



### 저작자표시-비영리-동일조건변경허락 2.0 대한민국

이용자는 아래의 조건을 따르는 경우에 한하여 자유롭게

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

다음과 같은 조건을 따라야 합니다:



저작자표시. 귀하는 원저작자를 표시하여야 합니다.



비영리. 귀하는 이 저작물을 영리 목적으로 이용할 수 없습니다.



동일조건변경허락. 귀하가 이 저작물을 개작, 변형 또는 가공했을 경우에는, 이 저작물과 동일한 이용허락조건하에서만 배포할 수 있습니다.

- 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](#)

이학석사 학위논문 초고

# Growth of Large-Domain Graphene

큰 사이즈의 그래핀 형성 및  
액정의 특성을 이용한 도메인 관찰

2012년 8월

서울대학교 대학원

물리천문학부 물리학 전공

한진화

# Growth of Large-Domain Graphene

큰 사이즈의 그래핀 형성 및  
액정의 특성을 이용한 도메인 관찰

지도 교수 국 양

이 논문을 이학 석사 학위논문으로 제출함  
2012년 8월

서울대학교 대학원  
물리천문학부 물리학 전공  
한 진 화

한진화의 석사 학위논문을 인준함  
2012년 8월

위 원 장 이 탁 희 (인)

부위원장 국 양 (인)

위 원 유 재 준 (인)

# Abstract

Graphene is made out of carbon atoms tightly packed into a two-dimensional honeycomb lattice, and is a basic structure corresponding to carbon-carbon connected materials. Graphene has received attention because of its unique properties. These properties, have shown it to have great potential in a number of interesting fields, including in electronics in the construction of graphene transistors, integrated circuits, and ultracapacitors (due to their high conductivity).

The electrical properties of graphene, which has astonished many researchers, are very curious as to use commercialized semiconductors as well as scientific researches. For enhancing these electrical properties, researchers feel the need to grow graphene's domain. Because the size of domain is influenced on graphene's quality, domain size enhancement is necessary to develop more upgraded graphene materials. Also, it is newly known that using liquid crystal for examining the size of graphene domain is quite easy due to polarized microscope.

In this paper, we will report the growth of graphenes by using our home-made CVD furnace system, and we will show that the size of domains are quite reasonable compared to other research group's results by using liquid crystals.

**주요어** : Graphene, Graphene Domain, Graphene growth, CVD, Liquid Crystal.

**학 번** : 2010-23153

# List of Contents

<b>Part 1. Introduction.....</b>	<b>4</b>
<b>Part 2. Graphene .....</b>	<b>6</b>
2. 1 Properties of graphene .....	6
2. 2 Growth of graphene .....	10
<b>Part 3. Liquid Crystal.....</b>	<b>16</b>
3.1 The properties of liquid crystal .....	16
3.2 The types of liquid crystal .....	19
3.3 Light and nematic liquid crystal.....	20
3.4 Confirmation of liquid crystal.....	22
3.5 Graphene and liquid crystal.....	23
<b>Part 4. Visualization of large-domain graphene .....</b>	<b>25</b>
4.1 Growth process .....	25
4.2 Transfer of graphene.....	26
4.3 Polarized optical microscope images.....	33
<b>Part 5. Conclusion.....</b>	<b>40</b>
<b>References .....</b>	<b>41</b>
<b>Abstract (Korean) .....</b>	<b>44</b>

## List of Tables

[Table 2.1] .....	9
-------------------	---

## List of Figures

[Fig. 1.1] .....	4
[Fig. 2.1] .....	8
[Fig. 2.2] .....	15
[Fig. 2.3] .....	15
[Fig. 3.1] .....	20
[Fig. 3.2] .....	22
[Fig. 3.3] .....	24
[Fig. 4.1] .....	28
[Fig. 4.2] .....	28
[Fig. 4.3] .....	30
[Fig. 4.4] .....	31
[Fig. 4.5] .....	32
[Fig. 4.6] .....	33
[Fig. 4.7] .....	35
[Fig. 4.8] .....	36
[Fig. 4.9] .....	37
[Fig. 4.10] .....	38
[Fig. 4.11] .....	39

# Part 1. Introduction

Carbon-based composition materials can be seen around the world—Fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid or tube. The progress of the study of carbon allotropes has been expanded to the study of graphene since the 1970s, the time of the presentation of a paper about a fullerene. Graphene, one of the most issued materials recently, has been researched by many groups.

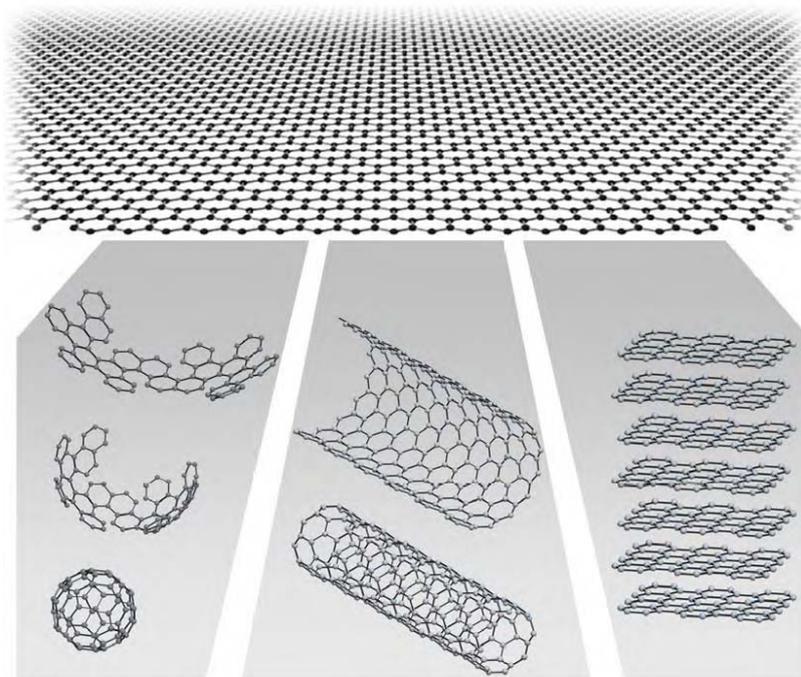


Figure 1.1 Graphitic Forms of Carbon (Illustration from article by A. K. Geim and K. S. Novoselov, *The Rise of Graphene*)

Many useful characteristics graphene has, which will be

mentioned below section, let us reach the possibility of new and innovative electronics. The electronic properties of graphene are closely related to graphene's domain size. Therefore, many groups have researched on enlarging the domain size of graphene. When it comes to its domain size, there have been some progresses on the growth of graphene domain.

However, it is true that we have not had the simple and quick observation tool which measures the domain size of graphene. Though graphene's domains are observed by Scanning Tunneling Microscopy (STM), Scanning Electron Microscope (SEM), Atomic Force Microscopes (AFM) or some other microscopes, these tools are quite difficult to prepare and use. Fortunately, according to recent research by KAIST, it is said that using liquid crystals makes the domain measurement easy due to the birefringence of liquid crystals.

In this paper, we will show our large-grown domain of graphene and demonstrate it by using liquid crystals. This experiment offers that the quality of graphene samples we have made and whether our graphene domain is reasonably large or not.

## Part 2. Graphene

### 2.1 Properties of Graphene

Graphene is made out of carbon atoms tightly packed into a two-dimensional honeycomb lattice, and is a basic structure corresponding to carbon-carbon connected materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite. Graphene has been studied for sixty years and widely used for describing properties of various carbon-based materials[1]. Fullerenes can correspond to wrapped-up graphene. Carbon nanotubes are obtained by rolling graphene along a given direction, reconnecting the carbon-carbon bonds. Graphite can be thought as stacks of graphene layers that are weakly coupled by van der Waals forces. After the invention of the pencil in 1564, it takes 440 years until graphene is obtained by Novoselov et al., 2004. The reason is that no one expected graphene to exist in the free state, and graphene from the pencil's flakes cannot be shown as one-atom-thick layer.

Graphene possesses some very interesting unique properties; Graphene's structure is one-atom-thick planar sheets of  $sp^2$ -bonded carbon. Its carbon-carbon bond length in graphene is

about 0.142 nanometers. Graphene sheets stack to form graphite with an interplanar spacing of 0.335 nm. Also, it has a particularly high electron mobility, a high thermal conductivity. These properties, have shown it to have great potential in a number of interesting fields, including in electronics in the construction of graphene transistors, integrated circuits, and ultracapacitors (due to their high conductivity). The electrical properties of graphene, which has astonished many researchers, are very curious as to use commercialized semiconductors as well as scientific researches. This thin material has a mobility of  $200,000\text{cm}^2/\text{V} \cdot \text{s}$ . Also using cryogenic temperatures and high magnetic fields, graphene undergoes half-integer quantum hall effect and Landau level splitting.

The most explored aspect of graphene physics is its electronic properties. Charge carriers in condensed matter physics are described by the Schrödinger equation with an effective mass  $m^*$  different from the free-electron mass. Relativistic particles in the zero rest mass follow the Dirac equation, charge carriers in graphene are called massless Dirac fermions. Electrons propagating through the honeycomb lattice completely lose their effective mass, which results in quasi-particles that are described by a Dirac-like equation rather than the Schrödinger equation. Electron waves in graphene propagate within a layer that is only one atom thick, which makes them accessible and amenable to various scanning probes as well as sensitive to the

proximity of other materials such as high- $k$  dielectrics, superconductors, ferromagnets, etc. Graphene exhibits an astonishing electronic quality. Its electrons can cover submicrometer distances without scattering, even in samples placed on an atomically rough substrate, covered with adsorbates, and at room temperature. As a result of the massless carriers and little scattering, quantum effects in graphene are robust and can survive even at room temperature. The transport properties of real graphene devices have turned out to be much more complicated than theoretical quantum electrodynamics predicts, and some basic questions about graphene's electronic properties have yet to be answered. For example, there is no consensus about the scattering mechanism that currently limits the mobility, and in addition, this property seems to strongly depend on the type of graphene sample been investigated (i.e. exfoliated or prepared via thermal desorption of Si in SiC) [2].

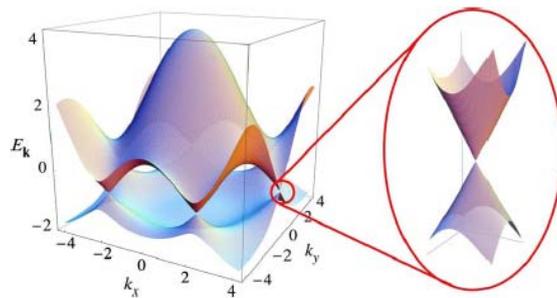


Fig. 2.1. The Fermi Surface of Graphene [2].

Table. 2.1 : comparison of Graphene Production Methods

Method	Advantages	Disadvantages
Mechanical exfoliation	Low-cost and easy No special equipment needed SiO <sub>2</sub> thickness is tuned for better contrast	Serendipitous Uneven films Labor intensive (large-scale impossible)
Epitaxial growth	Most even films Large scale	Difficult control of morphology and adsorption High temperature process
CVD	Continuous plane films as large as metal substrates	Possibility to have more impurities and wrinkles

## 2.2 Growth of Graphene

We will explain the graphene growth with three methods ; Mechanical exfoliation, Epitaxial growth, Chemical vapour deposition. The best quality graphene is obtained by mechanical cleavage of highly oriented pyrolytic graphite [3]. Although pristine graphene has very low concentration of structural defects, the flake thickness, size and location are uncontrollable. Another example is the conversion of SiC(0001) to graphene via sublimation of silicon atoms at high temperatures. High quality wafer scale graphene with switching speeds of up to 100GHz has been demonstrated using this technique. Although the price of the initial SiC wafer is relatively high compared to that of silicon, the technique maybe suitable for radio and THz frequency electronics where the excellent performance of the devices could offset the cost of the wafers. The most promising, inexpensive and reasonable high quality graphene can be obtained by chemical vapor deposition (CVD) onto transition metal substrates such Ni, Pd, Ru, Ir or Cu. Recent developments on uniform single layer deposition of graphene on copper foils over large areas have been researched.

## 2.2.1 Mechanical Exfoliation

Mechanical exfoliation, which was introduced in 2004, is still the method which consistently produces high-quality samples with the best properties, though of a limited size. This method uses a wafer of Highly Ordered Pyrolytic Graphite (HOPG), which is composed of many stacked layers of graphene. A diamond scribe was used to cut wafers of SiO<sub>2</sub> into small pieces roughly 5mm<sup>2</sup> to be used as substrates for graphene. It has been determined in other work such as that of P. Blake et al. that 300nm thick SiO<sub>2</sub> is ideal as a graphene substrate because it allows a single atom-layer of graphene to be visible with the naked eye under white light, unlike pure silicon's mirror-like surface. The contrast between a graphene flake and a substrate has to be relatively high for the flake to be visible to the naked eye, which, in the case of a SiO<sub>2</sub> on Si substrate, relies on the relative indices of refraction of the SiO<sub>2</sub>, Si, and graphene. The behavior of light as it encounters each of these 10 transitions can be described using the Fresnel equations. Indeed, the contrast was so high-quality that not only could graphene/graphite flakes be identified, but flakes with larger numbers of carbon layers appeared darker than those with fewer layers. About six inches of tape from a mount was discarded, including the piece of tape that had been exposed

previously to the air collecting dust. A fresh piece was removed and pressed firmly adhesive-side down to the shiny side of the HOPG for about ten seconds. The tape was gently peeled away with thick, shiny layers of graphite stuck to it.

Next, the part of the tape with layers from the HOPG was refolded upon a clean adhesive section of the same piece of tape; the two layers were then pressed firmly together for several seconds. The tape was gently unfolded so that two mirrored graphite areas on the tape remained. This process was repeated with the original area removed from the HOPG on the tape until a large portion was no longer shiny, but dull, dark grey. It was preferable that the area be more graphite and less bare tape so that more graphite and less glue residue would be transferred to the substrate; despite the fact that tape residue does not seriously affect the quality of the graphene flake samples, it does make those samples more difficult to find on the substrate. One of the small SiO<sub>2</sub> wafers was placed shiny-side down on that dull area with a pair of tweezers and pressed firmly to the tape for several seconds. It was then gently removed and placed in a labeled sample box. This process could be repeated separately for each SiO<sub>2</sub> wafer, or the same dull graphite area on the tape could be used for the production of several different wafers.

## 2.2.2 Epitaxial Growth On SiC

Ultrathin epitaxial graphite films were produced on the Si terminated(0001) face of single-crystal 4H-SiC and 6H-SiC by thermal desorption of Si[4-7]. Surface preparation by oxidation or H<sub>2</sub> etching is needed because of removing the scratches of the sample. The samples are usually etched in a furnace atmosphere of 5% H<sub>2</sub> and 95% Ar at 1 atm pressure. A general furnace hydrogen etching cycle consists of ramping to between 1500~1600° C at a rate of 100° C/min followed by a 30min soak at 1600° C. The sample is cooled at a rate 50° C/min down to 800° C and allowed to cool rapidly down to room temperature. It is important that the samples are cooled slowly after the maximum temperature to remove the crystallized Si deposits produced during etching. After undergoing this process samples were heated to 950~1100° C for 6 min by electron bombardment in ultrahigh vacuum (UHV; base pressure 1\*10<sup>-10</sup> Torr) in order to remove the oxide (some samples were oxidized/deoxidized several times to improve the surface quality). After verifying by Auger electron spectroscopy (AES) that the oxide was removed, samples were heated to temperatures ranging from 1250 ° C to 1450 ° C for 1-20 min. Under these conditions, thin graphite layers are formed, with the layer thickness determined predominantly by

the temperature. Multilayered graphene film thicknesses were estimated by modeling the ratio of measured intensities in the Si 92-eV and C 271-eV Auger peaks (3 keV incident energy) [6].

### 2.2.3 Chemical Vapor Deposition

In CVD, a metal substrate such as copper is put into a furnace and heated under a vacuum to around 900~1100° C. The heat anneals the copper as increasing its domain size. Methane and hydrogen gases are then flowed through the furnace [8–9]. The hydrogen catalyzes a reaction between methane and the surface of the metal substrate. This process causes carbon atoms from the methane to be deposited onto the surface of the metal through chemical adsorption. After passing deposition time, The furnace is quickly cooled to keep the deposited carbon layer from aggregating into bulk graphite, which crystallizes into near graphene layer on the surface of the metal [10]. The graphene produced by this method is more likely to carry impurities due to the various materials required for CVD. However, research has shown that such impurities can be sufficiently minimized to create graphene as pure as exfoliated flakes [3]. Additionally, the graphene from CVD tends to wrinkle due to the difference in thermal expansion between graphene and copper. This is

decreased via proper annealing, but still needs an research challenge. Most importantly, graphene from CVD is a continuous plane film as large as the underlying metal substrate.

Our CVD graphene method is almost same as above description. Copper (Alfa Aesar, 99.9% 0.025mm) is cut out for 1.7 centimeter \* 1.7 centimeter square size, and is etched with 40°C acetic acid during 10min for the elimination of oxidation on copper surface. After rinsing the residues of acetic acid with distilled water, copper slice is soaked into 99% ethanol. Then, copper slice is put into the prepared sample holder. Sample holder with the copper slice is put in the quartz tube of the homemade furnace system which can pump up to  $10^{-8}$  torr with a drypump and a turbo molecular pump. When reaching the proper pressure of the system (low  $10^{-6}$  torr), our furnace is ready to grow CVD type-graphene.



Fig. 2.2 Our home-made furnace



Fig. 2.3 The sample holder

## Part 3. Liquid Crystal

Liquid crystal can be seen in everyday life. These days, liquid crystal plays a crucial role especially in visual media technology. Every time people open a laptop, a smartphone, or a brand new television, they see the material in the display panel. Be that as it may to the public, from the physical point of view, however, it is a mysterious material. The term “liquid crystal” itself looks odd: is it a liquid, or is it a solid? Can anything be liquid and at the same time, solid? In order to utilize the material to observe graphene domain, we need to look into its properties first[11–12].

### 3.1 The Properties of Liquid Crystal

In fact, liquid crystal refers to a state of matter, not a certain material: a material can be at a state of liquid crystal. It is neither of the three classical states—gas, liquid, and solid, although it is still a “state” which is stabilized by thermodynamic mechanism and resembles some properties of both liquid and solid.

Generally, a material exists in one of the classical states, which is specified by a function of pressure and temperature. In solid states, molecules are bound tight with each other to

compose a certain arrangement. They are forced to stay only in fixed positions. In liquid states, they are relatively free from such restriction and can move: there is no arrangement as seen in solids. Still, they undergo a certain amount of force so that they sustain their positions somewhat close to each other. Gaseous states give molecules even more freedom—binding forces in between are insufficient to keep them close to each other.

As temperature varies, the binding forces between the molecules change. A material is said to undergo a phase transition if the binding forces have changed such that it cannot maintain stability anymore and arrive at another state.

So, can there be any other state other than those three classical states? The answer is yes. Although irrelevant to the liquid crystal, plasma is one example of such exceptional states. At extremely high temperatures, a material is partly ionized—particles of opposite charges are separated from each other. Look here at another state, “liquid crystal.” In order to understand it specifically, look into the transition of benzoic acid cholesteryl. It is solid at room temperature (25°C). When it is heated, it melts down to form liquid around 146°C. This liquid, however, is turbid. Only after it is heated above 179°C it becomes transparent. This turbid liquid is liquid crystal, the transparent one is a general liquid that we are familiar with.

In that it is fluid and can vary its shape regardless of where it is contained, liquid crystal is equivalent to general liquids.

However, it is different from them in that it is turbid. Then, is liquid crystal the middle point between the solid and liquid? If not, is it more closer to one of solid and liquid? When solid melts down to liquid crystal, the order that the solid state has had disappears, and only the mere array remains. Liquid crystal has more freedom to align molecules' position compared to solid state. In other words, liquid crystal is more similar to liquid than it is to solid.

What is the order solid states have? In a solid state, molecules are confined in two ways. First, molecules are confined in certain positions. This represents the positional order. Second, they are aligned in some directions. This represents the orientational order. When solid melts down to liquid, it loses both its positional and orientational order. In liquid crystal, on the other hand, it loses its positional order but maintains its orientational order slightly.

However, not every solid can transform into liquid crystal when heated. It has to have a distinct feature in order to achieve the goal: its constituent molecules must have a certain geometrical shape. It is revealed that, to become liquid crystal, the molecules should have a length much larger than its width. Empirically, it is known that liquid crystal is formed when the ratio  $L/D$  is greater than about 3. Energy stability can well be

achieved when long bar-type molecules are parallel to their major axis (i.e., the direction along its “length” ).

In a liquid crystal state, bar-type molecules are free to move as they are in liquid states, aligning to a certain direction. There is a parameter that describes this special alignment, which is called the “director.” The major alignment of the molecules is the mean value of the directions of all molecules. This mean value, “director” approaches  $0^\circ$  in solid states, around  $57^\circ$  in liquid states. Therefore, for a liquid crystal, the value serves as an indicator that tells which of either solid or liquid is it closer to.

### 3.2 The Types of Liquid Crystal

In a nematic liquid crystal, the positions of molecules are in a disorder, but their major axis are aligned to a certain direction. That is, of the two “orders,” the orientational order survives. In a cholesteric liquid crystal, the structure is twisted compared to nematic liquid crystals. If such twist is uniform, it is said to have reached one complete rotation ( $360^\circ$  ).

This length of  $360^\circ$  Rotation means one pitch. Such type of liquid crystal is also called the “Chiral nematic liquid crystal.” In a smectic liquid crystal there are both of some orientational and positional order. The major axes of its constituent

molecules are aligned to a certain direction, and at the same time, the molecules tend to form layers.

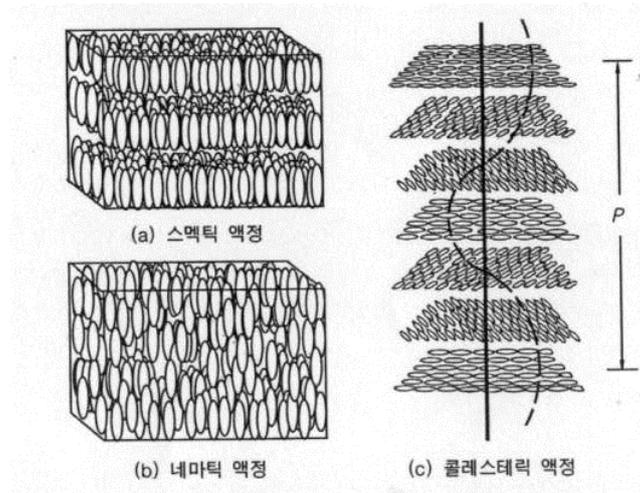


Fig. 3.1 The types of liquid crystal

### 3.3. Light and Nematic Liquid Crystal

One of the best ways to observe liquid crystal is to use the Polarized Optical Microscope (POM). After X-axis and y-axis linearly polarized light passing through a target, the angle between the boundary of target and light. From this angle, we can induce an index of refraction. The index of refractions of most targets such as glass, water, large sodium chloride crystals have same values on x-axis and y-axis linearly polarized incident light. On the other hand, the case of crystal and calcite, they have different refraction index on x-axis and y-axis linearly polarized incident light, because the

transmission velocity is different depending on the polarized direction of light. The former substances have an isotropy and only one index of refraction, the latter have anisotropy and several indexes of refraction. The anisotropy materials have different indexes of refraction about x-axis and y-axis polarized incident light, therefore, lights progress two directions in those materials. The birefringence, or double refraction indicates these phenomena.

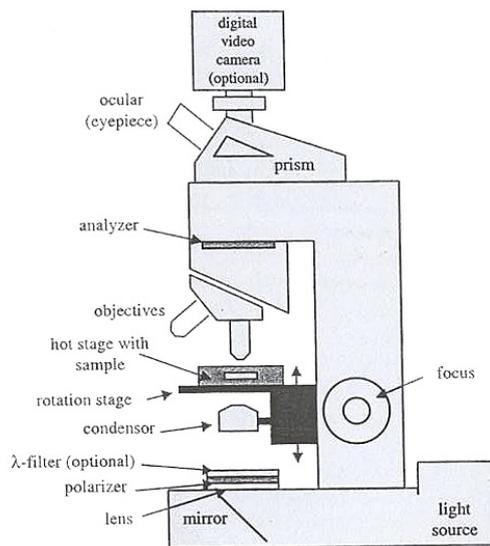
All consequences about the index of refraction work dissimilarly depending on the direction of polarization. Using this result, there is one method for confirming the polarization; The polarizer and analyzer. The polarizer makes light pass through special direction in materials. The analyzer makes light block same direction along to light polarization.

The light polarized along to the nematic liquid crystal's director in parallel progresses with different velocities compared to light in perpendicular, which is caused by the anisotropy of nematic liquid crystal. In other words, nematic liquid crystal has birefringence. Consider the situation in which nematic liquid crystal is located between two polarizers. Think of the polarization which is parallel to the director or different from the direction of director, when the light passes through from the 1<sup>st</sup> polarizer. These polarized lights are splitted into the light parallel to the director and perpendicular to the director in no phase transition. The phase of 2 polarized lights

varies while passing through liquid crystal. Generally, elliptically polarized light appears. This light is parallelized to the axis of polarizer twice per one period, because electric field of elliptically polarized light makes one rotation regularly during each period. For that reason, some light can pass through 2<sup>nd</sup> polarizer.

### 3.4. Confirmation of Liquid Crystal : Polarizing Microscope

Polarizing microscope is the essential piece of equipment for texture studies[13]. A typical setup of a polarizing microscope is shown in Fig. 3.2. It consists of a light source, which is generally a halogen light bulb emitting white light. The light is



reflected upwards by a mirror, passes through a lens. Then the light is linearly polarized by a sheet polarizer, which can be rotated by 360 °. We use Nikon microscope MM-40 model.

Fig. 3.2 General polarized microscope

### 3.5. Graphene and Liquid Crystal

In this experiment, we use 4'-pentyl-4-biphenylcarbonitrile (98%, Aldrich) which is the same nematic liquid crystal '4-Cyano-4'-pentylbiphenyl(5CB)'(Fig. 3.3). 5CB is crystalized below 23°C, but the nematic liquid crystal between 23°C and 35°C, and isotropic state above 35°C. How to visualize the graphene domain shows Fig. 3.3 schematically[14]. The alkyl chains of 5CB form the long-bar type structure of nematic liquid crystal, and these chains can occupy alternate positions on the graphene hexagons. The driving force for the change in the orientation of nematic liquid crystals, is induced by graphene domains. It has been reported that the graphene hexagons induce highly ordered packing of liquid crystals which contains cyanobiphenyl groups and alkyl tails and this combination is caused by strong  $\pi$ -stacking interactions. In addition, the matching with the distance of hexagon graphene lattice(2.42) and that of alternate alkyl tails of 5CB(1.52) means that the instantaneous dipole-induced dipole force might play a role in aligning liquid crystal molecules on the graphene. The orientations of 5CB will vary depending on the lattice direction of each graphene domain. The different 5CB orientatations on graphene cause the different birefringence in

polarized optical microscope so that the angle-dependent polarizability can be identified.

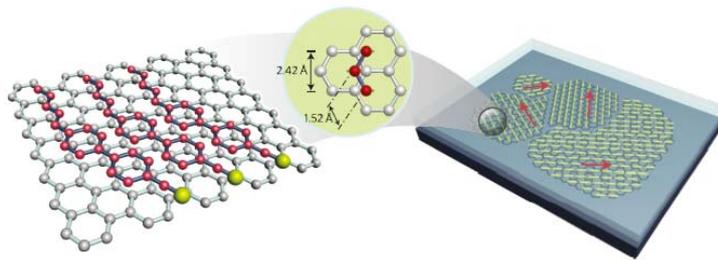


Fig. 3.3 Schematic diagram of visualizing graphene domains [14]

## Part 4. Visualization of Large-domain graphene

### 4.1. Growth Process by CVD

Generalized process of Chemical Vapor Deposition is skipped. (It is expressed in detail above chapter 2.2.3 For large-domain graphene (LD graphene), it has been researched by many groups. In this research, we referred to papers of Ruoff group to set an adequate condition for LD graphene growth [9].

We need to control some conditions of graphene growth when operating the furnace by CVD; the time for exposing methane gas, the growth temperature, the existence of pre-annealing H<sub>2</sub> gas, and the cooling time. Due to our furnace's structural condition, we cannot adjust the cooling time of graphene growth to influence the size of LD graphene. It is critical point of the growth of LD graphene condition. We only can set the fan for cooling. If the cooling system is developed better, it will outperform this results for the LD graphene growth. Therefore, actually we could test the growth temperature and the pre-annealing time.

First, controlling the growth temperature to 995~1020°C, we could observe the quality of graphene and how the LD graphene growth would be revealed in these condition. Next we set the

H<sub>2</sub> pre-annealing time 0min, 10min before injecting methane gas in quartz tube. The outline of our chemical vapor deposition is same as a rough explanation CVD growth of the chapter 2. In this level, the detailed CVD procedure on our graphene growth will be described. Cu foil(purity 99.9%, Alfa Aesar) is cut into a square that has one edge of 1.7cm. Cutting Cu foil is cleaned by Aceton during 10 min, which eliminates the oxidation of Cu surface. After rinsing Cu foil several times with distilled water and 99% ethanol, all residues and solution are removed using N<sub>2</sub> gun. Then, the Cu foil puts into the sample holder to be loaded in the furnace.

## 4.2. Transfer of Graphene

Graphene which is completed each growth conditions experiences transfer process. Copper taken out on the sample holder is conducted the Polymethyl Metacrylate(PMMA) coating using spin-coat machine with 2000 rpm during 1min 30sec. After spin-coating, copper is heated about 170°C on the hotplate. Then, it is cut out by 0.7cm X 0.7cm and etched with copper etchant for about 2 hours. Copper dissolves in the etchant from this process. After dissolving, we can see PMMA-coated graphene floating on the surface of etchant. Using the piece of dummy silicon, graphene is scooped and rinsed several

times on the distilled water, then rinsed and dried graphene is transferred on SiO<sub>2</sub> substrate. For removing PMMA on the graphene surface, graphene on SiO<sub>2</sub> substrate is soaked in acetone during 20min. After taking it out in acetone, pure graphene on SiO<sub>2</sub> substrate is washed over isopropyl alcohol(IPA). By evaporating IPA, it is ready to observe the graphene quality using Optical Microscope and Raman Spectroscopy.

When observing the liquid crystal on LD graphene, sample preparation is very easy. LD graphene on SiO<sub>2</sub> on which liquid crystals drop and is spin-coated about 2,000 rpm during 1min. Ending the spin-coating operation, graphene with liquid crystals is transferred on a slide glass to observe the graphene domains using a polarized optical microscope. There is the prepared sample structure diagram in Fig. 4.2

The confirmation of the condition for full graphene domains is carried out by optical microscope, also Raman spectroscopy can check whether the graphene is a monolayer or not. Full-size domain graphene is usually gained to the vicinity of temperature of 1,000°C, growth time of 2 hours. Copper that was just pulled out from the furnace, can be shown domains to us(Fig. 4.1). These copper domains contribute to graphene's domain structures[14].

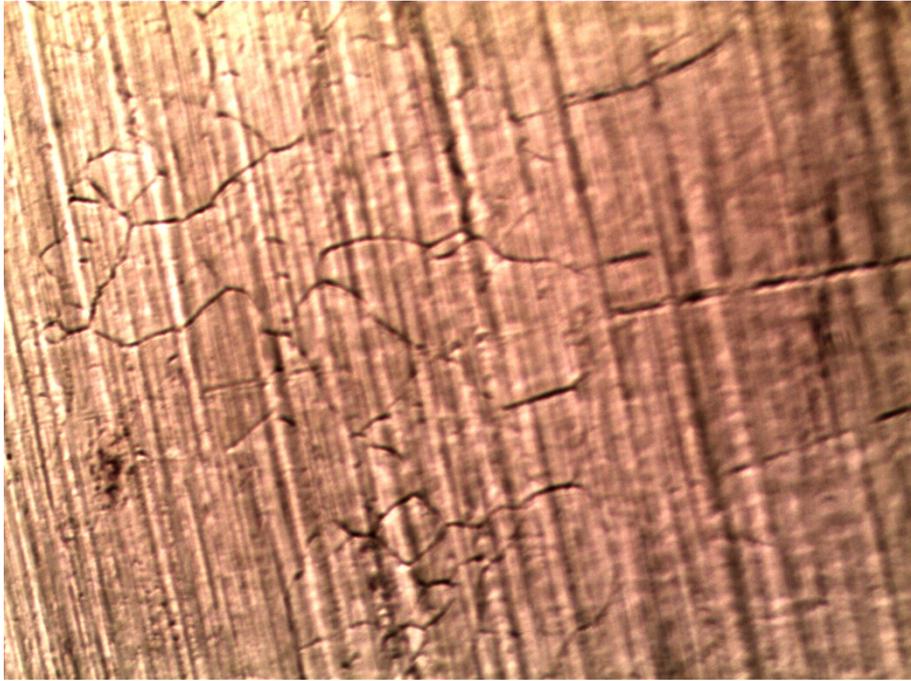


Fig. 4.1 Copper domains after heating around 1010°C

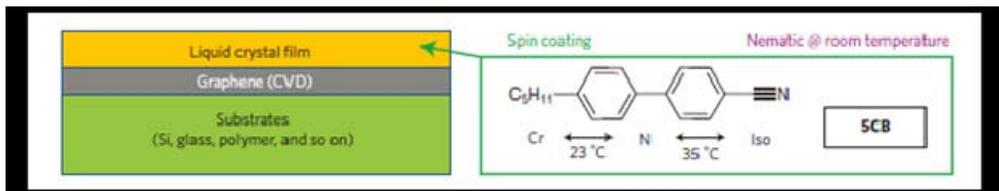


Fig. 4.2 Illustration from article by Dae Woo Kim et al, *Direct visualization of large-area graphene domains and boundaries by optical birefringency*

As growing graphenes many times for setting full-size graphene, the uncertainty whether the graphene is a monolayer or not is revealed. In order to check the graphene monolayer, we performed the Raman spectroscopy (Fig. 4.4). Through Raman spectroscopy, it is confirmed that our graphene is a well-growing monolayer. According to Raman spectra for graphenes [15] (Fig. 4.3), the 514nm Raman spectra shows that the two most intense features are the G peak at  $\sim 1580 \text{ cm}^{-1}$  and a band at  $\sim 2700 \text{ cm}^{-1}$ , historically named G' (2D peak). A bilayer graphene has a much broader and up-shifted 2D band with respect to a monolayer graphene. Thus Raman spectroscopy can clearly distinguish a single layer, from a bilayer from few (less than 5) layers.

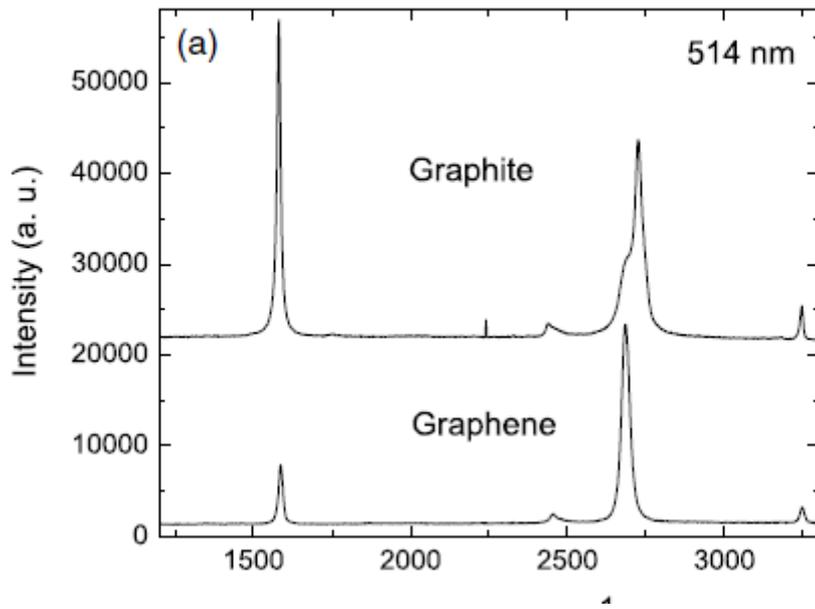


Fig. 4.3 Comparison of Raman spectra at 514 nm for bulk graphite and graphene. They are scaled to have similar height of the 2D peak at  $\sim 2700 \text{ cm}^{-1}$ . (Image from article by A. K. Geim et al, *Raman Spectrum of Graphene and Graphene Layers*)

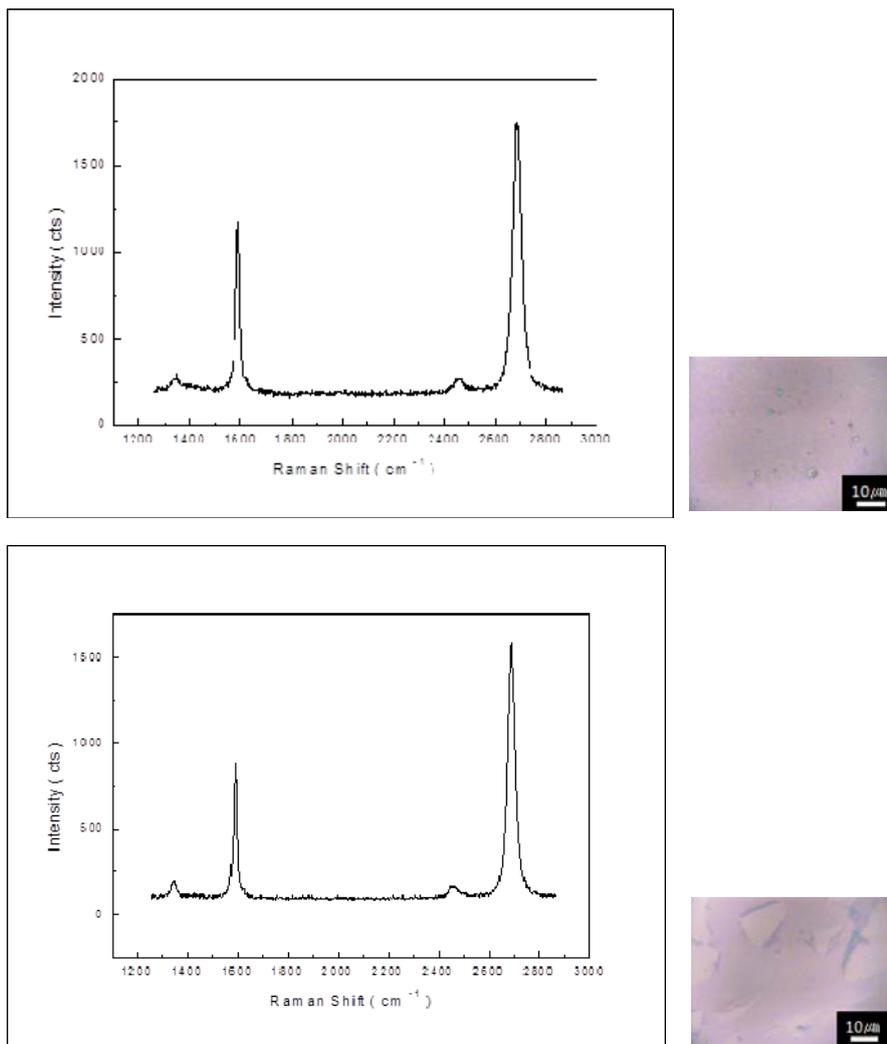


Fig. 4.4 (upper) 999°C, 50min, partial growing graphene.  
(lower) 999°C, 2hr, monolayer graphene.

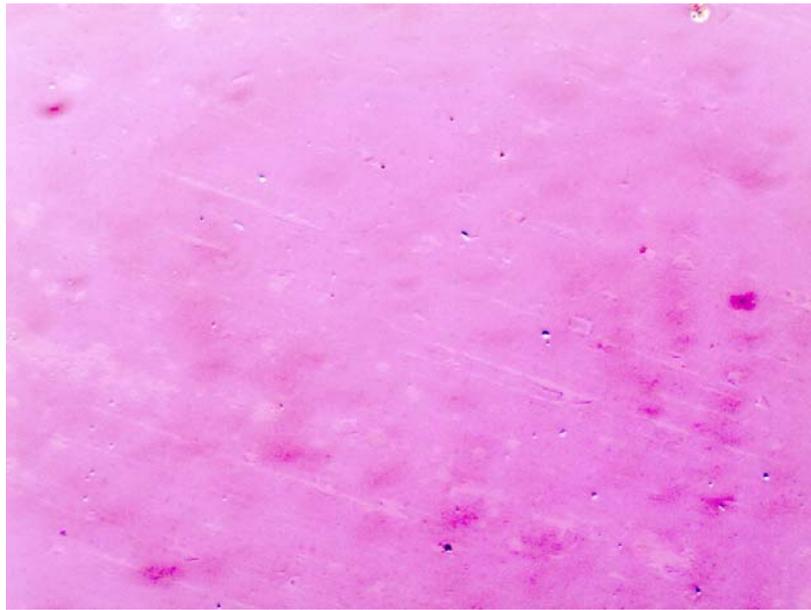


Fig. 4.5 The image of optical microscopy with full-size graphene monolayer (transferred on  $\text{SiO}_2$ )

Fig. 4.5 is the optical microscopy image which corresponds to the growth condition  $\sim 1,000^\circ\text{C}$ , methane exposure time 2hr. Average full growth condition in our furnace ranges between  $995^\circ\text{C}$  and  $1020^\circ\text{C}$  in case of the 1~2 hours of methane exposure time. This long methane exposure time is generally not compatible with the result of Li, X. et al group. They suggest that copper growth more than 60min yields similar structure to growth performed for  $\sim 10$ min. However, the inconsistency in the growth time is assumed that the growth time depends on the difference in geometrical structure of furnace. Actually, our full-size graphene condition was changed because our furnace

had been repaired during doing experiments. The same full-size graphene is slightly different before and after repairing each other.

### 4.3. Polarized Optical Microscope Images

The observing liquid crystals on LD graphene conducted at the laboratory of Prof. Kee Hoon Kim to use polarized microscope by permission. The magnifying power of an eyepiece is 10, and we use the magnifying power of 5, 10 an object lens.

Due to the characteristics of liquid crystals, liquid crystals on LD graphene might result in various birefringent colors, which can verify large domains of graphene. First, we could check the shapes of graphene domains in priority (Fig. 4.6)

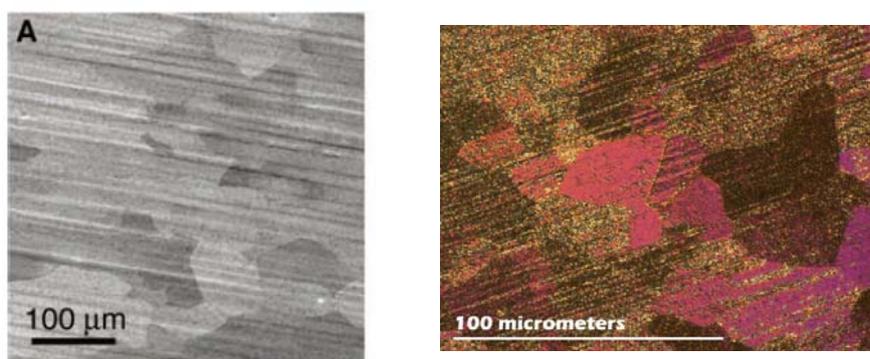


Fig. 4. 6 Left : Domains of graphene by SEM. (Image from the article by Li. X et al, *Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils*) Right : Domains of our graphene on  $\sim 1,000^{\circ}\text{C}$  during methan exposure 2hr,

annealing 10min.

Fig 4.6 shows that our graphene's general domains agree with the SEM result of Li. X. et al group. The size of graphene domains is less than  $100\mu\text{m}$ , but the graphene is well grown. When the direction of polarized light is rotated, the colors of graphene domains are changed (Fig. 4.7). The one changed area means that there is one graphene domain, generally copper domains correlate with them.

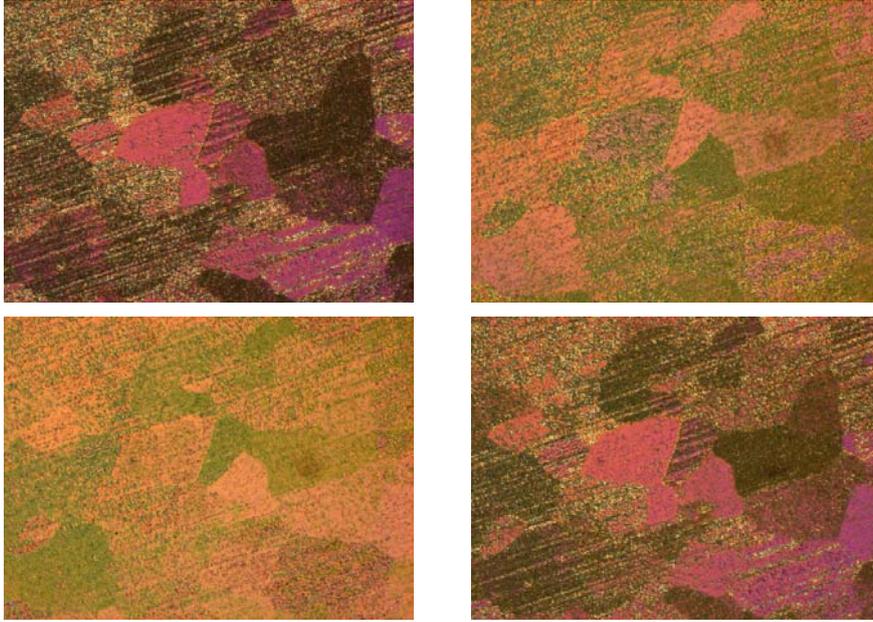


Fig. 4.7 The birefringence of liquid crystals on the LD graphene of Fig. 4.6. The first image and last image are same each other, because the rotation angle is  $180^\circ$

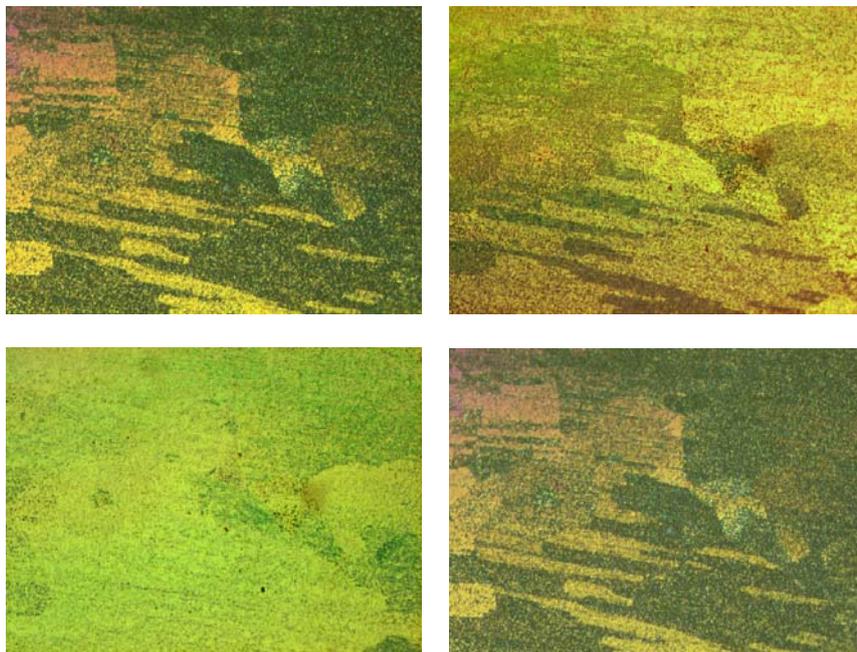


Fig. 4.8 The birefringence of liquid crystals on the LD graphene with no annealing. The image scale is exactly same as Fig. 4.6

Compared to Fig. 4.7, the domains of Fig. 4.8 are rather slim. With this fact, it is assumed that an annealing in graphene growth should be needed to enlarge the domains size of graphene. Another results with no annealing condition are represented in Fig. 4.9.

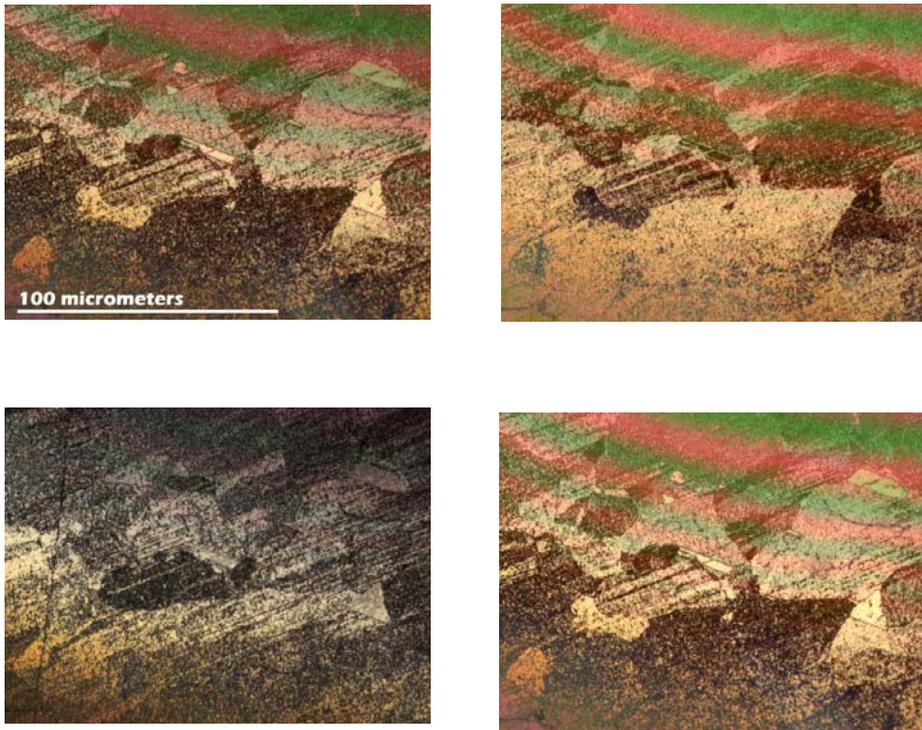


Fig. 4.9 The birefringence of liquid crystals on the LD graphene with no annealing,  $\sim 1,000^{\circ}\text{C}$ , 1hr.

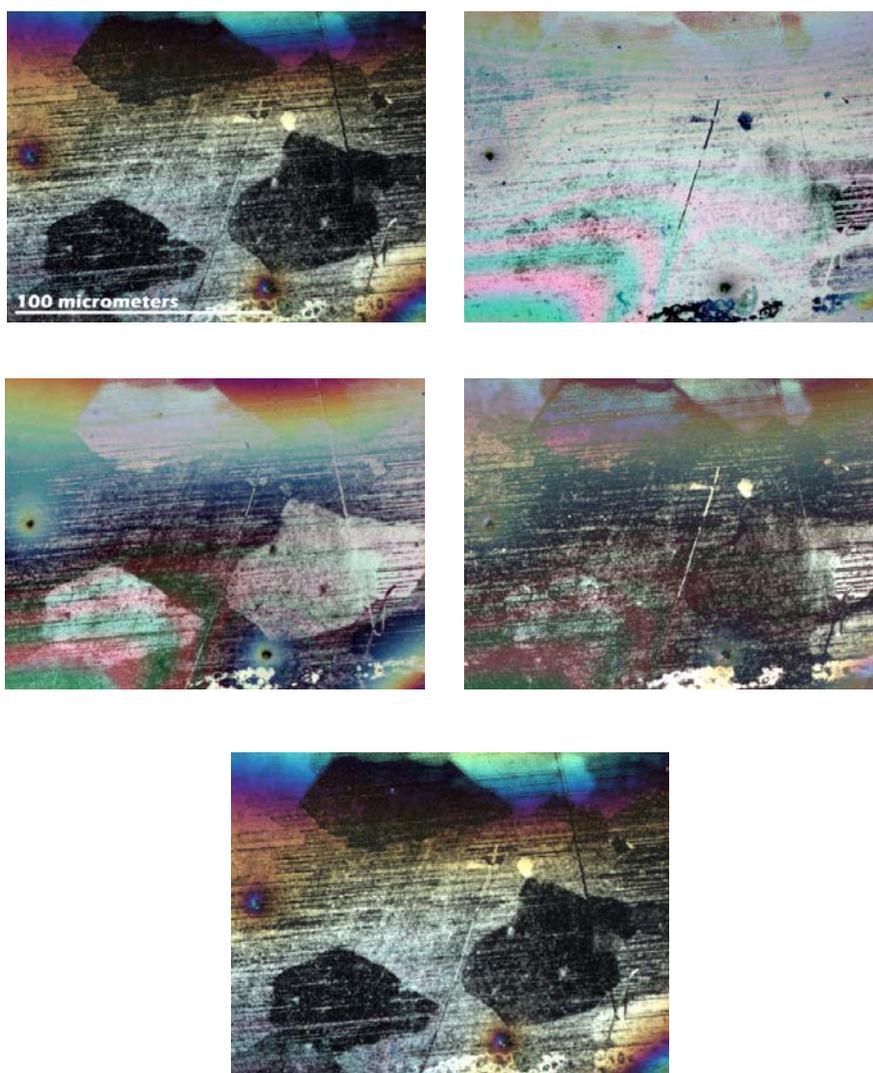


Fig. 4.10 The birefringence of liquid crystals on the LD graphene with 10min annealing during methan exposure time 1hr 30min,  $\sim 1020^{\circ}\text{C}$ .

Let's compare Fig. 4.10. with no annealing condition results. Fig. 4.10 is the result that is increased temperature a little more. Though the size of domains are not superiorly good to compare with that of no annealing conditions, more arranged and clear shapes are observed. We concluded that the high temperature below threshold temperature is sufficient to grow LD graphene, although there is not very critical effect. This temperature condition is required when good quality graphene is needed, and if more annealing time increases, the domain size might be good, which is assumed that we need to research the enlargement of copper domain size.

In case of partial growth (low temperature), it is certain that the domain size is quite small (Fig. 4.11a). We estimated that this resulted from Cu CVD principle—the surface absorption. Full-size domain images (~1010°C, 2hr growth, 10min annealing) are stated as comparison (Fig. 4.11b).

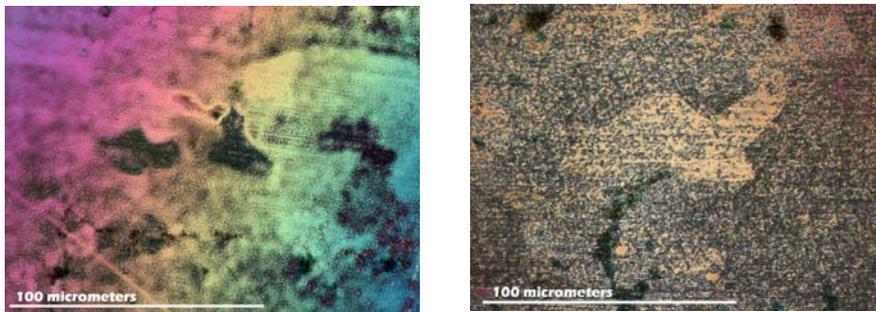


Fig. 4.11 (a) Domains of partial growing—graphene.

(b) Domains of full—size graphene.

## Part 5. Conclusion

As described, we can show that our graphene has quite large domains, but not larger domains than other recent researches. When we check the domain size by using liquid crystal, the temperature dependence seems to be weak concerning the domain size of graphene. We assume that it is caused by sensitive growth condition—our homemade furnace's operation has the fluctuation on the growth condition recently. However, we conclude that domain size is related to the domain of copper, so if copper domains are expanded, we would expect the larger size of graphene domain. Also, more precise details about 2-step growth method and other growth methods are needed because of the larger domain possibility [16–19].

## References

- [1] A. K. Geim, K. S. Novoselov, “ The Rise of Graphene” , *Nature Materials* **6**, 183 – 191 (2007)
- [2] Castro Neto *et al.*, “The electronic properties of graphene” , *Rev. Mod. Phys.*, Vol. 81, No. 1, January–March 2009
- [3] Cecilia Mattevi *et al.*, “A review of chemical vapour deposition of graphene on copper” , *J. Mater. Chem.*, 2011,21, 3324–3334
- [4] EPITAXIAL GRAPHENE FILMS ON SiC: GROWTH, CHARACTERIZATION, AND DEVICES
- [5] D. Kurt Gaskill *et al.*, “Epitaxial Graphene Growth on SiC Wafers” , *ECS Trans.* 19, 117 (2009)
- [6] Claire Berger *et al.*, “Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphene–based Nanoelectronics” , *J. Phys. Chem. B* 2004, *108*, 19912–19916
- [7] J Hass, W A de Heer and E H Conrad, “The growth and morphology of epitaxial multilayer graphene” , *J. Phys. : Condens. Matter* 20 (2008) 323202
- [8] Xuesong Li, *et al.* “Graphene Films on Copper Foils Large–Area Synthesis of High–Quality and Uniform” , *Science* 324, 1312 (2009)

- [9] Rodney S. Ruoff et al., “Synthesis and Characterization of Large–Area Graphene and Graphite Films on Commercial Cu–Ni Alloy Foils” , *Nano Lett.* 2011, 11, 3519–3525
- [10] Rodney S. Ruoff et al., “Evolution of Graphene Growth on Ni and Cu by Carbon Isotope Labeling” , *Nano Lett.*, Vol. 9, No. 12, 2009
- [11] 최이준 ; 진정일 공저 , 『 액정고분자 』 , 문운당, 2001
- [12] 피터 콜링스 저, 이신두 역, 『액정 : 자연의 미묘한 상』 , 전파과학사, 1994
- [13] Ingo Dierking, 『Textures of liquid crystals』 , Wiley–VCH, 2003
- [14] Daewoo Kim et al., “Direct visualization of large–area graphene domains and boundaries by optical birefringency” , *Nature Nanotech.* 2011, 198, 29–34
- [15] A. C. Ferrari et al., “Raman Spectrum of Graphene and Graphene Layers” , *PRL* 97, 187401 (2006)
- [16] Li Tao, Rodney S. Ruoff, “Synthesis of High Quality Monolayer Graphene at Reduced Temperature on Hydrogen–Enriched Evaporated Copper (111) Films” , *Nano lett.* 2012, vol 6, NO. 3 , 2319–2325
- [17] Bin Zhang et al., “Low–Temperature Chemical Vapor Deposition Growth of Graphene from Toluene on Electropolished Copper Foils” , *Nano let.* 2012, VOL. 6, NO. 3, 2471–2476
- [18] Xuesong Li et al., “Large–Area Graphene Single Crystals

Grown by Low-Pressure Chemical Vapor Deposition of Methane on Copper” , J. Am. Chem. Soc. 2011, 133, 2816–2819

[19] Xuesong Li et al., “Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process” , *Nano Lett.* 2010, 10, 4328–4334

## 국문초록

그래핀은 탄소가 2차원 벌집 구조로 결합된 물질로, 탄소-탄소 결합 물질의 기본적인 형태라고 할 수 있다. 그래핀은 여러 가지 특성들로 인해 주목받고 있는데, 이 전기적 특성들은 그래핀 트랜지스터, 집적회로 등등 여러 곳에 사용될 수 있는 잠재력을 지니고 있다.

이 그래핀의 전기적 특성을 높이기 위해서, 그래핀 도메인 사이즈를 키울 필요성이 요구된다. 그래핀의 전기적 특성은 그래핀의 도메인이 크면 클수록 좋아지며, 따라서 그래핀 도메인 사이즈의 확대는 더 나은 그래핀 관련 물질을 개발하는데 필수적이다. 이 그래핀의 사이즈 확대를 확인하는데, 최근에 액정을 이용하여 편광 현미경만으로도 간편히 볼 수 있는 방법이 알려져 있다.

이 논문에서는 자체적으로 제작된 CVD 방식 그래핀 제작을 통해 큰 도메인 사이즈의 그래핀을 만들어 보며, 그 도메인 사이즈를 액정으로 확인하여 다른 리서치 그룹의 결과와 비교해 보려 한다.

**주요어 :** 그래핀, 그래핀 도메인, CVD, 액정

**학 번 :** 2010-23153