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Investigation of Solvent Effect on the Electrical Properties of Triisopropylsilylethynyl (TIPS) Pentacene Organic Thin-film Transistors

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In this paper, we investigated the electrical properties of triisopropylsilyl (TIPS) pentacene organic thin-film transistor (OTFT) depending on solvent type. We spin coated TIPS pentacene by using chlorobenzene, p-xylene, chloroform, and toluene as solvents. Fabricated OTFT with chlorobenzene shows field-effect mobility of 1.0×10^{-2} $cm^2/V\cdot s$, on/off ratio of 4.3×10^{3} and threshold voltage of 5.5 V. In contrast, with chloroform, the mobility is 5.8×10^{-7} $cm^2/V\cdot s$, on/off ratio of 1.1×10^{2} and threshold voltage of 1.7 V. Moreover we measured the grain size of each TIPS pentacene solvent by atomic force microscopy (AFM). From these results, it can be concluded that a solvent with higher boiling point results in better electrical characteristics due to large grain size and high crystallinity of TIPS pentacene layer. In this paper TIPS pentacene with chlorobenzene shows the best electrical properties.

Keywords : OTFT, TIPS, Pentacene, Solvent effect.

Ⅰ. Introduction

Organic thin−film transistors (OTFTs) have attracted a considerable amount attention in various display application due to their potential advantages such as simple device architecture, large−area compatible fabrication and low−temperature process for flexible applications. Fabrication processes of OTFTs are much less complex compared with conventional Si technology, which involves high−temperature and high−vacuum deposition processes and sophisticated photo lithographic patterning methods. OTFTs have great potential for a wide variety of applications, especially for new products that rely on their unique characteristics. Such applications may include active−matrix flat−panel−displays (FPDs), active−matrix flexible−displays, radio frequency identification (RFID) tags, electrode paper (E−paper), smart cards, inventory tags, and large area sensor arrays [1−8]. There has been great progress in both the materials' performance and development of new fabrication techniques for replacing conventional inorganic TFTs in many applications. However OTFTs are limited by their switching speed and field−effect mobility.

In general, conjugated polymers, oligomers, or small molecules are used as organic active layer.

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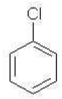
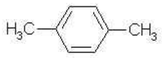
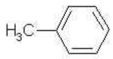
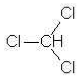
Table 1. Chemical structure and physical properties of solvents

Solvent	Chemical Structure	Formula	Boiling Point (℃)
Chlorobenzene		C_6H_5Cl (CHCHCHCHCHCCl)	131.72
P-xylene		C_8H_{10} (C(CH3)CHCHC(CH3)CHCH)	138.37
Toluene		C_7H_8 (C(CH3)CHCHCHCHCH)	110.63
Chloroform		$CHCl_3$	61.17

Especially, pentacene is one of the most promising organic compounds for many applications. OTFTs using the evaporated pentacene have been reported, that exhibited field-effect mobility 7.0 $cm^2/V·s$ [9]. Despite the high performance, expensive high vacuum processes are needed for making OTFTs using the evaporated organic materials. Also, using shadow mask is unsuitable for large-area applications. But the solution processes enables the fabrication of large-area and low-cost applications such as the large size flat panel displays [10-11]. Also they can be adapted for the roll-to-roll process. There are various solution processes for OTFTs fabrication such as spin coating, dip coating, drop casting, screen printing, blade coating, bar coating, rubber-stamp printing, ink-jet printing [12-15]. Ink-jet printing is one of the solution processes that reduced wasting of organic semiconductor materials [16]. All organic semiconductors cannot be used in solution process because many small-molecules are not dissolved in a solvent. So, polymers are commonly used in solution processed OTFTs. However several functional small-molecules having solubility are recently been tried.

Ⅱ. Experiments

First, We fabricated the device as shown in the structure such in figure 1. We deposited Al-Si (Si 1 wt%) with thickness of 100 nm on a cleaned glass substrate at room temperature by DC sputtering equipment with power of 400 W, and deposition pressure of 6 mTorr. Next we patterned the gate electrode by standard lithography process. Prior to the deposition of gate electrode, the surface of bare glass was cleaned with acetone, methanol, and deionization water. As a gate dielectric, Poly 4-vinyl phenol (PVP) was deposited on the gate electrode by spin coating. The concentration of curing agent of PVP melamine-co-formaldehyde was fixed at 5 wt% and Poly 4-vinyl phenol was fixed at 10 wt%.

We first put the sample in a convection oven set at 90°C for 5 minutes to remove the excess solvent. Then, the PVP was thermally cured at 200°C for one

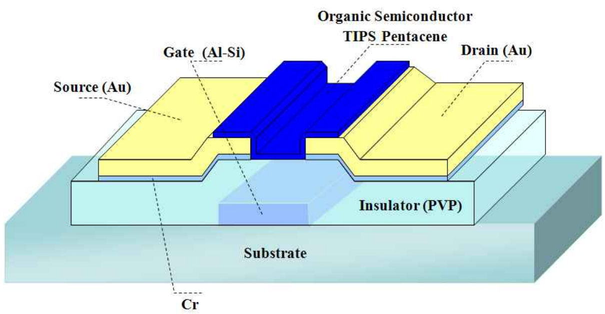


Figure 1. The vertical structure of OTFT with bottom gate/bottom contact

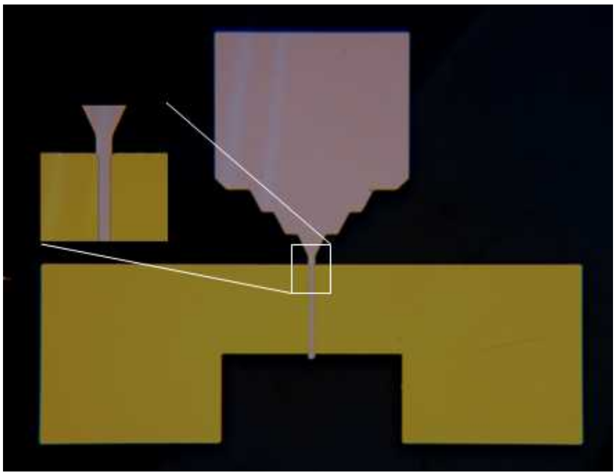


Figure 2. An image of OTFT device fabricated with TIPS pentacene as an active layer.

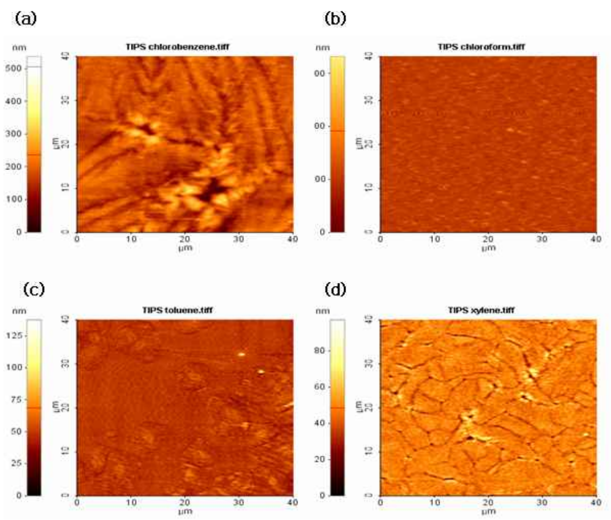


Figure 3. AFM images of pentacene layer spin-coated from different solvent. (measured rage is 40μm×40μm) (a) chlorobenzene (b) chloroform (c) toluene (d) p-xylene

hour to crystallization. For source/drain electrode, we used the Cr/Au double layer. Cr layer of 5 nm was deposited on the PVP insulator to improve adhesion of Au and gate insulator by e-beam sputtering system. Au contacts of 100 nm were deposited by thermal evaporation. It is well known that gold is very good material of source and drain electrodes for OFTFs [17-18]. Before spin coating TIPS pentacene, hexa-methyldi-silazane (HMDS) was spin coated for surface modification by spinner. The HMDS treatment has already been known to enhance the hole mobility of pentacene-based OTFTs [19], in our research, we used the treatment to examine its effects on the channel/Source-Drain interface state. Finally, TIPS pentacene (1 wt%) with four different solvents: chlorobenzene, p-xylene, chloroform and toluene, was spin coated on Source-Drain electrode. Chloroform is a general solvent for OTFT's active layers. However, its low boiling point and rapid evaporation limit the time for crystallization during the spin-coating process. Chang et al., investigated a range of solvents with higher boiling points that is chloroform, thiophene, xylene, cyclohexylbenzene (CHB), and 1,2,4-trichlorobenzene (TCB) [20].

Table 1 is the chemical structure and physical properties of each solvent which was used as our TIPS pentacene solvent [21]. The OTFT device has bottom/top gate and bottom/top contact type structure. Our pentacene TFT device was made by bottom contact with Cr/Au as source and drain electrodes.

Ⅲ. Results & Discussion

Figure 2 is the optical microscopy image of the OTFT and boxed portion is spin-coated active layer where TIPS pentacene solvent was used as an active layer. Figure 3 shows the AFM image of the different TIPS pentacene solvent. 50 nm-thick pentacene thin-film on PVP was fabricated for AFM measurements. Each image range is 40 μm × 40 μm. The grain size of pentacene layer is larger for solvents with higher boiling point.

We can see the clear crystalline structure of pentacene thin film from Figure 4. TIPS pentacene film showed a preferential orientation of (001) direction. The crystallinity of the film was strongly dependent on the solvent. The TIPS pentacene film coated from chlorobenzene solution showed the highest crystal-

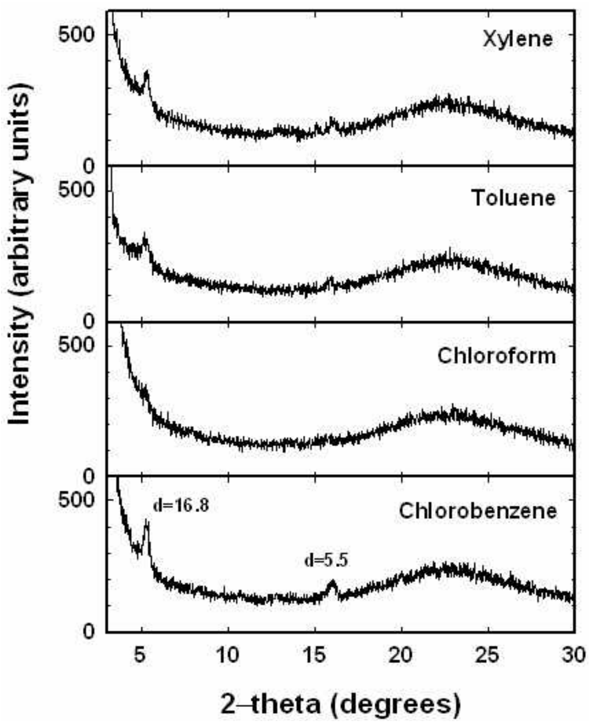


Figure 4. XRD measurements of the pentacene layer formed by different solvent ((a) p-xylene (b) toluene (c) chloroform (d) chlorobenzene)

Figure 5. Transfer characteristics of TIPS pentacene OTFTs favricated with different solvent.

linity, while the film coated from chloroform had nearly no crystalline phase.

In the figure 5, the best performance can be found in devices made by chlorobenzene. The entire current-voltage characteristics of our fabricated pentacene OTFTs were measured by a parameter analyzer (KEITHLEY 4200).

Figure 6. The transfer curves of an OTFT device fabricated with TIPS pentacene. The source-to-drain voltages were −40 V and −80 V respectively.

Figure 7. Output curves of an OTFT device fabricated with TIPS pentacene. The gate-to-source voltages were changed from 0 V to −80 V with −20 V step

Figure 6 shows the logarithmic plot of I_{ds} and represents the properties of TIPS pentacene in the Chlorobenzene. Then, Drain-Soure voltage bias is −40 V, −80 V. And figure 7 shows the output characteristics of an OTFT made with TIPS pentacene in

Table 2. The variation of electrical properties of pentacene OTFTs

Solvent	mobility (cm2/V ·s)	Ion/Ioff	Threshold Voltage (V)
Chlorobenzene	0.01	4.3×103	5.5
Chloroform	5.8×10−7	1.1×102	1.7
P-xylene	1.2×10−3	1.4×103	−0.8
Toluene	6.6×10−4	3.4×102	5.4

chlorobenzene.

As clearly seen in the graph, the solvent of TIPS pentacene has significant effect on the electrical properties of OTFT device.

The field effect mobility μ and the threshold voltage V_{th} are extracted from saturation region of the transfer characteristic using the following equation.

$$I_{ds} = \mu C_i \frac{W}{2L}(V_{gs} - V_{th})^2$$

Where I_{ds} is the drain current, L is the channel length, W is the channel width, C_i is the capacitance per unit area of the insulating layer, V_{gs}=−80 V is the gate voltage and V_{th} is the threshold voltage. The insulator capacitance C_i= 6.5 nF/cm^2 is a 600 nm thick insulator, and the device channel width W and length L are 2400 μm and 15 μm, respectively.

Ⅳ. Conclusion

Generally, grain size strongly depends on substrate temperature, deposition rate, and surface treatment. Through experiment, we knew that grain size is also influenced by the solvent. Therefore we investigate a range of solvents with higher boiling points in this paper. With chlorobenzene as a solvent of higher boiling point, the device showed the highest saturation field-effect hole mobility of 1.0×10^{-2} cm^2/V·s, on/off ratio of 4.3×10^3 and threshold voltage of 5.5 V. In contrast, chloroform with lower boiling point showed poor electrical properties with field-effect mobility of 5.8×10^{-7} cm^2/V·s, on/off ratio of 1.1×10^2 and threshold voltage of 1.7 V. The electrical characteristics of OTFT devise made with different solvent are listed in Table 2. We are unable to fully understand this phenomenon yet. However, we conclude that the solvent of pentacene film is not a unique indicator in determining the grain size.

Acknowledgement

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용제에 따른 TIPS(triisopropylsilyl) Pentacene을 이용한 유기박막 트렌지스터의 전기적 특성에 관한 연구

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(2008년 6월 3일 받음, 2008년 7월 10일 수정, 2008년 7월 17일 확정)

본 논문은 TIPS Pentacene을 유기반도체로 사용한 유기박막 트렌지스터의 용제에 따른 전기적 특성에 대한 연구로서, 용제로는 chlorobenzene, p-xylene, chloroform, toluene을 사용하였으며, 회전 도포 방법을 사용하여 TIPS pentacene을 혼합하여 적층하였다. chlorobenzene을 사용하여 만들어진 유기박막 트렌지스터는 1.0×10^{-2} $cm^2/V\cdot s$의 전계효과 이동도, 4.3×10^3의 on/off 비율, 5.5 V의 문턱전압의 특성을 보였다. 반대로, chloroform을 사용하여 만들어진 유기박막 트렌지스터는 5.8×10^{-7} $cm^2/V\cdot s$의 전계효과 이동도, 1.1×10^2의 on/off 비율, 1.7 V의 문턱전압의 특성을 보였다. 또한 각 용제에 따른 TIPS pentacene 결정크기를 AFM을 통하여 측정하였다. 이와 같은 결과들을 통하여, 더 높은 끓는점을 가진 용제는 TIPS Pentacene의 더 큰 결정 크기와 높은 결정화 성향으로 인하여 더 좋은 전기적 특성을 가지는 것을 확인할 수 있었으며, 본 실험에서는 끓는점이 가장 높은 chlorobenzene을 사용한 TIPS Pentacene 유기박막 트렌지스터가 가장 좋은 전기적 특성을 나타내는 것을 확인하였다.

주제어: 유기박막 트랜지스터, TIPS(triisopropylsilyl), 펜타신(Pentacene), 유기용제

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