# Control of threshold voltage in organic thin-film transistors by modifying gate electrode surface with MoO<sub>x</sub> aqueous solution and its application to circuits

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## Abstract

Control of threshold voltage  $(V_{TH})$  in organic thin-film transistors (OTFTs) is an important technique which would realize organic circuits. Several methods have been studied to achieve  $V_{TH}$  control in the OTFTs. However, these methods mainly used thermal evaporations, so there are no reports using a printing method. Here we report on a novel method for control of  $V_{TH}$  by modifying gate electrode surface with a drop casting method. Also, we fabricated inverter circuits and obtained satisfactory good characteristics by using our technique, indicating that our technique is useful for circuit design and performance improvement.

# 1. Introduction

Organic thin-film transistors (TFT) have been attracting much attention as fundamental devices for printed electronics. Organic TFTs can be fabricated on inexpensive and flexible plastic substrates with coating and printing processes at room temperature in air. These features are ideal for large-area electronic applications, such as flexible display drives and radio frequency identification (RFID) tags.

When we design a circuit with organic TFTs, it is important to control the threshold voltage ( $V_{TH}$ ) of the transistors. Controlling  $V_{TH}$  simplifies the design of logic circuits and maximizes circuit performance. Several methods of controlling the  $V_{TH}$  of organic TFTs have been demonstrated, by floating gate structures[1,2], Oxygen plasma irradiations[3], self-assembled monolayers (SAMs)[4,5], and tuning work function (W.F.) of gate electrode[6,7], for example. However, there are not reports using printing-method. In this study, the  $V_{TH}$  of pentacene TFTs was controlled by modifying the surfaces of aluminum (Al) gate electrodes with a molybdenum oxide (MoO<sub>X</sub>) aqueous solution.

# 2. Experimental

Fig. 1 schematically shows the structure of the fabricated organic TFTs. A 30-nm-thick Al layer was deposited by thermal evaporation on glass substrates. A  $MoO_X$  aqueous solution (0.03wt. % or 0.1 wt. %) was drop-casted (2 µl constant) on the Al gate electrodes at room temperature and in air ambient, and annealing was performed at 100°C for



Fig. 1 Schematic diagram of bottom-gate, bottom-contact organic TFTs.

10 min. A polychloro-p-xylylene layer (KISCO, dix-C) was then formed by a chemical vapor deposition for the gate dielectric layer. Silver nanoparticle ink (NPS-JL, Harima Chemical) was patterned with an ink-jet printer (FUJIFILM Dimatix, DMP2831) to form the source/drain electrodes. Finally, a 50-nm-thick pentacene layer was deposited by thermal deposition.

## 3. Results and Discussions

Fig. 2 (a) plots the W.F. of Al electrode surfaces as a function of the concentration of aqueous  $MoO_X$ . The W.F. increased from 4.1 eV to 5.7 eV with the drop-casting method. This graph clearly shows that the W.F. of Al electrode surfaces can be changed by a treatment in aqueous  $MoO_X$ .



Fig. 2. (a) W.F. of Al electrodes as a function of concentration of  $MoO_X$  in aqueous solution. (b) Transfer characteristics of fabricated organic TFTs treated with drop casted  $MoO_X$  aqueous solution on the same substrate. The channel dimensions are W/L = 5300 µm/ 110µm.

Fig.2 (b) shows the transfer curves of TFTs made with the drop-casting MoO<sub>X</sub> treatment. Mobility was more than  $0.3 \text{ cm}^2/\text{Vs}$ , and the on/off ratio was more than  $10^6$ .  $V_{TH}$ =-5.5 ± 0.1 V without the treatment,  $V_{TH} = -4.2 \pm 0.5$  V with a 0.03 wt. % MoO<sub>X</sub> treatment, and  $V_{TH} = -3.2 \pm 0.4$  V with a 0.1 wt. % treatment.  $V_{TH}$  shifted by up to +2.3 V. These results show that our method can selectively control the  $V_{TH}$  of devices on the same substrate by using methods such as ink-jet printing and dispenser printing. In addition, the MoO<sub>X</sub> layer formed on the gate electrodes strongly affected the  $V_{TH}$  of the fabricated TFTs, but did not affect other key parameters such as mobility, device hysteresis, on/off current ratio, and device yield. Indeed, the device yield was 98% for untreated TFTs and 92% for TFTs treated with a drop casted 0.1 wt. % MoO<sub>X</sub> solution.

To demonstrate the usability of our  $V_{TH}$  control technique with the design of integrated circuits we fabricated zero- $V_{GS}$  load inverters with selectively treated gate electrodes (Fig. 3 (a)). The zero- $V_{GS}$  load inverters with the untreated gate electrodes were not operated because the load TFT was of the normally off (enhancement) type. On the other hand, the zero- $V_{GS}$  load inverters with the treated load TFT (M<sub>2</sub>) operated with a relatively high inverter gain of 30 at an operation voltage of 20 V and a low operation voltage of 5V (Fig. 3 (b)). The on-current at  $V_{GS} = 0$  V increased as a result of the MoO<sub>X</sub> treatment, which enabled the device to function as an inverter.



Fig. 3 (a) Circuit diagram of zero- $V_{GS}$  load inverter circuit. (b) Input-output characteristics of zero- $V_{GS}$  load inverters. Solid lines represent the output characteristics with M<sub>2</sub> treated inverters, and dashed lines represent the output characteristics with untreated inverters.

Now, let us consider the reason why  $V_{TH}$  shifts as a result of modifying the Al gate electrode surface. We consider that the flat-band voltage of a capacitor that consists of metal, dielectric, and organic semiconductor affects the  $V_{TH}$  of organic TFTs[7]. The flat-band voltage ( $V_{FB}$ ) of an Metal-Insulator-Semiconductor (MIS) capacitor is expressed in terms of the difference between the work functions of the gate electrode and semiconductor ( $\Phi_{MS}$ ), the charges at the dielectric/semiconductor interface ( $Q_{if}$ ), and the dielectric capacitance ( $C_i$ ), as follows[7,8]:

$$V_{FB} = \Phi_{MS} - \frac{Q_{if}}{C_i} \,. \tag{1}$$

Hence, shifts in  $V_{FB}$  can be estimated from the difference between the work functions of the gate electrodes by postulating a constant Fermi level for the semiconductor layer. On the other hand, onset voltage ( $V_{ON}$ ) shifts in organic TFTs are similar to the difference between the work functions of gate electrodes, as described in the literature[9]. Therefore,  $V_{ON}$  shifts consequently caused  $V_{TH}$  shifts.

#### 4. Conclusions

In summary, we controlled the  $V_{TH}$  of organic TFTs without changing other key parameters by modifying the gate electrode surface with a MoO<sub>X</sub> aqueous solution. We could control  $V_{TH}$  over range of +2.3 V with the drop casting method. Therefore, it will be possible to control the  $V_{TH}$  of TFTs systematically and selectively in a patternable solution process, such as ink-jet printing and dispenser printing. Using this technique, the control of the threshold voltage can be in-lined in a fully solution process. Moreover, we controlled the driving voltage of the inverter circuits with a MoO<sub>X</sub> aqueous solution.

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