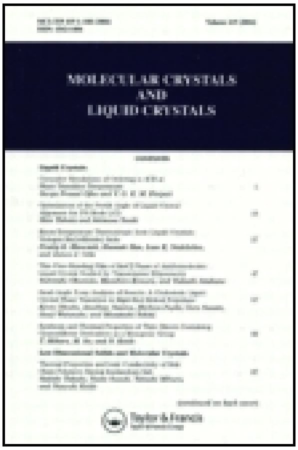

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Electrical Characteristics of Pentacene Thin Film Transistors in Volatile Compound Vapors

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Electrical Characteristics of Pentacene Thin Film Transistors in Volatile Compound Vapors

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We have systematically investigated the real-time I_{DS} responses and electrical characteristics of pentacene OTFTs exposed to six volatile compound vapor flows of acetone, ethanol, methanol, water, chloroform, and toluene, which could be classified into two group according to the influence on the electric performance of OTFTs. The first three compounds caused remarkable and irreversible degradation of electric performance of OTFTs. However, the latter three compounds caused slight and reversible changes of their electric performance. Moreover, the good linearity existed in plot of changes of the normalized I_{DS} as a function of their concentrations in N_2 flow.

Keywords: degradation; electrical performance; organic thin film transistor; pentacene; volatile compound

INTRODUCTION

Organic thin film transistors (OTFTs) have recently attracted a great deal of attentions for low-cost electronic application, such as smart

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cards, identification (ID) tags, display, gas sensors, and large-area sensors [1–6]. Extensive research interests have been focusing on synthesizing organic semiconductor materials with high mobility and high ON-OFF current ratios, as well as on improving OTFT performance by device engineering and optimizing processing conditions [7–9]. Pentacene as a very promising material of OTFTs has been drawing intensive attentions, which exhibits the hole mobility greater than 1 $\text{cm}^2/\text{V}\cdot\text{s}$ and an on/off ratio over 10^5 [10]. However, few reports related to the stability and operational reliability of such OTFTs at the ambient conditions. Several research groups have reported the performance degradation of pentacene OTFTs exposed to humidity [11–14]. In addition, Gundlach *et al.* [15] reported that, after pentacene OFETs were dipped into organic solvents such as acetone, isopropanol, or ethanol and then blown dry, their performance was dramatically degraded, which derived from a solvent-induced phase transition in pentacene thin films from a "thin film" phase to a bulk-like phase.

In this work, we have systematically investigated electrical characteristics and real-time sensing measurements of penacence OTFTs exposed to volatile compound vapors including acetone, methanol, ethanol, water, chloroform, and toluene, which are used as common solvent in laboratory and in which pentacene is nominally insoluble. In the light of the influence on the electric performance of OTFTs, the six compounds could be classified into two groups. The first group, including acetone, methanol, ethanol, caused the remarkable and irreversible degradation of electric performance of such OTFTs. On the other hand, the second group, including water, chloroform, and toluene, only caused slight and reversible degradation of their electric performance.

EXPERIMENTAL

Fabrication Process

In the typical fabrication process of pentacene OTFT, pentacene thin film was firstly deposited by thermal evaporation onto heavily doped thermally oxidized Si substrates with 330 nm thickness of SiO_2 at a typical base pressure of ca. 5×10^{-5} Pa. The substrate was not heated deliberately and pentacene film with a final average thickness of 30 nm was deposited at the mean deposition rate of ca. 0.1 nm/min. The n-doped silicon substrate is also directly served as the gate electrode and thermally grown SiO_2 layer as the gate dielectric layer. Finally, we fabricated top-contact source and drain electrodes by thermally evaporating gold with 50 nm thickness at ca. 10 nm/min deposition rate through a shadow mask at a base pressure of ca. 2×10^{-4} Pa. The channel length (L) and width (W) were 50 and 1200 μm, respectively.

Electric Characteristics and Real-time Sensing Measurements

The electrical characteristics and real-time sensing measurements of pentacene OTFTs were carried out by using two coupling Keithley 2400 SourceMeters units in dark and semi-enclosed chamber with free volume of ca. $10 \times 5 \times 2\,\text{mm}^3$ at the ambient temperature of 25 ± 1°C. High-purity N_2 as carrier gas was introduced in the chamber by a syringe with 0.6 mm diameters and 30 mm lengths. In the experiments of acetone, ethanol, and methanol as volatile source, the 10 ml/min N_2 flow directly passed through a corresponding bubble cuvette. On the other hand, the concentrations of water, chloroform, and toluene in N_2 flow, ranged from 1.0 to 0.4 times of P_0 (P_0: vapor pressure of these compounds at 25°C), were controlled by two paths of N_2 flow with the total flux of 10 ml/min. One path passed through a bubble cuvette and then pre-mixed with another one before introducing into the chamber. Vapor pressure of acetone, ethanol, methanol, water, chloroform, and toluene corresponds to 0.304, 0.079, 0.165, 0.031, 0.256, and 0.037 atm., which, except for water, were calculated by the Antoine equation: $\log p = A - (B/t + C)$. The A, B, and C values as well as vapor pressure of water are derived from Ref. [16]. The flux increment caused by compound vapor could not be considered. The electrical characteristics and real-time sensing measurements of OTFT were alternately carried out. Namely, after the saturation I_{DS} at V_{DS} and V_{GS} of -40 V reached to quasi-steady state, the real-time sensing measurement paused, and then electrical characteristics measurement was rapidly performed, subsequently, the sensing measurement restarted. During the sensing measurements, a continuously sampling mode was adopted. To recover from the depleted state, each sampling was followed by reverse gate bias of $+40$ V for 2 seconds.

RESULTS AND DISCUSSIONS

The typical output and transfer characteristics of the original OTFTs in dark and air ambient are displayed in Figure 1. The output characteristic was shown in the inset of Figure 1, which was plotted the drain-source current (I_{DS}) as a function of drain-source voltage (V_{DS}) for several values of gate-source voltage (V_{GS}) from -40 to 10 V with a step of -10 V, which indicated typical I–V plot for p-type pentacene OTFTs. The saturation I_{DS} of transfer characteristic can be modeled by the equation:

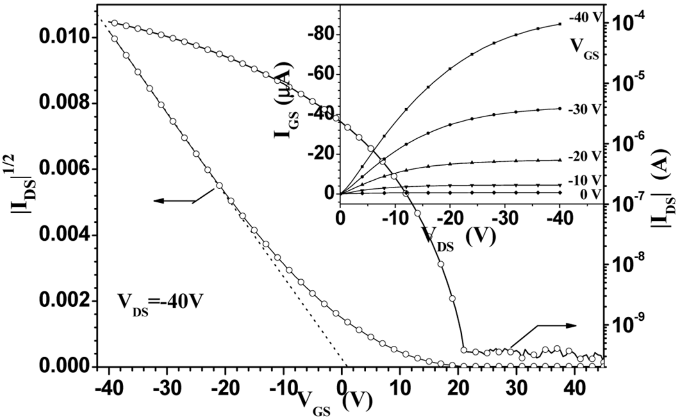

FIGURE 1 Typical output (inset) and transfer characteristics of the original pentacene OTFT with 30 nm thickness measured in dark and air ambient. The channel length L and width W were 50 and 1200 μm, respectively.

$$I_{DS} = -\frac{W}{2L} C_i \mu (V_{GS} - V_{th})^2 \tag{1}$$

where C_i is ca. 10 nF/cm^2, the capacitance of the dielectric layer, μ is the hole carrier mobility, and V_{th} is the threshold voltage. Thus, the mobility (μ) of 0.36 cm^2/V·s and V_{th} (x-intercept of the linear fit) of 1.0 V were easily extracted from a plot of the square root of the saturation I_{DS} as a function of V_{GS} for the OTFT biased in saturation region. ON-OFF current ratios were ca. 3×10^5 at the minimum OFF current.

Figure 2 displays time dependence of the saturation I_{DS} of pentacene OTFTs at V_{DS} and V_{GS} of -40 V, exposed to N_2 flow saturated by the volatile compound vapors of acetone, methanol, and ethanol, and then restored to pure N_2 flow. After introducing these saturated vapors, all I_{DS} firstly fell quickly and then slowly tended to steady state. The decreases of the saturation I_{DS} were 85.5, 92.0, and 92.1%, in turn. The mobility also greatly reduced from ca. 0.27 cm^2/V·s to 0.09, 0.04, and 0.15 cm^2/V·s. The threshold voltage changed from ca. -0.7, -3.7, and $+1.8$ V to -21.1, -27.9, and -15.9 V, correspondingly. After restored to pure N_2 flow, in the case of methanol, I_{DS} firstly increased rapidly and then slowly tended to steady state. However, in the case of acetone and ethanol, I_{DS} both increased slowly and did not reach to steady state in the long run. Finally, I_{DS} only recovered to ca. 26.9, 35.7, and 33.5% of the original level, in turn, about one of three equal parts. The mobility also only

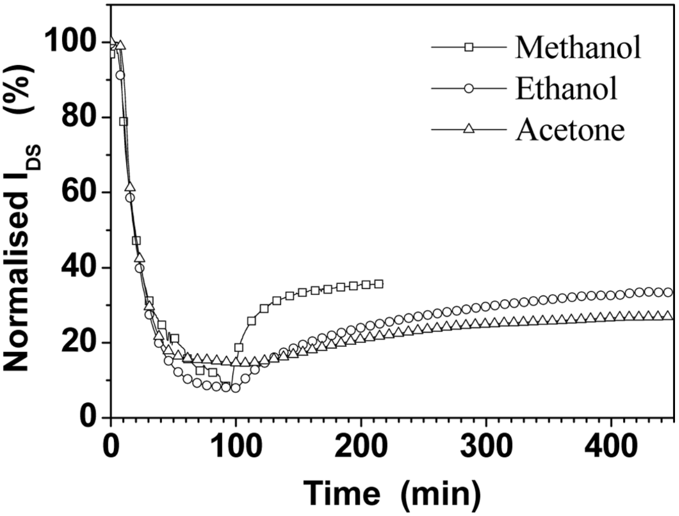

FIGURE 2 Time dependence of the normalized I_{DS} of pentacene OTFTs at V_{DS} and V_{GS} of -40 V, exposed to N_2 flow saturated by the volatile compound vapors of acetone, ethanol, and methanol, and then restored to pure N_2 flow.

recovered 0.17, 0.14, and 0.20 cm^2/V·s. The threshold voltage corresponded to –18.0, –14.9 and –13.4 V. The obvious changes of threshold voltage were inconsistent with the reported that, after solvent exposure, the change of threshold voltagewas negligibly small [15]. These results clearly indicated the electric performance was remarkably degraded and irreversible after exposing OTFTs to N_2 flow saturated by the volatile compound vapors of acetone, methanol, and ethanol.

Figure 3(a) shows time dependence of the saturation I_{DS} of pentacene OTFTs at V_{DS} and V_{GS} of -40 V, alternately exposed OTFTs to pure N_2 flow and N_2 flow containing variable concentration level (from 1.0 P_0 to 0.4 P_0) of the volatile compound vapors of water, chloroform, and toluene. After exposing to their saturated vapor flows, the saturation I_{DS} decreases were only 16.9, 9.2, and 3.6%, respectively. The mobility only decreased slightly. Interestingly, after restored to pure N_2 flow, the electrical performance could basically recover to the original level. All saturation I_{DS} could rapidly come to steady state after altering the atmosphere. Furthermore, the saturation I_{DS} response directly related to the concentrations of these three vapors in N_2 flow, shown in Figure 3(a). When the changes of normalized I_{DS} were plotted as a function of concentrations of these three compounds in

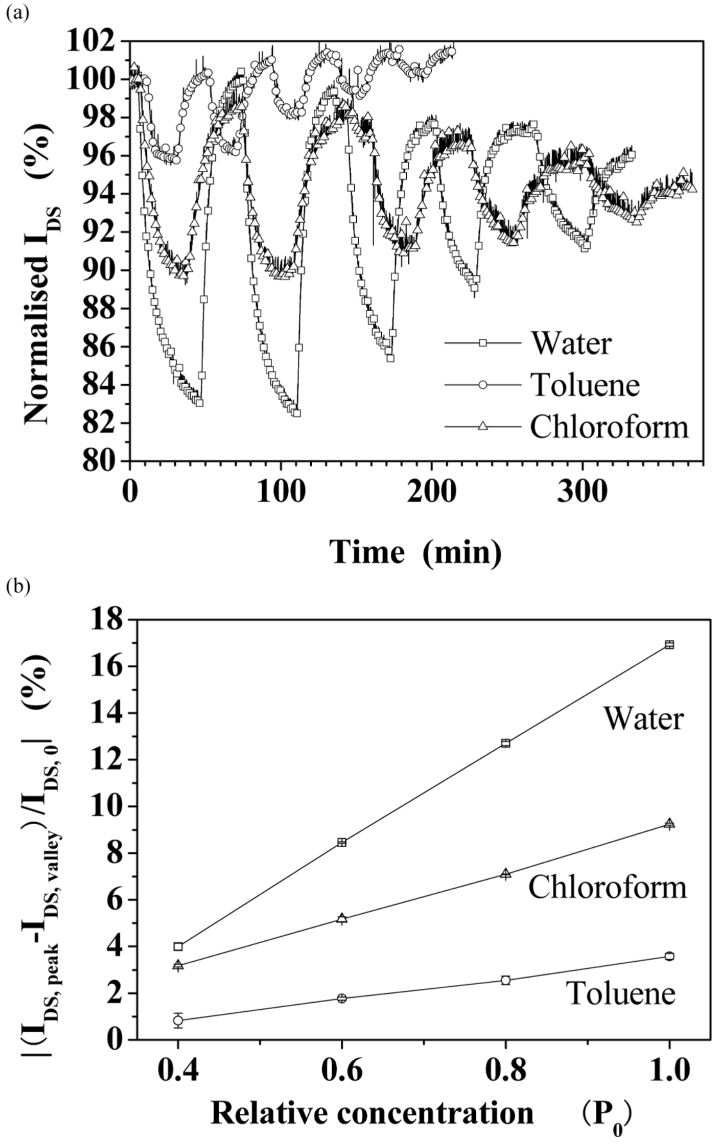

FIGURE 3 (a) Time dependence of the normalized I_{DS} of pentacene OTFTs at V_{DS} and V_{GS} of $-40\,V$, alternately exposed to pure N_2 flow and N_2 flow contained the variable concentration levels of the volatile compound vapors of water, chloroform, and toluene. The vapor concentrations in N_2 flow were 1.0, 1.0, 0.8, 0.6, and 0.4 P_0, in turn. (b) Changes of normalized I_{DS} as a function of concentrations of compound vapors in N_2 flow, corresponding to (a).

N_2 flow, the good linearity existed in the concentration range of 1.0 and 0.4 P_0, as indicated in Figure 3(b). It implied that such OTFTs might be applied as sensors for exploring these three compound vapors. Therefore, according to the apparent effect on the electric performance of such OTFTs, the six volatile compounds can be classified into two groups, i.e., acetone, ethanol, and methanol as a group while water, chloroform, and toluene as other group.

According to the AFM observations, pentacene films had the terraced dendritic morphology with micron size crystal domains like that of Ref. [15]. Since the OTFT device size was much greater than the average grain size of pentacene, the device properties were influenced by both intragrain and intergrain transport. Although bulk pentacene is relatively insoluble and nonreactive in the above volatile compounds, these gaseous molecules of volatile compounds can easily diffuse into these crevices. And then they were able to interact with the trapped carriers by altering the electric field at the grain boundaries. To the group of acetone, ethanol, and methanol, the great irreversible performance degradation of such OTFTs seemed to be attributed to two effects at least: (1) the irreversible solvent-induced phase transition of pentacene intragrain [15] and (2) charge trapping at grain boundaries reducing the rate of charge transport by reversibly adsorbing these polar molecules. In contrast, to the group of water, chloroform, and toluene, the degradation should only relate to the reversible interaction between these polar molecules and pentacene molecules located on the grain surface. What caused to the above-mentioned difference of the electric response in the atmosphere of the volatile compound vapors? The further investigation is underway.

CONCLUSIONS

We systematically investigated the real-time I_{DS} responses and electrical characteristics of pentacene OTFTs, exposed to six volatile compound vapor flows, i.e., acetone, ethanol, methanol, water, chloroform, and toluene in N_2 flow and then restored to pure N_2 flow. To the first three volatile compounds, the electric performance was remarkably degraded and irreversible after exposed OTFTs to N_2 flow saturated these three compound vapors. For example, the decreases of the saturation I_{DS} of pentacene OTFTS were more than 85%. The mobility also evidently reduced from ca. $0.27\,\mathrm{cm^2/V{\cdot}s}$ to 0.09, 0.04, and $0.15\,\mathrm{cm^2/V{\cdot}s}$. The threshold voltage obviously changed from ca. -0.7, -3.7, and $+1.8\,\mathrm{V}$ to -21.1, -27.9, and $-15.9\,\mathrm{V}$. After restored to pure N_2 flow, I_{DS} only recovered to ca. one of three equal parts of the original level. However, after OTFTs exposed to N_2 flow saturated by water, chloroform, and toluene vapors, the saturation I_{DS} decreases were only 16.9, 9.2, and 3.6%, respectively, and the mobility only decreased slightly. After restored to pure N_2 flow, the electrical performance could basically recover to the original level. Moreover, the good linearity of the changes of normalized I_{DS} as a function of their concentrations in N_2 flow existed in the concentration range of 0.4 and 1.0 P_0, which implied that such OTFTs might be applied as sensors for exploring these three compound vapors.

REFERENCES

[1] Dimitrakopoulos, C. D. & Malenfantols, P. R. L. (2002). *Adv. Mater.*, *14*, 99.

[2] Baude, P. F., Ender, D. A., Haase, M. A., Kelley, T. W., Muyres, D. V., & Theiss, S. D. (2003). *Appl. Phys. Lett.*, *82*, 3964.

[3] Drury, C. J., Mutsaers, C. M. J., Hart, C. M., Matters, M., & de Leeuw, D. M. (1998). *Appl. Phys. Lett.*, *73*, 108.

[4] Rogers, J. A., Bao, Z., Baldwin, K., Dodabalapur, A., Crone, B., Raju, V. R., Kuck, V., Katz, H., Amundson, K., Ewing, J., & Drzaic, P. (2001). *Proc. Natl. Acad. Sci. USA.*, *98*, 4835.

[5] Crone, B., Dodabalapur, A., Gelperin, A., Torsi, L., Katz, H. E., Lovinger, A. J., & Bao, Z. (2001). *Appl. Phys. Lett.*, *78*, 2229.

[6] Someya, T. & Sakurai, T. (2003). *Tech. Dig.-Int. Electron Devices Meet.*, 203.

[7] Katz, H. E., Lovinger, A. J., Johnson, J., Kloc, C., Siegrist, T., Li, W., Lin, Y. Y., & Dodabalapur, A. (2000). *Nature*, *404*, 478.

[8] Merlo, J. A., Newman, C. R., Gerlach, C. P., Kelley, T. W., Muyres, D. V., Fritz, S. E., Toney, M. F., & Frisbie, C. D. (2005). *J. Am. Chem. Soc.*, *127*, 3997.

[9] Kymissis, I., Dimitrakopoulos, C. D., & Purushothaman, S. (2001). *IEEE Trans. Electron Devices*, *48*, 1060.

[10] Kato, Y., Iba, S., Teramoto, R., Sekitani, T., Someya, T., Kawaguchi, H., & Sakurai, T. (2004). *Appl. Phys. Lett.*, *84*, 3789.

[11] Li, D. W., Borkent, E. J., Nortrup, R., Moon, H., Katz, H., & Bao, Z. (2005). *Appl. Phys. Lett.*, *86*, 042105.

[12] Zhu, Z. T., Mason, J. T., Dieckmann, R., & Malliaras, G. G. (2002). *Appl. Phys. Lett.*, *81*, 4643.

[13] Qiu, Y., Hu, Y., Dong, G., Wang, L., Xie, J., & Ma, Y. (2003). *Appl. Phys. Lett.*, *83*, 1644.

[14] Ye, R. Y., Baba, M., Suzuki, K., Ohishi, Y., & Mori, K. (2004). *Thin Solid Films*, *437*, 464–465.

[15] Gundlach, D. J., Jackson, T. N., Schlom, D. G., & Nelson, S. F. (1999). *Appl. Phys. Lett.*, *74*, 3302.

[16] Dean, J. A. (1998). *Langes Chemistry Handbook*, 15th ed. McGraw-Hill Professional.