



저작자표시-비영리-변경금지 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

- 이 저작물을 복제, 배포, 전송, 전시, 공연 및 방송할 수 있습니다.

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



변경금지. 귀하는 이 저작물을 개작, 변형 또는 가공할 수 없습니다.

- 귀하는, 이 저작물의 재이용이나 배포의 경우, 이 저작물에 적용된 이용허락조건을 명확하게 나타내어야 합니다.
- 저작권자로부터 별도의 허가를 받으면 이러한 조건들은 적용되지 않습니다.

저작권법에 따른 이용자의 권리는 위의 내용에 의하여 영향을 받지 않습니다.

이것은 [이용허락규약\(Legal Code\)](#)을 이해하기 쉽게 요약한 것입니다.

[Disclaimer](#)

공학석사 학위논문

**Completely dry transfer printing of
graphene for organic electronic devices**

유기전자소자에 응용하기 위한 그래핀의 건식전사
공정에 대한 연구

2014년 8월

서울대학교 대학원

융합과학부 나노융합전공

차민정

Abstract

Completely dry transfer printing of graphene for organic electronic device

Minjeong Cha

Program in Nano Science and Technology

Department of Transdisciplinary Studies

Seoul National University

Despite extensive research on using graphene as transparent electrodes, its application to organic electronic devices has been rather limited. In the most commonly used fabrication technique, graphene-polymer stack floating on water is transferred onto a target substrate, and the polymer layer is subsequently removed by an organic solvent. As a result, in most previous applications, graphene has been deposited on a substrate before organic layer depositions, and it has been used mostly as a bottom electrode. Furthermore, when one works with wet chemicals that are known not to damage a given organic material, patterning of the graphene on the organic layer is likely to involve chemical and/or physical processes that may adversely affect the electrical and/or optical properties of the underlying

organic layer.

Here, we describe a completely dry technique capable of transfer printing a graphene monolayer onto an organic layer. In this process, a CVD-grown graphene monolayer is first transferred onto a PDMS stamp by scooping a graphene-support layer stack floating on a liquid with the PDMS stamp, following the conventional wet-transfer process except two important differences. First, we decrease the surface tension of the liquid by mixing ethanol and water. This enhances the wetting of the hydrophobic PDMS surface by the liquid, which is crucial to obtain a graphene monolayer with a low defect density on the PDMS stamp. Second, as a support layer deposited on graphene on a copper foil, we use a thin film of gold as opposed to commonly used polymers, such as PMMA and polystyrene. This allows us to use an aqueous chemical to remove the support layer, and hence prevents the swelling of PDMS, which would severely degrade the quality of the graphene monolayer on the PDMS stamp.

We discuss the effects of the surface tension of the liquid on the quality of a graphene monolayer transferred on an organic material commonly used in organic electronic devices, such as PEDOT:PSS, PVP and ZnPc.

Keywords: graphene, dry transfer, organic materials, transfer printing, organic electronics

Student Number: 2012-22454

Contents

Abstract	i
Contents	iii
List of figures and tables	v
1. Introduction	1
2. Theory	7
2.1 Graphene transfer methods	7
2.2 Sheet resistance measurement	14
2.3 Raman spectroscopy	25
3. Experimental Methods	29
3.1 Dry transfer of monolayer graphene	29
3.2 Patterning of graphene and aligned stamping	
3	1

3.3 Characterization of transferred graphene	6
3	
4. Results and Discussion	38
4.1 Transfer of monolayer graphene onto substrates via three methods	38
4.2 Patterning of monolayer graphene and dry transfer it onto substrates	49
4.3 Dry transfer of patterned graphene onto organic materials	6
5	
5. Conclusion	63
Reference	66
초록(국문)	69

List of figures and tables

Figure 1.1	Limitation of conventional method for graphene onto the organic layers	3
Figure 2.1	Conventional graphene transfer process.....	12
Figure 2.2	Sheet resistance of the sample that is composed of several squares ..	16
Figure 2.3	The two point probe and four point probe method.....	19
Figure 2.4	Sheet resistance measurement using linear four point probe method.....	22
Figure 2.5	Sheet resistance measurement using van der Pauw method.....	24
Figure 2.6	Correction factor function in van der Pauw method.....	24
Figure 2.7	Schematics of Rayleigh, Stokes Raman, and Anti-Stokes Raman scattering	26
Figure 2.8	Evolution of the Raman spectrum with the number of graphene layers respectively	28
Figure 3.1	Patterns for stamping graphene in well alignment with the substrates	33
Figure 3.2	Alignment stamping setup design	34

Figure 3.3	The stamping setup mated to the mask aligner.....	35
Figure 4.1	Key factor of graphene conventional graphene transfer method.....	42
Figure 4.2	Surface tension of water-ethanol mixtures according to the volume ratio of them.....	43
Figure 4.3	Schematic of graphene transfer method using gold and ethanol-water mixtures	43
Figure 4.4	The transferred graphene monolayer on the glass substrates	45
Figure 4.5	Transmittance of transferred graphene via three different methods ..	46
Figure 4.6	Sheer resistance measurement using van der Pauw method.....	47
Figure 4.7	Raman spectrum of monolayer graphene on 285 nm SiO ₂ /Si wafer ..	48
Figure 4.8	Patterning of graphene using gold pattern	51
Figure 4.9	Transfer of graphene pattern in alignment with the substrates	54
Figure 4.10	Sheet resistance measurement using patterned graphene.....	55
Figure 4.11	Edge on and face on ZnPc	58
Figure 4.12	Transferred graphene onto the face on ZnPc layer	58
Figure 4.13	Raman spectrum of graphene on face-on ZnPc layer.	59
Figure 4.14	Graphene monolayer on PEDOT : PSS	61
Figure 4.15	Graphene monolayer on PVP	62

Table 1.	Transmittance at 550nm of transferred graphene via four different methods	46
Table 2.	Sheet resistance data of transferred graphene via four different methods	47

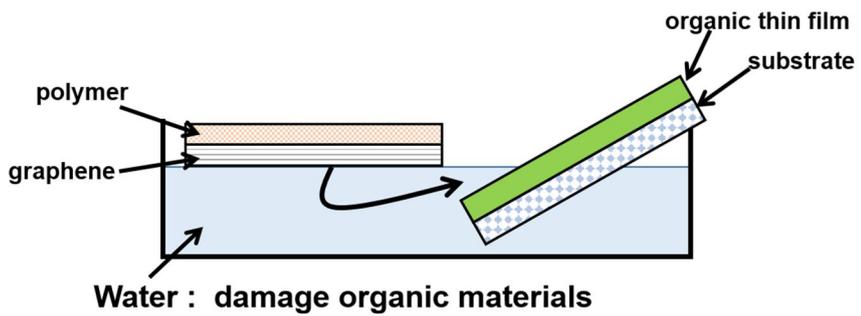
1. Introduction

Graphene is a crystalline allotrope of carbon with two-dimensional structure. In graphene, sp²-bonded carbon atoms are densely packed in a honeycomb crystal lattice. Graphene can carry 1,000 times the electrical current of copper wire and 100 times faster than single crystalline silicon. Besides, graphene has high thermal conductivity, mechanical strength, chemical resistance, flexibility and transparency. These properties enable graphene to be applicable to flexible and transparent electrodes, energy electrode materials, heat transport materials, bio materials, and so on. Especially, the development of the CVD (chemical vapor deposition) method that succeeded in growing larger than 30 inch mono-layer graphene on copper foil has made graphene research more diverse [1].

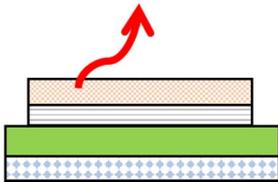
In order to apply graphene to various research fields, graphene on copper foil should be patterned and transferred to particular substrates. The most widely used process to date is based on polymer supported etching and transfer. In this process, graphene monolayer firstly is coated by thick film of PMMA (poly(methyl methacrylate)), which provides mechanical support for the graphene when copper foil is etched away. Then floating graphene / polymer stack is scooped up with target substrates and finally polymer film is removed by organic solvents, such as acetone [2]. However, in this transfer method, the target substrates are exposed to

water and organic solvents which limits the types target substrate. For example, if a graphene layer is transferred onto an organic thin film through this method, the water and the organic solvent, used in this process, would damage the organic materials under the graphene layer as shown in Figure 1.1.

Transfer graphene onto organic thin films



Removed by an organic solvent



: Dissolve organic thin films



Figure 1.1 Limitation of conventional method for transferring graphene onto the substrates that are vulnerable to wet environment and organic solvents.

Therefore, the substrates should be stable to wet environment and organic solvents. As a results, formal studies have shown that a graphene monolayer has not been transferred onto various substrates and mainly transferred onto SiO₂ / Si and glass substrates.

Also, in graphene patterning process, a graphene monolayer has been transferred onto a target substrate prior to forming photoresist pattern through photolithography method. Subsequently, areas that are not covered by photoresist pattern is removed by O₂ RIE (reactive ion etching) process. This patterning method also limits the types of target substrate because it is inevitable to use organic solvents during developing and removing photoresists.

Therefore, it is necessary to develop new graphene patterning and transfer methods in order to transfer patterned large area graphene onto different substrates for example, organic thin films, which are vulnerable to organic solvents. Until now, there have been various attempts to transfer monolayer graphene onto organic thin films. Firstly, a PDMS (polydimethylsiloxane) stamp has been used. PDMS has a low Young's modulus of less than 3 MPa, which enhances conformal contact between a PDMS stamp and a substrate. Furthermore, its low surface energy less than 20 mJ/m² helps to be separated from transferring materials well [3]. In the transferring method using a PDMS stamp, a cross-linked PDMS stamp is attached

to graphene grown on copper or nickel substrates and used as a supporting layer of graphene when growing substrates are etched away. Subsequently, graphene monolayer on the PDMS stamp is transfer printed onto a target substrate. In contrast to method using spin casted polymer, it is possible to transfer graphene monolayer on a PDMS stamp onto target substrates through a dry process and thus it enables to place graphene onto organic thin films. Despite this advantages, the use of the PDMS stamp is limited by the non-conformal contact with the graphene surface because of roughness of growing metal substrates. Consequently, it is hard to put monolayer graphene with low defect density on a PDMS stamp.

In the second place, graphene on copper foil is spin casted by self-released polymer and the polymer film is removed by orthogonal solvents lastly. To be specific, in this process, a PDMS block is attached to the polymer film followed by spin casting of it on graphene on copper foil to make it more convenient of handling. The PDMS / polymer / graphene stack is picked and placed on the destination substrate after the copper foil is etched away. Finally, the PDMS block is peeled off and self-released polymer is removed by orthogonal solvents which do not damage the destination substrate. This method is available only when sacrificial layer is dissolved in orthogonal solvents that is not harmful to the substrates. However, it is hard to find proper orthogonal solvents matching particular substrates and although it is possible to ensure that the solvent used for removing

polymer supporting layer does not dissolve the underlying layer, the solvent effect cannot be eliminated entirely [4].

In this thesis, a new method which enables monolayer graphene and graphene patterns to be transferred onto arbitrary substrate through dry transfer printing will be described. Toward this end, a graphene layer is placed on a PDMS stamp firstly and transfer printed onto various organic semiconductor thin films. As well as, graphene patterning and transfer method which is totally different from conventional photolithography methods will be discussed. This method allow us to transfer graphene patterns onto the desired position of the arbitrary substrates, such as organic thin films. Therefore, this study could be applied as a core technology for the realization of various graphene based organic, inorganic devices.

2. Theory

2.1 Graphene transfer methods

2.1.1 Mechanical exfoliation

The very first graphene layer was obtained by exfoliating a piece of highly oriented pyrolytic graphite (HOPG) with Scotch tape. Since HOPG graphite is composed of three-dimensional graphene structure, it is necessary to peel the graphite layers repeatedly and a single-layer and few-layer graphene flakes are yielded in the end [5]. Otherwise, graphene monolayer can be separated from HOPG by using AFM (atomic force microscope) tip [6]. These graphene pieces obtained from HOPG are isolated from natural graphite rather than made by chemical synthesis. They are high quality and have well-ordered crystal structure. They have electron mobility of $2.5 \times 10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature, Young's modulus of 1 TPa, and thermal conductivity of $3,000 \text{ W mK}^{-1}$ [7]. However, this exfoliating method limits the size of graphene flakes to a few micrometers and it is difficult to gain large areas of monolayer graphene flakes, which has rendered the existing mechanical exfoliation process highly empirical. Moreover, exfoliated graphene flakes are not controllable in their shapes and

position on substrates, which makes it hard to fabricate various devices using them.

There is another method of mechanical separation of graphene except exfoliation of a graphene sheet from HOPG, where the graphene is synthesized on transition metal substrates, such as copper and nickel by CVD process. The greatest advantage of mechanical separation of graphene is that chemical etching can be avoided. The most widely used etchants of copper and nickel, including iron chloride and ammonium persulfate, are harmful for the environment or expensive to dispose. In addition, formal research has shown the unwanted chemical doping effect and degradation of graphene by these chemical etchants. As a result, excluding etching process seems reasonable if it is possible and there are several preceding research. For example, E. H. Lock et al reported the method that allows graphene on copper foil to be detached from its growth substrate by a covalent bonding force of linker molecules and graphene [8]. The linker molecule, N-ethylamino-4-azidotetra-fluorobenzoate (TFPA-NH₂) could make strong covalent carbene bond with graphene surface and this bonding force is much stronger than adhesion between graphene and copper foil. Also, another method was demonstrated by Yoon et al. They used a thin layer of epoxy to separate graphene from copper foil [9]. Although these have merits as etch-free processes, they need extra steps for removing linker molecules or epoxy film.

2.1.2 Polymer supported etching and transfer

Graphene can be synthesized by CVD process using catalytic action of copper or nickel. The metal substrates that graphene is grown on is only needed for catalytic purpose and is superfluous after the synthesis is completed so the metal should be removed after the growth step. Copper and nickel growing substrates can be etched away in iron nitrate, iron chloride or ammonium persulfate aqueous solution, but cannot be etched without the supporting layers. This is because ultrathin graphene tend to get ruffled and torn when they float in liquid surface independently. As supporting layer of graphene, polymer thin films such as PDMS (polydimethylsiloxane), PMMA (poly(methyl methacrylate)), PS (polystyrene), and TRT (thermal release tape) have been widely used.

First, PDMS is undoubtedly the most generally used material for soft lithography because of its properties of moldability, durability, low surface energy, and so on. Due to the low adhesion force between PDMS and substrates, when transferring materials get reach the substrate, they prefer to adhere to the substrate rather than the PDMS. Similarly, graphene monolayer can be transferred to a target substrate by the PDMS. Graphene grown on metal substrates is attached to the PDMS and the PDMS support the graphene sheet when metal substrates are etched away. Since the PDMS is quite thick, it is easy to handle the graphene and the

PDMS stack. After the etching, graphene get released from the PDMS and stamped onto the substrate through the dry process. Despite this method seems easy and could be done by dry process, it is hard to make perfect conformal contact between the graphene and the PDMS. Because the severe roughness of metal surfaces that graphene is grown on and extremely low surface energy of the PDMS hinder the good contact between graphene and the PDMS and make air gaps between them. Therefore, the quality of transferred graphene on a substrate by this method is very poor [10]. To solve this problem, Hansun Kim et al. coated DMSO (dimethyl sulfoxide) on PDMS to enhance adhesion force between graphene and the PDMS and stamped graphene onto a target substrate but some unwanted chemicals left on graphene has been still unsolved [11].

PMMA is also widely used polymer for supporting CVD graphene when it is transferred to a substrate. PMMA can be easily coated on graphene grown on metal substrates and moved to target substrates, thus the PMMA transfer method is the most conventionally used way of transferring CVD grown graphene. The method is fairly simple; PMMA dissolved in chlorobenzene is spin casted on graphene on its growth metal, the metal is then etched to release the graphene / PMMA on water surface and it is scooped up on a destination substrate, usually glass or SiO₂/Si wafer. Finally, the PMMA layer is removed by acetone and graphene on the substrate is washed and dried. The transfer process using PMMA as the supporting

layer is described in Figure 2.1 [12]. However, this PMMA-based transfer technique has some drawbacks; 1) the complete removal of PMMA residues is difficult, and 2) most flexible substrates including organic materials and polymer films such as PET dissolve in acetone or cannot resist the annealing temperature up to 200 °C. PMMA residues on a graphene layer especially tend to have a p-doping effect on graphene and cause carrier scattering effect. This can degrade the electrical and physical characteristic of pristine graphene [13]. In addition, PMMA residues on graphene surface can influenced on molecular orientations of the upper layer which is deposited on the graphene since polymer residues hinder $\pi - \pi$ interaction between the graphene and molecules [14].

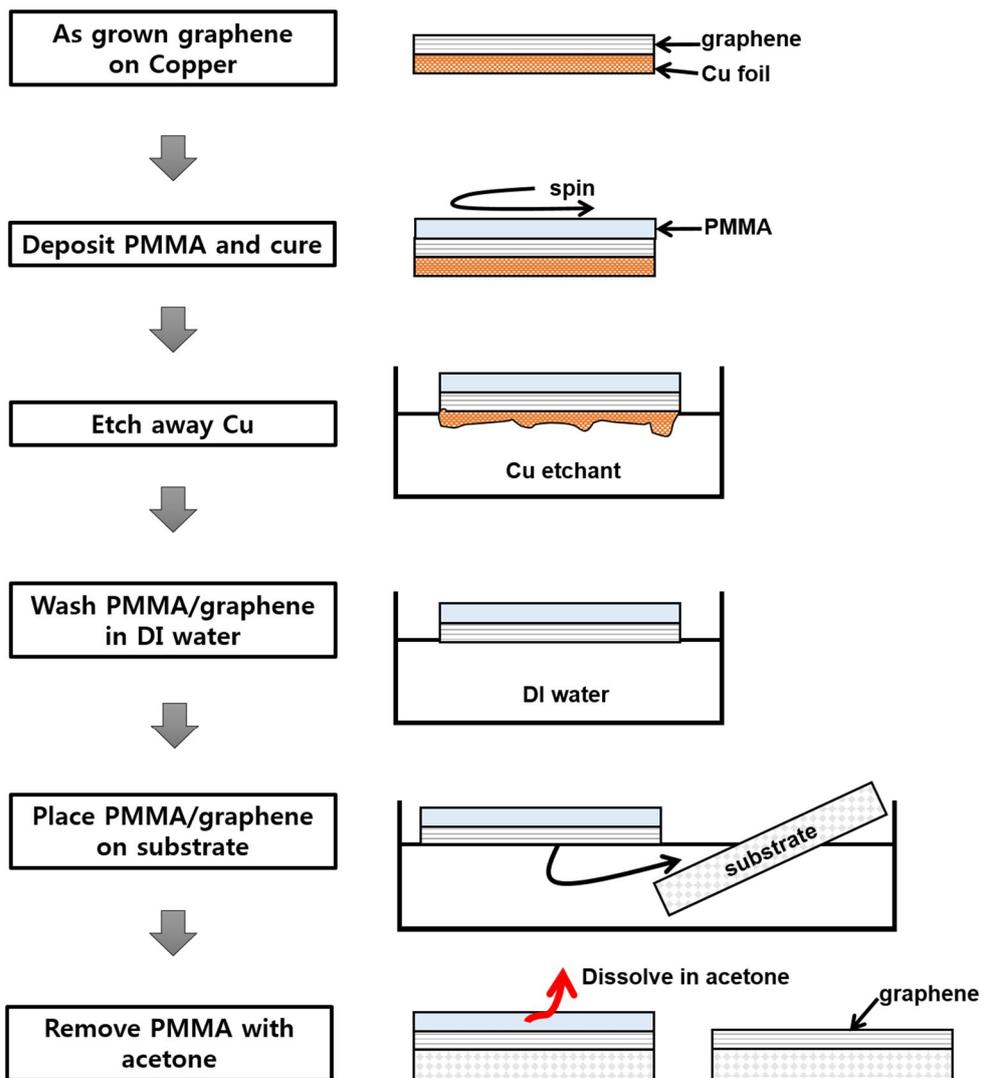


Figure 2.1 Conventional graphene transfer process using a PMMA layer as the supporting layer.

Also thermal release tape can be used as an alternative supporting layer of graphene. Thermal release tape has a special properties that it lose its adhesive strength when it is heated. Using this, graphene on growing metal is attached to the tape and metal is etched away. Afterward the graphene / thermal release tape stack is transferred onto a target substrate and heated over 100°C to release the tape. Thermal release tape is not simply a supporting layer of graphene, but its real advantage is that it can be applied to roll-to-roll transfer of graphene. The process can be scalable easily and allows continuous and mass production of materials thus bring graphene research one step closer to industrial application [15, 16]. Despite its advantages, intimate contact between graphene and thermal release tape and remaining residue after removing the tape are still challenging.

2.1.3 Transfer of graphene onto organic layers

Up to now, there are a few attempt to transfer of graphene onto organic layers. For example, Jie Song et al reported the method for transferring graphene onto soft surfaces. In this article, they used PMMA, PS (polystyrene), PIB (poly(isobutylene)) etc. as supporting layers for monolayer graphene, and then attach the PDMS blocks on the polymer layer. They made the handle of graphene layer easy. After the copper foil was etched and the graphene/polymer supporting

layer could be moved to organic layers with the help of PDMS blocks. Finally the PDMS were detached and the polymer supporting layer on graphene should be removed by the orthogonal solvents that are not harmful to only the specific organic layer that graphene was transferred [4]. If there is no solvent that does not destroy the bottom organic layer, this method does not work. Therefore, it is hard to declare that this is the general method for transferring graphene onto soft surfaces.

Another research about water-free transfer method for CVD-grown graphene was reported by Hyun Ho Kim et al. They suggested the new scooping substrate, a sample holder with square hole, and the floated graphene/supporting polymer layer in water was scooped by it. After baking the graphene/polymer layer on the holder to remove the water, they were transferred to the soft substrate and attached to the substrate by nitrogen gas pressing. Finally the holder was peeled off and they did not remove the polymer supporting layer and used them as an encapsulation layer of graphene devices [17]. However, the left polymer layer limits post process that need to do on the transferred graphene onto the soft surface. Consequently, the water-free transfer method reported in this research is not really effective.

2.2 Sheet resistance measurement

Sheet resistance is resistance of thin films that have uniform thickness. Since a sheet can be considered as two-dimensional entity, sheet resistance implies that the

current is along the surface of the sheet, not perpendicular to it. Generally, resistance of three-dimensional conductor can be expressed as below equation [18]

$$R = \rho \frac{L}{A} = \rho \frac{L}{Wt}$$

(ρ is the resistivity, A is the cross –

sectional area which can be split into the width W and the sheet thickness t ,

L is the length)

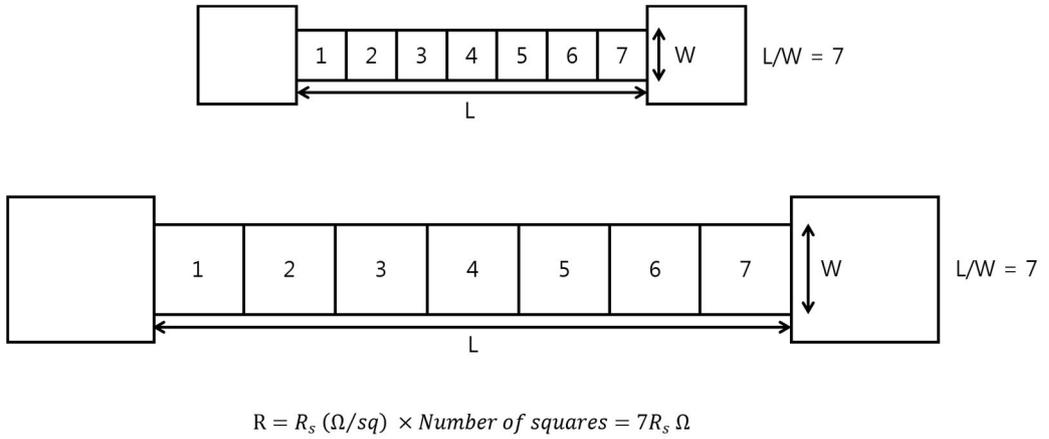
Combining resistivity with thickness, the following equation is obtained.

$$R = \frac{\rho L}{t W} = R_s \frac{L}{W} , \rho = R_s \cdot t$$

The unit of sheet resistance seems to be Ohm (Ω), which is $\Omega \cdot \text{cm}$, the unit of resistivity divided by cm , the unit of thickness. However, sheet resistance (R_s) is not the resistance of the test sample, it should be distinguished from the resistance of the sample, so use Ω/sq as its unique unit. The resistance of the test sample can be written as:

$$R = R_s \frac{L}{W} \text{ Ohms}$$

Also the test sample can sometimes be divided into several pieces of square as shown Figure 2.2 and in this case, the resistance is written as following equation.



$$R = R_s (\Omega/sq) \times \text{Number of squares} = 7R_s \Omega$$

Figure 2.2 Test samples that are composed of several squares and their sheet resistance [18].

2.2.1 Four – point probe method

Four-point probe method is the most generally used to measure the resistivity of semiconductor materials. It seems that two-point probe method is much easier way of measuring the resistivity since it need only two controllable tip, but even more difficult to analyze the measured data. Figure 2.3 represents two-point probe and four-point probe. Total resistance R_T in two-point probe system can be expressed as:

$$R_T = V/I = 2R_W + 2R_C + R_{DUT}$$

(R_W : resistance of lines or probes, R_C : contact resistance , R_{DUT} : resistance of device under test)

Resistance of device under test (R_{DUT}) can be determined by above equation but R_{DUT} cannot be found out according to the equation of R_T , so four-point probe method is proposed as a solution. In the four-point probe method, the current flows from one of the end of the probe to the other end of the probe as same way of two-point probe case. However, the voltage is measured by two additional contact and the contact sites is positioned between the both ends, which current source is injected. Although the probes where the voltage is measured include R_W and R_C , the current rarely flows between the voltage measured probes since the input

impedance of the voltmeter is very high. Accordingly, the measured voltage is considered as a voltage drop due to R_{DUT} and voltage drop due to R_W and R_C can be ignored. This is the principle of four-probe contact measurement, in other words, Kelvin measurement. Moreover, Wenner suggested a new four-point probe method where the distance between probes are all same, called Wenner's method. One probe system can be simply considered to derive the resistivity using Wenner's method [18].

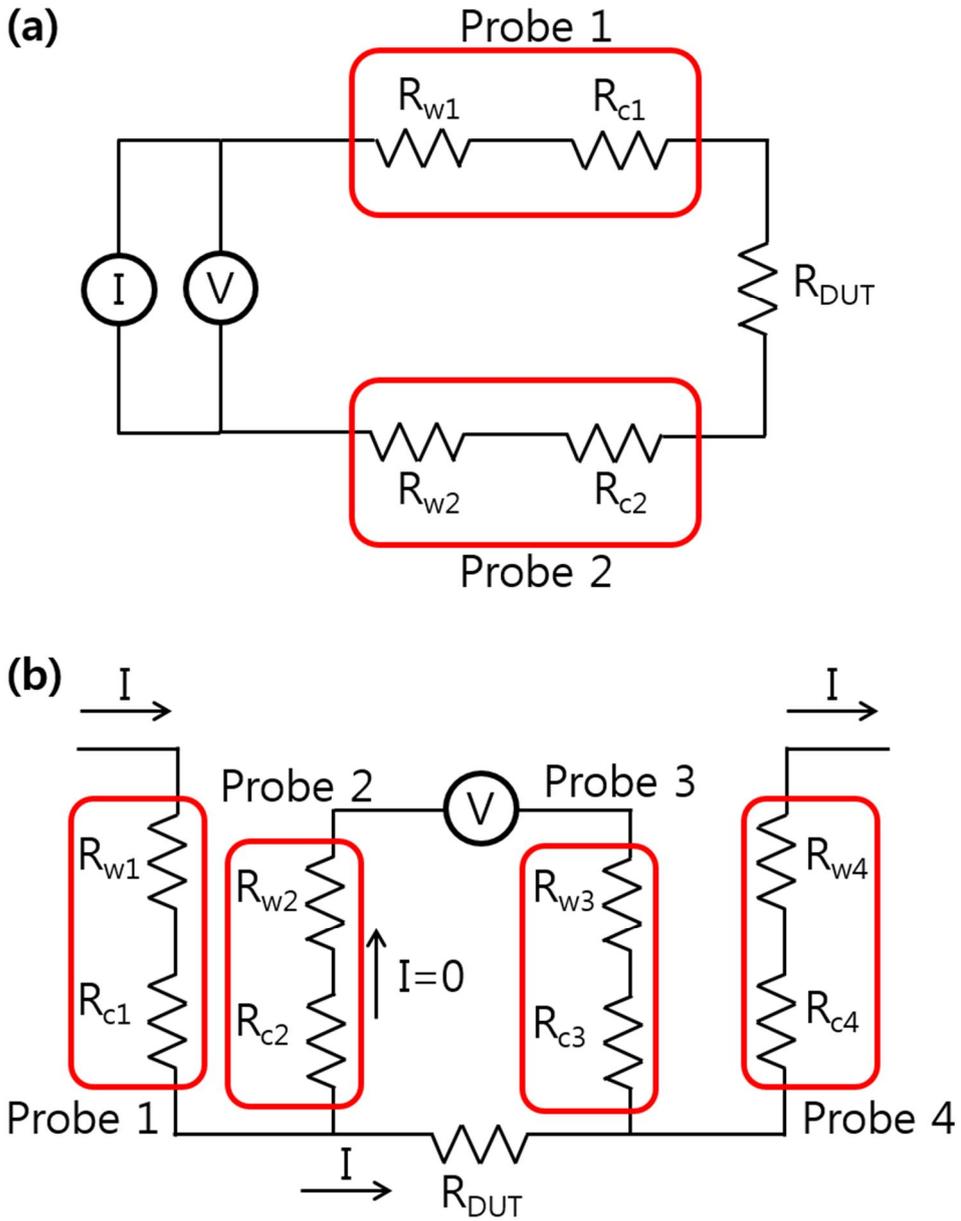


Figure 2.3 (a) The two point probe method and (b) the four point probe method, the voltage drop is depending on only the R_{DUT}

In this system, when a point is apart from a probe with the distance of 'r', the below relations are valid.

$$E = J\rho = -\frac{dV}{dr} ; J = \frac{I}{2\pi r^2}$$

$$\int_0^V dV = -\frac{I\rho}{2\pi} \int_0^r \frac{dr}{r^2} \Rightarrow V = \frac{I\rho}{2\pi r}$$

The voltage of second probe in Figure 2.4 can be written as in accordance of the formal relations :

$$V_2 = \frac{I\rho}{2\pi} \left(\frac{1}{s_1} - \frac{1}{s_2 + s_3} \right)$$

The voltage of third probe can be also written as :

$$V_3 = \frac{I\rho}{2\pi} \left(\frac{1}{s_1 + s_2} - \frac{1}{s_3} \right)$$

Therefore, the measured total voltage $V = V_{23} = V_2 - V_3$ is :

$$V = \frac{I\rho}{2\pi} \left(\frac{1}{s_1} - \frac{1}{s_2 + s_3} - \frac{1}{s_1 + s_2} + \frac{1}{s_3} \right)$$

In the case of $s = s_1 = s_2 = s_3$, the resistivity ρ can be expressed as :

$$\rho = 2\pi s \frac{V}{I}$$

Furthermore, if the correction factor is considered for very thin test sample, ρ

can be expressed as :

$$\rho = \frac{\pi}{\ln 2} t \frac{V}{I} = 4.532 t \frac{V}{I}$$

Also the sheet resistance R_s is [17] :

$$R_s = \frac{\rho}{t} = \frac{\pi}{\ln 2} \frac{V}{I} = 4.532 \frac{V}{I}$$

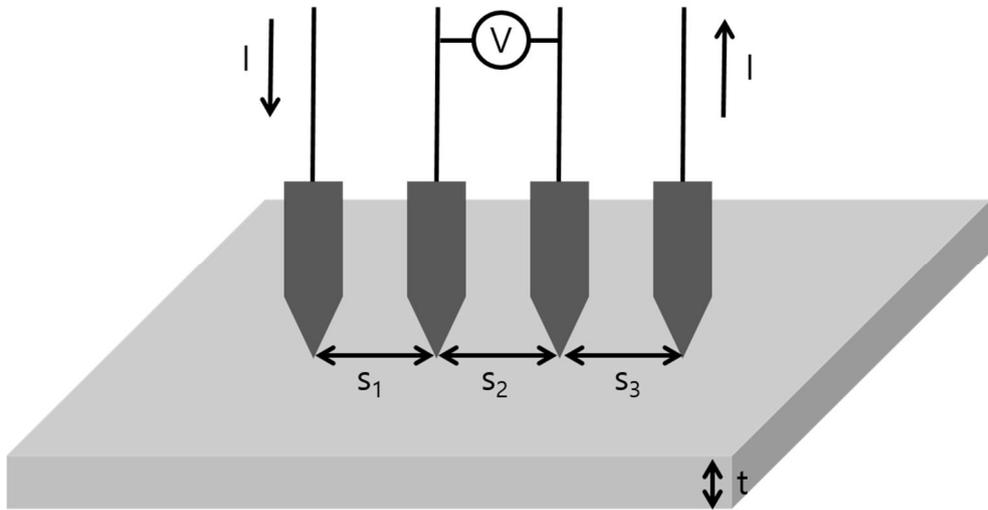


Figure 2.4 Sheet resistance measurement with the four point probe method when the probes are located linearly.

2.2.2 van der Pauw method

The sheet resistance of an arbitrary shaped sample can be measured through a method which is developed by van der Pauw, and the method called van der Pauw method. van der Pauw showed that the resistivity can be obtained if any sample that has flat surface satisfy the following conditions : 1) the contact sites are on the boundary of the sample, 2) contact sites are small enough, 3) the thickness of the sample is uniform, and 4) the surface of the sample is continuous and homogeneous.

As shown in Figure 2.5, there are four contact sites, A, B, C, and D, and the resistance R_A and R_B is defined as following equations.

$$R_{AB,CD} = \frac{V_{AB}}{I_{DC}} ; R_{BC,DA} = \frac{V_{AD}}{I_{BC}}$$

$$R_s = \frac{\pi}{\ln 2} \left(\frac{R_{AB,CD} + R_{BC,DA}}{2} \right) f \left(\frac{R_{AB,CD}}{R_{BC,DA}} \right)$$

Here, f is a function of $\frac{R_{AB,CD}}{R_{BC,DA}}$ and Figure 2.6 shows the relation between f and

$\frac{R_{AB,CD}}{R_{BC,DA}}$. If the contact length is less than 10% of the length of side, R_s can be

calculated very precisely [18, 19].

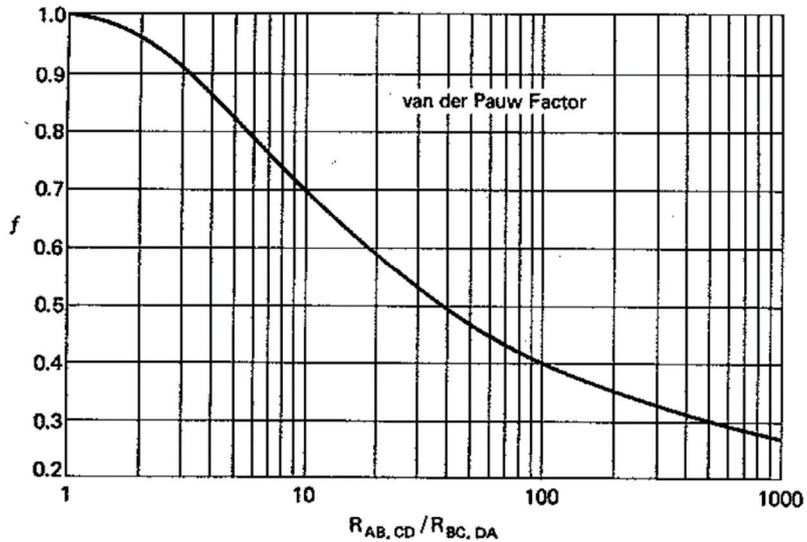
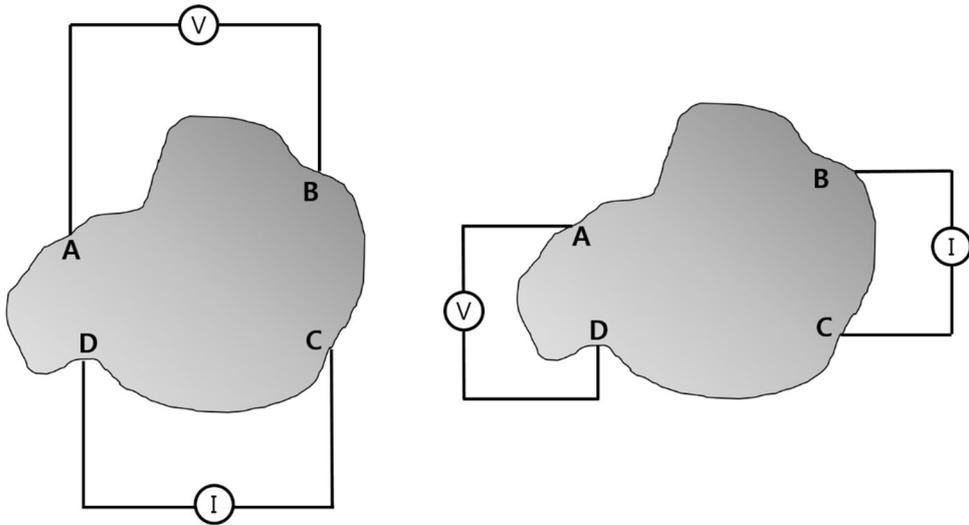


Figure 2.5 Sheet resistance measurement of an arbitrary shaped conductor sheet with the van der Pauw method

Figure 2.6 The correction function of the ratio $\frac{R_{AB,CD}}{R_{BC,DA}}$ in the van der Pauw method

[19]

2.3 Raman spectroscopy

Raman spectroscopy is a spectroscopic technique based on inelastic scattering of monochromatic light from a laser source. There are several mechanisms of light scattering when the light meets the surface. Scattered light induced by elastic interaction between incident light and the matter is called Rayleigh scattering, scattered light which is caused by interaction between incident light and acoustic phonon is Brillouin scattering, and lastly, interaction between incident light and optical phonon occurs Raman scattering. Raman spectroscopy is based on the Raman scattering effect which is reported by Raman in 1928. The Raman effect is originated from molecular deformations in electric field E determined by molecular polarizability α . The laser beam can be considered as an oscillating electromagnetic wave and this wave can be interact with the sample. The interaction between them includes electric dipole moment, $P = \alpha E$, which deforms molecules. Since the deformations are periodic, molecules vibrate with specific frequency. If incident photons from the laser beam apply energy to the lattice of matters in the form of phonons, the incident light scattered into the light with low energy and this phenomena is called Raman Stokes shifted scattering. On the other

hand, if photons absorb phonon and scattered as the light with high energy, this is Raman anti-stokes shift scattering. However, since Raman anti-stokes shifted scattering mode is much

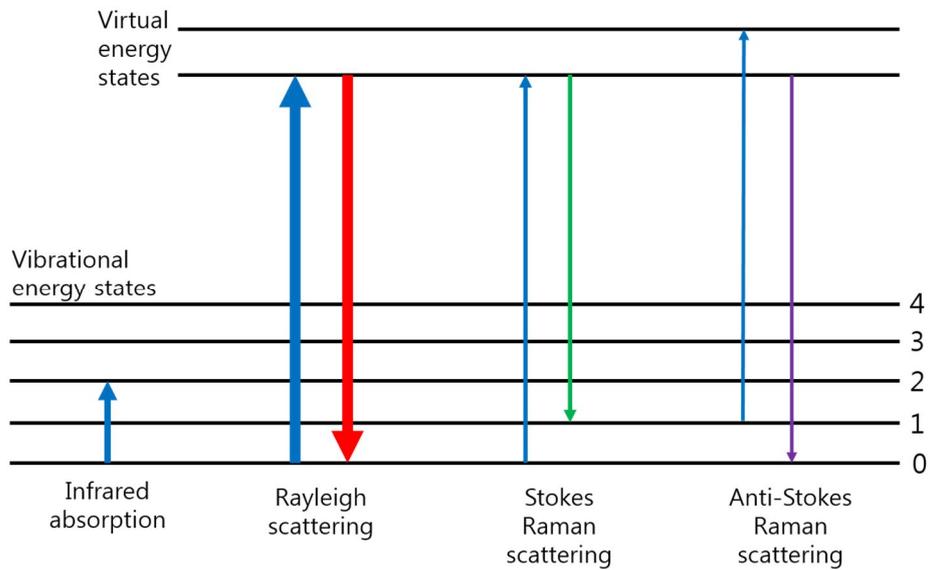
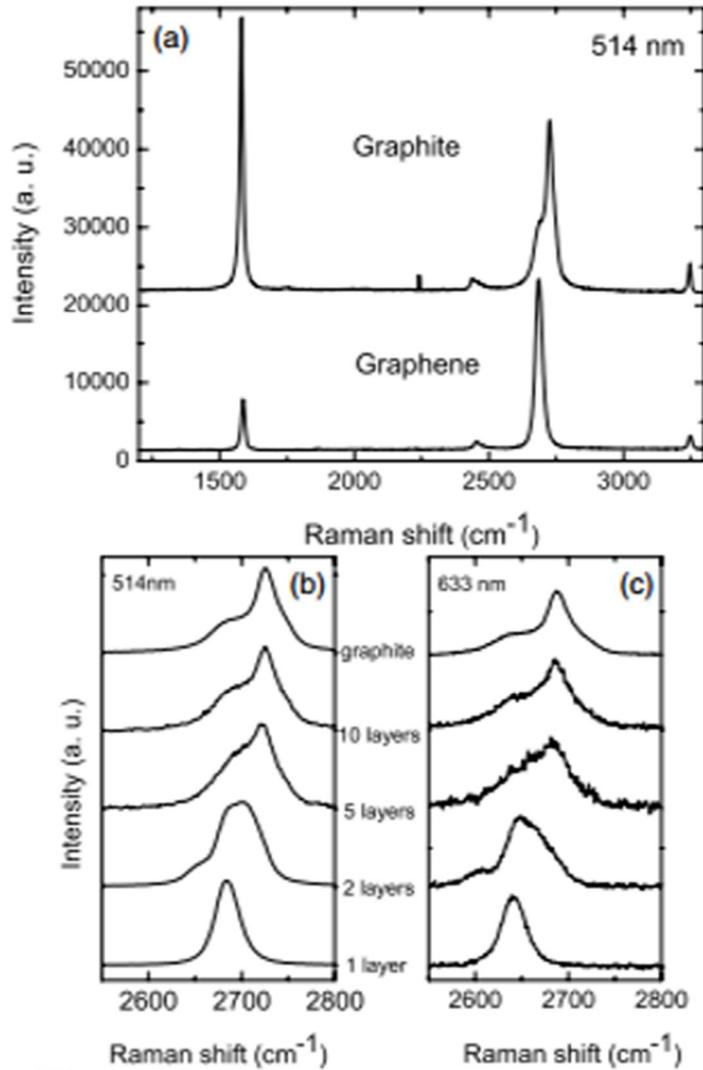


Figure 2.7 Schematic figure about Rayleigh scattering, Stokes Raman scattering, and Anti-Stokes Raman Scattering.

weaker than Raman Stokes shifted scattering mode, Stokes modes are observed in most cases [18].

In graphene, the Raman spectroscopy can be used as a fingerprint of graphene. The Stokes phonon energy shift of graphene occurred by laser excitation creates two main peaks in the Raman spectrum : G (1580 cm^{-1}), a primary in-plane vibrational mode, and 2D (2700 cm^{-1}), a second-order overtone of a different in plane vibration [20]. Otherwise, D (1350 cm^{-1}) peak appears when zone boundary phonon satisfies the Raman fundamental selection rule so it is not seen in the Raman spectrum of defect-free graphene. D and 2D peak positions are dependent on the laser excitation energy. The position cited here are from a 514nm excitation laser.

As the number of graphene layers increases, the spectrum of Raman shift changes from that of monolayer graphene. Since there are additional forces caused by the interaction between layers of stacked graphene, a splitting of the 2D peak is occurred and it can be divided into several modes that combined to make a wider, shorter, higher frequency peak [21]. The G peak also changes as the graphene



layers are stacked up. It moves to the direction of red shift and its intensity increases [22]. Therefore, the number of graphene can be derived from the ratio of peak intensity, I_{2D}/I_G , also the position and the shape of these peaks [21].

Figure 2.8 (a) Comparison of Raman spectra at 514 nm for graphite and graphene.

(b), (c) Evolution of the spectra at 514 nm and 633 nm with the number of graphene layers respectively [21]. (ref: Raman Spectrum of Graphene and Graphene Layers, PRL)

3. Experimental Methods

3.1 Dry transfer of monolayer graphene

Used monolayer graphene was grown on copper foil with thickness of 25 μm and bought from Graphene Supermarket or Graphene Square. First of all, 100 nm of gold was deposited with thermal evaporator mated to a glove box and load lock and the deposition process was proceeded in high vacuum below 5×10^{-7} Torr. The evaporating rate was 1 $\text{\AA}/\text{s}$ and the thickness and rate were controlled by gold crystal sensor. Graphene synthesized on the back side of the copper foil was etched by O_2 plasma treatment, at 300 W, for 20 minutes using YES-G1000 plasma cleaner. (Yield Engineering System, USA) A Copper foil / graphene / gold stack was floated in 0.1 M ammonium persulfate (Sigma-Aldrich, USA) aqueous solution in sequence to etch copper foil. After the copper foil was removed completely, graphene / gold stack was moved to a bath of DI-water and rinsed several times to eliminate etchant remainders and some impurities. The next step is

scooping the stack up on a hydrophobic PDMS stamp (Sylgard 184 kit, Dow Corning, USA). Toward this end, the graphene and gold stack was floated in a solution, a mixture of water and ethanol (water : ethanol = 3:7) and the stack was scooped up on the PDMS stamp. As soon as the stack was scooped on the PDMS stamp, spread liquid formed between the graphene and the PDMS stamp, thus the liquid had to be removed by nitrogen blow drying and then, the gold layer on graphene / PDMS stamp etched by dropping iodide aqueous solution (LAE 202, COWON SOLAR, Korea). To make the stamp clean, graphene on the PDMS stamp should be rinsed in DI-water several times and dried. The final step is transfer of graphene from the PDMS stamp to a target substrate. To achieve the high quality of transferred graphene on the substrate, the conformal contact between the stamp and the substrate was kept for more than one hour and the stamp was peeled off slowly followed by annealing at 100°C for 10 minutes. The PDMS stamp made using Sylgard 184 kit (Dow corning, USA), the kit is composed of liquid pre-polymer base and curing agent. To create PDMS stamps structure, liquid PDMS pre-polymer is mixed at a 10 : 1 weight ratio with curing agent and poured onto the master. The master was pattern free ITO substrates which were cleaned sequent with detergent, de-ionized water, acetone, and isopropyl alcohol, followed by basking at 200 °C in a vacuum oven. Afterward, the mixed liquid PDMS on the substrates were degassed in a vacuum chamber under 0.1 Torr for over 12 hours

and finally cured at 80 °C for more than 1 hour.

3.2 Patterning of graphene and aligned stamping

To create graphene patterns, 30 nm thick of gold was thermally deposited on graphene copper foil with desired pattern under high vacuum below 5×10^{-7} Torr. The evaporation rate was 1 Å/s and the gold pattern was made from the pattern of steel masks. Graphene area which did not cover with gold pattern and graphene grown backside of the copper foil were etched by Oxygen plasma treatment at 300 W, for 20 minutes using YES-G1000 plasma cleaner. Through this process, graphene pattern which was same as the shape of the gold pattern was created on the copper foil. Afterward, copper foil should be etched, but, parts of the pattern were disconnected on the copper foil, so for the connectivity of them, 100nm thick of gold was deposited again on the graphene and gold pattern on copper foil with the rate of 1 Å/s. In the next step, the copper foil/graphene pattern/gold stack were floated in 0.1 M ammonium persulfate solution and etched copper foil, in sequence, as explained 3.1, the patterned monolayer graphene and

gold stack was scooped with a PDMS stamp and etched gold followed by stamping the pattern onto a target substrate.

To transfer the graphene pattern on a PDMS stamp to the desired position on the target substrate, align marks as shown in Figure 3.1 (b) were formed in advance by thermal deposition of metal and the align mark of graphene on the stamp and that of the substrate was matched subsequently using MDA-400M mask aligner (MIDAS SYSTEM, Korea). Toward this end, an alignment setup that can be mated to the mask aligner was fabricated as shown in Figure 3.2 Since the PDMS stamp is transparent, graphene pattern on the below side of the stamp and align marks of the substrate could be watched and matched. After matching the align marks between graphene pattern and the substrate, the substrate stage was moved to upper position along the z axis to touch the stamp. The fabricated alignment setup mated to the mask aligner can be shown in Figure 3.3. The setup can be fixed in the mask fixing site in the mask aligner.

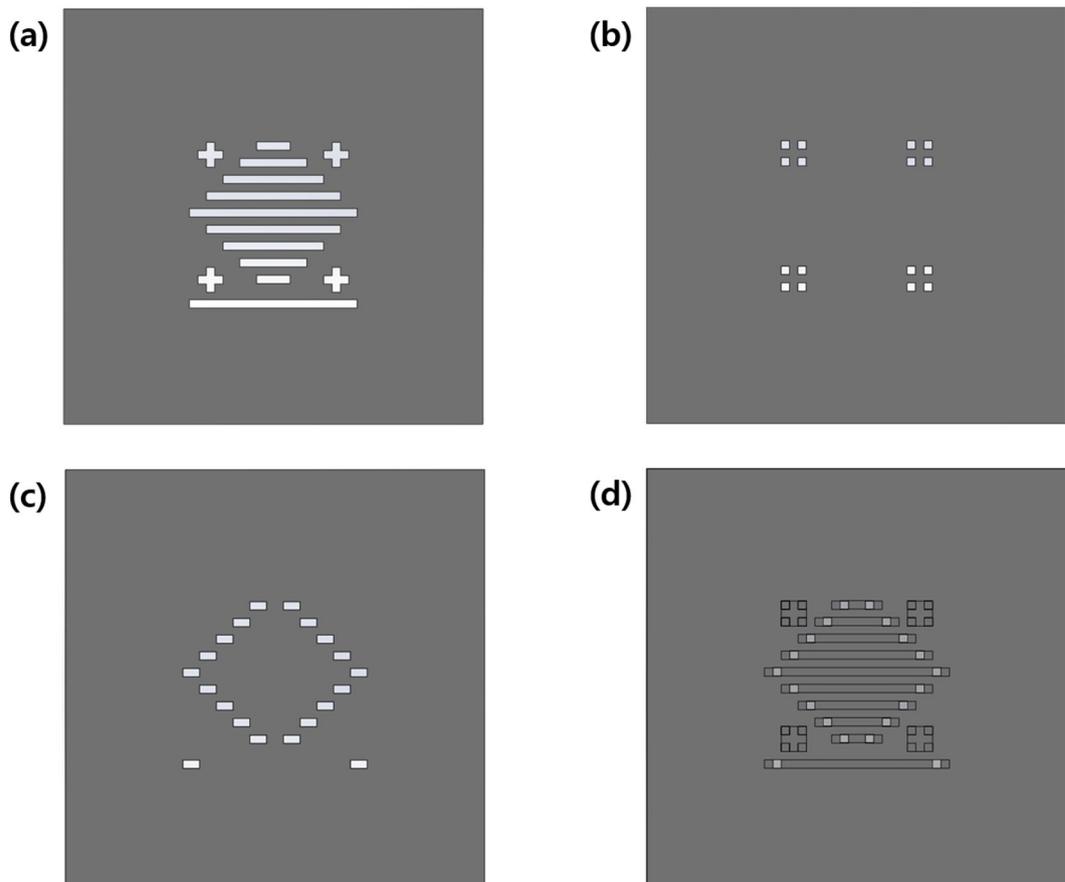


Figure 3.1 (a) A pattern for gold and graphene, and the four align marks are shown in the vertices. (b) An align mark pattern for the substrate. (c) A pattern for graphene contact and (d) the figure of completely aligned all three patterns.

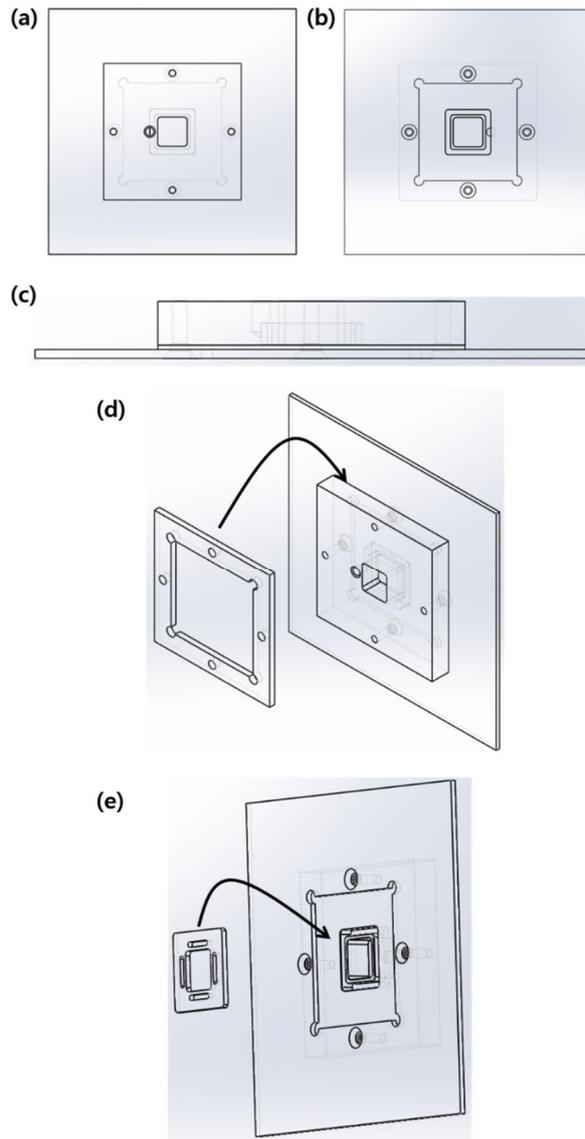


Figure 3.2 (a) The top view of the alignment setup (b) The bottom view of it, the stamp can be fixed at the center by vacuum. (c) The side view of it (d) if the stamp is thicker than 20 mm, a spacer can be inserted in the site that the arrow pointed and make room for the thick stamp. (e) On the other hand, if the stamp is thinner than 20 mm, the other spacer can be fixed in the site that the arrow pointed and fill the gap between the stamp and the substrate.

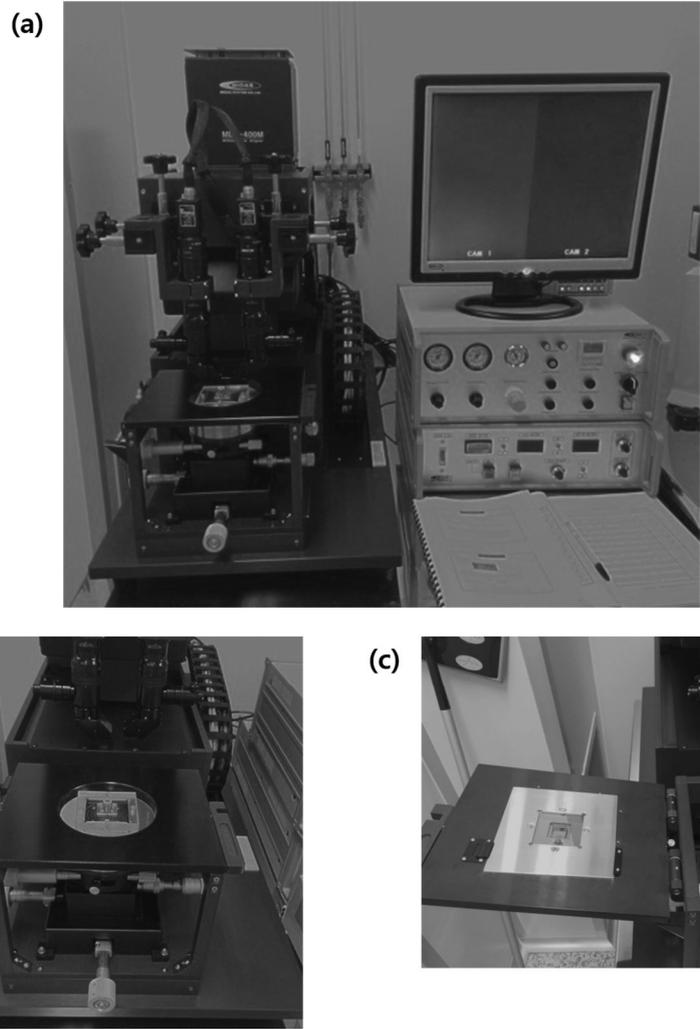


Figure 3.3 (a) The stamping setup mated to the mask aligner. (b), (c) The setup fixed in the mask fixing site of the mask aligner. The stamp is fixed to the set up, and the substrate stage can be moved to align with the mark of the stamp.

3.3 Characterization of transferred graphene

The surface of monolayer graphene placed on a PDMS stamp or a target substrate was observed by Olympus BX51 optical microscope (USA). The sheet resistance of monolayer graphene transferred onto substrates, such as a piece of glass and 285nm of SiO₂ / Si wafer was measured using van der Pauw method and also could be cross-checked by detecting the resistance of graphene patterns having different length. When the sheet resistance was measured by van der Pauw method, 1 mA of current was applied using Keithley 2400 source-meter (USA) between the two vertexes which are on the same side of the square and voltage drop between the other two points on the opposite side was measured by Agilent 34410A multi-meter (USA) and then, same measurement was proceeded with 90 degree rotation of the substrates. Furthermore, when the sheet resistance was measured using patterned graphene having different length, the patterned graphene was transferred onto the specific position of the substrate using self-fabricated stamping set-up, and then, to make contact the both ends of the graphene pattern, gold was thermally evaporated on the both ends edge with a steel mask which is precisely designed to work with the patterns beforehand. Afterward, the current-voltage characteristics of the graphene pattern were measured by Keithely 2400 source meter contacting the gold contact sites on both ends of the graphene with gold-wires.

The transmittance of the graphene was obtained using a PerkinElmer Lambda 35 UV/VIS Spectrometer (USA) within the wavelength of 420 nm to 800 nm, after the monolayer graphene was transferred onto a 0.63 mm thickness of BK7 glass substrate (AMG glass, Korea).

The analysis using Raman spectroscopy is performed using laser and light detection system. The laser used here was a LASOS LGK 7872 GL 514.5 nm Argon laser (Germany). The laser focused on the sample at normal incident to excite the sample and induce the Raman scattering. Since Raman scattering signal was too weak to detect, the Rayleigh scattering signal was filtered and only the Raman scattering signal was collected by an Olympus BX53F microscope lens (USA) at normal incidence and then detected using an Andor iDus DU401A CCD camera (UK) cooled to $-55\text{ }^{\circ}\text{C}$.

4. Results and Discussion

4.1 Transfer of monolayer graphene onto substrates via three methods

The most effective way of transferring monolayer graphene with dry process is to make stamps and transfer print the graphene sheet onto a target substrate using them. For this, proper stamp materials should be chose first and then, high quality of monolayer graphene could be placed on the stamps. As the stamp material, PDMS, the most widely used in soft-lithography field, has been chosen. Since PDMS has low Young's modulus below 3 MPa and low surface energy of 20 mJ/m², it does not need large pressure to transfer materials onto target substrate and also transferring materials can be easily separated from the PDMS stamp. Due to these properties, PDMS is undoubtedly the most proper as a stamp material for dry transfer printing of monolayer graphene.

In most previous research, a sheet of graphene has been placed on the PDMS stamp by attaching PDMS to graphene on its growing metal substrate and etching the metal. However, since the PDMS stamp adheres to the graphene only by van der Waals force, adhesive strength of the PDMS is insufficient to hold the graphene

on metal substrates completely. Also the roughness of metal substrates hinders the intimate contact between the graphene and the stamp, because of the roughness, some air gaps are made between them. Therefore, when the metal substrates are etched, the etchant permeates through the gap and destroy the quality of the graphene sheet. For this reason, the PDMS attaching methods is usually used for transfer of multi-layer graphene grown on nickel substrate and it is hard to make the high quality of monolayer graphene put on the PDMS stamp.

Another way for placing monolayer graphene on a PDMS stamp is to apply the polymer supported etching transfer method. In this process, floated graphene and polymer stack in water is scooped up with the PDMS stamp followed by etching copper foil in 0.1 M ammonium persulfate aqueous solution, but polymer layer coated on graphene, working as a supporting layer can be removed by organic solvents such as acetone, toluene and so on, and these solvents can swell the PDMS stamp, as a result, graphene monolayer on the stamp may be destroyed by the expansion of it. To prevent the swelling of the PDMS stamp during dissolving the supporting layer, it is necessary to find the supporting layer material which does not deform the stamp and the gold is used as the supporting layer of the graphene. Thin film of gold deposited on the monolayer graphene via thermal evaporation seems to work well as the supporting layer because it supports graphene to float in the water and dissolve in iodide aqueous solution that does not

make the PDMS swell. However, another problem come up. When floated gold / graphene stack in water is scooped up with the PDMS stamp, water droplets get trapped between the hydrophobic PDMS stamp and the graphene and gold. These droplets are hardly flowed out by nitrogen blow drying and finally they burst, destroying the graphene sheet either.

Generally a graphene layer covered with a supporting material is scooped by hydrophilic substrate including glasses after the graphene stack is floated in liquid and copper is etched. In this case, since the substrate is hydrophilic, the water can be spread between the graphene and the substrate and the spread water layer is easily flowed out by nitrogen blow drying as shown in Figure 4.1. In order to take advantage of this phenomenon, even if the hydrophobic PDMS stamp is used as the scooping substrate, the surface tension of the liquid should be controlled. The surface tension of water is 72 mN/m and that of ethanol is 22 mN/m, so the surface tension of liquid can be modulated by mixing them as shown in Figure 4.2. In this experiment, water and ethanol are mixed in volume ratio of 3:7 and the surface tension of the mixture becomes ~ 25 mN/m and it spreads well between the graphene and the PDMS stamp similar to the case of scooping graphene in water with a glass substrates. The Figure 4.3 shows the graphene transfer method flow through dry process using gold supporting layer, water and ethanol mixtures, and the PDMS stamp. In addition, Figure 4.4 represents the optical microscope image

of transferred monolayer graphene layers on the glasses via three transfer method;

- 1) attaching the PDMS stamp on the graphene on copper foil to support the graphene before etching copper foil
- 2) scooping the gold/graphene floated in water with a PDMS stamp after etching copper foil
- 3) scooping the gold/graphene floated in water-ethanol mixture with a PDMS stamp after etching copper foil.

As expected, the graphene transferred by the method 3) has the least defect among three. Also, as the graphene has less defect, the transmittance was more similar to the graphene transferred by conventional wet process, so the graphene transferred by the method 3) was 97.8%, it was different from the reference by only 2% as shown in Figure 4.5 and Table 1. Furthermore, the sheet resistance of that was the least among three dry transfer method, only the third sample has the sheet resistance of $\sim 1000 \Omega/\text{sq}$, less than $2000 \Omega/\text{sq}$. (Table 2). The sheet resistance is quiet large, but it was the smallest among the transferred graphene using the PDMS stamp [23], and the size of the graphene that sheet resistance was measured was quite large which is almost 1 cm^2 . Also, the stamping process may make the defect on the graphene. Figure 4.7 presents the Raman spectrum of transferred monolayer graphene via the method 3), there are G peak (1598 cm^{-1}) and 2D peak (2698 cm^{-1}).

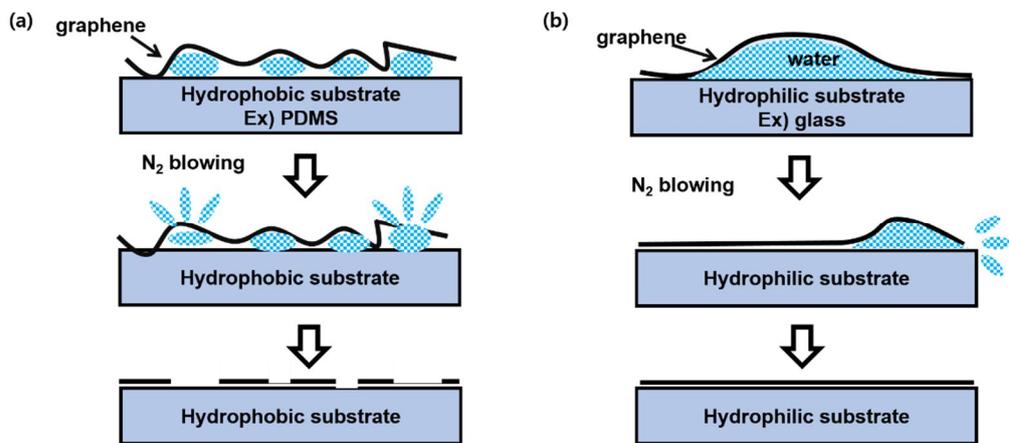


Figure 4.1 (a) If graphene floated in water is scooped with a hydrophobic substrate such as a PDMS stamp, some water droplets will be trapped between the graphene layer and the substrate, and the graphene gets destroyed by blow drying process. (b) If graphene floated in water is scooped with a hydrophilic substrate, water will be spread well between the graphene layer and the substrate, and the water can be removed easily by nitrogen blow drying.

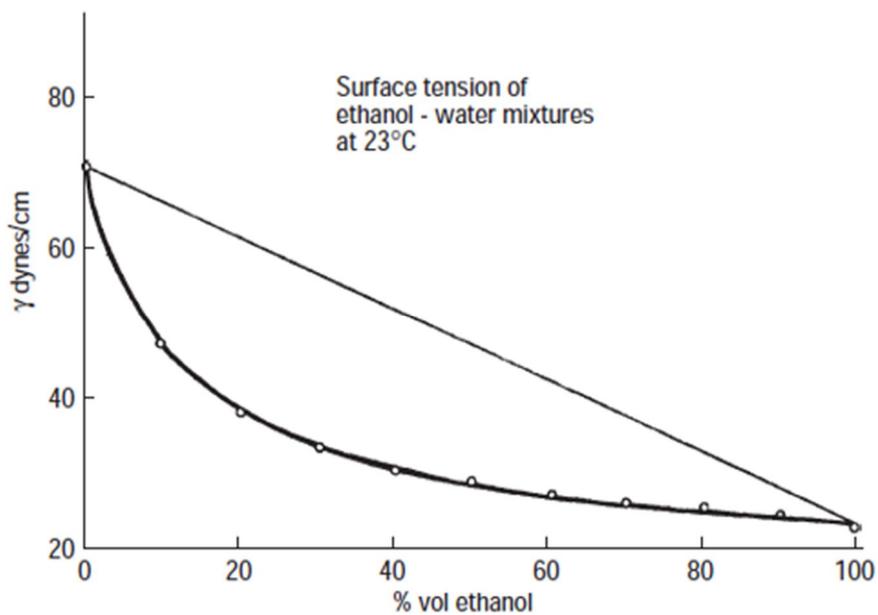


Figure 4.2 Surface tension of ethanol-water mixtures according to the volume ratio of two. dynes/cm is same as mN/m [24].

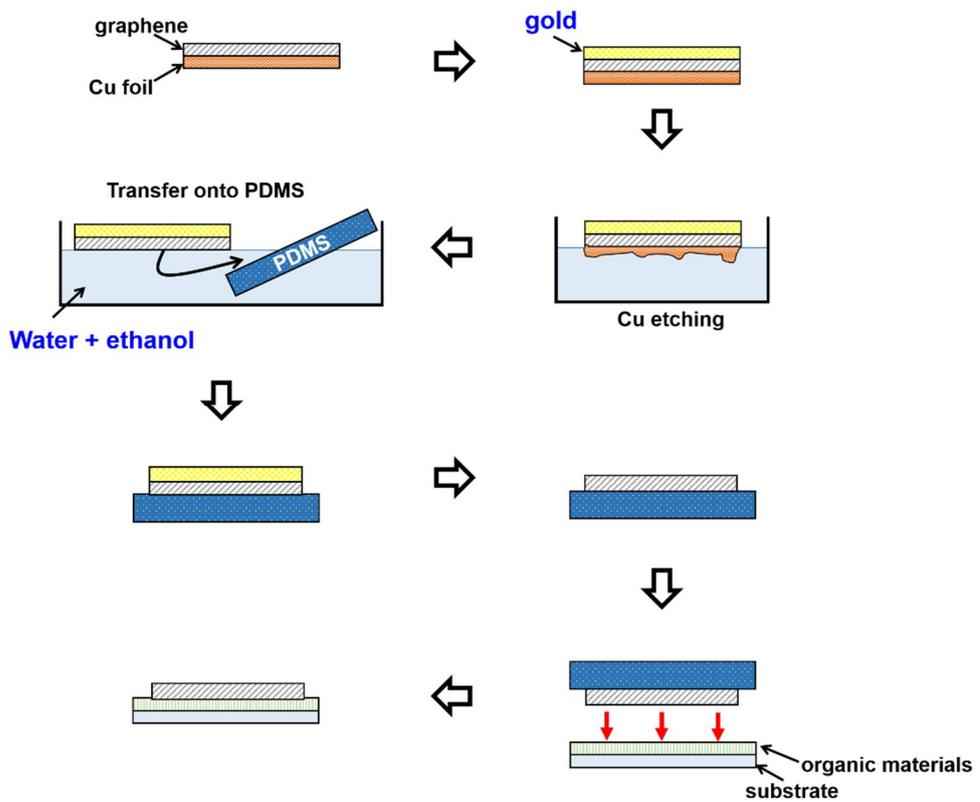


Figure 4.3 The graphene transfer method flow through dry process using gold supporting layer, water and ethanol mixture, and PDMS.

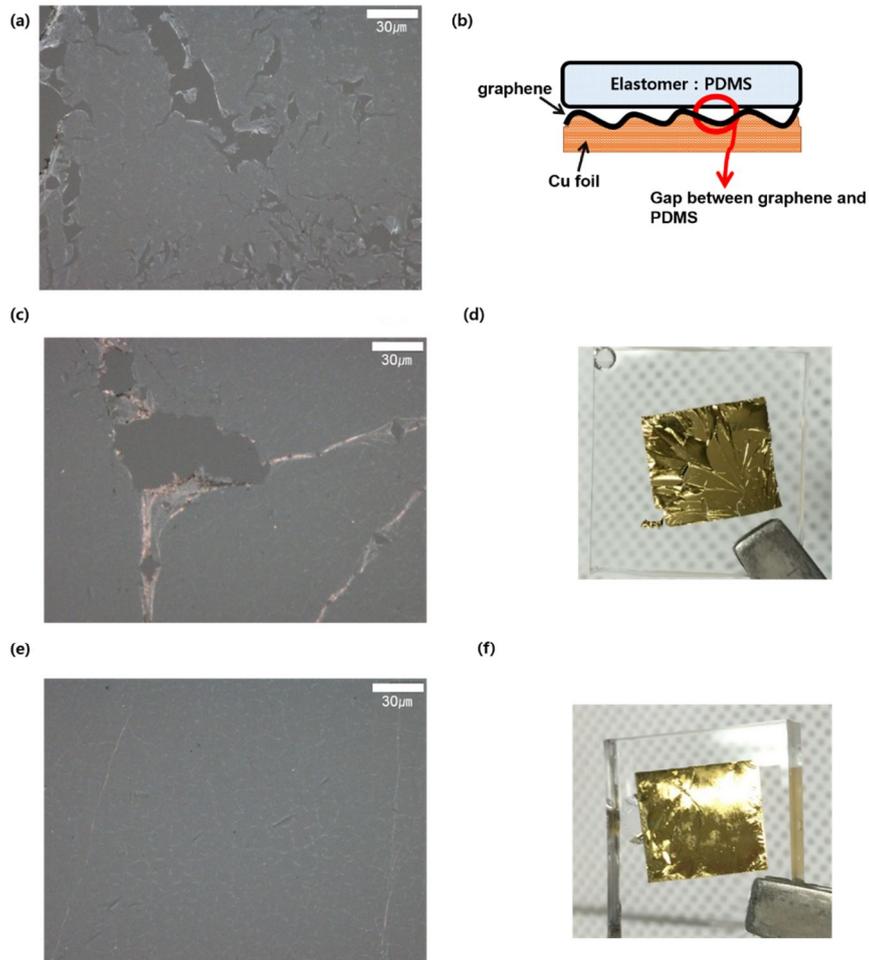


Figure 4.4 (a) The transferred monolayer graphene on the glass substrate using attaching PDMS stamp method (b) When the PDMS stamp was attached to the graphene on copper foil before the copper is etched, the stamp and the graphene cannot make an intimate conformal contact due to the gap between them and the gaps caused the crack on graphene after the transfer process. (c) The transferred monolayer graphene on the glass substrate by scooping the gold/graphene film with the PDMS stamp in water (d) some water trapped between graphene and the PDMS stamp and the trapped water is hardly removed and destroyed the graphene. (e) The transferred monolayer graphene on the glass substrate by scooping the gold/graphene film with the PDMS stamp in water-ethanol mixture (f) The water-ethanol mixture spread well between graphene and the hydrophobic PDMS stamp and this make the liquid removed easily.

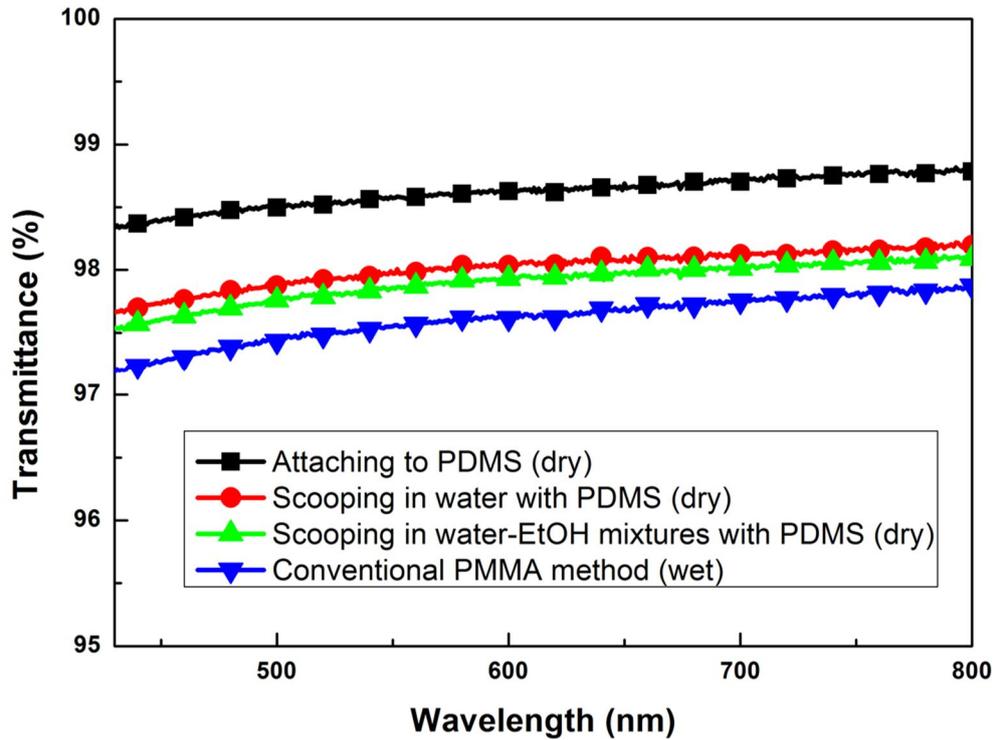


Figure 4.5 The transmittance of transferred graphene monolayers on glass substrates, according to the transfer methods

Sample	Transmittance at 550 nm
PMMA	97.6 %
PDMS attach	98.6 %
Water	98.0 %
Water - Ethanol	97.8 %

Table 1 The transmittance of transferred graphene monolayers on glass substrates at 550 nm, according to the transfer methods

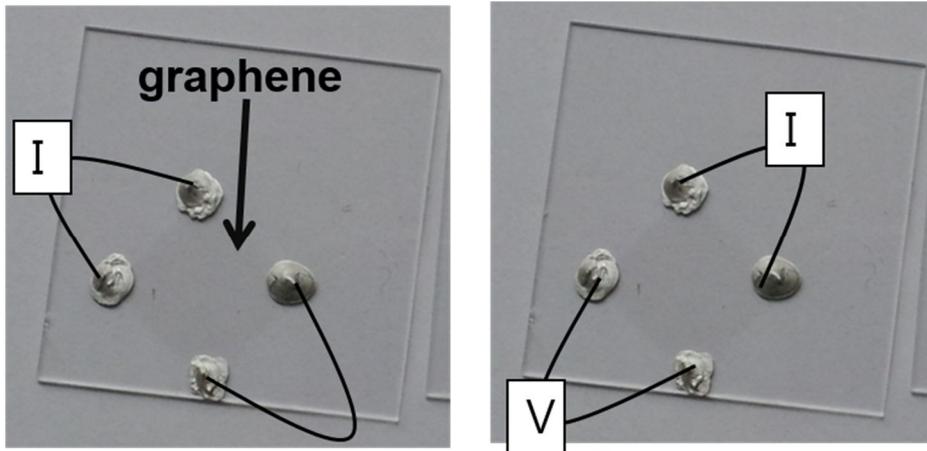


Figure 4.6 To measure the sheet resistance of transferred graphene on the substrates, silver paste was applied to contact the edge of the graphene monolayer.

Sample		Sheet resistance (Ohm/sq)
PMMA		567
PDMS attach		∞
Water		4500
Water - Ethanol		1700

Table 2 The sheet resistance data of the transferred graphene on glasses depending on the transfer methods.

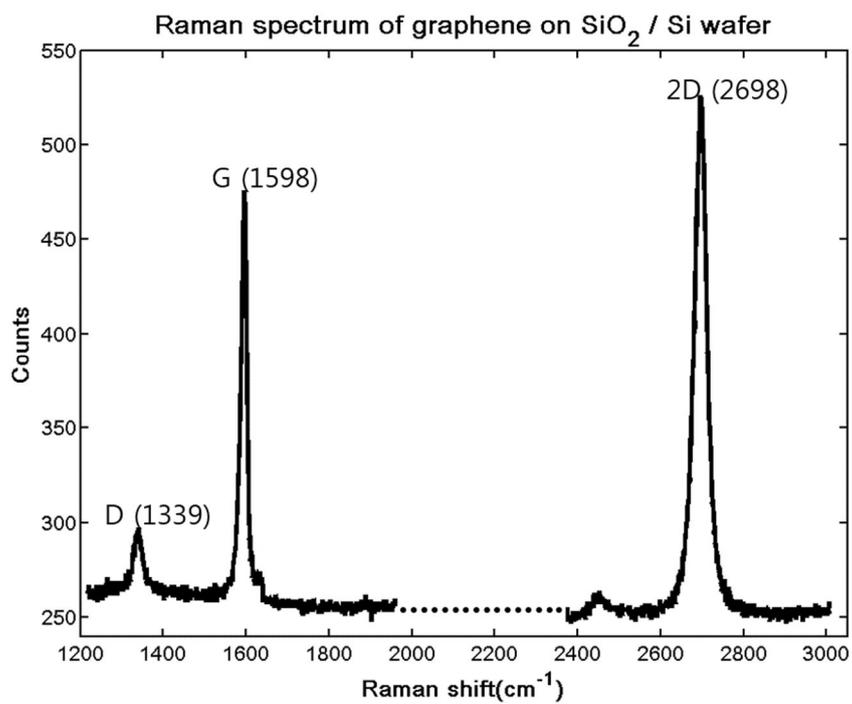


Figure 4.7 Raman spectrum of monolayer graphene on 285 nm SiO₂/Si wafer

4.2 Patterning of monolayer graphene and dry transfer it onto substrates

In this study, graphene pattern is made before graphene is transfer printed onto a target substrate and also the transfer proceeded through dry process. As a supporting layer of the graphene, a gold thin film is used, as well as gold can be used as a etch mask for the graphene. Since graphene is composed of sp² carbon – carbon bonding, the graphene layer can be etched easily by O₂ plasma treatment. Therefore, Graphene area uncovered with graphene can be removed easily followed by the gold pattern layer is created on the graphene on copper foil. After the graphene pattern that is same as that of gold is made on copper foil, the graphene pieces may disconnected according to the pattern design, so if the copper is etched right away, the graphene pattern pieces will get took apart each other. To maintain the sheet of pattern array, gold film is deposited one more time for the connectivity among graphene pattern pieces and the supporting of them, and then copper foil is etched, graphene pattern / gold stack is scooped with the PDMS stamp, gold is etched, and the graphene pattern on the stamp is transferred onto the substrate in order. The advantages of these patterning methods are that since the

process proceeded before the graphene is placed on the substrate, the process does not have a bad effect on the substrate. Also the patterns of the gold determines that of the graphene, so if the gold is patterned in nanoscale on graphene on copper foil, the graphene nano-pattern can be fabricated easily. Figure 4.8 shows the process of patterning of graphene monolayer as explained above.

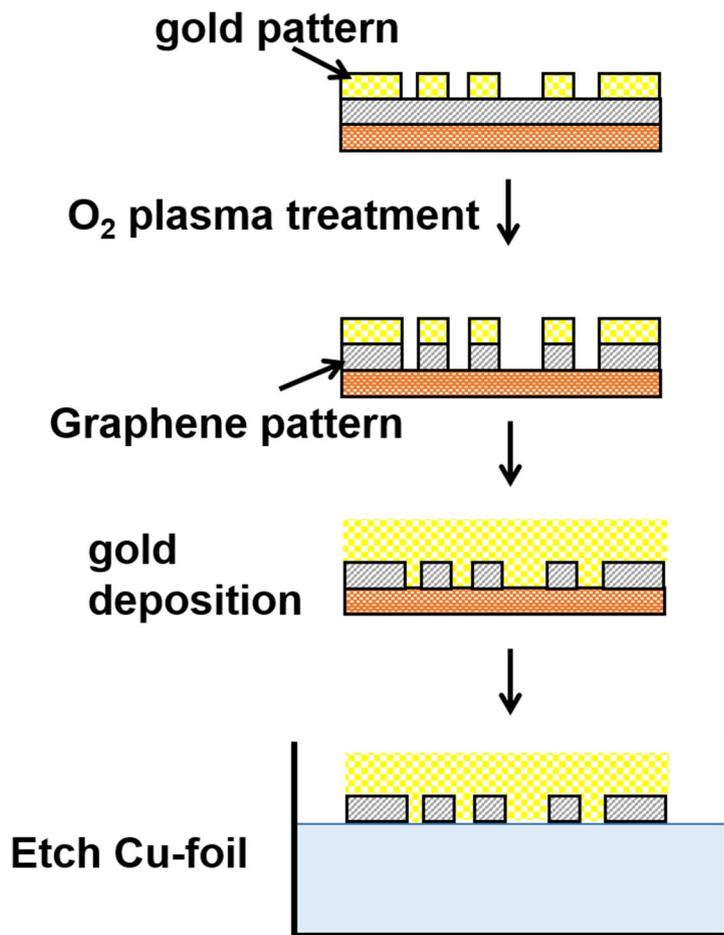


Figure 4.8 The graphene patterning method using gold. Graphene patterns that are same as that of gold are created through this method and after copper foil is etched, the gold/patterned graphene stack is scooped with the PDMS stamp and the graphene is transferred onto the substrate as same method explained in Figure 4.3

To demonstrate the graphene patterning method using gold pattern, gold pattern was made by thermally deposited on graphene on copper foil with pre-designed stainless mask as shown in Figure 3.1. The pattern is designed for measure the sheet resistance and the contact resistance. The length of the rectangular shaped graphene sheets are different but width of them are same in the pattern, and this graphene pattern was firstly placed on the stamp and then transferred onto the specific position of the target substrate. There were align marks on both the stamp and the substrates, the marks on the stamp were made from graphene pattern and that of the substrate were made from thermally deposited metal. Because the PDMS stamp is transparent, both patterns can be observed by microscope camera through it and matched. Toward this aligned stamping process, mask aligner and self-designed set-up was used. Figure 4.9 shows the patterned graphene on 285 nm SiO₂ / Si wafer and the graphene pattern was transferred in align with the mark on the substrate. Using this graphene pattern, graphene resistance according to the length can be obtained and by the below equation, the sheet resistance and the contact resistance can be found out. There are more than three types of the graphene pattern depending on the length, the below equation can be solved.

$$R_T = R_{graphene} + R_{contact}$$

$$= R_s \frac{L}{W} + R_{contact}$$

As shown Figure 4.10 according to the equation of R_T , if y axis is R_T and x axis is $\frac{L}{W}$, the slope will be the sheet resistance and the y-intercept will be the contact resistance in the linear plot.

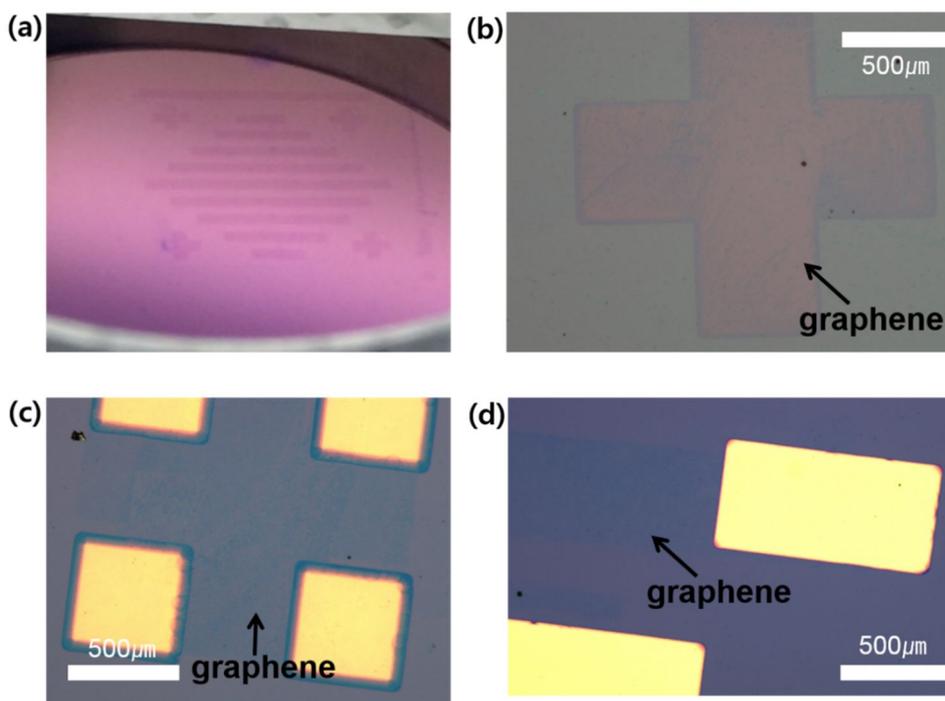


Figure 4.9 Transferred graphene monolayer pattern 285 nm SiO₂/Si wafer (a) and (b) are just transferred pattern on the substrate. (c) The square align marks on the substrate and cross pattern of the graphene on the stamp are mated. (d) To contact the graphene pattern with a tip, gold patterns are deposited.

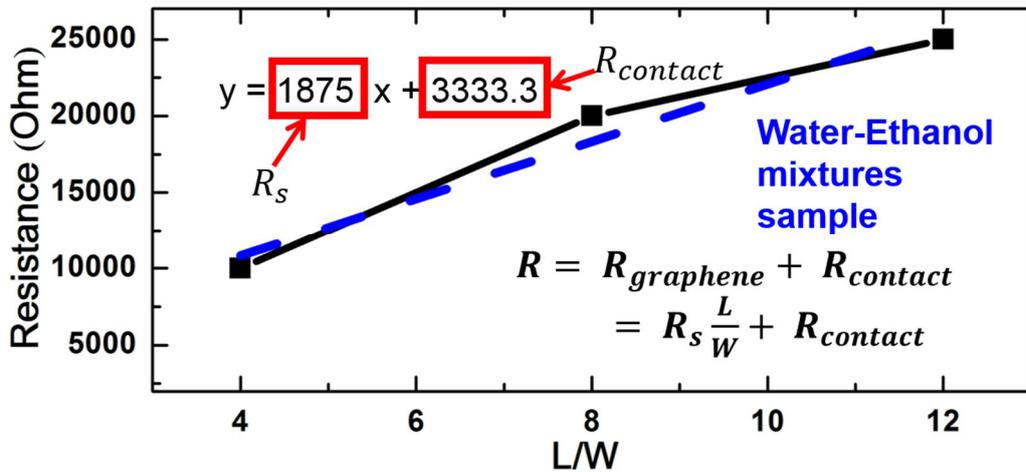


Figure 4.10 The measured sheet resistance by detecting current-voltage characteristics of different length of graphene patterns. The slope of the graph means the sheet resistance.

4.3 Dry transfer of patterned graphene onto organic materials

Graphene patterns were transferred onto the organic thin films that are prone to organic solvents and wet processes using the new method developed in this study.

The first organic thin film which graphene pattern would be transferred was ZnPc (zinc phthalocyanine). ZnPc is widely used organic semiconductor material as a donor material in small molecular organic solar cell fields and it is easily evaporated thermally. Recent study by Barry et al, ZnPc is oriented face-on when the CuI thin film is worked as a template layer, but without CuI, ZnPc is oriented edge-on as shown in Figure 4.11 [25, 26]. In addition, Susmit Sihgha Roy et al proposed that a monolayer graphene sheet also worked as a template layer of phthalocyanine materials due to strong pi-pi interaction between the graphene and phthalocyanine molecules. According to this report, CuPc (Copper phthalocyanine) was template in favorable lying-down orientation with large crystal sizes on the graphene layer [27]. Graphene transfer quality is also affected by the molecular orientation of the organic thin films. In this study, a monolayer graphene was transferred onto both the face-on ZnPc and edge-on ZnPc. However, it was

transferred onto only the face-on ZnPc as shown in Figure 4.12. This is because for the case of face-on ZnPc, the molecules would make the stronger pi-orbital overlap with the graphene and this helped the dry transfer process. Figure 4.13 shows the Raman spectrum of the graphene monolayer on the face-on ZnPc. The solid line is the graphene transferred sample and the dot line is the bare face-on ZnPc layer. G peak is hardly distinguished from the ZnPc film, but 2D peak can be noticed clearly.

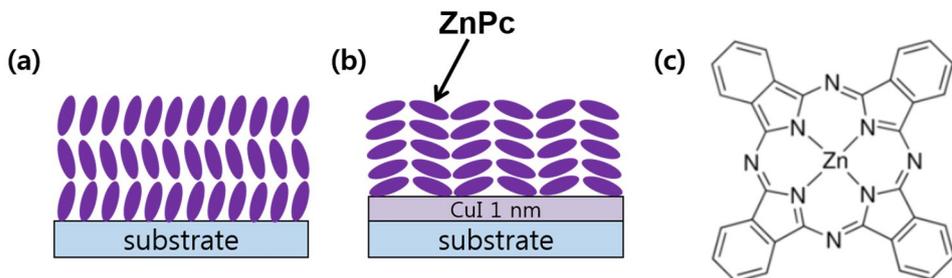


Figure 4.11 (a) Edge on ZnPc layer on the substrate, (b) face on ZnPc on the 1 nm of CuI film on the substrate, (c) the molecular structure of ZnPc

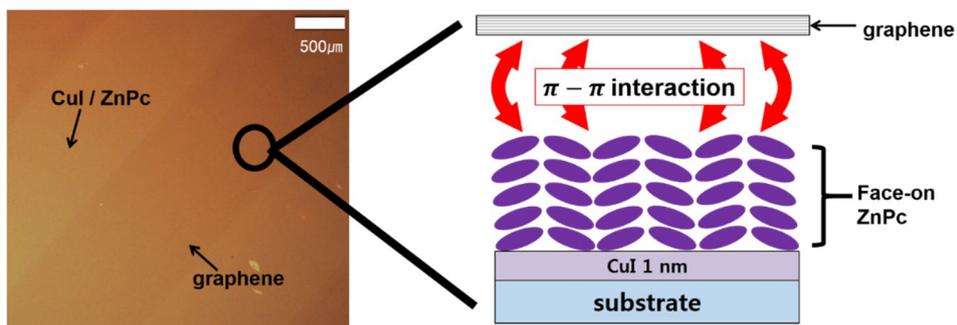


Figure 4.12 Transferred graphene line pattern on face on ZnPc layer due to strong $\pi - \pi$ interaction between graphene and face on ZnPc due to its molecular structure.

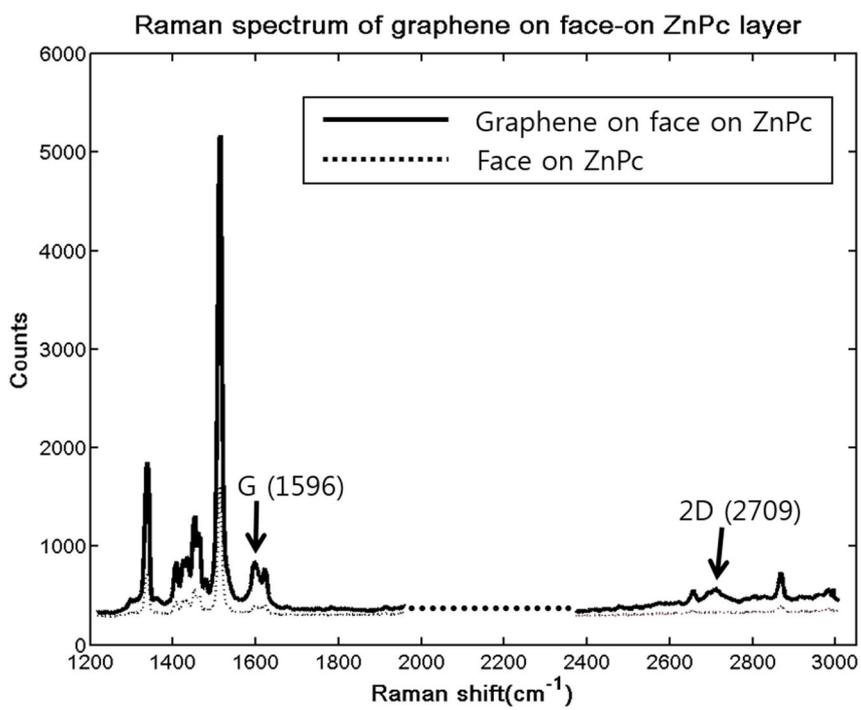


Figure 4.13 Raman spectrum of graphene on face-on ZnPc layer.

The second organic thin film is PEDOT : PSS (Poly(3,4-ethylenedioxythiophene) : Polystyrene sulfonate). It is transparent and conductive polymer and used as a hole transport and electron blocking layer in organic solar cells. Since its surface is hydrophilic, the graphene monolayer can be transferred easily onto it. Figure 4.14 represents the transferred monolayer graphene onto the PEDOT : PSS layer on glass. The dark square area indicates that the graphene was transferred onto the film. Also Raman spectrum of the graphene on the PEDOT : PSS can be seen in Figure 4.14 (c). As similar to the graphene on face-on ZnPc, the G peak is hardly distinguished from the bare PEDOT : PSS, but the 2D peak is clearly shown at 2704 cm^{-1} .

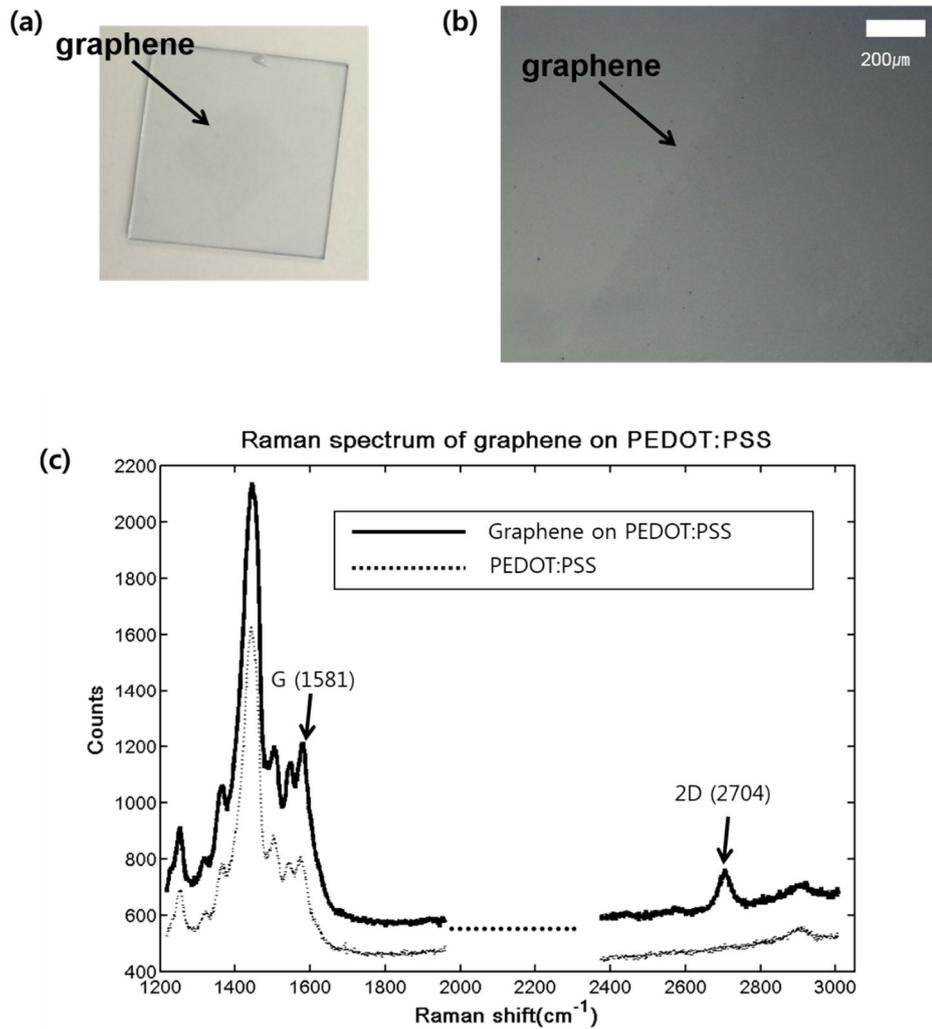
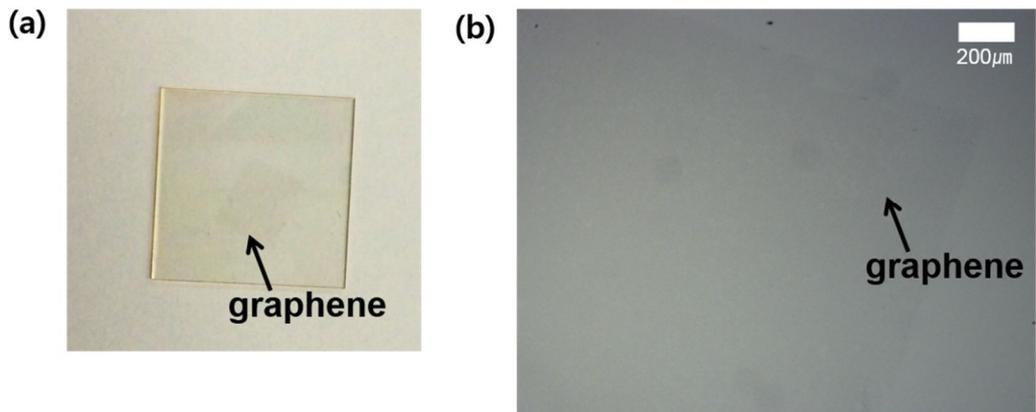


Figure 4.14 (a) Graphene monolayer on the PEDOT : PSS film on a glass substrate (b), Optical microscope image of the (a), (c) Raman spectrum of the graphene on PEDOT : PSS layer.

The third organic thin film is PVP (poly(4-vinylphenol)). It is transparent and insulating polymer and used widely as a polymer dielectric layer in thin film transistor. Figure 4.15 shows the transferred monolayer graphene onto the PVP layer on glass. The dark square area indicates that the graphene was transferred



onto the film.

Figure 4.15 (a) Transferred graphene on PVP layer on a glass substrate, (b) Optical microscope image of (a)

5. Conclusion

In this thesis, a new graphene transfer method by dry process is discussed. For the first of the steps, the monolayer graphene grown on copper foil is transferred onto a PDMS stamp with low defect density. Since the PDMS surface is hydrophobic, when the graphene layer floating in water was scooped by the PDMS stamp, the water could not wet it, thus the graphene layer attached to the stamp irregularly and some water drops trapped between them which destroyed the graphene layer. To overcome the wetting problem, water and ethanol was mixed by volume ratio of 3:7, and this mixture wetted well on the PDMS surface because its surface tension is nearly 22 mN/m, which is three times lower than water.

In addition, although many kind of polymer layers are generally used as a supporting layer of the graphene, the gold layer is used in this thesis to prevent the swelling of the PDMS when the supporting film is removed. Gold can be dissolved in an iodide aqueous solution and it does not swell the PDMS. On the other hand, conventionally used polymer layers are dissolved in organic solvent, which make the PDMS expand and the graphene on them also gets expanded together and degraded.

Also the advantage of using gold is that it makes the graphene patterning process

easier. Gold pattern on graphene can be work as a etch mask of the graphene. As gold pattern is formed on the graphene on its growing substrate, the graphene uncovered with gold pattern can be removed by O₂ plasma treatment. Through this process, the gold pattern can be transferred to the graphene pattern and the following process is same as the non-patterned case. As a result of the using water-ethanol mixture and gold supporting layer, the better quality of transferred graphene was obtained comparing to conventional dry transfer process. The sheet resistance was less than 2000Ω/sq, which is the best among the transferred monolayer graphene by dry transfer printing process. Also the transmittance and Raman spectrum was similar to that was made by conventional wet transfer process.

The monolayer graphene was transferred onto the variety of organic thin films such as ZnPc, PEDOT:PSS, and PVP successfully. In the case of face-on ZnPc especially, they made strong $\pi - \pi$ interaction with pi-orbital of graphene and this helped the dry transfer of the graphene onto the face-on ZnPc. Above this, graphene layer also can be transferred onto the polymer thin films which are widely used in organic electronics. This can be a supporting evidence that the technique discussed in this thesis is effective in transfer of graphene onto general organic thin films.

In conclusion, the dry transfer printing technique for graphene developed in

this thesis has a strength in the respect that graphene pattern can be placed onto the variety of thin films that have not been done with the conventional wet process. Therefore, this will be a basic technique for the new graphene research field that overcomes the limits of present graphene process.

Reference

- [1] Xuesong Li, Weiwei Cai, Jinho An, Seyoung Kim, Junghyo Nah, Dongxing Yang, Richard Piner, Aruna Velamakanni, Inhwa Jung, Emanuel Tutuc, Sanjay K. Banerjee, Luigi Colombo, and Rodney S. Ruoff. "Large-area synthesis of high quality and uniform graphene films on copper foils", *Science*, **324**, 1312 (2009).
- [2] Xuesong Li, Yanwu Zhu, Weiwei Cai, Mark Borysiak, Boyang Han, David Chen, Richard D. Piner, Luigi Colombo, and Rodney S. Ruoff. "Transfer of large-area graphene films for high performance transparent conductive electrodes", *Nano Letter*, **9**, 4359 (2009).
- [3] Maaiké L. van Poll, Saghar Khodabakhsh, Paul J. Brewer, Alex G. Shard, Madeleine Ramstedt, and Wilhelm T. S. Huck. "Surface modification of PDMS via self-organization of vinyl-terminated small molecules", *Soft Matter*, **5**, 2286 (2009).
- [4] Jie Song, Fong-Yu Kam, Rui-Qi Peng, Wei-Ling Seah, Jing-Mei Zhuo, Geok-Kiang Lim, Peter K. H. Ho, and Lay-Lay Chua. "A general method for transferring graphene onto soft surfaces", *Nature Nanotechnology*, **8**, 356 (2013).
- [5] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A.A. Firsov. "Electric field effect in atomically thin carbon films", *Science*, **306**, 666 (2004).
- [6] Y. Zhang, J. P. Small, W. V. Pontius, and P. Kim. "Fabrication and electric field dependent transport measurements of mesoscopic graphite devices", *Applied Physics Letters*, **86**, 073104 (2005).
- [7] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, and M. G. Schwab & K. Kim. "A roadmap for graphene", *Nature*, **490**, 192 (2012).
- [8] Evgeniya H. Lock, Mira Baraket, Matthew Laskoski, Shawn P. Mulvaney, Woo K. Lee, Paul E. Sheehan, Daniel R. Hines, Jeremy T. Robinson, Jacob Tosado, Michael S. Fuhrer, Sandra C. Hernandez, and Scott G. Walton. "High quality uniform dry transfer of graphene to polymers", *Nano Letters*, **12**, 102 (2012).

- [9] Taeshik Yoon, Woo Cheol Shin, Taek Yong Kim, Jeong Hun Mun, Taek-Soo Kim and Byung Jin Cho. "Direct measurement of adhesion energy of monolayer graphene as grown on copper and its application to renewable transfer process", *Nano Letters*, **12**, 1448 (2012).
- [10] Kwanghyun Yoo, Yusuke Takei, Sungjin Kim, Shohei Chiashi, Shigeo Maruyama, Kiyoshi Matsumoto, and Isao Shimoyama. "Direct physical exfoliation of few-layer graphene from graphite grown on a nickel foil using polydimethylsiloxane with tunable elasticity and adhesion", *Nanotechnology*, **24**, 205302 (2013).
- [11] Hansun Kim, Min-wook Jung, Sung Myung, Daesung Jung, Sun Sook Lee, Ki-jeong Kong, Jongsun Lim, Jong-Heun Lee, Chong Yun Park, and Ki-Seok An. "Soft lithography of graphene sheets via surface energy modification", *Journal of Materials Chemistry C*, **1**, 1076 (2013).
- [12] Alfonso Reina, Xiaoting Jia, John Ho, Daniel Nezych, Hyungbin Son, Vladimir Bulovic, Mildred S. Dresselhaus, and Jing Kong. "Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition", *Nano Letters*, **9**, 30 (2009).
- [13] A. Pirkle, J. Chan, A. Venugopal, D. Hingojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace. "The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂", *Applied Physics Letters*, **99**, 122108 (2011).
- [14] Wi Hyoung Lee, Jaesung Park, Sung Hyung Sim, Soojin Lim, Kwang S. Kim, Byung Hee Hong, and Kilwon Cho. "Surface directed molecular assembly of Pentacene on monolayer graphene for high performance organic transistor", *Journal of the American Chemical Society*, **133**, 4447 (2011).
- [15] Sukang Bae, Hyeongkeun Kim, Youngbin Lee, Xiangfan Xu, Jae-Sung Park, Yi Zheng, Jayakumar Balakrishnan, Tian Lei, Hye Ri Kim, Young Il Song, Young-Jin Kim, Kwang S. Kim, Barbaros Ozyilmaz, Jong-Hyun Ahn, and Byung Hee Hong & Sumio Iijima. "Roll-to-roll production of 30 inch graphene films for transparent electrodes", *Nature Nanotechnology*, **5**, 574 (2010).
- [16] Junmo Kang, Soonhwi Hwang, Jae Hwan Kim, Min Hyeok Kim, Jaechul Ryu, Sang Jae Seo, Byung Hee Hong, Moon Ki Kim, and Jae-Boong Choi. "Efficient transfer of large area graphene films onto rigid substrates by hot pressing", *ACS Nano*, **6**, 5360 (2012).

- [17] Hyun Ho Kim, Yoonyoung Chung, Eunho Lee, Seong Kyu Lee, and Kilwon Cho, "Water-free transfer method for CVD-grown graphene and its application to flexible air-stable graphene transistors", *Advanced Materials*, **26**, 3213 (2014)
- [18] Dieter K. Schroder, "Semiconductor Material and Device Characterization, third edition", *A JOHN WILEY & SONS, INC., PUBLICATION*, 4502 (2008).
- [19] L. J. van der Pauw. "A method of measuring the resistivity and Hall coefficient on lamellae of arbitrary shape", *Philips Technical Review*, **20**, 220 (1958).
- [20] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, M. S. Dresselhaus. "Raman spectroscopy of graphene and carbon nanotubes", *Advances in Physics*, **60**, 413 (2011).
- [21] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth, and A. K. Geim. "Raman spectrum of graphene and graphene layers", *Physical Review Letters*, **97**, 187401 (2006)
- [22] A. Gupta, G. Chen, P. Joshi, S. Tadigadapa, and P. C. "Raman scattering from high frequency phonon in supported n-graphene layer films" *Nano Letters*, **6**, 2667 (2006).
- [23] Seok Ju Kang, Bumjung Kim, Keun Soo Kim, Yue Zhao, Zheyuan Chen, Gwan Hyoung Lee, James Hone, Philip Kim, and Colin Nuckolls, "Inking elastomeric stamp with micro-patterned, single layer graphene to create high-performance OFETs", *Advanced Materials*, **23**, 3531 (2011)
- [24] Charles M. Hansen. "New simple method to measure polymer surface tension" *Pigment & Resin Technology*, **27**, 374 (1998).
- [25] B. P. Rand, D. Cheyons, K. Vasseur, N. C. Giebink, S. Mothy, Y. Yi, V. Coropceanu, D. Beljonne, J. Cornil, J. Brédas, and J. Genoe. "The impact of molecular orientation on the photovoltaic properties of a phthalocyanine/fullerene heterojunction", *Advanced Functional Materials*, **22**, 2987 (2012).
- [26] Hyo Jung Kim, Hyun-Sub Shim, Ji Whan Kim, Hyun Hwi Lee, and Jang-Joo Kim. "CuI interlayer in lead phthalocyanine thin films enhance near-infrared light absorption", *Applied Physics Letters*, **100**, 263303 (2012).

- [27] Susmit Singha Roy, Dominick J. Bindl, and Michael S. Arnold. "Templating highly crystalline organic semiconductors using atomic membranes of graphene at the anode/organic interface", *The Journal of Physical Chemistry Letters*, **3**, 873 (2012)

요약 (국문초록)

지난 5년간 투명전극으로써의 그래핀에 대한 연구가 많이 이루어져 왔지만 유기전자소자에 그래핀 투명전극을 응용하는 데에는 다소 한계가 있다. 지금까지 그래핀의 전사방법으로 대부분 고분자 지지층을 그래핀 위에 코팅하고 이를 물 위에 띄워 전사하고자 하는 기판으로 견지는 방법을 사용해왔는데, 이때 고분자 지지층을 제거하기 위해 유기용매를 사용한다. 따라서 그래핀을 유기전자소자의 유기재료 위에는 전사하지 못하고 유기재료를 증착하기 전에 기판 위에만 그래핀을 전사해 전극으로 활용했다. 게다가 그래핀을 패터닝하기 위해서는 그래핀을 전사한 후 포토리소그래피 공정을 이용하기 때문에 그래핀 패터닝 시 유기재료를 증착하기 전에 형성해야만 했다.

본 연구에서는 그래핀 단일층, 또는 그래핀 단일층 패터닝을 유기재료 위에 전사하기 위해 건식공정을 이용하여 그래핀을 패터닝하고 전사하는 방법에 대해 연구하였다. 공정 중에, 먼저 액체 위에 떠 있는 그래핀 단일층을 PDMS 도장으로 견져 전사하였다. 이때 기존의 습식공정방

식과는 다른 점이 두 가지 있는데, 첫 번째는 그래핀을 띄운 액체의 표면장력을 조절하여 소수성의 PDMS 표면 위에 잘 퍼질 수 있도록 한 점이다. 두 번째는 그래핀의 지지층으로 고분자를 사용하는 것 대신 금 박막을 열 증착하여 사용했다는 것이다. 고분자를 제거할 때 사용하는 유기용매가 PDMS를 팽창시키는 것을 방지하기 위해 수용액에 녹을 수 있는 금을 이용하였다. 또한 그래핀위에 금을 패터한 후 금이 패터되지 않은 부분의 그래핀을 산소 플라즈마로 제거하면 금 패터와 동일한 모양의 그래핀 패터를 얻을 수 있다. 따라서 금을 지지층으로 하여 그래핀을 패터하여 전사할 수 있게 되었다.

본 연구에서 개발한 방법을 이용하여 그래핀 단일 층 및 그래핀 패터를 임의의 유기재료 위에 전사할 수 있게 되었으며, 전사한 그래핀의 질은 그 동안 PDMS에 그래핀을 붙이고 구리포일을 녹이는 방식으로 전사한 그래핀 보다 매우 향상된 것을 볼 수 있었다. 본 연구를 통해 PEDOT:PSS, PVP, 또는 ZnPc와 같이 유기전자소자에 많이 이용되는 유기재료 위에 그래핀 또는 그래핀 패터를 건식으로 형성할 수 있게 되었고 유기전자소자 또는 무기전자소자의 투명전극으로써의 그래핀 패터를 원하는 위치에 전사할 수 있게 되었다.

.....

주요어 : 그래핀, 투명전극, 건식전사공정, 그래핀 패터, 유기재료

학 번 : 2012-22454

