Fabrication of the solution-processible OLED/OTFT by the gravure printing/contact transfer: role of the surface treatment

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Keywords : OLED, OTFT, Gravure printing, Self-assembled monolayer, PEDOT:PSS

Abstract

We have investigated the effectiveness of a gravure printing method for the fabrication of organic light-emitting diode (OLED) and Organic Thin Film Transistor (OTFT). Printing of the organic layers was performed with a small-scale gravure coating machine, while the metallic layers were vacuum-evaporated. Devices with gravure-printed layers are at least comparable with the spin-coated devices. Effects of the solvent formulation and surface energy mismatch between the organic layer materials on the printed patterns and device performance were discussed. We will present the initial design and experimental data of OTFT fabricated by roll-type soft contact transfer process.

1. Introduction

Conducting or semiconducting organic materials (both polymeric and molecular materials) are advantageous in terms of their capability for solution processing, such as spin/blade coating, inkjet printing, and other roll-type printing methods. Spin coating allows a fabrication of thin and homogeneous films. However, material usage is not efficient since large fraction of the solutions is wasted during the spin coating. Furthermore, direct line patterning should accompany the additional patterning process such as photo-lithography or laser imaging. Therefore, investigation of the direct printing process for both area-coating and fine-line patterning is required, which can be applied for the fabrication process of organic light emitting device (OLED) or organic thin film transistor (OTFT). [1.2]

Among the various direct contact printing, flexography and gravure printing have features which are cost effective, high throughput, and compatibility for roll-to-roll processing. However, the quality of the printed layer/patterns by these processes is strongly affected by surface/interfacial properties of substrate, ink formulation of organic materials, force between impression and engraved cylinders, and speed of printing.

In this paper, we have employed a gravure coating process, specifically investigating the role of ink formulation (by solvent mixing and additive) and control of surface properties (by hydrophobic/ hydrophilic treatment) on the uniformity of coated layers and device properties of polymeric OLEDs and OTFTs.

2. Experimental

Gravure coating and printing method could transfer the ink embedded at engraved disk surface to substrate. During printing, the printing ink is filled into the engraved cells, while the use of a flexible doctor blade removes the excess amount [3]. We have used 33um-depth engraved disk with triangular continuous patterns for this experiment. Fig.1 shows scheme of printing process and image of tester machine. When extended to process for roll to roll web-coating, continuous fabrication of flexible devices with organic layer thickness of 30nm-200nm (individual) and 50um-scale line patterns might be possible with carefully prepared engraved disk roll.

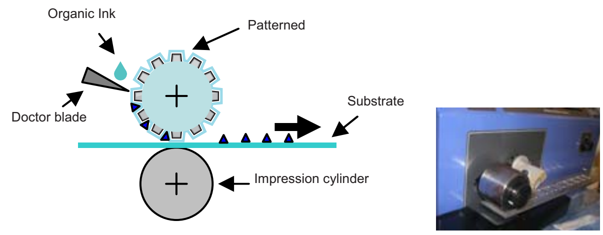


Fig. 1 The scheme of gravure printing process and equipment image of tester (*IGT-G1*, *Netherland*)

It is possible to improve the adhesion between ITO and organic materials by the modification of ITO surface. In order to uniformly coat the PEDOT:PSS on the ITO surface, hydrophilic substrate surfaces are preferred. The substrates are treated with the ultra-thin layer of self-assembled monolayer (SAM) during our process, using 3-aminopropyltriethoxysilane (APTES) and methacryloxypropyltrimethoxysilane (MPS) as hydrophilic surface modifier. It changes the properties of ITO surface depending on the molecular structure of the silane-based materials under usage. APTES layer has amide group (-NH_3) in a molecule terminal, so that it is supposed to improve the adhesion between substrate and PEDOT:PSS. Fig.2 indicates the scheme of hydrophilic and hydrophobic surface treatment of ITO [4,5].

The patterned ITO substrates with a pixel size of 2.0mm×2.0mm were cleaned by ultra-sonication in deionized water, rinsed with hot isopropyl alcohol, and dried at hot plate (150^{o}C). OLEDs were fabricated in order to compare the efficiency and brightness of devices prepared by spin coating and gravure printing. First, we have verified charge injection through thin SAM layer. APTES dissolves various ratios in methanol: water (95:5 v/v) and ITO glasses were immersed in this solution. The ITO was subsequently annealing at 60℃ hotplate. PEDOT:PSS was mixed with various methanol content, which is subjected to spin coating (3000rpm/60sec) or gravure printing (1.0N/m, 0.2m/s, set for overall processes).

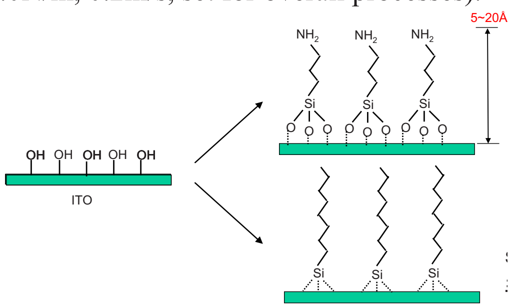


Fig. 2 The scheme of the ITO surface treatment by APTES or octadecyltrichlorosilane (OTS) as self-assembled monolayer

Fluorene-based copolymers (Lumation* NRP5, and Green 1304 light emitting polymers, *Trademark of Dow Chemical; now Sumitomo Chemical, for red and green) were employed for OLED fabrication. They were dissolved at 1.0wt% in p-xylene, subjected to gravure or spin coating process, and then annealed at 150^{o}C hotplate in nitrogen atmosphere. LiF/Al cathode was deposited at pressure less than 2x10^{-7}Torr.

3. Results and discussion

3.1. Gravure printing for OLED fabrication

In order to confirm the existence of SAM layer as a surface-modifying material, we have measured x-ray photoelectron spectroscopy (XPS, see Fig. 3). Using the monochromatic Al Kα radiation, photoelectron peaks of In, Sn, Si, N, C, O were monitored. Since the molecular structure of APTES surface can be characterized by the presence of the nitrogen and silicone species, peaks at N1s spectrum (398eV) shows the presence of APTES thin film, as well as the C1s and Sip2 spectral data compared to bare ITO film [6].

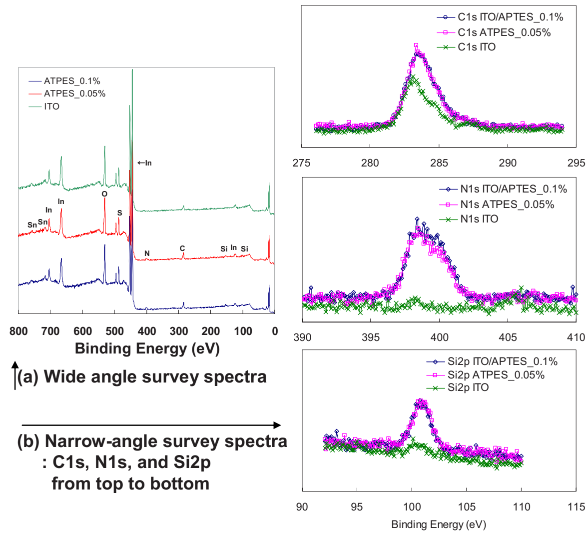


Fig. 3 XPS spectral survey analysis of the APTES (self assembled monolayer) –coated ITO surfaces

As a hole injection/transport layer in OLED structure, PEDOT:PSS (Baytron P TP AI4083) was employed. In order to facilitate the evaporation of solvent media, pristine AI4083 PEDOT:PSS was mixed with methanol, yielding the general improvement of the macro-uniformity of gravure printed films. Both the condition of SAM layer (APTES or MPS) on ITO surface and the concentration of methanol affected the optical clarity of PEDOT:PSS film, as seen in Fig. 4: optical microscopy image of gravure printed conditions

Generally, in a gravure printing, viscosity of the ink is higher than the case of other process such as spin coating or inkjet printing [7]. We prepared three PEDOT:PSS samples: pure PEDOT:PSS, PEDOT:PSS with 50% (v/v) methanol, and PEDOT:PSS with 30% methanol. We found that optical clarity (hence representing the macroscopic uniformity of coated film) of PEDOT:PSS/methanol ratio 5:5 (v/v) is better than 7:3 (v/v), in case of ITO substrate treated with APTES. At the surface of MPS treated ITO, PEDOT:PSS shows inferior optical clarity compared with APTES-treated ITO.

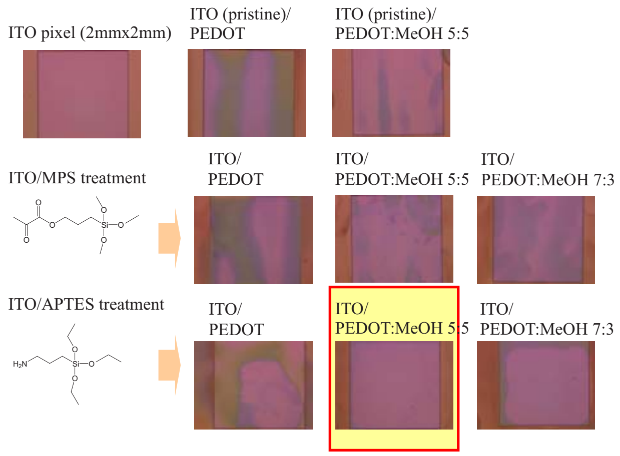
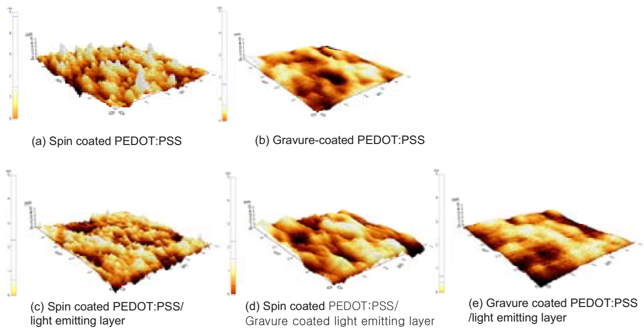


Fig. 4 Microscopic image for the evaluation of optical clarity, which will govern the macroscopic uniformity of gravure printed PEDOT:PSS on ITO

The morphology of the printed surface of PEDOT:PSS on ITO was characterized by atomic force microscope (AFM, Fig. 5). AFM topographic image of demonstrate morphologies of PEDOT:PSS AI4083:Methanol (50/50) by spin coating, gravure printing, and PEDOT:PSS/light emitting layer prepared with combination of spin/gravure processes. Comparing the root mean squre (rms) value, gravure printed PEDOT:PSS shows lower value than spin coated one. A phosphorescent light emitting layer was composed of 4,4'-N,N'-dicarbazole-biphenyl (CBP) as host, poly(9-vinyl carbazole) (PVK) as co-host and matrix, and fac-Tris(2-phenylpyridine) iridium(III) [$Ir(ppy)_3$] as dopant in p-xylene solution. The control of viscosity was performed by the variation of solid contents in the mixed solution.

In order to compare the charge injection and efficiency of device using ITO/APTES structure, concentration of APTES for dip coating on ITO surface was varied. The results were shown in Fig.6. Reference is a device without APTES layer between spin-coated PEDOT:PSS and ITO (note that gravure coating of PEDOT:PSS on bare ITO yields highly non-uniform surface with poor optical clarity). The spin-coated device with pristine ITO surface (UV-ozone treated) shows better brightness and efficiency than APTES-treated ones. However, gravure-printed device shows that SAM-treated surfaces are at least comparable brightness and efficiency than device with pristine surface of ITO. We are currently under investigation of the variation of thickness and microscopic surface roughness of gravure-printed organic layers. In our experiments, we have found that covering the thin layer of APTES on ITO does not hinder the charge injection for OLED performance.



sample	(a)	(b)	(c)	(d)	(e)
rms	0.75	0.34	0.45	0.596	0.25

Fig. 5 AFM image of spin or gravure coated PEDOT:PSS and PEDOT:PSS/light emitting layers on ITO glass treated with 0.05% APTES.

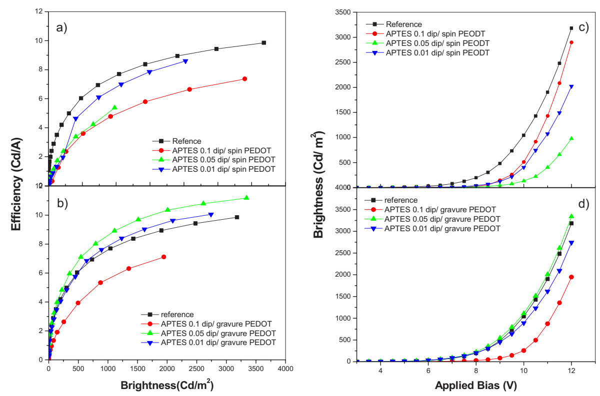


Fig. 6 Brightness and efficiency graph of spin coated/ gravure printed devices

3.2. Contact transfer process for OTFT fabrication

Contac transfer method using the soft material is a novel technique for the fabrication of micro- or nano-structures on large surfaces. The method is based on the excellent replication fidelity obtained with polymers and combines thermo-plastic molding with common pattern transfer methods. Fig. 7 illustrates the soft lithographic transfer method based on roll-type coating process, which is beneficial for large are and flexible device fabrication. Various micro- or nano-patterns will be investigated for a fabrication of patterned substrates and transistors, especially OTFT with patterned source/drain structure. Conceptual roll (either gravure or flexo) coating process will be applied for a peeling/transfer step, with the control of impression pressure, rolling speed, surface coating of pattern roll, and type of transferred materials (silver patterns or transparent, semiconducting oxide).

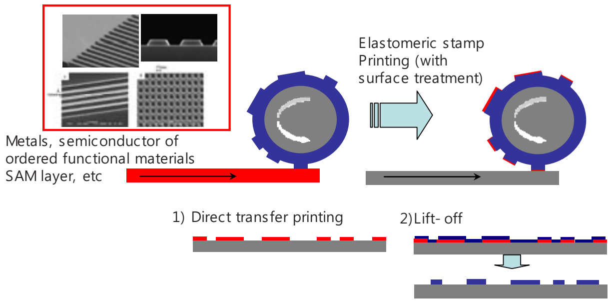


Fig. 7 Schematics of Soft contact transfer method based on roll-type coating process, providing patterned substrates and electrodes for OTFT.

4. Summary

Both the formulation of inks and modification of the substrate are essential for an application of gravure printing for OLED fabrication process. In the present paper, we have confirmed the validity of gravure printing process using SAM-treatment on the ITO surface and PEDOT:PSS ink formulation. Such an interfacial modification technique is essential for a fabrication of large scale or high resolution devices, especially for integrated OTFT and other organic devices.

Acknowledgement.
This research was supported by the Seoul R&BD support program (10848) and "SystemIC2010" project, Ministry of Knowledge Economy, Korea.

5. References

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