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Multi-layer Fluorinated Graphene for pH Sensing Membrane of LAPS

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Abstract

A multi-layer fluorinated graphene (FG) is firstly applied as the pH sensing membrane of light-addressable potentiometric sensor (LAPS). 3 mono-layer graphene were transferred on Si_3N_4 surface and then treated with CF_4 plasma for 30 min with filter. Significant difference could be found in the photocurrent versus bias voltage curves between FG and Si_3N_4. A good pH sensitivity of 59.9 mV/pH and linearity of 99.9% is obtained in this proposed 3FG-LAPS. A clear 2D chemical image could be collected by the light source scanning by X-Y stage and LAPS measurement system.

1. Introduction

A light-addressable potentiometricsensor (LAPS) is derived from an electrolyte-insulator-semiconductor (EIS) structure for the ability of ion concentration and 2 dimensional (2D) sensing by an extra scanning illumination modulated with ac frequency. [1] Conventional material of pH sensing membrane of LAPS could be Si_3N_4 deposited by low-pressure chemical vapor deposition (LPCVD). [2] However high dielectric constant material, such as NbOx is also approved to have a high pH sensitivity. [3]

Recently, graphene has received increased attention owing to itsunique electrical, electrochemical, mechanical and optical properties. [4] In particular, application to sensors has been explored due to its electrical characteristics influenced from the surrounding chemical and biological environment. [5]Moreover, Modulation of fluorinated doping on graphenecan be used to modify the properties of-bandgap,and conductivity. [6] In this study, a CF_4 plasmatreatment on stacking3-layer graphene is firstly proposed to be the pH sensing membrane of LAPS.

2. Experiments

Thermally grown SiO_2 and Si_3N_4 deposited by LPCVDwere fabricated on P-type Si wafer. Back-side Si_3N_4 and SiO_2 layers were removed by reactive-ion etching (RIE) and buffer oxide etchant (BOE) before Al evaporation with metal shielding mask as back-side contact. Monolayer graphene were fabricated by LPCVD and then transferred to Si_3N_4 for 3 stacking layers. A CF_4 plasma treatment was processed at RF power of 100W for 30 min with a filter. [6] A cross-sectional schematic plot and picture of 3FG-LAPS is shown in Fig. 1(a) and (b). The measurement setup of LAPS with X-Y stage could be seen in our previous publication. [2]

3. Results and Discussion

As shown in Fig. 2, the frequency response of photocurrent (PC) versus bias voltage curves of 3FG-LAPS could be found. Current optimized frequency is 1 kHz could be determined by the condition of Si wafer doping and illumination by the chosen red laser. pH sensing performance could be firstly investigated by the photocurrent versus bias voltage curve measured in different buffer solution from pH 4 to 8 as shown in Fig. 3. A representative bias voltage of a pH value could be calculated of 60% of maximum photocurrent. pH sensitivity of 59.9 mV/pH and linearityof 99.9% could be calculated as shown in the inset of Fig. 3. To study the stability of this 3FG-LAPS, a long-term measurement in pH 7 buffer solution is shown in Fig. 4(a). The drift coefficient is 0.01mV/h by the linear fitting of bias voltage from 300 to 720 min. In the meantime, hysteresis measurement in the pH loop of pH 7-4-7-10-7 with a period of 5 min in each pH solution was performed. The hysteresis response is shown in Fig. 4(b). Hysteresis width is 16 mV, which could be further improved by the CF_4 plasma treatment and graphene synthesis modification. This pH sensing performance could be acceptable for certain application such as biomedical environment. To verify the 2D chemical imaging, the whole device with 3 different surface including Si_3N_4, $3G/Si_3N_4$, and $3FG/Si_3N_4$ was used to measure the photocurrent at a fixed bias voltage of 0V. The OM picture of 3 surfaces is shown in Fig. 5(a). Only a boundary could be seen between graphene and Si_3N_4. In the meantime, photocurrent versus bias voltage curves measured with the matrix setting of 10*10 pixels controlled by X-Y stage movement with 3FG-LAPS. It can be clearly seen negative bias voltage by graphene and much negative bias voltage shift by 3FG in Fig. 5(b), which could be explained by the hole doping. Also a clear difference in 2D chemical image could be observed in Fig. 5(c).

4. Conclusion

A fluorinated graphene is firstly verified to be a pH sensing membrane by using CF_4 plasma treatment on 3 mono layer transferred graphene on Si_3N_4 LAPS. A clear chemical image is obtained in area with fluorinated graphene, graphene and Si_3N_4 surface. Further studies on the graphene relative sensing membrane could be suggested for biomedical applications in the future.

References

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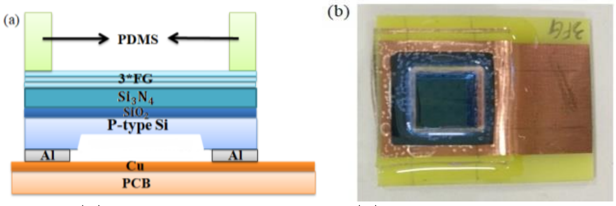


Fig. 1 (a) schematic plot and(b) picture of this fabricated 3FG-LAPS.

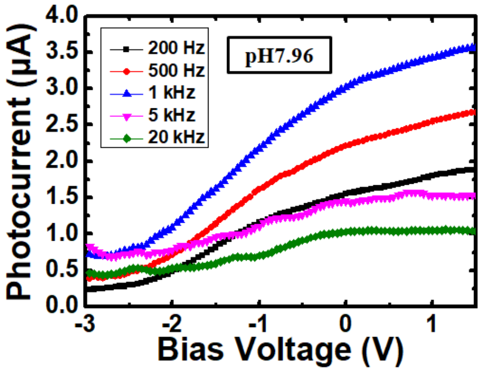


Fig. 2 Frequency response of PC-V curve of 3FG-LAPS.

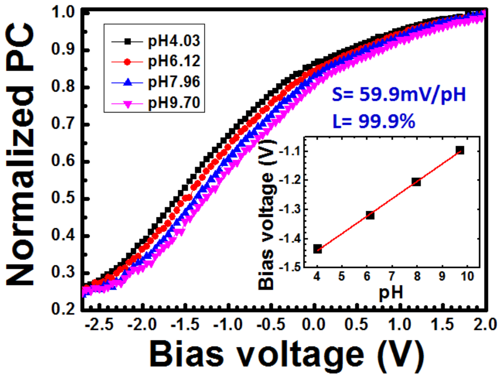
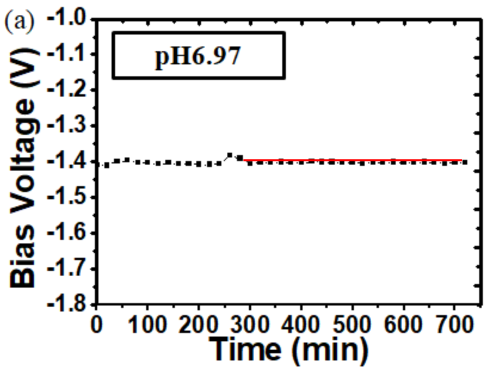


Fig. 3 pH response of PC-V curve of 3FG-LAPS and linear fitting curve of pH and bias voltage is shown in the inset.



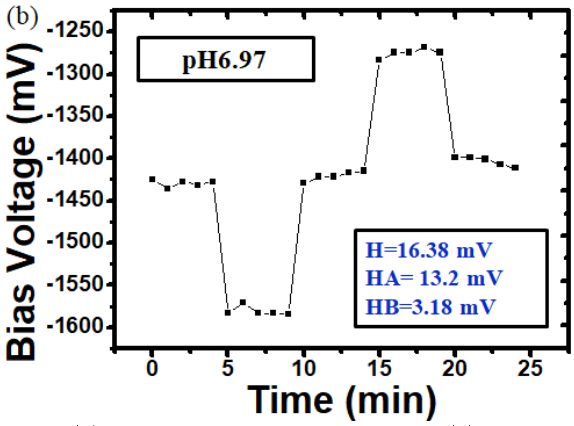


Fig. 4 (a) long-term stability and (b) hysteresis measurement of 3FG-LAPS.

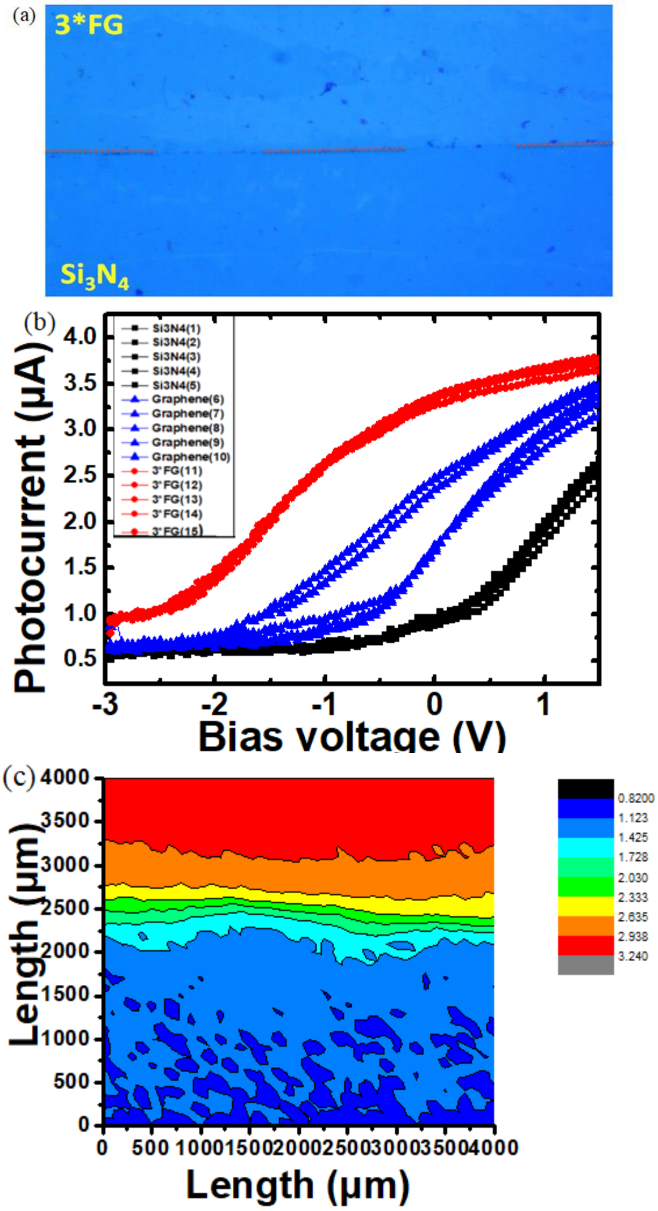


Fig. 5 (a) OM picture, (b) PC-V curves and (c) 2D chemical image of Si3N4 and 3FG-LAPS.