Journal of Industrial and Engineering Chemistry 21 (2015) 126–128

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Short communication

Electroimmobilization of DNA for ultrafast detection on a microchannel integrated pentacene TFT

Rohit Chand [a,1], Jun-Ho Jeun [b,1], Min-Ho Park [a], Jung-Min Kim [c], Ik-Soo Shin [d], Yong-Sang Kim [a,*]

[a] School of Electronic and Electrical Engineering, Sungkyunkwan University, Suwon, Gyeonggi 440-746, South Korea
[b] Research & Development Center, Amkor Technology Korea Inc., Seoul 133-703, South Korea
[c] Materials & Devices Lab, Corporate R&D Institute, Samsung Electro-Mechanics Co. Ltd., Suwon, Gyeonggi 443-743, South Korea
[d] Department of Chemistry, Soongsil University, Seoul 156-743, South Korea

ARTICLE INFO

Article history:
Received 6 October 2013
Accepted 22 February 2014
Available online 2 March 2014

Keywords:
Pentacene thin film transistor
Microfluidic
Gate electric field
DNA sensor
Label free

ABSTRACT

We report a pentacene thin-film transistor integrated with microfluidic channel as an ultrafast DNA sensor. The microchannel assisted in easy transport of sample onto the pentacene active layer. The DNA immobilization time on active layer was drastically shortened by applying low positive electric field at the gate electrode. This helps by attracting the negatively charged DNA toward the pentacene layer. This device was evaluated for the label-free detection of single stranded DNA. The electrical property of the device fiercely changed due to the adsorption of DNA. Furthermore, the electrical characteristics were studied as a function of immobilization voltage and time.

1. Introduction

Organic thin-film transistors (OTFTs) are attractive candidates for a broad range of low-cost electronic applications, including memory devices, photodetectors, and chemical and biosensors. Genetic and microbial disease diagnosis requires a low-cost and fast biomolecule detection tool. Conventional methods of DNA detection mainly encircle spectroscopic or fluorescence based detections which are built on labeling or tagging of the targets. Label-free electronic methods are inexpensive and promise to offer better sensitivity and selectivity for the detection of DNA [1,2]. Pentacene based organic thin-film transistor as a DNA sensor is an excellent candidate and affirms the development of a handheld device in the near future. This sensor is of various advantages due to its effortless fabrication process and biocompatibility. The advancement and usefulness of OTFTs as sensors has been extensively discussed in some reviews [3,4].

In spite of all the research done, there still lacks a substantive and feasible use of these sensors in a practical world. Recently, a number of groups fabricated OTFTs for sensing DNA [5–7]. Among them, Zhu et al. and Zhang et al. employed SiO_x based FET with a pentacene layer for DNA immobilization [5,6], while Yan et al. used gold surface for the immobilization of thiolated DNA probe [7]. A common feature and disadvantage of these devices is the prolonged DNA immobilization time. Zhang et al. reported an immobilization time of 30 min with an overnight storage in nitrogen whereas Zhu et al. immobilized DNA for 1 h with an 8 h of drying time. Yan et al. in their report used 4–48 h for thiolated ssDNA probe deposition followed by 2 h of target DNA immobilization. However, Liu et al. have accelerated the DNA immobilization but by introducing a high electric bias of +50 V for 30 min [8]. 30 min is still a long time and is comparable to several other reports which did not use any special means. Such an extended time and high electric bias for DNA immobilization make the process tedious and also eliminate the practicality of the sensor.

In this work, we used a low electric field to immobilize DNA on pentacene surface resulting in a drastic reduction of immobilization time, compared to 60 min as reported earlier [9]. Furthermore, a polydimethylsiloxane (PDMS) based microfluidic channel was also integrated with the OTFT to make a self-sustained device.

* Corresponding author at: School of Electronic and Electrical Engineering, Sungkyunkwan University, Seobu-Ro 2066, Suwon, Gyeonggi 440-746, South Korea. Tel.: +82 31 299 4323; fax: +82 31 290 5828.
E-mail address: yongsang@skku.edu (Y.-S. Kim).
[1] Both these authors contributed equally to this work.

http://dx.doi.org/10.1016/j.jiec.2014.02.039
1226-086X/

2. Experimental

Top contact pentacene based TFTs fabricated on glass substrate were used for the DNA sensors. At first, Al bottom gate electrode was deposited on a clean glass surface up to a height of 80 nm by thermal evaporation. PMMA gate insulator was then spin-coated and cured in the oven at 100 °C for 10 min to remove the solvent followed by 160 °C for 30 min. For the active layer, pentacene was deposited to about 70 nm thickness through a patterned shadow mask in a high vacuum thermal evaporator at a rate of 0.1 Å/s. The source/drain Au electrodes were patterned to about 100 nm thickness by thermal evaporation using shadow mask defining a pentacene channel width of 1000 μm and length 100 μm. Finally, we integrated PDMS microchannel with pentacene based TFT.

The negatively molded PDMS microchannel was fabricated using a photo-patterned SU-8 2075 on a silicon wafer mold. Access holes were manually drilled at the ends of the microchannel. The uncured PDMS gel was brushed on the bottom surface of the PDMS layer containing engraved microchannel. The microchannel was then aligned on the pentacene active layer using a microscope and finally baked in oven at 75 °C for 1 h, for bonding.

DNA oligonucleotides (ssDNA, 25mer Poly-A, Bionics Inc., Korea) were diluted in deionized (DI) water to a concentration of 100 pmol/μl. To immobilize ssDNA on pentacene film, 1 μl of ssDNA was injected into the microfluidic channel through the inlet and a positive voltage was applied to the gate electrode for few minutes. Later air was blown using a syringe to remove the leftover solution and lastly the device was subjected to drying for 30 min at room temperature. The electrical performance of OTFTs was analyzed using Keithley 236 source measure unit with the LabVIEW assisted automated data acquisition system.

3. Results and discussion

The schematic of the device is shown in Fig. 1. The OTFTs had a pentacene active layer for immobilizing the DNA and a microfluidic channel to contain the DNA. The microfluidic channel helped in easy sample introduction and cleaning of the active layer and also helped in insulating the OTFTs from external environmental factors. In past, a few groups attempted to integrate a microfluidic delivery channel on the OTFTs system [10,11]. Zhang et al. fabricated a photolithographically produced SU-8 microchannel on the OTFTs which is tedious and expensive. Herein, we used a simple PDMS based microchannel to combine with the OTFTs.

Fig. 2(a) shows the transfer characteristic of the device with drain current (I_{DS}) as a function of the gate voltage (V_{GS}) measured at a constant drain-source voltage (V_{DS}) for different immobilization positive gate voltage. ssDNA injected into the microfluidic channel was subjected to +5 V positive gate voltage for 2 min. After air-drying the microchannel for 30 min, the change in electrical response was measured. Immobilization of ssDNA at +5 V (gray)

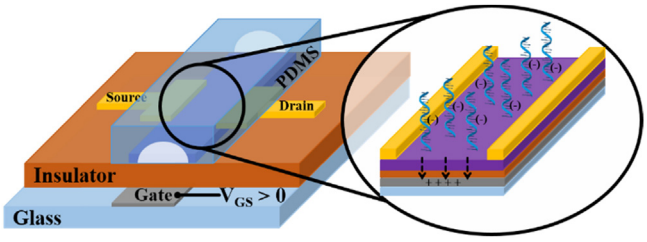

Fig. 1. Schematic of microchannel-integrated pentacene based TFT showing the principle of DNA immobilization at positive gate electric field. PDMS microchannel: 100 μm width and 120 μm height, pentacene channel: 1000 μm width and 100 μm length.

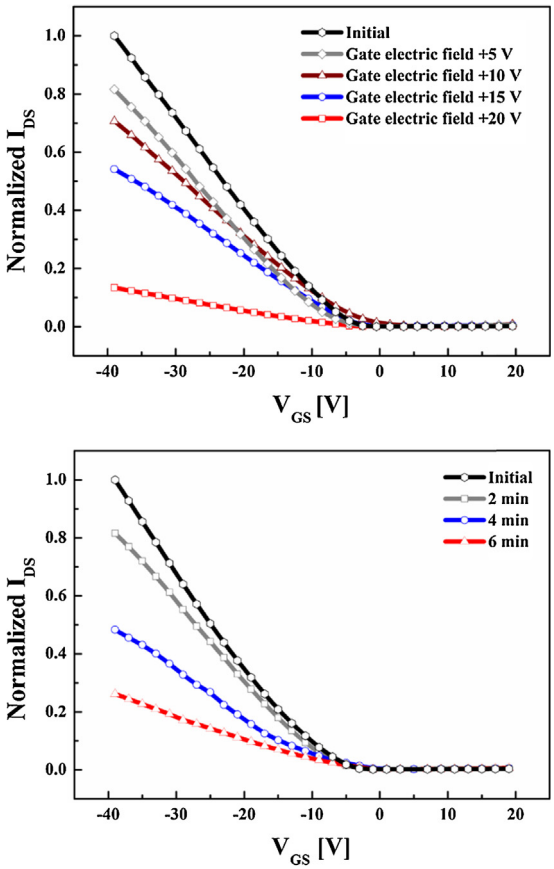

Fig. 2. Normalized transfer characteristics of pentacene based TFTs at V_{DS} = 20 V: different condition of ssDNA immobilization on pentacene: (a) positive gate electric field and (b) time. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

reduced the initial drain current (*i*, at V_{GS} = −40 V, V_{DS} = −20 V) by approximately 20% from the initial value (black) and also the mobility (μ_{fet}) by 42%. Application of positive voltage on the gate electrode attracted the negatively charged ssDNA deep into the pentacene layer and sped up the immobilization. A positive electric field resulted in dismissal of stearic hindrance and re-orientation of the DNA. Low electric field also ensured that there was no degradation of DNA. The ssDNA molecules physically adsorbed on the hydrophobic pentacene surface due to the electrostatic attraction and hydrophobic interactions (Fig. 1). The negative charge of the immobilized ssDNA on the pentacene surface scattered the holes. For this reason, drain current and mobility decreases depending upon the amount of immobilized ssDNA on the active layer. The ssDNA solution was prepared in DI water instead of common buffers such as Tris, PBS, etc., to avoid interference of ionic species present in the buffers with the performance of pentacene based TFTs. The negative ions present in these buffers can also be attracted into the pentacene layer when positive gate electric field is applied which can alter the output of the device. As shown in Fig. 2(a), increasing immobilization voltage led to an increase in ssDNA adsorption thereby decreasing the drain current with respect to initial device response. A control device without any ssDNA and ssDNA immobilized at −10 V for 2 min showed no accountable change in the electrical performance of OTFTs. The negative gate electric field repelled the DNA preventing it to immobilize on the active layer.

For the confirmation of immobilization, we hybridized the electrically immobilized polyA ssDNA with complimentary polyT ssDNA and used fluorescence imaging [11]. The resultant dsDNA

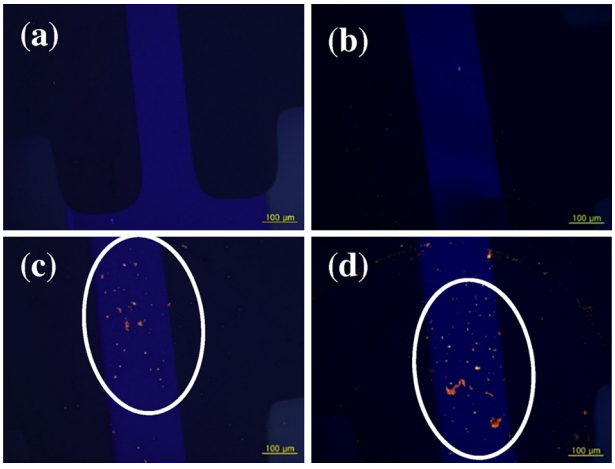

Fig. 3. Microscopic image of pentacene channel showing orange red fluorescence of DNA intercalated with EtBr: (a) no DNA, (b) polyA ssDNA, (c) polyA ssDNA immobilized at +5 V and hybridized with polyT ssDNA, (d) polyA ssDNA immobilized at +20 V and hybridized with polyT ssDNA. (For interpretation of the references to spectra in this figure legend, the reader is referred to the web version of this article.)

was intercalated with ethidium bromide dye (EtBr) for 15 min. The fluorescent images were obtained using a fluorescence microscope (Olympus BX50, Japan). For control, pristine pentacene channel of a device was treated with EtBr, which showed no fluorescence upon exposure (Fig. 3(a)). Another device, electro-immobilized with ssDNA and further interacted with EtBr also did not produce any fluorescence (Fig. 3(b)). Lastly, the device with dsDNA, produced orange red fluorescence upon exposure. Fig. 3(c and d) represents the device with DNA immobilized at +5 V and +20 V, respectively. It can be clearly seen that +20 V increased the amount of immobilized DNA on pentacene channel. The positive fluorescence affirmed that the ssDNA did not lose its property even after the electro-immobilization.

Later on, we calculated the application time of positive electric field for effective immobilization of ssDNA. Fig. 2(b) shows the electrical characteristic of OTFTs in relation to the time of immobilization at +5 V. When +5 V of the electric field was applied at the gate electrode for 2 min (gray), drain current and mobility reduced approximately by 20 and 42% respectively (Fig. 2(b)). As the immobilization time increased to 4 min (blue) and 6 min (red), the current reduced by 55 and 70%, respectively. Increasing the time of the applied positive electric field resulted in higher immobilization of ssDNA on the pentacene layer, thereby reducing the drain current and mobility.

The performance of pentacene based TFT with different immobilization voltage and time is summarized in Table 1. The average drain current response and mobility of various devices ($n = 5$) with respect to the different DNA immobilization voltage and the duration for which immobilization voltage was applied is shown in Table 1. These results indicate the possibility of reducing the DNA immobilization time on the pentacene based TFTs leading to an overall shorter analysis time.

Table 1
Performance of pentacene based TFTs at $V_{GS} = -40$ V and $V_{DS} = 20$ V, where $I_{DS(i)}$ = initial drain current and $I_{DS(DNA)}$ = drain current after ssDNA immobilization.

	$I_{DS(DNA)}/I_{DS(i)}$	% μ_{fet}
Voltage (V)		
05	0.82 ± 0.010	60.35
10	0.73 ± 0.018	51.80
15	0.58 ± 0.042	26.05
20	0.18 ± 0.046	04.70
Time (min)		
02	0.82 ± 0.010	60.35
04	0.45 ± 0.013	19.48
06	0.27 ± 0.020	08.17

4. Conclusion

We demonstrated a pentacene based TFTs that could sense the ssDNA immobilized on the active layer. The OTFTs had a PDMS based microchannel to store the DNA. Electroimmobilization concluded in faster absorption of ssDNA. The results validates that higher and longer the positive electric field, higher is the adsorption of DNA. Performance of OTFTs critically changed following the immobilization of DNA which is a result of hole scattering due to negatively charged phosphate group on the DNA. An increase in the amount of DNA adsorbed leads to a greater decrease in the drain current. An immobilization voltage of +5 V for 2 min was found to be optimum which will be used for future experiments. Therefore we propose a label-free OTFT based DNA sensor with a microfluidic channel to realize a quick and effortless detection platform having a potential use in the various diagnostics lab. The future work includes development of the device as a hybridization sensor and to sense the real biological sample.

References

[1] P. Estrela, P. Migliorato, J. Mater. Chem. 17 (2007) 219.
[2] X. Tang, S. Bansaruntip, N. Nakayama, E. Yenilmez, Y.L. Chang, Q. Wang, Nano Lett. 6 (2006) 1632.
[3] P. Lin, F. Yan, Adv. Mater. 24 (2012) 34.
[4] F. Yan, H. Tang, Expert. Rev. 10 (2010) 547.
[5] Q. Zhu, F. Xing, C. Liu, Y. Hu, N. Liu, J. Wang, Appl. Phys. Lett. 99 (2011) 073301.
[6] Q. Zhang, V. Subramanian, Biosens. Bioelectron. 22 (2007) 3182.
[7] F. Yan, S.M. Mok, J. Yu, H.L. Chan, M. Yang, Biosens. Bioelectron. 24 (2009) 1241.
[8] N. Liu, Y. Hu, J. Zhang, J. Cao, Y. Liu, J. Wang, Org. Electron. 13 (2012) 2781.
[9] J.-M. Kim, S.K. Jha, R. Chand, D.-H. Lee, Y.-S. Kim, Biosens. Bioelectron. 26 (2011) 2264.
[10] Q. Zhang, L. Jagannathan, V. Subramanian, Biosens. Bioelectron. 25 (2010) 972.
[11] P. Lin, X. Luo, I.-M. Hsing, F. Yan, Adv. Mater. 23 (2011) 4035.