.2±0.1%). As the transparency of the back electrode decreases, the luminance emitted by the device decreases al well. The device formed by the thinnest film (6 µm wet thickness) emits a luminance of 124 ± 5 cd/m^2, while for the thickest film (wet coating of 80 µm), the detected luminance was close to zero.

The conductivity of printed MWCNT films remains constant under bending, and the overall performance of the devices remains unchanged after twenty bending cycles to 180^o.

In summary, we presented the use of metallic and CNT-based inks, methods for obtaining metallic conductive printed patterns without heating, and obtaining transparent conductive arrays based on self assembly combined with printing.

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