Thermal annealing effect on the crack development and the stability of 6,13-bis(triisopropylsilylethynyl)-pentacene field-effect transistors with a solution-processed polymer insulator

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A R T I C L E   I N F O
Article history:
Received 10 December 2009
Received in revised form 16 January 2010
Accepted 17 January 2010
Available online 25 January 2010

Keywords:
TIPS-pentacene FET
Solution-processed
Cracks
Trapping sites

A B S T R A C T
We report the thermal annealing effect on the field-effect mobility enhancement, the crack development, and the stability of 6,13-bis(triisopropylsilylthynyl) (TIPS)-pentacene field-effect transistors (FETs) with a solution-processed polymeric insulator. A high value of the field-effect mobility (0.401 cm²/V s) is achieved by thermally annealing the TIPS-pentacene FET at 60 °C which corresponds to the baking temperature of the TIPS-pentacene film. We demonstrate that thermal cracks, resulting primarily from side chains of the TIPS-pentacene, play a critical role on the degradation of the electrical properties of TIPS-pentacene FET, particularly in air under atmospheric pressure. The annealing effect is found to suppress both the development of the cracks and the increase of the off-current with time in the ambient environment. It is suggested that the cracks act as trapping sites of moisture and/or oxygen for the off-current flow and thus deteriorate the electrical performances of the TIPS-pentacene FET.

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that this behavior is very different from that of a vacuum-deposited film of pentacene with no side chains, showing an increased behavior of the mobility with increasing $T_a$ [10]. The annealing effect is found to suppress both the development of the cracks and the increase of the off-current with time in air under ambient pressure. It is suggested that the cracks act as trapping sites of moisture and/or oxygen for the off-current flow.

A top contact FET structure, shown in Fig. 1, was used in our study. A solution-processed polymer showing the low current leakage and negligible hysteresis, poly(4-vinylphenol) (PVP) mixed with methylated poly(melamine-co-formaldehyde) (MMF) of 125 wt.% as a cross-linker [11], was selected as a gate insulator. The PVP with MMF, dissolved in propylene glycol methyl ether acetate (PGMEA) in 10 wt.%, was spin-coated on the top of the pre-patterned ITO gate electrode, baked at 100 °C for 1 min to remove any residual PGMEA, and subsequently baked for 5 min at 200 °C to produce thermal cross-linking in the PVP layer. The thickness of the cross-linked PVP film was about 540 nm and the capacitance per unit area was 6.4 nF/cm². A solution of the TIPS-pentacene, dissolved in 1,2-dichlorobenzene (1,2-DCB) in 1.0 wt.%, was drop-casted on the top of the PVP insulator and was baked at 60 °C for 1 min to evaporate the 1,2-DCB solvent. The baking temperature of 60 °C is known to improve the crystallinity of the TIPS-pentacene film itself [6]. It should be noted that the cross-linked PVP layer is chemically inert against the residual PGMEA, and subsequently baked for 5 min at 200 °C to produce thermal cross-linking in the PVP layer. The thickness of the cross-linked PVP film was about 540 nm and the capacitance per unit area was 6.4 nF/cm². A solution of the TIPS-pentacene, dissolved in 1,2-dichlorobenzene (1,2-DCB) in 1.0 wt.%, was drop-casted on the top of the PVP insulator and was baked at 60 °C for 1 min to evaporate the 1,2-DCB solvent. The baking temperature of 60 °C is known to improve the crystallinity of the TIPS-pentacene film itself [6]. It should be noted that the cross-linked PVP layer is chemically inert against the residual PGMEA, and subsequently baked for 5 min at 200 °C to produce thermal cross-linking in the PVP layer. 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![Fig. 1. The chemical structure of a soluble organic semiconductor, TIPS-pentacene, and the schematic diagram of our TIPS-pentacene FET with a solution-processed polymer insulator. The channel length and the channel width are denoted by $L$ and $W$, respectively.](image-url)
the corresponding transfer characteristic curves of our TIPS-pentacene FETs annealed at the optimum value of $T_a = 60 \degree C$, respectively. From the characteristic curves, the field-effect mobility was determined to be 0.401 cm$^2$/V s. Note that without the help of an extra passivation layer and the optimization of the work function [6], and blending of the TIPS-pentacene [15], the high value of about 0.401 cm$^2$/V s has not been attained so far in a TIPS-pentacene FET fabricated on a solution-processed polymer gate insulator.

The annealing temperature ($T_a$) dependence of the field-effect mobility is shown in Fig. 3c. The mobility for the as-prepared TIPS-pentacene FET case was 0.152 cm$^2$/V s, and that annealed at $T_a = 60 \degree C$ was 0.401 cm$^2$/V s. For $T_a$ above 60 $\degree C$, the mobility decreases as low as 0.029 cm$^2$/V s at $T_a = 150 \degree C$ due to the appearance of thermal cracks in the TIPS-pentacene film. This behavior does not exist in thermally-deposited films of pentacene with no side chains but a simple increased behavior is observed with...
increase in the annealing temperature [10]. The on–off current ratio varies from $9 \times 10^2$ to $3 \times 10^4$ depending on $T_a$.

Let us investigate the thermal annealing effect on the stability of our TIPS-pentacene FETs in terms of the field-effect mobility and the off-current with time. Three different types of the TIPS-pentacene FETs (with no thermal treatment, annealed at 60 °C, and annealed at 150 °C) were studied at three different storage times of 0, 600, and 4000 h in air under atmospheric pressure. The OM images, taken after 4000 h, showing the morphology for each case were presented in Fig. 4a–c. In the non-annealed TIPS-pentacene FET, the cracks that did not exist initially were developed in time while in the annealed cases, no considerable change in the morphology was observed irrespective of the presence of the cracks. It is clear from Fig. 4d that after 4000 h, the mobility value for the non-annealed TIPS-pentacene FET decreases drastically by about 90% from 0.152 to 0.011 cm²/V s while the mobility values of the annealed cases decrease rather slowly by about 50% from 0.401 to 0.205 cm²/V s for $T_a = 60$ °C and from 0.029 to 0.016 cm²/V s for $T_a = 150$ °C. This implies that in relation to the cracks, the annealing effect plays a critical role in the stability of the TIPS-pentacene FETs. It is found that the thermal treatment at the optimum value of $T_a = 60$ °C avoids the crack development and enhances the crystallinity in the TIPS-pentacene film. This is why the TIPS-pentacene FET annealed at 60 °C exhibits the highest mobility (0.401 cm²/V s) and the best stability in time among the three types of the TIPS-pentacene FETs we studied.

Fig. 4e shows both the relative change of the off-current and the resulting on–off current ratio with time for three different devices to address the temporal degradation in relation to the cracks. After 4000 h stored in air under atmospheric pressure, the values of the off-current for the TIPS-pentacene FETs with cracks shown in Fig. 4a and c increase as large as 80 times while the value for the TIPS-pentacene FET annealed at the optimum value of $T_a = 60$ °C, showing no cracks, increases by about a factor of 10. From the fact that the moisture and/or oxygen diffused into an organic semiconductor film deteriorate the electric properties of the FETs [16–18], it is reasonable to conclude that the physicochemical adsorption of air and/or moisture onto the cracks dictates primarily the long-term stability of the TIPS-pentacene FETs with time. After 4000 h, the on–off current ratio for the TIPS-pentacene FET annealed at the optimum value of $T_a = 60$ °C is on the order of $10^3$, while that for the non-annealed case is below $10^2$.

In summary, we demonstrate how the thermal annealing affects the mobility enhancement, the development of cracks and the resultant degradation mechanism of the electrical properties, and the temporal stability of the TIPS-pentacene FETs fabricated on a single, solution-processed polymer insulator. The annealing process at the optimum temperature of 60 °C results in the highest field-effect mobility of 0.401 cm²/V/s among the TIPS-pentacene FETs we studied. Such high value has not been obtained so far in the TIPS-pentacene FET having a solution-processed polymer insulator without an additional buffer layer or a blending process. It is found the annealing effect suppresses both the development of the cracks and the increase of the off-current with time in the ambient environment. The cracks act as trapping sites of moisture and/or oxygen for the off-current flow and thus deteriorate the electrical performances of the TIPS-pentacene FET. Finally, further studies on the structural arrangement of side chains of the TIPS-pentacene in relations to the cracks as a function of temperature and the nature of the solvent used will provide a scientific platform for developing all solution-processed printed electronics.

![Fig. 4.](image-url) The optical microscopic images, taken after 4000 h stored in air under atmospheric pressure, of the TIPS-pentacene film, (a) without the thermal treatment, (b) annealed at 60 °C, (c) annealed at 150 °C and (d) the field-effect mobility of each case as a function of the storage time. Open squares (dashed line), open circles (solid line), and open triangles (dotted line) represent the non-annealed case, the annealed case at 60 °C, and the annealed case at 150 °C, respectively, (e) the relative change of the off-current (open symbols) and the resulting on–off current ratio (filled symbols) of each case as a function of the storage time in the ambient environment.
Acknowledgement

This work was supported by Korea Ministry of Knowledge Economy through the System IC-2010 Project.

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