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Ammonia gas sensing using a graphene field–effect transistor gated by ionic liquid

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ABSTRACT

We propose a low-voltage-driven graphene field–effect transistor (GFET) gas sensor that is electrochemically gated by an ionic liquid (IL). The IL-gate GFET (ILGFET) consists of a graphene channel, located between the source and drain electrodes, and an IL, which covers the channel. Gate voltage is applied to the graphene through an electric double layer of the IL. The nanometer-thick double layer enables low-voltage operation compared with solid-gate materials, such as silicon dioxide (SiO_2). The ILGFET was fabricated from chemical vapor deposition (CVD)-grown graphene. To test the gas sensing property, the ammonia (NH_3) gas response of the fabricated ILGFET was measured. In response to 9–2400 ppm NH_3, the current–voltage curve shifted toward negative voltage for the range of −0.8 to 0.8 V of gate voltage. The curve shifted 0.057 V per 10-fold increase in NH_3 concentration. The calculated detection limit was 130 ppb. The fabricated sensor yielded a response time of 33 s. The sensitivity and response time of the proposed sensor were similar to those of a conventional GFET with an SiO_2 gate. Additionally, the IL-gate structure was capable of decreasing the operating gate voltage.

1. Introduction

Graphene, which is a sp^2-bonded honeycomb structure of single-layer carbon atoms, exhibits high carrier mobility and a large surface area per unit volume [1]. These inherent characteristics make graphene a promising material for chemical sensors. Graphene's large surface/volume ratio make it highly sensitive to certain environmental conditions, and its high mobility reduces the thermal noise, improving the detection limit. Due to these features, gas sensors that use graphene were studied and developed to measure O_2, CO, CO_2, H_2O, NH_3, and NO_2 [2–6]. Graphene gas sensors also exhibit low power consumption compared with conventional gas sensors, such as metal oxide semiconductors (MOSs). To enhance the reactivity to target gases, a MOS requires heating at approximately 300 °C [7]. A graphene gas sensor can detect low concentrations of gases at room temperature [8]. Therefore, a graphene gas sensor requires no power consumption for heating. This characteristic is important when applying graphene to low-power sensor devices and multiple-sensor systems.

The majority of the graphene gas sensors that have been previously examined were resistive sensors. However, sensors based on graphene field–effect transistors (GFETs), as illustrated in Fig. 1(a), demonstrate certain advantages. For example, a GFET exhibits excellent gas sensitivity in the range of parts per million to the single-molecule level [2], and the FET structure is more applicable to electronic devices [5]. However, a conventional GFET requires several tens of volts of gate voltage due to the 300-nm-thick solid-gate insulator of silicon dioxide (SiO_2). High drive voltage is a critical problem regarding the application of GFETs to low-power and low-voltage sensor devices, such as battery-powered, energy-harvesting, and CMOS-integrated sensors.

To reduce drive voltage, we utilized an ionic liquid (IL), which consists of organic salts that are molten at room temperature, as the liquid gate material of the GFET. The IL has demonstrated chemical stability, negligible vapor pressure, and an extensive potential window [9]. These characteristics make it an ideal liquid gate material for the GFET [10,11]. In a typical GFET, i.e., a back-gate GFET, the gate voltage is applied between graphene and silicon under the 300-nm-thick SiO_2 layer to create a field effect. In the case of the IL-gate GFET (ILGFET), graphene is coated with the IL. Gate voltage is applied between graphene and a gate electrode, which is connected to the IL, to form a 1-nm-thick electric double layer at

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Abbreviations: ILGFET, ionic liquid-gate graphene field–effect transistor.

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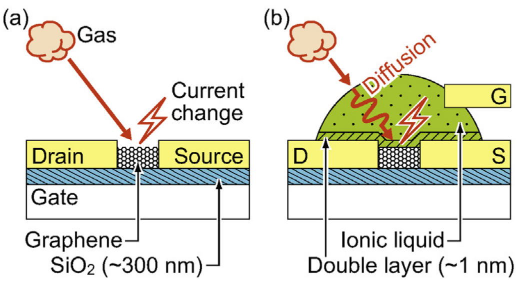

Fig. 1. Comparison of (a) the conventional back-gate GFET gas sensor and (b) the proposed IL-gate GFET gas sensor.

the graphene/IL interface. The double layer serves as a gate insulator. Due to the thickness of the double layer, the ILGFET can be driven by approximately 100 times lower voltage than the back-gate GFET [1,10–12]. Although the use of ILGFETs as transistors has been examined, their gas-sensing characteristics have not been reported [10,11]. When the ILGFET is used for gas sensing, the gas molecules can diffuse through the IL to reach the graphene/IL interface and can modify the electrical properties, as shown in Fig. 1(b), because ILs can absorb various gases [13,14]. The ILGFET is capable of detecting gas concentration in a manner similar to the back-gate GFET.

In this paper, we discuss ammonia (NH_3) gas sensing using an ILGFET. The ILGFET was fabricated from graphene grown by chemical vapor deposition (CVD). The variation in the electrical property of the ILGFET was attributed to an increase in NH_3 concentration. These results demonstrate that the ILGFET gas sensor had a lower drive voltage than the back-gate GFET, while the sensitivities and response times of the two GFETs were similar. We previously reported on the static NH_3 response of the ILGFET at the 26th IEEE International Conference on Micro Electro Mechanincal Systems [15]. This paper reports on the dynamic response, including the time response, recovery, and repeatability.

In the proposed sensor, IL and graphene act as the gas absorption medium and sensing material, respectively. Ionic liquid can absorb NH_3 as well as other gases [14]. The concentration gradient of the absorbed NH_3 from the IL surface to the graphene/IL interface activates diffusion to transport the NH_3 toward the graphene until the concentration in the IL reaches a uniform equilibrium state. Some of the NH_3 molecules near the graphene/IL interface adsorb on the graphene. In air or vacuum, the NH_3 molecules adsorbed on the graphene transfer negative charges to the graphene due to the interaction of the molecular orbitals, as reported in Refs. [2,5,26]. A similar charge transfer occurs in the IL, which was experimentally verified as described in Section 3.

2. Materials and methods

2.1. Graphene field–effect transistor fabrication

The ILGFET was fabricated by patterning source, drain, and gate electrodes around a channel of CVD-grown graphene and then covering the channel and the electrodes with an IL. The fabrication process was divided into three steps: graphene preparation, electrode formation, and IL placement.

In the first step of the process, a graphene sheet was transferred onto a SiO_2/Si wafer. Graphene was synthesized on a Cu foil (CU-113263, Nilaco Corp., Tokyo, Japan) by CVD. The growth condition was based on the condition described in Ref. [16], whereas ethanol vapor was used as a carbon source and substitute for methane gas [17,18]. After the Cu was annealed in Ar/H_2 (3% H_2) at 900 °C for 10 min in the CVD process, ethanol vapor was flowed at the same temperature for 5 min to absorb carbon on the Cu surface. The cooling of the wafer converted carbon into graphene. Subsequently, the Cu foil with graphene was placed on liquid polydimethylsiloxane (PDMS, KE-106, Shin-Etsu Chemical Corp., Tokyo, Japan), and the PDMS was cured. The Cu foil was etched in iron(III) chloride solution (H-1000A, Sunhayato Corp., Tokyo, Japan); only graphene remained on the PDMS. The PDMS was placed with the graphene side down on the target SiO_2/Si wafer. A small amount of pure water was inserted between the graphene and wafer for adhesion enhancement; the wafer was subsequently heated to dry the water. The PDMS was removed by dipping it in acetone at 70 °C; only graphene remained on the wafer.

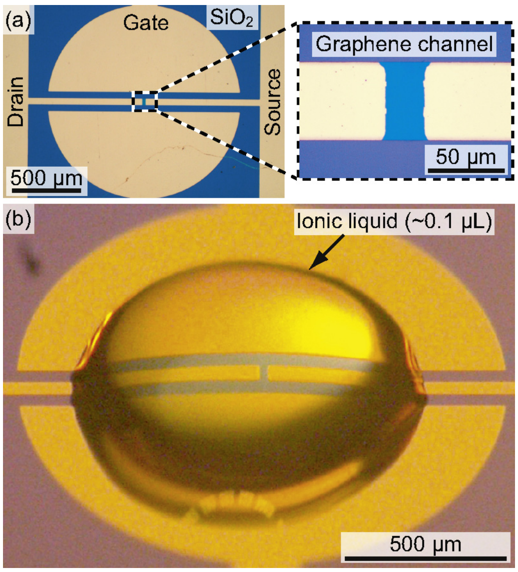

Fig. 2. Optical photographs of the fabricated ILGFET (a) before dropping the IL and (b) after dropping the IL.

In the second step of the process, the source, drain and gate electrodes and a graphene channel were fabricated. A photoresist (ZPN 1150-90, Zeon Corp., Tokyo, Japan) was patterned on the wafer, and Cr/Au was deposited on the surface. The electrodes were formed via lift-off of the photoresist, and the graphene channel between the source and drain electrodes was not exposed but rather covered with Au to mask the channel during subsequent plasma ashing. After the undesired graphene was removed by oxygen plasma, the Cr/Au on the graphene channel was etched by wet etching to expose the channel.

In the third step of the process, a droplet of 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4], Merck KGaA, Darmstadt, Germany), which was reported to be able to absorb NH_3 gas [14], was manually placed on the wafer using a sharp needle. After a droplet from the IL bottle was picked up at the tip of the needle, we placed the droplet on the wafer by bringing the tip closer to the wafer. The graphene channel was fully covered with the droplet, which was in contact with all of the electrodes. The height of the IL above the channel is directly related to the response time of the gas because gas molecules react with the graphene only after they diffuse through the IL to reach graphene. For this reason, the height was controlled in the range of 20–100 μm and was established for each device by laser scanning microscopy (VK-9710, Keyence, Osaka, Japan). When a lower height was required, we sponged the droplet with a paper towel or expanded the droplet by using the needle.

Fig. 2 presents optical micrographs of the fabricated ILGFET before and after liquid dropping. The ILGFET contained a graphene channel, with a length of 20 μm and width of 50 μm, between the source and drain electrodes. The slight color variation in the