

Graphene-enhanced Carrier Mobility and Air Stability in Organic Polythiophene Field Effect Transistors

Gen-Wen Hsieh¹, Zong-Rong Lin¹, Chun-Yi Hung¹, Sheng-Yu Lin¹, Chii-Rong Yang²

¹ College of Photonics, National Chiao Tung University
301, Gaofa 3rd Road, Guiren District
Tainan 71150, Taiwan

Phone: +886-6-303-2121 E-mail: cwh31@nctu.edu.tw

² Department of Mechatronic Engineering, National Taiwan Normal University
162, Section 1, Heping East Road
Taipei City 106, Taiwan

Abstract

Multifunctional graphene nanostructure as charge carrier mobility enabler and moisture and air barrier for organic field effect transistors is investigated. Primary results show that graphene flakes can enhance field effect mobility by a factor of up to ten. CVD graphene via direct polymer-free transfer reveals significant barrier capability for organic active channels.

1. Introduction

Two-dimensional graphene nanomaterials have attracted extensive attentions for both fundamental investigations and potential applications due to their fascinating optoelectronic, mechanical and physical characteristics. Recent advances show that the sp^2 -hybridized carbon honeycomb framework of graphene can enable π - π interactions with other organic and inorganic materials. Hence, different forms of graphene nanostructures have been considered as a viable additive to organic polymeric or molecular matrices, with the hope of constituting hybrid architectures with augmentative performance.

Moreover, the need for high barrier encapsulation to active device components in organic optoelectronics is particularly demanding since moisture and air are the most detrimental and life-limiting factors. Toward this end, thin film encapsulation that can enable reduction in the weight and thickness of devices is the most popular means since conventional glass lid capsulation is inappropriate for flexible devices. Notably, flexible and transparent graphene films could serve as an excellent barrier to gases because of their densely packed six-carbon ring framework. For instances, gas barrier properties of CVD-grown graphene films as a top electrode layer in organic photovoltaic devices have been investigated [1]. Laminating polymer-supported graphene sheets as top passivation layers can extend device functionality in polymer light emitting diodes [2] and organic field effect transistors [3]. However, there have been no reports of utilizing solitary graphene as gas barriers without any intermediate supporting film for organic active channels.

Here we report a novel strategy for fabricating organic-based field effect transistors (FETs) with multifunctional graphene nanostructures that relies on (i) a solution-processed active channel containing graphene flakes

and organic semiconducting polythiophene polymers, and (ii) an additive passivation layer of CVD graphene film atop transistor active channels (Fig. 1).

2. Results and Discussion

We first investigated the impact of the amount of graphene flakes on the graphene-polythiophene blend device characteristics. Primary results show that graphene flake density plays a crucial role in the organic active channel, which substantially influences the polymer morphology and transistor performance. Different concentrations of homogeneous graphene-poly(3-hexylthiophene-2,5-diyl) (Gr-P3HT) blend solutions ranging from 0 to 10 wt% were prepared for transistor fabrication in which the few layer graphene flakes were ~ 200 – 500 nm in diameter. As shown in Fig. 2, a tiny amount of graphene flakes (only 1 wt%) blended in the polythiophene active channel could reach a ten-fold increase in effective transistor mobility (from $6.3 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for pristine P3HT to $6.2 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ for Gr-P3HT blend). This enhancement is a clear indication of that polythiophene-graphene-polythiophene acts as the preferential path where charge carriers can travel much better than those in pristine polythiophene.

In order to investigate the barrier capability of graphene, we conducted a polymer-free approach for direct transfer of CVD graphene to our target substrates. Densely packed honeycomb CVD graphene for efficient moisture and air shielding is firstly applied on organic active channels without any supporting polymer, resulting in mild mobility degradation in ambient environment with respect to unprotected polythiophene devices. Fig. 3a summarizes the relative carrier mobilities of a bare P3HT FET and different graphene-passivated P3HT FETs before and after 700 h under ambient air at room temperature (23 – 25 °C, relative humidity ~ 50 – 60%) with dim light. Obviously, the bare P3HT device revealed a pronounced degradation by $\sim 62\%$ in mobility due to the absorption of water and oxygen at the P3HT and P3HT/dielectric interface. In contrast, the P3HT transistor with PMMA-assisting transferred graphene and the device covered with direct transferred graphene were relatively stable in ambient conditions. The former revealed that more water and oxygen could penetrate the transferred graphene film through the PMMA residual-induced defects [4];

in addition, the prior acetone stripping step for PMMA removal may likely damage the functionality of organic semiconducting films. With increased exposure time to ambient air, more localized trap states formed and the bulk conductivity of active channel increased, leading to a mobility reduction of $\sim 29\%$. Noteworthy is the later case possessing the best stability with a minor mobility reduction of $\sim 16\%$, which is associated with the fine protection of low-defect direct transferred graphene. These results clearly demonstrate that the graphene-passivated polythiophene FETs could exhibit relatively longer lifetime in ambient air. The graphene passivation layer via direct polymer-free transfer method could greatly keep moisture and air away from the charge transport pathway near the semiconducting/dielectric interface and thus alleviate mobility degradation. This beneficial effect on air stability is probably attributed to the bilayer structures of our CVD-grown graphene sheet, which can cover undesired point defects or cracks in the overlapped graphene network (Fig. 3b). This bilayer network can give rise to extensive horizontal diffusion and slow vertical penetration of moisture and air. Considerably, it should also be possible to use multilayered graphene for higher impermeability to moisture and air. Finally, we showcased that the integrated hybrid graphene-polythiophene blend transistors laminated with graphene passivation layers exhibited significantly superior and prolonged performances over 1400 hours, whereas the hybrid devices without graphene passivation have become unswitchable in 600 hours, as shown in Fig. 3c & 3d.

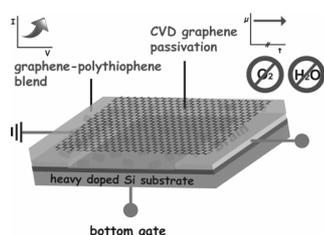


Fig. 1 Schematic illustration of proposed hybrid graphene-polythiophene blend FETs with an additive passivation layer of laminated CVD graphene sheet.

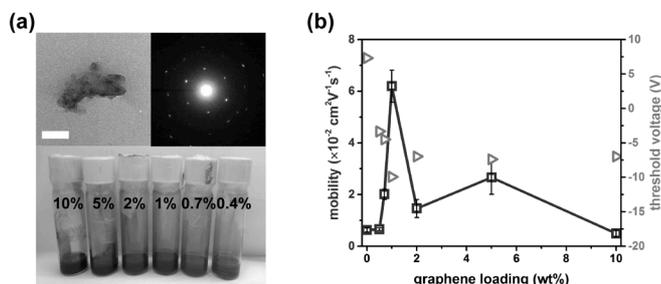


Fig. 2 (a) TEM image of a few layer graphene flake with the corresponding electron diffraction pattern (scale bar: 50 nm) and optical image of a series of Gr-P3HT blend solutions with different graphene loading. (b) Saturation field effect mobility and threshold voltage of the hybrid FETs with various graphene loadings ranging from 0-10 wt%.

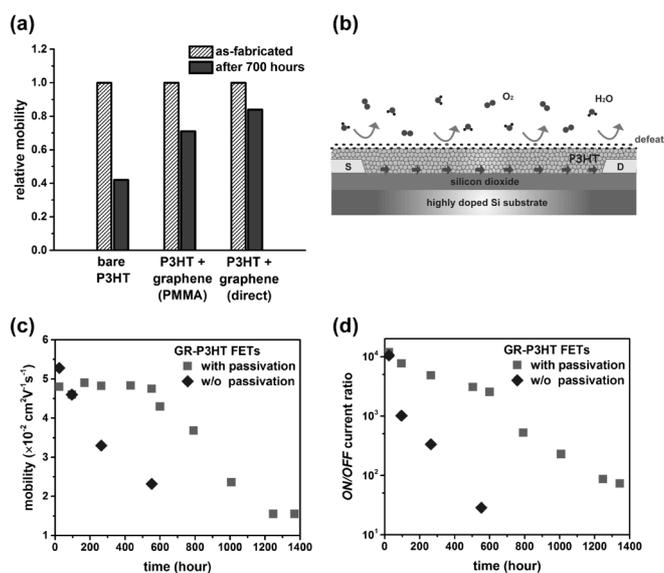


Fig. 3 (a) Summary of the relative carrier mobilities of a bare P3HT FET, a graphene-passivated P3HT FET via PMMA-assisted transfer, and a graphene-passivated P3HT FET via direct polymer-free transfer before and after 700 hours exposure to air. (b) Schematic diagram of water and oxygen barrier effect for a bilayer graphene-passivated P3HT FET. Device performance data of (c) saturation mobility and (d) ON/OFF current ratio versus time plots for a graphene-passivated hybrid Gr-P3HT FET (graphene loading: 1 wt%) and a bare Gr-P3HT FET, respectively.

3. Conclusions

Overall, we successfully fabricated hybrid graphene-polythiophene FETs with our direct graphene passivation method, which can integrate the merits of accelerating charge transport and encapsulating organic active channel from ambient moisture and air. We expect that this approach, with several advantages of low processing temperature ($< 150^\circ\text{C}$), solution processability, and flexibility of both graphene and polythiophene, is applicable to a wide range of organic conjugated molecules and polymers for air stable and high performance field effect transistors and large-area flexible electronics.

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References

- [1] Z. Liu *et al.*, *Adv. Mater.* **25** (2013) 4296.
- [2] H.-K. Seo *et al.*, *ACS Appl. Mater. Interfaces* **8** (2016) 14725.
- [3] K. Choi *et al.*, *ACS Nano* **9** (2015) 5818.
- [4] J. Chan *et al.*, *ACS Nano* **6** (2012) 3224.