

Triisopropylsilyl pentacene organic thin-film transistors by ink-jet printing method

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Abstracts

By ink-jet printing method, organic thin-film transistors (OTFTs) having soluble 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) as an active material were fabricated. The TIPS pentacene solution was made with chlorobenzene and anisole. The solutions were printed on poly (4-vinylphenol) (PVP) dielectric layers and source/drain electrodes by piezo-type heads for bottom contact OTFTs. The dielectric layers had untreated or HMDS-treated conditions. The chlorobenzene device showed the highest field effect mobility of $0.016 \text{ cm}^2/\text{Vs}$ and the anisole HMDS-treated device shows the highest $I_{\text{on}}/I_{\text{off}}$ ratio of 10^5 .

1. Introduction

Organic thin-film transistors (OTFTs) have been improved the performance in the last several years and their field-effect mobility and on/off current ratio values are comparable to those of amorphous-silicon TFTs [1]. Many organic semiconductors are used for OTFTs. Especially the pentacene is one of the most promising organic compounds for many applications. OTFTs with field-effect mobility up to $7.0 \text{ cm}^2/\text{Vs}$ using the evaporated pentacene have been reported [2]. Despite the high performance, the high vacuum deposition process is difficult to dramatically lower the manufacturing cost. Also, using shadow mask is unsuitable for large-area applications. The solution process, on the other hand, may enable the fabrication of large-area and low-cost applications such as the large size flat panel displays [3][4]. Also it is a method that can be adapted for the roll-to-roll process.

Various solution processes are used to fabricate OTFTs such as spin coating, dip coating, drop casting, screen printing, blade coating, bar coating, rubber-stamp printing and ink-jet printing [5-8]. Each of the

solution processed films shows the different uniformity, molecular ordering and thickness. Usually Spin coating and dip coating are the methods for depositing uniform films. Films that deposited by drop casting shows a better ordering than those of deposited by spin coating, but with sample-to-sample variation. In this work, organic semiconductor films are deposited by ink-jet printing method.

Ink-jet printing method is one of the solution processes that reduced wasting of organic semiconductor materials [9]. There are two most common types of ink-jet dispensers, piezoelectric crystal dispensers (piezoheads) and thermoelectric dispensers (bubble jet heads). Piezoheads work through use of a piezoelectric crystal. By applying a potential across the crystal, it will create a pressure wave that expels ink droplets. The ink droplet volume variation is impact factor to ensure that the smallest possible lines and gaps can be repeatedly and precisely made.

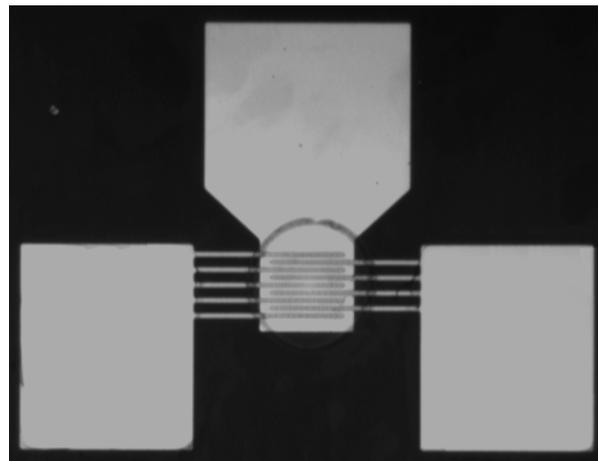


Figure 1. OTFT device with TIPS pentacene solution was printed for a channel layer.

Usually soluble organic semiconductors such as poly (3-hexylthiophene) (P3HT) and functionalized pentacene are used for OTFTs by solution processes. In this study, 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS pentacene) was used for OTFT fabrication. Figure 2 shows the structure with TIPS pentacene where added bulky groups at the 6 and 13 positions of the pentacene molecule. TIPS pentacene is known to have a pi-type molecular crystal packing and also same crystal packing in solution process [5].

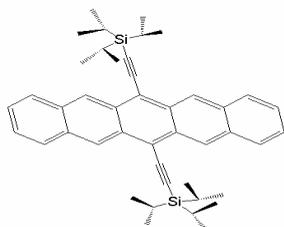
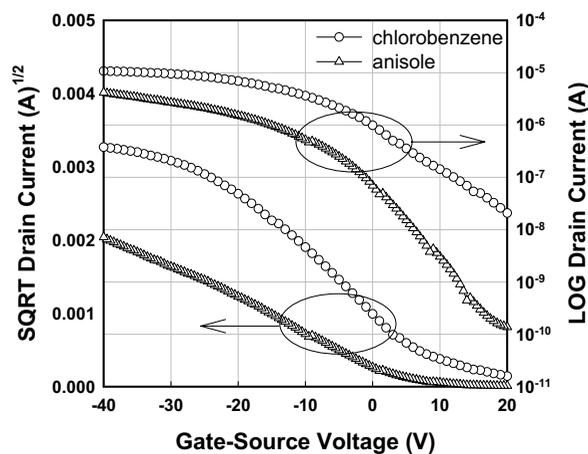


Figure 2. 6,13-bis (triisopropylsilylethynyl) pentacene (TIPS pentacene)

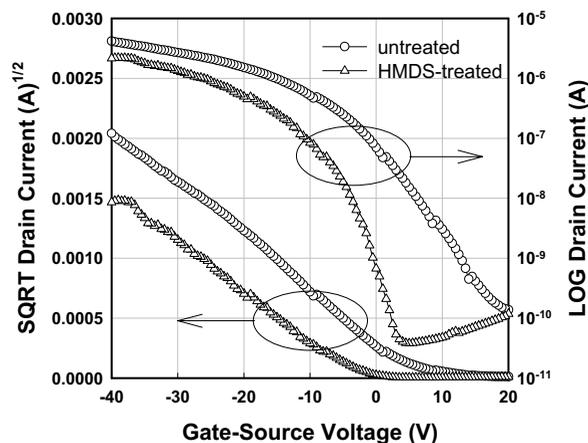
2. Results

OTFTs for ink-jet studies were made with a bottom-gate, bottom-contact configuration. A 100-nm-thick Al-Si (Si 1 wt%) gate electrode was deposited by DC sputtering method at the room temperature. Poly (4-vinylphenol) (PVP) was used for the gate dielectric layer by the spin-coating method with a thickness of 600 nm. Propylene glycol monomethyl ether acetate was used as a solvent and 5 wt% poly (melamine-co-formaldehyde) methylated was used as a curing agent for the 10 wt% PVP solution. The spin coated film was annealed in an oven at 200°C for 60 min and cooled down to room temperature. In order to fabricate source/drain electrodes, e-beam-deposited Cr (5 nm-in-thickness) with a thermally evaporated Au (100 nm-in-thickness) layer was used. The gate and source/drain electrodes were patterned by a conventional photolithography method. Then some films were treated with hexamethyldisilazane (HMDS) by spin coating. HMDS was spun on the sample and maintained for 2 minutes and then spin-coated at rate of 3000 rpm/min. Chlorobenzene and anisole were used as the solvent for dissolving TIPS pentacene with 1 wt% in concentration. The TIPS pentacene solutions were deposited by ink-jet printing method for channel layers (see Fig. 1). The ink-jet printing machine (UniJet UJ2100) had 30 μm-size piezoheads (microfab) and XY-motion stage. The average ink drop diameter was 31 μm, volume of 16.9

pl and with average drop velocity of 3.0 m/s. The gap between the end of the piezo-head and the surface of the devices was 1 mm. The sizes of the ink-jet printed drops were different with the solution used. The chlorobenzene drop size was almost 10 percent larger than the anisole drop size. And the size of a drop on the untreated dielectric layer was almost 10 percent larger than those of a drop on the HMDS-treated one. This effect is due to the difference in the surface tension of the gate dielectric surface. As a result, it was difficult to make patterns accurately on the HMDS-treated surface with anisole-solution.



(a)



(b)

Figure 3. The transfer characteristics of the TIPS pentacene OTFTs ink-jet printed (a) from chlorobenzene and anisole on the untreated dielectric surface (b) from anisole on the untreated and the HMDS-treated dielectric surface.

Table 1. Transistor parameters for the variation solvents and surface condition in Figure 2

	mobility (cm ² /V-s)	I _{on} /I _{off}	threshold voltage (V)	subthreshold slope (V/dec)
chlorobenzene untreated	1.6x10 ⁻²	10 ^{3.5}	10.5	
anisole untreated	4.3x10 ⁻³	10 ^{4.5}	4.5	
anisole HMDS-treated	4.1x10 ⁻³	10 ⁵	-3.2	2.5

Figure 3 shows drain to source current (I_{DS}) versus gate to source voltage (V_{GS}) characteristics with a drain to source voltage (V_{DS}) of -30V (a) using chlorobenzene and anisole solutions on the untreated PVP dielectric surface, and (b) from anisole solutions on the untreated and HMDS-treated PVP dielectric surface.

The untreated device from chlorobenzene solution shows the highest field effect mobility (0.016 cm²/Vs), which is more than 3 times higher than that of untreated one from anisole solution (see Fig. 3 (a)). But the anisole device shows the higher current I_{on}/I_{off} ratio (10^{4.5}), and lower subthreshold slope than those of the devices from chlorobenzene (10^{3.5}). The leakage current (off current) of the chlorobenzene device was relatively high, which might be related to residual impurities, and oxidative doping by the solvent [10]. The reduced leakage current of both the devices may be achieved by several factors; (1) a sharp pattern of the ink-jet printed TIPS channel layer, (2) a passivation layer for isolation from air [11].

Figure 3 (b) shows the effect of the dielectric surface treatment. Both the devices had similar field effect mobility (~0.004 cm²/Vs), but the HMDS-treated one showed higher current on/off ratio (10⁵), and lower subthreshold slope (~2.5 V/decade) than the untreated one. In addition to the HMDS-treatment, the threshold voltage shifted towards more negative values. It may be caused by the dipole moment depending on the electron acceptance property of the HMDS's head group (CH₃)₃Si [12].

3. Conclusion

Here, OTFTs with ink-jet printed TIPS channel layer were fabricated. The device made from chlorobenzene solution had the highest field effect mobility than that of the device from anisole solution. But the chlorobenzene device had lower I_{on}/I_{off} ratio, larger threshold voltage and subthreshold slope.

When anisole solution was ink-jet printed on untreated and HMDS-treated dielectric layers, the HMDS-treated device showed higher I_{on}/I_{off} ratio and lower subthreshold slope. However it was difficult to make patterns accurately on the HMDS-treated dielectric layers with anisole solution. It might be arranged by using the hydrophobic treated bank layers.

5. References

- [1] S F Nelson, Y Y Lin, D J Gundlach, T N Jackson, Appl. Phys. Lett. Vol 72, 1854(1998)
- [2] M P Hong, B S Kim, Y U Lee, K K Song, J H Oh, J H Kim, T Y Choi, M S Ryu, K Chung, S Y Lee, B W Koo, J H Shin, E J Jeong, L S Pu, SID Dig. 23(2005)
- [3] Z Bao, A Dodabalapur, and A J Lovinger, Appl. Phys. Lett. Vol 69, 4108-4110 (1996)
- [4] T W Kelley, D V Muryes, P F Baude, T P Smith, and T D Jones, Mater. Res. Soc. Symp. Proc. Vol 771, L6.5 (2003)
- [5] S K Park, C C Kuo, J E Anthony and T N Jackson IEEE International Electron Devices Meeting (IEDM) Technical Digest, 105-108 (2005)
- [6] Y H Kim, D G Moon, W K Kim and J I Han, J. SID, Vol 13, 829-833 (2005)
- [7] C C Kuo, M M Payne, J E Anthony and T N Jackson, 2004 IEDM Technical. Digest, 373-376 (2004)
- [8] M Plotner, T Wegener, S Richter, S Howitz, W J Fischer, Synth. Met. Vol 147, 299-303 (2004)
- [9] S K Volkman, S Molesa, B Mattis, P C Chang, V Subrmanin, Mater Res. Soc. Symp. Proc. Vol 769, H11.7.1/L12.7.1 (2003)
- [10] J F Chang, B Sun, D W Breiby, M M Nielsen, T I Solling, M Giles, I McCulloch, H Sirringhaus, Chem. Mater. Vol 16, 4772-4776 (2004)
- [11] H Sirringhaus, N Tessler, and R H Friend, Synth Met. Vol 102, 857-860 (1999)

[12] K P Pernstich, S Haas, D Oberhoff, C Goldmann,
D J Gundlach, B Batlogg, A N Rashid, G Schitter,

J. Appl. Phys. Vol 96, 6431-6438 (2004)