

Highly Sensitive pH-EGFET Sensors with Oxygen-Plasma-Treated Reduced Graphene Oxide Films Sprayed on the Reverse Pyramid Substrate

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Abstract

The oxygen-plasma-treated reduced graphene oxide films (RGOFs) are firstly used as the sensing membranes in extended-gate field-effect transistors (EGFETs) for the pH sensors. A large amount of oxygen-containing functional groups are effectively decorated on the RGOFs, resulting in increasing the sensing sites. Furthermore, the reverse pyramid (RP) structure is used as the substrate to increase surface roughness with fixed sensing window. The pH-EGFET current sensitivity of the plasma-treated RGOF on the RP structure can achieve as high as $1.09 \mu\text{A}^{1/2}/\text{pH}$ with excellent linearity of 0.999, and a wide sensing range from pH 1 to 13.

1. Introduction

pH sensing is the foundation of numerous biosensors and intensely demanded in environment monitoring, medicines, and analytical chemistry. Because of the merits of low power consumption and rapid pH response, the ion-selective field-effect transistor (ISFET) is widely studied. However, there are several fatal disadvantages of ISFETs such as low current sensitivity and device instability. Unlike the integration of an ion-selective electrode and a FET in an ISFET, the isolated FET of the Extended-gate field-effect transistor (EGFET) [1] keeps the FET away from the chemical environment and the sensing head is extended from the gate electrode through a metal wire, resulting in long-term stability. Up to the present, most of the sensing membranes utilized in EGFETs are metal oxides, such as zinc oxide (ZnO) [2], tin oxide (SnO_2) [3], indium tin oxide (ITO) [4]. Nevertheless, the brittleness of these metal oxides might restrict their practical applications in the future.

Recently, graphene has been seen as the promising sensing material due to its great electrical properties, outstanding mechanical strength, and good chemical inertness. However, it has been reported that graphene transistors are insensitive to pH changes due to its ideal hydrophobic surface with little dangling bonds [5]. According to site binding model [6], the decent sensing films require sufficient sensing sites to respond to the ions of interest in a buffer solution. In this study, the reduced graphene oxide (rGO) solution is employed as sensing membrane because of its imperfect structure and high surface-to-volume ratio. The oxygen plasma and reverse pyramid (RP) substrate were utilized to graft the oxygen-containing functional groups on

the rGO and increase the sensing area with a fixed sensing window.

2. General Instructions

Device structure and fabrications

The reduced graphene oxide solution was spray-coated on two kinds of substrates: Si substrate and RP-structured Si substrate. A RP structure etched with 30 wt. % KOH solution was employed on (100) Si substrate to increase the surface roughness. Then, the reduced graphene oxide films (RGOFs) were annealed under the nitrogen ambience at 400°C for 1 hr to remove the residues. Subsequently, the samples were functionalized with the oxygen plasma via the high-density-plasma reactive ion etching (HDPRIE) system at 10^{-2} torr with the oxygen flow rate of 20 sccm under the inductively coupled plasma power of 100 W and bias power of 20 W for 60 s. Finally, the sensing head was bound to metal wires with the silver paste and then baked at 120°C for 30 min. Epoxy resin was used to avoid the leakage current and define the sensing window at $4 \times 4 \text{ mm}^2$. The Keithley 236 parameter analyzer was utilized to measure the output characteristics of the pH-EGFET sensors in the pH=1, 3, 5, 7, 9, 11, and 13 phosphate buffer solutions (PBSs). The commercial reference electrode was adopted as the reference electrode, offering constant potential when measuring. The sensing membrane connected to the gate of a commercial standard MOSFET and the reference electrode (Ag/AgCl) were both immersed into the PBSs.

Results and discussions

Fig. 1(a) shows the cross-sectional FE-SEM of the RP-structured Si substrate. The aim of this microstructure is to provide more sensing regions with the fixed sensing window of $4 \times 4 \text{ mm}^2$. The depth of the RP and the spacing between two RPs are 37 and 69 μm , correspondingly. The Raman spectra of the as-deposited RGOF and plasma-treated RGOF are presented in Fig. 1(b). There are four featured peaks of the graphene-based materials: D ($\sim 1350 \text{ cm}^{-1}$), G ($\sim 1595 \text{ cm}^{-1}$), 2D ($\sim 2680 \text{ cm}^{-1}$) and D+D' ($\sim 2930 \text{ cm}^{-1}$). Both of the samples exhibit a strong D-band and G-band assigned to the structural disorder and the graphitized structure, respectively. After oxygen plasma treatment, the I_D/I_G ratio increase from 1.36 to 1.58, resulting from the attachment of the functional groups such as hydroxyl, epoxide on the carbon skeleton.

Fig. 2(a) and 2(c) shows the output characteristics (drain current versus drain voltage, $I_{\text{DS}}-V_{\text{DS}}$) of the RGOFs in the saturation region for the pH-EGFET sensors before and after oxygen plasma treatment for V_{DS} varied from 0 to

6 V with V_{REF} fixed at 3 V. It is observed that the saturation current decreases with increasing the concentration of OH^- ion. According to the principles of the basic MOSFET, the pH current sensitivity and linearity can be extracted from the change in $I_{DS}^{1/2}$. Fig. 2(b) shows the low sensitivity of $0.87 \mu\text{A}^{1/2}/\text{pH}$ with poor linearity of 0.956 for the as-deposited RGOF on Si substrate. Encouragingly, the plasma-treated RGOF on the RP structure exhibits the outstanding sensitivity of $1.09 \mu\text{A}^{1/2}/\text{pH}$ with excellent linearity of 0.999.

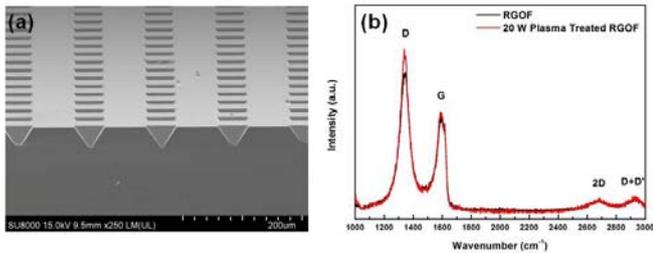


Fig. 1 (a) FE-SEM image of the RP-structured Si substrate. (b) Raman spectra of the as-deposited RGOF and the oxygen-plasma-treated one, respectively.

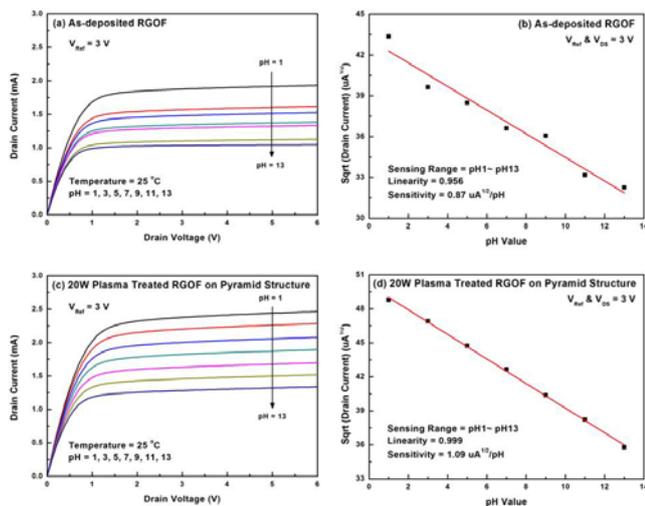


Fig.2 (a) and (c) show the output sensing characteristics of the as-deposited RGOF and plasma-treated one. (b) and (d) exhibit the extracted pH current sensitivities and linearities without and with oxygen plasma treatment, respectively.

3. Conclusions

In summary, the oxygen plasma treatment is an effective way to decorate the surface of RGOF with oxygen-containing groups. Besides, we utilized the RP microstructure to enhance the surface roughness, resulting in creating more sensing sites at a fixed sensing window. By the means of the oxygen plasma treatment and the use of RP microstructure, the sensitivity is greatly increased from 0.87 to $1.09 \mu\text{A}^{1/2}/\text{pH}$ and the linearity is substantially improved from 0.956 to 0.999 in a wide sensing range of $\text{pH} = 1$ to $\text{pH} = 13$.

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