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Reduced graphene oxide field-effect transistor with indium tin oxide extended gate for proton sensing

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ABSTRACT

In this study, the reduced graphene oxide field-effect transistor (rGO FET) with indium tin oxide (ITO) extended gate electrode was demonstrated as a transducer for proton sensing application. In this structure, the proton sensing area of the ITO extended gate electrode is isolated from the active area of the rGO FET. The proton sensing properties based on the rGO FET transducer were analyzed. The rGO FET device with encapsulation by a tetratetracontane (TTC) layer showed good stability in electrolytic solutions. The device showed an ambipolar behavior with shifts in Dirac point as the pH of the electrolyte is varied. The pH sensitivity based on the Dirac point shift as a sensing parameter was about 43–50 mV/pH for a wide range of pH values from 2 to 12. The ITO extended gate rGO FET may be considered a potential transducer for sensing of H^+ in electrolytes. Its sensing area can be modified further for various ions sensing applications.

1. Introduction

In most bio-chemical processes, it is crucial to understand the basic conditions of the physiological environment [1–8]. In analytical biosensing and chemical sensing, pH measurement is the most important task [2–6,8–10]. In fact, it can be used to detect any kind of substance that interacts with protons in bio-chemical processes, such as cell metabolism [2–8,10] and in DNA sequencing [4]. Therefore it is important to develop a proton sensor with a large dynamic range, high sensitivity, high selectivity, and high signal – to – noise ratio [2].

The ion sensitive field-effect transistors (ISFETs) have been extensively investigated for pH sensing since 1970 [1,3,10]. The ISFET structure originated from the metal – oxide – semiconductor FET (MOSFET), except the gate electrode, which was replaced by the gate biasing between the chemical sensitive membrane and the solution under the reference electrode, which induced a gate potential shift [5]. The first Si-based ISFET employed the SiO_2 gate oxide as sensing layer [6] and Si ISFET is already commercialized. To improve its performance, various oxide materials were investigated for H^+ sensing, such as Al_2O_3, Si_3N_4, Ta_2O_5, ZrO_2, HfO_2, Y_2O_3, and Gd_2O_3 [7,11,12].

The gate oxide of ISFET is typically exposed directly to a solution [1,5,10]. It is easy for ions to penetrate into the channel or move through the gate oxide, causing leakage that contributes to device instability [8]. Therefore, the structure still has the drawback of the isolation between the solution and the active area of the device [8,13]. The extended gate FET (EGFET), which can overcome this isolation problem by separating the sensing area from the device area, was introduced for the first time by Spiegel et al., in 1983 [14]. In fact, the sensing layer is at the end of the extended conductive gate electrode line, and the FET bottom gate electrode is at the head of the line [13]. This structure offers some advantages: first, it provides convenient packing of the active devices because of a conductive plane, which is the extended gate electrode [15,16]; second, the FET can be tested and characterized in the usual manner without using the solution, as in the traditional ISFET [15]; and third, the sensing area can be readily modified for selective

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detection of various ions [15]. The deprotonization or protonization at the extended gate electrode material, which depends on the pH at the electrode, can change the surface potential and a change in surface potential can induce a gating effect on the FET structure [13]. The change in threshold voltage (V_{th}) can be described by the current voltage method [7]. The pH sensing mechanism can be explained by the theoretical combination of the Gouy–Chapman–Stern theory, the site – binding model and MOSFET theory; it showed the maximum sensitivity of 59 mV/pH following the Nersntian behavior [5,7,11]. Various conductive proton sensing materials such as V_2O_5 xerogel [13], tin oxide (SnO_2) [16], iridium oxide (IrO_x) [17] and indium tin oxide (ITO) [8,18,19] have been used as the extended gate electrode for high sensitivity. Among these materials, ITO is considered the best candidate for the extended gate electrode because it has high electrical conductivity and high optical transmittance in the visible range [8,20]. High optical transmittance ITO electrode allows integration of ITO sensing layer with optical and fluorescence imaging of cells which enables simultaneous electrical and optical detection in cell-based biosensing [21,22].

Besides the selection of the sensing material for the extended gate electrode, the channel for extended gate FET transducer should be considered. Even though the Si-based ISFET has been commercialized, its use is limited by cost and fabrication complexity. Besides the Si ISFETs, organic semiconductors have been considered because of light weight, low cost, mechanical flexibility, and high compatibility to large area applications [23]. But the unstability issue of organic semiconductors limits their applications in ambient environment [24]. Nowadays, nanomaterials and nanostructures have been applied in many fields because of their unique properties. They have been integrated as channels in ISFETs [25]. Nanostructure FETs based on carbon nanotube [26], Si nanowire [27], and graphene [28] show outstanding electrical properties and thus, are considered ideal candidates for bioelectronics applications [25]. Among these materials, graphene has received much attention because of its high electrical performance [28]. Graphene FET shows unique ambipolarity in transfer characteristics, which means that two branches, n-type and p-type, are separated by a Dirac point, which is the gate voltage at minimum current [29]. In fact, the concept of a Dirac point in graphene FET is the same as the concept of a threshold voltage in MOSFET theory [30]. Moreover, the Dirac point is strongly related to the type and density of the trap charge at the interface between the graphene channel and the gate dielectric and charge doping in graphene [29]. These relations mean that the Dirac point is very sensitive to the environment and therefore, is a useful sensing parameter [30,31].

Recently, the graphene based FET (GFET) has been extensively researched and developed as the next generation post-silicon device for electronics and bioelectronics devices [29]. Graphene can be produced by micromechanical cleavage, epitaxial growth, and chemical vapor deposition approaches [32–36]. In these approaches, graphene is transferred, so the fabrication of GFET becomes complicated [33,37,38]. A chemical route with low cost and high yield production has been introduced and developed: the reduction of graphene oxide (GO), which can be easily applied to a large range of substrates. Generally, hydrazine hydrate is used as the agent to reduce GO to graphene, which is also called reduced graphene oxide (rGO) [39,40].

In our work, we report the successful fabrication of the rGO channel FET with the ITO extended gate electrode for proton sensing. Tetratetracontane (TTC), a hydrophobic polymer, was used for the encapsulation layer of the rGO channel. With the TTC layer, the device showed good electrical performance in ambient environment. In pH sensing, the device showed sensitivity as high as 43–50 mV/pH in the range of pH values from 2 to 12. The device showed potential in proton sensing.

2. Experiments

Fig. 1(a) shows the device fabrication procedure, Fig. 1 (b) is the cross-sectional view of the device structure, and Fig. 1 (c) is the schematic diagram for pH sensing. rGO FET devices with ITO extended gate electrodes were fabricated on glass substrates. The ITO coated glass substrate which was purchased from Fine Chemicals Co., Ltd (Korea) had a resistivity of 20 ohm/□, thickness of

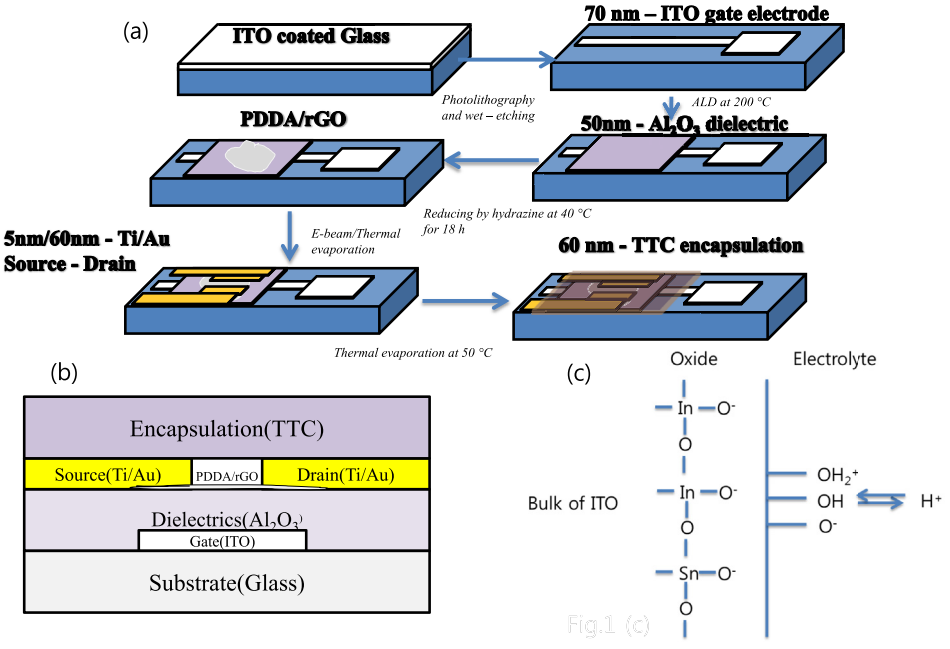

Fig. 1. The device fabrication procedure (a) and cross-sectional view of the device (b), and the schematic diagram for pH sensing (c).