Gravure Printability of Conducting Polymer Inks

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Abstract

The present work considers the suitability of gravure printing in electronics manufacture. Different engraving methods are described in terms of resolution and quality. The properties influencing printability of conductive polymer inks, more specifically surface tension and substrate wetting are discussed in greater detail.

Introduction

Organic materials used in the manufacture of electronics are becoming more and more attractive since the discovery of a certain class of polymers being able to transport the charge and thus conduct electricity [1]. Nowadays, organic electronics give a rise to increasing interest due to potentially lower cost, easier processability and rapid progress in performance of such devices in recent years [2]. The most important cost advantage of organic materials used in the electronics manufacture is the solution processability, because it eliminates the need for time consuming fabrication processes in expensive high vacuum chambers. However, to fully utilize this advantage, all of the functional layers comprising electronic components should be deposited using methods that do not involve vacuum [3].

One of the very promising solutions toward the lower price of electronics and microelectronics is implementation of different printing technologies into their manufacture [4]. Printing of patterns with inks having functional electrical conductivity provides the opportunity to print electrical circuitry or RFID antennas [5]. Printing patterns with functionalities like semi-conductivity and electrical insulation open routes to print polymer transistors and LED's [6]. However, the potential of different printing technologies is yet very often not known.

General Considerations for Printing of Electronics

Patterning issues that are crucial to electronics manufacturing include resolution, design rules, accuracy, registration, and yield. In the past, printing of visual images was the only application of printing and technologies were very well optimized to meet these requirements, such as the resolution limits of 100 - 150 µm, which is sufficient for human eyes [7]. Additionally, the printed image consists of printed dots that are printed side by side or they are slightly overlapping. On the other hand, for the printing of electronic components, disrupted traces would be undesirable. For instance, in the manufacture of thin film transistors, continuous lines are substantial for functional electrodes with resolution in the micrometer range. Very thin, homogeneous, defect free layers of semiconductor and dielectric materials and gate electrodes must be deposited onto source and drain electrodes as accurately as possible, in order to create properly functioning devices [8]. Furthermore, the presence of additives that are commonly included in regular printing ink formulations in order to meet process requirements [9] (such as viscosity, wettability, and end-use properties, etc.) may cause undesired change of electrical properties of the materials and consequently performance of the final device.

Gravure Printing

Among conventional printing processes, gravure printing is the premier process in terms of high quality and ability to print at very high speeds. Robustness of its image carrier is also advantageous, contributing to very good printing stability over time. These advantages of gravure printing make it a very promising process for electronics manufacture, smart packaging and RFID [10]. There are specific requirements to be met in order to achieve the best print quality possible. These include both the substrate properties (smoothness, compressibility, porosity and ink receptivity, wettability, etc.) and ink properties (ink chemistry, viscosity, rheological behavior, solvent evaporation rate, drying, etc.) [11]. Furthermore, process parameters, such as doctor blade angle and pressure, impression pressure and speed, have tremendous effect on quality of printed ink films [12]. In addition, the engraving method used to prepare the image carrier is an important factor, because ink release from engraved cells will depend on the width and depth of cells and their overall shape [13].

Preparation of Image Carrier

In gravure printing, the image is almost always broken up into separate cells and a solid image is then created by the ink spreading on the substrate. Walls between individual cells provide a supporting surface for the doctor blade as it wipes the ink off the non-image areas of the gravure cylinder (Figure 1). There are several different methods of image carrier preparation. These include chemical etching, electromechanical engraving and laser engraving [13]. Recently, a new engraving method based on electrolytic copper removal was introduced by Creo and Acigraf - Thermal Gravure Technology (EXACTUS™) [14]. Each of these techniques produces different type of cells. Even though the electromechanical engraving dominates the engraving industry, for printed electronics the chemical etching or laser might be more suitable. However, latest advances in electromechanical engraving are pushing this technology toward higher resolutions and smoother continuous edges [15].

Resolution, determining the line width, is limited by the engraving process used. Electromechanical engraving produces image as rows of discrete dots. Substrate wetting and ink spreading are very important here in order to produce continuous lines. Ragged edges are very common with this type of engraving. With laser engraving, a minimum beam size of about 40 microns is used and therefore the minimum line width is also roughly 40 microns. Engraving based on chemical etching nowadays employs laser technology to image a photoresist, leaving the image areas unprotected so it can be chemically etched. Some of the imaging systems use the indirect laser, which is based on splitting of the laser beam into four beams of equal power. Therefore it typically works with a beam size of 10 microns for gravure applications and hence the minimum line width is also about 10 microns, or a little more due to the sidewall etching [16].

Gravure printing tends to be a directional process when fine lines are printed. The smoothest edges and the most uniform lines are usually produced in the print direction. Printing in perpendicular direction often results in more pronounced "sawtooth" edge or poor line contour. Additionally, it is likely that more ink will be transferred onto the substrate in the print direction, resulting in more conductive traces. Directionality effect of the printed lines is also connected to the quality of engraving at different angles to print directions. Figure 2 shows the 37 micron wide lines prepared by indirect laser imaging and chemical etching. Evidently the quality of engraved grooves is higher in the same direction as the laser beam travels (vertical direction).

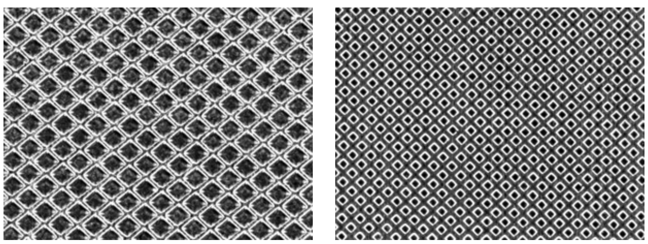
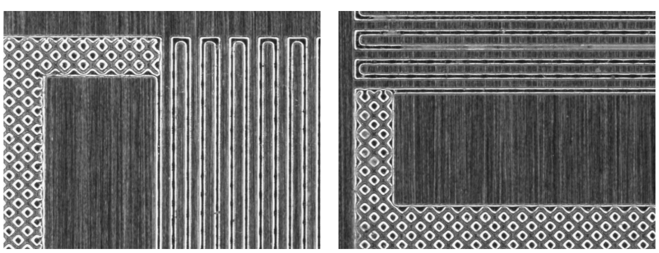


Figure 1: *Electromechanically engraved cells with resolution of 150 l/cm (left) and chemically etched gravure cells at 400 l/cm (right) (Images were taken using the ImageXpert system by KDY, Inc.)*



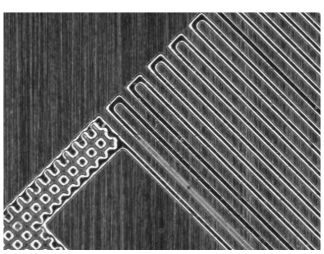


Figure 2: *Fine lines (37 micron) engraved by indirect laser imaging and chemical etching method. Upper Left is parallel, upper right is perpendicular and lower left is in 45 degrees angle to printing direction. (Images were taken using ImageXpert system by KDY, Inc.)*

Conductive Polymer Inks Requirements

The term conductive polymer ink is used to generally characterize printing inks that are used for printing of conductive layers, such as electrodes or wires. Conductivity can be achieved by different mechanisms, such as incorporating metallic or other conductive particles into a non-conducting polymer vehicle, or by using polymers that exhibit electrical conductivity in a suitable solvent. From conductive polymers, solvent based (xylene, toluene) polyaniline inks [17, 18] and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) inks [19] are under study for gravure printing of conductors.

Surface Tension and Spreading of Inks

Surface tension is probably the most obvious difference between solvent and water based inks. Water has a high surface tension and thus water based inks are very often formulated with alcoholic co-solvents and/or surfactants in order to lower surface tension for printing. Under dynamic press conditions, the ink is under constant compositional change. A new liquid-air interface is created characteristically in the order of milliseconds. Dynamic surface tension of inks containing surfactants and other polymers is determined by diffusion, adsorption and desorption processes and it is typically higher than equilibrium (static) surface tension [20, 21].

Addition of alcohols lowers the surface tension monotonically with increasing concentration, due to a preferential adsorption of the organic molecule at the liquid-air interface. Surfactants, however, quickly reduce the surface tension at very low concentrations up to the critical micelle concentration (CMC), due to a strong adsorption of the surfactant at the liquid-air surface. At concentrations higher than the CMC, the surface tension is practically constant since additional surfactants will form micelles in bulk [22].

Figure 3 shows the decrease of dynamic surface tension with addition of ethylene glycol (Sigma Aldrich) to an aqueous solution of PEDOT-PSS (Baytron P by HC Starck). Static surface tension of initial and final ink is also shown. Dynamic surface tension was measured using the maximum bubble pressure method (SensaDyne 900). The pendant drop method (FTA200) was used for static surface tension. In addition to lowering of surface tension, it was found that the presence of ethylene glycol (EG) dramatically decreases surface resistivity of resulting polymer films [23]. This phenomenon is believed to be due to increased interchain interactions and conformational change from coil to expanded-coil or even linear chain conformation in the presence of EG [24]. Figure 4 shows decrease of dynamic surface tension with addition of surfactant TWEEN80 (Sigma Aldrich) to EG-PEDOT-PSS conductive polymer ink. It can be seen that CMC of such system is reached at around 0.5 g/l.

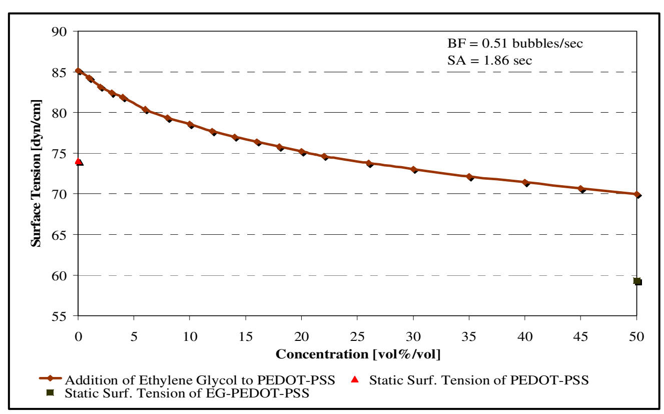


Figure 3: *The effect of addition of ethylene glycol to PEDOT-PSS aqueous solution. (BF= bubble frequency; SA= surface age)*

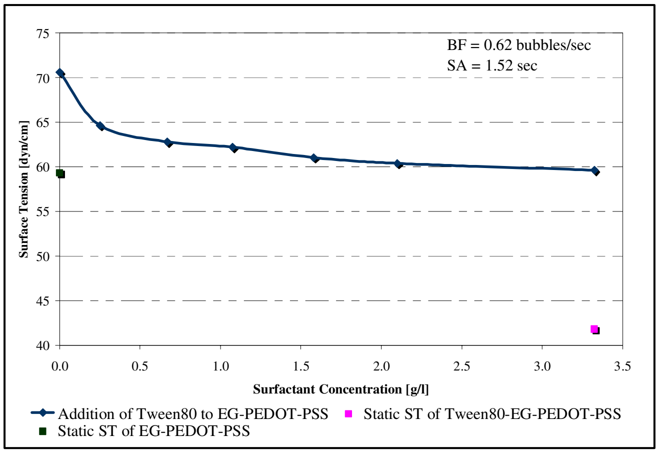


Figure 4: *The effect of addition of surfactant (TWEEN 80) to EG-PEDOT-PSS ink. (BF= bubble frequency; SA= surface age)*

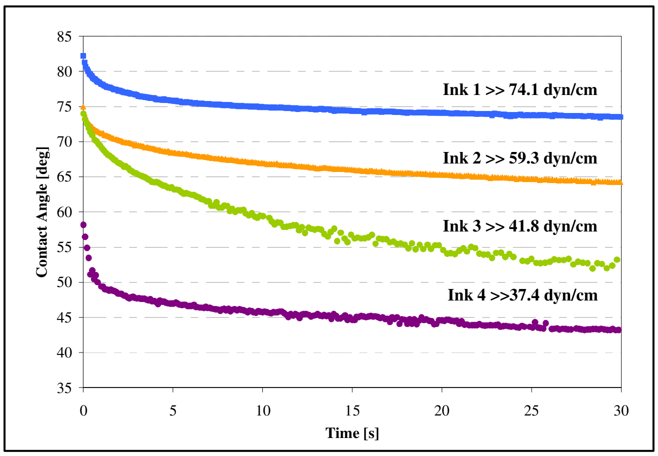


Figure 5: *Dynamic contact angle of different PEDOT-PSS based inks on PET substrate.*

Surface tension of an ink has a tremendous effect on spreading and wetting properties on particular substrates. Dynamic contact angle (measured with the FTA200) for PEDOT-PSS based inks with different surface tensions on PET substrate (DuPont) is presented in Figure 5. Ink 1 represents initial PEDOT-PSS aqueous solution, inks 2 and 4 were prepared with addition of ethylene glycol and ethanol respectively and ink 3 was prepared with addition of surfactant. It is evident that the time for surfactant molecules to migrate to the liquid-air surface is longer than that of alcohols and thus the equilibrium contact angle was not reached within the tested time period. The escape of the solvents from printed polymer films determines the film quality. The development of surface tension gradients due to fast evaporation of alcohols can cause printing defects such as discontinuity of printed lines (Figure 6). This is especially undesirable when printing conductive traces for electronics. In order to minimize these defects, all solvent should evaporate at the same rate providing the same medium for ink components [22].

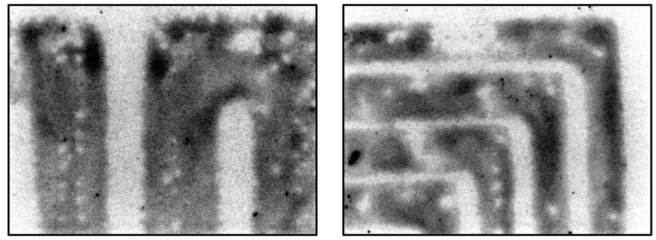


Figure 6: *Illustration of printing defects caused by surface tension gradient due to faster evaporation of co-solvent.(EG-PEDOT-PSS ink printed on synthetic paper Valéron™ using Gravure K-Proofer)*

Rheological Behavior of Inks

Printing inks are typically shear thinning materials, meaning that viscosity of an ink decreases with increasing shear rate. Flow curves (viscosity vs. shear rate) can provide information about ink's processing and performance and thus it is very important to monitor. Low shear rates can be related to storage conditions of material, such as sedimentation, phase separation and structure retention. The flow curve of a polymer solution depends on polymer concentration, molecular weight, temperature and the applied stress. More concentrated polymer solutions deviate from Newtonian behavior more than diluted solutions due to higher number of chain entanglements per unit volume [25].

Figure 7 shows the flow curves (TA Advanced Rheometer 2000) of three different PEDOT-PSS based inks. Initial polymer solution (PEDOT-PSS) first shows increase in viscosity with increasing shear rate. This can be due to orientation of polymer chains with applied shear and thus increasing the polymer-polymer interaction up to the point of maximum viscosity, after which it slowly shear-thins. Addition of EG to PEDOT-PSS solution lowers the concentration of polymer, however, as already mentioned, it causes the polymer chain to expand causing even stronger interchain interactions. This effect results in increased viscosity at lower shear rates. It was already shown that CMC for TWEEN80 for EG-PEDOT-PSS system is about 0.5g/l (Figure 4). In our case, the concentration of surfactant was above the CMC (3 g/l), which resulted in possible formation of rod-like micelles and generating of additional entanglements within the polymer system [25]. This caused even further viscosity increase at lower shear rates.

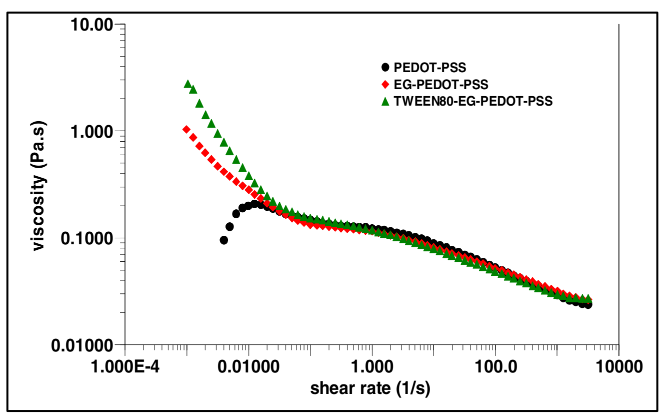


Figure 7: *Flow curves for different PEDOT-PSS based inks.*

Conclusions

There are many advantages and challenging disadvantages of using printing processes in the manufacture of electronic devices. The main advantages include high-speed fabrication, low cost manufacturing, and possibility of using flexible substrates, less waste and roll-to-roll capability. On the other hand, each of the available printing processes has its limitations, such as resolution, registration and uniformity of the printed layer. Among printing processes, gravure printing is considered to deliver the highest quality print and thus it is believed that it also has a big potential in printed electronics. Gravure printing and materials are very well established for printing of visual images. But, there is very little known about the printability of materials needed for electronic devices. And therefore there is a need for deeper investigation of conductive inks properties and performance. Working properties of inks, such as surface tension, rate of evaporation, and rheology, are very important in the process of evaluating new functional materials for electronics printing. In addition, the effect of different additives used in optimization of ink's press performance on quality and electrical properties of printed layers needs to be evaluated.

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