ION-SENSITIVE FIELD EFFECT TRANSISTOR SENSORS USING SUSPENDED GRAPHENE NANORIBBON PATTERNED BY SHRINK LITHOGRAPHY

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ABSTRACT

Low-cost and facile shrink lithography derived graphene nanoribbon (GNR) was suspended on the channel to form an ion-sensitive field effect transistor (ISFET), and its pH sensing application is presented. By combining a thermoplastic film with a molding process, GNR patterns 50 nm wide were achieved in a low-cost and simple way. Ambipolar characteristics of annealed suspended GNR ISFET present an enhanced ambipolar effect. In comparison, unsuspended GNR and microscale graphene sheets based ISFETs were characterized under the same design, fabrication, and measurement conditions, showing that the suspended GNR ISFET is superior in sensitivity and detection limits.

INTRODUCTION

Graphene nanoribbons (GNRs) become an attractive nanostructure with superior electrical, chemical, and mechanical properties [1-3]. Several GNR synthesis approaches were developed, including lithographic patterning [4] and unzipping of carbon nanotubes [5]. More recently, GNR has been employed as a sensing structure for the detection of various ions, providing unique advantages due to its tunable ambipolar field-effect characteristics [3], relatively low $1/f$ noise, and biocompatibility [6]. However, the potential applications of GNR are hampered by its limited availability due to the complexity and high-cost fabrication methods. In the meanwhile, current study has been focused on graphene attached on silicon oxide substrates [7], and charge traps at the interface and in the oxide have been reported as external scattering centers and degrade electrical properties in graphene [8].

Therefore, in this paper, an ion-sensitive field effect transistor (ISFET) using a suspended GNR formed by low-cost and facile shrink lithographic patterning was demonstrated. Herein, shrink lithography combines a thermoplastic film with a molding process to successfully achieve GNR patterns in a low-cost and simple way. The ambipolar characteristics of the suspended GNR ISFET were measured in different pH solutions. Moreover, its low electrical noise due to the suspension structure and annealing effect gives a very promising way to achieve relatively high sensitivity. In comparison, an unsuspended GNR and microscale graphene sheets based biosensors were characterized under the same design, fabrication, and measurement conditions, demonstrating that the suspended GNR ISFET is superior in its sensing performance.

DESIGN AND FABRICATION

The fabrication process of the suspended GNR ISFET is illustrated in Fig. 1. We started with a graphene plate generated by mechanical exfoliation method. A photoresist layer (Shipley S1818) was used as a transfer stamp to exfoliate graphene patterns from highly oriented pyrolytic graphite (HOPG), and transferred patterns onto a SiO_2/Si substrate. First, patterns in microscale were formed on the surface of HOPG by photolithography followed by an oxygen plasma etching with STS etcher (Model 320, 30 seconds). A layer of S1818 was spun on the pre-treated HOPG, and a thermal releasing tape was used to gently peel graphene flakes off, and transferred them onto the SiO_2/Si substrate. The substrate was pre-patterned with marks for alignment and location.

After stripping photoresist off, a microscale graphene plate was generated on the SiO_2/Si substrate.

Figure 1: Schematic of fabrication process of a suspended GNR ISFET by shrink lithography.

Next, a typical mold is fabricated by conventional photolithography, KOH etching, and subsequent electroplating. A cleaned silicon wafer with SiO_2 300 nm thick was patterned by photolithography with photoresist of Shipley S1813 about 1 μm thick spin-coated at 3,000 rpm for 30 s and exposed for 6 s, followed by buffered HF (BOE 10:1) etching for 7 minutes. The patterned wafer was etched by 20% KOH at 80°C for 10 minutes, and the SiO_2 was the passivation layer. To impenetrate the shrink film, an additional KMPR (MicroChem Inc.) layer around the patterns was deposited. Chromium/gold layers 50/50 nm thick were deposited on the substrate by an AJA sputter system (Model ATC 2000). Nickel electroforming was conducted on a nickel plating station (SE-101, Digital Matrix Co., U.S.) using the patterned wafer as mandrel. A nickel sulfamate bath and a pulse reverse power were used to obtain uniform and stress free nickel mold. After electroforming, the silicon wafer was completely removed by 20% KOH at 80°C. The fabricated nickel mold was cleaned by acetone and de-ionized water.

The mold is embossed against a polyolefin (PO) thermoplastic film to obtain impenetrated patterns. After preparation of the

mold, it was embossed against the shrink film and held for 2 minutes by a Manual Presser (Model Grimco 12-1-HT). The shrink film (Sealed Air Nexcel multilayer shrink film 955D) formed by 5 layers of co-extruded polyolefin (PO) was purchased from Sealed Air. The mold was released, and the PO shrink film with impenetrated patterns was made. Sequentially, the patterned PO shrink film was placed between two silicon wafers for uniform heating to desired temperatures in a slowly rising process for approximately 5 minutes and held for 10 minutes for shrinkage in a convection oven (Model 280A). Due to the adhesion of shrink polymer film at high shrink temperature, the PO shrink film bonded with silicon very well, as the shadow mask for Al_2O_3 deposition. After that, oxygen plasma was applied to pattern the graphene nanoribbon 50 nm wide. By using shrink lithography, extreme narrow patterns were obtained on the PO shrink film. A layer of Al_2O_3 8 nm thick was deposited, and the shrunk PO film was acting as a shadow mask. After the PO film was stripped, an Al_2O_3 nanoribbon was left on the graphene as the mask. The substrate was followed by oxygen plasma etching with STS etcher (Model 320, 10 seconds). The masks on the substrate assisted the alignment and location. The substrate was immersed into a KOH solution to remove the Al_2O_3 mask. Chromium/gold electrodes 50/200 nm thick were deposited and patterned on the two ends of graphene nanoribbon by an electron-beam evaporation (Model SEC 600) and metal lift-off. The SiO_2 layer 300 nm thick underneath graphene ribbons was etched away by buffered HF (BOE 10:1) for 7 minutes. The suspended structure was obtained by SF_6 etching followed by Super Critical Dryer (Model 915 B).

Figure 2: (a) Schematic of a suspended GNR ISFET. (b) SEM image of the suspended GNR structure. The width of the GNR is about 50 nm.

Fig. 2a shows the structure of the suspended GNR ISFET. Target solutions were introduced into the recording chamber, and

an Ag/AgCl reference electrode was immersed to apply a desired gate voltage. Electrical measurements were carried out using a semiconductor analyzer (HP 4145B). The suspended GNR was inspected by scanning electron microscope (SEM). As shown in Fig. 2(b), the GNR about 50 nm wide is successfully suspended by the dry etching of silicon.

RESULTS AND DISCUSSIONS

Figure 3: Ambipolar characteristics of GNR ISFET are measured in a PBS buffer solution at room temperature. Annealing bias voltage at a set point of 3.3 V is applied by V_{ds} without a gate voltage. The annealing process contributes the enhanced ambipolar behavior.

Drain-to-source current versus solution gate voltage was recorded to investigate the electrical properties of the suspended GNR ISFET. Fig. 3 presents ambipolar characteristics of GNR ISFET measured in a PBS buffer solution at room temperature, showing the transition from p-type region to n-type region at the Dirac point of about 0.2 V. After applying the annealing bias voltage to a predefined set point of 3.3 V, the enhanced ambipolar behavior demonstrates larger intrinsic bandgap of GNR due to the annealing process, compared with the device before annealing. The enhanced ambipolar behavior after annealing is contributed by the thermal energy [9] and the suspended structure change [10] introduced by annealing. The annealing effect is responsible for the larger energy band gap, comparable to those of possibly much narrower ribbons [10].

The pH electrical characteristics were also investigated. First, the annealed suspended GNR ISFET was used to detect different pH solutions, and compared with unsuspended GNR prior to annealing and a normal graphene sheet in microscale under the same design, fabrication and measurement conditions. As shown in Fig. 4(a), solutions from pH5 to pH9 were delivered to the suspended GNR ISFET sequentially. The electrolyte gate response of the device drain-to-source current was measured for each solution. While the ISFET was biased at V_{ds} of 1 V, and the gate voltage was applied from -1.8 to 1.8 V. It is obviously observed that the Dirac point of GNR shifts positively from pH5 to pH9, suggesting that H^+ ions act as n-type dopants to the GNR. Adsorption of a positively charged H^+ induces additional negative charge in the GNR, thus the n-type doping of the GNR shifts the Dirac point to more negative gate voltages. The suspended GNR behaves as a p-type material when negative gate potential is applied, and the I_d of the ISFET increases with the increase of pH values. On the contrary, when the gate potential is switched to be

positive, transition from p-type region to n-type region occurs, and the I_d of the ISFET decreases with the increased pH values.

Figure 4: (a) Ambipolar characteristics of suspended GNR ISFET with different pH solutions. The Dirac point of suspended GNR shifts significantly from pH 5 to pH 9. (b) Normalized sensitivity of different types of ISFET is measured. In order to get a clear readout, a normalized sensitivity is deduced. I_d for pH 9 solution is used as an initial current I_0 , and other I_d tested under different pH subtracted I_0 to get ΔI . Normalized sensitivity is represented as $\Delta I/I_0$. Suspended GNR presents better sensitivity than the unsuspended GNR and normal graphene.

The sensitivity of different types of ISFET was also investigated. The ISFET was biased at V_{ds} of 1 V, and the gate voltage was fixed at 1.8 V. Different solutions from pH5 to pH9 were introduced to the suspended GNR ISFET, unsuspended GNR ISFET and normal graphene ISFET, respectively. The width of the suspended GNR and unsuspended GNR is about 50 nm, and the normal graphene sheet is in micrometer scale. For a clear readout, a normalized sensitivity was deduced. I_d for a pH9 solution was used as an initial source-drain current, and other I_d values tested under different pH values subtract, and then divided by the initial I_d to get the normalized sensitivity. As shown in Fig. 4(b), the normalized sensitivity was compared among the three types of ISFET, demonstrating that suspended GNR ISFET was superior in pH sensing performance. Two factors play important roles for the better sensitivity of suspended GNR. One factor is due to the suspended gap under the GNR. The H^+ ion concentration becomes

non-uniform due to the field presented in the suspended gap [11]. The other one is that the charge traps at the interface and in the oxide, which act as external scattering centers and degrade transport properties [12, 13] greatly by suspension.

Figure 5: Ambipolar characteristics of suspended GNR ISFET with different PSA solutions induced. The Dirac point of suspended GNR does not shift as significantly as pH detection.

Furthermore, we also investigated the cancer bio-marker detection by modifying the surface of GNR with receptor antibodies. Cancer bio-markers are molecules in blood or tissue, associated with cancer and whose measurement or identification is elucidated very critical and efficient in disease prediction, diagnosis, and monitoring [14]. In the meanwhile, the clinical utility of PSA to discriminate health and disease requires the capability to detect extremely low concentration [15], which is also especially important to understand cellular processes and to search for new protein biomarkers [16]. Herein, after the surface modification of suspended GNR, the anti-PSA was immobilized on the surface of a suspended GNR, and the ISFET was blocked with bovine serum albumin. Given that the conductance of graphene is determined by the charge carrier density and mobility, it is evident that changes in density and/or mobility of charge carriers must be responsive when molecules or ions are absorbed [17]. Therefore, the conductance of the suspended GNR modified with the PSA capture antibody shifts as the concentration change of PSA solutions.

As shown in Fig. 5, different concentrations of PSA solutions from 0 to 4 ng/ml were introduced to the surface modified suspended GNR ISFET sequentially. The ambipolar characteristics of suspended GNR ISFET were measured at different PSA solutions. The ISFET was biased at V_{ds} of 1 V, and the gate voltage was applied from -1.8 to 1.8 V. There is a small right shift of the Dirac point of suspended GNR from 0 to 4 ng/ml in the PSA solutions with a much less shift compared with a pH detection. The shift of Dirac point is due to the electrostatic gating effect from the adsorbed charge species adopted to explain the shift of I_d - V_g curve of carbon nanotube transistors. The positive shift of Dirac point is due to the negative charges of the adsorbed PSA which can only be balanced by a positive gate voltage. However, the interaction between GNR and PSA immunoreaction bonding is relative weak compared to the H^+ . Therefore, the positive shift of Dirac point is not obvious, and the conductance change becomes dominant.

CONCLUSIONS

In summary, we have investigated the fabrication of suspended GNR ISFET using shrink lithography, which is very cost effective due to the inexpensive thermoplastics and the molding process. The pH value was characterized based on the suspended GNR ISFET to show positively shift of the Dirac point with the increase of pH values. Annealing effect on the ambipolar characteristics of a suspended GNR was also investigated. In comparison, the ISFETs based on unsuspended GNR and microscale graphene sheets were characterized under the same design, fabrication, and measurement conditions, showing that suspended GNR ISFET was superior in sensitivity. Moreover, this low-cost detection platform can be extended to the recognition of other antigens, which may open a new way to diagnose cancer and other complex diseases.

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