

Origin of the ambipolar operation of a pentacene field-effect transistor fabricated on a poly(vinyl alcohol)-coated Ta₂O₅ gate dielectric with Au source/drain electrodes

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(Received 23 December 2008; accepted 6 February 2009; published online 24 February 2009)

Pentacene field-effect transistors (FETs) were fabricated on a poly(vinyl alcohol) (PVA)-coated Ta₂O₅ gate dielectric using Au source/drain electrodes. Their device characteristics were examined before and after annealing the FETs in a vacuum. Before annealing, the pentacene FET showed an ambipolar operation with hole mobility of 0.1 cm² V⁻¹ s⁻¹ and electron mobility of 0.005 cm² V⁻¹ s⁻¹. After annealing at 50 °C, however, the *p*-type operation characteristics almost diminished and an enhanced *n*-type operation was observed. Na⁺ ions in the PVA are supposed to change the character of the injection barrier at the Au/pentacene junction and enable the *n*-type operation. © 2009 American Institute of Physics. [DOI: 10.1063/1.3089692]

Organic field-effect transistors (OFETs) have been the focus of intense research efforts.¹ Many of the OFETs fabricated to date show only a unipolar operation. However, some applications, such as organic complementary circuits, require both *p*- and *n*-channel operation. For realizing the organic complementary circuits, ambipolar devices have a significant potential because they can eliminate the need to separately pattern *p*- and *n*-channel materials.² In addition, the ambipolar circuit is also useful for fabricating a light-emitting organic device, in which the light-emitting recombination of the hole and electron can be switched by the gate potential.³

One approach to accomplish the ambipolar OFET is the use of blends or bilayers of the hole and electron transporting materials as the active layer.⁴ The ambipolar operation has also been reported for single-agent OFETs in which metal elements with different work functions are properly chosen as the source and drain electrodes.⁵ Another successful approach in which only Au is deposited as the source/drain electrodes on the pentacene active layer uses a spin-coated film of poly(vinyl alcohol) (PVA) as the gate dielectric. In previous reports by Singh and co-workers,^{6,7} the pentacene FET fabricated on the PVA gate dielectric showed significantly high hole and electron mobilities such as 0.3 cm² V⁻¹ s⁻¹ and 0.04 cm² V⁻¹ s⁻¹, respectively, although the pentacene OFETs directly fabricated on oxide gate materials, such as SiO₂, Al₂O₃, or Ta₂O₅, show no *n*-type operation when Au is used as both the source/drain electrodes. In their study, however, a high working voltage was required to operate the pentacene OFETs on PVA because the PVA layer must be thick (1–1.5 μm) enough to avoid the breakdown of the gate dielectric.

In our study, pentacene OFETs were fabricated on thinner PVA films with which anodized Ta₂O₅ substrates were spin-coated. The dielectric constant of the anodized Ta₂O₅ is far higher (about 25–27)^{8,9} than that of PVA (about 7–8) (Ref. 6) so that the operation voltage of the OFET on the

PVA/Ta₂O₅ bilayer gate can be lowered if the thickness of the PVA layer is small. In addition, we followed the changes in the operation characteristics during the annealing of the fabricated ambipolar pentacene OFETs in an ultrahigh-vacuum (UHV) chamber to elucidate the origin of the *n*-type operation on PVA.

Ta sheets (Nilaco, 99.99%, 0.2 mm thickness) were used as the substrate for the OFETs. First a Ta sheet was electrochemically polished in a mixed solution of aqueous HF and concentrated H₂SO₄ to make a very smooth surface. Its surface was then anodically oxidized by applying 100 V in a 1 × 10⁻⁴ M aqueous solution of tetraethylammonium iodide ((C₂H₅)₄NI), which results in the growth of a Ta₂O₅ layer as thick as 200 nm. The detailed process of the polishing and anodization is shown in Ref. 9. The typical capacitance of the anodized Ta₂O₅ layer measured by an LCR meter (Tecpel LCR-612) was about 130 nF cm⁻². The anodized Ta₂O₅ surface was spin-coated with an aqueous solution of PVA (Sigma-Aldrich Mowiol® 40–88, weight-average molecular weight *M_w* ~ 127 000). The concentration of the solution was 5 wt %, and the rotation speed was 1500 rpm. The thickness of the PVA film estimated by the capacitance was about 600 nm. The typical gate capacitance of the PVA/Ta₂O₅ bilayer was about 10 nF cm⁻². Another Ta₂O₅ substrate was also spin-coated with a thinner PVA film of about 100 nm using a 3 wt % PVA solution at 5000 rpm in order to observe the dependence of the OFET characteristics on the PVA thickness. The coated substrate was then baked in an Ar atmosphere at 60 °C for 20 h and introduced into an UHV apparatus where the film growth and the FET characteristics measurement were performed.

The as-purchased pentacene (Sigma-Aldrich, 98% purity) was evaporated from a Knudsen cell under the vacuum of ~1 × 10⁻⁷ Pa. The substrate temperature was maintained at room temperature (RT: ~25 °C). The growth rate of the pentacene film was about 1 nm min⁻¹, and the typical thickness of the pentacene films was 100 nm. To complete the top-contact-type FET structure, the Au source/drain electrodes were deposited over the pentacene layer through a

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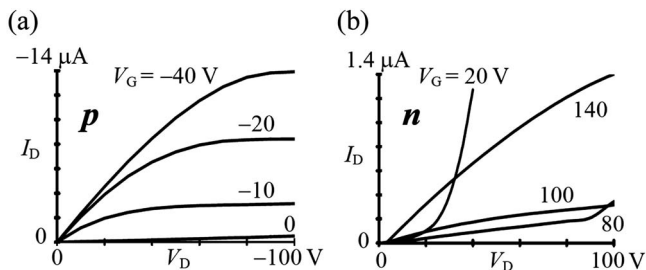


FIG. 1. (a) *p*-type and (b) *n*-type output characteristics of a pentacene OFET fabricated on a Ta₂O₅ gate dielectric coated with a 600 nm PVA film measured before the thermal annealing.

shadow mask. The channel width and the channel length were 1 and 0.1 mm, respectively.

Electrical characterization of the OFETs was performed in the UHV chamber without exposure to air using the combination of a Keithley 6517 A electrometer and a Keithley 487 picoammeter/voltage source. The measurements were performed at RT before and after annealing of the fabricated OFETs at 50 °C for 18 h under UHV conditions. Pentacene films were also deposited on a PVA/Ta₂O₅ bilayer at the substrate temperature of 50 °C for 2 h. In this case, the pentacene film was thermally annealed before the deposition of the Au source/drain electrodes.

Before the annealing, the pentacene OFETs fabricated at RT on the PVA(600 nm)/Ta₂O₅ bilayer gate dielectric showed the usual *p*-type operation, and the *n*-type operation was also observed when a high positive gate voltage (V_G) was applied. Figure 1 shows the *p*-channel and *n*-channel operations of the ambipolar pentacene OFET. In the ambipolar OFET, increasing the drain voltage (V_D) above a certain value, which is gate bias dependent, results in a characteristic increase in the drain current (I_D) when the absolute value of V_G ($|V_G|$) is low. For the present output characteristics of the *p*-type operation shown in Fig. 1(a), such an increase in I_D is barely observed only at $V_G=0$ V. For the output characteristics of the *n*-type operation shown in Fig. 1(b), however, a steep increase in I_D , which is due to the hole injection from the drain electrode, is observed in the increased V_D region for a $|V_G|$ lower than 80 V. For the higher $|V_G|$, the device shows an enhanced I_D and exhibits a normal *n*-type operation with the saturated regions. The hole and electron mobilities calculated from the transfer characteristics in the saturated regions using the theoretical equation¹ are 0.1 and 0.005 cm² V⁻¹ s⁻¹, respectively. The observed hole mobility of the pentacene OFET on the PVA/Ta₂O₅ bilayer is comparable to that of the OFET fabricated on a bare SiO₂ or Ta₂O₅ gate using the same pentacene source and UHV apparatus, although the *n*-type operation was never observed on the bare oxide surfaces.

After the annealing of this sample, the operating characteristics showed drastic changes. Figure 2 shows the *p*-channel and *n*-channel operations after the annealing at 50 °C for 18 h. In the annealed OFET, the I_D of the *p*-type operation is heavily reduced. In addition, a steep increase in I_D , which is due to the electron injection from the drain electrode, is observed in the increased V_D region for the low $|V_G|$ as shown in Fig. 2(a). The hole mobility of the annealed OFET is calculated to be 0.0008 cm² V⁻¹ s⁻¹. In contrast, the *n*-type operation is fairly improved after the annealing. As shown in Fig. 2(b), a six times larger I_D is observed at

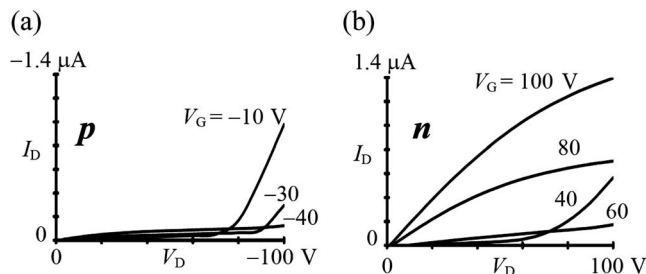


FIG. 2. (a) *p*-type and (b) *n*-type output characteristics of a pentacene OFET fabricated on a Ta₂O₅ gate dielectric coated with a 600 nm PVA film measured after the thermal annealing at 50 °C for 18 h.

$V_D=100$ V and $V_G=100$ V. The electron mobility of the annealed OFET was calculated to be 0.006 cm² V⁻¹ s⁻¹.

When we deposited the pentacene film on the PVA/Ta₂O₅ gate dielectric at 50 °C, similar *p*- and *n*-type performances were observed compared with those measured before the annealing of the OFET fabricated at RT. This result indicates that only the annealing after the deposition of the source/drain Au electrodes changes the performance of the OFET on the PVA/Ta₂O₅ bilayer gate dielectric.

The OFETs were also fabricated on a 100 nm PVA/Ta₂O₅ bilayer gate dielectric because a thinner PVA coating is favorable for the low-voltage operation. The *n*-type operation, however, could not be observed on the thinner PVA film, and only the usual *p*-type unipolar characteristics were observed before and even after the annealing.

Here, it must be considered that the PVA reagent is synthesized from poly(vinyl acetate) by the saponification with sodium hydroxide so that it contains Na impurity. In reality, a preliminary quantitative analysis by inductively coupled plasma spectrometry has revealed that a 5 wt % aqueous solution of PVA includes 7 ppm Na by weight. It is known that alkali metal elements have small work functions and change the barrier height against the electron injection from the cathode into the active layer of an organic light-emitting device.¹⁰ It is also reported that the pentacene OFET using Ca as the source/drain electrodes shows the ambipolar operation due to its small work function.⁵ It was also observed in our preliminary experiments that the doping of Li into the pentacene active layer at RT never caused the *n*-type operation, but the usual *p*-type operation was still observed.

Therefore, we postulate that the Na impurity in the PVA film changes the condition of the junctions at the Au/pentacene interface during annealing of the fabricated OFETs. The behavior of the Na impurity is schematically shown in Fig. 3. During the deposition of the evaporated “hot” Au atoms onto the pentacene/PVA surface, warmed Na⁺ ions existing in the PVA film [Fig. 3(a)] are allowed to diffuse. Some of them might intrude into the pentacene film

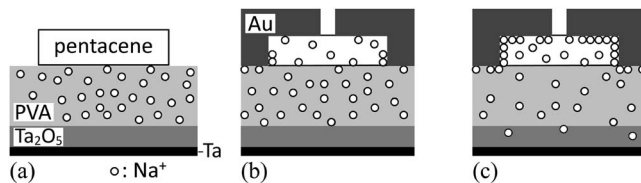


FIG. 3. Schematic view of the diffusion of Na⁺ ions from a PVA film to Au/pentacene interface. (a) Before and (b) after the deposition of Au electrodes. (c) After the successive thermal annealing of a fabricated OFET.

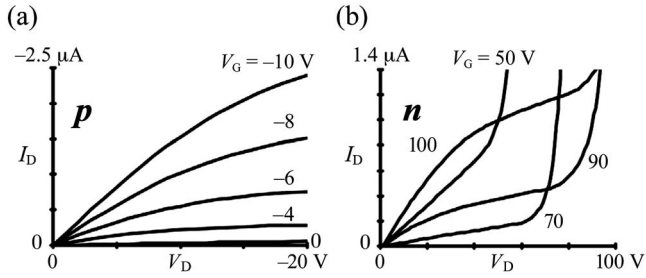


FIG. 4. (a) *p*-type and (b) *n*-type output characteristics of a pentacene OFET fabricated on a Ta₂O₅ gate dielectric coated with a thinner (350 nm) PVA film including a higher concentration of a Na⁺ impurity (700 ppm) measured before the thermal annealing.

and reach the Au/pentacene interface, as shown in Fig. 3(b). Such Na⁺ ions reduce the work function of the source/drain electrodes, which is favorable for the electron injection but unfavorable for the hole injection into the pentacene channel. The just fabricated OFETs then show the ambipolar operation due to the limited change of the injection condition. Further annealing of the OFETs promotes the diffusion of Na⁺ ions so that the injection condition is almost fully changed, as shown in Fig. 3(c). Then the OFETs show improved *n*-type and deteriorated *p*-type operation characteristics. Therefore, annealing of the sample during the deposition of the pentacene film, namely, before the deposition of Au electrodes, has no direct effect on the change in the injection condition. The annealing only after the deposition of Au electrodes can gather the Na⁺ ions at the Au/pentacene interface and change the injection condition.

If the PVA film is too thin, the total amount of Na⁺ ions becomes insufficient for changing the work function of the source/drain electrodes. The ambipolar operation might be observed on the thinner PVA film if a higher positive V_G was applied, but it usually causes a breakdown of the PVA/Ta₂O₅ gate. Then, we tried to add excess Na⁺ ions to the PVA film. If the concentration of Na⁺ is higher, it is expected that the ambipolar operation also occurs on a thinner PVA film. We added an aqueous NaOH solution to the 5 wt % aqueous PVA solution and prepared a solution including 700 ppm Na⁺ by weight. Next, the 200 nm thick Ta₂O₅ was spin-coated with this PVA solution at 2000 rpm, which results in a 350 nm thick Na⁺-rich PVA film. Figure 4 shows the output characteristics of a pentacene OFET that was fabricated on this thinner PVA/Ta₂O₅ bilayer gate and not annealed before the electric measurement. Although the PVA film is thinner, this OFET shows the ambipolar opera-

tion. The calculated hole and electron mobilities of the present OFET are 0.47 and 0.03 cm² V⁻¹ s⁻¹, respectively. In addition, the thinner PVA film makes it possible to operate the ambipolar OFET with lower bias voltages. In the *p*-type operation region of the previous OFET shown in Fig. 1(a), the I_D of $-2.0 \mu\text{A}$ was obtained with $V_D = -20 \text{ V}$ and $V_G = -10 \text{ V}$. However, in the present OFET shown in Fig. 4(a), the same I_D flows with $V_D = -15 \text{ V}$ and $V_G = -10 \text{ V}$. In the *n*-type operation region of the previous OFET shown in Fig. 1(b), the I_D of $0.3 \mu\text{A}$ was obtained with $V_D = 100 \text{ V}$ and $V_G = 100 \text{ V}$. In the present OFET shown in Fig. 4(b), the same I_D flows with $V_D = 10 \text{ V}$ and $V_G = 100 \text{ V}$. Therefore, it is concluded that the addition of the Na⁺ impurity is effective for decreasing the PVA film thickness and reducing the operating voltage of the ambipolar pentacene OFET.

In summary, the pentacene OFETs were fabricated on the PVA-coated Ta₂O₅ gate dielectric using Au source/drain electrodes. The as-fabricated pentacene OFETs showed an ambipolar operation, but the *p*-type operation character almost diminished, and an enhanced *n*-type operation was observed after the annealing in a vacuum. Na⁺ ions in the PVA are supposed to change the character of the injection barrier at the Au/pentacene junction and enable the *n*-type operation.

This work was supported by a Grant-in-Aid for Creative Scientific Research (Grant No. 14GS0207) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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