

Mechanical Exfoliation Of Single Layer Graphene From HOPG At Room Atmosphere Environment

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Abstract- In this paper we demonstrate an exfoliation technique with which single layered graphene can be acquired from a patterned highly ordered pyrolytic graphite (HOPG) mesa (20 μm x 20 μm x 1 μm) under room-temperature atmosphere environment using a micropipette and a high-precision nano-stage. The acquired thin layered graphene was analyzed through atomic force microscope (AFM) and Raman spectra for verification of its thickness. The results showed that the acquired graphene had a single layer and its lateral size of 20 μm x 20 μm with well-defined boundary features as patterned on the HOPG mesa. This result indicates that highly pure, size-controllable, and patterned graphene can be obtained via a mechanically controllable way such as the one studied in this paper.

Keywords – Graphene, Mechanical exfoliation, HOPG

I. INTRODUCTION

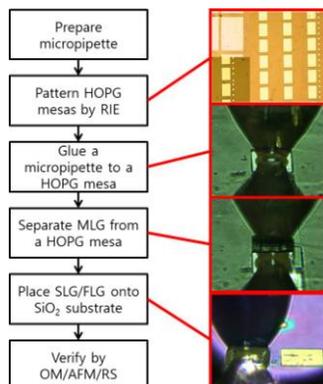
Graphene is a next generation emerging material that has a large potential in industrial, scientific and medical applications. Many techniques acquiring single layer graphene have been proposed recently in two categories, i.e., bottom-up and top-down method [1-6]. Chemical vapor deposition (CVD) is a well-known bottom-up method to make large-sized graphene, but the quality of the acquired graphene from this method is not as good as that of pure graphene. On the contrary, the mechanical exfoliation technique which produces single layer graphene from HOPG block/mesa is a good top-down method to acquire pristine-quality of single layer graphene from the view point of chemical contamination. So far many research groups have tried to produce graphene but there has been no report in which well-defined single layer graphene could be obtained with relatively large size (over 5 μm lateral dimension) in a mechanically controllable way. Pre-patterned graphite pillars on HOPG and an AFM tip were used to obtain thin graphitic layers [7, 8]. However, since the obtained size of the thin graphitic layers depends on controlling an AFM tip and its size, only a few micron size of graphene was obtained.

In this study we have succeeded in acquiring a single layer graphene with high purity and well defined features by using a small micropipette and a high precision nano-stage. The obtained graphene was confirmed as single layer by AFM and Raman spectroscopy as well as optical microscopy. From a pre-patterned HOPG mesa (20 x 20 x 1 μm^3), the acquired graphene had well defined boundary geometry (20 x 20 μm^2). The lateral size of the acquired graphene was ~20 μm , which is much greater than what was obtained in the previous research [9]. From well-defined geometries of graphene, one can relate its geometry to its performance in physical properties. As we know, it is extremely important to know physical properties from known or well-confined geometries of materials since physical properties strongly depend on materials geometrical confinement.

In order to obtain few layered or single layered graphene (FLG or SLG), normal forces were exerted on pre-detached graphitic thin layers from patterned HOPG mesas through micropipette manipulators. The applied normal force would have been sufficiently balanced with the interlayer bonding force between adjacent carbon layers so that the layered material could be exfoliated by a shear force which was also made possible through the micropipette manipulator. Parametric investigations have been performed using the applied forces, and accelerations of lateral movements of the micropipettes. AFM and Raman spectroscopy for confirming the number of layers of graphene after the acquisition process were conducted.

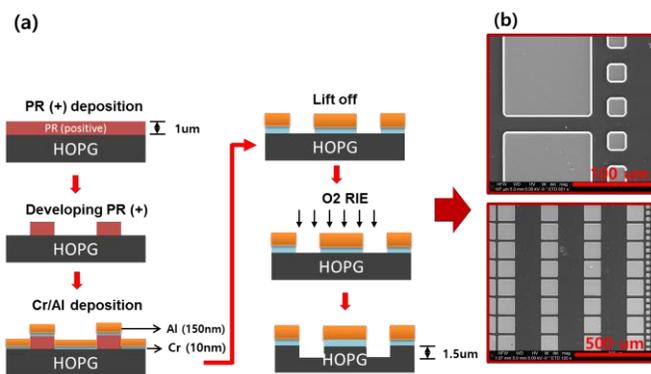
II. EXPERIMENTAL DESIGN AND METHODS

2.1 Acquisition single graphene –



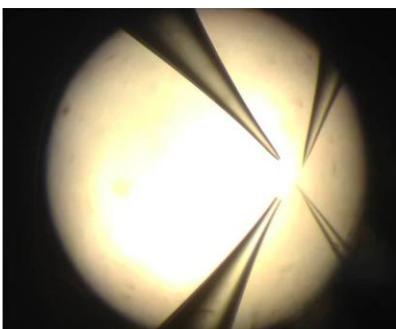
The fabrication process to acquire a single layer graphene from patterned HOPG mesas. MLG: multi-layer graphite, SLG/FLG: single layer/few layer graphene, OM: optical microscope, AFM: atomic force microscope, and RS: Raman spectroscopy.

Figure 1 is a flow chart of the process for acquiring SLG from a patterned HOPG mesa in room temperature atmosphere environment. We fabricated HOPG mesas using reactive ion etching (RIE) on a pre-patterned HOPG block (SPI supplies, grade: ZYA, 1 cm x 1 cm x 2 mm); standard lithography steps have been taken to generate a photoresist pattern on HOPG as shown in figure 2. The Al/Cr layer has been deposited for multiple purposes: 1. to protect the mesa during patterning and 2. to promote better adhesion between the micropipette and the mesa and to provide even force during exfoliation of the graphene. In the RIE process, oxygen was used as a reactive gas. Chamber pressure was maintained at 5 mTorr and the gas flow rate was 20 sccm. Plasma power of 300 W and bias power of 50 W were used respectively. An etching time of 10 min created an etching depth of 1.5 μm in HOPG. As can be seen in figure 2, various sizes of HOPG mesa whose lateral dimensions of 100 and 20 μm were created



Pattern of HOPG mesa fabricated by RIE. (a) fabrication steps; (b) patterned mesa

2.2 Fabrication of micropipette –



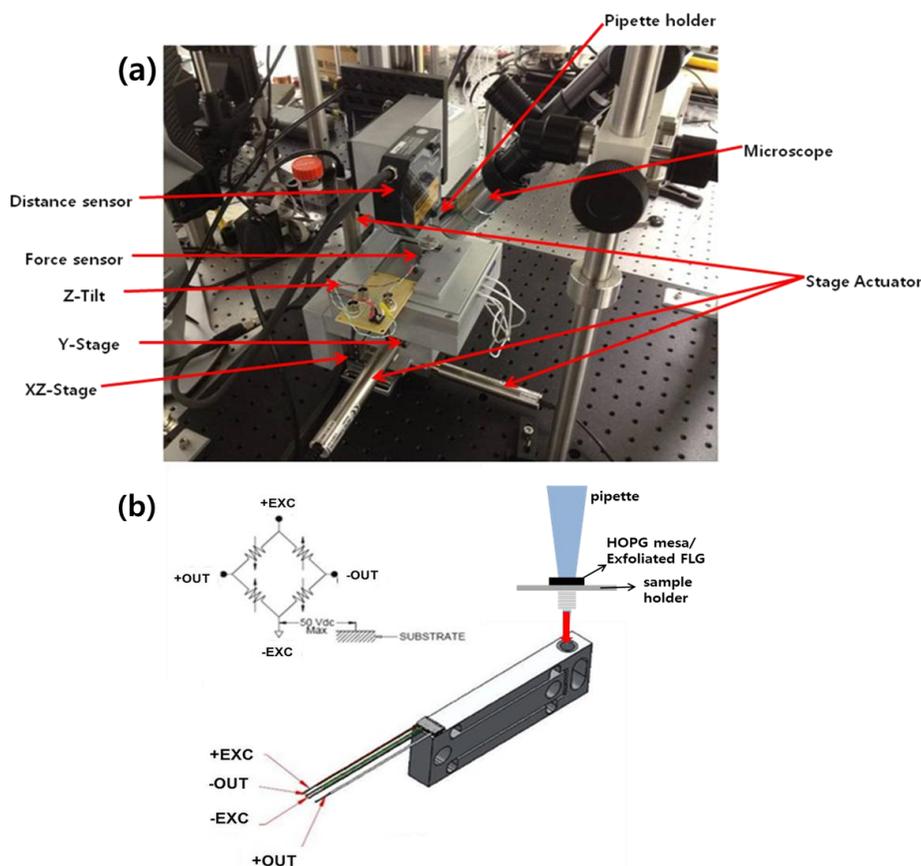
Various micropipettes for the experiment of graphene exfoliation

We used micropipettes with a tip size of $\sim 15 \mu\text{m}$ for attaching and manipulating the patterned mesas and the glass pipette puller was used for production of micropipettes (Sutter Instrument) as shown in figure 3. The tip size of micropipette can be determined by equipment parameters i.e., heat, pulling velocity, and time. For good adhesion between the micropipette and mesas to enable graphene exfoliation, the tip diameter used in this paper should be around $15 \mu\text{m}$ which is 75% of the size of HOPG mesa ($\sim 20 \mu\text{m}$) in this work, which is the appropriate size for good adhesion between the pipette and the HOPG mesa.

2.3 Acquisition of graphene –

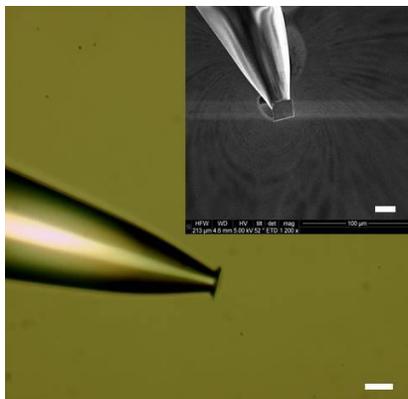
2.3.1 Exfoliation of MLG from the mesas

A precision nano-stage assembly has been constructed to acquire graphene as shown in figure 4. The assembly divides into two parts: a micropipette manipulator at the top and nano-stage at the bottom. A micropipette is fixed to a holder which has a v-groove for ease of mounting. The nano-stage has three actuators, each of which moves in x-, y- and z-direction, respectively and a precision tilting stage which rotates in θ_x - and θ_y - directions is attached on top of the x-y-z stage. Also, there is a manual tilting stage which is attached to the precision tilting stage for a coarse adjustment of the tilt. A substrate (oxide wafer) holder is located on top of the manual tilting stage to which a force sensor is attached for measuring the contact pressure between the mesa and the substrate.



(a) Precision nano stage setup and (b) force sensor with operational circuit

Initially, leveling of the HOPG mesa was conducted using a distance sensor (Keyence LK series) and nano and manual tilting stages. Final adjustment of leveling has been made by examining the two optical images at a certain distance ($\sim 1 \text{ mm}$) in both x and y directions; for a final leveled substrate, two clean, focused images were supposed to be obtained. Epoxy (loctite® super glue) was used to glue the micropipette to the HOPG mesa (see step 3 in figure 1, Glue a pipette to a HOPG mesa). Curing was needed for 15 hours for secure adhesion of the pipette to the mesa. After that, a lateral shear force was applied through the mesa with a speed of 5 to $100 \mu\text{m/s}^2$ that was controlled by an external stage controller. Figure 5 shows an optical image of the separated micropipette with detached multi-layer graphite (MLG, with a few thousands of graphene) from the HOPG mesa. The inset shows the SEM image taken from the bottom of the mesa.

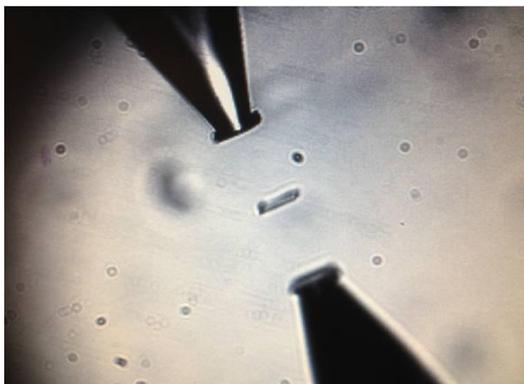


(a) Optical image of micropipette with detached MLG. The inset is its SEM image taken from the bottom of the mesa. The scale bar is 20 μm .

2.3.2 Acquisition of graphene from MLG

In order to obtain graphene from the detached MLG, the micropipette with MLG was moved to the desired site on the substrate where graphene would be exfoliated by applying a similar shear force between the mesa and substrate. We used an oxide wafer as a substrate with 300 nm thickness of SiO₂ film. We could observe exfoliated graphene with an optical microscope. Figure 6 is a CCD image representing the micropipette, MLG, and graphene which was obtained on the oxide substrate.

In this stage of acquisition of graphene from MLG, a normal force to the detached MLG which was placed at the desired site through the micropipette was applied. Voltage reading with the force sensor (S256, Strain Measurement Devices Inc.) could measure the applied force since its resolution was 1 μV in 10 mV which corresponded to a part in 10,000. Therefore, 1 mg was able to measure in the specified 10 g output range of the sensor. The reason why the normal force was applied is that since the interatomic repulsive energy keeps increasing as the interatomic distance of the graphite interlayers of MLG reduces through the normal force. Eventually the interatomic repulsive energy in the bonding energy is so dominant in the bonding energy of the interlayers that there could be no attractive energy between the layers. This will in turn lead to easy exfoliation of few layers of graphene (FLG) or SLG through later shear force applied to the MLG.

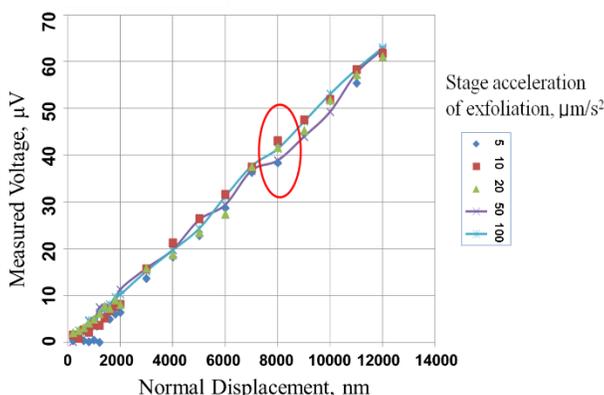


CCD image after exfoliation of graphene on SiO₂ substrate. The graphene exfoliated from MLG with the micropipette is shown in the middle of the image. The bottom image of the pipette is reflection of the real top image III. results and discussions

We have conducted a series of experiments with varying stage acceleration and normal force (output as voltage). In the acquisition process of graphene from MLG, among other parameters the stage acceleration of 100 $\mu\text{m}/\text{s}^2$ and the normal force of $406.01 \pm 9.8 \mu\text{N}$ (measured at $41.43 \pm 1 \mu\text{V}$ in the voltmeter under 10V applied bias to the force sensor; the sensitivity of the sensor was 1 mg/1 μV so that the measured voltage corresponded to $41.43 \pm 1 \text{mg}$) resulted in FLG including a single layer graphene. Figure 7 shows the controlling parameters that were used in obtaining FLG. The circled data indicated in the graph showed the best results out of trials using various parameters: around 400 μN of the normal force with 100 $\mu\text{m}/\text{s}^2$ acceleration. Since MLG had the area of 20 x 20 μm^2 , the stress applied to MLG was around 1MPa for the best results. We believe that beyond a certain value of applied stress most

of energy used to press MLG are dissipated through the mechanical system, not being used for reducing the interlayer distance since larger energies than the interlayer bonding energy induce larger interlayer repulsive energy. This might be a reason that larger stress than what is required for the best results (~1 MPa) were not useful to obtain FLG or SLG. However, more detailed studies to address this should be needed.

The condition on acquisition of SLG was not clearly understood in this study since SLG was not acquired at one single condition. The yield of 20 x 20 μm² lateral sized SLG was only 5% (one out of 20 trials of the exfoliation process) and there was no repeatable trend regarding the exfoliation condition for SLG. Repeatable results were not obtained because of the unknown interlayer force in MLG, which is likely to be different in each layer. For SLG acquisition, the breakage of the layers must be occurred at the bottommost interlayer. We believe that interlayer forces between each layer could be different layer by layer since grain boundaries and defects inside each layer were not known. We might have to accept a fact that physical conditions for obtaining SLG with a mechanical exfoliation means are challenging because they reside in a microscopic level of uncertainty. Defects, and grain boundaries, inside of the layers were impossible to identify. Additionally, inhomogeneity of applied normal and shear stress and surface conditions of the substrate (SiO₂) such as surface roughness, particles, and defects were also unknown parameters. Hundreds of trials with similar conditions can provide a few successes of obtaining SLG. This makes us recall “scotch tape method of obtaining graphene” in resemblance of randomness.



Control parameters for exfoliating graphene on SiO₂ substrate. Normal displacement means the stage movement in downward z-direction to create pressure on MLG. Circled data in the graph are the controlling parameters to successfully obtain FLG including a single layer graphene

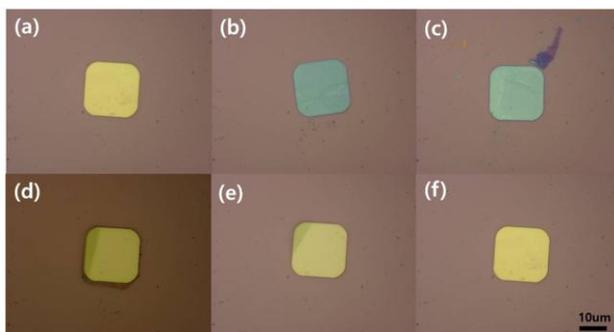
In addition, theoretically there has been no way to obtain exact values of the exfoliation energy, which is the energy for separation of layers of graphite. In 1972 theoretical studies of forces between graphene layers have been made [10]. They have employed the modified Thomas-Fermi-Dirac method considering inhomogeneities of electron configuration. This method involves with an energy term related with a configuration of electron distributed on the plane of graphite. This method describes well the interlayer bonding energy of graphite. However, one should know the exchange-correlation energy in (Eq. 1) in the total cohesive energy of graphite to exfoliate graphene from a host graphite with specified calculation as the cohesive energy of solid is defined as the energy needed to disassemble it into constituent atoms or molecules. Therefore, the system such as a layered system in our case, this definition can be referred to the exfoliation energy, which is the energy required to separate all layers of graphite to infinity. The total cohesive energy E_{coh} of graphite calculated from density functional theory (DFT) can be written in terms of a function of electron density, n ,

$$E_{coh} = T(n) + U(n) + Ex(n) \quad (1)$$

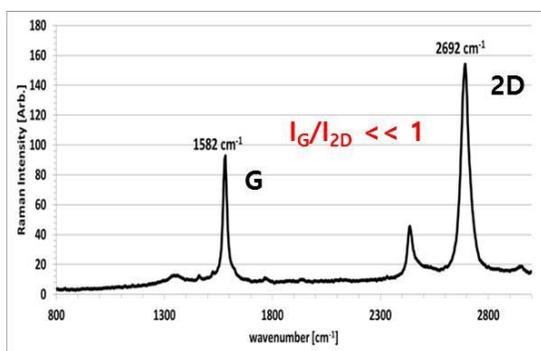
where $T(n)$ is the kinetic energy, $U(n)$ the potential energy, and $Ex(n)$ the exchange-correlation energy [11,12].

However, a problem arises from the fact that the exact exchange-correlation energy is not known, especially in a long-range order. This leads to make it impossible to obtain exact calculation for the exfoliation energy.

Nevertheless, surpassing the aforementioned theoretical limitation the process used in this study was successful to provide well-defined graphene flakes with 20 x 20 μm² lateral area (figure 8) with high frequency. Even SLG was successfully created. Therefore, it would be better to say that the method used in this research may provide much higher yield of SLG as compared to any other mechanical ways.

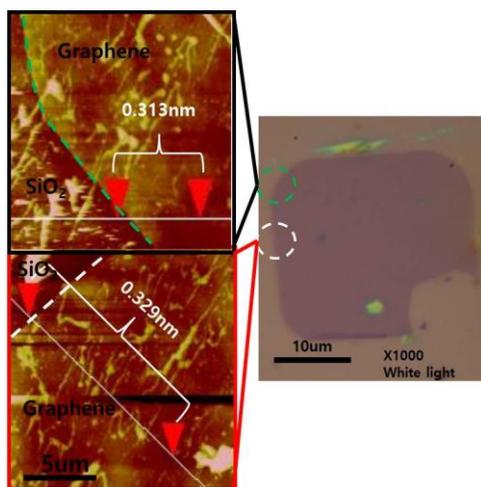


20 x 20 µm² graphene flakes obtained in this study. Based on their optical colors and Raman spectroscopy, their number of layers of graphene are in range of 5~10 for (b) and (c) and more than 10 for (a), (d), (e), and (f).



Raman spectrum for the obtained SLG. The intensity ratio of IG/I_{2D} was less than 1. The 2D band FWHM was found to be 30 cm⁻¹

For confirmation of a few layers of graphene, a Raman scattering spectrum can serve as a fingerprint to measure the number of thin graphene layers [13-17]. Raman G and 2D peaks (around 1580 and 2700 cm⁻¹, respectively) are shifted depending on the number of layers of graphene. The relative intensity ratio of the G band and 2D band, IG/I_{2D}, also signifies the number of layers of graphene. A ratio of less than 1 indicates only a few layers of graphene. And the FWHM of the 2D peak is used to determine single (30 cm⁻¹) or multi-layer (60 cm⁻¹) [17, 18].



AFM images for the placed graphene (left). Two sites corresponding to the corner and side edges in the optical image (right) were investigated by AFM scanning. Green and white dotted lines in the AFM image are indicators for boundaries of graphene and SiO₂.

The conventional method of obtaining atomic resolution of graphene is scanning tunneling microscope (STM) [19, 20] or atomic force microscope (AFM). AFM provides height profiles which can be used to determine the number of atomic layers. In this study, we utilized Raman (Thermo Electron Almega XR at 532 nm excitation wavelength) and AFM (Veeco Nanoscope III) to confirm the thickness or the number of layer of the placed graphene on SiO₂. Raman spectrum showed the placed graphene was SLG (figure 9). The G and 2D peaks were shifted from 1580 and 2700 cm⁻¹ (which are peak positions in HOPG) and the intensity ratio between IG and I2D was greatly reduced to much less than 1. The 2D band FWHM was found to be 30 cm⁻¹. This indicated that the placed graphene had one single layer (more than 2 layers graphene shows ~60 cm⁻¹). AFM results showed the height of the placed graphene were 0.313 and 0.329 nm measured respectively at one corner and side edge (figure 10). Since SLG has around 0.34 nm thickness, the resultant height profiles were close to a single layer. From the Raman and AFM analyses, we found that the placed graphene was indeed SLG.

IV. CONCLUSION

In this study we demonstrate an exfoliation technique with a top-down approach which was able to acquire single layered graphene. HOPG mesas patterned with RIE were used as a host graphitic thin layer provider. In room temperature atmosphere environment with a micropipette and a highly precision nano-stage, relatively large area (20 x 20 μm²) graphene was successfully obtained. Even though repeatability of obtaining graphene with the same condition was not sustained, well-defined and large area MLG and FLG were continuously obtained by this approach with high yield. This result demonstrates that highly pure and controllable sized and patterned graphene can be obtained via a mechanically controllable way.

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