Review

Nano-scale interface controls for future plastic transistors

Kazuhito Tsukagoshi a,b,*, Iwao Yagi a, Yoshinobu Aoyagi a,c

a RIKEN, Hirosawa 2-1, Wako, Saitama 351-0198, Japan
b PRESTO, JST, Honcho 4-1-8, Kawaguchi, Saitama 332-0012, Japan
c Department of Information Processing, Tokyo Institute of Technology, Nagatuda 4259, Midori, Yokohama, Kanagawa 226-8502, Japan

Received 11 October 2005; accepted 11 January 2006
Available online 20 March 2006

Abstract

Recent fundamental research on nano-scale interface control for organic thin film transistors is presented. The interfaces between the organic channel and the substrate, and between the organic channel and the metal electrodes have the greatest influence on transistor performance. The interface properties also drastically change the operation-stability of the transistor performance. This paper shows the results of a series of experimental investigations on the interfaces in the pentacene OTFT.

© 2006 NIMS and Elsevier Ltd. All rights reserved.

Keywords: Organic thin film transistor; Pentacene; Interface; Contact; Substrate

Contents

1. Introduction ........................................... 231
2. Effect of surface conditions ........................... 232
3. Effect of grain boundaries ............................ 233
4. Effect of contact interface properties ............... 233
5. Conclusion ........................................... 236
Acknowledgements ...................................... 236
References .............................................. 236

1. Introduction

Organic thin film transistors (OTFTs) have great potential in future electronics, particularly in flexible circuits [1–17]. Currently, the most reliable organic transistors are fabricated from pentacene molecules, and the fabrication process is surprisingly simple: a pentacene film is formed on insulator/conductive-substrate by sublimation in a vacuum chamber. The evaporated pentacene forms a polycrystalline film on the substrate through molecular self-assembly, which also provides performance superior to other OTFTs. However, improvements in the reproducibility and performance of pentacene transistors remain necessary before the technology can be applied for practical use. For example, the stability of the operating threshold and field-effect mobility is dependent on the strict control of several interfaces within the transistor structure. The interfaces that have the greatest influence transistor performance are those between the organic channel and the substrate, and between the organic channel and the metal electrodes. The polycrystalline grain–grain interface also suppresses carrier movement in the film, resulting in low transistor mobility, and carrier transport between the self-stacked molecule layers must also be considered. To integrate functional devices as plastic electronics, the interface between the organic channel and the passivation film is also crucial. This paper presents the results of a series of investigations on the interfaces...
between the substrate and electrodes, which can be tuned to stabilize pentacene OTFT performance.

2. Effect of surface conditions

The first step in the fabrication of pentacene OTFTs is the thermal evaporation of pentacene onto the substrate. The thin film thus formed tends to assume a polycrystalline grain structure (Fig. 1(a)). To examine the effects of surface conditions, a basic substrate consisting of thermally grown SiO₂ (200 nm in thickness) on conductive Si (Fig. 1(b)) was employed, where the former acts as a gate insulator and the latter as a gate electrode. Surface cleaning of the substrate is necessary to ensure reproducibility of transistor properties. Without cleaning, the device characteristics vary substantially from one device to the next due to the variability of surface conditions. Residual particles on the substrate surface affect the grain size of the evaporated pentacene film (Fig. 2) by acting as nucleation centers. A common surface cleaning procedure was employed in this study, involving ultrasonication in acetone followed by rinsing in isopropyl alcohol, then exposure to O₂ plasma and baking at 180 °C oven.

Transistor performance is also strongly dependent on the molecular surface conditions [4,5]. To examine the effect of surface molecular state, the substrate cleaned by the above procedure was compared to the same substrate after further treatment with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (Fig. 3), which has short molecular length, can be obtained in high purity, and is stable with respect to moisture. The HMDS acts as a silane coupling reactant, the chemical action of which changes the OH termination of SiO₂ to (CH₃)₃–Si termination. HMDS was applied to the substrate by spin-coating, followed by baking in an oven. Although the water contact angle changed substantially from 6.8° (Fig. 3(a)) to 70° (Fig. 3(f)) with HMDS treatment, atomic force microscopy (AFM) measurements confirmed that the surface roughness had not increased (Fig. 3(b) and (g)). To probe the conduction properties near the interface, a number of monolayer-channel OTFTs were fabricated on the substrates. The OTFT channels were deposited to a thickness of 5 nm, as determined from the deposition monitor. AFM cross-sectional analysis indicates that the channels consisted of two bottom layers with nucleating dendritic grains. The OTFTs on the untreated and HMDS-treated substrates did not exhibit clear differences in morphology, yet had distinctly different electrical properties. The OTFT on the untreated substrate displayed a weak gate voltage modulation and had a normally on state, whereas the OTFT on the HMDS-treated substrate exhibited large gate voltage modulation and had a normally off state. The dramatic change induced by HMDS treatment can also be seen in the $\sqrt{I_{sd}}$–$V_g$ plot of the transfer characteristic, where $I_{sd}$ is the source-to-drain current, and $V_g$ is the gate voltage. $I_{sd}$ decreases with decreasing gate voltage for the OTFT on an untreated substrate, yet does not reach a sufficiently low value to achieve the off state at $V_g < 20$ V. In contrast, $I_{sd}$ for the OTFT on the HMDS-treated substrate increased in proportion to the square of $V_g$–$V_T$ from a clear off state of the order of $10^{-10}$ A. The extracted field-effect mobility of the OTFT on the HMDS-treated substrate was 0.2 cm²/(V·s), and the threshold voltage was $-0.8$ V. Comparing the two OTFTs, the OTFT of the HMDS-treated substrate exhibits higher on-current and lower off-current, resulting in higher field-effect mobility. The achieved off-state and negative threshold voltage contribute to the clear saturation observed in the output characteristic of the OTFT on the HMDS-treated substrate. Molecular scale surface modification is therefore very effective for stabilizing transistor properties. The output and transfer characteristics of a pentacene OTFT formed on a 50-nm-thick SiO₂ film treated with HMDS are

Fig. 1. (a) Surface of a typical pentacene film on an SiO₂/Si substrate. (b) Schematic of OTFT in top-contact configuration.

Fig. 2. AFM images of SiO₂ substrates (a,b) and pentacene polycrystalline film (c,d), showing the cleaned substrate surface (a), a rough substrate surface with residual photoresist (b), and pentacene films formed on the cleaned (c) and rough (d) substrate surfaces.
shown in Fig. 4. Low-voltage operation was achieved, despite the use of SiO$_2$ as the gate insulator.

### 3. Effect of grain boundaries

Control of grain boundary properties in the thin films formed on the substrate also has a substantial influence on OTFT properties [6–8]. The evaporated pentacene film exhibits clear grain boundaries under AFM. AFM has been used extensively to image the surface of such pentacene films, and is an effective tool for determining grains structures and molecular steps. However, AFM is not a sensitive technique for detecting areas where the pentacene film is not contiguous. Using a low-voltage (0.3 kV) scanning electron microscopy (SEM) technique, serious flaws in the films have been recognized (Fig. 5). Low-voltage SEM allows the surface image of second electron emission to be captured. Second electron emission provides information on the surface material, and the images show strong contrast between the pentacene film and the SiO$_2$ substrate. The layer stepping seen by AFM can also be observed by low-voltage SEM. The discontinuity of the polycrystalline pentacene film reduces the conductivity of the film. The larger-grained films exhibit larger holes through which the underlying substrate is exposed, particularly films formed at higher substrate temperature. However, it is generally believed that larger-grained films provide better transistor characteristics, such as mobility. This is consistent with the higher field-effect mobility observed for single grains than through grain boundaries [8]. Nevertheless, poor interconnection between grains results in lower conductivity through the film. In film formation, it is therefore essential to consider both the size of grains and the continuity of the evaporated film. This type of treatment for improving film conductivity can be expected to be a key feature of optimized OTFT fabrication.

![Fig. 3. Comparison of as-cleaned SiO$_2$ surface (a–e) and HMDS-treated SiO$_2$ surface (f–j), showing the water contact angle (a,f), AFM images (5 μm × 5 μm) before (b,g) and after (c,h) pentacene deposition, output characteristics (d,i), and transfer characteristics (e,j).](image)

![Fig. 4. (a) OTFT output under low-voltage operation, and (b) the transfer characteristic](image)
4. Effect of contact interface properties

A patterning method with low damage will be useful for characterizing OTFTs. As pentacene films are sensitive to many kinds of solvents and solvent vapors [9–12], the solution process in device fabrication is difficult to optimize. Dry fabrication processes may therefore be more appropriate for avoiding excessive damage to organic thin films [13,14]. As a dry-etching method, laser ablation was investigated for the formation of a four-terminal device for direct contact resistance measurement. Fig. 6(a) shows a schematic of the instrument developed for dry-etching. A laser pulse from an Nd:YAG laser
(wavelength, 532 nm; maximum output power, 2.0 mJ/pulse) is guided through an optical microscope system to a sample mounted on an x–y moving stage. Fig. 6(b) shows a 30-nm-thick pentacene film formed on an SiO2/Si substrate by this method. The best resolution in this system is 1 μm. This laser patterning technique may also be applied to C60 (Fig. 6(c)) and poly-3-hexylthiophene (P3HT) (Fig. 6(d)) thin films. The area etched by laser patterning was sufficiently insulated, as confirmed from the channel width dependence (Fig. 6(e) and (f)). Dry-etching of the channel in the pentacene OTFT was repeatable, and consistent electrical properties were obtained. The current $I_{sd}$ at a given $V_g$ changed with channel width, and the insulating resistance at a channel width of 0 μm was greater than 10 GΩ, demonstrating that high insulation resistance was obtained in the etched area.

The change in contact resistance with gate voltage was examined using a four-terminal device (Fig. 7(a)). The pentacene film in this device was patterned by the laser ablation system. The variation in source-drain current ($I_{sd}$) in the two-terminal configuration and the voltage drop between electrodes 2 and 3 ($V_{23}$) with varying source-drain voltage ($V_{sd}$) is shown in Fig. 7(b) and (c). From the ohmic $I_{sd}–V_{sd}$ region, the two-terminal resistance $R_{14}$ was determined as the sum of the pentacene channel resistance ($R_{ch}$) and the contact resistances ($R_{c1}$ and $R_{c4}$). The ohmic region in the $I_{sd}–V_{23}$ characteristic gives the channel resistance between electrodes 2 and 3 ($R_{23}$). The pentacene channel resistance (two-terminal resistance) can then be obtained by multiplying $R_{23}$ by the channel length ratio $L_{14}/L_{23}$. From $R_{14}$ and $R_{ch}$, the total contact resistance $R_{c1} + R_{c4}$ can also be determined. The contact resistance and pentacene channel resistance were thus separated using this method. The dependence of $R_{ch}$, $R_{c1} + R_{c4}$, and $R_{14}$ on gate voltage is plotted in Fig. 7(d). At $V_g=0$ V, $R_{ch}$ was comparable to $R_{c1} + R_{c4}$. With increasing negative gate voltage, $R_{ch}$ and $R_{c1} + R_{c4}$ decreased. The $R_{c1} + R_{c4}$ component exhibited a more sensitive dependence on gate voltage than $R_{ch}$, and was reduced to be smaller than 1% at a gate voltage of −80 V. The contact resistance therefore primarily governs $I_{sd}$ in pentacene OTFTs. The temperature dependence of $R_{14}$, $R_{ch}$ and $R_{c1} + R_{c4}$ is shown in Fig. 7(e) for the range of 100–300 K at a gate voltage of −80 V. The $|V_{sd}|<2$ V region retained its ohmic property regardless of the temperature. At room temperature, $R_{ch}$ was larger than $R_{c1} + R_{c4}$, but both increased with decreasing temperature. $R_{c1} + R_{c4}$ became equivalent to $R_{ch}$ at 120 K, and became larger than $R_{ch}$ below 120 K. At 100 K, $R_{14}$ was mainly determined by $R_{c1} + R_{c4}$. This result indicates that contact resistance is dominant at low temperatures. The activation energies for $R_{ch}$ and $R_{c1} + R_{c4}$, determined by fitting the experimental temperature-dependence data to an Arrhenius equation, are shown in Fig. 7(f). The estimated
thermal activation energy of 80 meV for $R_{c1} + R_{c4}$ is twice that for $R_{ch}$ (42 meV). This feature is also expected to hold for OTFTs fabricated using other channel materials. Optimization of the channel/electrode interface is therefore another crucial issue in improving the performance of OTFTs. Structural modifications and doping control around the electrodes will also contribute to the enhancement of OTFT characteristics [15–17].

5. Conclusion

The present experiments on interfaces in pentacene transistors have shown that interface properties are critical to the control and stabilization of organic transistor performance. Therefore, while pentacene OTFTs are a very promising technology for advanced plastic electronics, it remains necessary to examine the effect of interfaces in the devices in order to increase our fundamental understanding of basic organic transistors.

Acknowledgements

The authors would like to thank Dr S. Shigeto for helpful discussions. This work was supported in part by a Grant-In-Aid for Scientific Research (No. 16GS50219) from the Ministry of Education, Culture, Sport, Science and Technology of Japan.

References

[1] G. Horowitz, Organic field-effect transistors, Adv. Mater. 10 (1998) 365–377.
[2] S. Ditlea, The electronic paper chase, Sci. Am. 285 (2001) 50–55.
[3] C.D. Dimitrakopoulos, D.J. MasCaro, Organic thin-film transistors: a review of recent advances, IBM J. Res. Dev. 45 (2001) 11–28.
[4] M. Shtein, J. Mapel, J.B. Benziger, Stephen R. Forrest, Effects of film morphology and gate dielectric surface preparation on the electrical characteristics of organic-vapor-phase-deposited pentacene thin-film transistors, Appl. Phys. Lett. 81 (2002) 268–270.
[5] I. Yagi, K. Tsukagoshi, Y. Aoyagi, Modification of the electric conduction at the pentacene/SiO$_2$ interface by surface termination of SiO$_2$, Appl. Phys. Lett. 86 (2005) 103502.
[6] G. Horowitz, M.E. Hajlaoui, Mobility in polycrystalline oligothiophene field-effect transistors dependent on grain size, Adv. Mater. 12 (2000) 1046–1050.
[7] F.-J. M. zu Heindorf, M.C. Reuter, R.M. Tromp, Growth dynamics of pentacene thin films 412 (2001) 517–520.
[8] T. Minari, T. Nemoto, S. Isoda, Fabrication and characterization of single-grain organic field-effect transistor of pentacene, J. Appl. Phys. 96 (2004) 769–772.
[9] D.J. Gundlach, N. Jackson, D.G. Schlor, S.F. Nelson, Solvent-induced phase transition in thermally evaporated pentacene films, Appl. Phys. Lett. 74 (1999) 3302–3304.
[10] T.N. Jackson, Y.Y. Lin, D.J. Gundlach, H. Klauck, Organic thin-film transistors for organic light-emitting flat-panel display backplanes, IEEE J. Selected Topics Quantum Electron. 4 (1998) 100–104.
[11] D. Li, E.-J. Borkent, R. Nortrup, H. Moon, H. Katz, Z. Bao, Humidity effect on electrical performance of organic thin-film transistors, Appl. Phys. Lett. 86 (2005) 042105.
[12] Z.-T. Zhu, J.T. Mason, R. Dieckmann, G.G. Malliaras, Humidity sensors based on pentacene thin-film transistors, Appl. Phys. Lett. 81 (2002) 4643–4645.
[13] I. Yagi, K. Tsukagoshi, Y. Aoyagi, Direct observation of contact and channel resistance in pentacene four-terminal thin-film transistor patterned by laser ablation method, Appl. Phys. Lett. 84 (2004) 813–815.
[14] K. Tsukagoshi, I. Yagi, K. Shigeto, K. Yanagisawa, J. Tanabe, Y. Aoyagi, Pentacene transistor encapsulated by poly-para-xlylene behaving as gate dielectric insulator and passivation film, Appl. Phys. Lett. 87 (2005) 183502.
[15] R. Hajlaoui, G. Horowitz, F. Garnier, A. Arce-Brouchet, L. Laigre, A. El Kassmi, F. Demanze, F. Kouki, Improved field-effect mobility in short oligothiophenes: quaterthiophene and quinquethiophene, Adv. Mat. 9 (1997) 389–391.
[16] J. Wang, H. Wang, J. Zhang, X. Yan, D. Yan, Organic thin-film transistors with improved characteristics using lutetium bisphthalocyanine as a buffer layer, J. Appl. Phys. 97 (2005) 026106.
[17] I. Yagi, K. Shigeto, K. Tsukagoshi, Y. Aoyagi, Alignment-free top-contact formation for organic thin film transistors with submicron-length channel, Jpn. J. Appl. Phys. 44 (2005) L479–L481.