Adhesive Layer for Robust Graphene Transferred on Solid Support and Its Application to Graphene Microelectrode Manufacturing

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We describe an originally developed fabrication process of introducing an adhesive layer that fixes a graphene layer on a substrate via π–π interactions. The adhesive layer is prepared with an easy and highly reproductive wet chemical reaction that modifies the surface of the substrate before transferring the graphene layer. By using the process, we can greatly reduce the damage of the graphene layer that occurs during the manufacturing of a graphene microelectrode (GME). The process enables us to produce almost damage-free GMEs in high yield. The durability of a GME during an electrochemical measurement was also improved and the GME can be used stably even after repeating the electrochemical measurement, rinsing with water, and air drying.

1. Introduction

Graphene is an atomically thin two-dimensional sheet of sp²-bonded carbon atoms. Not only does it have a unique shape and structure, graphene shows many distinguished physical and chemical properties, e.g., superior carrier mobility and excellent fluorescence quenching properties, is highly thermally and chemically stable, and has biocompatibility. Thus, it has been attracting great promise as a functional material in various different fields such as chemical sensors, electronic or mechanical devices, and biomedical applications.1 Recently, the synthesis of high-quality and large-area graphene in more than 100 cm² has become possible by chemical vapor deposition (CVD).2 Therefore, CVD is one of the most popular methods of graphene synthesis for device applications such as bio/chemical sensing,3,4 field-effect transistors (FETs),5 and wearable electronics devices.6 However, since graphene is CVD-grown on a catalytic metal surface such as Cu or Ni, we must transfer the graphene layer from the metal substrate to an insulating substrate in order to integrate a graphene layer on a device.7

The problem with using a transferred graphene layer is that it is often accompanied by damage during each stage of transferring graphene, subsequent device patterning, and using the device. If we try to avoid using a transferred graphene layer, we must consider using a graphene layer synthesized by a method other than CVD. However, the yield of a mechanical
In exfoliation method to obtain single-layer graphene is low and not effective for manufacturing devices on a large scale\(^{(8)}\). In addition, a mechanically exfoliated graphene layer is small; thus, it is not sufficient for manufacturing most devices. An epitaxial graphene layer grown on a SiC surface is another candidate material. However, the first graphitic layer on SiC transforms to a buffer layer because of strong coupling with a semiconductor SiC substrate\(^{(9)}\). Transferring the graphene layer from the SiC substrate to an insulating substrate such as SiO\(_2\) is required, but is not as easy as transferring CVD-grown graphene. To expand the applications of these graphene-based devices, it is urgent to realize an effective method that allows us to minimize damage during processing and to maintain the durability of the patterned graphene layer even when repeatedly using the device after being manufactured.

In this work, we successfully developed a fabrication process to prevent, as much as possible, the CVD-grown graphene layer from being damaged during the manufacturing of a device. We considered that a small aromatic molecule, such as pyrene, must work as an excellent adhesive layer for graphene via \(\pi-\pi\) interactions and enables us to hold graphene stably on a substrate. In this strategy, bonding pyrene covalently to the surface of a solid substrate to transfer graphene is the key point. As a concrete example of evaluating this method, we fabricated a graphene microelectrode (GME) in a form of interdigitated array (IDA) electrodes that require a precise patterning process in the micrometer scale over a graphene layer of few millimeters square. We used a SiO\(_2\)/Si wafer as a general insulator substrate. To form the adhesive layer between SiO\(_2\) and graphene layers, we first modified the SiO\(_2\) surface with 3-aminopropyltriethoxysilane and subsequently bonded 1-pyrenebutanoic acid-succinimidyl ester (I) to immobilize pyrene, which works as an excellent adhesive layer to graphene via \(\pi-\pi\) interactions. The entire surface modification process is an easy and highly reproducible wet chemical reaction. We transferred a graphene layer onto the substrate and then patterned the graphene layer into a microelectrode by photolithography to obtain a GME. We evaluated the effect of introducing the adhesive layer by observing the graphene layer via optical and Raman microspectroscopy and digital microscopy. We also studied the stability and durability of a GME during a cyclic voltammetry (CV) measurement.

2. Materials and Methods

2.1 Reagents and chemicals

A CVD-grown single-layer graphene on Cu foil was purchased from Graphene Platform Corporation (Tokyo, Japan). 3-Aminopropyltriethoxysilane (APTES, Shin-Etsu Chemical Co., Ltd.), 1-pyrenebutanoic acid-succinimidyl ester (I) (Invitrogen), \(N,N\)-dimethylformamide (DMF, Kanto Chemical Co., Inc.), ethanol (Kanto Chemical Co., Inc.), 45 wt\% Fe(III)Cl\(_3\) solution (Aldrich), and \([\text{Ru(III)(NH}_3\text{)}_6]\text{Cl}_3\) (Aldrich) were used as received. Polymethyl methacrylate (PMMA) solution (495 PMMA Series Resists in Anisole, A6, Microchem) and a photoresist (S1813G, Microchem) were used as received. 0.05 M Carbonate-bicarbonate buffer (preweighed buffer powder in a capsule, Aldrich, pH 9.6) was prepared by dissolving the powder in 100 mL of deionized (DI) water. DI water (Millipore, >18 M\(\Omega\)-cm) was used throughout the work.
2.2 Apparatus

We measured CV curves by employing an ALS/CHI 800D electrochemical analyzer (CH Instruments, Inc.). Figure 1 shows the overall picture and structure of the GME that we used in this study. Since the GME was fabricated in the form of IDA, it consists of a pair of generator (WE1) and collector (WE2) electrodes as shown in Fig. 1 (a, right). Although metal electrode patterns for a counter electrode (CE) and a reference electrode (RE) were also integrated in the same chip [Fig. 1 (a, left)], we did not use them for this study. Instead, a standard Pt wire and a Ag/AgCl (3 M NaCl) electrode (BAS, Inc.) were used as a CE and a RE for [Ru(III)(NH₃)₆]³+/²⁺ measurements, respectively. The setup for the CV measurement is shown in Fig. 1(b).

We measured Raman spectra by employing a Raman microprobe system (inVia Reflex/StreamLine microRaman spectrometer, Renishaw) using a CCD detector. The excitation light source was the 532 nm line of a laser-diode continuous-wave laser. The maximum laser power focused on the sample with an objective lens (×50, NA 0.55) was about 35 mW for all the measurements. The spot size and focal depth on the sample were <2 and <10 μm, respectively. The scattered light was collected by using a 180° backscattering geometry, and the grating in the polychromator was 1800 line/mm. We performed all the measurements at room temperature. We measured stitched optical microscopy images employing a digital microscope (VHX-5000, Keyence).

3. Results and Discussion

3.1 Fabrication of GME

Figure 2 shows our newly developed procedure for fabricating a GME. As a substrate of a GME, we used a 0.5-mm-thick Si(100) wafer with a 285-nm-thick SiO₂ layer (Si/SiO₂, SUMCO) and cut it into 12 × 20 mm² chips. We first patterned metal pads on a chip by photolithography...
and then deposited a 10-nm-thick Ti layer, followed by a 100-nm-thick Pt layer. The metal pad pattern was obtained after a lift-off process in acetone. We then carried out the oxygen plasma treatment of the chip with metal pads to make the SiO$_2$ surface hydrophilic [Fig. 2(a)]. To modify the SiO$_2$ surface with amine groups, we immersed the entire chip in 1 vol % APTES solution dissolved in a 20:1 mixture of ethanol and DI water containing 1 mM acetic acid for >1 h at room temperature, rinsed with ethanol, and then dried in a nitrogen stream [Fig. 2(b)]. We then covered the chip with a drop of 5 mM DMF solution of I for 1 h at room temperature, rinsed with DMF, and then dried in nitrogen stream [Fig. 2(c)]. With this process, the amine group was bonded to I by a dehydration reaction and thus the pyrene group was immobilized on the SiO$_2$ surface of the chip. Since pyrene adsorbs firmly on a graphene surface via π–π interactions, a pyrene-modified surface works as an excellent adhesive layer to graphene. Here, APTES does not bond with the Pt surface and thus the pyrene group is not immobilized on the Pt surface of the chip. Therefore, the graphene layer attached directly to the Pt surface on the metal pad pattern. Thus, it makes sufficiently good electrical contact between the graphene layer and the Pt metal pad. Subsequently, we transferred a single-layer graphene on the chip in the same manner as we previously reported for preparing a graphene aptasensor [Fig. 2(d)]. In brief, a CVD-grown graphene on Cu foil was cut into a piece of the required size. The graphene surface was covered with PMMA by spin coating. The piece was floated on FeCl$_3$ solution for about 2 h to etch the Cu foil. The FeCl$_3$ solution was replaced with DI water to wash the bottom graphene surface with a PMMA top layer. The graphene layer floating on water was then transferred on the pyrene-modified surface of the chip. The PMMA film was
removed in hot acetone. Next, we formed the photoresist pattern on the graphene surface by photolithography and used it as a mask to etch the graphene layer using oxygen plasma into the GME pattern [Fig. 2(e)]. The photoresist mask was then removed using acetone. The final gap between pairs of electrodes and the width of the electrodes were 5 and 10 μm, respectively.

For reference, we also fabricated GMEs without introducing an adhesive layer. To prepare GMEs without an adhesive layer, we skipped the APTES-pyrene modification process and transferred a single-layer graphene on the chip immediately after the oxygen plasma treatment of the chip with metal pads. Other processes were all the same.

3.2 Analysis by optical and Raman microscopy image

Figure 3 shows the microscopy images of GMEs fabricated (a) without and (b) with an adhesive layer. As described in the following section, the dark part is the area covered with a graphene layer. Without an adhesive layer, graphene peeled off in a large area and the microelectrode pattern was not correctly formed. In contrast, for the GME with an adhesive layer, damage was greatly reduced and a desirable electrode pattern was obtained in a wide area. This result shows that the new process that introduces an adhesive layer is greatly effective for reducing damage of a graphene layer and enables us to manufacture high-quality GMEs with high yield.

Figure 4 shows the results of analyzing the representative parts of GMEs by using optical and Raman microscopy images. The characteristic Raman bands of graphene, G (~1580 cm\(^{-1}\)) and 2D bands (~2680 cm\(^{-1}\)), change in shape, position, and relative intensity with the number of graphene layers; thus, Raman spectroscopy can be efficiently used to monitor the structure and quality of graphene.\(^{(10)}\) The dark parts in the optical images (a-1, a-2) correspond to the dark parts in the Raman images (b-1, b-2) that show a high 2D band intensity. Therefore, we considered these parts as areas covered with graphene. The bright parts in both the optical and Raman images do not show Raman peaks (c-1, c-2). Therefore, we considered these parts as areas not covered with graphene. Moreover, the relative intensity of G and 2D bands showed

![Fig. 3. Stitched microscopy images of GMEs (a) without and (b) with adhesive layer.](image-url)
that graphene is mainly a monolayer. As described above, without an adhesive layer, graphene peeled off in a large area and the microelectrode pattern was not correctly formed. In contrast, for the GME with an adhesive layer, damage was greatly reduced and a desirable electrode pattern was obtained in a wide area.

3.3 Stability and durability of GMEs during electrochemical measurement

Figure 5 shows the typical results of dual-mode CV measurements obtained by using GMEs, (a) without and (b) with an adhesive layer. We fabricated four electrodes for both GMEs without and with an adhesive layer. Without an adhesive layer, the response of the collector electrode was very noisy and the current was smaller by two orders of magnitude than that with an adhesive layer in the entire potential region [Fig. 5(a), superimposed graph]. The responses of four different GMEs without an adhesive layer were all unusual as shown in Fig. 5(a). On the other hand, with an adhesive layer, the responses of the generator and collector electrodes were both noiseless and almost symmetrical for the four different GMEs as shown in Fig 5(b). Moreover, the responses were stable for 50 cycles of the potential sweep of the generator electrode (results not shown).

Figure 6(a) shows the typical results of the single-mode CV measurements obtained by rinsing with water and air drying 10 times using GMEs with an adhesive layer. From the 1st
Fig. 5. Dual-mode CV curves for 1 mM \([\text{Ru(III)(NH}_3)_6]^{3+/2+}\) in 0.05 M carbonate-bicarbonate buffer obtained by using GMEs (a) without and (b) with adhesive layer. The superimposed graph is the same plot as (a) enlarging the y-axis by two digits.

Fig. 6. (a) Single-mode CV curves for 1 mM \([\text{Ru(III)(NH}_3)_6]^{3+/2+}\) in 0.05 M carbonate-bicarbonate buffer obtained by rinsing with water and air drying 10 times using the GME with adhesive layer. (b) Stitched microscopy image obtained after repeating CV measurement, rinsing with water, and air drying 10 times.
CV measurement to the 4th CV measurement, the peak intensity slightly decreased, but after the 5th CV measurement, the responses became stable and the difference in current level was within ±1% for both the oxidation and reduction peaks. Figure 6(b) shows a microscopy image obtained after repeating CV measurement, rinsing with water, and air drying 10 times. As described in the previous section, the dark part is the area covered with a graphene layer. Damage was hardly observed and the electrode pattern was kept in good condition in a wide area. These results clearly show that introducing an adhesive layer provides sufficient durability for the repeated use of GMEs.

5. Conclusions

We proposed an originally developed fabrication process to prevent, as much as possible, a CVD-grown graphene layer from being damaged during the manufacturing of graphene-based microdevices. The point of our strategy was introducing an adhesive layer, namely, a pyrene-modified surface that strongly fixed a graphene layer on a substrate via π–π interactions, between graphene and a SiO₂ substrate. As a concrete example of evaluating this method, we fabricated a GME that requires a precise patterning process in the micrometer scale over a graphene layer of few millimeters square. We compared the Raman and optical microscopy images of GMEs fabricated with and without an adhesive layer and found that introducing an adhesive layer enables us to manufacture GMEs with an almost damage-free graphene layer in high yield. CV measurements also showed that the GME response was stable and durable during repeating cycles of electrochemical measurements, rinsing with water, and air drying. We believe that the surface modification method that we developed in this study has a major impact on manufacturing many different graphene-based microdevices in a large scale.

References

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