

博士論文（要約）

Control of threshold voltages of organic thin-film transistors by self-assembled monolayers and their structural analysis

（自己組織化単分子膜による
有機薄膜トランジスタの
閾値電圧制御と微細構造評価）

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Organic thin-film transistors (OTFTs) have been developed since the first demonstration in 1983. Recently the performance of OTFTs is greatly increased, thanks to the development of the materials and fabrication methods. In 2007, the mobility and the power consumption of the OTFTs became well competitive to the that of amorphous Si-based TFTs. The advantages of the OTFTs such as mechanical flexibility, robustness, and easiness and inexpensiveness in the process.

For the design of complex circuits, the parameters of single devices such as mobility and threshold voltage must be accounted, or, ideally, must be controllable. In this research, the control of the threshold voltage is of the interest. To maximize the characteristics of organic electronics, the process to control the threshold voltage must be simple and deterministic.

Among several methods to control the threshold voltage, the author focused on the use of alkylphosphonic acid-based self-assembled monolayers (SAMs) to modify the surface the gate dielectrics, because of the process simplicity, effect to lower driving voltage, and contrability of the surface potential. The tail group of a SAM-forming molecule affects the dipole moment along the molecular axis, which induces built-in potential. Control of the surface potential is demonstrated by utilizing SAMs with various dipole moments. Control of the threshold voltage is segmented to three elements: (1) Determination the threshold voltages of OTFTs by SAMs, (2) control the threshold voltage of individual OTFTs, and (3) investigation of the relationships between the state of SAM surface and threshold voltage. In this thesis, this topic is approached in three steps.

1. Spatial control of threshold voltage by stamping

In this chapter, the control of the threshold voltage of OTFTs with cm-scale stamping (microcontact printing) is demonstrated. To control the threshold voltage, SAMs of n-tetradecylphosphonic acid (HC14-PA) and 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecylfluoro-n-octadecylphosphonic acid (FC18-PA) were utilized. In a conventional SAM-forming method, substrates are immersed into the solution of the SAM-forming molecule, during which the entire substrate is covered by a single species of SAMs. In this work, stamping was applied to form more than one species of SAMs to different area on a substrate.

OTFTs with top-contact and bottom-gate structure were fabricated. First, on Si substrate, Al was deposited as a gate electrode. The surface of the gate electrode was oxidized by plasma, then SAMs were formed by stamping. Organic semiconductor of dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]-thiophene and Au source/drain electrodes were formed. By applying the stamping method, two species of SAMs were successfully transferred to the sample surface. The threshold voltage of the OTFTs with HC14-PA was -1.19 V, while that of the OTFTs with FC18-PA was -0.36 V, under the driving voltage of -2 V. The electric characteristics of the OTFTs with stamped SAMs were compared to those of OTFTs with SAMs by the conventional

dipping method. Figure 1 shows the comparison of transfer characteristics of the OTFTs composed of stamped SAMs and dipped SAMs. The performance of the OTFTs was equivalent regardless of the forming method of the SAMs. The morphology of the DNTT grains on the SAMs were observed by AFM. The size of the DNTT grains on the stamped SAMs was smaller than that of DNTT on the dipped SAMs, which indicated the rough surface of the stamped SAMs.

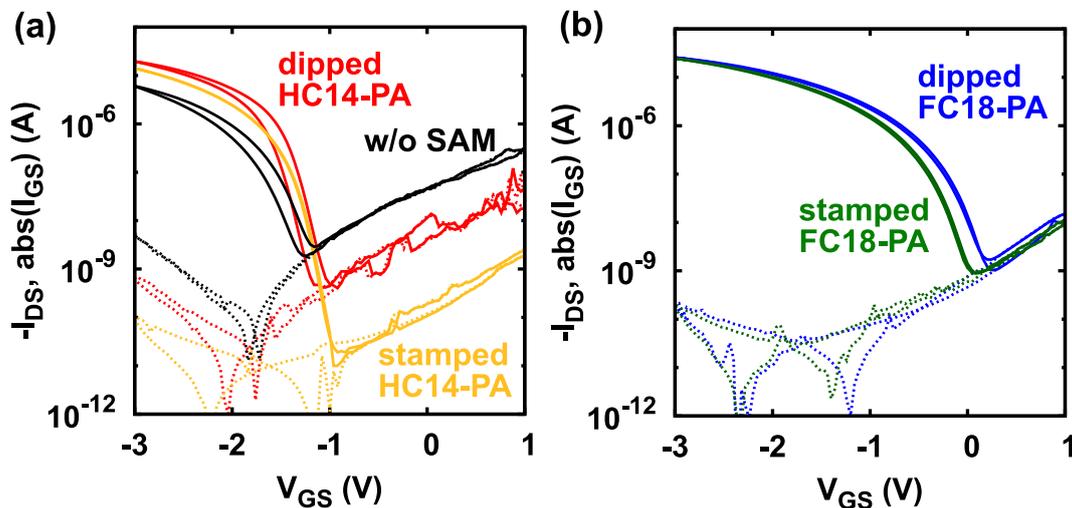


Figure 1. Comparison of transistor characteristics of OTFTs with stamped SAMs and OTFTs with dipped SAMs. (a) OTFTs with HC14-PA, (b) OTFTs with FC18-PA

To assess the effect of the excess of the SAM-forming molecules, the quality of the SAMs formed by SAMs was also evaluated by water contact angle (WCA), transmission electron microscopy (TEM), and near-edge x-ray absorption fine structure (NEXAFS). Most interestingly, NEXAFS result showed that the SAMs formed by stamping had the similar molecular structure to the SAMs by dipping in respect of the molecular orientation, coverage, and tilt angle.

Finally, the OTFTs with controlled threshold voltage were utilized in load inverters. With driving voltage of 3 V, the switching voltage was shifted by 2.6 V at the maximum. The gain and output voltage drop of the load inverters was governed by the conductivity and the subthreshold swing of the OTFTs.

2. Control of threshold voltage by co adsorption of SAMs

In this chapter, the coadsorbed SAMs of 3,3,4,4,5,5,6,6,7,7,8,8,8-terdecylfluoro-n-octylphosphonicacid (FC8-PA) and n-octylphosphonicacid (HC8-PA) were utilized as gate insulator modifiers to perform the continuous control of the threshold voltages. Also, the coadsorbed SAMs were observed by WCA, x-ray photoelectron spectroscopy (XPS), NEXAFS, and Kelvin-probe force microscopy (KFM). By changing the molecular composition of FC8-PA in the mixture of the SAM-

forming solutions, $\chi_{\text{sol}}^{\text{F}}$, the threshold voltages of OTFTs were controlled from -1 to 0.4 V. Figure 2 shows the transfer curves and threshold voltages of the OTFTs with coadsorbed SAMs. The shift of the threshold voltage was corresponded to the difference of the surface potential observed by KFM, induced by the use of SAMs. At the same time, smooth surface of the SAMs with higher $\chi_{\text{sol}}^{\text{F}}$ was observed.

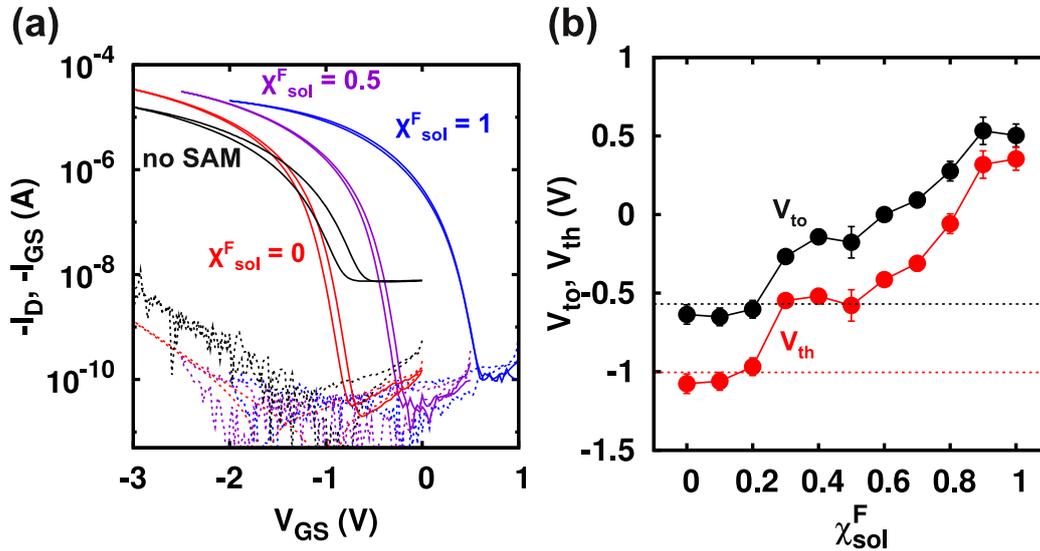


Figure 2. (a) Transfer curves of OTFTs with coadsorbed SAMs. (b) Threshold voltage (red) and turn-on voltage (black).

The composition of the coadsorbed SAMs was determined by XPS. From the analysis of the atomic composition, it was concluded that the molecular composition of FC8-PA and HC8-PA on the surface followed $\chi_{\text{sol}}^{\text{F}}$, yet unexpectedly the mixture of the solutions of FC8-PA and HC8-PA cannot be handled as the ideal two-dimensional solution.

The molecular structure of the coadsorbed SAMs was investigated by NEXAFS and the change of the molecular orientation of FC8-PA corresponding to $\chi_{\text{sol}}^{\text{F}}$ was observed. It was concluded that in coadsorbed SAMs, the orientation and the order of the FC8-PA domains were greatly affected by $\chi_{\text{sol}}^{\text{F}}$, while the molecular structure of HC8-PA domains were constant regardless of $\chi_{\text{sol}}^{\text{F}}$.

3. Spatial control of threshold voltage with high resolution

In this chapter, the control of the threshold voltage of OTFTs in an array was demonstrated. To control the threshold voltage spatially, SAMs were patterned either by stencil printing or by hybrid formation, the combination of microcontact printing and dipping. By either method, OTFTs in 25 \times 20 array was controlled so that the neighboring OTFTs had different threshold voltages.

The cross-contamination of the SAMs by hybrid formation was evaluated by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). Figure 3 shows the ToF-SIMS images of the ions of Al, CH, and F of the SAMs formed by hybrid formation. FC10-PA was first formed by microcontact printing, then HC10-PA was formed by dipping. In the case that FC10-PA was formed earlier, the cross-contamination was negligible, while, in the case of HC10-PA, some cross-contamination was observed. In either case, AlO_x surface was completely covered by SAM-forming molecules and the diffusion length of the printed molecules was negligibly small.

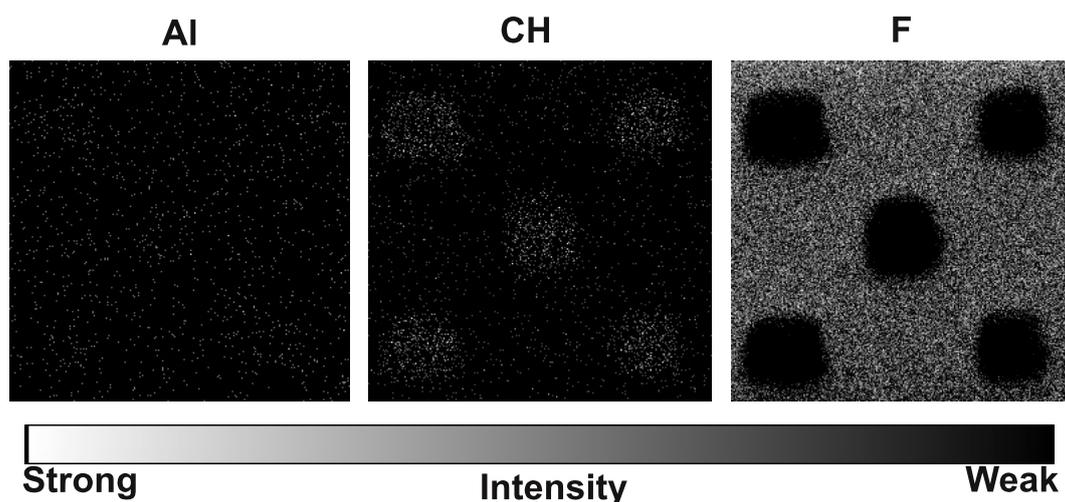


Figure 3. ToF-SIMS images of SAMs by hybrid formation method. The image area is $15 \times 15 \mu\text{m}^2$.

As a summary, the control of the threshold voltage of organic thin-film OTFTs was performed by using coadsorption and the spatial formation of SAMs. Beside the control of the threshold voltage, the quality and molecular structure of coadsorbed SAMs was assessed. For the application of the spatially formed SAMs, the cross-contamination was investigated.

A new method to control the threshold voltages of OTFTs on a same substrate was demonstrated in this research. The use of SAMs with microcontact printing is simple and easily applicable to solution-based fabrication methods for OTFTs. Thanks to its low cross-contamination, the hybrid formation method is expected to be applicable to other species of SAMs. The combination of functional SAMs and the spatial formation will enhance the feature of the OTFTs.