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| <b>Title</b>       | <b>Pentacene thin-film transistors with HfO<sub>2</sub> gate dielectric annealed in NH<sub>3</sub> or N<sub>2</sub>O</b>  |
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# Pentacene Thin-Film Transistors with HfO<sub>2</sub> Gate Dielectric Annealed in NH<sub>3</sub> or N<sub>2</sub>O

L. F. Deng, W. M. Tang, C. H. Leung, P. T. Lai\*, J. P. Xu, and C. M. Che

**Abstract** –Pentacene-based Organic Thin-Film Transistor (OTFT) with HfO<sub>2</sub> as gate dielectric is studied in this work. The HfO<sub>2</sub> dielectric was prepared by RF sputtering at room temperature, and subsequently annealed in N<sub>2</sub>O or NH<sub>3</sub> at 200 °C. The OTFTs were characterized by IV measurement and 1/f noise measurement. The OTFTs show small threshold voltage and can operate at as low as 3 V. Results indicate that the OTFT annealed in NH<sub>3</sub> shows higher carrier mobility, larger on/off current ratio, smaller sub-threshold swing and smaller Hooge parameter than the OTFT annealed in N<sub>2</sub>O. Therefore, NH<sub>3</sub>-annealed HfO<sub>2</sub> is a promising gate dielectric for the fabrication of high-performance OTFTs.

## I. INTRODUCTION

Organic thin-film transistors (OTFT) have got wide attention from researchers due to their advantages such as low cost and flexible substrate. They are considered as good candidates for applications like electronic paper, RFID tags, smart cards and large-sized flat-panel display [1], [2]. OTFTs with pentacene as active layer and SiO<sub>2</sub> as gate dielectric have achieved a performance which is comparable to amorphous Si thin-film transistors [3]. However, OTFTs with SiO<sub>2</sub> as gate dielectric often work at high operating voltage, which is commonly greater than 15 or 20 V. High operating voltage usually leads to high power consumption and causes inconvenience to the development of portable equipment. One way to decrease the operating voltage is to reduce the thickness of the gate dielectric [4]. However, too thin gate dielectric will cause large gate leakage. The other way to decrease the operating voltage is to replace the low-k SiO<sub>2</sub> with high-k dielectric [5], [6]. Hafnium (Hf) -based oxides (e.g. HfO<sub>2</sub>, HfON) are being actively investigated to act as the gate dielectric of inorganic transistors because of their better interface quality with the semiconductor [7], [8] as well as higher dielectric constant. The carrier transport in the OTFTs is

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decisively determined by the characteristics of the interface between the gate dielectric and organic semiconductor. In order to realize high-quality interface, one common method is to passivate the gate-dielectric surface by nitridation before the evaporation of organic layer. In this work, HfO<sub>2</sub> was prepared by sputtering method and then annealed in N<sub>2</sub>O or NH<sub>3</sub> respectively to form the gate dielectric of pentacene OTFTs. The IV characteristics of the devices were measured, and used to deduce the field-effect carrier mobility, threshold voltage, sub-threshold swing and on/off current ratio. Moreover, 1/f noise was measured to evaluate the interface quality of the OTFTs.

## II. EXPERIMENTAL DETAILS

Fig. 1 shows the cross-sectional view of the OTFT to be fabricated as follows. N-type <100> silicon wafers with a resistivity of 0.2 ~ 0.5 Ωcm were cleaned according to the standard RCA method. Then 5% hydrofluoric acid was used to remove the native oxide of the wafers. Subsequently the wafers were sputtered with a layer of HfO<sub>2</sub> as gate dielectric at room temperature. The sputterer was Denton Vacuum LLC Discovery 635. Before the sputtering, the vacuum in the chamber was kept below  $2 \times 10^{-6}$  Torr. The sputterer worked on RF (radio frequency) mode and the power was 30 W. The material of the target was HfO<sub>2</sub>. Argon flowed in the reactive chamber at a rate of 24 sccm. In order to improve the interfacial characteristics, the samples were divided into two groups, each annealed in N<sub>2</sub>O and NH<sub>3</sub> respectively with a gas flow rate of 1000 mL/min. The annealing process lasted for 10 minutes at a temperature of 200 °C. Hydrofluoric acid with 20% concentration was used to remove the back oxide of the silicon substrate which would be used as the gate electrode. Then pentacene (from Aldrich) was deposited on the dielectric in an Edwards Auto 306 evaporator. The substrate was not heated and the vacuum in the chamber was  $4 \times 10^{-6}$  Torr. The deposition rate was 1.1 nm/min and the final thickness of the pentacene film was 30 nm, which was detected by a quartz-crystal oscillator. Finally gold was evaporated on the pentacene layer through a shadow mask to form drain and source electrodes. The channel length L and width W are 30 μm and 200 μm respectively. Before the gold

evaporation, the vacuum in the chamber was about  $8 \times 10^{-6}$  Torr.

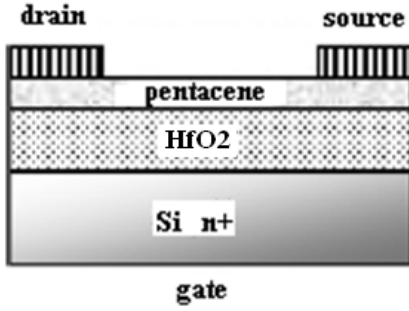


Fig. 1. Cross-sectional view of top-contact OTFT

The devices were characterized by HP4145B Semiconductor Parameter Analyzer, Berkeley Technology Associates FET Noise Analyzer Model 9603 and HP 35665A Dynamic Signal Analyzer to measure the I-V curve and  $1/f$  noise characteristics of the organic thin-film transistors. The measurements were taken by a probe station in the ambient atmosphere.

### III. RESULTS AND DISCUSSION

Fig. 2 and Fig. 3 reveal the output characteristics of the OTFTs with HfO<sub>2</sub> as the gate dielectric annealed in N<sub>2</sub>O and NH<sub>3</sub> respectively. The OTFTs can work at very low operating voltage (less than 3.0 V), which is much lower than that of OTFT with SiO<sub>2</sub> as gate dielectric. The gate leakage is low when the former works at low drain-source voltage. Fig. 4 displays the comparison of the transfer characteristic of the two transistors. The on/off current ratio is about  $4.3 \times 10^3$  for the former and  $1.5 \times 10^4$  for the latter. Carrier mobility  $\mu$  and threshold voltage  $V_{th}$  are two of the most important parameters to evaluate the performance of OTFTs. To deduce their values, the transfer characteristics curve of the OTFTs is plotted as  $\sqrt{-I_d} = f(V_g)$ , as shown in Fig. 4. According to the standard formula when OTFT operates in the saturation regime

$$I_d = -\frac{W}{2L} \mu C_{ox} (V_g - V_{th})^2 \quad (1)$$

we can get

$$\sqrt{-I_d} = \sqrt{\frac{W}{2L} \mu C_{ox}} (V_g - V_{th}) \quad (2)$$

where W and L are the width and the length of the channel respectively;  $C_{ox}$  is the oxide capacitance per unit area. From (2),

$$\mu = \frac{2L}{WC_{ox}} \left( \frac{\partial \sqrt{-I_d}}{\partial V_g} \right)^2 \quad (3)$$

After calculation, the carrier mobility is  $0.399 \text{ cm}^2/\text{Vs}$  for the N<sub>2</sub>O-annealed device and  $0.655 \text{ cm}^2/\text{Vs}$  for the NH<sub>3</sub>-annealed one. By extrapolating the  $\sqrt{-I_d} = f(V_g)$  curve to the X-axis, the threshold voltage can be calculated. Besides, sub-threshold swing is also of great significance to analyze the switching characteristics of OTFTs. By plotting the transfer characteristics in the semi-logarithmic representation as in the inset of Fig. 4, the sub-threshold swing (SS) is found to be  $0.361 \text{ V/dec}$  and  $0.229 \text{ V/dec}$  for the N<sub>2</sub>O-annealed and NH<sub>3</sub>-annealed OTFTs respectively.

$$SS = \frac{1}{\frac{\partial \text{Log}(-I_d)}{\partial V_g}} \quad (4)$$

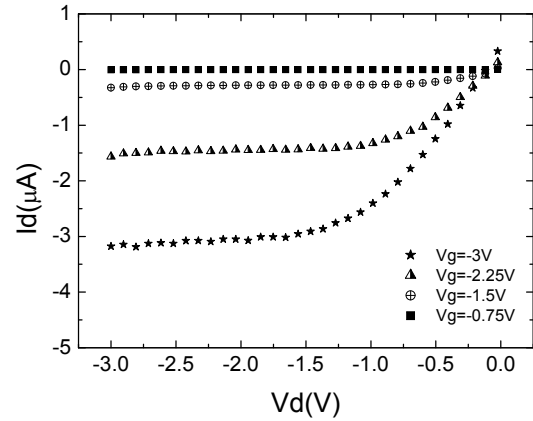


Fig. 2. Output characteristic of the OTFT annealed in N<sub>2</sub>O

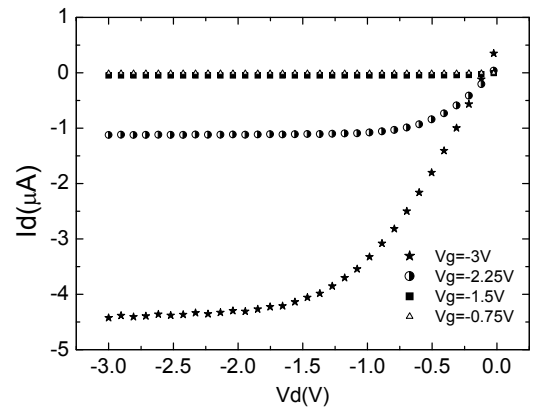


Fig. 3. Output characteristic of the OTFT annealed in NH<sub>3</sub>

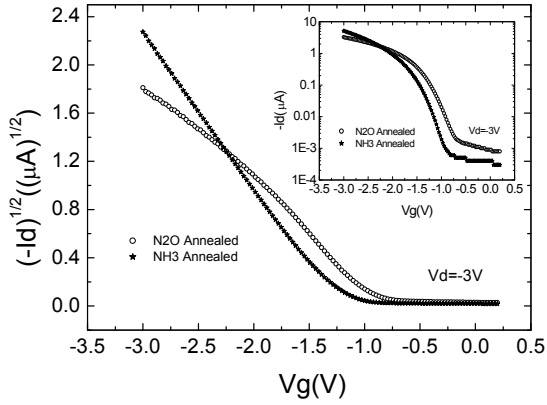


Fig. 4. Transfer characteristic of the OTFTs annealed in N<sub>2</sub>O or NH<sub>3</sub> (Inset shows the  $I_d$ - $V_g$  curve in semi-logarithmic scale)

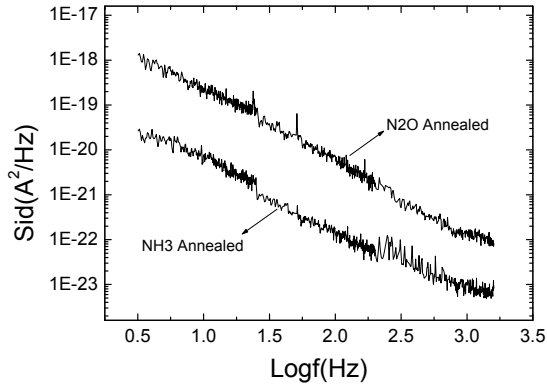


Fig. 5. 1/f noise characteristics of the OTFTs annealed in N<sub>2</sub>O or NH<sub>3</sub>

To further study the interface quality of the organic thin-film transistors, their 1/f noise spectrum was measured. The 1/f noise was tested in the frequency ( $f$ ) range of 3.125 Hz and 1.6 kHz. Fig. 5 shows the comparison of the 1/f noise for the two transistors. The noise level of the transistor annealed in the NH<sub>3</sub> ambient is about 2 orders lower than that of its counterpart annealed in the N<sub>2</sub>O ambient. It reveals that the device gain better interfacial quality through the NH<sub>3</sub> annealing than the N<sub>2</sub>O annealing. In order to analyze the 1/f noise characteristic further, the Hooge parameter  $\alpha$  is extracted according to the Hooge's empirical formula for the 1/f noise [9]

$$\frac{S_{id}(f)}{I_d^2} = \frac{\alpha}{Nf} \quad (5)$$

where  $S_{id}$  is spectral density of the 1/f noise of drain current  $I_d$ ; and  $N$  is the total number of carriers in the channel. For the case of organic thin-film transistors, (5) can be approximated as [10],

$$\alpha = \frac{fS_{id}(f)L^2}{e\mu V_{ds}I_d} \quad (6)$$

where  $e$  is the electron charge. In this work,  $f = 30\text{Hz}$  is used for the calculation of  $\alpha$ . In the case of transistor which experienced the N<sub>2</sub>O annealing at 200 °C, the Hooge parameter is 50.1. By contrast, the Hooge parameter is 0.274 for the transistor annealed in NH<sub>3</sub> at 200 °C. This means that the current fluctuation due to the 1/f noise in the former is more severe than the latter. In terms of sub-threshold swing, the transistor annealed in NH<sub>3</sub> is 0.229, which is better than 0.361 of the transistor annealed in N<sub>2</sub>O. As a result, organic thin-film transistor annealed in NH<sub>3</sub> shows better switching characteristics than its counterpart annealed in N<sub>2</sub>O. Besides, the former has higher carrier mobility than the latter. All these advantages of the transistor annealed in NH<sub>3</sub> over its counterpart annealed in N<sub>2</sub>O can be attributed to its more nitrogen incorporation at the dielectric surface, and hence better interface quality between the gate dielectric and organic semiconductor. In other words, higher carrier mobility means weaker trap-related scattering for the carriers. Smaller 1/f noise and sub-threshold swing mean less traps in the channel / at the interface. On the other hand, the transistor annealed in NH<sub>3</sub> has a larger threshold voltage than the transistor annealed in N<sub>2</sub>O, possibly because more nitrogen incorporation results in more positive oxide charges in the former. More quantitative analysis lies in better understanding of the carrier transport mechanism in the interface between the organic layer and the high- $k$  dielectric layer of the organic thin-film transistors.

TABLE I

Device parameters of the OTFTs annealed in N<sub>2</sub>O or NH<sub>3</sub>

|                                      | Annealing gas    |                 |
|--------------------------------------|------------------|-----------------|
|                                      | N <sub>2</sub> O | NH <sub>3</sub> |
| $C_{ox} (\mu\text{F} / \text{cm}^2)$ | 0.458            | 0.551           |
| $t_{ox} (\text{nm})$                 | 11.2             | 10.9            |
| $k$                                  | 5.8              | 6.8             |
| $\mu (\text{cm}^2 / \text{Vs})$      | 0.399            | 0.655           |
| $V_{th} (\text{V})$                  | -0.801           | -1.26           |
| SS (V/decade)                        | 0.361            | 0.229           |
| on/off ratio ( $10^4$ )              | 0.432            | 1.52            |
| $I_d _{V_d=V_g=-3V} (\mu\text{A})$   | 3.17             | 4.42            |
| $\alpha$                             | 50.1             | 0.274           |

#### IV. CONCLUSION

The application of HfO<sub>2</sub> as gate dielectric to pentacene thin-film transistors is studied in this paper. OTFTs with HfO<sub>2</sub> as gate dielectric were realized by RF sputtering and subsequent annealing in N<sub>2</sub>O or NH<sub>3</sub> at 200 °C. Both can operate under a supply voltage of as low as 3 V. The OTFT annealed in NH<sub>3</sub> displays higher carrier mobility, larger

on/off current ratio, smaller Hooge parameter and smaller sub-threshold swing than its counterpart annealed in N<sub>2</sub>O. All these advantages make the organic thin-film transistor suitable in low-voltage and low-power applications. To conclude, HfO<sub>2</sub> annealed in NH<sub>3</sub> is very promising to act as the gate dielectric of high-performance OTFTs.

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#### REFERENCES

- [1] C. D. Dimitrakopoulos, and P. R. L. Malenfant, "Organic thin film transistors for large area electronics," *Adv. Mater.*, vol.14, p.99, 2002.
- [2] G. Horowitz, "Organic field-effect transistors," *Adv. Mater.*, vol.10, p.365, 1998.
- [3] S. F. Nelson, Y. Y. Lin, D. J. Gundiach and T. N. Jackson, "Temperature-independent transport in high-mobility pentacene transistors," *Appl. Phys. Lett.*, vol.72, p.1854, 1998.
- [4] L. A. Majewski, R. Schroeder, M. Grell, "Organic field-effect transistors with ultrathin gate insulator," *Synth. Met.* Vol.144, p.97, 2004.
- [5] J. Tardy, M. Erouel, A.L. Deman, A. Gagnaire, V. Teodorescu, M.G. Blanchin, B. Canut, A. Barau and M. Zaharescu, "Organic thin film transistors with HfO<sub>2</sub> high-k gate dielectric grown by anodic oxidation or deposited by sol-gel," *Microelectronics Reliability*, vol.47, p.372, 2007.
- [6] C. D. Dimitrakopoulos, S. Purushothaman, J. Kyriassis, A. Callegari and J. M. Shaw, "Low-voltage organic transistors on plastic comprising high-dielectric constant gate insulators," *Science*, vol.283, p.822, 1999.
- [7] T. J. Park, S. K. Kim, and J. H. Kim, "Electrical properties of high-k HfO<sub>2</sub> films on Si<sub>1-x</sub>Ge<sub>x</sub> Substrates," *Microelectronic Engineering*, vol.80, p.222, 2005.
- [8] N. Wu, Q. C. Zhang, C.X. Zhu, D. S. H. Chan, M. F. Li, N. Balasubramanian, Albert Chin and Dim-Lee Kwong, "Alternative surface passivation on germanium for metal-oxide-semiconductor applications with high-k gate dielectric," *Appl. Phys. Lett.*, vol.85, p.4127, 2004.
- [9] F. N. Hooge, "1/f noise source," *IEEE TRANSACTIONS ON ELECTRON DEVICES*. Vol.41, p.1926, 1994.
- [10] M. J. Deen, O. Marinov, J. F. Yu, S. Holdcroft, and W. Woods, "Low-Frequency Noise in Polymer Transistors," *IEEE TRANSACTIONS ON ELECTRON DEVICES*, vol.48, p.1688,2001.