Extended Abstracts of the 2017 International Conference on Solid State Devices and Materials, Sendai, 2017, pp361-362

Intrinsic response of protein adsorption to graphene film on SiC substrate

Yoshiaki Taniguchi, Tsubasa Miki, Yasuhide Ohno, Masao Nagase, Yukihiro Arakawa, Yasushi Imada, Keiji Minagawa, and Mikito Yasuzawa

Graduate School of Advanced Technology and Science, Tokushima University
2-1 Minamijyousanjima, Tokushima 770-8506, Japan

Abstract

Protein adsorption characteristics to the epitaxial graphene film on a SiC substrate were investigated. The transfer characteristics of the epitaxial graphene film shifted in the negative gate-voltage direction after introduction of the proteins with both of negative and positive charges. To confirm the protein adsorption, adsorption characteristics to a phosphorylcholine-modified graphene film were also studied. As a result, smaller shifts were observed, indicating that these negative gate-voltage shifts were derived from positively or negatively charged proteins adsorption. These electric properties are different from other results which has been reported.

1. Introduction

Since the discovery of graphene, various applications have been attempted owing to its unique mechanical and electrical properties. Among them, graphene based field-effect transistor (GFET) is expected to be a highly sensitive biosensor. However, many fundamental properties related to intrinsic graphene film have not been clarified yet. Toward realization of graphene-based biosensor, it is essential to understand basic properties about protein adsorptions on graphene surface. In this study, we investigated the response of the positively and negatively charged protein adsorptions to an epitaxial graphene film on a SiC substrate. Since epitaxial graphene film on the SiC substrate is single crystal with large scale, it is expected that the intrinsic characteristics of various sensing properties on graphene are obtained. However, there are few reports of biosensing applications based on epitaxial graphene film on the SiC substrate. Moreover, in order to confirm a protein adsorption, the electrical characteristics of the protein adsorption to phosphorylcholine (ChoP)-modified epitaxial graphene film were studied. The ChoP group on graphene surface can suppress non-specific adsorption because this molecule acts to keep the protein electrostatically away [1].

2. Experiments

The monolayer graphene films were prepared by heating 10 mm square 4H-SiC (0001) substrates at 1650 °C for 5 min in Ar 100 Torr atmosphere using rapid thermal annealing. Thereafter, in order to obtain electric characteristics only in the region immersed in the solution, a 6-terminal graphene Hall bar having a 3 mm square channel was formed by a typical stencil mask lithography with PET film and air plasma etching. Such fabrication processes need no photo and e-beam resist, hence, the device were free from these residues. Raman spectroscopy and Hall measurement were carried out to evaluate the device characteristics. Figure 1(a) shows a full width at half maximum (FWHM) map of a 2D peak in a range of 9 mm square measured after the device patterned. FWHM of 2D peak is almost 40 cm^{-1}, which indicates monolayer graphene on a SiC substrate [2]. In addition, since the Hall mobility exceeded 1,000 $cm^2(Vs)^{-1}$ and the carrier type was n type, these results show that these devices were a typical high quality graphene films on the SiC substrate.

In this work, bovine liver-derived alpha-chymotrypsin (CHT, SiGMA C 3142) and bovine serum albumin (BSA, SiGMA A 7030) were prepared as target proteins. The isoelectric points of the CHT and the BSA are 8.75 and 5.3, respectively. Therefore, CHT was negatively charged in 10 mM borate-buffered solution (BBS, pH: 9.2) and BSA was positively charged in 10 mM acetate-buffered solution (ABS, pH: 4). An electrolyte-gated GFET was constructed as shown in Fig. 1 (b). Electric properties depending on the protein concentration were measured.

The ChoP-pyrene derivatives [Fig.1(c)] were modified on the graphene surface [3]. It has been confirmed that the synthetic molecule can be modified to GFET and suppressed non-specific adsorption of positively charged BSA [1].

3. Results and discussion

Figures 2(a) and 2(b) show the drain current (I_D) – gate voltage (V_G) characteristics for the various concentration of

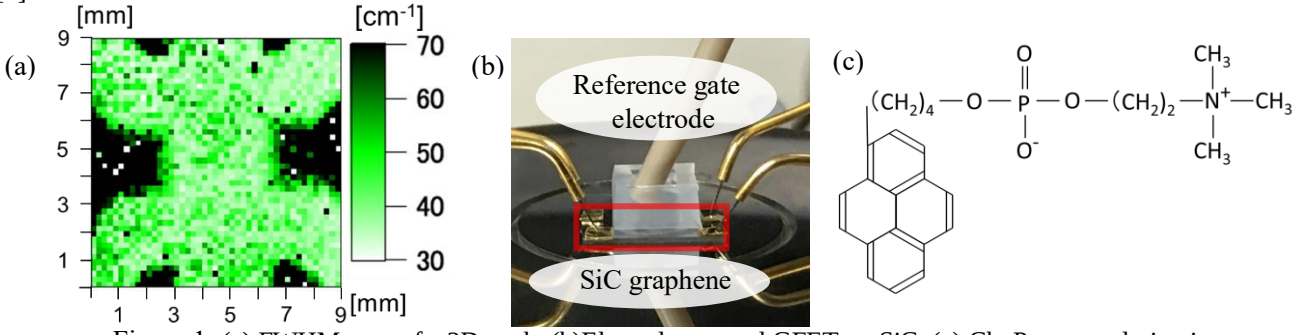

Figure 1: (a) FWHM map of a 2D peak, (b)Electrolyte-gated GFET on SiC, (c) ChoP-pyrene derivative

proteins. The minimum point of the slope indicates the charge neutrally point (CNP), and it shifted widely in the negative gate voltage (~0.2 V) to the left with increasing both of protein concentrations less than 5 nM. These results were different from previous reports about protein adsorption on graphene obtained from the chemical vapor deposition and mechanical exfoliation from a bulk graphite. Their shifts depended on the charge type of adsorbed proteins [4].

Figure 3(a) shows the negatively charged CHT concentration dependence of transfer characteristics in ChoP-modified GFETs. The shift amount was smaller than bare GFET in highly CHT concentration (~0.12 V in 10 μM CHT). Also, the net voltage changes at the CNP are plotted in Fig. 3(b), which estimates that the sensitivity to CHT adsorption reduced to about 12 %. It was confirmed that non-specific adsorption of proteins can be suppressed by modifying ChoP group despite of the charge types of proteins. These results indicate the protein adsorption generated the negative shifts shown in Figs. 2.

It can be considered that the strongly n-doped epitaxial graphene film on a SiC substrates [5, 6] causes such negative voltage shifts. It is expected that electrons in the epitaxial graphene film attracted to the positively charged parts of the proteins. Since the size of the proteins is larger than the electric-double layer, the graphene might not detect whole charges of the proteins. In order to elucidate the adsorption mechanism, it is necessary to cut off the bond between the SiC and graphene using such as a H_2 intercalation method or to measure the transfer characteristics to DNA adsorption with fully negative charged.

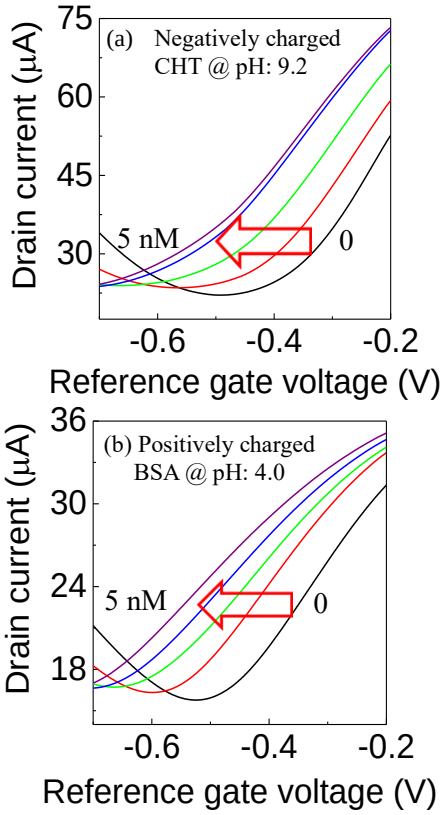

Figure 2: I_D - V_G characteristics of bare GFET. (a) negatively charged CHT at pH 9.2, and (b) positively charged BSA at pH 4.0

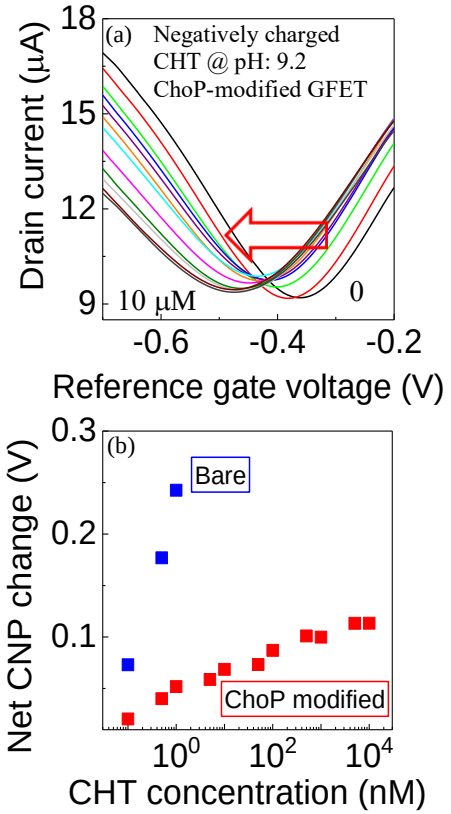

Figure 3: (a)I_D - V_G characteristics of ChoP-modified GFET, (b)CNP shift vs protein concentration

4. Conclusions

In this work, we studied the intrinsic response of protein adsorption to graphene surface on a SiC substrate. The bare GFET was n-doped by protein adsorption under each any condition, which was different from the typical results reported ever. Since ChoP-modified GFET was able to suppress this doping, it was found that graphene on the SiC was preferentially n-doped regardless of protein charge.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers 15H03551 and 15H03986, and JST CREST Grant Number JPMJCR15F4, Japan.

References

[1]Y. Taniguchi *et al*., *29th International Microprocesses and Nanotechnology Conference* (2016) 11P-11-16.

[2] Y. Ohno *et al*., Jpn. J. Appl. Phys. **55** (2016) 06GF09.

[3] Y. Taniguchi *et al*., Phys. Status Solidi B **254** (2017) 1600524.

[4] Y. Ohno *et al*., J. Am. Chem. Soc. **132** (2010) 18012.

[5] C.Berger *et al*., *Numerical Data and Functional Relationships in Science and Technology* (2017).

[6] T. Aritsuki *et al*., Jpn. J. Appl. Phys. **55** (2016) 06GF03.