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# Molecular Crystals and Liquid Crystals

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## Role of Oxidation Layer of Aluminum Base Electrode in Metal-Base Organic Transistors

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Metal base organic transistor (MBOT) is a new type of vertical organic transistor that has simple organic/metal/organic layered structure. MBOT showed a high output current modulation for very low operation voltage, but large off-current resulted in poor ON/OFF ratio around several tens. We found that leaving the device under atmospheric condition caused decrease of the OFF current and the ON/OFF ratio reaching 330 was attained. The effect of exposure to air was investigated from the viewpoint of oxidation layer of electrode surface.

Keywords: metal base organic transistor; on/off ratio; oxidation layer; vertical transistor

#### INTRODUCTION

Organic transistors have a great potential for low-cost processing, flexible circuits, leading to flexible displays or smart tags [1,2]. So far, organic field-effect transistors (OFETs) have been studied most extensively, and the performance has been mainly discussed in terms of the charge mobility of the organic film. There have been many reports on organic materials or preparation methods to obtain high crystallinity [3]. On the other hand, some other structures of organic transistors have been proposed to improve the performance drastically. The vertical structure is a promising structure to attain high current and low voltage operation, where the channel carriers flow across the thin film

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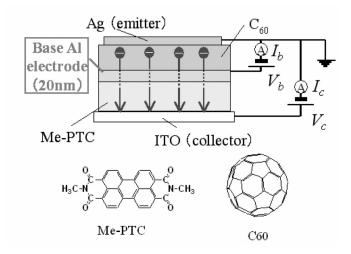
in vertical direction to the substrate. Since in these devices, the channel length can be controlled by the thickness of organic layer, a short channel length less than 1  $\mu$ m can be achieved easily. There have been a few reports using a vertical structure; polymer grid transistors [4], organic static induction transistors (SIT) [5], FET with a top and bottom contact configuration (TBC-FET) [6], charge injection controlled transistors (CICT) [7], and unique vertical organic transistors (VOFET) [8].

Recently, we have proposed a metal base organic transistor (MBOT), which is a new type of a vertical organic transistor that has a thin sheet electrode inserted in the middle of organic sandwich cell [9]. This simple organic/metal/organic structure can be prepared by conventional vacuum deposition without a fine lithography technique. In spite of such a simple structure, this device shows very high performance of a large modulation current density exceeding 100 mA/cm<sup>2</sup> with low operation voltage of several volts. This remarkable current modulation is attributed to transmission of electrons injected from the emitter, which can be controlled by the base voltage. The capability to modulate a sheet current is expected to be applied for display devices. For example, the MBOT can be integrated into the organic light-emitting diodes (OLED). Such a device can exclude an area of driving transistors in the active matrix system and bring a high aperture number in the OLED display.

One problem of this device is the large OFF current, resulting in poor ON/OFF ratio around several tens. Such a problem is often observed in vertical transistors because the leakage current is prone to flow through the short channel. Recently, it was found that the ON/OFF ratio was improved by leaving the device under atmospheric condition. In this study, we report the effect of exposure to air in the MBOT devices, resulting in improvement of ON/OFF ratio, and discuss the role of oxidation layer of the aluminum base electrode.

#### **EXPERIMENT**

The device structure and measurement system of MBOT are shown in Figure 1. The device was fabricated by vacuum evaporation under  $1\times 10^{-3}\,\mathrm{Pa}$ . N-type organic semiconductor of 3,4,9,10-perylenetetra-carboxylic 3,4:9,10-bis-methylimide (Me-PTC, Dainichiseika Color and Chemicals Manufacturing Co. Ltd.) was deposited on a cleaned ITO glass substrate with a thickness of 500 nm. The inserted electrode of aluminum was deposited with a thickness of 20 nm. The upper organic layer of n-type semiconductor of  $C_{60}$  (100 nm, Tokyo Chemical Industry Co., Ltd.) and the top electrode of Ag (30 nm) were prepared



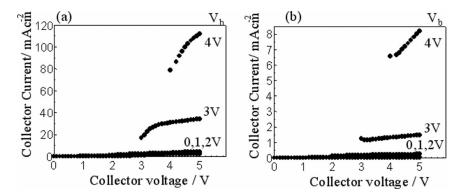
**FIGURE 1** The schematic illustration of device structure and measurement system of MBOT.

in the same way. The active area where the three electrodes were overlapped was  $0.04 \, \text{cm}^2$ . Hereafter, we called the top Ag the emitter and the embedded Al the base, and the ITO the collector.

The device performance was measured using two source-measure units (Keithley Instruments Inc., model 236). The collector voltage  $(V_c)$  was applied between the collector and emitter electrodes using a negative bias on the emitter. The base voltage  $(V_b)$  was applied between the emitter and base electrodes using a negative bias on the emitter. The output current (collector current,  $I_c)$  and the input current (base current,  $I_b)$  were measured for various  $V_c$  and  $V_b$ . The measurements were performed under vacuum condition  $(10^{-1}\,Pa)$ , but the device was preserved under atmospheric condition for evaluating the time dependence of the performance in air.

#### RESULTS AND DISCUSSION

Figure 2(a) shows the modulation characteristics of this device measured immediately after the deposition. Current-voltage curves between the emitter and collector ( $I_c$ - $V_c$  curves) were plotted for different constant  $V_b$ . When the input base voltage ( $V_b$ ) was not applied, the output collector current ( $I_c$ ) was low value. On the other hand, applying the base voltage ( $V_b = 4\,V$ ) causes remarkable increase of the  $I_c$ , exceeding  $100\,\text{mA/cm}^2$ . This means that very high current density,



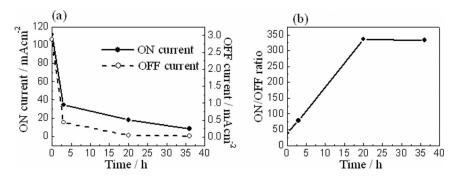
**FIGURE 2** Current modulation at initial state and after preservation for 36 hours under atmosphere condition.

which is enough to drive OLED devices, can be modulated by low external voltage. It should be noticed that the base current ( $I_b$ ) was not increased for applying  $V_b$ . As a result, the current amplification factor ( $h_{\rm FE}$ ), defined as a ratio of change of  $I_b$  to  $I_c$ , was estimated to be around 30, which means that current amplification occurred.

The output collector current ( $I_c$ ) observed for  $V_b=0\,V$  (shorted) is defined as an OFF current, and an ON current is evaluated for  $V_b=4\,V$ . The ON/OFF ratio is one of the most important features as a switching device. However, the OFF current at  $V_c=5\,V$  was large value around  $3\,\text{mA/cm}^2$  in Figure 2(a), which resulted in poor ON/OFF ratio around several tens. Because MBOT achieves shigh current density for the ON current, the most important requirement is to improve the ON/OFF ratio by reducing the OFF current.

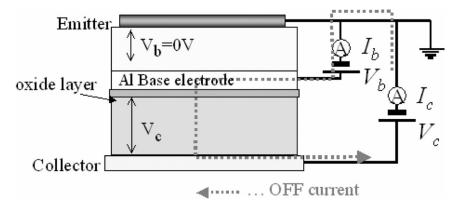
Figure 2(b) shows the effect of exposure to air on the modulation characteristics. The device was preserved under atmospheric condition for 36 hours and measured in vacuum condition. The shape of modulation curves did not change very much, but the OFF current was drastically reduced from  $3\,\text{mA/cm}^2$  to less than  $0.02\,\text{mA/cm}^2$ . We traced the exposure time dependence of ON current, OFF current (Fig. 3(a)) and ON/OFF ratio (Fig. 3(b)). Both the ON and OFF current decreased with exposure time, but the OFF current was suppressed stronger. The ON current after 36 hours was still high value around  $8\,\text{mA/cm}^2$ . As a result, the ON/OFF ratio was improved from 36 to 330.

In order to understand the effect of exposure to air, it is important to consider how the ON and OFF current flows in the device. Figure 4 shows a simplified model indicating the current flow in the device. The



**FIGURE 3** Time dependance of the device performance. (a) Current at OFF state ( $V_b=0\,V$ ) and ON state ( $V_b=4\,V$ ) with  $V_c=5\,V$  and (b) ON/OFF ratio.

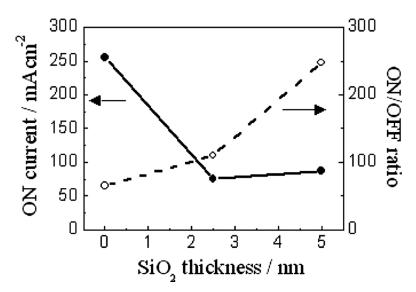
current modulation and amplification can be observed by that the emitted current from the emitter electrode passes through the thin base electrode, although the detailed mechanism has not been clarified. In the OFF states of  $V_{\rm b}=0$ , the potential of the base electrode is controlled to be the same as that of the emitter electrode, and consequently, the electron emission from the emitter is not promoted. This means that the OFF current is mainly composed of the current between the base and collector. On the other hand, the ON current mainly flows between the emitter and collector. From these considerations, the observed decrease of the OFF current is attributed to suppression of the current between the base and collector.



**FIGURE 4** Schematic illustration of the current flow at OFF state in the device.

There are several ways to explain the decrease of the current. For example, the current may be suppressed by degradation of the organic film owing to adsorption of moisture or oxygen in air. However, they can be desorbed during evacuation before the measurement. We are now presuming partially oxidation of the Al base electrode (Fig. 4). It is known that Al film is easily oxidized by oxygen in air, and changes itself to insulating  $Al_2O_3$ . Although the insulating layer should also prevent the ON current, the transmission probability of electrons, which is calculated from the value of  $h_{\rm FE}$ , did not change very much. These facts indicate that the thin oxide layer can block electron injection from the base electrode, but can pass the electrons from the emitter through.

Assuming that the effect of exposure to air is attributed to surface oxidation, an intentional oxide layer should improve the ON/OFF ratio. We fabricated a device with an insulating silicon oxide layer (SiO<sub>2</sub>) under the base electrode. Figure 5 shows dependence of the ON current and ON/OFF ratio on the thickness of the SiO<sub>2</sub> layer. The performances of these devices were measured under vacuum condition immediately after device preparation. The ON current decreased with increasing thickness of SiO<sub>2</sub> layer, but the OFF current was suppressed stronger. As a result, the ON/OFF improved from 70 to 250 for a 5 nm-thick layer. These results indicate that the



**FIGURE 5** Dependence of the ON current and ON/OFF ratio on the thickness of SiO<sub>2</sub> insulating layer.

insertion of an insulating layer under the base electrode has the same effect as exposure to air. Therefore, we concluded that leaving the device under atmospheric condition caused partial oxidation of Al electrode surface that worked as an insulating layer blocking the OFF current. Thus, the intentional control of the oxide layer is effective to suppress the OFF current and to achieve high ON/OFF ratio in the MBOT devices.

#### CONCLUSIONS

The effect of exposure to atmospheric condition in the MBOT devices was investigated. Exposure for 36 hours caused remarkable decrease of the OFF current and improvement of the ON/OFF ratio from 36 to 330. The mechanism was attributed to surface oxidation of the Al base electrode. The intentional oxide layer brought the same effect achieving high ON/OFF ratio. These results suggest important guiding principles to design the MBOT devices.

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