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Graphene device array using transfer-free patterned growth on insulator for an electrolyte-gated sensor

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Abstract

We report transfer-free graphene growth on insulated substrates and the fabrication of a sensor array from the synthesized graphene. The insulated substrate coated with amorphous carbon and catalyst metals was annealed under an Ar atmosphere. After annealing, graphene was synthesized between the metal layer and the insulated substrate. We fabricated a sensing array based on the graphene growth method and used it for pH measurements. Our sensor had as a high resolution of pH as that of graphene synthesized by chemical vapor deposition. This

technique allows graphene arrays to be synthesized simply and is suitable for industrial sensing applications.

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1. Introduction

Many kinds of sensing devices have been developed to detect ions or biomolecules by methods such as cyclic voltammetry and spectral fluorescence [1, 2]. Recently, sensors based on electrical measurements using field-effect transistors (FETs) have been investigated owing to their simple, rapid detection of biomolecules without the need for special facilities [3, 4]. FETs based on Si modified with ion-selective membranes or DNA have demonstrated selective detection of ions or DNA, respectively [5, 6]. However, Si FET sensors require insulators on the channels in solution because of the narrow potential window of Si, which decreases the sensitivity for detecting biomolecules.

Graphene is an ideal two-dimensional carbon material. Carbon materials, including graphene, are electrochemically stable in solution, and have a wide potential window, which is important for measuring biomolecules in solution [7-10]. Additionally, changes in tiny amounts of charge caused by adsorption or desorption of analytes on the graphene channel in solution are detected as large changes in the conductance of the device owing to its high carrier mobility [11, 12]. In terms of these properties, graphene is well suited to detecting biomolecules with high sensitivity in solution. Our group reported high-sensitivity detection of pH, proteins, or DNA using graphene FETs, where the graphene was obtained by mechanical exfoliation [13-15]. However, mechanical exfoliation for graphene is not suitable for industrial applications because of the method's low productivity. Recently, chemical vapor deposition

(CVD) has been investigated for graphene synthesis. In CVD, there are two types of synthesis mechanisms, classified according to the catalytic metal. For a metal with low carbon solubility, such as Cu [16-19], graphene is synthesized by carbon adsorption on the metal surface [20]. For a metal with high carbon solubility, such as Ni [21-23], graphene is formed when carbon atoms leave the metal during cooling. Although CVD can synthesize large areas of high-quality graphene, the graphene must be transferred to insulated substrates for electronic devices [24, 25]. Graphene transfer requires many steps and is complicated. The transfer process often degrades the graphene through the formation of wrinkles or folds [26]. Thus, a graphene growth method that does not require transfer is desirable [27-29]. In this paper, we have fabricated a graphene-FET array through direct graphene synthesis on a Si/SiO₂ substrate. Graphene was synthesized by annealing amorphous carbon (a-C)/catalyst metal films. Moreover, we demonstrated simultaneous pH sensing and measurements of solutions with the graphene-FETs array. This growth method has great advantages for the simple fabrication of graphene-FET arrays.

2. Experimental

Graphene was directly synthesized by annealing as follows (Fig. 1). First, a-C (1 nm) was deposited on a Si substrate with a thermally grown SiO₂ layer (285 nm). The a-C layer functioned as carbon source for synthesizing graphene without reactive gases. Subsequently,

the a-C layer was coated with Ni (40 nm) and Pd (10 nm) layers as catalysts, which were deposited by an electron beam evaporator (EB350-8L, EIKO) without exposure to air. The metals were patterned in stripes ($15 \times 50 \mu\text{m}$) by conventional photolithography and lift-off processes (Fig. 1a). Then, the samples were annealed in an electric furnace at 850°C for 10 min in an Ar flow (350 sccm). The heating and cooling rates were 17 and $15^\circ\text{C}/\text{min}$, respectively. During the heating stage, the carbon atoms entered the metal layer (Fig. 1b), and during cooling, the carbon atoms left the metal layer as graphene (Fig. 1c). After annealing, the metal layers were etched with FeCl_3 (Fig. 1d). The synthesized graphene was characterized by using an optical microscope and Raman spectroscopy (HR800 UV, HORIBA Jobin Yvon) excited by a He-Ne laser at 632.8 nm. Moreover, the source and drain electrodes (Ni 20 nm/Au 10 nm) were formed on the graphene by using photolithography and lift-off processes to obtain the graphene-FET array. The channel length and width were approximately 3 and $15 \mu\text{m}$, respectively. Finally, a silicone rubber barrier was attached to the array to measure pH in solution. The pH was varied from 4.0 to 8.6 by injecting a phosphate buffer solution at pH 6.9 and a borate buffer solution at pH 9.0.

3. Results and Discussion

Fig. 2a and b show optical microscope images of the samples after metal deposition, and after annealing and metal etching, respectively. The Raman spectra revealed that graphene

was synthesized in the patterned area, and the contrast between the substrate and the graphene layer indicated the layer number of the graphene was relatively uniform. Fig. 2c shows the Raman mapping image of the G/G' peak intensity ratio of the sample in the square area in Fig. 2b. The mapped area had an average G/G' ratio of 3.0 and a standard deviation of 0.6; therefore, the synthesized graphene was estimated to have three layers [30-32]. The results indicate that the position-controlled synthesis of graphene on the insulators was achieved by annealing the a-C/metal structures.

To fabricate a graphene electrical sensing array, Ni and Au electrodes were formed on the graphene by photolithography and a lift-off process. After electrode formation, the device was annealed in an Ar/H₂ atmosphere at 300 °C for 1 h to remove residual contamination from the graphene surface. Fig. 3a shows the typical transport characteristics of the graphene FET in a vacuum chamber. The back-gate voltage was swept from 30 to -30 V with a drain voltage of 0.1 V with semiconductor parameter analyzer (B1500A, Keysight Technologies). For the graphene FET, the Dirac point was observed at a back-gate voltage of ~17 V and the graphene FET showed ambipolar transport characteristics. Moreover, Fig. 3b shows the histogram of the mobility in the graphene FETs. The average and maximum mobilities were estimated to be 210 and 410 cm²/(V·s), respectively. The results indicate that the graphene formed by annealing has as high mobility as few-layer graphene synthesized by CVD [24].

Subsequently, a silicone rubber barrier was attached to the array to measure pH (Fig.

4). First, a 10 mM phthalate buffer solution at pH 4.0 was injected into the rubber barrier. A gate voltage was applied with an Ag/AgCl reference electrode (Cypress Systems EE-009). Fig. 5a shows the drain current plotted as a function of the electrolyte-gate voltage for a graphene FET in various electrolytes at pH 4.0 to 8.6, which was obtained by adding a 10 mM phosphate buffer solution at pH 6.9, and a 10 mM borate buffer solution at pH 9.0. The transfer curves of the graphene FET shifted in a positive direction as the pH increased, which is consistent with previous research [24, 33]. This shift is considered to be attributed to trapped charges on the graphene surface [34, 35]. The plot of the electrolyte-gate voltages at 16 μ A versus pH value reveals that a linear relationship between pH and electrolyte-gate voltage was obtained from pH 4.0 to 8.3 (Fig. 5b).

Fig. 5c shows real-time simultaneous measurements of pH using two devices in the array. In the measurements, the pH was changed from 4.0 to 8.6 and then from 8.6 to 6.2, with the drain and electrolyte-gate voltages fixed at 100 and 50 mV, respectively. The drain current changed noticeably after injection of a solution with a different pH. The drain current increased stepwise with increasing pH and decreased with decreasing pH. The detection limit of the pH resolution (signal-to-noise ratio of 3) for each device was calculated to be 0.10 and 0.17. A previous study of single-CNT sensing reported a pH resolution of 0.65 [35]. The pH resolution for the CVD-grown graphene-FET was 0.18 [24]. Therefore, the pH resolution for

the annealed graphene device was as high as that for the CVD graphene-FET.

4. Conclusion

We have fabricated a graphene sensing array by direct growth on an insulated substrate. This growth method does not require a transfer process or reactive gas. Additionally, graphene FETs were used in a sensor array for pH detection. The graphene FETs had as a high resolution of pH detection as that of CVD-grown graphene. The results indicate that although this growth method only requires a simple annealing process, it produces graphene with similar characteristics to CVD-grown graphene. Our graphene synthesis technique is expected to be useful for fabricating sensors.

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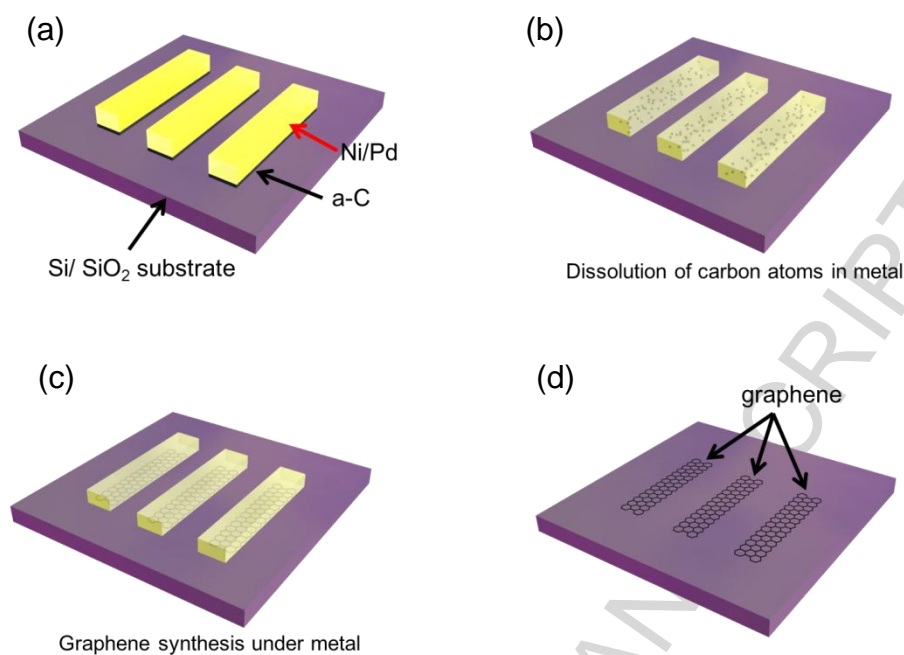


Fig. 1. (Color Online) Schematic of direct graphene growth on a SiO₂/Si substrate (a) as deposited a-C/Ni/Pd, (b) during heat treatment, (c) after annealing, and (d) after metal removal.

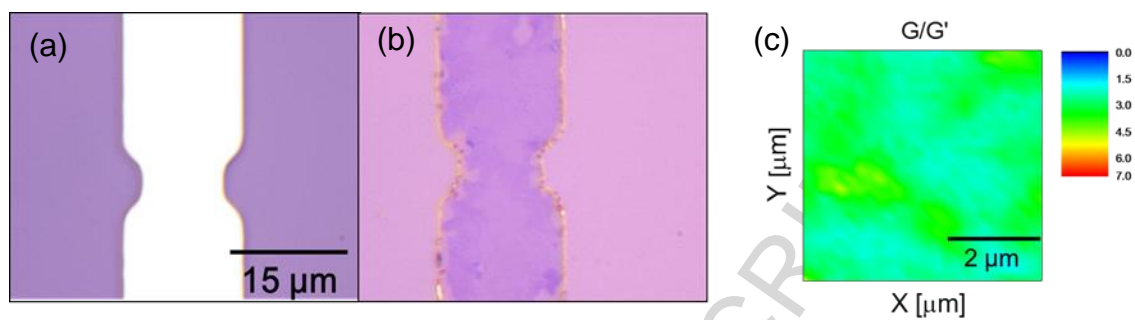


Fig. 2. (Color Online) Optical microscope images of (a) as-deposited metal and (b) after annealing and etching, and (c) Raman mapping image of G/G' peak intensity ratio.

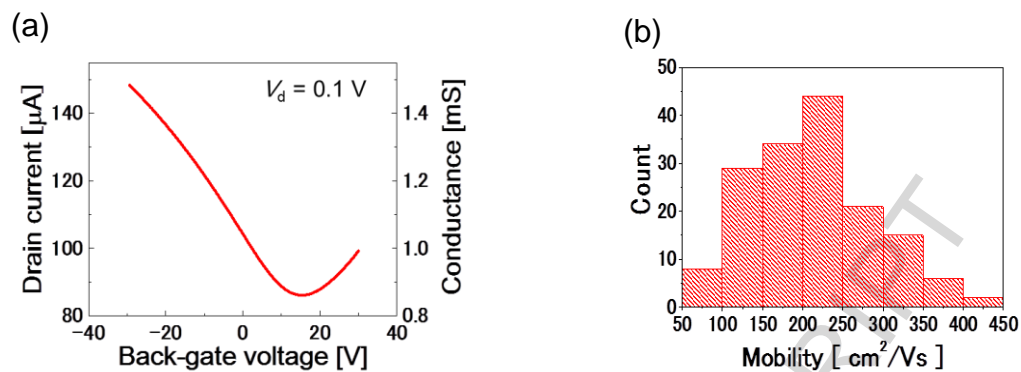


Fig. 3. (Color Online) (a) Transfer characteristic of the graphene FET and (b) histogram of the mobility in the graphene FETs.

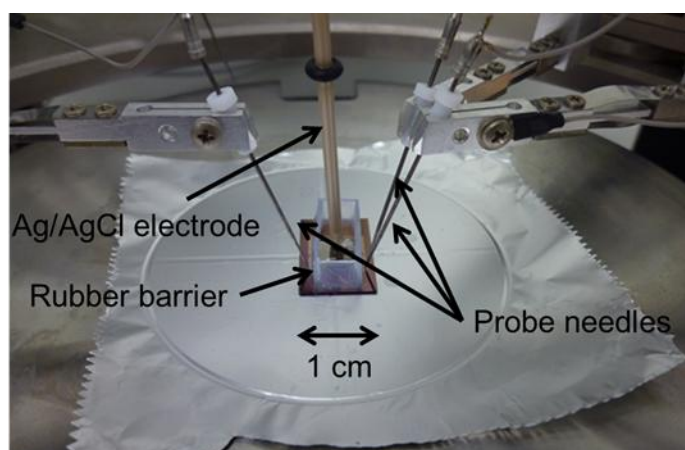


Fig. 4. (Color Online) Setup for pH measurements of electrolyte.

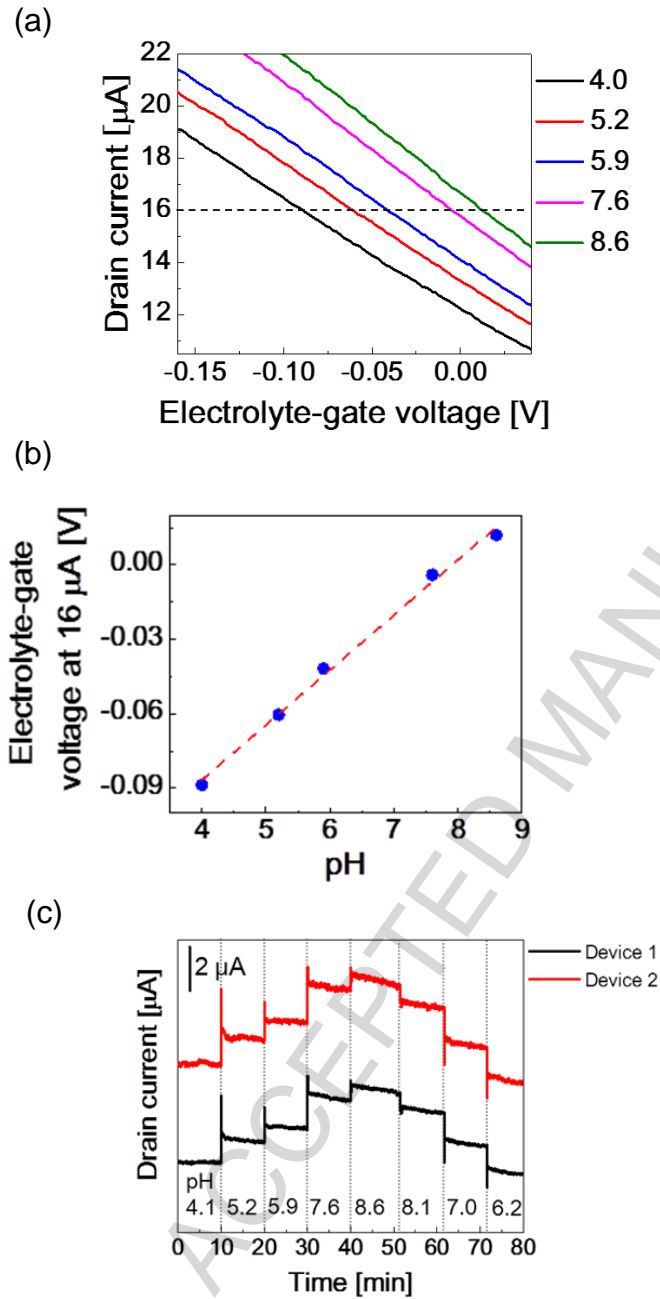


Fig. 5. (Color Online), (a) Drain current as a function of the electrolyte-gate voltage of a graphene FET at pH 4.0 to 8.6 and (b) electrolyte-gate voltage shift at 16 μA as a function of pH. Red dashed line shows the linear fit to experimental data. (c) Real-time drain-current observations at pH 4.0 to 8.6 with a drain voltage of 0.1 V and electrolyte-gate voltage of 0.05 V.

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Highlights

1. Graphene sensing array was fabricated by direct growth on an insulated substrate.
2. The graphene formed by annealing has as high mobility as that synthesized by CVD.
3. The linear shift of the transfer curve was observed from pH 4.0 to 8.3.
4. The pH resolution for each device in the array was calculated to be 0.10.