

Mechanical Exfoliated Large Scale CVD-Graphene using Water-Soluble WO₃ Supporting Layer

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Keywords: Chemical Vapor Deposition, Mechanical Exfoliation, Graphene, Tungsten Oxide

ABSTRACT

We will introduce a large area clean graphene transfer method that solves the problems encountered during the transfer process of CVD graphene. WO₃ can transfer high-quality graphene synthesized on a Ge substrate without a defect, and there is no chemical etching process due to its water-soluble nature.

1 INTRODUCTION

Mechanical exfoliation has yielded graphene with a layer of atomic thickness with a carbon atom in the honeycomb structure^[1], and due to its remarkable thermal, mechanical and electrical properties^[2], numerous studies have been made to utilize graphene. For high performance and development of graphene-based applications, there have been studies to obtain graphene through thermal decomposition of SiC^[3] and reduction of graphene oxide^[4]. After the synthesis of graphene using chemical vapor deposition (CVD) method in 2009^[5], the technique of synthesizing high quality graphene of large area has been studied steadily. However, in order to utilize it as a synthesized electronic device, it is essential to transfer a desired substrate. Through advanced researches, graphene synthesized on catalyst substrates such as Cu, Ni, and Ge^[6-8] has high crystallinity and comparable properties to the highly oriented pyrolytic graphite (HOPG), but there are various obstacles to transfer it to a desired substrate without degrading performance. Problems arising from transfer of graphene can be divided into physical defect, chemical contamination, and the need for further processing. The physical defect can be observed on the surface of graphene transferred by tearing and cracking. This is mainly observed in a wet-transfer method in which a substrate is mainly etched using polymethyl methacrylate (PMMA) or poly (bisphenol A carbonate) ^[9]. Because there is no supporting layer, the catalyst and polymer layers directly attached to the surface of the graphene form a strong interaction with the graphene, resulting in structural discontinuities in the etching process, resulting in the aforementioned defects. ^[10] Also, the polymer layer can be etched using an organic solvent, but residues are inevitably present on the surface of the graphene, which causes chemical contamination with the graphene and causes deterioration of performance. ^[11-13] When graphene is transferred using a supporting layer

such as an inorganic metal, most of the above problems can be solved. However, additional chemical etching process is required to remove the problem, and defects and contamination on the graphene surface can not be avoided^[14,15]. The material transferred from the mother board has a complex structure through the individual processes in device manufacturing, which causes performance degradation, additional cost and time to occur in the process. Solving the above-mentioned damage of the graphene transfer process and solving the complexity of the process is essential for the development of the graphene industry. We will introduce a large-area clean graphene transfer method that solves the preceding problems in this reunion. WO₃ can transfer high-quality graphene synthesized on a Ge substrate without a defect, and there is no chemical etching process due to its water-soluble nature. In addition, it is expected that it will be useful for the development of the field using graphene by suggesting the possibility of using the composite structure of WO₃ and graphene in an application.

2 EXPERIMENT

Synthesis of Graphene: Ge (110) wafer was used for the synthesis of graphene. After loading the prepared substrate into the CVD chamber, the vacuum to $\approx 10^{-6}$ torr. Afterwards, H₂ gas is flowed in the middle of the temperature increase, and when the chamber temperature reaches 900 ° C, GeH₄ gas (20 sccm, 30 torr) is flowed for 30 minutes to deposit. After the deposition, the mixture gas of CH₄ / H₂ (1/100 ratio) was flowed at 930 ° C for 2 hours to synthesize graphene. Finally, turn off CH₄ and cool down to room temperature.

Graphene Transfer: For mechanical exfoliation of as-grown graphene, first, a 30 nm WO₃ thinfilm is deposited on an substrate using an e-beam evaporator. After the deposition, the heat treatment is performed at 300 ° C for 1 hour in an air atmosphere. Then spincoating the PMMA (A6) layer (2500 rpm, 60s). The graphene layer comprising WO₃ is mechanically exfoliated using TRT and the TRT is removed by hot press (120 ° C). Finally, PMMA and WO₃ layers are removed by acetone dipping and DI water dipping.

3 RESULTS

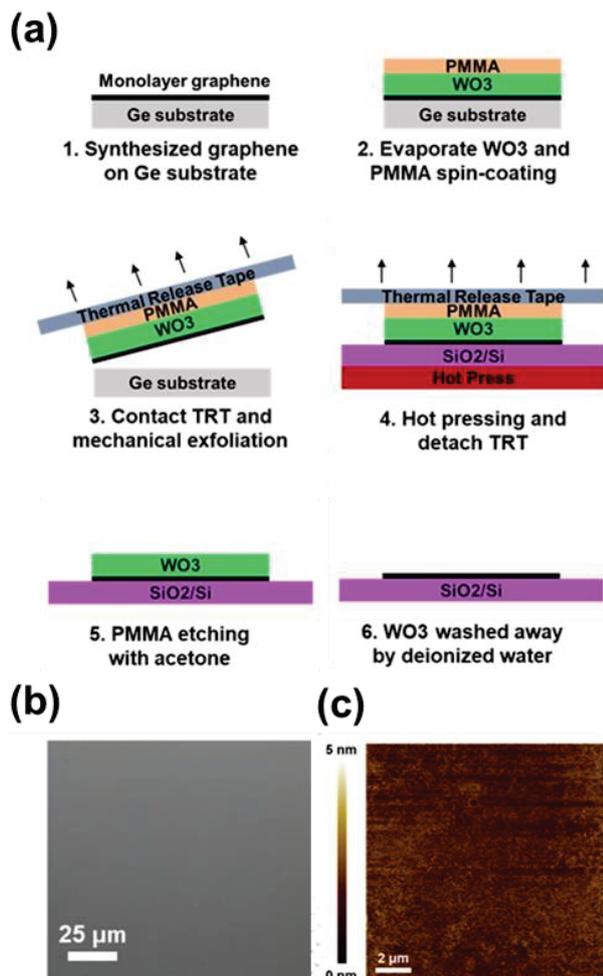


Fig. 1 Schematic of mechanical exfoliation process and images of transferred graphene on SiO₂/Si substrate

a) Graphene synthesized on Ge substrate exfoliated through WO₃ thin film and transfer onto target substrate. b) OM image of graphene on SiO₂/Si substrate. c) photograph images of graphene after mechanical exfoliation and etching process. d) AFM images of graphene on SiO₂/Si substrate. RMS roughness is 0.577 nm.

Fig. 1a Shows the mechanical exfoliation process of graphene using WO₃ as a supporting layer. After the monolayer graphene is synthesized using low-pressure CVD on a Ge substrate, a WO₃ thin layer is deposited on the graphene layer via an e-beam evaporator. The PMMA layer is then spin-coated for conformal contact and then bake on hot plate. Contacted thermal release tape (TRT) and WO₃ / graphene layers are mechanically exfoliated on the Ge substrate and transferred onto SiO₂ without damage. The TRT, which was in contact with the top layer of the graphene layer, is removed using a hot press that applies heat and pressure. When the process of etching the PMMA in acetone ends, only the graphene and WO₃ layers remain on the SiO₂ substrate. As a final step, when Deionized (DI) water is deeply depleted, the WO₃ layer is

easily removed and only the clean transferred graphene remains. The adhesion energy of Ge substrate and graphene is lower than that of other metals used as transition metal catalyst substrates for CVD. Due to these properties, deposited WO₃ acts as a supporting layer to protect the graphene, as well as allowing the Ge substrate and graphene layer to be mechanically exfoliated easily. Therefore, the synthesized graphene can be transferred to another substrate without damage. To confirm the large area transfer, we synthesized graphene on a 1 cm² Ge substrate and transferred it to SiO₂, and confirmed it through a photograph image (Fig. 1b). Transferred graphene is continuous without defect such as wrinkle and tearing, and optical image enlarged by it can be seen in fig.1c. In addition, atomic force microscopy (AFM) was performed to confirm the flatness of the transferred graphene surface, and root mean square (RMS) value of 0.577 at a size of 10 μm × 10 μm was obtained (Fig. 1d).

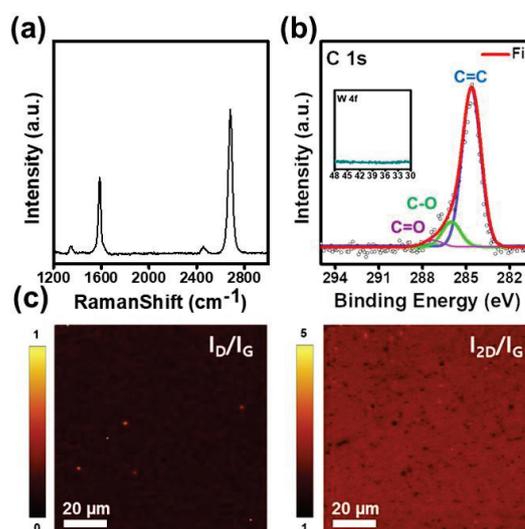


Fig. 2 Surface measurement of mechanical exfoliation graphene for chemical inspection

a) Raman spectra of graphene after mechanical exfoliation process. b) XPS spectrum of C 1s and W 4f peak of graphene on SiO₂/Si substrate. c) Raman mapping images of intensity ratio of D peak /G peak and 2D peak/G peak.

Raman spectra were measured not only for the physical defects of the Graphene surface but also for the high quality and chemical effects of the graphene after transfer. It can be seen that the D peak indicating the atomic defect of Graphene is very low through fig. 2a. The calculated 2D / G ratio of 2.32 confirmed that the synthesized high-crystalline monolayer graphene was transferred without crystallinity degradation or defect. In order to confirm the transferred graphene uniformity, the raman mapping was measured and the D / G ratio and the 2D / G ratio were shown as the results (Fig. 2c). The graphene in the whole area demonstrates uniformity of

G and 2D peak intensities, demonstrating uniformity and confirming that the defect free monolayer graphene is transferred to a large area with a low D / G ratio and a high 2D / G ratio. Fig. 2b shows x-ray photoelectron spectroscopy (XPS) measurements of graphene transferred on a SiO₂ substrate. Fitting was performed with high C 1s as the major peak, and the C-C peak of sp² bonding was 284.6 eV. In addition, sp³ bonding C-O and C = O peaks were identified as low intensity values and observed at 286.1 and 287.1 eV. Inset image is the result of measuring the range of W 4f, which is the main peak of WO₃ acting as supporting layer, and it shows that WO₃ washed away from Di water is cleared away from graphene surface.

4 DISCUSSION

The CVD graphene synthesized on the Ge(110) substrate was mechanically exfoliated using a WO₃ supporting layer and transferred to another substrate. After the transfer, it was confirmed by OM image and AFM that physical defect of graphene does not exist. In addition, WO₃ has a water-soluble property and is removed by Di-water without chemical etchant used in the conventional transfer method. XPS was measured to confirm that WO₃ etched with di-water was completely removed from the graphene surface. XPS was measured to confirm that the WO₃ etched with di-water was completely removed from the graphene surface. A sharp C 1s peak was obtained and W 4f peak was not present. The Raman spectra result confirmed that the monolayer without degradation of quality or doping was transferred, and the large-scale clean transfer was confirmed through mapping data.

5 CONCLUSIONS

Mechanically exfoliated graphene using WO₃ as a support layer clearly addresses the limitations of conventional transfer methods, as mentioned above. In particular, the chemical effect of the etching of the support layer on the graphene using chemical etchant is solved by the water-soluble nature of the inorganic metal oxide. Clean transfer of graphene is essential for the fabrication of devices and applications that utilize it. We have achieved this goal in this study, and further work is going to confirm the electrical properties of the transferred graphene. In addition, WO₃, which is used as a supporting layer, is being used in various ways such as a photodetector and a gas sensor. Therefore, it can be used as a graphene / WO₃ heterostructure device. We believe these studies will bring positive developments to graphene-based projects.

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