

A DETAILED STUDY ON CONTROLLED SYNTHESIS AND DEVICE INTEGRATION OF
MONOLITHIC GRAPHENE-GRAPHITE STRUCTURES

BY
SUNGGYU CHUN

THESIS

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Advisor:

Professor SungWoo Nam

ABSTRACT

This thesis presents the controlled synthesis and the characterization of monolithic graphene and graphite through low pressure chemical vapor deposition (LPCVD) method. Selective patterning of heterogeneous metal catalysts enables a simultaneous and controlled growth of graphene and graphite with varying number of graphene layers. The number of graphene layers and graphite thickness can be controlled by using different catalytic metals or by modulating the thickness of source catalytic metal. Using the presented synthesis technique, we have successfully grown monolithic structure of graphene and graphite ranging from single to few hundred in number of graphene layers. Graphene based field-effect transistor (FET) is fabricated with monolithic graphene-graphite structures. Especially, superior mechanical flexibility of the fabricated graphene FET enables it to be transferred onto a variety of substrates, including soft materials. This thesis also explores the fabrication of crumpled three-dimensional (3D) graphene structure through thermally-activated shrinkage of the base substrate, which can be exploited as 3D biological sensor mechanism. A detailed analysis on synthesis and characterization of monolithic graphene-graphite structures is explained in detail.

*This thesis is dedicated to my beloved family for their limitless love,
endless support, and encouragement.*

*Particularly to my parents,
whose love have sustained me throughout my life.*

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CHAPTER 1

INTRODUCTION

Over the past several years, graphene has drawn worldwide interest because of its extraordinary electrical and mechanical properties such as high carrier mobility, mechanical stiffness, elasticity, and high electrical and thermal conductivity[1, 2]. Superior material properties of graphene have motivated the development of various graphene synthesis processes and graphene-integrated devices for wide ranges of applications, including electronic, bioelectronics, and photonic applications such as flexible touch screen, foldable OLED, transistor applications, and polarization controller, photodetector, and etc. [3]. Especially, graphene electronics are considered to be potential supplements for current silicon CMOS devices, such as transistors, chemical sensors, and biosensors.

Graphene is known to be the first two-dimensional (2D) atomic crystal that has been found. Graphene was initially introduced to the world by the micromechanical cleaving of graphite, or so called the Scotch-tape method [1]. The Scotch-tape method was able to fabricate graphene with reasonable structural and electromechanical qualities, but the method itself was not efficient and reliable. It lacked the stability in production of graphene with a reasonable quality, which was not suitable for large-scale or mass production of graphene. The production efficiency of graphene became more reliable by the method using reduction of graphene oxide via chemical reduction and/or thermal annealing [4]. This method involved prior oxidation of graphite, followed by subsequent aqueous exfoliation, deposition as thin film onto a substrate, and finally reduction back to graphene [5-7]. Nonetheless the reduced graphene oxide (rGO) improved the efficiency and yield rate, it lacked in uniformity in thickness and the size of graphene was limited to a few

micrometers. Epitaxial growth of graphene on Silicon carbide (SiC) seemed to resolve the problems. This method fabricated graphene via sublimation of SiC surface at high temperature and/or high vacuum, which produces high quality of graphene crystal domains with the size of several micrometers [8-12]. Even if this multilayer graphene reduced from SiC via thermal annealing had great electromechanical quality [13], there were technical difficulties to transfer graphene to other substrates. Also, the high temperature condition was required for sublimation, but it was not compatible with existing electronic device fabrication processes.

The introduction of chemical vapor deposition (CVD) method to graphene synthesis resolved some of those problems [14-17]. A great advantage of CVD was that it was compatible with large scale synthesis unlike all other synthesis methods introduced earlier. CVD method first enabled centimeter-scaled sized monolayer graphene with gaseous methane (CH_4) and hydrogen (H_2) as precursors on copper foil [15, 16, 18]. This was followed by the fabrication of a 30 inch graphene film for transparent electrodes by using CVD and roll-to-roll transfer method [19]. Graphene synthesized by CVD not only had electromechanical properties that are comparable to those grown from SiC, but was also easily transferable onto many other substrates by using wet-etching of the catalytic metal substrate. As the transfer process of graphene after synthesis became improved and optimized, the defects or damages of transferred graphene were minimized.

Recently developed monolithic graphene-graphite synthesis method [20] has demonstrated a great potential for one-step direct synthesis of graphene-graphite electronics. A careful analysis and characterization of monolithic graphene-graphite synthesis is required to accurately control the structure morphology and improve the synthesis reproducibility. In addition, an efficient transfer method needs to be developed for device integration of synthesized monolithic graphene-graphite structures. This thesis presents a detailed study on controlled growth and transfer of

monolithic graphene-graphite structures by exploring the new synthesis approach for thin layer graphene and thick graphite using various catalytic substrates, such as copper (Cu) and cobalt (Co). The investigation of the relationship between the thickness Co catalytic metal and the thickness of resultant graphite structure provide a quantitative analysis of monolithic graphene-graphite synthesis. Moreover, this thesis demonstrates the fabrication of all-carbon FETs using the developed synthesis and transfer methods of graphene-graphite structures. The fabrication of crumpled 3D graphene-graphite structure via thermally-activated shrinkage of the base substrate also helps to pave the way for the 3D sensing capability as well as the intracellular recording of living cells in the future.

CHAPTER 2

SYNTHESIS AND TRANSFER OF GRAPHENE

Among the number of different graphene synthesis methods, the synthesis via CVD has become the most popular nowadays because of its capability of synthesizing graphene with good quality and feasibility of large-scale synthesis of graphene. The basic CVD process is composed of heating, annealing, synthesizing, and cooling. Even though the synthesizing period is the most crucial factor that determines the quality of graphene, the importance of annealing and cooling periods should not be ignored. The heating and hydrogen annealing periods are important since they have capabilities of modulating the number of defects by removing excessive copper oxide on the surface of Cu substrate or enlarge the grain sizes of Cu substrates by suppressing nucleation sites [21]. Figure 2.1 shows the LPCVD system that is used to grow graphene and graphite under the low pressure close to 520 mTorr and the temperature of around 1050 °C. It is connected to three gas tanks, hydrogen, methane, and argon (Ar).



Figure 2.1 Actual LPCVD system for graphene and graphite synthesis: entire system (left), load lock (right).

The quality of graphene is determined by various synthesis parameters, such as gas flow rate, gas flow ratio, set pressure, annealing time, synthesis temperature, and synthesis time. These parameters are quantifiable and scalable so the quality of graphene is stable under same synthesis conditions. Hydrogen and methane gases are the most popular precursor for graphene synthesis. The amount of gas flow or partial pressure of synthesis gases determines the thickness or the quality of graphene. Increasing methane flow rate would provide more carbon sources and result in thicker graphene, while increasing hydrogen flow rate would enhance the chances of getting thinner graphene. Higher ratio of hydrogen to methane significantly reduces the chance of carbon depositing on the surface of Cu catalyst because excessive hydrogen gas prevents formation of carbon nucleation sites. The annealing temperature and time are also important. Hydrogen annealing at high temperature (above 900 °C) cleans the surface of a Cu substrate by removing native copper oxide or impurities. Pre-synthesis annealing also enlarges grain sizes of a Cu substrate, which results large area single crystalline graphene synthesis. However, the most important parameters should be synthesis temperature and time. A low-pressure mixture of methane and hydrogen flowing over Cu substrate heated to a temperature close to the melting temperature of Cu (~1100 °C) [22]. Even if high synthesis temperature is necessary in the synthesis of high quality graphene, it also induces a dewetting or evaporation of catalytic metal film. The dewetting is undesirable because it decreases uniformity of the metal film and causes defects or breakage on resultant graphene film. The excessive annealing or synthesis time also induces dewetting of the catalytic metal film. Therefore, synthesis of graphene with good quality requires the optimized conditions of time and temperature.

CVD graphene synthesis requires catalytic metals such as Cu, nickel (Ni), and Co to dissociate hydrocarbon gas molecules (usually methane) into carbon and hydrogen. Each catalyst

has its own level of carbon solubility so the process of graphene synthesis and results are different from metal to metal. Unlike Ni and Co, which are known to possess high carbon solubility [15, 23], Cu has only negligible carbon solubility [16]. This self-limiting characteristic of Cu allows a few layers of graphene when graphene was grown on a Cu catalytic surface [16, 24, 25]. When methane and hydrogen gases are introduced to the CVD chamber, hydrogen reduces Cu surface and also facilitate reverse reaction of methane decomposition. Carbon atoms decomposed from the methane are then deposited onto the surface of the metal through chemical adsorption, resulting in a single layer or few layers of graphene. Graphite or thick multilayers graphene tend to be synthesized on Ni and Co catalytic metals due to their high carbon solubility. Carbon atoms are absorbed into Ni or Co catalytic metal films at the beginning of the synthesis. As temperature of metal film decreases, the solubility of the catalytic metals decreases. As a result, the dissolved carbon appears on the surface and form multilayer or thick graphene film.

2.1 Graphene synthesis on Cu foil

Graphene growth on Cu foil is a popular way to synthesize graphene because of its low cost and accessibility. Before the CVD synthesis, Cu foil is pretreated with hydrochloric acid for 10mins. The main purpose of the pretreatment is to remove native copper oxide [26, 27] and impurities on the surface of Cu foil. Remaining copper oxide residue on the surface of Cu foil is also stripped under high temperature environment during hydrogen annealing. As previously discussed, hydrogen annealing not only removes an oxide layer on copper surface, but also helps to produce enlarged grain size, which would improve the electromechanical properties of graphene. Figure 2.2 shows a schematic illustration of a typical CVD graphene growth process including heating, annealing, synthesizing, and cooling conditions.

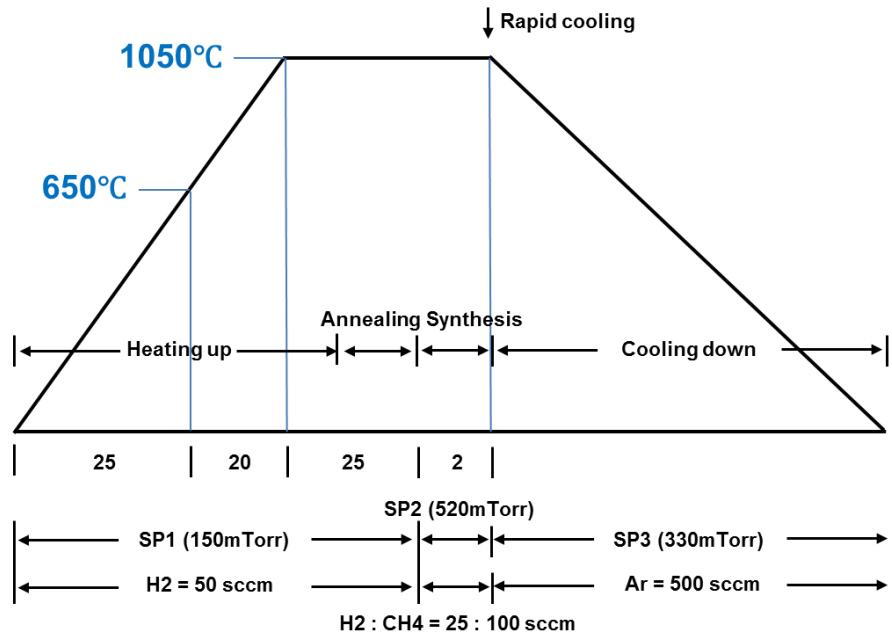


Figure 2.2 A schematic illustration of a typical CVD graphene growth process including heating, annealing, synthesizing, and cooling phases

When the Cu foil is placed into the CVD chamber, the chamber is pumped down below 1mTorr and heated up to synthesis temperature. During the heating period, the pressure of the CVD chamber raises to 150mTorr as 50sccm of hydrogen begins to flow. After the temperature of the chamber raises above 1000 °C, the Cu foil is annealed with hydrogen gas for 20 minutes to enlarge grain size of Cu and also to remove Cu oxide, which result in a better quality of graphene. After the annealing period, the pressure of the CVD chamber increases to 520mTorr with inflow of 50sccm of hydrogen and 100sccm of methane. When the pressure of CVD chamber stabilizes, the synthesis period begins and the actual growth of graphene occurs at 1050 °C for 2 minutes. Both hydrogen and methane gases are involved in the reaction. The ratio between hydrogen and methane gases is one of the most critical factors to determine the quality of graphene. After the synthesis phase, the substrate is cooled for characterization and fabrication. During the cooling period, both hydrogen and methane tanks are turned off and only argon flows to regulate the pressure of the chamber close to 330mTorr. The cooling rate of the substrate also affects the quality

of graphene by dominating the amount of carbon segregation. The cooling rate of the substrate is about 14 °C/s. By adopting a rapid cooling technique, the carbon segregating sites can be reduced [28].

The synthesized graphene is transferred onto a clean SiO₂/Si substrate for characterization. The transfer of graphene film is performed via wet transfer method, which is explained in detail at the end of the chapter. Figure 2.3 shows the optical microscope images of synthesized graphene with different magnifications after graphene is transferred on a SiO₂/Si substrate for characterization. There is no distinctive damage or defect visible on the graphene surface. Therefore, the current synthesis process has capability of producing graphene of a good quality with a negligible level of defects.



Figure 2.3 Optical microscope images of graphene synthesized on Cu foil and transferred on a clean 285nm thick SiO₂/Si substrate with different magnifications.

Raman spectra results provide reliable information to determine the quality of graphene. Raman spectra exhibit three characteristic bands of graphene and graphite: (1) D band centered at $\sim 1,350\text{cm}^{-1}$, (2) G band centered at $1,590\text{cm}^{-1}$, and (3) 2D band centered at $\sim 2,690\text{cm}^{-1}$ [20]. Figure 2.4 shows the Raman spectra to demonstrate the effect of pretreatment. A graphene sample with pretreatment (shown in red) not only shows much lower D band intensity than that of the graphene sample without pretreatment (shown in black), but also much higher 2D to G band intensity ratio (~ 2.3). This 2D to G band intensity ratio demonstrates the existence of only single or bi-layer of graphene. The higher 2D band intensity of graphene film with pretreatment indicates its higher crystalline quality compared to the graphene synthesized without pretreatment.

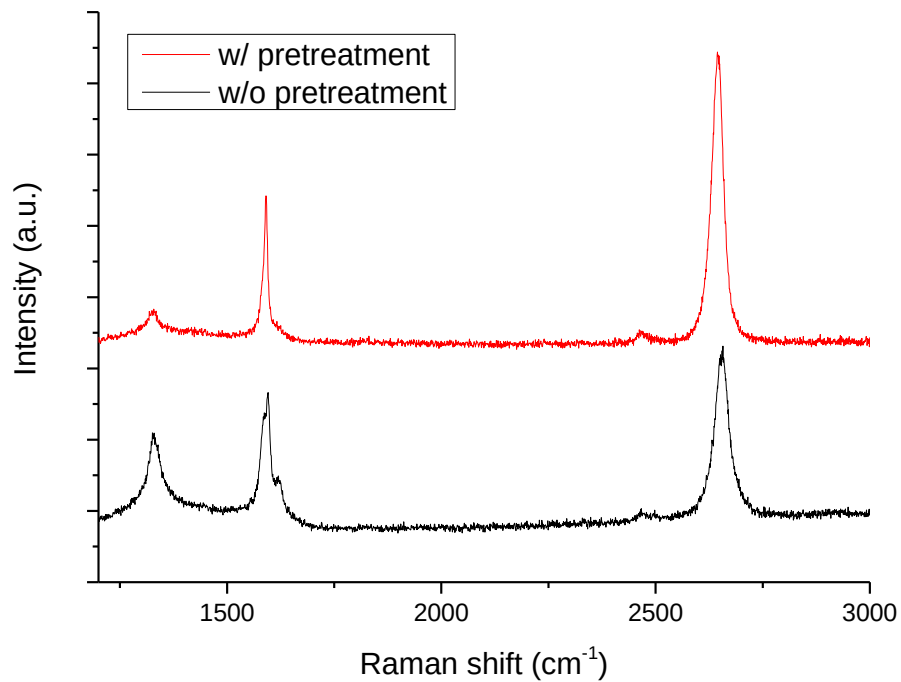


Figure 2.4 Raman spectra of graphene prepared with pretreatment (red) and without pretreatment (black). The graphene samples were transferred on a clean 285nm thick SiO₂/Si substrate to be measured.

2.2 Graphene synthesis on Cu film

The overall synthesis process of graphene on a Cu film is almost similar to that on a Cu foil. For the graphene synthesis on a Cu film, 700nm thick Cu catalytic metal is deposited on top of a clean SiO₂/Si wafer with a sputter or thermal evaporator. Graphene growth on a Cu film has some advantage over that on a Cu foil. Backside graphene layer frequently occurs at graphene synthesis on a Cu foil because graphene synthesis happens on the both sides of the Cu foil. During the transfer process, the backside graphene induces contamination and additional mechanical defects such as wrinkles or breakages. Unlike the Cu foil, a Cu film on a SiO₂/Si substrate has no Cu layer on the backside of the substrate. The SiO₂ on the backside of the substrate can prevent graphene from growing on the backside of the substrate. As a result, transfer of graphene film becomes much easier and more stable.

Furthermore, the evaporated Cu film guarantees surface cleanness and better uniformity than a Cu foil, so the graphene synthesis on the Cu film does not generally require hydrochloric acid pretreatment. The major difference between synthesis processes with these two substrates is the duration of the annealing period. A long annealing period induces much severe dewetting in the case of the copper film [27]. If the dewetting becomes really severe, graphene film grown across the voids missing Cu film tends to attach to the SiO₂ substrate. When this happens, the bonding between graphene film and SiO₂ substrate does not allow the graphene film to detach from the substrate even after all the Cu film is etched away.

Figure 2.5 shows the graphene film on dewetted Cu film before and after Cu etching. Circular regions indicate that dewetting happened during lengthy exposure of the substrate to high temperature in CVD chamber. For the samples without dewetting, Cu etching normally takes 5 to 6 hours. It is notable that Cu film cannot be completely etched even with an elongated etching time

(1 or 2 days). The dewetting becomes more severe if the thickness of the Cu film is thinner. The uniformity of graphene film quality cannot be guaranteed if the thickness of Cu film is less than 500 nm [27].

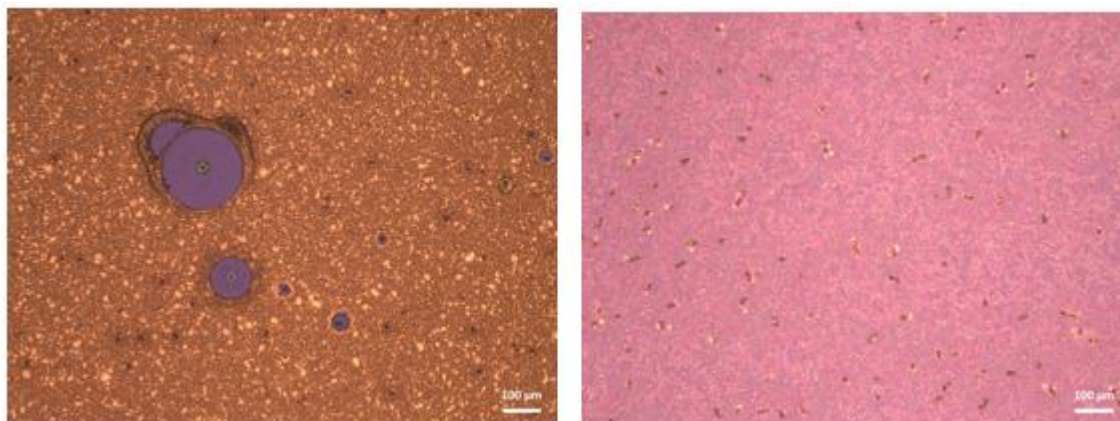


Figure 2.5 Optical microscope images of dewetted Cu film before Cu etching (left) and optical microscope image of dewetted graphene film after Cu etching (right).

To reduce such dewetting of Cu film, the optimization of synthesis temperature, and annealing and synthesis time is required. Figure 2.6 shows the optical microscope images of graphene film synthesized on a Cu film with optimized conditions and transferred onto a clean SiO₂/Si substrate. The transferred graphene film appears to be highly uniform. There are no visible defects or wrinkles present on the surface of transferred graphene. The substrate is exposed to high temperature of 1050 °C for a total of 4 minutes, including 2 minutes of annealing time and 2 minutes of synthesis time. If the substrate is exposed to high temperature longer than 4 minutes, it can deteriorate the uniformity of Cu film, resulting in discontinuous graphene film. Even if the quality of graphene seems to be better as time of annealing is close to 5 minutes, the disconnection of film becomes more severe. Even though the synthesized graphene has good quality, it is impossible to use it for fabrication of any devices if those physical disconnections or breakages exist on resultant graphene film.



Figure 2.6 Optical microscope images of graphene synthesized on Cu film and transferred on a clean 285nm thick SiO₂/Si substrate with different magnifications.

Figure 2.7 shows the Raman spectra of graphene transferred on a clean SiO₂/Si substrate in order to investigate the effect of different amount of annealing time on graphene samples. All the graphene samples are synthesized at 1050 °C for 2 minutes with 50sccm of hydrogen and 100sccm of methane. The graphene sample without annealing (black) shows a small 2D band intensity, and noticeable G and D band intensity without distinctive peaks, which indicate the existence of amorphous carbon, rather than graphitic material. There is not much difference in the 2D to G band intensity ratio (~1.55) between graphene samples with 2 minutes of annealing (red) and 5 minutes of annealing (blue). It is notable that the intensity for the D band intensity is dramatically decreased as the annealing time is increased from 2 minutes to 5 minutes. This proves that the graphene sample with 5mins of annealing time has much better crystalline quality and

fewer defects than that with 2 minutes of annealing time. However, longer annealing time induces disconnection of the graphene film, which deteriorates the uniformity of the graphene film.

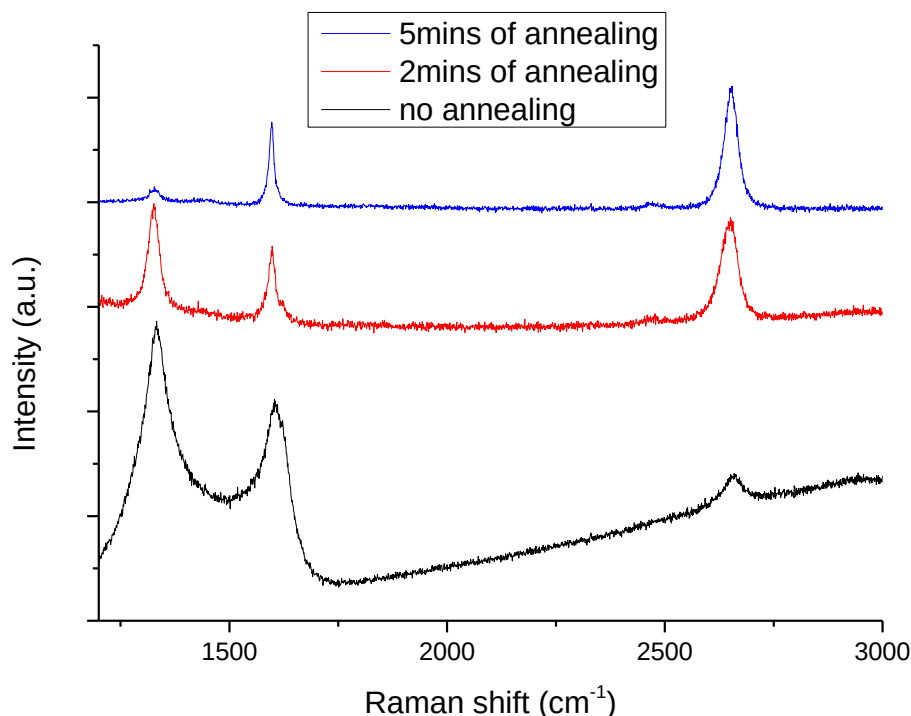


Figure 2.7 Raman spectra of graphene with different annealing times: no annealing (black), 2mins (red), and 5mins (blue). The Raman characterization were performed after the graphene was transferred on a clean 285nm thick SiO₂/Si substrate.

2.3 Graphite synthesis on Co/Cu film

Unlike graphene synthesis, graphite (or multilayer graphene) synthesis requires the catalytic metal that possesses high carbon solubility, such as Ni and Co. These catalytic metals can produce graphite or multilayer graphene by segregation and precipitation of the carbon on the metal surface [17, 20, 24]. To prepare the samples for graphite synthesis, a Cu film is deposited on a clean SiO₂/Si substrate by a sputter. The thickness of underlying Cu film should be thicker than 700nm to minimize the dewetting of the catalytic metal film. After the Cu film is deposited,

a Co film is then deposited. The overall synthesis process of graphite after the Co/Cu film preparation is the same as that of graphene on Cu film.

Figure 2.8 shows the optical microscope images of graphite synthesized on sputtered Co/Cu film and transferred on a clean SiO₂/Si substrate for characterization. The thicknesses Co and Cu catalytic metals are 400nm and 700nm, respectively. The color contrast of the graphite look greener or bluer compared to that of the graphene shown in Figure 2.3 and Figure 2.6. The color of the SiO₂/Si substrate is usually shown in pink or violet through our optical microscope. A single or bi-layer graphene does not change the color contrast so that the microscope images of graphene are not much different from those of bare SiO₂ substrate. As the thickness of graphene increases, the multilayer graphene or graphite film changes the color contrast on microscope images. A difference in color contrasts between Figure 2.3 and Figure 2.8 can support the fact that the thickness of the synthesized material is much thicker than graphene film. As shown in Figure 2.8, the color contrast tends to be slightly different from region to region. This indicates that the synthesized graphite does not have perfect uniformity. Some areas have thicker graphite film shown in bright or intense blue, while some other areas have thinner graphite film shown in pink or light blue.

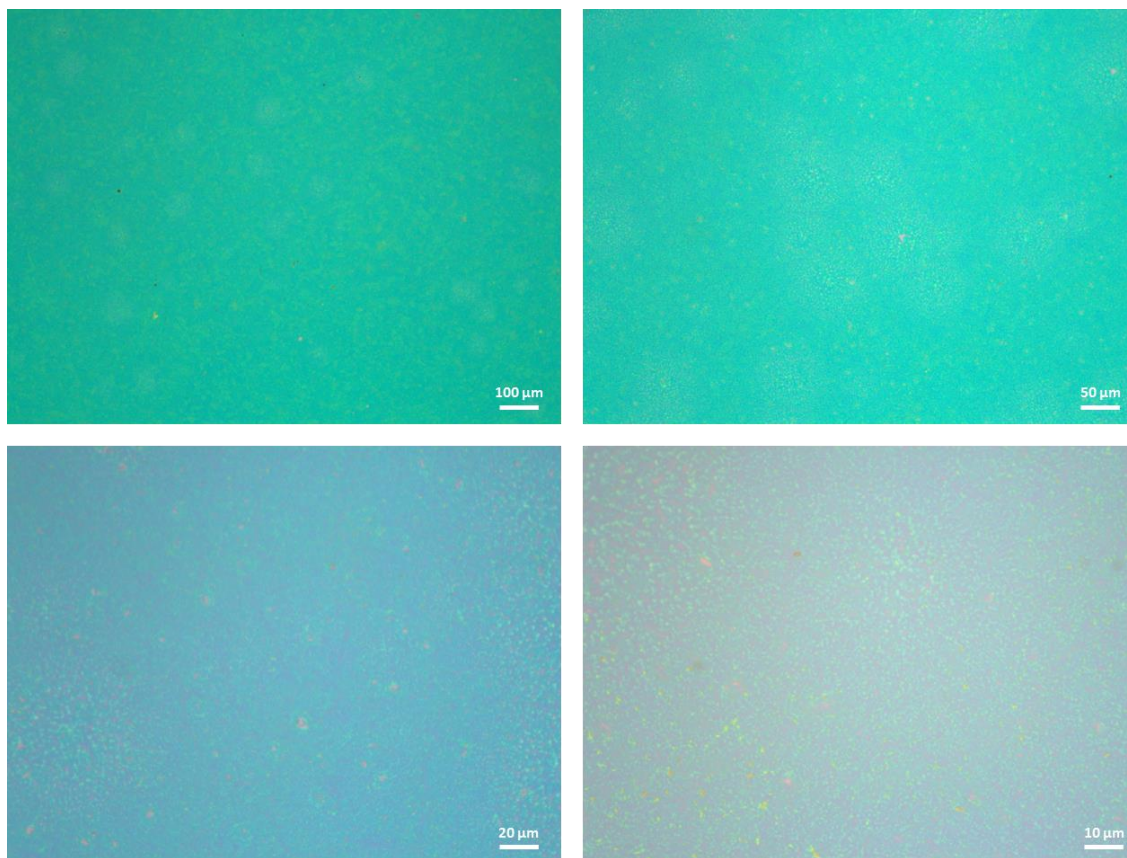


Figure 2.8 Optical microscope images of graphite synthesized on a Co/Cu film and transferred on a clean 285nm thick SiO₂/Si substrate with different magnifications.

Figure 2.9 shows the Raman spectra of synthesized graphite film after transfer onto a SiO₂/Si substrate. Unlike high 2D to G intensity ratio of single layer graphene (~ 2.3) shown in Figure 2.4, the 2D to G intensity band intensity is only about 0.6. Low 2D to G band intensity ratio is a positive evidence of an existence of thick graphite. The region with relatively thinner graphite shows a slightly higher 2D to G band intensity ratio (~ 0.8) than the region with relatively thicker graphite. The uniformity of graphite film should be improved to achieve better quality of graphite for further fabrication.

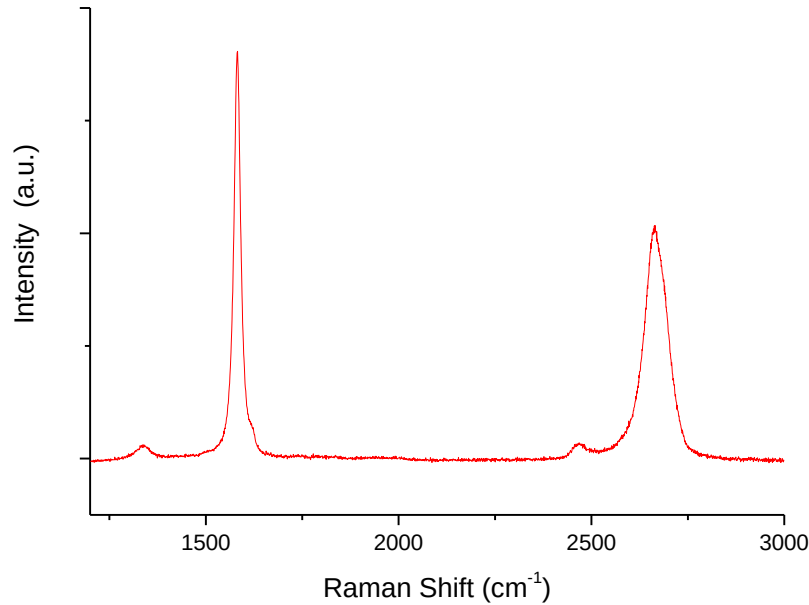


Figure 2.9 Raman spectra of graphite synthesized on Co/Cu film with the thickness of 400nm/700nm and transferred on a 285nm thick SiO₂/Si substrate.

2.4 Graphene and graphite transfer

As mentioned in the beginning of the chapter, one advantage of graphene film synthesized via CVD is its capability of easy transfer compared to the other synthesis methods such as exfoliation through reduction of graphite oxide or epitaxial growth on SiC. After graphene or graphite is grown on Cu or Co catalytic metal substrate, it has to be transferred to other substrates for further characterization or device fabrication. One of the most popular transfer methods is wet transfer using a thin film of poly-methyl-methacrylate (PMMA). Figure 2.10 shows a schematic illustration of a simple PMMA assisted wet transfer process. After graphene/graphite growth via CVD, a thin PMMA supporting layer is spin-coated on the synthesized graphene/graphite-metal substrate and baked on a hot plate at 180 °C for 90 seconds to evaporate excessive solvent in PMMA. This PMMA layer on the surface maintains the shape of graphene/graphite film. Otherwise, a

graphene/graphite film would break into pieces during the catalytic metal etching process. The catalytic metal film is then etched in a diluted sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) solution, which is capable of etching both Cu and Co and compatible with PMMA. The PMMA-graphene/graphite film floats on the surface of the solution due to surface tension. The sample is then transferred onto a surface of DI water bath for cleaning and finally transferred to the surface of a clean SiO_2/Si substrate. The transferred PMMA-graphene/graphite film is exposed with a gentle N_2 flow to get rid of water and kept in ambient atmosphere for complete drying. After the PMMA supporting layer is removed with acetone and isopropyl alcohol (IPA), the graphene sample is ready for characterization or further device fabrication. If the film was not completely dried, water residue breaks the film or makes holes while the PMMA layer is removed with acetone. There are some drawbacks in this kind of wet transfer method, such as inducing wrinkles, cracks and tears. PMMA capturing between graphene films during graphene film transfer also deteriorates the quality of film. The advanced transfer approaches can be utilized to improve the process [19, 29].

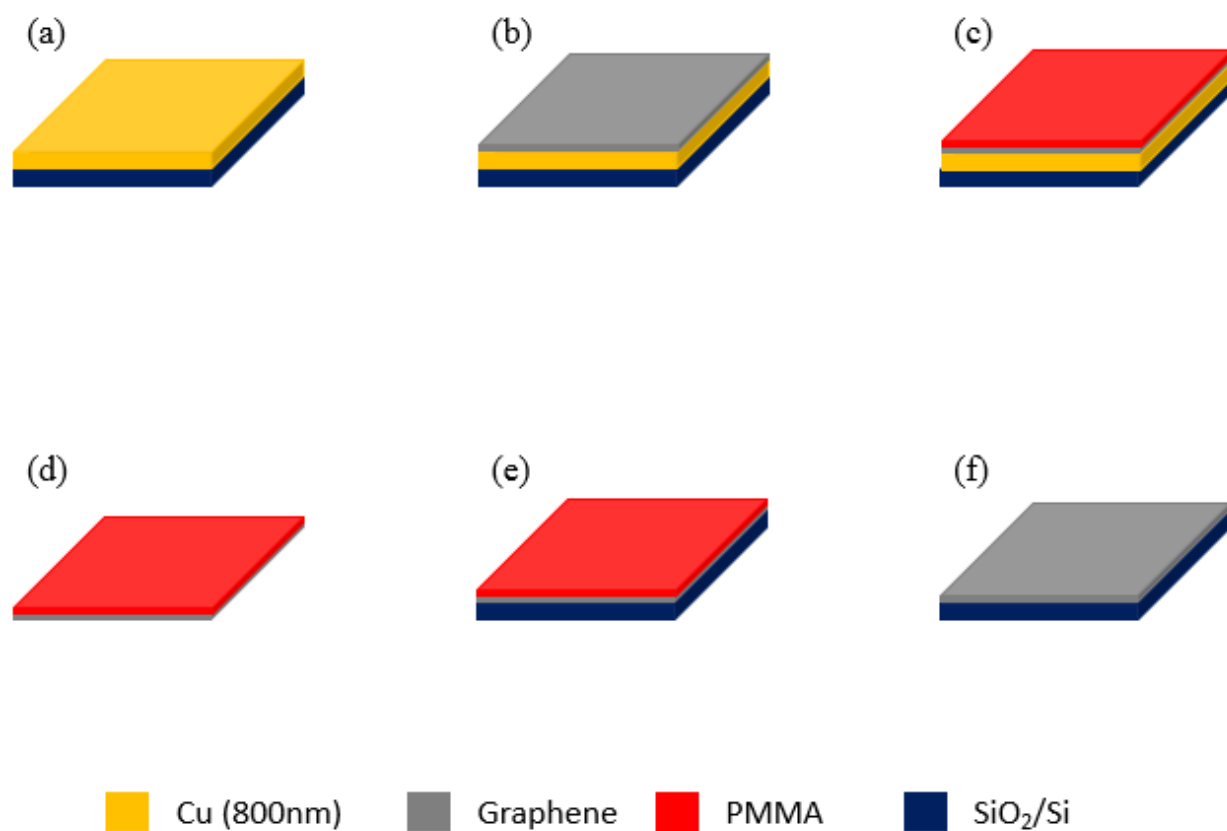


Figure 2.10 Overview of PMMA assisted wet etching transfer process of graphene. (a) Cu deposition on a SiO₂/Si wafer (b) graphene grown on substrate (c) spin coating of PMMA (d) wet etching of the Cu film in the Na₂S₂O₈ (e) transfer on a clean 285nm thick SiO₂/Si wafer and (f) PMMA removal after complete drying.

CHAPTER 3

CONTROLLED SYNTHESIS OF MONOLITHIC GRAPHENE AND GRAPHITE STRUCTURE

The synthesis of individual graphene or graphite film was respectively introduced in the previous chapter. By locally patterning different catalyst metals, the monolithic structure of graphene-graphite can be synthesized via LPCVD. The controlled monolithic graphene-graphite structure can be synthesized by utilizing differences of carbon solubility in heterogeneous catalytic metals during CVD synthesis [20]. By patterning different catalytic metals on localized areas, graphene or graphite with different thicknesses are grown on selective areas. After Cu film with thickness of 700nm is evaporated on a clean SiO₂/Si substrate with a sputter, a photoresist (PR) layer is spin-coated and patterned with simple photolithography techniques. When the PR pattern is developed, the sample is cleaned and dried for further Co deposition with a sputter. The entire substrate is submerged into a stripper to lift off undesirable regions of a Co layer.

After synthesis via LPCVD, thick multilayer graphene, or graphite is grown on patterned Co regions by segregation and precipitation of the dissolved carbon on the surface of Co catalytic metals (>1.3 at.% at 1000°C) [17, 19, 20]. Thin or single layer graphene is synthesized by adsorption of carbon on the surface of background Cu catalyst metal, which only has negligible carbon solubility as mentioned in previous chapter (<0.0001 at.% at 1000°C) [19, 25, 30]. As the temperature increases above 1000°C during CVD synthesis, intermixing of Co and Cu happens at the interface between Co film and Cu film, forming a Co-Cu alloy interlayer. After the catalytic metal is etched away, the monolithic structure of graphene-graphite is produced and transferred on a clean SiO₂/Si substrate for characterization or fabrication. Figure 3.1 shows optical microscope

images of localized graphite letters on graphene background to demonstrate the capabilities of modulating the thickness of graphene and graphite. The letters ‘UIUC’ are patterned with different thicknesses of Co on a Cu background. The image on top shows the graphite synthesized on the Co film with a thickness of 200nm, while the image on the bottom shows the graphite synthesized on the Co film with a thickness of 650nm. The difference in thicknesses between the two synthesized graphite is easily noticeable due to the difference in color contrast.

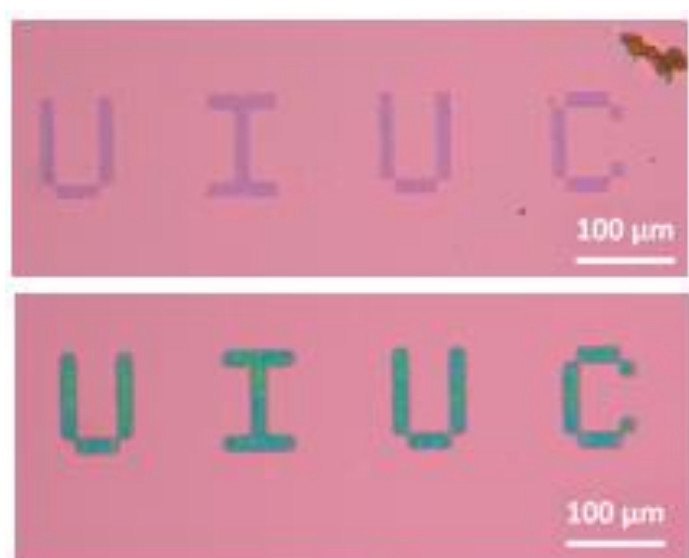


Figure 3.1. Synthetic control of graphene layers. Optical microscope images of graphene with different number of layers. Letters on top are composed of thinner graphite and letters on bottom are composed of thicker graphite. Background is composed of bi-trilayer graphene on a 285nm thick SiO₂/Si substrate.

The control of thickness of graphene and graphite are demonstrated by using different catalytic metals or by modulating the thickness of catalytic metal. The electromechanical properties of graphene can be controlled by changing the thickness of graphene layers. It is known that the conductivity or sheet resistance of multilayer graphene can be controlled more than two orders of magnitude by performing controlled synthesis of graphene multilayers on different metal catalysts [20].

Figure 3.2 shows the optical microscope images of graphite letters patterned on graphene background synthesized with different catalytic metals. Vowels (i.e. E's) are patterned with thicker Co (750 nm) on Cu background (700 nm), while consonants (i.e. C, H, M and S) are patterned with thinner Co (200 nm). According to atomic force microscope (AFM) results, consonants are composed of 10~20 layers of graphene, while vowels are composed of a few hundred layers of graphene. The color contrast between vowels and consonants reveals that the thickness of graphene in vowels is much thicker than that of graphene in consonants.



Figure 3.2. Synthetic control of graphene layers. Optical microscope images of graphene with different number of layers. Consonants are composed of thinner graphite and vowels are composed of thicker graphite. Background is composed of bi- to tri-layer garphene on a 285 nm thick SiO₂/Si substate. Scale bars, 100 μ m (top) and 10 μ m (bottom).

Figure 3.3 shows the Raman spectra characterizations performed on different regions of the monolithic graphene-graphite sample to support the results of synthetic control of graphene and graphite thickness. The background graphene shows a smaller G band intensity compared to the 2D band intensity ($2D/G \sim 1.6$), indicating bi- or tri-layer graphene. The graphite on vowel regions shows a much lower 2D to G band intensity ratio ($2D/G \sim 0.45$) compared to that on consonant regions ($2D/G \sim 0.79$). Lower 2D to G intensity ratio and non-symmetric tendencies of the peak prove that the graphite on vowels represents much thicker graphite than that on consonants. A slight blue-shift due to interlayer binding also indicates the thickness of graphite on vowels is much higher than that of graphite on consonants. All the Raman spectra results show a relatively small D band intensity. The low D to G band intensity ratio close to 0.1 proves that the resultant graphene and graphite films have small number of defects, and are expected to possess superior electrical and mechanical properties.

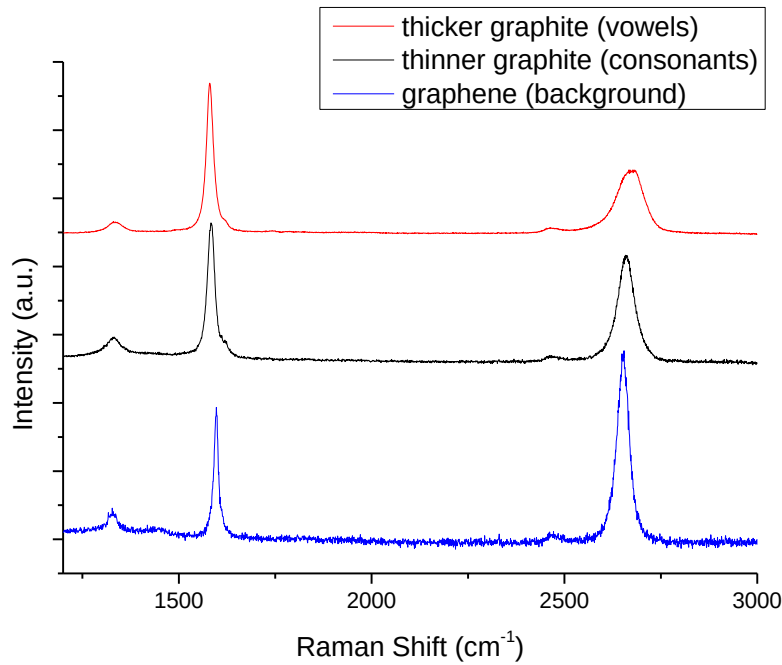


Figure 3.3. Raman spectra of graphite and graphene with different thicknesses: red (thicker graphite; vowels), black (thinner graphite; consonants), and blue (bilayer graphene; background).

Figure 3.4 shows the step height difference of the catalytic Co patterns before and after the synthesis. Even though the surface of both Co and Cu catalytic metals are rough or spiky, there is a distinct height difference between Co region and Cu region after synthesis with a high temperature condition. This shows that there was relatively negligible intermixing of Co and Cu during the synthesis, possible due to short synthesis time.

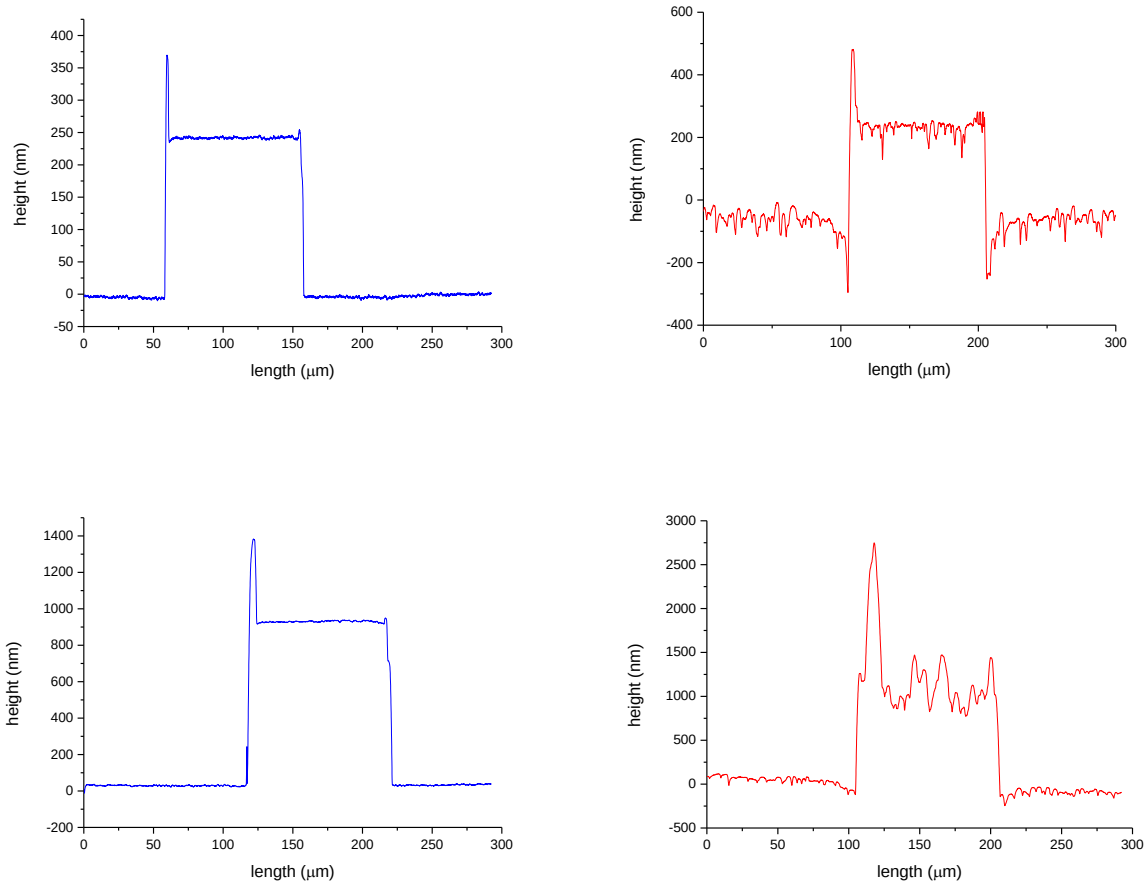


Figure 3.4 Height profile images of catalytic Co patterns with varying thicknesses, $t_{\text{Co}} \sim 250\text{nm}$ (top) and $t_{\text{Co}} \sim 950\text{nm}$, before (blue) and after CVD synthesis (red).

To investigate the effect of modulating thickness of Co film on thickness of resultant graphite, monolithic graphene-graphite samples with four different thicknesses are prepared. The thicknesses of Co films are 250nm, 450nm, 650nm, and 950nm respectively. Figure 3.5 shows optical microscope images of cross shaped graphite patterns with varying thicknesses on a same

graphene background. As the thickness of Co film increases, the color of graphite gradually changes from blue to deep blue and finally to bright green. This gradual change in color contrast demonstrates that the thickness of graphite linearly increases as the thickness of Co film increases.

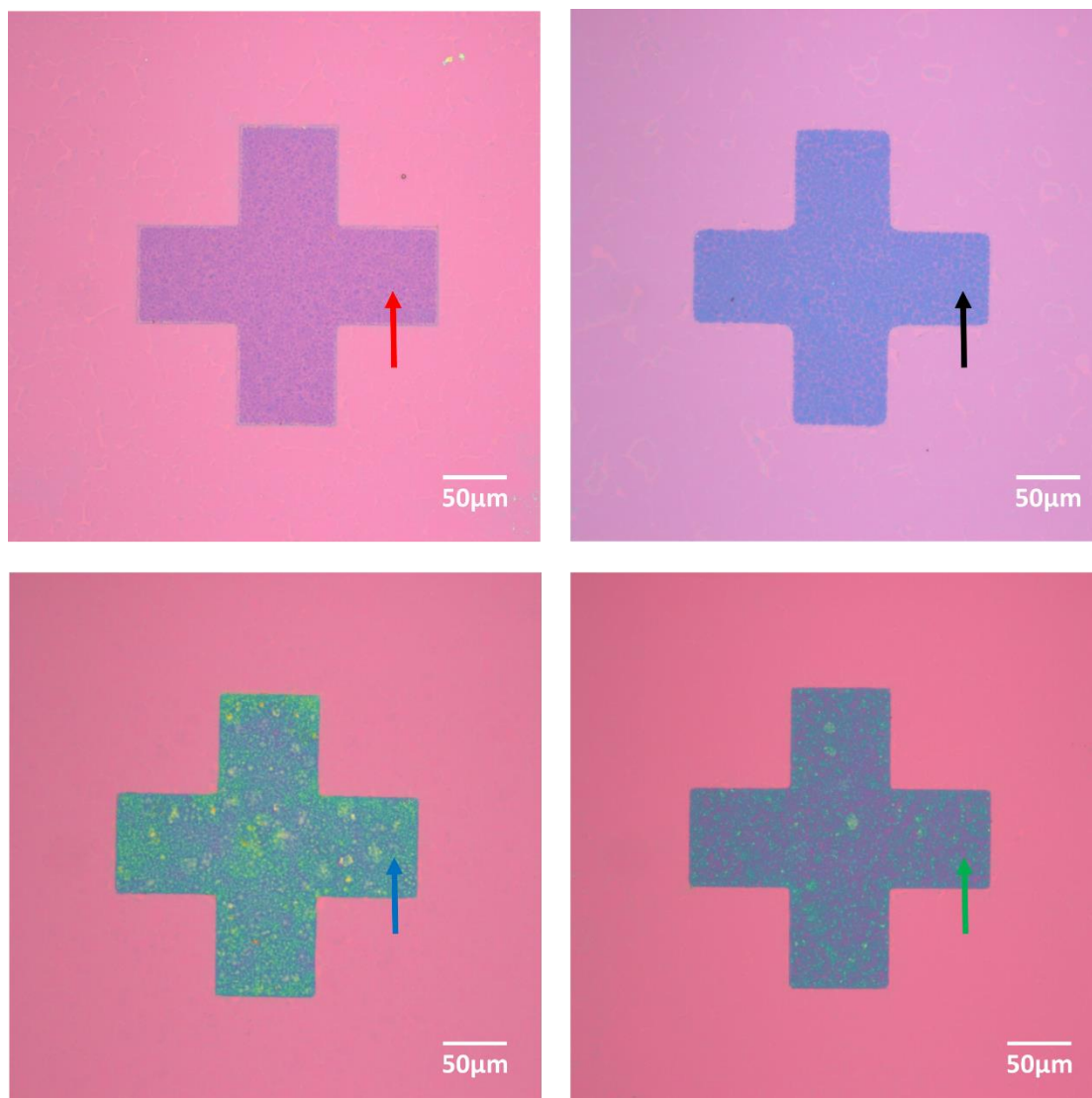


Figure 3.5 Optical microscope images of monolithic graphene-graphite samples with varying thicknesses. Thickness of initial Co catalytic metal (removed in the images) for each sample is 250nm, 450nm, 650nm, and 950nm (clockwise direction).

Figure 3.6 shows atomic force microscope (AFM) images of graphite thickness to show that each graphite sample has different thickness compared to each other. There is some variation

in thickness of graphite due to unwanted dewetting and evaporation of Co catalytic film. Since the synthesis happens in conditions with low pressure and high temperature, the Co catalytic metal easily evaporates. Also, some of Co film are lost during intermixing between Co film and underlying Cu film, forming a Co-Cu alloy. Even if we consider the variation of graphite thickness, it is not hard to observe that the average thickness of graphite actually increases as the thickness of initial Co film increases. A possibility of contamination or dust on the surface of graphite which sticks to the tip of AFM cantilever during the measurement explains the unreasonably tall spikes. The average thickness of each graphite sample is measured to be about 4nm, 10nm, 24nm, and 35nm respectively.

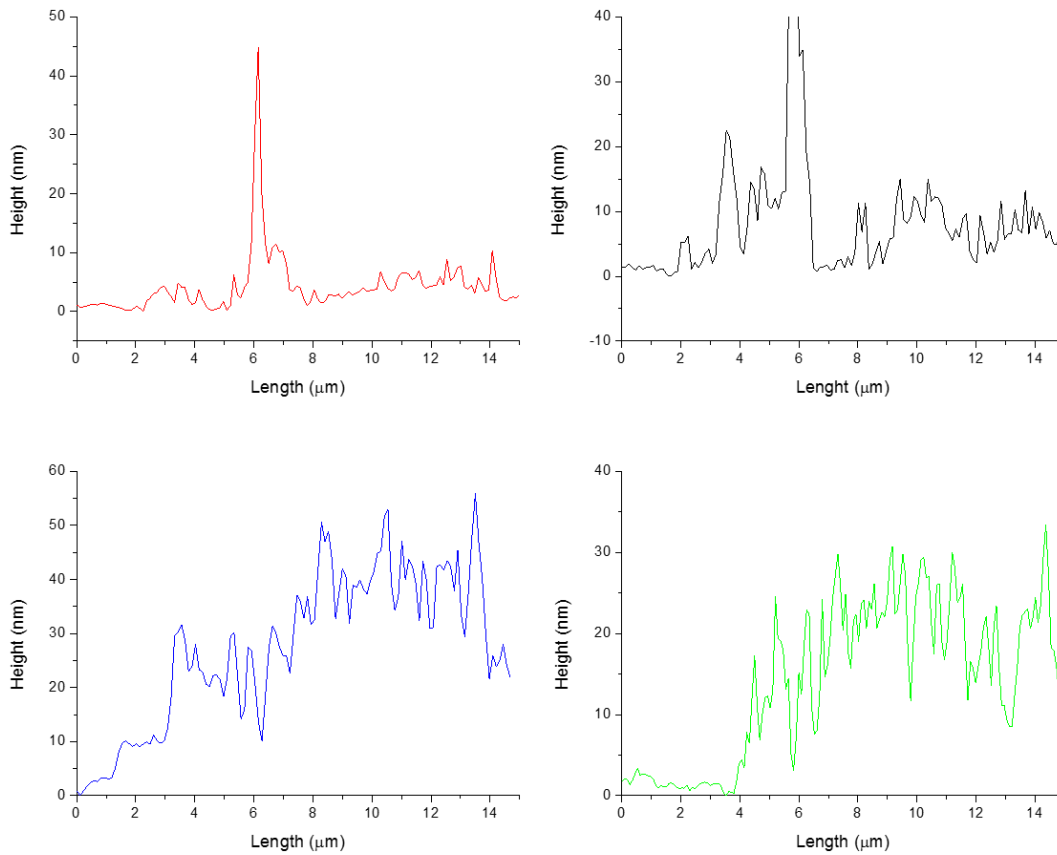


Figure 3.6 AFM scans of graphite synthesized on Co catalyst patterns with varying thicknesses after CVD synthesis.

Figure 3.7 shows the relationship between the thickness of Co film and that of resultant graphite. It clearly shows the linear increase of graphite thickness as the thickness of initial Co catalytic metal increases. The average thickness of each graphite sample is shown with an error bar.

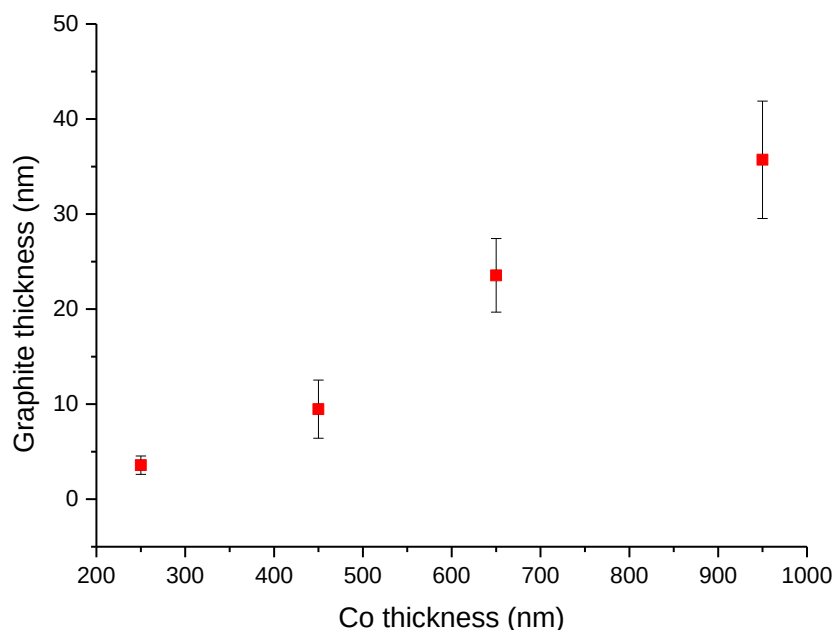


Figure 3.7 The average thickness of resultant graphite as a function the thickness of initial Co film.

Figure 3.8 shows the relationship between the thickness of initial Co film and 2D to G band intensity ratio of resultant graphite. The average 2D to G band intensity ratio gradually decreases as the thickness of initial Co film increases. Even though a wide range of error bar indicates the resultant graphite does not have perfect uniformity, it certainly shows the inverse relationship between 2D to G band intensity ratio and the thickness of graphite, or the thickness of initial Co catalytic metal.

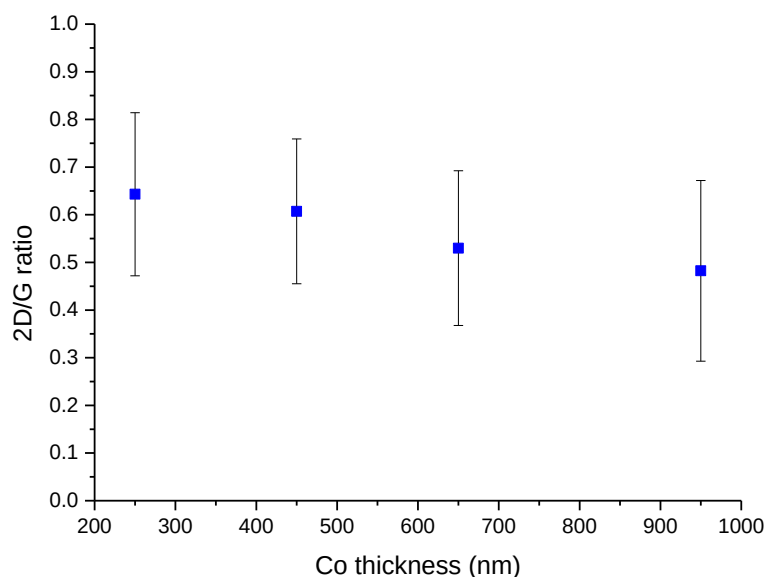


Figure 3.8 The average 2D to D band intensity ratio of resultant graphite as a function the thickness of initial Co film

The thickness of synthesized graphite seems to be smaller than previously reported graphite thickness with the same thickness of the initial Co film [20]. The reason might be that carbon sources from methane are not enough to saturate the Co catalytic metal during synthesis. There are a number of different ways to increase the carbon content during synthesis, such as increasing the flow rate of methane or switching carbon precursor gas from methane to ethylene. The quality of the monolithic graphene-graphite structure is expected to be improved by optimizing the synthesis condition to decrease the standard deviation of the thickness of each graphite sample or to increase the uniformity of the graphite sample.

CHAPTER 4

DEVICE CHARACTERIZATION

One of the ultimate goals of synthesizing monolithic graphene-graphite structure is to apply this technique in actual applications, especially in chemical or biological sensor devices. To demonstrate graphene as a good candidate material for sensor devices, fabrication of graphene field-effect transistors (FETs) is carried out. The superior transconductance level of the bi-layer or a few layer graphene is known to be appropriate for the active channels of FETs [20]. Figure 4.1 shows the graphene FET device fabricated on a SiO_2/Si substrate. The design for graphene FET is based on the monolithic graphene-graphite FET sensor [20]. The device consists of 4 segments of graphene FET arrays and each segment has 9 individual FETs. The electrodes are used for electrical contacts to graphene field-effect channels and SU-8 passivation is carried out for further water-gate measurements.

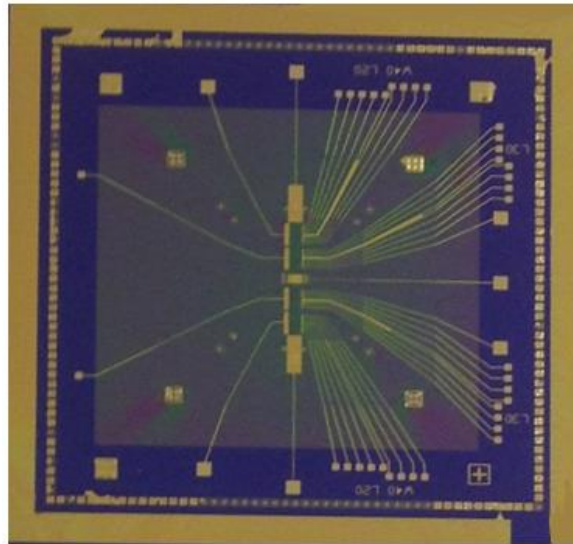


Figure 4.1 A photo of graphene-FET device fabricated on a 285nm SiO_2/Si substrate.

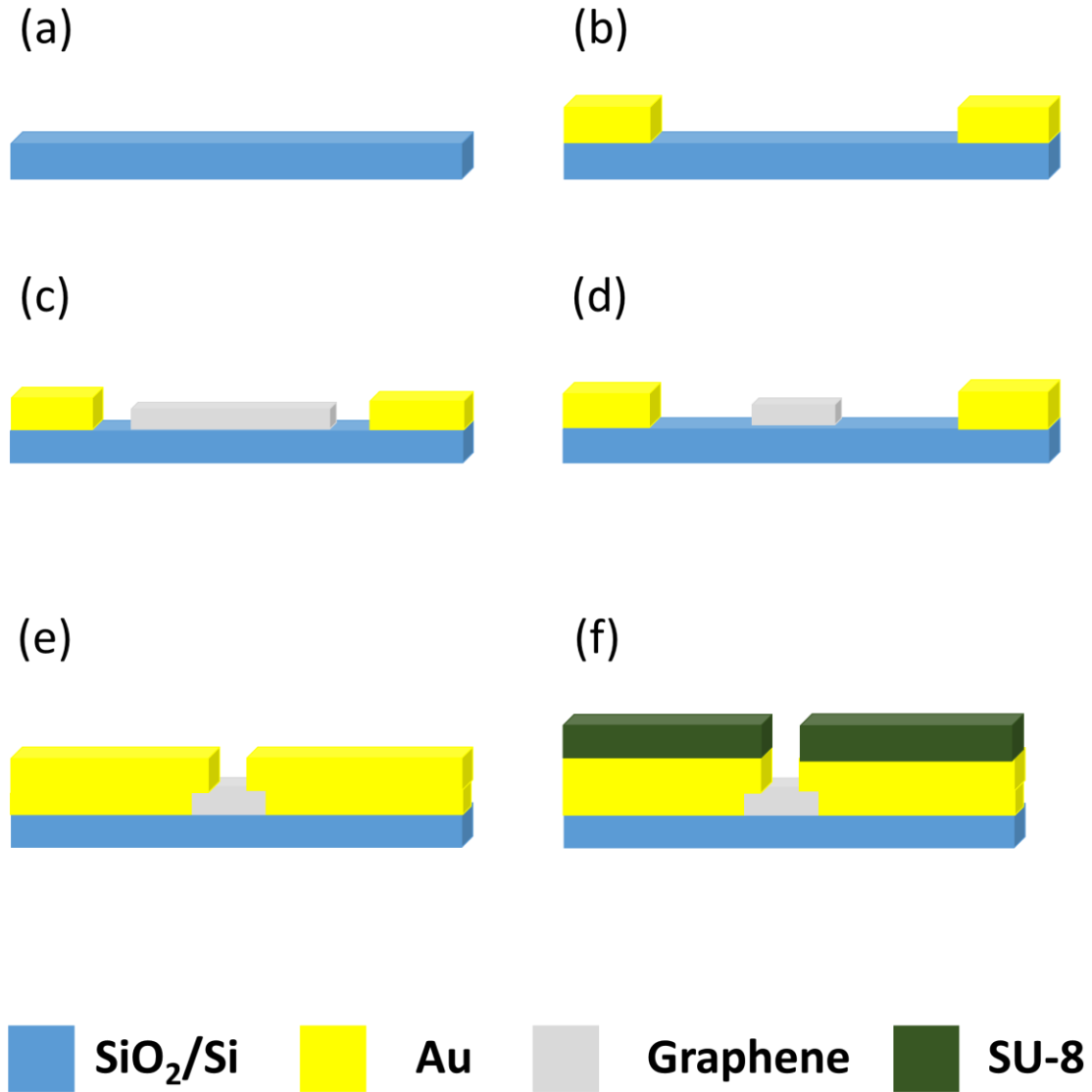


Figure 4.2 Overview of fabrication process of graphene FETs (a) 285nm-thick SiO_2/Si wafer, (b) Au aligning marker formation, (c) graphene transfer, (d) graphene channel patterning with O_2 plasma, (e) Au electrode fabrication (f) patterned deposition of SU-8 passivation layer

Figure 4.2 shows a schematic illustration of a fabrication process for graphene FET device. After graphene film is synthesized on a Cu foil via LPCVD, it is transferred on a clean SiO_2/Si wafer with pre-deposited aligning markers. The graphene film is selectively etched and forms a FET arrays as shown in Figure 4.2(d). The fabricated device has four segments of graphene FET arrays, each of which contains nine individual FETs. Then a selective deposition of 100 nm thick

gold (Au) film is done on the substrate with patterned graphene by a thermal evaporator as shown in Figure 4.2(e). The SU-8 is spin coated to be a passivation layer for further electrical characterization. Figure 4.3 shows the optical microscope image of fabricated graphene FET device with Au electrodes. There is no SU-8 passivation layer to show a better image of graphene FET design. It shows one of the four segments of graphene FET arrays. All of nine FETs are clearly visible without distinct defects or contamination.

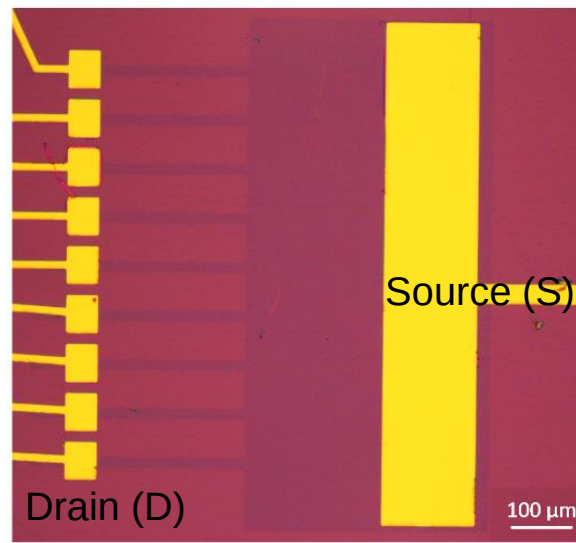


Figure 4.3 An optical microscope image of the fabricated graphene FET device with Au electrodes.

After the fabrication of graphene FET devices, the electrical characterization of graphene FETs is carried out. Figure 4.4 shows a current-voltage (I_{ds} - V_{ds}) characterization of the graphene FETs at room temperature. A linear behavior of I_{ds} - V_{ds} curve indicates Ohmic contact behavior. The resistance of graphene FETs is measured to be about 1.0 k Ω which shows a high conductance of synthesized graphene. Figure 4.5 shows a water-gate characterization, indicating the ambipolar I_{ds} - V_{gs} behavior of graphene FET devices with a Dirac point at ~ 0.1 V with the use of the Au reference electrode. Figure 4.6 shows source/drain current (I_{ds}) versus back-gate bias (V_{gs}) characterization of the graphene FET structures, which is also measured at room

temperature. The result shows that the fabricated device showed p-type behavior within a gate voltage (-100V, 100V), possibly due to adsorbates from the air [31].

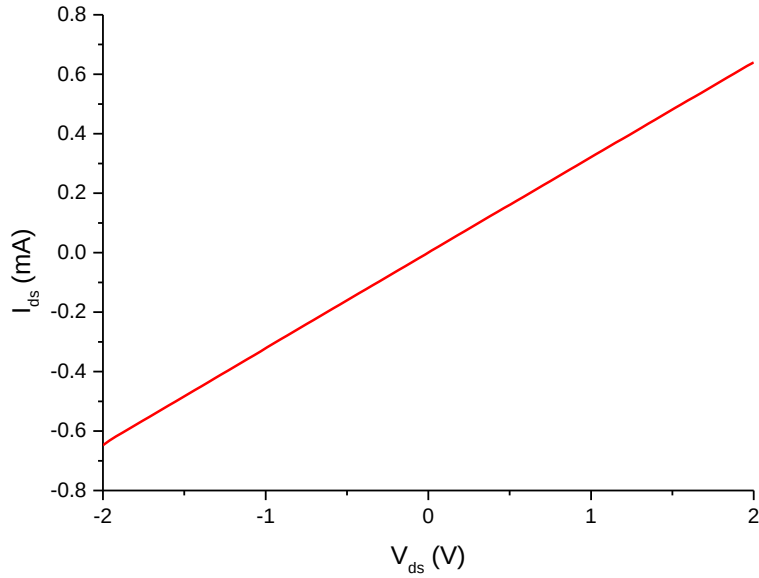


Figure 4.4 I_{ds} - V_{ds} electrical characterizations of the graphene FET devices.

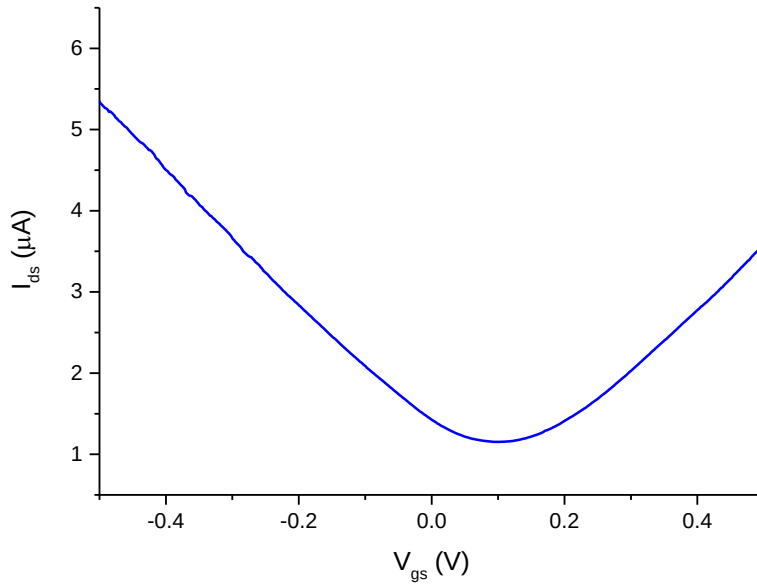


Figure 4.5 Watergate I_{ds} - V_{gs} electrical characterizations of the graphene FET devices. Au reference electrode is used in the watergate measurement.

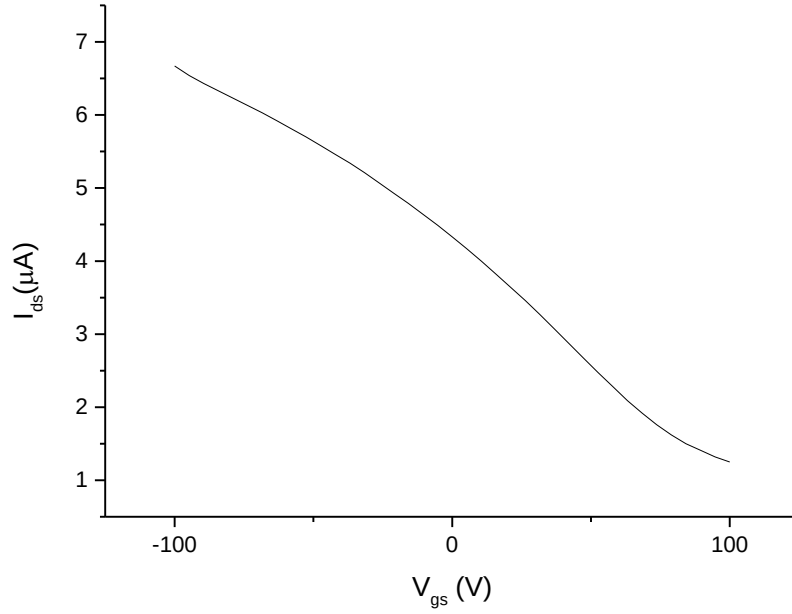


Figure 4.6 Backgate I_{ds} - V_{gs} electrical characterizations of the graphene FET devices.

By combining concepts of graphene FETs and monolithic interface between graphene and graphite, the fabrication of all-carbon graphene FET with monolithic integration of graphite electrodes would be possible. This all carbon monolithic graphene FET devices with superior electromechanical properties can be exploited in both soft and biological electronics. This multiplexed graphene FET with monolithic integration of graphite electrodes is expected to have higher sensitivity, electron mobility, and mechanical flexibility than current FETs which are based on Silicon.

CHAPTER 5

CRUMPLED STRUCTURE

As mentioned in previous chapters, the intrinsic electric or mechanical properties of graphene can be modulated by controlling a number of parameters during the synthesis process. Unlike this, there have been efforts to modulate the properties of graphene by altering its shape or geometry. Localized bending of graphene alters the electrical properties of graphene, such as electronic band structures [32-39]. A sufficient amount of mechanical strain can induce large crumpled morphology on graphene film, which leads to localized three dimensional (3D) texturing. This 3D morphology of graphene is applicable to 3D electrodes and sensors [20, 30]. For this 3D graphene structure, the graphene sample is first synthesized on a Cu foil via the LPCVD method. The synthesized graphene film is then transferred on a centimeter-scale polystyrene (PS) sheet, a polymeric thermoplastic materials widely used for material shrinkage. PS substrate is shrunk when it is heated up to its glass transition temperature. The 3D texturing of graphene film is accomplished by glass transition of PS substrate.

Figure 5.1 shows the SEM images of crumpled graphene film after thermally induced shrinkage. It shows the various levels of graphene film crumpling with gradual increases in strain for the uniaxial case (18%, 46%, and 71%) and equi-biaxial case (58%). The wrinkles are aligned with almost uniform gaps on the uniaxial case, while there are only chunks of graphene, resembling checkerboard structures [40, 41] on the equi-biaxial case. According to sheet resistance characterization performed during crumpling with simultaneous 4-point probe electrical characterization, the sheet resistance of graphene is not significantly changed up to a 73% macroscopic compressive stain. It shows that properties of graphene can be maintained even with high percentage of compressive strain.

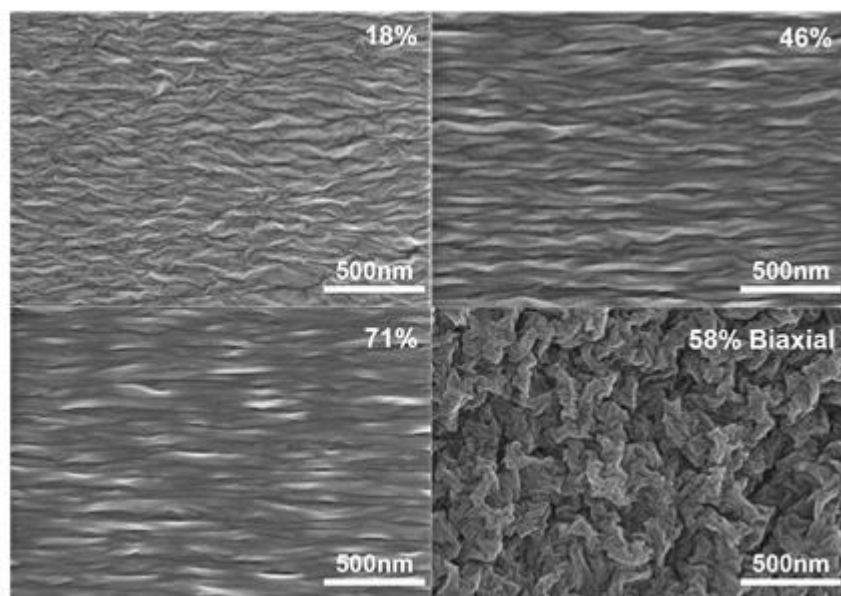


Figure 5.1 SEM images of uniaxially (18%, 46%, 71%) and equi-biaxially (58%) textured graphene.

The monolithic graphene-graphite structure is used to investigate the thickness effect on crumpling. The cross pattern of Co catalytic metal is patterned on Cu catalytic metal background by photolithography. A graphite film is then synthesized on cross pattern, which is monolithically connected to a background graphene film. Figure 4.2 shows the SEM images of monolithic graphene and graphite substrate after undergoing thermally induced uniaxial compressive strain. The cross pattern of graphite, which was originally a symmetric cross (white dotted line), becomes asymmetric (black solid line) after inducing 70% of uniaxial shrinkage. It is notable that there exists bigger crumples on thicker graphite region (in blue box) than on thinner graphene region (in red box), which proves that the thicker graphite actually develops crumples with higher density and thickness.

The result shows that 3D texture of graphene and graphite can be simply modulated by changing the size of thermal strain of base substrate. The electrical properties of graphene and

graphite can be preserved up to a 73% of compressive strain. This monolithic integration of 3D and 2D structure of graphene and graphite can be applied to advanced 3D biosensors in the future.

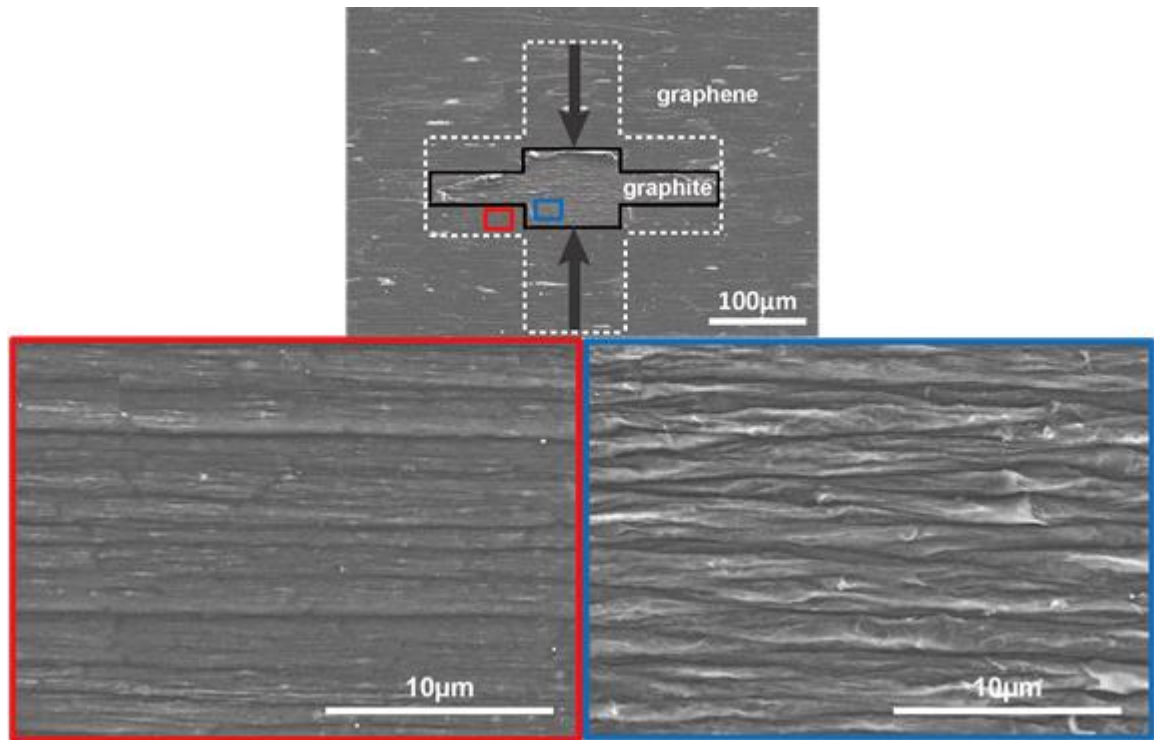


Figure 5.2 SEM images of heterogeneous graphene-graphite cross pattern subjected to ~70% uniaxial strain (top). Smaller crumples on the thinner graphene region (bottom left) than the thicker graphite region (bottom right).

APPENDIX

Graphene/Graphite synthesis and transfer recipe and Graphene FET device fabrication

0. Wafer Material

Wafer specification: SiO₂/Si Wafer <100>, Diameter: 100mm (or 4 inches)

Thermal Oxide thickness: 285 nm ± 5%, Resistivity: 0.001-0.005 Ohm*cm

Handle thickness: 500-550 μm

Wet Thermal Oxide on both sides

1. Graphene on Cu foil

1.1 Pretreatment

Equipment: Acid Bench (MNTL)

Recipe: HCl solution (37-38%wt)

Time = 10mins

Rinse with DI water, Acetone, IPA, DI Water, IPA, and dry with nitrogen gun

1.2 Synthesis

Equipment: LPCVD (RMV RMR-2000)

Recipe: Heating, Annealing, Synthesis, and Cooling

Time = Heating (60mins), Annealing (25mins), Synthesis (2mins), and Cooling (60mins)

Gas ratio = Heating (H₂=50sccm), Annealing (H₂=50sccm),

Synthesis (H₂:CH₄=50sccm:100sccm), and Cooling (Ar=500sccm)

1.3 Graphene transfer

Appendix 5

2. Graphene on Cu film

2.1 Catalytic Cu deposition on SiO₂/Si wafer

Equipment: AJA metal sputter (MNMS)

Recipe: Cu thickness 700nm

Time: 60mins

2.2 Synthesis

Equipment: LPCVD (RMV RMR-2000)

Recipe: Heating, Annealing, Synthesis, and Cooling

Time = Heating (60mins), Annealing (5mins), Synthesis (2mins), and Cooling (60mins)

Gas ratio = Heating ($H_2=50\text{sccm}$), Annealing ($H_2=50\text{sccm}$),
Synthesis ($H_2:CH_4=50\text{sccm}:100\text{sccm}$), and Cooling ($Ar=500\text{sccm}$)

2.3 Graphene transfer

Appendix 5

3. Graphite on Co/Cu film

3.1 Catalytic Cu deposition on SiO_2/Si wafer

Equipment: AJA metal sputter (MNMS)

Recipe: high deposition rate

Thickness: 800nm

Time: 60mins

3.2 Catalytic Co deposition

Equipment: AJA metal sputter (MNMS)

Recipe: high deposition rate

Thickness: 200-950nm

Time: 10-50mins

3.3 Synthesis

Equipment: LPCVD (RMV RMR-2000)

Recipe: Heating, Annealing, Synthesis, and Cooling

Time = Heating (60mins), Annealing (5mins), Synthesis (2mins), and Cooling (60mins)

Gas ratio = Heating ($H_2=50\text{sccm}$), Annealing ($H_2=50\text{sccm}$),

Synthesis ($H_2:CH_4=50\text{sccm}:100\text{sccm}$), and Cooling ($Ar=500\text{sccm}$)

3.4 Graphene transfer

Appendix 5

4. Monolithic graphene-graphite on Co/Cu film

4.1 Cu deposition on SiO_2/Si wafer

Equipment: AJA metal sputter (MNMS)

Recipe: high deposition rate

Thickness: 800nm

Time: 60mins

4.2 Shipley 1813

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin Shipley 1813 at 500rpm for 5sec (acceleration 250rpm/sec)

and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 115 °C for 5mins

4.3 Photolithography of Mask #1 (letters)

Equipment: Karl Suss Mask Aligner

Recipe: Exposure
Hard contact mode
Expose: 13.5sec
Development: CD 26, around 45sec
Rinse with DI water and dry with nitrogen gun
Hardbake: hotplate 110 °C for 60sec

4.4 Catalytic Co deposition

Equipment: AJA metal sputter (MNMS)

Recipe: high deposition rate

Thickness: 200-950nm

Time: 10-50mins

4.5 Metal Liftoff

Equipment: Wet Bench

Recipe: Soak the substrate in removal PG bath at 70 °C

Time: Overnight

4.6 Synthesis

Equipment: LPCVD (RMV RMR-2000)

Recipe: Heating, Annealing, Synthesis, and Cooling

Time = Heating (60mins), Annealing (5mins), Synthesis (2mins), and Cooling (60mins)

Gas ratio = Heating ($H_2=50\text{sccm}$), Annealing ($H_2=50\text{sccm}$),

Synthesis ($H_2:CH_4=50\text{sccm}:100\text{sccm}$), and Cooling ($Ar=500\text{sccm}$)

4.7 Graphene/Graphite transfer

Appendix 5

5. Transfer

5.1 PMMA Coating

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin 950 PMMA C2 at 500rpm for 5sec (acceleration 250rpm/sec)
and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 180 °C for 90sec

5.2 Backside graphene etching (only on Cu foil)

Equipment: TI Planer Plasma System

Recipe: O_2 plasma with 300W

Time: 1mins 15sec

5.3 Catalytic metal etching

Equipment: Wet bench

Recipe: Soak (wafer) or float (foil) the sample on Na_2SO_8 solution bath (Na_2SO_8 : DI=1:9)

Time: 3 to 6 hours

5.4 Graphene cleaning

Equipment: Wet bench

Recipe: Use a clean glass slide to transfer graphene film on DI water bath for cleaning
Time: 5-10mins

5.5 Graphene transfer

Appendix 5

5.6 PMMA removal

Equipment: Wet bench

Recipe: Soak the sample on Acetone bath

Time: Acetone bath for 5mins, Acetone, IPA, and dry with nitrogen gun

5.7 Quality check

Equipment: Zeiss

Recipe: N/A

Bright field optical microscope image, Dark field optical microscope image

Equipment: Renishaw

Recipe: N/A

Raman spectra image

6. Device Fabrication

6.1 SPR 220

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin SPR 220 at 500rpm for 5sec (acceleration 250rpm/sec)
and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 110 °C for 90sec

6.2 Photolithography of Mask #2 (alignment markers)

Equipment: Karl Suss Mask Aligner

Recipe: Exposure

Hard contact mode

Expose: 13.5sec

Development: AZ 400K solution (AZ 400K: DI=1:5), around 45sec

Rinse with DI water and dry with nitrogen gun

Hardbake: hotplate 110 °C for 60sec

6.3 Au deposition

Equipment: Kurt J. Lesker Thermal Evaporator (Nano 36)

Recipe: low deposition rate

Thickness: 60nm

Time: 1 hour

6.4 Metal Liftoff

Equipment: Wet Bench

Recipe: Soak the substrate in Acetone bath at room temperature

Time: 1 hour

6.5 Graphene transfer

Appendix 5

6.6 SPR 220

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin SPR 220 at 500rpm for 5sec (acceleration 250rpm/sec)
and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 110 °C for 90sec

6.7 Photolithography of Mask #3 (graphene channel)

Equipment: Karl Suss Mask Aligner

Recipe: Exposure

Hard contact mode

Expose: 13.5sec

Development: AZ 400K solution (AZ 400K: DI=1:5), around 45sec

Rinse with DI water and dry with nitrogen gun

Hardbake: hotplate 110 °C for 60sec

6.8 Graphene patterning

Equipment: TI Planer Plasma System

Recipe: O₂ plasma with 300W

Time: 2mins 30sec

6.9 SPR 220

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin SPR 220 at 500rpm for 5sec (acceleration 250rpm/sec)
and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 110 °C for 90sec

6.10 Photolithography of Mask #4 (Au electrodes)

Equipment: Karl Suss Mask Aligner

Recipe: Exposure

Hard contact mode

Expose: 13.5sec

Development: AZ 400K solution (AZ 400K: DI=1:5), around 45sec

Rinse with DI water and dry with nitrogen gun

Hardbake: hotplate 110 °C for 60sec

6.11 Au deposition

Equipment: Kurt J. Lesker Thermal Evaporator (Nano 36)

Recipe: high deposition rate

Thickness: 100nm

Time: 1.5 hour

6.12 Metal Liftoff

Equipment: Wet Bench

Recipe: Soak the substrate in Acetone bath at room temperature

Time: 1 hour

6.13 SU-8 2005

Equipment: Spinner (MNTL)

Recipe: dehydration bake

Spin SU-8 2005 at 500rpm for 5sec (acceleration 250rpm/sec)

and 4000rpm for 40sec (acceleration 1000rpm/sec)

Softbake: hotplate 65 °C for 1min and 95 °C for 1min

6.14 Photolithography of Mask #5 (SU-8 passivation)

Equipment: Karl Suss Mask Aligner

Recipe: Exposure

Hard contact mode

Expose: 9.5sec

Postbake: hotplate 65 °C for 1min and 95 °C for 1min

Development: SU-8 developer around 90sec

Rinse with IPA and dry with nitrogen gun

Hardbake: hotplate 65 °C for 1min and 180 °C for 5mins

Cooling: natural cooling on hot plate

6.15 Device final check

Equipment: Keithley 2614b

Recipe: N/A

I-V, backgate I-V, and leakage current check

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