Fluorophilicity as Selection Criterion of Solvents for Printed Organic Electronics

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Abstract The deteriorations of carrier mobility of organic thin film transistors after immersing into various solvents containing fluorine were investigated. The deteriorations showed the correlation with the fluorophilicity, the partition ratio between solvents containing fluorine and without fluorine. The fluorophilicity will be a useful parameter for screening the process solvent.

Keywords: Printed Electronics, Organic Semiconductor, Orthogonal Solvents.

1. Introduction

Printing is one of good candidate processes for fabricating flexible devices, because it is expected to have high throughput and require merely low temperature process enough to apply the plastic substrates. For printing process, the organic semiconductor is a good candidate to be used as semiconductor ink rather than inorganic ones, because it doesn't require high temperature annealing process such as 300°C.

As the printing is a kind of wet process, organic solvents play important roles to achieve the good productivity. If the lower layer is soluble to the solvent of the upper layer, the intermixing occurs at the interface of these layers, and the performance of the device will be much worse than designed. So, the solvents for the printing process should be carefully selected. The inertness of the solvent to the lower layer is called 'orthogonality', and the 'orthogonal' combination of the material and solution is one of the big issues on the wet process.

On the other hand, the fluorine containing solvents, such as Fluorinert™ (3M), Vertrel™ (DuPont) and CT-Solv™ (Asahi Glass), are empirically known to be inert to most of the ordinary hydrocarbon molecules. So they are useful in designing the orthogonal combination. We have been developing the fluorinated polymer coatings applicable to printed organic electronics these years1). CYTOP™, poly-(perfluorobutenylvinylether), is one of those materials2). It is soluble to the fluorine containing solvent such as CT-Solv™, and insoluble to the solvent without fluorine. So CYTOP™ can be used as the orthogonal coatings to any organic layers. For example, CYTOP™ is used as a gate insulator of top gate structure device which requires the coatings directly onto the organic semiconductors.

Recently the orthogonality of the solvents was thoroughly examined and discussed by A. M. Gaikwad et al.3). And to our knowledge, there is no report on the criteria to select the fluorinated solvents for organic electronics processes such as polymer coating, cleansing, lift-off, and so on. In this paper, we investigated the damage to the organic thin film transistors caused by various kinds of fluorine containing solvents.

2. Experiment

We fabricated the organic thin film transistors (OTFTs) by wet or dry process, and performed the immersing test, on which we characterized them before and after immerse into the various solvents.

2.1 OTFT

Figure 1 shows the cross-sectional view of the OTFT for our investigation. The structure is the inverted staggered type, so-called top-contact-bottom-gate.

The source and drain electrodes are made of 40nm thick Au (gold) coated by evaporation, and the gate electrode is the highly doped n+-Si (silicon) substrate. The gate insulator is 100nm thick SiO2. Channel dimension is : L/W=200/2000µm.

We prepared three organic semiconductors (OSC) : 3, 11-Didecyldinaphtho[2,3-d:2',3'-d']benzo[1,2-b:4,5-
b’-dithiophene (C10-DNBDT) [4], Dinaphto[2, 3-b:2’,3’-f]thieno[3,2-b]thiophene (DNTT), or 2,7-Diphenyl[1]benzothieno[3,2-b][1]benzothiophene (DPh-BTBT). The reason we chose these materials was that they were known to show high carrier mobilities over 1 cm/Vs which made us easy to measure. The chemical formula of them are shown in Figure 2. C10-DNBDT was wet coated[4], on the other hand DNTT and DPh-BTBT were dry coated with evaporator.

2.2 Solvents

Table 1 shows the solvents for this immersing test. For characterizing the solvents, we adopted three parameters: fluorine contents, molecular weight, and the fluorophilicity (Pf)[5-6]. Pf is experimentally determined by the partition ratio of the fluorine containing solvent to the organic solvent without fluorine. If the molecule has the affinity or compatibility to the fluorine containing solvent, the partition ratio increases, then Pf becomes large. In this paper, we adopted the toluene as the solvent without fluorine because OSCs are slightly soluble to the aromatic solvent, and perfluoro-methylcyclohexane as the fluorine containing solvent, because it is alike in chemical structure but not compatible to the toluene.

Fluorine content is the weight ratio of fluorine atoms to the molecule, defined as (NF x 19)/Mw, in which NF is the number of fluorine atoms in the molecule and Mw is molecular weight.

2.3 Measurement

OTFTs were immersed into the various solvents for 5 minutes. The temperature of the solvents was 20-25 degree Centigrade. After the immersion, OTFTs are dried in vacuum at room temperature. We achieved transfer curves of OTFTs before and after the immersion. The gate voltage (Vg) varied from –30V to 20V, and the drain voltage was –30V when source

| No. | Name         | Structural formula | Fluorine content | Mw   | Pf  |
|-----|--------------|--------------------|------------------|------|-----|
| 1   | FC-43        | C_{14}F_{25}N-C_{14}F_{9} | 76%              | 671.09 | >20 |
| 2   | AC2000       | C_{14}F_{25}N-C_{14}F_{9} | 77%              | 320.05 | 12  |
| 3   | AC6000       | C_{14}F_{25}N-C_{14}F_{9} | 71%              | 348.10 | 5.6 |
| 4   | HFE-7300     | C_{14}F_{25}N-C_{14}F_{9} | 71%              | 350.08 | 8.2 |
| 5   | Vertrel-XF   | C_{14}F_{25}N-C_{14}F_{9} | 75%              | 252.05 | 3.7 |
| 6   | 1H, 1H, 2H, 2H-perfluorooctanol | C_{14}F_{25}N-C_{14}F_{9} | 68%              | 364.10 | 1.1 |
| 7   | AE3000       | C_{14}F_{25}N-C_{14}F_{9} | 64%              | 200.05 | 0.6 |
| 8   | HCFC-225ca/cb (45/55) | C_{14}F_{25}N-C_{14}F_{9} | 47%              | 202.94 | 0.3 |
| 9   | Perfluorobenzene | C_{14}F_{25}N-C_{14}F_{9} | 61%              | 186.05 | 0.3 |

| No. | Name         | Structural formula | Fluorine content | Mw   | Pf  |
|-----|--------------|--------------------|------------------|------|-----|
| 10  | Hexafluoro-2-propanol | F_{3}C-CF_{3}OH   | 66%              | 168.04 | 0.24 |
| 11  | 1H, 1H, 7H-perfluoroheptanol | F_{3}C-CF_{3}OH   | 69%              | 332.08 | 0.23 |
| 12  | Isopentane   | H_{2}C-CF_{3}H_{2} | 0%               | 72.15  | 0.18 |
| 13  | 1H, 1H, 9H-perfluoropentanol | F_{3}C-CF_{3}OH   | 65%              | 232.07 | 0.1 |
| 14  | 2-propanol (IPA) | H_{2}C-CF_{3}OH   | 0%               | 60.1   | 0.04 |
| 15  | PGMEA        | H_{2}C-CF_{3}OH   | 0%               | 132.16 | 0.02 |
| 16  | EDM          | H_{2}C-CF_{3}OH   | 0%               | 148.2  | 0.01 |
| 17  | 1,2-propanediol | H_{2}C-CF_{3}OH   | 0%               | 74.12  | 0.01 |
| 18  | Ethanol      | CH_{3}CH_{2}OH   | 0%               | 46.07  | 0   |
electrode was on the earth potential.

3. Results and discussions

3.1 Deterioration of carrier mobility

In order to quantify the damage, deterioration of carrier mobility was analyzed. As the typical example, Figure 3 shows the transfer curves and the plots for square root of drain current ($I_d$) of C10-DNBDT TFTs. The solid lines show the initial curve achieved before immersion, and the dotted lines show the curve after the immersion.

The solvent for Figure 3(a) is FC-43™ (perfluoro(tributylamine) by 3M), and (b) is AE-3000™ (a hydrofluoroether by Asahi Glass). Figure 3(a) shows little difference between before and after immersion. On the other hand, (b) shows obvious difference between them, showing the deterioration of carrier mobility ($\mu$) which is derived from the slope of the square root of $I_d$. Here we quantified the damage to the organic semiconductor as the carrier mobility deterioration ratio ($\Delta \mu$). The $\Delta \mu$ for (a) is 3% ($\mu$ changed from 3.3 to 3.4 cm$^2$/V$\cdot$s), and (b) is 46% (2.4 to 1.3 cm$^2$/V$\cdot$s).

3.2 Relationship between the damage and the parameters of solvent

In order to clarify the trend, we tried plotting the data with the parameters of solvent. Figure 4 shows the plot of the degrees of damage to C10-DNBDT TFTs by each solvent, with the horizontal axis of molecular weight (Mw) and the vertical axis of fluorine contents. Each number near the plot is correspondent to Table 1.

Considering the fabrication and measurement errors, we classified the degree of $\Delta \mu$ in three levels: no damage (less than or equal to 10%), medium damage (10–20%), damaged (more than 20%). It is natural that the solvent with high fluorine content doesn't bring about the damage in the Figure 4. However, in the low Mw region, this rule is not consistent. For example, the solvent 10 (Hexafluoro-2-propanol) with the fluorine content as high as 68% showed a high damage, as well as 9 (Perfluoro benzene) etc. This result shows that the fluorine content is not always the good criterion for select the inert solvent, and we should consider the chemical structure.

On the other hand, Figure 5 shows the result plotted with Mw and Pf. At the Pf larger than 1.0, we found no
damage on this OTFT. This is reasonable when we think that Pf reflects the incompatibility to the ordinary organic materials. And in the smaller Pf region, large Mw is advantageous in the view of less-damage. This is also reasonable because the smaller Mw has the higher compatibility which brings about damages on the organic semiconductors. From this result, we think that Pf is better criterion to select the inert solvent than the fluorine content.

We tried the same analysis with the other OSCs. Figure 6 shows the same plot as the Figure 5 on DNTT TFTs (a) and DPh-BTBT TFTs (b). The number of plot points decreased due to the fabrication failures.

In these plots, the Pf border of no-damage decreases to nearly zero, and Mw seems to be a dominant parameter. We think this is reasonable because both DNTT and DPh-BTBT are not soluble to the organic solvents. The solubility and inertness to the solvent will be in the trade-off relation.

From the result above, Pf border will vary for each OSC molecule, so we can’t decide the suitable solvent a priori without experiment. However, we believe that considering the Pf will be a good guideline for screening the solvent.

4. Conclusion

We investigated the deterioration of carrier mobility of organic TFT after immersing into various solvents containing fluorine. Although there were some variances by the OSC molecules, the deterioration was correlated with the fluorophilicity, the partition ratio between solvents containing fluorine and not containing fluorine. The fluorophilicity will be a useful parameter for screening the process solvent.

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