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İSTANBUL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES IN
SCIENCE AND ENGINEERING**



Ph.D. THESIS

**INVESTIGATION OF STRUCTURAL, OPTICAL AND
ELECTRICAL PROPERTIES OF GRAPHENE/GRAPHENE OXIDE
HYBRIDS**

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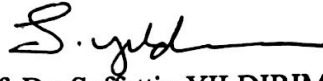
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LIST OF SYMBOLS AND ABBREVIATIONS

Symbol	Explanation
$\text{\AA}$	: Angstrom
e	: Electron charge
ϵ_0	: Permittivity of free space
ϵ_r	: Relative permittivity for silica
n	: Charge carrier density
μ	: Mobility
σ	: Conductivity
t	: Thickness of silica
V	: Volt
V_g	: Gate voltage

Abbreviation	Explanation
2D	: Two dimensional
AFM	: Atomic force microscopy
C-AFM	: Contact mode of Atomic force microscopy
CVD	: Chemical vapor deposition
EBL	: Electron beam lithography
FET	: Field effect transistor
FT-IR	: Fourier transform infrared
I-AFM	: Current mode of Atomic force microscopy
ITO	: Indium tin oxide
LFM	: Lateral force microscopy
MBE	: Molecular beam epitaxy
PMMA	: Polymethylmethacrylate
RIE	: Reactive ion etch
SEM	: Scanning electron microscopy
UV-vis	: Ultraviolet visible
XRD	: X ray diffraction

ÖZET

DOKTORA TEZİ

GRAFEN/GRAFENOKSİT HİBRİT YAPILARIN YAPISAL, OPTİK VE ELEKTRİKSEL ÖZELLİKLERİNİN İNCELENMESİ

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Yüksek kristal kalitesine sahip grafen numuneleri litografik tekniklerle oksitlenerek hibrit yapılar elde edilmiştir. Elde edilen hibrit malzemeden alan etkili transistör üretilerek elektriksel özellikleri incelenmiş ve yapının stabilitesi sıcaklığa bağlı olarak karakterize edilmiştir. Bu amaçla, tek katmanlı grafen numuneleri için e-demet ve maskesiz fotolitografi teknikleri kullanılarak, grafen numunelerinin oksitlenmemesi gereken kısımları maskelenmiş oksitlenmesi planlanan kısımları ise hazırlanan kimyasal çözelti ile başarılı bir şekilde homojen olarak oksitlenmiştir.

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Anahtar kelimeler: Grafen, grafenoksit, FET

SUMMARY

Ph.D. THESIS

INVESTIGATION OF STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF GRAPHENE/GRAPHENE OXIDE HYBRIDS

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In this study, apart from the literature, we are proposing to locally oxidize high-quality graphene samples through the lithographic techniques and characterize the hybrid structures in terms of electrical properties and material stability. For this purpose, we have used e-beam and maskless photolithography techniques for tailoring the single layer graphene samples. In e-beam lithography and photolithography techniques, the parts of the graphene samples that are not to be oxidized were masked and other parts were oxidized in a chemical solution similar to the Hummers method developed for oxidizing graphite.

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Keywords: Graphene, graphene oxide, FET

1. INTRODUCTION

Graphene is the name given to a flat monolayer of carbon atoms densely packed in a hexagonal lattice structure. The crystal structure of graphene can be seen as the building block of carbon materials such as graphite, carbon nanotubes and fullerenes [1]. Hence, the theoretical studies of graphene goes back several decades [2]. However, the physical realization of graphene in research laboratories has become possible only in 2004 [3]. The experimental techniques developed afterwards have allowed researchers to isolate monolayer and multilayer graphene samples by micro-mechanical cleavage (that is mechanical exfoliation from graphite or Scotch tape method) [3], thermal decomposition of SiC [4], chemical vapor deposition (CVD) [5], molecular beam deposition [6] and etc. While mechanical exfoliation is performed on SiO₂/Si substrates, epitaxial growth has been achieved on SiC. In CVD and molecular beam deposition methods, some metal surfaces such as nickel are used.

Graphene is the first two dimensional (2D) material which has unique electrical properties. Since 1859, many scientists were looking for graphene using complex experiments. But the first crystals of graphene were discovered in 2004 using a very simple and effective method namely ordinary 'scotch tape'. Andre Geim and Konstantin Novoselov were the two scientists who made this simple but groundbreaking experiments and they were awarded the Nobel prize in physics in 2010. Thanks to the scotch tape method, this area of science grew extremely quickly. And today, hundreds of laboratories all over the world deal with the different aspects of graphene research. What makes graphene are really super material is the combination of as unique properties. Graphene is the thinnest object ever obtained and also the lightest one. It is the worlds' strongest material which is harder than diamond and 300 times stronger than steel. Graphene conducts electricity much better than copper. It is a transparent material. It can take any form because it is bendable. Moreover, this super material with unique properties gave birth to a new class of crystals that are also just one atom thick which is MoS₂, boron nitride, fluorographene, graphane, NbSe₂, and MgB₂. To engineer new materials on demand, these 2D crystals can be shuffled with each other to meet the special needs of different industries. All these factors move graphene swiftly from the graphene research laboratory to the graphene market place driven by demand from industries where such super materials are required as in

aerospace, automotive, electronics, energy storage, communications, sensors, solar, the oil industry etc.

The unprecedented attention in graphene originates from the interesting physical phenomena observed on it and from the fact that graphene can shape the future of electronics technology owing to its superior electrical properties. In graphene, the conduction and valence bands meet at two inequivalent, charge-neutral points in momentum space around which the dispersion is linear, leading to so-called Dirac cones. This electronic dispersion is similar to that of relativistic, mass-less fermions and provides a model system for testing the ideas about such fermions. This peculiar band structure leads to intriguing new phenomena such as half-integer quantum Hall effect (HE) and non-zero Berry's phase [7]. In addition, electrical measurements on suspended graphene have resulted in the measurement of highest electron mobility of $200,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ even at room temperature [8, 9] where supported graphene shows a mobility value of $10,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [10]. Graphene nanoribbons are shown to have metallic or semiconducting characteristics depending on the edge type (armchair or zigzag) and the width of the nanoribbon [11]. In the light of properties such as high electron mobility and adjustable band-gap, graphene comes up as a material of high potential for future electronic applications. If the current technical problems can be resolved, graphene will be one of the strongest alternatives to silicon technology which is reaching to its theoretical limits. With this new material, the electronic processor can be built from a single 2D material rather than using the current complicated production procedures and the circuits will work at a higher speed and consume less energy.

The interest in graphene continued to increase over the years and recently new materials based on graphenes such as graphene oxide [12], graphane (hydrogenated graphene) [13] and fluorinated graphene (fluorographene) [14] are being synthesized and characterized. Recently, scientists have begun to synthesize graphene-based new materials with different electrical and mechanical properties. In this respect, graphene oxide and graphane are two noteworthy materials. In contrast to graphene, both of these materials are insulators.

Graphene oxide can be easily obtained by oxidizing and exfoliating graphite in a chemical solution and then transferring to substrates of our choice. Such materials are attracting much interest as they can be produced in large quantities and used to coat large areas of surfaces [15].

In addition, the so-called “reduced graphene oxide” which is obtained by removing the oxygen via several methods is a conductive material [16]. As a result, new conducting graphene-based materials covering large areas are obtained by reducing the graphene oxide sheets. However, such materials have many crystal defects and their conductivity is lower than that of pristine graphene sheets [17]. Nevertheless, we are seeing new research efforts directed towards the formation of graphene/graphene oxide hybrid structures without preparing solution based graphene flakes. To do that, we will produce our single-layer graphene flake by mechanical exfoliation; then we will apply wet chemical procedures on it to make graphene oxide for hybrid structure. Again, the goal is to get new material properties using this hybrid structure.

Briefly in this dissertation, apart from the literature, we are proposing to locally oxidize high-quality graphene samples through lithographic techniques and characterize the hybrid structures in terms of electrical properties and material stability. For this purpose, we have used e-beam and maskless photolithography techniques for tailoring the single layer graphene samples. In e-beam lithography and photolithography techniques, the parts of the graphene samples that are not to be oxidized have been masked and other parts have been oxidized in a chemical solution similar to the Hummers method developed for oxidizing graphite [18]. Unlike oxidized region of the graphene flake, the conducting regions are of high crystalline quality with high electron mobility. As a result, we have obtained a hybrid structure rather than graphene and graphene oxide at the end of this procedure. Furthermore, we have expected to obtain hybrid structures which are of better quality in comparison to that of colloidal suspensions of reduced graphene oxide hybrids. Since the fabricated hybrid device is on a single layer graphene flake, to investigate the physical properties of the chemically modified material is very important for the semiconductor industry and sensor applications. It will be a basic research study for such kind of materials. The samples have been tested for electrical conductivity and mobility as a function of temperature, current and time in order to determine material stability and working limits. In addition, due to potential nano-electromechanical systems (NEMS) applications, the mechanical properties of graphene and graphene oxide have been investigated by atomic force microscopy measurements.

1.1. BACKGROUND AND THEORY OF GRAPHENE

Graphene has almost been explored by the scientists for seventy years. The first study that can be related to the graphene was ‘the band theory of graphite’ by P. R. Wallace [2]. He estimated

the band structure of graphite with a tight-binding approach for mono graphite layer and showed that graphene has an unusual semi-metallic manner theoretically. A certain number of studies about the band structure of graphite was performed during the following years [19-26]. These studies have occupied a significant importance on the fundamental theory of the band structure of graphene. On the other hand, planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes due to that of theory until 2004 [3].

Graphene is the first real 2D crystal experimentally produced. In Figure 1.1 a schematic structure of graphene is shown. Since it was awarded the Nobel prize in 2010, a huge attention to the graphene and 2D materials has been increased in recent years [1]. During the past decade much more information has become available on graphene and there is a large volume of published studies describing the role of graphene in different research areas ranging from conductive ink to chemical sensors, light emitting devices, energy, touch panels, composite materials and flexible electronics due to its fascinating physical properties like thermal conductivity, exceptional charge mobility, high fraction strength values and etc. [27-31]. This multifunctional nature of graphene has been emerged using a number of measurements with different fabrication techniques such as micromechanical cleavage (Scotch tape method) [32], chemical vapor deposition (CVD) [33], epitaxial growth [34], colloidal suspensions [35-39] and etc. What makes graphene so famous and attractive for the science world is originated from its peculiar and interesting electrical behavior in an applied electric field [3].

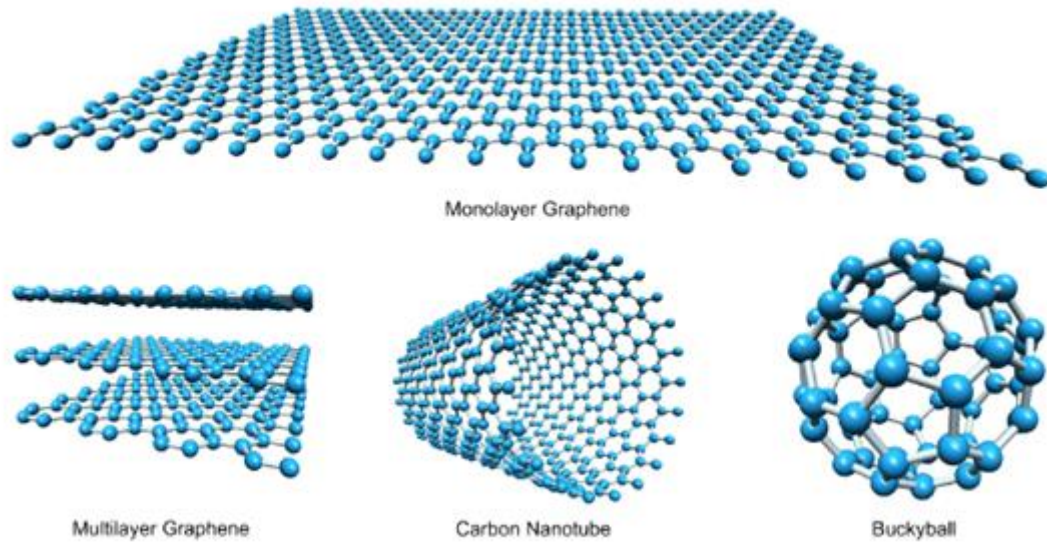


Figure 1.1: Schematic illustration of graphene as a building block of other carbon-based materials such as graphite, nanotube, and buckyball.

The revealed electrical properties of that one – atom thick material make it the best electricity conducting material ever discovered. In addition, it exhibits the best heat conductivity [40].

1.1.1. Electronic Structure

Graphene has an extraordinary electronic band form due to its crystal structure where carbon atoms arranged in a honeycomb (hexagonal) lattice in the 2D platform. In this crystal structure, each carbon atom possesses three electrons that tightly bond with the nearest neighbor atom electrons, thus creating chemical bonds with a bond length of $1.42 \text{ \AA}$ (in-plane). This bond is called as σ bond. For each atom, a fourth electron is delocalized on the whole graphene layer which allows the conduction of an electrical current. The other fourth bond is in the z -direction and called as π bond (out of plane). The π orbitals are centered on each carbon nucleus as a pair under and above it. This pair arises from the Pauli principle where π band is half filled by virtue of hybridization as π and π^* bands. As shown in Figure 1.2a, graphene has two triangular sublattices. Each atom in one sublattice ‘A’ has 3 nearest neighbors in another sublattice ‘B’. There are two carbon atoms in the one-unit cell. In Figure 1.2b, the first Brillouin zone of the single layer graphene is depicted with the reciprocal lattice which is defined by b_1 and b_2 .

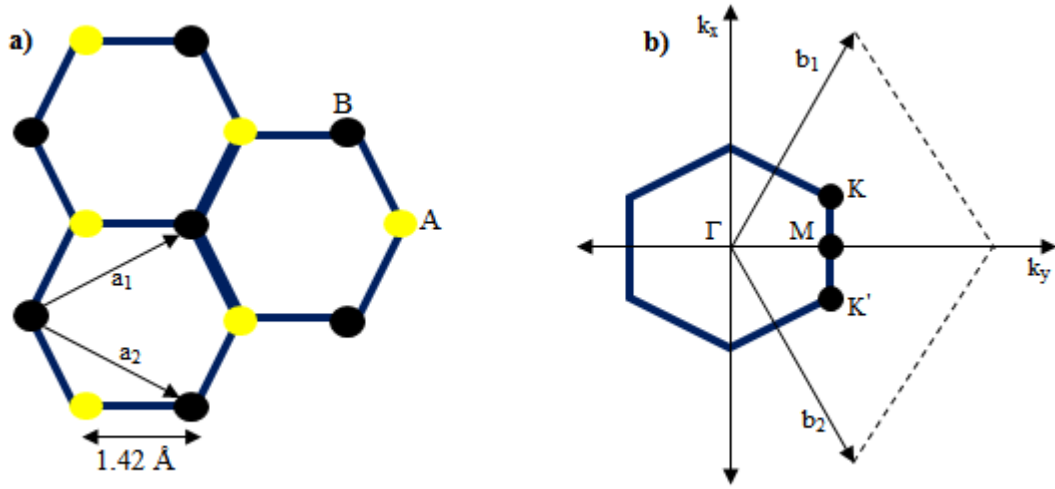


Figure 1.2: a) The sublattices of graphene **b)** The first Brillouin zone of graphene.

These π and π^* bands are determinant on the particular electronic properties of graphene such as charge mobility and electrical conductivity. On the other hand, the σ bond has a filled shell and specify the robustness of the structure. As a result of that σ bond is related to the hardness of the material and π bonds is determiner in its electrical properties. Below some outstanding properties refer to its electronic structure will be explained respectively.

1.1.1.1. Massless Dirac Fermions

Graphene is a zero band gap material. The vertex where the valence and conduction bands come across is called as Dirac points drawn in Figure 1.3. The each cones are the points in momentum space near the Brillouin zone of the graphene. The two distinct corners of Brillouin zone are called as K and K' where the Fermi level is located. Therefore, electronic properties are specified by the states near the K and K' points. As explained above that the Hamiltonian can be given by

$$H_{\vec{k}} = \begin{pmatrix} \epsilon_A & te^{\vec{i}\vec{k} \cdot \vec{a}_1} + te^{\vec{i}\vec{k} \cdot \vec{a}_2} + te^{\vec{i}\vec{k} \cdot \vec{a}_3} \\ c.c. & \epsilon_B \end{pmatrix} \quad (1.1)$$

Here ϵ_A and ϵ_B are zero which refers to the energies of carbon atoms of A and B. “ t ” is the nearest neighbor hopping element between these atoms and has a value of approximately 2.7 eV. $\vec{a}_1 = a(1,0)$, $\vec{a}_2 = a(-1/2, \sin [\pi/3])$, $\vec{a}_3 = a(-1/2, -\sin [\pi/3])$ are the position vectors of the nearest neighbors and c.c. is the complex conjugate. Figure 1.3 shows the eigenvalues of that equation in momentum space.

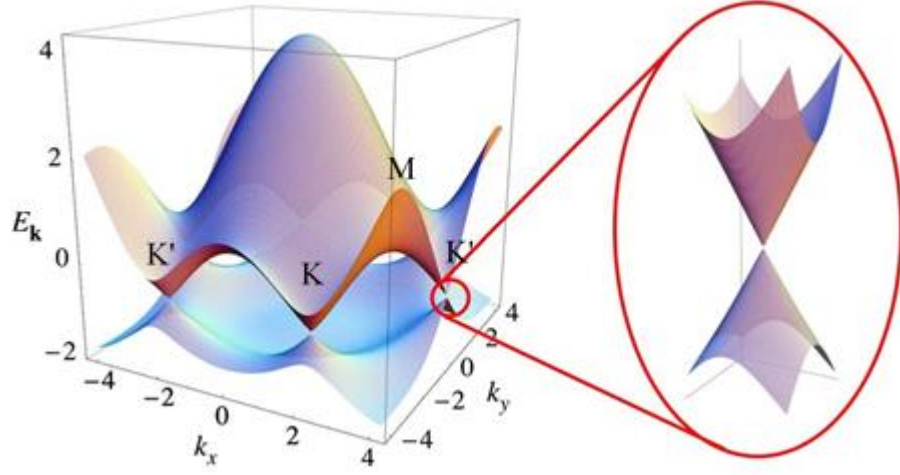


Figure 1.3: First Brillouin zone and the band structure of graphene where Dirac cones are illustrated as a function of $\vec{k} = (k_x, k_y)$. K and K' are the points where conduction and valence bands meet. M is the midpoint.

In the expanded part of the Figure 1.3, the energy bands in the vicinity of the K and K' points are seen. The linear dispersion relation is observed at an energy level of 1 eV. This linearity is fine fitted by the equation of Dirac for massless fermions. Here, there is no any effective mass for the charge carriers. Equation 1.2 usually reveals this dispersion relation near the K point as indicated below:

$$E_{\pm}(k) \approx \pm \hbar v_F |k - K|, \quad (1.2)$$

$$H_K = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} = \hbar v_F \vec{\sigma} \cdot \vec{k}. \quad (1.3)$$

Equation 1.3 is corresponded to tight binding Hamiltonian from the Eq.1.2 near the K for $\hbar v_F = 3ta/2$. If the same approximation is tackled for the K', the Hamiltonian becomes $H_{K'} = \hbar v_F \vec{\sigma}^* \cdot \vec{k}$. Here, $\vec{\sigma} = (\sigma_x, \sigma_y)$ is the two dimensional vector and * symbolise the complex conjugate, $\vec{k}$ is the wavevector and v_F is the Fermi velocity $\approx 10^6$ m/s. Since the speed of light in vacuum is $\approx 3 \times 10^8$ m/s, one can say that the charge carriers in graphene deal with like relativistic particles thanks to the Fermi velocity which is about 1/300 the speed of light. Consequently, this unconventional electronic property of graphene is the leading cause of global attention.

1.1.1.2. Chirality

Transport in graphene displays a novel chirality due to the graphene sublattices can be viewed like a responsible segment of the charge carrier motions. These dispersion segments communicate with each other washily. The chiral impact shows the presence of the pseudospin quantum number for carriers. The quantum number is undifferentiated from the turn, however, is totally free of the "genuine" turn. The pseudospin gives us a chance to separate between commitments from each of the sublattices. The freedom is called as chirality in consequence of the powerlessness to change one sort of scattering into another [41]. A regular case of chirality is that you can't change a privilege hand into a left hand with just interpretations, scaling, and turns. The chirality of graphene can likewise be caught on as far as the Pauli network commitments in the Dirac-like Hamiltonian portrayed in section (1.1.1.1).

1.1.1.3. Klein Paradox

A particular property of the Dirac Hamiltonian is that charge carriers can not be bound by electrostatic possibilities. In customary semiconductors, if an electron strikes an electrostatic boundary that has a tallness over the electron's motor vitality, the electron wave function will wind up plainly transitory inside the obstruction and exponentially rot with separation into the barrier. This implies that the taller and more extensive a hindrance is, the more the electron wave function will rot before achieving the opposite side. Therefore, the higher and wider the boundary is, the lower the likelihood of the electron quantum burrowing through the hindrance. In any case, if the particles are administered by the Dirac condition, their transmission likelihood really increases with expanding obstruction tallness. A Dirac electron that hits a high hindrance will transform into a gap and proliferate through the boundary until it reaches the opposite side, where it will transform once again into an electron. This marvel is called Klein contradiction. A clarification for this marvel is that expanding boundary stature prompts an expanded level of mode coordinating between the wave functions of the openings inside the obstruction also, the electrons outside of it. When the modes are impeccably coordinated (on account of a boundlessly tall obstruction), we have idealized transmission through the hindrance. On account of graphene, the chirality talked about before prompts a fluctuating transmission likelihood relying upon the edge of rate to the hindrance [42]. Some trial comes about have been deciphered as confirmation for Klein paradox. Klein tunneling has been seen

through electrostatic hindrances, which were made by entryway voltages [43]. Comparative impacts have likewise been seen in thin graphene full heterostructures [44].

1.1.1.4. A comparison with Conventional Semiconductors

Conventional semiconductors have a limited bandgap while graphene has not. Typically, the investigation of electron and hole movement through a semiconductor must be carried out with contrastingly doped materials. Be that as it may, in graphene the way of a charge carrier changes at the Dirac point from an electron to a gap or the other way around. In graphene, the Fermi level is dependable inside the conduction or valence band while in conventional semiconductors the Fermi level frequently falls inside the bandgap when stuck by debasement states. Due to the properties of Klein tunneling scattering in graphene is chiral. Moreover, graphene has a linear scattering connection while semiconductors have a tendency to have quadratic scattering. Numerous of the amazing physical and electronic properties of graphene can be thought to be results of this reality.

Graphene is significantly slenderer than a conventional 2D electron gas (2DEG). A conventional 2DEG in a quantum well or heterostructure has a tendency to have a successful thickness around 5–50 nm. This is expected to the limitations on development and the way that the limited electron wave functions have a transitory tail that extends into the hindrances. Graphene, on the other hand, is just a solitary layer of carbon particles, for the most part, respected to have a thickness of around $3 \text{ \AA}$ (double the carbon-carbon bond length).

1.1.2. Vibrational Properties

The vibrational properties are also important as much as electronic properties of graphene. Due to the electron-phonon and phonon-phonon interactions, both the structural information and electronic behavior of graphene can be revealed by Raman spectroscopy. Moreover, the vibrational property of graphene plays a key role in thermal conductivity.

1.1.2.1. Phonon Dispersion

Phonon dispersion of graphene can be explained by examining the lattice vibrational modes. There are two carbon atoms in one unit cell of graphene. This result in three acoustic (A) and three optical (O) phonon modes. Due to the two dimensional nature of the graphene, the vibrational modes vary as longitudinal (L), transverse (T) and flexural (Z). In addition, the

longitudinal and transverse modes are related to the in-plane vibrations where the flexural phonons correspond to the out-of-plane. So there are two out of plane vibrations as ZA and ZO modes, four in plane vibrations as LA, LO, TA and TO modes. The phonon dispersion is generally demonstrated with the phonon energy ($E = \hbar\omega$) versus the phonon wave vector (q). Figure 1.4a shows the schematic of the atomic arrangement in graphene with a unit cell drawn in dashed lines. Figure 1.4b plots the phonon dispersion in phonon energy as a function of wave vector from Γ to M point.

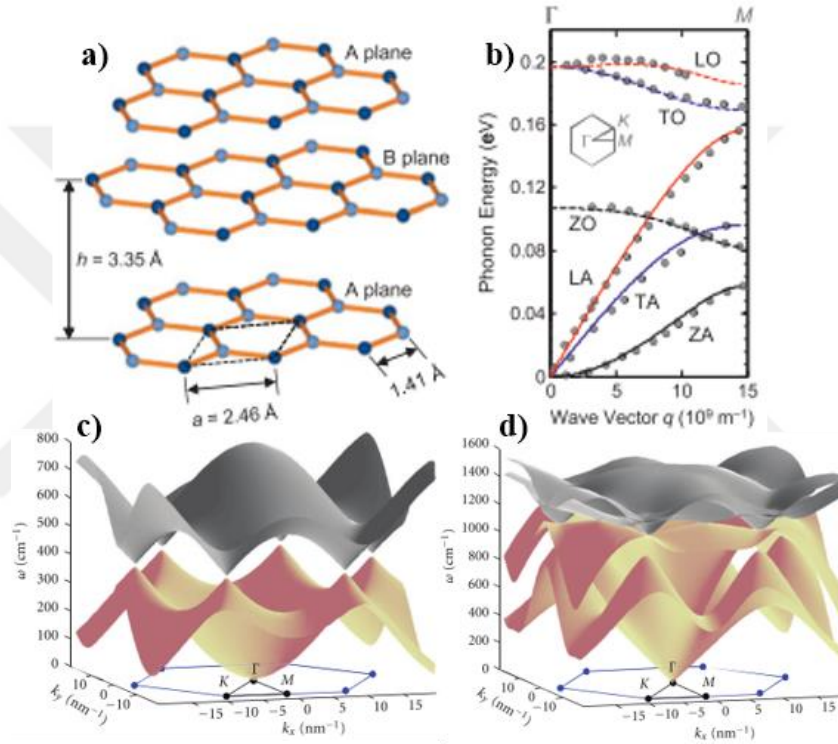


Figure 1.4: **a)** Schematic illustration of the graphene geometry within a unit cell showing the bond lengths in plane and out of plane **b)** The phonon dispersion in graphene depicted with experimental (symbols) and calculated (lines) data **c)** The out of plane phonon modes plotted with phonon frequency by momentum space for ZA and ZO **d)** The in plane phonon modes for TO, LO, TA and LA [45, 46].

On the other hand, the phonon dispersion relation can be calculated using the second-nearest-neighbor model. Figure 1.4c represents ZA (bottom surface) and ZO (top surface) modes as a function of phonon frequency by momentum space (reciprocal vector $\vec{k}$). In figure 1.4d, gray surfaces indicates the optical phonons TO and LO. The colored surfaces indicates the acoustic phonons TA and LA. As it is understood from the figure 1.4d, there is a linear dispersion for TA and LA near the Γ . This linear dispersion makes the group velocities of TA and LA higher than those in traditional semiconductors such as silicon and germanium with the velocities of

approximately 13,6 km/s and 21,3 km/s for TA and LA respectively [47-49]. Conversely, ZA modes do not exhibit a linear dispersion near the center of the Brillouin zone but it plays a key role for the thermal properties of graphene.

1.1.2.2. Thermal Conductivity

According to the kinetic theory of gases, the thermal conductivity of graphene can be calculated by the formula $\kappa \approx \sum C v \lambda$, where λ is the mean free path, v is the group velocity of phonons and C is the specific heat [50]. Since the group velocity is very high in graphene, a record thermal conductivity is easily anticipated which is the highest of any known material, above $2000 \text{ W m}^{-1} \text{ K}^{-1}$ for suspended graphene. Below the thermal conductivities of some materials are compared with suspended graphene.

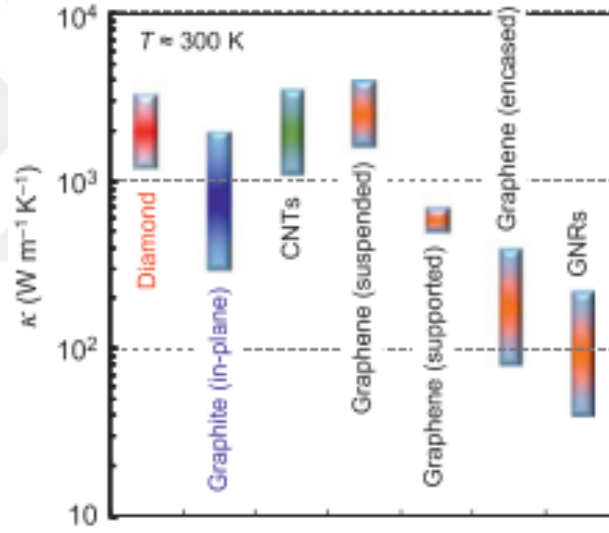


Figure 1.5: The thermal conductivities of diamond, graphite, carbon nanotubes, suspended graphene, SiO_2 -supported graphene, SiO_2 -encased graphene and graphene nanoribbons at room temperature[51].

Due to the scattering mechanism of phonons, any disorder or remnant from the experimental process cause extra phonon scattering comprising shorter mean free path decreases the thermal conductivity. As a result of this fact, supported graphene samples have lower thermal conductivity. In addition to supported graphene samples, graphene nanoribbons which have equal sample dimensions compared to the mean free path present lowest thermal conductivity.

1.1.3. Production Methods

Since graphene was discovered with a sticky tape by the scientists at the University of Manchester, it has attracted tremendous concern around the world due to its fascinating physical and chemical properties. But; there was a lack of in producing a vast amount of graphene in the early stages of the invention. Scientists have been developing multi-way of graphene production not only for graphene but also graphene derivatives such as graphene oxide, graphane. Upon many methods, the most known ones will be explained briefly below.

1.1.3.1. Scotch Tape (Mechanical Exfoliation)

The first and the most used method for the beginners in graphene research is the scotch tape method. It is also known as the mechanical exfoliation of the graphite. The method is practical and low cost. All the need is just a piece of graphite and a sticky tape and a specific substrate (Silicon substrate with a 300 nm thick oxide layer). Since graphite consists of many sheets which is composed of tightly bonded carbon atoms in-plane and weakly bonded with the van der Waals bond out-of-plane, each layer can be easily separated by a small force. And this separation or in other words “exfoliation” occurred with a sticky tape which was first used by its inventors. This method was unintentionally realized during a so-called Friday night experiments at the University of Manchester for the cleaning of the graphite surface. With this method, one can produce graphene flakes with the high crystal quality with no defects and the high mobility.

Table 1.1: Graphene production methods and their consequences. (a):[52], (b):[53], (c):[54], (d):[55], (e):[56], (f):[57].

Method	Layers	Size	Mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)
Exfoliation	1-10	1 mm ^a	15000 ^b
Thermal SiC	1-4	50 μm^c	2000 ^c
Ni-CVD	1-4	1 cm ^d	3700 ^d
Cu-CVD	1	65 cm ^e	16000 ^f

However; this process is restricted to small scale production. For the applications such as flexible touch screens, transistors, gas or chemical sensors and so forth, a large scale graphene production is required. For this purpose, several methods have been developed and these are

explained below. Table 1.1 represents the comparison of some graphene synthesis methods according to their number of layers, size, and mobility value. In our study, we also chose the exfoliation method. A detailed information about this process is well-depicted step by step in section 2.1.

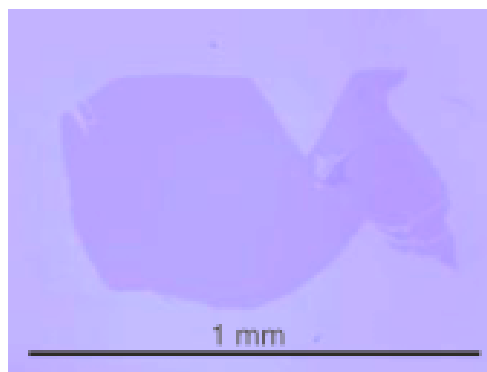


Figure 1.6: One of the largest graphene flakes obtained by scotch tape method (Courtesy of Graphene Industries Ltd.).

1.1.3.2. Thermal Decomposition of SiC

As the name of this method implies, thermal decomposition includes heating of the SiC at high temperatures (1000°C - 1500°C) in inert gas atmospheres for Si atoms to sublime from the SiC. In this method, to get a 2D formation of graphene with high mobility from SiC, high stable vacuum conditions are a necessity [54]. Unlike the exfoliation method, thermal decomposition of SiC provides large graphene flakes. On the other hand, the 2D crystal quality of the samples prepared with this method is not successful as much as exfoliation method due to the locally disordered carbon atoms. Preliminary work on thermal decomposition of SiC for graphene synthesis was undertaken by Walt A. de Heer and his colleagues who managed to produce few layer graphene sheets by epitaxial growth and proved it by low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements [58]. The process covers the oxidation or H_2 etching of a 6H-SiC crystal at the beginning in order to prepare the sample for the formation of graphene and improve the surface quality. Then the sample is treated to the electron bombardment in high vacuum to remove the oxide layer. After removal of the oxide

layer, it is heated to about 1250-1450°C temperature, to get a thin graphitic formation on the surface. Here the decomposition parameters play a key role to determine the layer thickness.

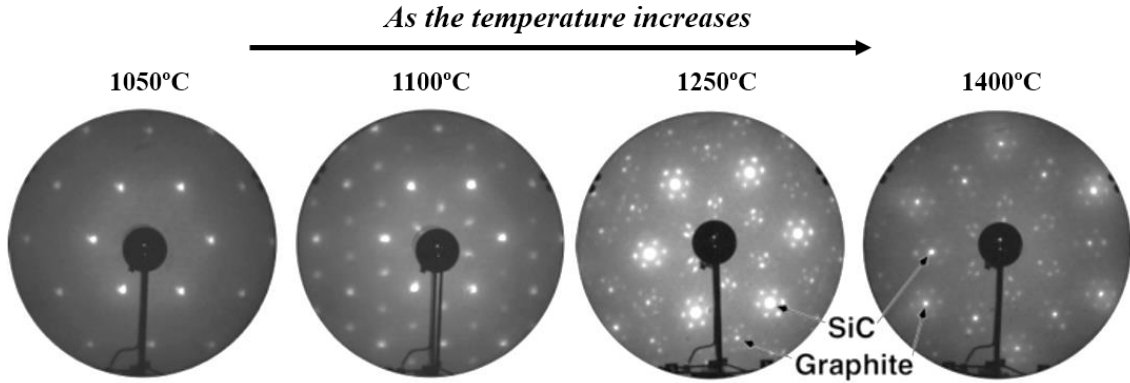


Figure 1.7: The LEED patterns obtained SiC in a series of heat treatment respectively [58].

The LEED pattern shows that when the sample was heated at 1050°C SiC 1×1 pattern was obtained. Heating at 1100°C for 3 minutes turns out $\sqrt{3} \times \sqrt{3}$ reconstruction. When the temperature is set to 1250°C for 20 minutes the electrons diffracted from a $6\sqrt{3} \times 6\sqrt{3}$ unit cell (~single layer graphene). The 1400°C temperature treatment gives ~2.5 layer graphene as well. The study of the structural behavior of epitaxially grown graphene samples was carried out by Emtsev et al. using atomic force microscopy (AFM) shown in figure 1.8 [54].

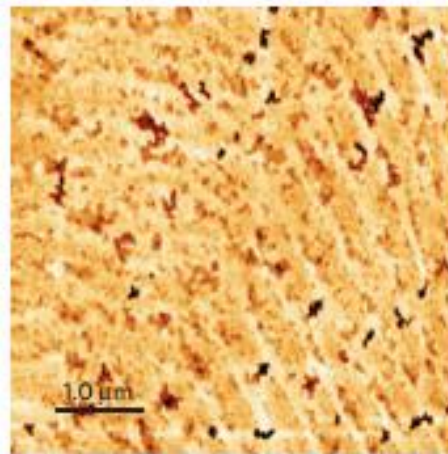


Figure 1.8: AFM image of graphene on 6H-SiC(0001) formed by annealing in UHV at a temperature of about 1280 °C.

They also obtained the electron mobilities of up to $2000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This technique enables to produce large scale graphene layers which can be a great potential for the semiconductor

industry. But; there are some drawbacks on layer thickness and the repeatability of the process for mass production.

A recent study by Juang et al. involved the synthesis of millimeter sized graphene on SiC substrates at low temperature (750°C) with a continuous growth using Ni thin films [59].

In another study, researchers have been successful on manufacturing single layer graphene in mm² using a process where gold/polyimide film was used to transfer graphene onto an insulating substrate for field effect transistor (FET) measurements [60].

1.1.3.3. Chemical Vapor Deposition

Unlike thermal decomposition of SiC method, chemical vapor deposition (CVD) technique involves an appropriate gas (hydrocarbons) supply onto a metal surface under low or ultra high vacuum (UHV) conditions in order to compose the graphene sheets. Here, the metal is used for both as a substrate and catalyst during the formation of graphene. Generally, nickel (Ni) and copper (Cu) foils are used in this technique.

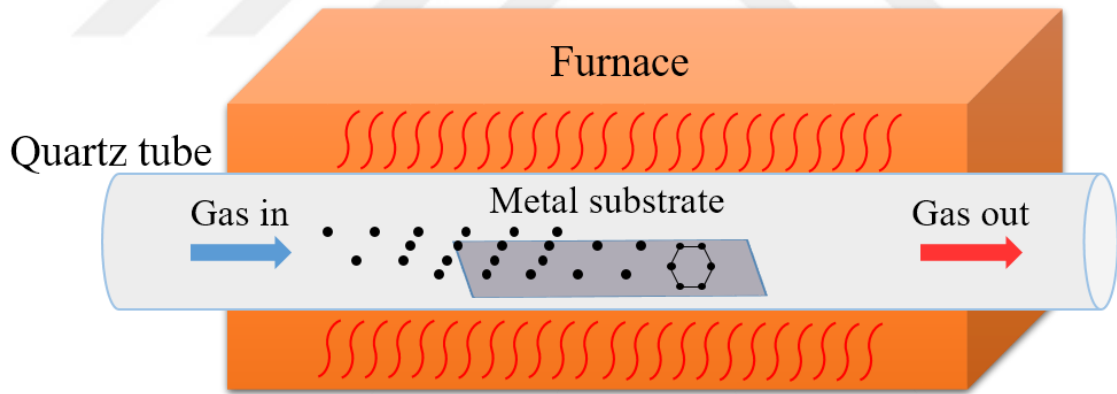


Figure 1.9: Schematic illustration of CVD process for graphene.

Briefly in this method, a hydrocarbon gas such as methane is flown through a quartz tube onto the Ni or Cu foil while the tube is heated in a furnace at approximately 1000°C. During the cooling process of the foils the number of the layers of graphene is determined by the cooling rate. It was observed that the very fast cooling of the Ni foil causes the carbon atoms to segregate into the foil inhomogeneously and moderate cooling brings about proper segregation onto the surface with composing graphene sheet [5]. After this step, the deposited surface of the Ni foil is often coated with poly(methyl methacrylate) (PMMA) for transfer operation. Since HNO₃

dissolves the Ni foil, the specimen is immersed into the HNO_3 solution to get rid of the nickel part. In recent years, there has been an increasing amount of literature on this method. For example, Reina and et al. presented their modified CVD technique which provides large area (cm^2) graphene samples with varying layer thicknesses on nickel films [61]. They also suggested that these graphene films can be lithographically patterned for electronics or other applications such as touch screens or displays due to the film homogeneity and light transmittance. On the other hand, Li et al. have performed a similar series of experiments in large scale graphene on copper foils [62]. In their process, 25 μm thick copper foils with an appropriate methane flow have been used and the layer thickness was verified as monolayer via Raman spectroscopy and SEM analysis. They also showed that the carrier mobility of graphene reached up to the $4050 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Bae et al. have recently developed a methodology for the roll to roll production of graphene with a diagonal of up to 30 inches which can take place commercially instead of indium tin oxide (ITO) (Figure 1.10) [56]. As shown in the figure, CVD grown graphene on copper was transferred to a polyethylene terephthalate (PET) substrate.

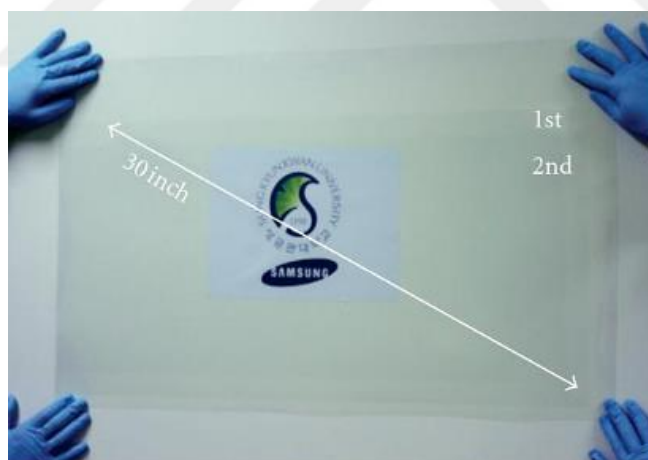


Figure 1.10: Large scale graphene sheets on PET substrate produced by CVD method.

The sheet resistance of this ultra-large graphene/PET film can be varied by the number of layers stacked on each other. For example, one layer of this film shows prominent sheet resistance of $125 \text{ } \Omega/\text{W}$. When the number of layer increased to four, the sheet resistance becomes approximately $30 \text{ } \Omega/\text{W}$ with an optical transmittance of 90%. Today, the commercial touch screens and flat panel displays are manufactured using ITO ($\sim 100 \text{ } \Omega/\text{W}$, sheet resistance for ITO) as transparent electrode. When the results of the electrical properties of this film compared to that of ITO, it is clearly seen that graphene is surpassing.

1.1.3.4. Molecular Beam Epitaxy (MBE)

In this method, large area and high quality graphene samples have been intended to be produced in ultra high vacuum ($\sim 10^{-10}$ Torr) on metal surfaces. But, it is difficult to obtain graphene samples with high crystal quality as much as exfoliated one due to the mismatch problems with the substrate. Differently from CVD method, the carbon atoms do not diffuse underneath the metal surface in MBE. And the layer formation can be controlled up to several layers by continuous growth contrary to the CVD method. For MBE method, ethylene or carbon filaments are used as a source material.

1.2. GRAPHENE OXIDE

Graphene oxide is prevalently produced using an aggressive acidic treatment developed by Hummers and Offeman [18]. Unlike graphene, graphene oxide is an insulating material, including carboxylic and carbonyl groups at the edges, epoxy and hydroxyl groups on the basal plane [63]. That makes the graphene oxide material possible to be functionalized for various applications. However, this method of analysis has a number of limitations. One of the key problems is that colloidal graphene suspensions are irreversible processes and it is very difficult to totally reduce and purify the graphene oxide sheets [16, 64, 65]. In addition, the corresponded measurements represent questionable results about the last product due to the dispersed graphene and graphite flakes in the suspension. On the other hand, a better understanding of the reaction mechanism is needed for nano-electronic devices and such sensor applications. The device design is also important and must be well patterned readily.

Graphene oxide can also be utilized to obtain graphene by using a series of reduction and cleaning procedures [38]. The reduction of graphene oxide can be made thermally or chemically.

1.2.1. Production Methods

There are several methods to produce graphene oxide. The most common way to get it is the wet chemical treatment of the graphite particles. Herein, we report a direct wet chemical oxidation of mechanically cleaved and lithographically shaped single layer graphene on SiO₂/Si substrate using a modified Hummer's method. We believe that a much more systematic approach would prove how graphene oxide formation affects the electrical properties with other

variables that are believed to be linked to both the chemical treatments and other methods. In the view of this approach, the different ways of getting graphene oxide is explained below.

1.2.1.1. Wet Chemical Synthesis

Graphene oxide can be easily obtained by oxidizing and exfoliating graphite in a chemical solution. This approach was discussed and improved in the early stages of 1960s by Hummers and Offeman [18]. But before them two methods by the scientists in the name of Brodie [66] and Staudenmaier [67] had been suggested. In all these methods, graphite is oxidized by acidic treatment in different rates with various chemicals. In Brodie and Staudenmaier method, the mixture of nitric acid and potassium chlorate has been facilitated to oxidize the graphite. On the other side, potassium permanganate and sulfuric acid were used in Hummers' method. Upon these methods, the recent studies on oxidizing graphite were published as modified Hummers' method [68-71]. Briefly in wet chemical process, a small amount of graphite flakes (~5-10 g) are mixed with acid (H_2SO_4) in a beaker and cooled in an ice bath. After stirring of the mixture for 1 hour, a certain amount of KMnO_4 is added slowly on magnetic stirrer to keep the solution agitated. Due to the oxidation reaction, the color of the mixture turns out green. The change of the color from green to pink shows that the reaction terminates and oxidation stops. Also, the viscosity of the pink mixture increases as the separation of graphene oxide sheets from the graphite flakes. Then a suspension of graphite oxide and graphene oxide mixture is obtained. After this step, a considerable amount of this mixture is washed with iced water and centrifuged until to get rid of the acid. Finally, the precipitate is prepared for a solution with any solvent such as water, acetone, dimethyl sulfoxide and etc. At the end of an ultrasonic treatment of this solution one could get graphene oxide colloidal suspensions because of the hydrophilic property of graphene oxide.

1.2.1.2. Plasma Functionalization

Due to the potential requirement of graphene in almost all industrial area, alternative ways to produce graphene oxide without any loss of time and chemicals have been developed recently. One of these alternatives is the plasma functionalization method or in other words glow discharge treatment. Vandsburger et al. have proven to oxidize the carbon allotropes with this method [72]. The main advantage of this method is not to need of strong acid usage and the process can be easily taken at room temperature very quickly without waiting day after day. For bandgap

manipulation of graphene, plasma treatment may take the place of Hummers' method by changing the electrical properties of graphene or few-layer graphites.

1.2.1.3. Scanning Probe Microscopy

A few attempts have been made to pattern the single layer graphene using atomic force microscopy (AFM) rather than chemical treatments [73-76]. Such studies present local anodic oxidation process for graphene nano-device fabrication where the AFM tip and the oxygen molecules in the ambient react on the surface of the graphene sheet. Perhaps the most serious disadvantage of this method is the shallow oxidation [77]. A much more systematic approach would prove how graphene oxide formation affects the electrical properties of other variables that are believed to be linked to both the chemical treatments and other methods.

As an alternative way to tailor graphene-based electronic devices, scanning probe lithography (SPL) has been frequently used in the last decade [73-75, 77, 78]. Local anodic oxidation (LAO) lithography is a kind of SPL technique where atomic force microscopy (AFM) and water meniscus between the AFM tip and substrate are used. In this technique, AFM tip is negatively biased and the substrate is grounded in order OH^- ions in moisture to oxidize the graphene [77]. LAO can also be used to pattern e.g. quantum dots [79], quantum point contacts [80] and graphene nanoribbons [73, 81]. In contrast to the conventional lithography applications, LAO lithography needs a conductive substrate in order to produce a current between the AFM tip and the substrate. Although LAO has a capability to pattern graphene in nanometer size, it is not practical for large-area applications because of the extended operation time. On the other hand, a range of measurements need to be carried out to get the optimized conditions to form graphene oxide bumps or trenches due to some variables such as tip bias voltage, set point voltage, the relative humidity in environment and scanning frequency. Because of that, the experimental data about the LAO lithography are rather controversial, and there is no general agreement about the graphene oxide formation.

2. MATERIALS AND METHODS

2.1. PREPARATION OF GRAPHENE

In preparation of graphene samples, micromechanical cleavage method (Scotch tape method) has been used. Through the method, graphite flakes are exfoliated by folding and unfolding the scotch tape repeatedly until thinner graphite residue remains on it. Si wafer with a 300 nm thick thermal oxide layer is handled for transferring graphene. In order to detect one atom thick graphene samples, we have used an optical microscope to scan the surface of the substrate with the naked eye and candidate graphene flakes were first obtained by recognizing the contrast difference between flake and substrate. To ensure and prove that the flake is single layer graphene or not; Raman spectrum is taken to detect related G and 2D peaks. For further study coordinates of graphene flakes are saved via a reference point on the desired substrate corner. Images of them in different magnification are also recorded as a reference for maskless and e-beam lithography processes.

2.1.1. Cleaning Procedure of the SiO₂/Si Substrate

Before transferring graphite flakes on the substrate, the wafer surface must be cleaned chemically to get rid of organic residue and dust particles in order to get a clean and hydrophobic surface. It is very important for further applications of graphene. Because; if there is any organic residue or dust, it would be an obstacle to measure proper electrical properties of graphene. To do that, a cleaning procedure is taken out through all our experiments. First, %35 H₂O₂ and %95-98 H₂SO₄ chemicals are mixed 1:3 ratios in a beaker within an ice bath. This mixture is also called 'Piranha' solution. Second, approximately 1×1 cm² substrates are cut from the bulk wafer with the help of a diamond cutter and placed into the prepared mixture. Third, the beaker is put in an ultrasonic bath for 30 minutes. Subsequently, substrates are taken out the beaker and rinsed with distilled water. Finally, rinsed wafers are dried with nitrogen gas. Through the cleaning process, we have used p-doped (0.005 Ω.cm) Si substrate with 300 nm thick thermal oxide layer. All these procedures and steps were followed in a clean room (Class 10,000).

2.1.2. Transfer Procedure of Graphite Flakes and Determination of Graphene

By folding and unfolding the tape, we had various graphite flakes with different thicknesses on the scotch tape. Then we attached tape onto the surface of cleaned Si/SiO₂ substrate. The tape

was provided to stick on the surface smoothly using a soft object. After letting the substrate wait approximately 10 minutes, the tape was uncovered from the surface very slowly. These steps are shown briefly in Figure 2.1.

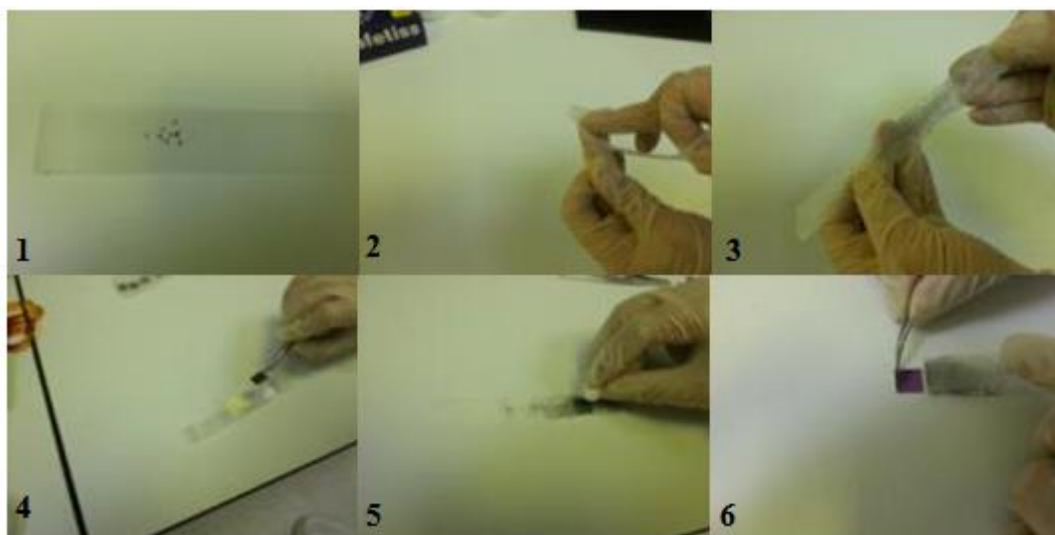


Figure 2.1: Preparation of graphene samples on SiO₂/Si substrate by scotch tape method shown in successive steps.

After uncovering the tape from the wafer surface, the substrate is scanned under an optical microscope to detect monolayer graphene. The difference in contrast between graphene and silica surface enables us to observe appropriate graphene flakes unlike graphene is one atom thick carbon sheet and has a light transmittance of ~%98. The coordinates of desired samples with respect to a reference point on the substrate are recorded for Raman analysis and further investigations. In Figure 2.2, mono and bilayer graphene samples detected under optical microscope is presented.

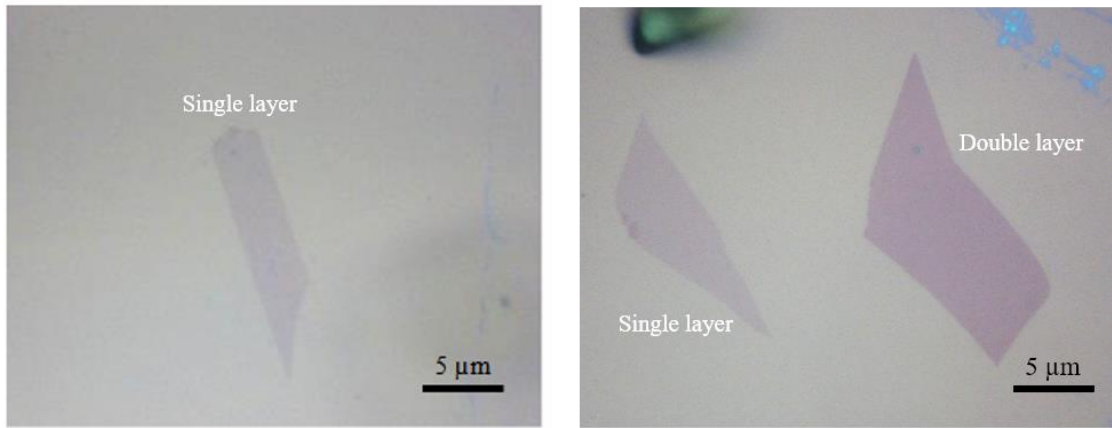


Figure 2.2: The optical images of single and double layer graphene samples in 50X magnification.

Raman analysis is the best known versatile technique to characterize carbon-based materials among other characterization methods. In order to be sure about the samples a Raman spectrum is taken. By looking at the spectrum we can easily understand whether flake is graphene or not. Because graphene has a Raman fingerprint as shown in below.

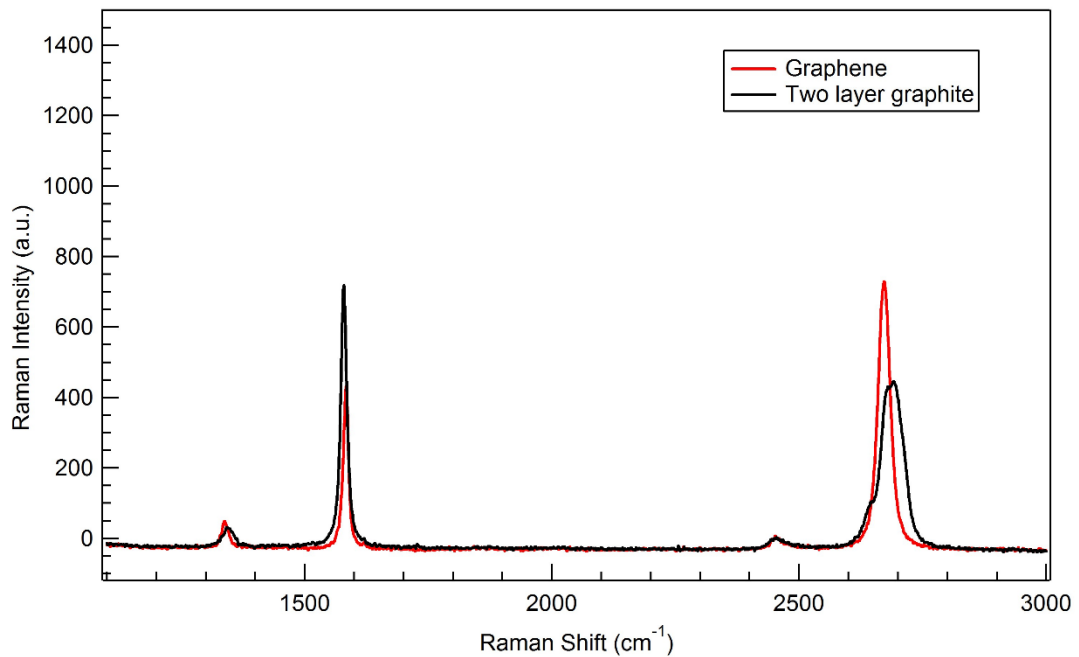


Figure 2.3: The Raman spectra of single and double layer graphene (graphite).

As it is seen in the spectra above, graphene has a specific spectrum that has two major peaks arise $\sim 1570 \text{ cm}^{-1}$ called G peak and $\sim 2700 \text{ cm}^{-1}$ called 2D peak. For a graphene sample, the 2D peak is sharp symmetric and greater than the G peak. Starting with the two-layer, 2D peak loses its sharpness and greatness. It is very obvious that graphene can be differentiated from

even two-layer graphene although it is almost difficult under an optical microscope with naked eye compared to the contrast (Figure 2.2). We used green laser with a 532 nm wave length with high brightness as a light source within Thermo DXR micro-Raman spectroscopy system. Figure 2.4 shows the micro Raman spectroscopy system allied with 4X, 10X, 20X, 50X and 100X objectives.



Figure 2.4: Raman Spectroscopy system (DXR, Thermo) used for graphene analysis.

2.2. RAMAN SPECTROSCOPY

As it is known, the light consists of photons. If these photons interact with matter for example, with substances such as particles, they get absorbed, scattered or pass through the matter without any interaction. In an absorption process, when the energy of a photon corresponds to the energy difference between the ground state and the excited state of the material it is interacting with, it will be absorbed and lead the material to have a higher energy than before. On the other hand, it may also get scattered as a result of the interaction with or without losing part of its energy. The energy, scattering direction and the intensity of these photons can be measured using a photodetector and analyzed to obtain information about the material interacting with the light. Such measurements can be utilized to determine the size of particles, type of chemical bonds involved within the material and even the electronic structure of the material.

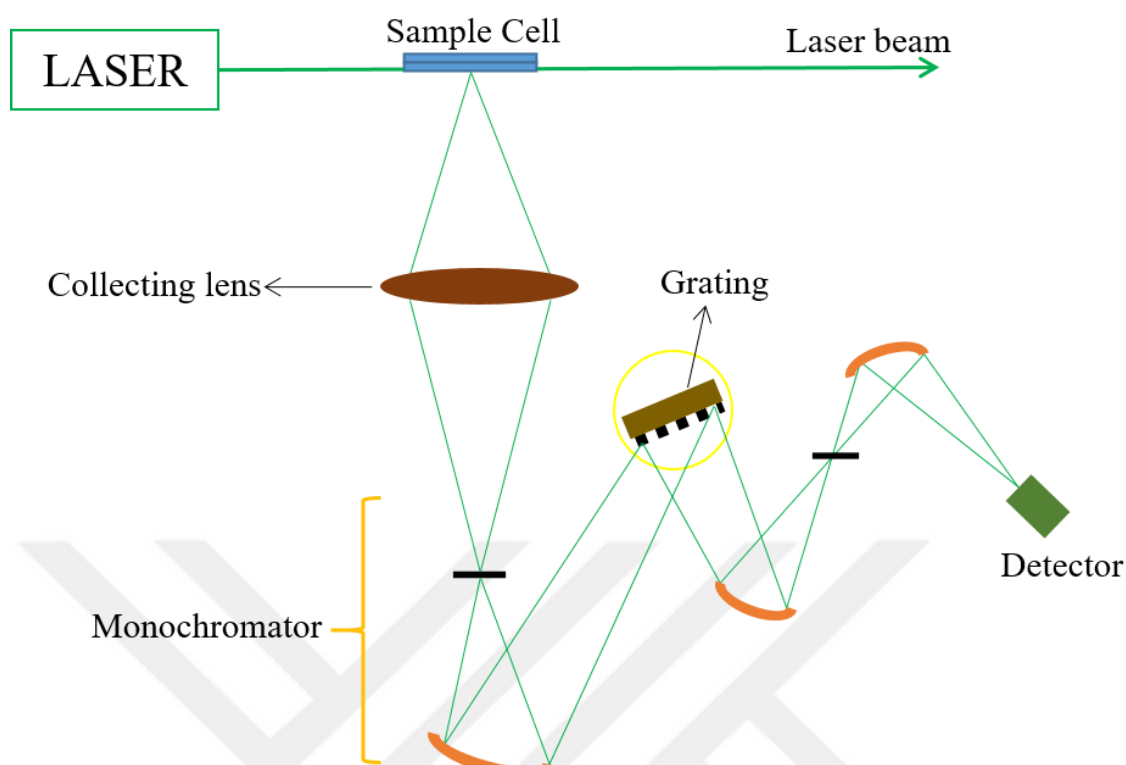


Figure 2.5: Schematic diagram of a Raman spectrometer.

Raman scattering is a technique which is used in Raman Spectroscopy to characterize and identify the molecules. In Raman spectroscopy, a single frequency of radiation is used to irradiate the sample. This is easy to achieve with the use of modern lasers and microscopes. Raman spectroscopy involves an interaction between the molecule and the photon. In addition to the backreflected and transmitted light as is commonly observed, light can get scattered through three different processes. In the so called Rayleigh scattering process, the photon gets absorbed and excites the molecule to a higher energy state (or a virtual state) and the molecule returns back to its initial level by emitting a photon with exactly the same energy in some other direction (Figure 2.6). Because, energy of the incident photon is equal to the photon emitted by the molecule, this scattering is similar to the elastic scattering process of particles.

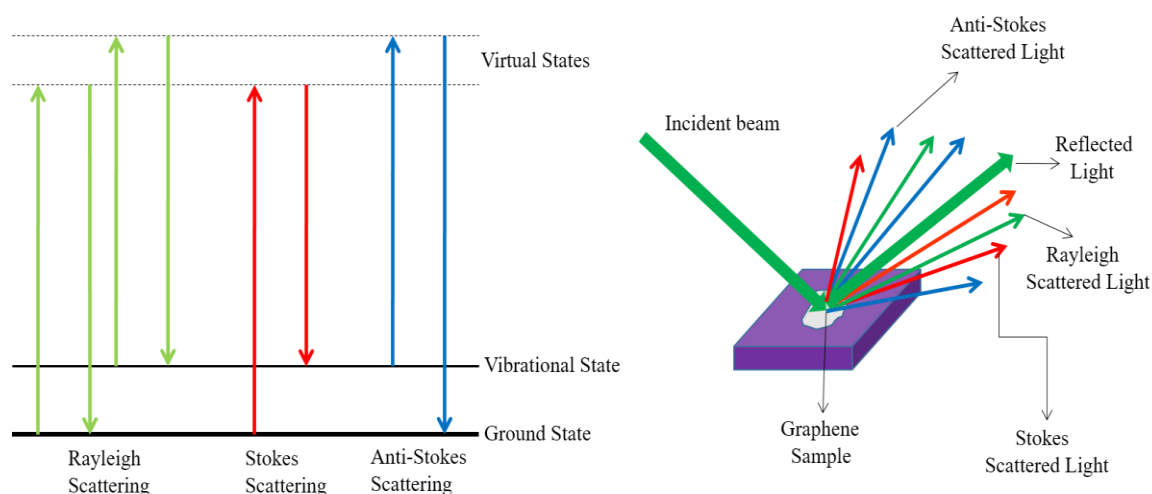


Figure 2.6: General illustration of three types of scattering processes of light with matter. The dashed lines indicate the virtual energy state of the molecules according to the energy of the incident photon. Diagram of Raman scattering among different scattered photons.

In addition to Rayleigh scattering, there are two other types of scatterings such as Stokes and Anti-Stokes scattering. The Stokes scattering is the name given to a process which takes over an inelastic scattering of a photon (Figure 2.6). In contrast to Rayleigh scattering, molecule absorbs energy and after the vibrational excitation of the molecule, lower energy photon is released by the molecule and there remains an excess energy. As a result of this, distorted molecule starts to vibrate in an upper vibrational energy state steadily. This is also called as a Raman scattering. The Stokes scattering is a much rarer case which includes only one in 10^6 - 10^8 of the photons scattered. Figure 2.6 illustrates this scattering as an example for a better comprehension. The anti-Stokes scattering is the inverse condition of Stokes scattering in basic terms. Contrary to the Stokes, molecule loses energy and after the vibrational excitation of the molecule, higher energy photon is released by the molecule. So, it takes place in the ground state or a lower vibrational energy state compared to the initial condition.

Generally, molecules vibrate in the lowest vibrational energy level at room temperature. Most molecules scatter from the ground state but; occasionally, some molecules are present in an excited state by the reason of thermal energy. If these molecules scatter from this excited state to the ground state, this process is called Anti-Stokes scattering. As it is mentioned above, Rayleigh scattering does not involve any energy change. Hence, the most intense process is the Rayleigh scattering with respect to the Stokes and Anti-Stokes scattering. The second intense process is the Stokes and the third one is Anti-Stokes. The scattering probability depends on the

number of molecules in the ground state or excited vibrational states. It can be calculated using the Boltzmann equation:

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} \exp\left(-\frac{E_n - E_m}{k_B T}\right) \quad (2.1)$$

where N_n is the number of molecules in the excited vibrational energy level n , N_m is the number of molecules in the initial vibrational energy level m , g_n and g_m are the degeneracies of the levels n and m respectively, $E_n - E_m$ is the energy difference between the two vibrational levels, k_B is the Boltzmann's constant, and T is the temperature.

2.3. MASKLESS OPTICAL LITHOGRAPHY

In this process, we use a maskless photolithography system that has 1-micrometer patterning resolution capability (SF-100, Intelligent Micro Patterning, LLC) shown in Figure 2.7. After defining the coordinate of graphene sample on the wafer, a maskless lithography process is started to build a contact circuit onto graphene. Also, four markers are patterned around the graphene for e-beam lithography process. For this purpose, the wafer is coated with positive photoresist (Micro resist, ma-P 1205) by a spin coater (G3, Specialty Coating Systems). Here, the coating parameter is very important to acquire intended thickness of photoresist which is 500 nm and essential for the optical lithography process.

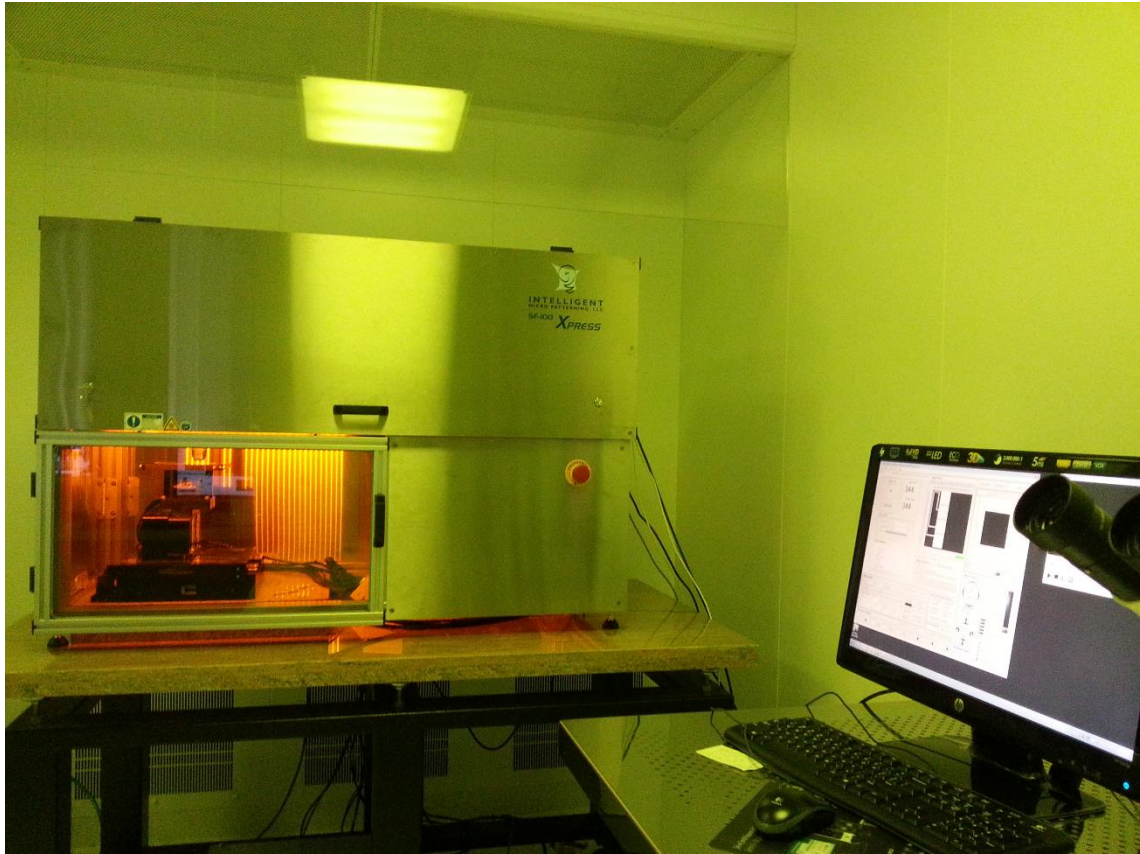


Figure 2.7: Maskless photolithography system in a clean room (Class 100).

2.3.1. Preparation of 500 nm thick photoresist film

In order to obtain an intended thickness of photoresist film, we have optimized the spin coater operation parameters. Utilizing from the literature we had tried much to find appropriate ramp times and rpm (revolution per minute) values of the spin coater. In our optimization, spin coater is started to operate at 500 rpm in 5 seconds and continued to run 5 seconds more at that speed. Then in 10 seconds, speed is increased at 3000 rpm and motion is kept going for 40 seconds. Subsequently, spinning is decelerated to stop in 10 seconds. Thereby 500 nm thick photoresist film is attained. We have confirmed the coated film thickness with a profile meter (NanoMap 500 LS). Last, the coated wafer is annealed at 100 °C on the hotplate for 90 seconds in order for photoresist film to solidify.

2.3.2. Optimization of the UV exposure time

After photoresist coating step the wafer is placed under the objective of the optical lithography system. Target graphene sample's location is adjusted by moving the automated stage to the corresponding coordinates that were taken under optical microscope relative to the reference

corner of the wafer. We can see the video image of graphene underneath thin and transparent photoresist film on the monitor by the help of lithography software called ‘Stage’.

Subsequently desired pattern is projected onto the surface of the photoresist film. In the sequel, ultraviolet light exposes the surface of the photoresist with a proper time. Afterward, the wafer is taken and dipped into the solution so called developer for 40 seconds. If the exposure time is not sufficient the pattern on the photoresist does not take shape properly. In Figure 2.8(a), as it is seen obviously the violet silica surface cannot be seen in some places of the pattern due to the undeveloped photoresist residue. On the other hand, in Figure 2.8(b) with a sufficient exposure time, the test pattern is seen very good and there is no any photoresist residue on the surface. Here the violet regions are silica surface in trench and the other parts are photoresist film.

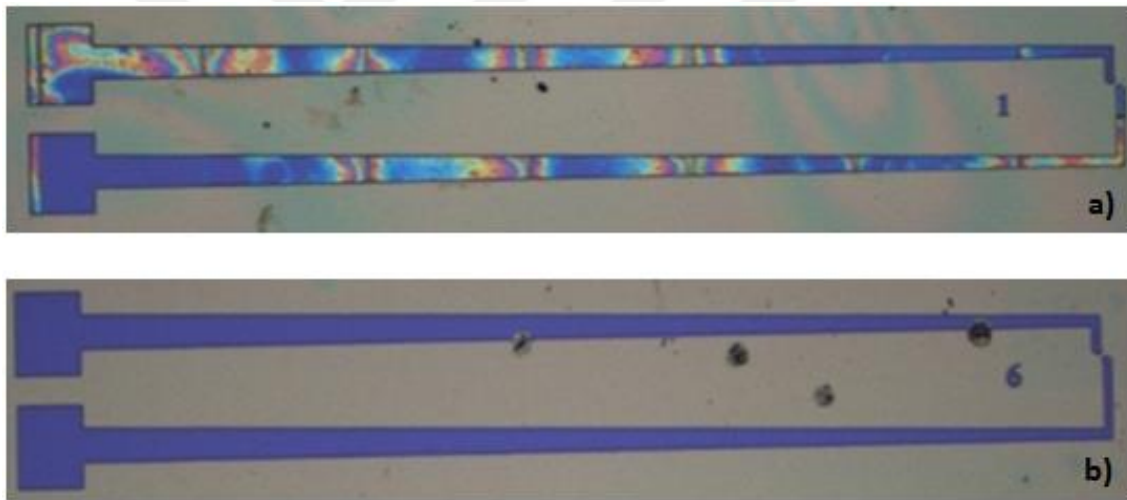


Figure 2.8: **a)** Image of a test pattern with insufficient exposure time **b)** with sufficient exposure time.

Here, the reason can also be development time but we had adjusted the development time by making a series of development at different times with constant exposure time and we find the optimal development time as 40 seconds. In order to optimize the UV exposure time, we had used exposure matrices with various exposure times. At the end of the development procedure, we achieve optimal exposure time controlling the patterns under an optical microscope. The exposure time may be different for each experiment because the lamp of the UV light runs out as the day goes on. So at the beginning of each lithography process, we first test and optimize the exposure time using a trial SiO_2/Si wafer.

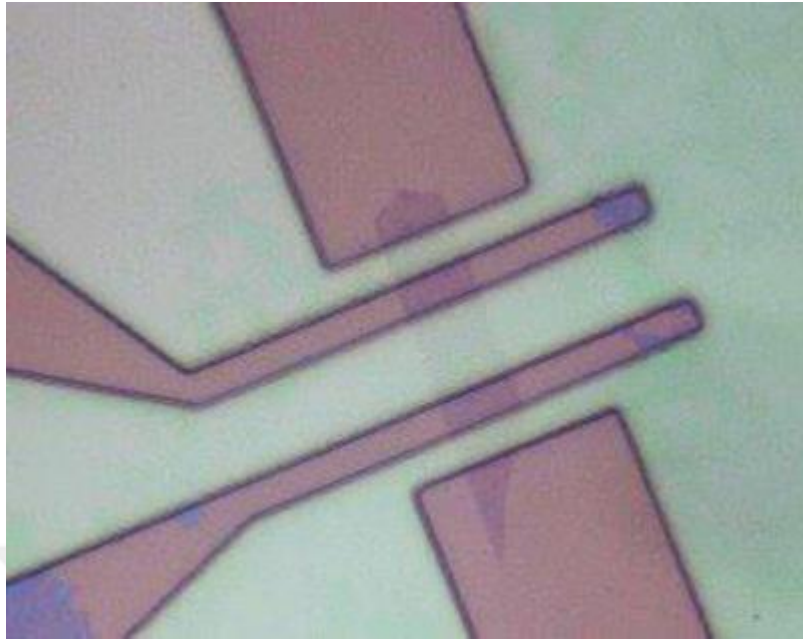


Figure 2.9: The optical image of the developed contact pattern on graphene for four-probe electrical measurements.

2.4. MAGNETRON SPUTTERING

In this step, we build up our circuit by coating titanium and the gold metal thin films respectively in an appropriate thickness ratio using magnetron sputtering system. Additionally, lift-off procedure is performed with acetone in an ultrasonic bath. In Figure 2.10, the constructed contact circuit and marks are shown. Here the marks around the center of the image are going to be used in e-beam lithography in order to make hybrid graphene structure.

2.4.1. Construction of Au/Ti Contact Lines and Pads on Graphene

After patterning the photoresist layer using optical lithography system, we first deposited 5 nm thick titanium metal on the surface of the wafer. Subsequently, 30 nm thick golden thin film was coated. Here the reason of depositing titanium at first is to make gold thin film adhere on the surface of silica very well by the means of titanium. If golden thin film is coated onto the surface of silica without titanium layer, we cannot get the desired contact

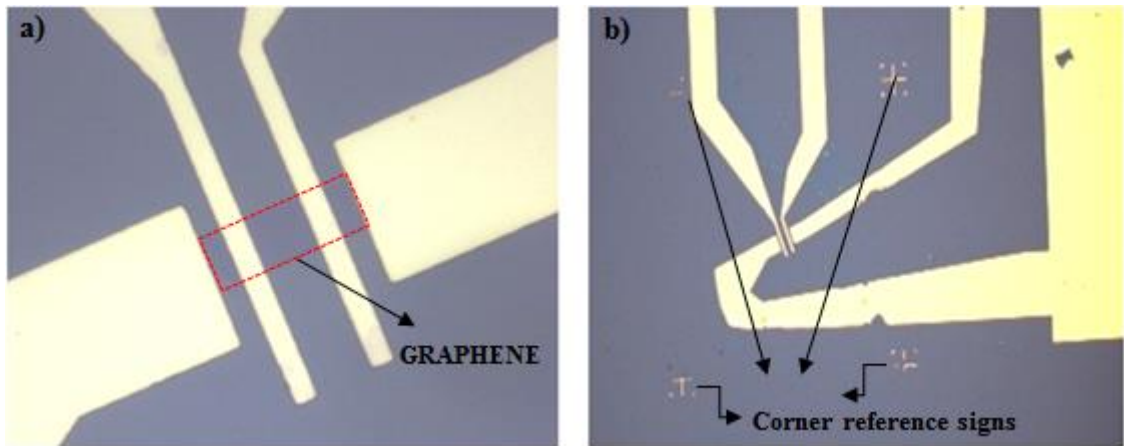


Figure 2.10: a) After metal deposition and liftoff process b) Marks around the contact lines will be used during the e-beam lithography for alignments.

patterns after lift-off process. Because; titanium thin film plays an adhesive layer role for the gold thin film. All the metal deposition processes are carried out in magnetron sputtering system due to the rapid growth ratio (Figure 2.11).



Figure 2.11: The magnetron sputtering system used for metal coatings.

In this system, the substrates can be coated quickly rather than e-beam evaporator or other coating ones with the help of RF and DC source. Using these units a plasma media is generated inside the chamber and ionized argon gas molecules strike the surface of metal target swiftly.

As a result, bombardment process leads to removal or sputtering of target atoms from the surface and condense on the substrate as a thin film.

In our work, we adjust the argon gas flow rate through the chamber as 20 sccm. Generally, we operate the system in 5×10^{-5} Torr. We have optimized gas pressure as 5 mTorr while coating titanium and 4 mTorr for gold. We also made a series of coating experiment to achieve optimal deposition parameters such as coating periods, powers of sources and the partial gas pressures during the coating for both metals. On the other hand, the thicknesses of coated films are very important to lift the photoresist off Si/SiO₂ substrate after coating Au/Ti. Because; our experiments showed that coated film thickness must be lower than 50 nm in order for removal of photoresist residue and forming contact pattern properly. Excess of this thickness causes the contact lines to break off the surface.

On lift off process, coated wafer is put in a beaker with approximately 40 ml acetone (%99 purity) and sonicated in the ultrasonic bath until photoresist layer lifts off the surface. When we encountered a problem in liftoff process, we also tried to keep the sample in a hot acetone for a long time before a harsh sonication in a jiff.

2.5. E-BEAM LITHOGRAPHY

In order to fabricate graphene/graphene oxide hybrid structure, e-beam lithography (EBL) technique was used to pattern the graphene surface. For this study, we have practiced on JEOL JSM-7001F model scanning electron microscope (SEM) allied with Elphy Quantum (Raith) software that enables us to perform lithography procedure down to a resolution of 50 nm (Figure 2.12). EBL system is operated in a Class 100 clean room.

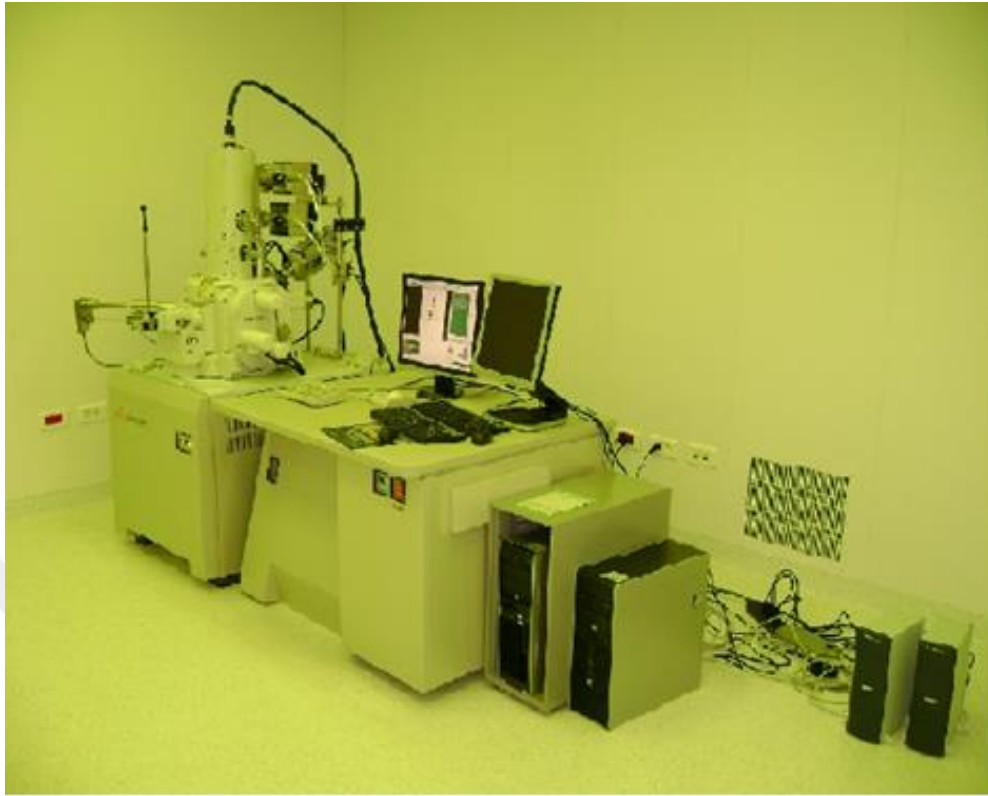


Figure 2.12: Scanning electron microscope(SEM, JEOL 7110) allied with e-beam lithography facility (EBL, Raith).

Unlike optical UV lithography, the EBL uses electrons to expose the resist layer. The whole SEM imaging and lithography process is carried out under high vacuum condition because; electrons can easily be absorbed or deflected by the particles (atoms, molecules or dust) in the medium. Therefore, if the pressure in the chamber is not low enough not only the homogeneity of e-beam but also the resolution of imaging will be unfavorable. This is the unsolicited status for SEM and EBL applications. In our system, EBL is run with a chamber pressure of 9.6×10^{-5} Pa ($\sim 10^{-7}$ mbar). The evacuation is provided by a diffusion pump backing with a rotary pump.

For the source of e-beam, a thermionic electron gun where electrons are emitted from the heated tungsten filament was used in former SEM systems. Today, most of the new instruments have a field emission electron gun that utilizes very high electric field to extract electrons from a metal filament. Our system is equipped with a field emission electron gun as well.

Before EBL the substrate's surface should be coated properly with an appropriate resist film by a spin-coater (Spincoat G3P-8) according to the type of application.



Figure 2.13: Spin-coater used for coating resists on wafers.

We used a positive e-beam resist (950 PMMA A2 Microchem Corp.) for our process. This e-beam resist is a kind of polymer called as Poly (methyl methacrylate) (PMMA). It is easily affected by the e-beam exposure due to the fact that the bonds between the polymer chains are broken by highly energetic electrons. Here the dose of e-beam exposure and development time play a key role in patterning the resist layer. The accelerated voltage, the emission, and probe current are also important parameters. Meanwhile, the different operating conditions of these parameters are effective in EBL. So, there should be a standard for the dose rate, accelerated voltage, emission and probe current values together for the best results. With this purpose in mind, we have optimized accelerating voltage, probe current, e-beam dose rate and development time on free wafers before performing EBL procedure on graphene samples. We have also optimized the recipe for spin-coater as well as to obtain an optimum and desired thickness of resist in order to be successful in the liftoff procedure. After all experiments, we decided to coat 100 nm thick PMMA resist layer on the wafers.

2.5.1. Preparation of 100 nm Thick PMMA Resist Film

In this procedure, the wafer is first preheated to 180°C temperature onto a hotplate for 60 seconds and blown with nitrogen gas immediately in order to eliminate the moisture, organic residue and another such kind of dusty particles which hinder the adhesion of the e-beam resist on the substrate's surface. After waiting for cooling at room temperature, the surface of the wafer is coated with positive e-beam resist (950 PMMA A2 Microchem Corp.) by a spin coater

(Figure 2.13). Here, the thickness of the resist becomes approximately 100 nm according to our optimized coating recipe that involves the ramping and dwells time with rpm (revolution per minute) values of spinning. Table 2.1 shows our program which is the recipe for coating PMMA with 100 nm thick by the spin-coater.

Table 2.1: The selected recipe to obtain 100 nm thick PMMA resist layer on wafers.

Step	Time (s)	Ramp (rpm)	Dwell time (s)
1	5	500	10
2	10	2000	40
3	10	0	0

Later, the wafer is post-baked at 100 °C temperature on a hotplate in 90 seconds for stiffening of e-beam PMMA resist. Figure 2.14 shows the PMMA coating results in a comparison between the random and selected recipe. In Figure 2.14a, it is seen that

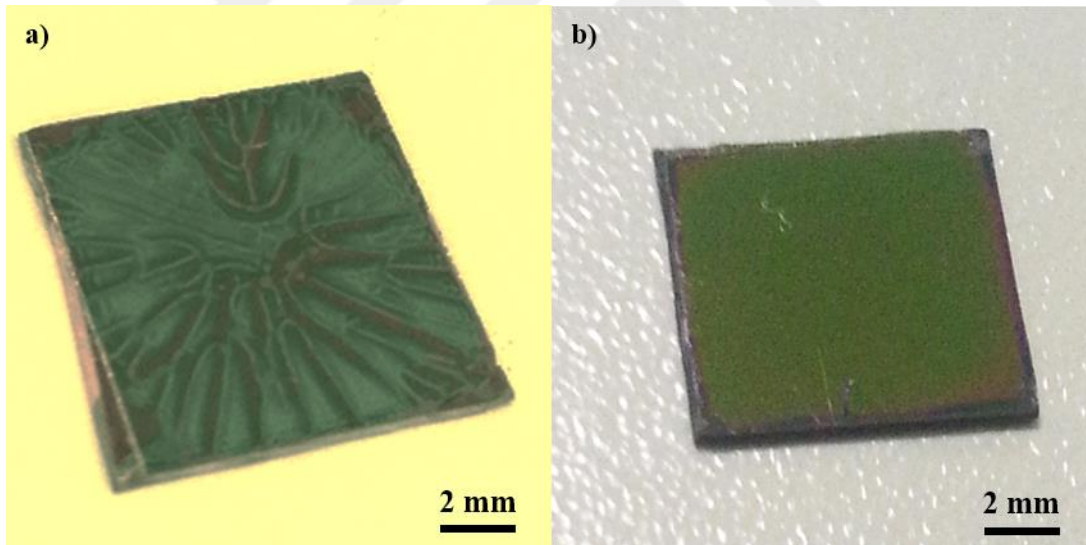


Figure 2.14: **a)** The inhomogeneous PMMA coated wafer because of the moisture **b)** The desired PMMA coating with a thickness of 100 nm.

there are some breaking points (dust or moisture residuals) block the homogenous overlay of PMMA resist. When we apply our procedure consists of preheating the wafer on a hotplate with the selected recipe, we are able to get a well smooth layered surface of PMMA coating as shown in Figure 2.14b. After this step, the wafer is loaded into the SEM chamber for further EBL process.

2.5.2. Executing e-Beam Lithography

As in optical lithography, the patterned design must be well aligned to the graphene sample sensitively. However; unlike optical lithography, alignment procedure and imaging of the PMMA coated surface without exposing to e-beam is not possible. Therefore, on behalf of realizing the procedure properly, we first patterned reference marks around the graphene sample by using optical lithography and magnetron sputtering techniques which provide us to define the graphene location on the substrate before performing EBL. In order to define the write field alignment, we first load the substrate to the SEM chamber without overlaying with PMMA on it. Then we monitor the substrate reference corner and assign it as the origin (x:0; y:0) of the stage's coordinate system. During the EBL, the origin is attributed to a reference point to find the graphene flakes. According to the origin, we drive the sample stage to the intended coordinates and monitors the graphene sample. When we find the graphene on the substrate, we start the write field alignment procedure. In this procedure, each marker around graphene is scanned respectively and set to fit in the $400\ \mu\text{m} \times 400\ \mu\text{m}$ writing field with a magnification of 150X.

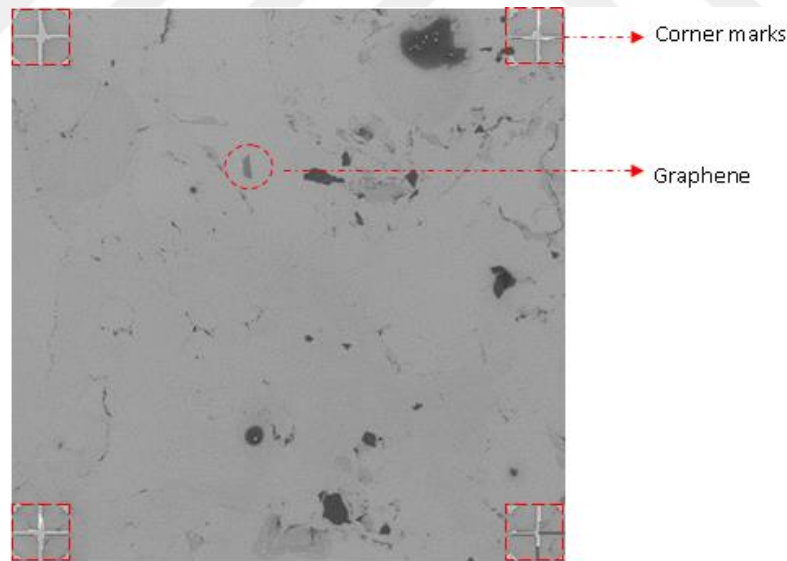


Figure 2.15: Graphene flake and corner marks. The image scanned after the alignment.

Figure 2.15 demonstrates the graphene flake and aligned marks around the corners. On the other hand, the e-beam is blanked by the blanking plates automatically during the stage is moved. Due to the e-beam blanking, resist is not exposed. When the stage movement is completed, blanking of the e-beam can be canceled by the user to get image again. After write field

alignment, the EBL process is completed by the exposure of drawn circuit design on graphene flake.

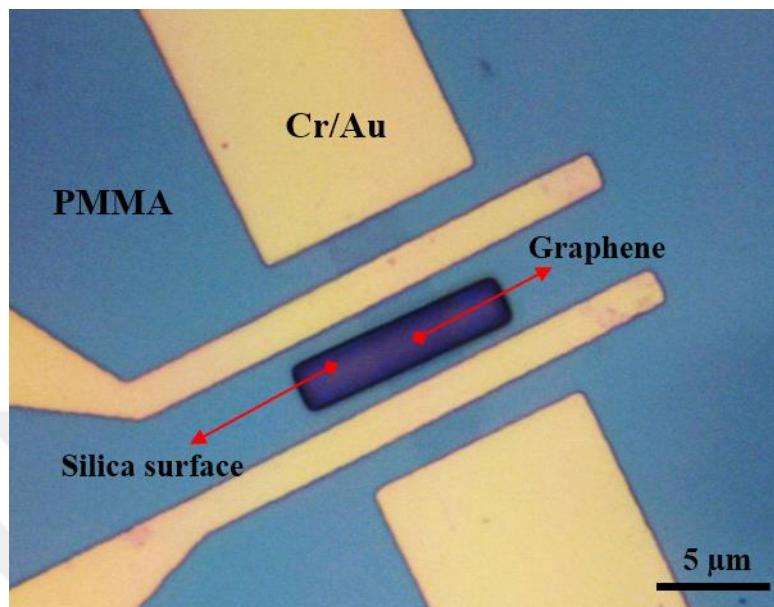


Figure 2.16: The optical image of the graphene FET device patterned with EBL to build hybrid.

Thereafter the substrate is immersed into the solution of MIBK/IPA 1:3 (MicroChem) for 45 s to develop the exposed regions of the resist. Subsequently, the substrate is adequately rinsed with isopropanol and dried under nitrogen gas flow. At the end of this step, a space in the middle of the graphene device is occurred and ready to the oxidizing reaction in solution which is preapred specifically. Figure 2.16 demonstrates the result of the EBL process which is essential for tailoring the surface in such a narrow dimensions. It is apparent that the desired space should be built with EBL because of the higher resolution capability.

2.6. ATOMIC FORCE MICROSCOPY

Another technique we use in the characterization of graphene specimens during our work is Atomic Force Microscopy (AFM). Basically this technique measures the forces resulting from the interaction between the needle and the sample at the atomic level with the help of a pointed needle at the end of a cantilever. Although various methods such as contact mode, non-contact mode, electrical force microscopy, magnetic force microscopy have been developed within this principle. But; three methods have been used predominantly in our studies. These methods are called contact mode, lateral force mode (LFM) and current (I-AFM) measurement mode, respectively. During our experiments, XE-100 model AFM manufactured by Park System was used that is shown below.



Figure 2.17: Atomic force microscopy system (XE-100, Park Systems).

Basically, AFM is operated with a laser deflected from the cantilever and a photodetector which the position of the laser is controlled. Actually, force is not measured directly; but calculated by the measurement of the position of the deflected beam.

2.6.1. Contact Mode

Contact mode (C-AFM) is the basic mode of atomic force microscopy. In this mode, the tip is in physical contact with the surface and applies a constant force to the surface. When the needle is moved parallel to the surface with the aid of piezo-crystals, the force is tried to be held constant by means of a feedback mechanism. For this, when the force between the surface and the specimen increases, the tip is lifted up through the piezocrystallites and lowered when the force is reduced. Surface topography images are generated using the pyroxocardial expansion and shrinkage data.

During our studies, Shocona-10 (APP NANO) model needles were used for C-AFM imaging operations. The force applied to the surface during the measurements has been 3nN. Figure 2.18 is an example of a topography image obtained from a single layer graphene. The sample and substrate can easily be distinguished from each other and the sample topography can be observed in detail. Using C-AFM, surface roughness can be measured, for example, the thickness can be measured and the small particles not visible under the optical microscope can be detected. In the following figure, the height between the SiO₂ substrate and the graphene was measured differently and was found to be around 1 nm in accordance with the literature values.

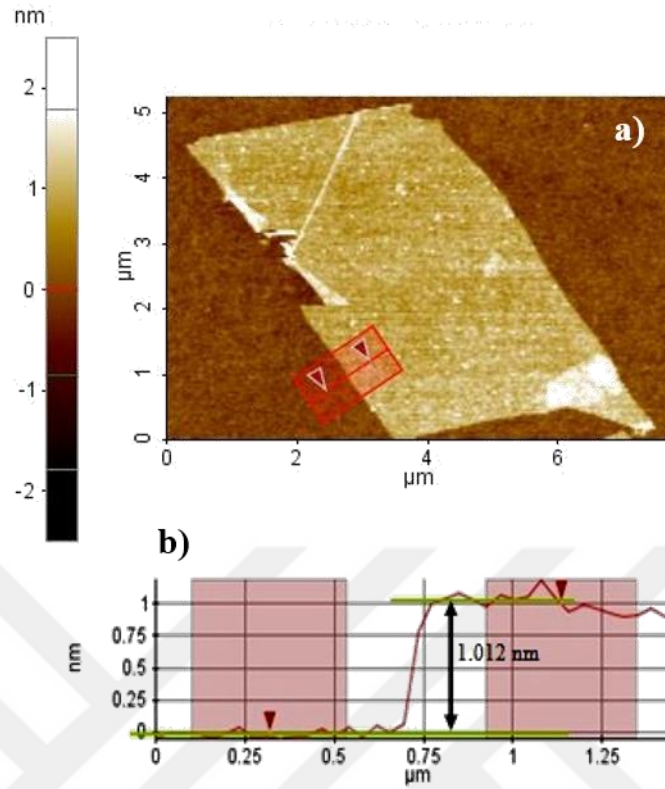


Figure 2.18: a) The topography image of single layer graphene on Si/SiO₂ substrate obtained in contact mode AFM. **b)** The thickness of graphene film by height profile.

Contact mode is the most common type of the other modes. It has a large usage area. In this mode, the tip is scanned across the surface by touching. To visualize this method in our minds, the tip can be thought as a needle which works in recording devices. In contact mode, the force between the tip and sample is kept constant by preserving a constant deflection. Contact mode can also be operated under fluids with a similar high resolution to that in the air. Generally, the spring constant of the cantilevers that used in contact mode is in the range of 0.01 to 10 N/m

2.6.2. Lateral (Frictional) Force Mode

In the frictional mode, as the tip is scanned across a surface the forces exerted on the tip in the x-direction or lateral direction is recorded at the same time. While working with the lateral mode, we have to take some important points into account for extracting quantitative data from measurements. These are, for example, normal force applied by the tip, the lateral spring constant of the cantilever, geometry of the tip apex, and the sensitivity of the optical lever to the torsional bending of the lever arm that holds the tip at the end of it [82, 83]. In Figure 2.19, a LFM image is shown taken from a graphene

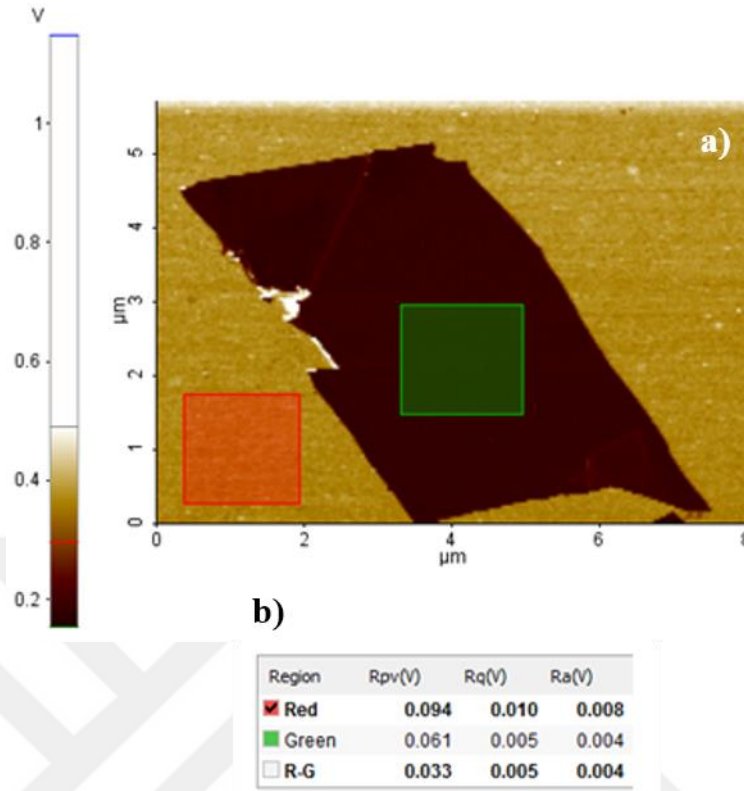


Figure 2.19: a) AFM image of graphene in lateral force mode. **b)** Table of the surface roughnesses in three different calculation type.

The LFM image analysis enables us to investigate the surface roughness as a mechanical behaviour of the graphene and substrate comparatively. In this figure, the red and green shaded areas are chosen for the frictional analysis. As it is seen obviously, the red area corresponds to the silica (Si/SiO_2) surface and the green one is single layer graphene surface. When the calculated average roughness values are compared, one can say that the frictional force exerted on the tip by the silica surface is two times greater than that of graphene.

2.6.3. Current (I-AFM) Mode

Unlike previous modes, a conductive tip is required. For this, conventional AFM tips are usually coated with Pt/Ir-like metals. In this method, a potential difference is applied between the needle and the sample in contact mode and the current passing from the needle to the surface is measured in a manner similar to the scanning tunneling microscope. An image is formed by measuring the change of the current passing through the surface while the force applied to the tip and the potential difference are kept constant. The obtained image is regarded as a measure of the regional conductivity of the sample surface. We have used SHOCONA-10 needle of APP NANO in our work. The length of the cantilever to which the needles are attached has a

dimension of 225 μm with a dimension of 46 μm and the needle has a radius of less than 10 nm. The reflective surface of these needles we use for conductivity measurements is covered with aluminum. Needles produced with N type Si have a conductivity of 0.01 - 0.025 ohm/cm. Below is an I-AFM image from these needles.

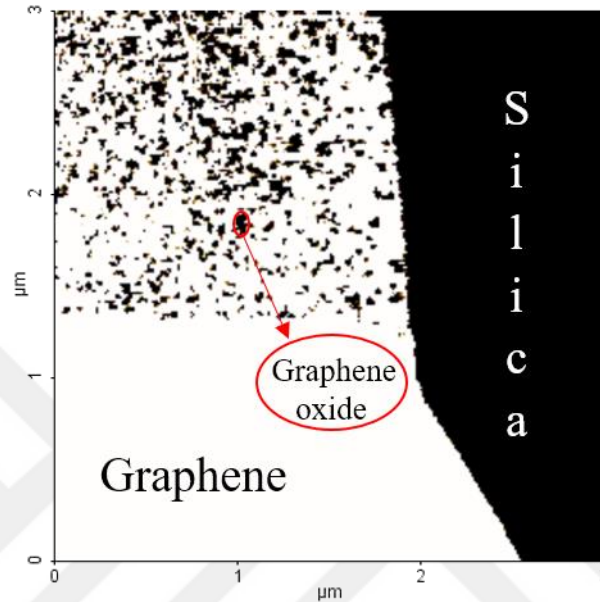


Figure 2.20: Current (I-AFM) image of oxidized graphene surface in which bright white regions are the conductive graphene and the dark black grains are the insulating graphene oxide.

In this figure, the color of black indicates the nonconducting parts (graphene oxide) which do not permit the current to flow. Conversely the color of white points the conducting portions (graphene). As an insulating substrate, silica seems black through this AFM image inherently. We have used this technique elaborative electrical properties of the graphene and graphene/graphene oxide hybrid structures.

2.7. REACTIVE ION ETCHING (RIE)

Large graphene specimens have to be shaped to the appropriate form as the Hall bar design for electrical measurements (Figure 2.21). In connection with this topic, we have conducted experiments to optimize the parameters of the plasma etching system. As a result of the experiments, we determined the minimum plasma power and erosion time required for etching one or two layers. For this process, the DC plasma source attached to the substrate holder of the magnetron sputtering system was used. In Figure 2.21, an optical microscope image is shown before and after a corroded graphene samples in this manner. A mixture of 20% O_2 and 80% Ar is used during the etching process and the etching time is 30 seconds with a DC power of

100 W. It is also possible to erode thicker specimens by increasing the time. We used these optimized parameters for tailoring the graphene surfaces which is partially covered with photoresist or e-beam resist. Figure 2.22 demonstrates the result of the plasma etching on single and few layer graphene flakes.

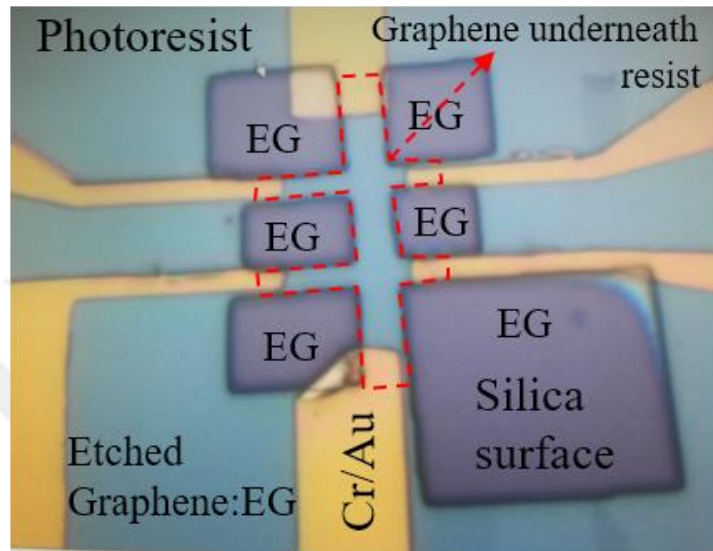


Figure 2.21: Optical image of Hall bar shaped graphene device by RIE.

Due to the RIE etching, the parts in which graphene exists are seen as silica surface. Using this method any shape can be obtained on graphene samples according to the request.

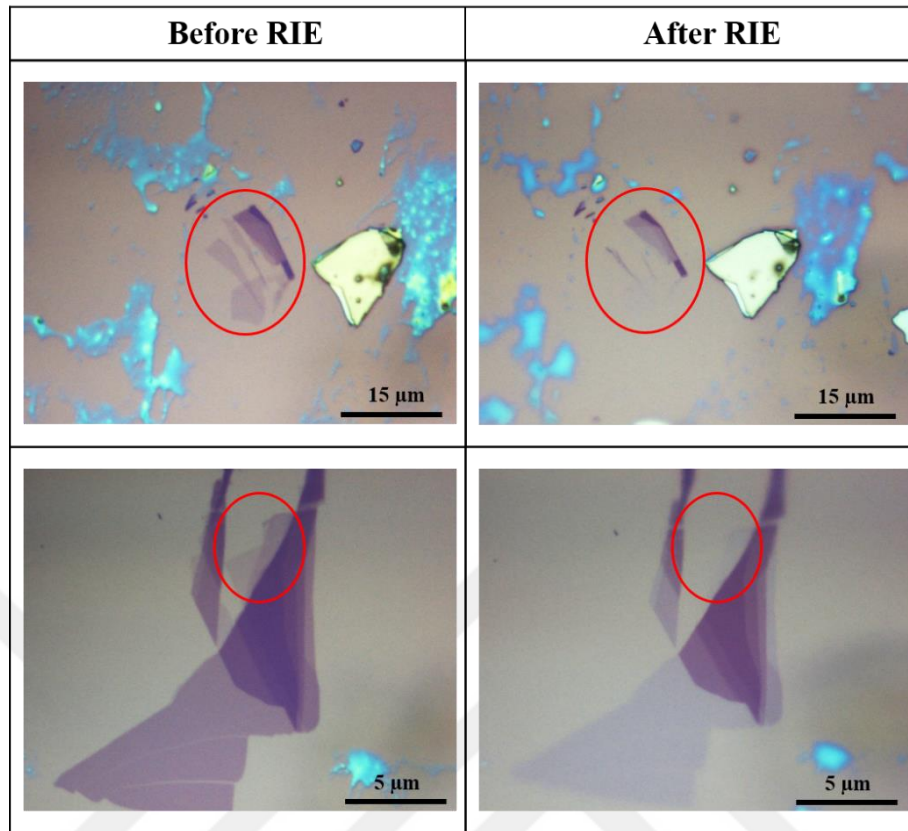


Figure 2.22: The effect of RIE to the graphene sheets.

As shown above, to optimize the reaction time two different regions on the same substrate were treated to the plasma etching and examined that single layer graphene flakes were facilely burnt up. On the other hand, it was observed that few layer graphene flakes were got thinner. If substrate is exposed to the plasma with sufficient time, even few layer graphites can vanish.

2.8. E-BEAM EVAPORATOR

During our research, e-beam evaporator was also used for the metal deposition due to the coating uniformity and precise layer controlling. When photoresist and optical lithography was chosen to tailor the graphene device, magnetron sputtering technique was carried out without any concern about the metal thickness for liftoff. But; when PMMA was coated on graphene for patterning the contact lines and pads, we have either tested e-beam deposition for metal covering with a big concern about thinner film deposition. Because the thickness of the coated metal must be one to three times the resist thickness for a successful liftoff procedure. The resist thickness covered during the photolithography is 500 nm and 200 nm in e-beam lithography. Therefore, the e-beam evaporation system, which has a more precise coating rate

for decreasing resist thickness, is required. In Figure 2.23, the e-beam deposition system that was used in our study is presented (Qprep deposition systems, Mantis).

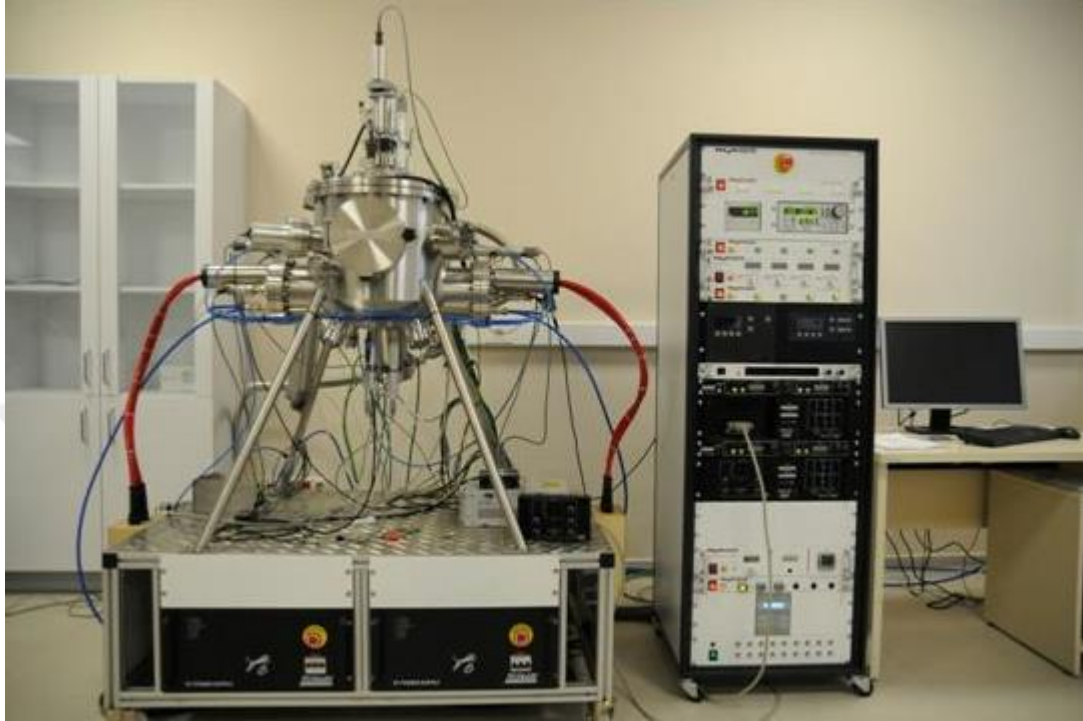


Figure 2.23: E-beam evaporation system with a controller unit.

The chamber pressure was kept under 3×10^{-6} mbar as starting pressure and during the metal deposition it decreased quite slowly according to the deposition rate of chromium (Cr) and gold (Au) metals. In this system, 5 nm Cr and 30 nm Au were coated according to 100 nm thick PMMA resist. The optimal coating parameters such as deposition rate, emission/filament current, DC output voltage and the coating pressure were experienced step by step and determined. Here, quartz crystal monitoring (QCM) enabled us to correlate the film thicknesses. We checked and proved the metal thicknesses by AFM analysis where height profile was generated.

2.9. ANNEALING SYSTEM WITH A QUARTZ TUBE

When we prepare the graphene samples by scotch tape method, we recognize tape residues on the surface of the wafer and graphene flakes. It was noteworthy to get rid of the residues from the surfaces because of the further experimental processes. But it should be non-destructive for monolayer graphene samples. Thereby, we performed the annealing procedure for the substrates by horizontal split tube furnace (Figure 2.24) in a clean room (Class 10000). In this

system, Argon (Ar) and Hydrogen (H_2) gases were used with a mass flow controller. During the annealing, a programmable temperature controller which provides temperature control using up to 8 segments was used. Each segment comprising of a ramp was followed by a dwell. Dwells may be set to zero time. In our case, the temperature was set to 250 °C in 30 minutes. After achieving 150 °C, Ar was flown into the tube with 400 sccm (standard cubic centimeter).

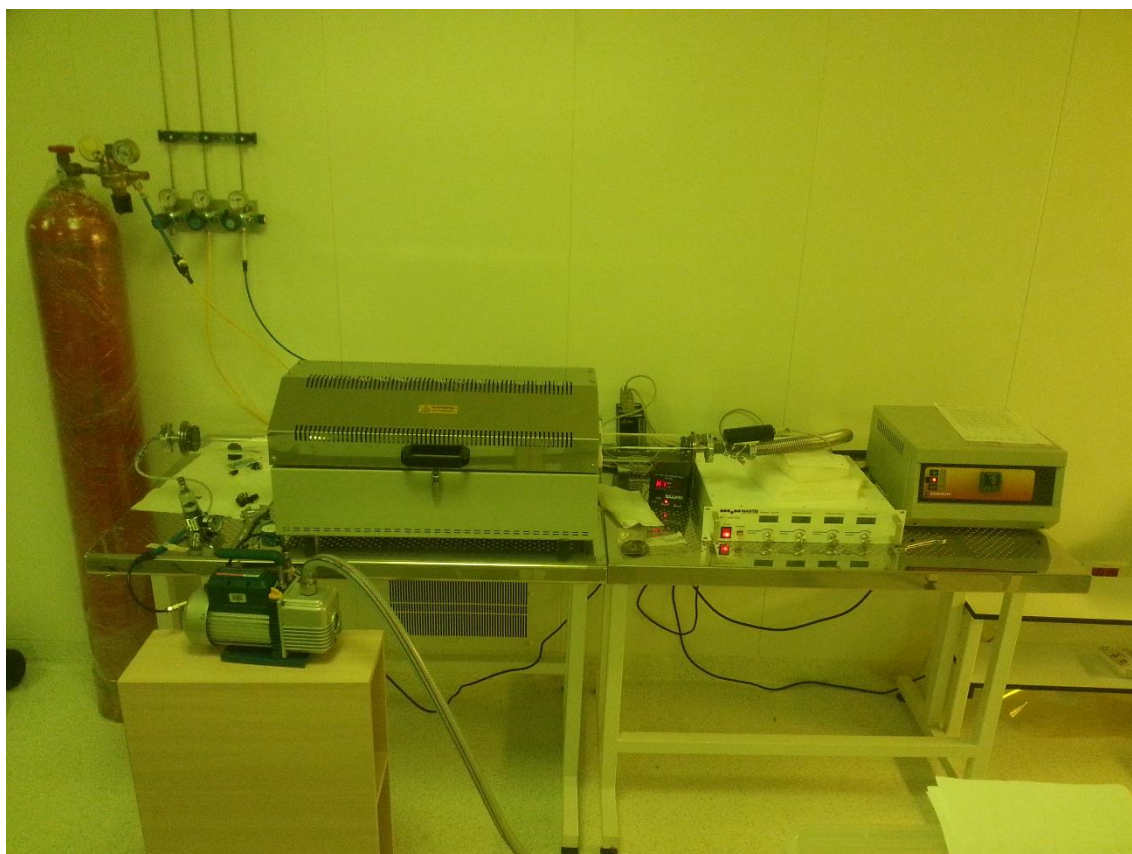


Figure 2.24: The quartz tube annealing system for graphene samples with gas and temperature controller.

200 sccm H_2 was included to the system when the temperature reached to 200 °C. This annealing dwell time was adjusted for 1 hour at 250 °C. By the way, the tube was first evacuated to approximately 10^{-4} mbar by a standard oil vacuum pump. This procedure enables to clean the organic residues on the wafer surface with tape residues on the graphene/graphite flakes as well.

2.10. WIRE BONDING SYSTEM AND ELECTRICAL CHARACTERIZATION SETUP

In the early stages of our research, we established a system for electrical measurements on our first graphene FET devices. For this purpose, we bonded the each contact pads of the device to the Cr/Au coated wafer surfaces. To apply backgate voltage to the device, the wafer grounded with silver tape on a patterned copper printed circuit board as shown in the figure below.

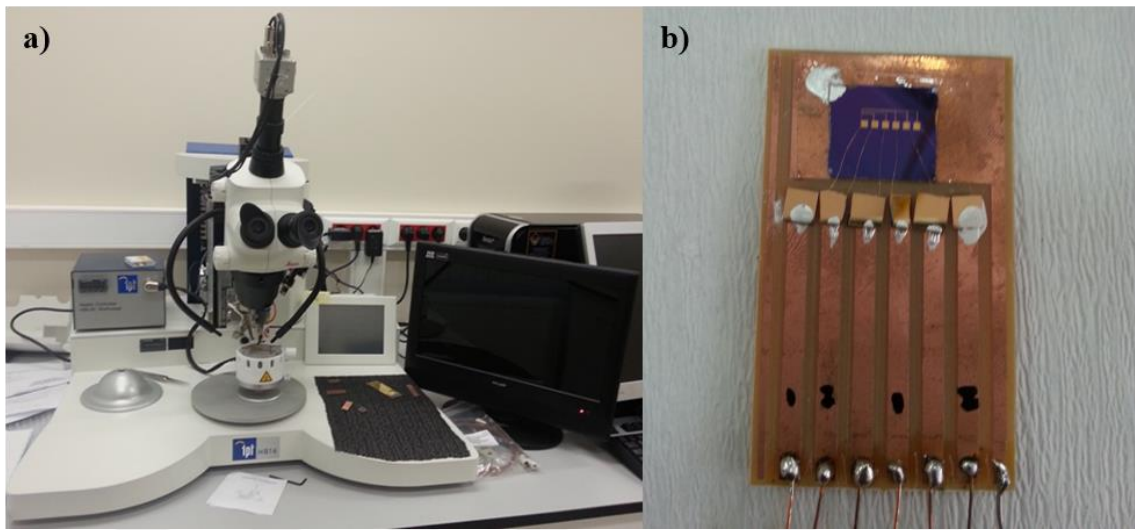


Figure 2.25: a) TPT HB-16 wire bonder system. **b)** The graphene device after wire bonded to contact pads before electrical measurements on Cu coated pcb.

After bonding and supplying connections for the measurements, the device was characterized by our electrical characterization set-up where various measuring devices were taken together and electrical characterization scheme was established and all software was developed so that the devices can be controlled and the data can be recorded on the computer. In addition to the KUSB-488B GPIB / USB Adapter and GPIB connection cables to provide a desktop computer, Keithley 6221 DC / AC current source, 2182A nanovoltmeter, 2400 sourcemeter, 6514 electrometer and these devices to communicate with the desktop computer, S-302 probe station was provided (Figure 2.26). In the tests performed, currents of up to 1mA were applied to the 6221 current source samples, while 2182A was used when the voltage on the sample was precisely measured. 2400 sourcemeters were used as a voltage source in cases where gate voltage had to be applied to the specimens and the electrometer was used for sensitive current measurements.

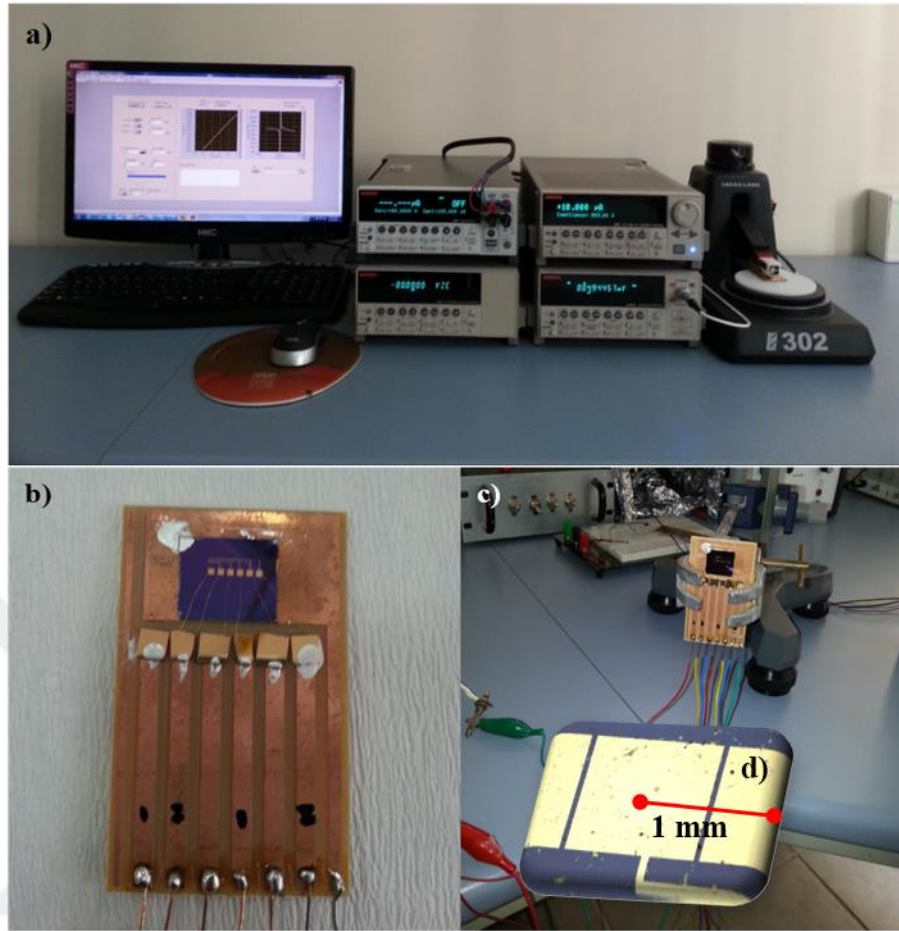


Figure 2.26: a) A four-point probe (Signatontest S-302) was added to the measurement instrument used for electrical characterization. The contact heads prepared on the specimens were adjusted according to the distance between the probe pins (inside figure) to enable measurement without connecting wires to the specimens b) Graphene FET device on PCB bonded by wire bonder c) ready to measure of the built electrical connections of the device d) Contact heads for the probe station.

The electrical connection between the devices was an important step in order to be able to take measurements from the graphene samples during the work. In these connections, conductive paths and contact heads connected to the specimens on the insulator substrate were formed using lithography. There are two ways to make electrical connections from these contact heads due to problems experienced in the wire binding system in our university. In the first method, the contact heads are placed in such a way as to be 1 mm between the side and the center as shown in the Figure 2.26d. It was thus possible to make electrical measurements by contacting the pins of the S-302 probe station directly to the contact heads. In the second method, the distance between the contact heads is increased and also gold wires are connected to the

contacts of the prepared circuit boards. A design was used to allow the measurement of circuit boards through direct probe station (explained in Section 2.11).

The four-probe method was used to measure the electrical conductivity of graphene specimens. Generally, care was taken to ensure that the specimens were of a rectangular geometry and four contact connections were made to the specimens. In this technique the current is passed through the sample with the outermost two contacts while those inside are used for voltage measurement. This geometry allows measurement of the voltage drop across the specimen, which is examined independently of the resistance of the connection wires and contact points. Care has been taken to create a uniform current on the specimen by placing wires parallel to each other in such a way as to cover the entire specimen. The current passed from the samples during the measurements is in the range of 1 mA.

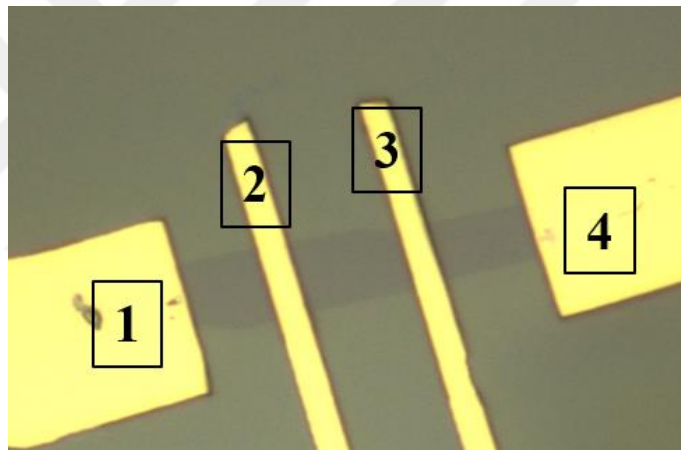


Figure 2.27: The four wire method used for electrical characterization.

Figure 2.27 shows the optical image of one of the devices we prepared with the numbers given to the contacts. Generally, the current is passed between the 1 and 4 and the voltage drop is measured with 2 and 3.

2.11. SEMICONDUCTOR ANALYZER

Another method and the most practical one with confidential measurement for electrical characterization of graphene devices was the semiconductor analyzer (Keithley 4200, Figure 2.27) system with a probe station. We have decided to make all the four-probe and FET measurements of the devices with this system when we found a chance during our research. Using this system we did not need to pattern the contact pads close each other or wire bonder to make the electrical connections to be able to make measurement with our first electrical

characterization system. Here, the Keithley 4200 plays a significant role in our graphene FET devices' electrical characterization due to its capability of the integrated computational programmable electrical analysis. The magnetically locked probe kits were on a benchtop vibration isolation platform hence, the measurements did not affected by the ambient noise and resulted with a high signal to noise ratio.

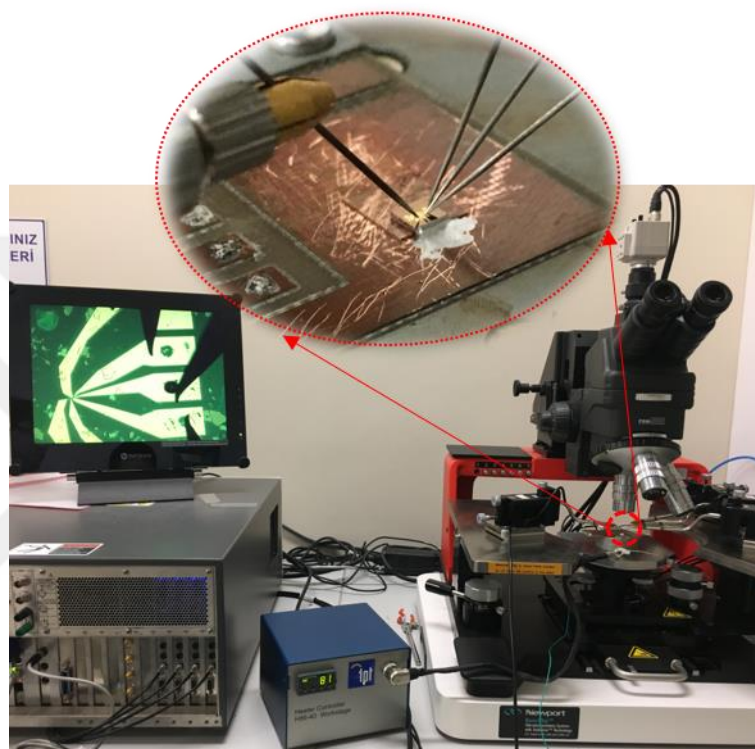


Figure 2.28: Keithley 4200 - Semiconductor analyzer system with a probe station used for the electrical measurement of the graphene/graphene oxide hybrid structures.

Three objectives with different magnifications of 5X, 10X and 20X provides the user to catch the features on the surface rapidly.

2.12. CLEAN ROOM FACILITIES

All the production and wet chemistry procedures were carried out in Class 10000 clean room. Optical and e-beam lithography were used in a Class 100 clean room illuminated with yellow light not to damage the photoresist film. The magnetron sputtering and the tube furnace were also deployed in the clean room. Until characterization step such as Raman, AFM and electrical analysis, graphene samples were not exposed to the ambient conditions. Under favor of the wet bench in the clean room, cleaning procedure of the wafers and all chemical steps especially oxidation treatment were done to obtain the hybrid device.

2.13. FT-IR AND UV-VIS SPECTROSCOPY

During our study we have carried out FT-IR spectroscopy for our graphene oxide samples to detect the functional groups bonded to the graphene flakes. A modified Hummers' method which is a wet chemistry process breaking the bonds between the carbon atoms by acidic treatment was used. Although graphene has a single crystal with no defects in the lattice, graphene oxide consists of carbonyl, hydroxyl and carboxyl groups. In order to see the formation of such groups on the graphene, it is needed to take a FT-IR spectrum from the samples. Since the vibrational energy states of these groups can be obtained by the spectroscopic analysis, we operated Thermo Scientific Nicolet 6700 FT-IR spectroscopy system which provides the vibrational frequencies of each groups.



Figure 2.29: FT-IR spectroscopy system.

Another spectroscopic analysis has been done on graphene oxide samples with the UV-vis spectroscopy system which is 'Evolution 300 UV-VIS Spectrophotometer' shown in Figure 2.30.



Figure 2.30: Ultraviolet – visible spectroscopy system.

While the spectral analysis of the graphene oxide is carried out, a Xenon light source which has the wave length varying between 190 – 1100 nm is used. It has a scanning rate of 1-3800 nm per minute with 0.5, 1.0, 1.5, 2.0, 4.0 nm spectral bandwidths.

3. RESULTS

Briefly, the results of the study were presented in three main topics as the structural, optical and electrical properties of the devices which were prepared by mechanically isolated graphene flakes on Si/SiO₂ substrates. For revealing the structural properties, AFM and LFM were used on different graphene samples and devices. In addition, force-distance measurements were also carried out on suspended graphene flakes to understand the mechanical behaviour of the graphene. Raman and UV-vis spectroscopy techniques were used for the optical properties of the samples. The electrical properties was investigated mainly by I-AFM and semiconductor analyzer system.

3.1. STRUCTURAL ANALYSIS

In order to examine the mechanical properties of the graphene, it is necessary to prepare graphene samples which are only supported by their edges and have no support at their lower and upper parts. It is called as suspended graphene. For the preparation of these samples, SiO₂/Si substrates having regular holes with a diameter of 5 micrometers were made. Optical lithography has been used to prepare these substrates. After the substrates were patterned with the hole arrays, the silica layer was etched by hydrofluoric acid. Various experiments have been carried out to optimize this process, taking into consideration the dimensions of the holes and the reaction conditions. If the conditions were not optimized, it was seen that the holes did not extend to the silica, widened more than the lithographic pattern, and worn away in the areas that should be protected by photoresist (Figure 3.1a). As a result, it was determined that the procedure performed in the ultrasonic bath for 5 minutes was the most appropriate method (Figure 3.1b). Finally, graphene was prepared by scotch tape method as described previously in section 2.1. Figure 3.1c shows a segment of single-layer and multi-layer regions obtained after this process. The single layer graphene sample completely covered one of the holes and formed a graphene zone suspended over the hole.

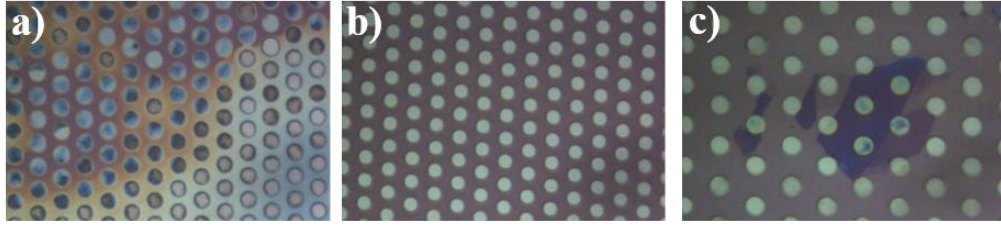


Figure 3.1: a) An unsuccessful attempt to prepare a perforated substrate b) Successful lithography and etching c) Multi layer and single layer suspended graphene on the perforated surface.

3.1.1. Nanomechanical behavior of graphene

The suspended graphene specimen was subjected to forces at the nanometer level with a Si tipped AFM needle to determine deformations or displacements. The procedures followed in nanomechanical measurements can be summarized as follows:

- Recording the microscopic images of the graphene flake on the perforated substrate
- Determination of the number of layers by Raman spectroscopy
- Recording of AFM topographical images
- Making force-distance measurements on it.

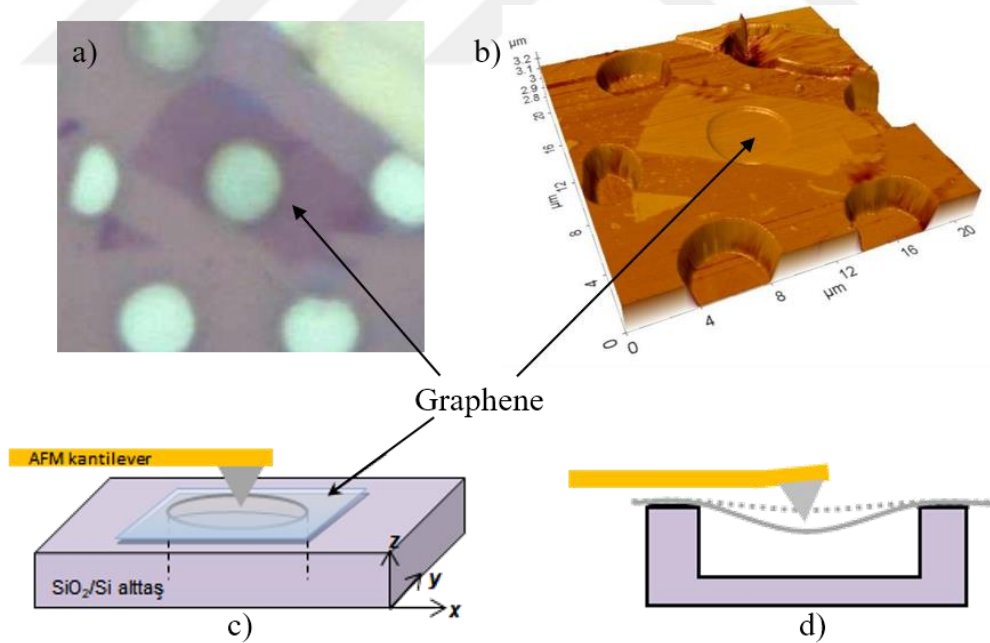


Figure 3.2: a) Microscopic view of the graphene sample obtained on the SiO₂ / Si perforated substrate. b) 3D topographic image recorded, for example, by the C-AFM method. c) and d) Schematic representation of the deformation of the force exerted by the AFM needle on it.

Figure 3.2a shows an example of a graphene obtained on photolithographic SiO₂/Si perforated substrate. A 3D topography image of this graphene flake obtained in the contact mode (C-AFM)

is shown in Figure 3.2b. The 3D-AFM image clearly shows the example of the graphene closing one of the 5 μm diameter holes. It is understood that this example has 4 layers compared to the result of the Raman spectrum previously taken. Figure 3.2c and d show the deformation in the z-direction of the force applied to the specimen by the AFM cantilever and needle and brought to the graphene field on the hole.

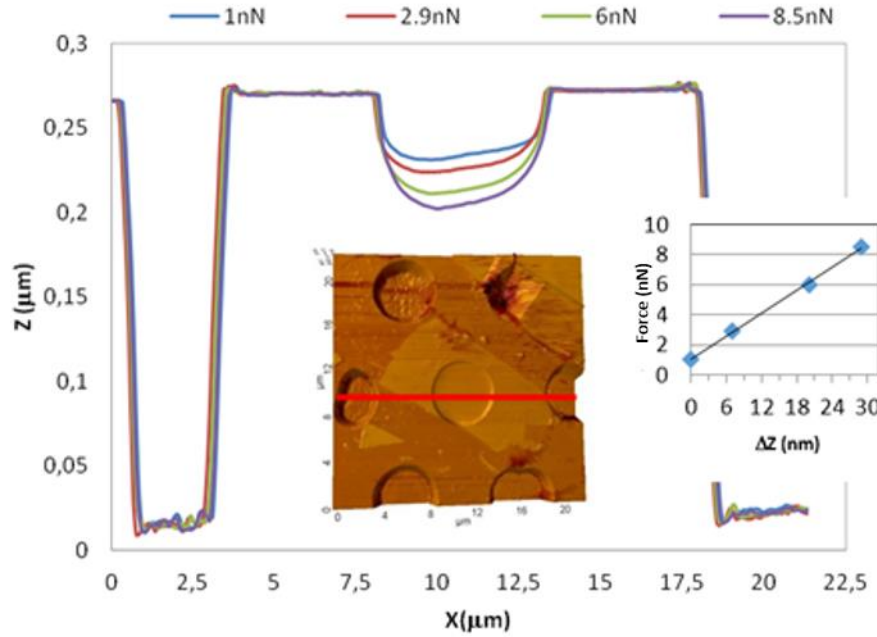


Figure 3.3: 3D-AFM image obtained by applying different pressing forces on the graphene on the hole with AFM needles and changes in the z direction along the red line. Inside the small graph shows the relative deformation of the graphene in the z direction with respect to the other forces with reference to the image obtained by applying a force of 1nN.

In order to reveal the nanomechanical deformation properties of the graphene, different pressure forces were applied to the C-AFM needle for scanning. In Figure 3.3, cross-sectional profiles along a line (indicated by the red line) of the 3D images obtained by applying the force of 1 nN, 2.9 nN, 6 nN and 8.5 nN with the AFM needle are given. From these cross-sectional views, it is obvious that as the force of the press increases, the deformation from the suspended graphene to the square of the hole is increased. The differences between the cross-sectional views show deformation from the graphene due to the applied pressure. This deformation resembles a flat circular membrane model under perpendicular force. With this model, for example, nanomechanical properties can be revealed. The relative deformation created by the other forces with reference to the z-direction deformation generated by the 1 nN compression force at the mid-point of the graphene on the hole is given in the inset of the Figure 3.3. According to this

graph, the deformation seems to increase linearly with the applied pressure, and the result is in line with Hooke's law. The force-deformation graph obtained according to Hooke's law gives the force constant of the gradient graph. Here the measurement can be thought as two springs in series which consists of the spring constants of the tip and the graphene. Due to the slope of the curve in the inset of Figure 3.3, the effective spring constant is found as ~ 0.26 N/m. Equation 3.1 gives the effective and local spring constant of graphene. The average spring constant of the tip is taken as 2.15 N/m experimentally. As a result, the spring constant of the graphene is obtained nearly 0.3 N/m. These observations are consistent with the results of the studies in the literature. On the other hand, in this experiment, it was observed that the graphene was not subjected to any displacement in the horizontal plane under these forces when AFM images were obtained in contact mode strongly between 1nN and 8.5nN. Here we show that the graphene is not dragged or displaced by the AFM needle because the interaction of graphene regions outside the hole with the silica surface is strong enough to keep the graphene unaffected during the force-distance measurements.

$$F = -kx \quad (\text{Hooke's Law}) \quad (3.1)$$

$$\frac{1}{k_{eff}} = \frac{1}{k_{tip}} + \frac{1}{k_{graphene}} \quad (\text{Springs in series}) \quad (3.2)$$

$$k_{eff} = \frac{k_{tip} \cdot k_{graphene}}{k_{tip} + k_{graphene}} \quad (3.3)$$

According to the local spring constant of the suspended graphene, the surface tension was acquired as 0.264 N/m neglecting the bending stiffness by the formula given in Equation 3.4 [84].

$$S \approx (k/2\pi) \ln(R/r) \quad (3.4)$$

where R is the radius of the suspended graphene on the hole (5 μm) and r is the radius of the tip (~ 10 nm). Since the tension on graphene is found, the Young modulus can be calculated by the formula below [85].

$$S \cong \left\{ \frac{FE}{4\pi R} \right\}^{\frac{1}{2}} \quad (3.5)$$

where F is the force applied to the tip, R is the AFM tip radius and E is the Young modulus of the suspended graphene. In addition, the force-distance (F - z) curves for the graphene sample obtained on the perforated substrate are recorded. The curves are obtained by slowly approaching the sample starting from a predetermined height and then by retracing the sample once it reaches a certain force value and then gradually removed from the sample. Figure 3.4 shows the F - z curves obtained from the silica surface, the graphene on the silica/silicon and the graphene hanging on the hole. The measurement points from which the F - z curves are obtained are marked as a, b and c on the 3D AFM image. The F - z curve obtained from the suspended graphene (Fig. 3.4b) appears to have different slopes when compared to the F - z curve of the graphene on the substrate. This difference is due to the deformation of the suspended graphene, that is, the displacement of the graphene in the z direction with the applied force. The blue curves indicates that the tip is in contact with the surfaces (Trace) and the red ones are the curves while the tip is leaving the surface. The lowest peak on the red curve refers to the point which the tip quits the surface completely. It was shown that the elastic modulus is related to the slope of the blue curve and can be used to reveal the sample hardness [86, 87].

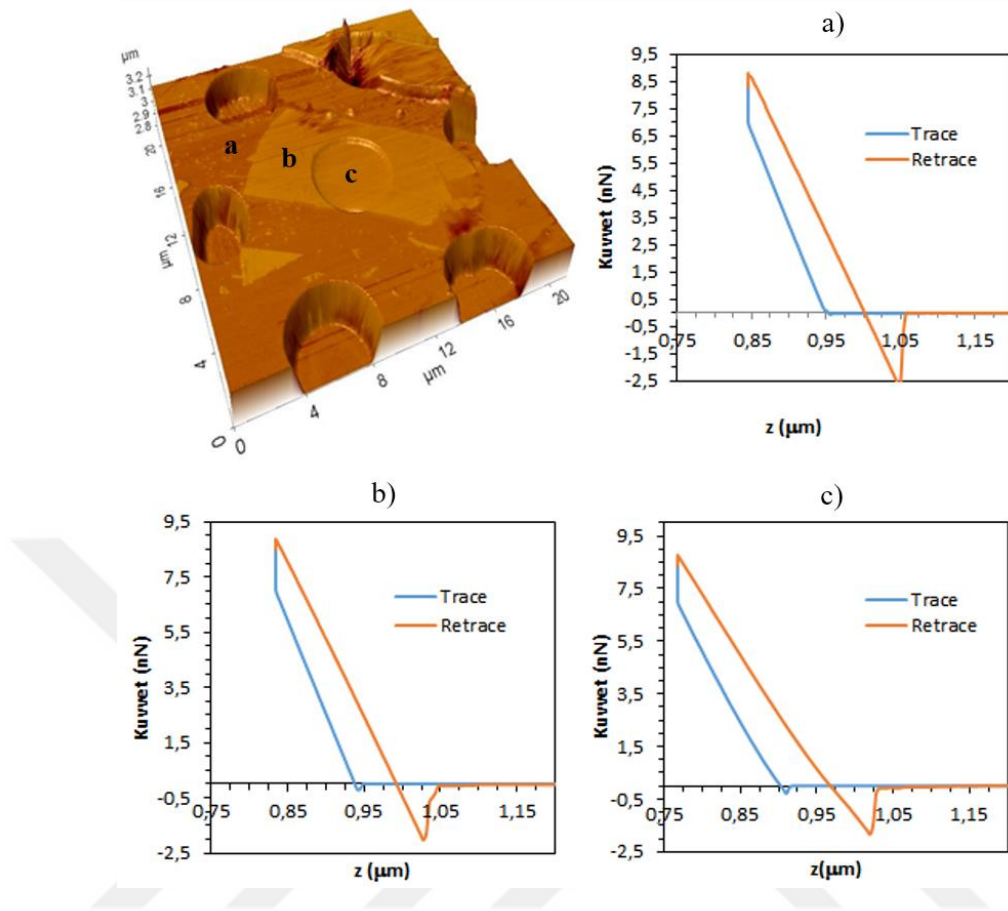


Figure 3.4: Force - distance (F-z) graphs. The points where the F-z measurements were made are indicated by a, b and c on the AFM image. **a)** Measurement on the silica surface **b)** on the graphene on silica **c)** on the suspended graphene.

3.1.2. AFM and LFM analysis on the hybrid structures

We have conducted both optical and e-beam lithography techniques for tailoring and obtaining the graphene/graphene oxide hybrid structure as mentioned in detail above. But for the oxidation process, it was needed to control which resist is durable in the oxidative solution with the optimal exposure time. So, both photoresist and PMMA coated and prepared graphene samples will be shown below for the structural analysis.

Figure 3.5a shows the optical image of the prepared graphene before the treatments (oxidation and optical lithography). Single layer graphene is at left-bottom part. Optical image of graphene sample after lithographic process is shown in Figure 3.5b. We immersed this sample into chemical solution for 10 minutes after lithography. After oxidation procedure, we removed the PMMA but during this procedure the few layer graphene part removed and single layer part rendered and turned (Figure 3.5c). After removing the PMMA film, we obtained the AFM image

(Figure 3.5d). Upper part of sample is oxidized and bottom part is the non-oxidized part which covered with PMMA. As it is estimated that oxidized part has high friction like silica and non-oxidized part has low friction. In addition, the LFM image shows that the oxidized part has the same contrast with the silica surface. As a result of it, to observe the oxidized part is very hard in LFM image.

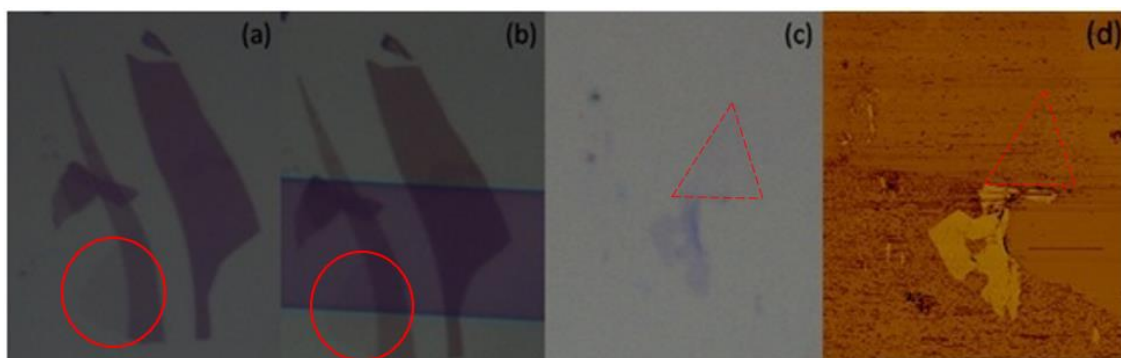


Figure 3.5: **a), b)** and **c)** Optical images of graphene sample before the oxidation and lithography, after optical lithography and 10 min oxidation respectively **d)** lateral force image after oxidation.

In order to examine the structure in detail, we obtained topography image of the oxidized region in high resolution illustrated in Figure 3.6. We noticed that the center of the oxidized part has a different contrast compared to the other sites. Bright and dark color indicates thick and thin part respectively. The height profile extracted through the red line is also seen in the Figure. It is clearly shown that this dark color region of single layer graphene is lower than the rest of the oxidized single layer graphene in height. There are two possible reasons to explain this height difference. This low part may be non-oxidized or it was etched through the oxidation process. LFM image also clearly indicates the difference between the oxidized and non-oxidized part where the oxidized region exhibits the same characteristic due to the frictional property.

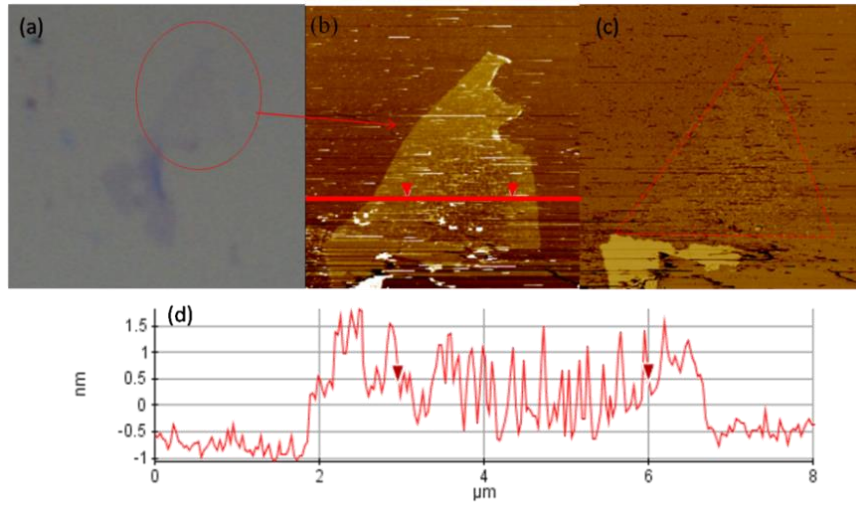


Figure 3.6: **a)** The optical image, **b)** the topography image of single layer graphene, **c)** the LFM image after oxidation, **d)** the height profile of the scanned graphene via red line.

This lower part of the single layer graphene was studied more carefully. Figure 3.7 shows nearly $1 \times 1 \mu\text{m}^2$ region of lower part of sample. Bright and dark color correspond to the amount of height. The brightest point indicates the highest feature and the darkest shows the lowest one. It is obviously seen in the Figure 3.7c that the bright region is approximately 1.3 nm higher than the dark region indicated with the cursors. We can conclude that this lower part was not oxidized. Oxidation starts from edge and it continues through the center of the graphene but it is not uniform at the center.

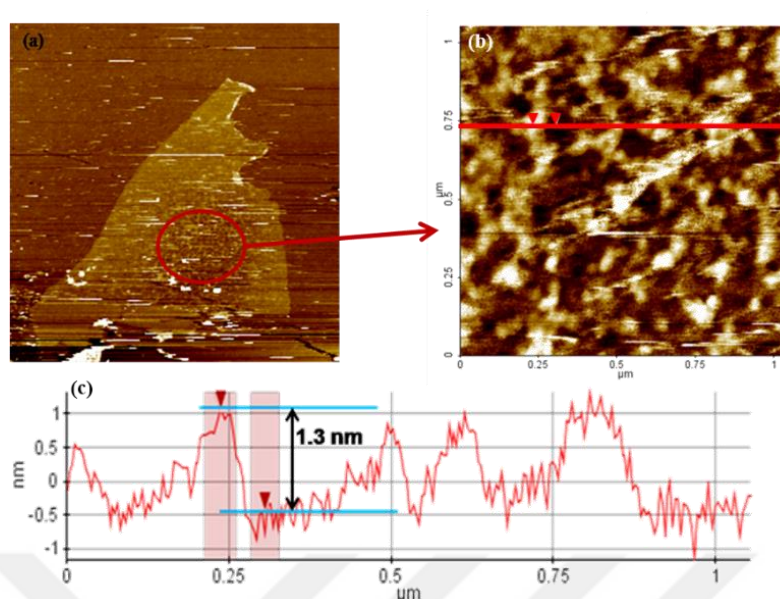


Figure 3.7: **a)** Topography image of the single layer graphene **b)** Height profile of the oxidized graphene surface extracted from the red line with the cursors.

During our study we have noticed that the size of the gap on the graphene flake was also effective in the oxidation because of the capillary effects. So the minimum size of the space which is exposed to the solution should be greater than 5 micron due to our experiences. We also checked the edge effect of the graphene flake where the oxidation takes place easily and proceed into the whole surface. Figure 3.8a and b demonstrates the optical images of the graphene flake before and after optical lithography. The unmasked region surrounds the whole graphene part and the oxidation was completed fairly as shown in the Figure 3.8c. Here the important property of the oxidized graphene is that the formation of the graphene oxide nano-islands which is our published work [88].

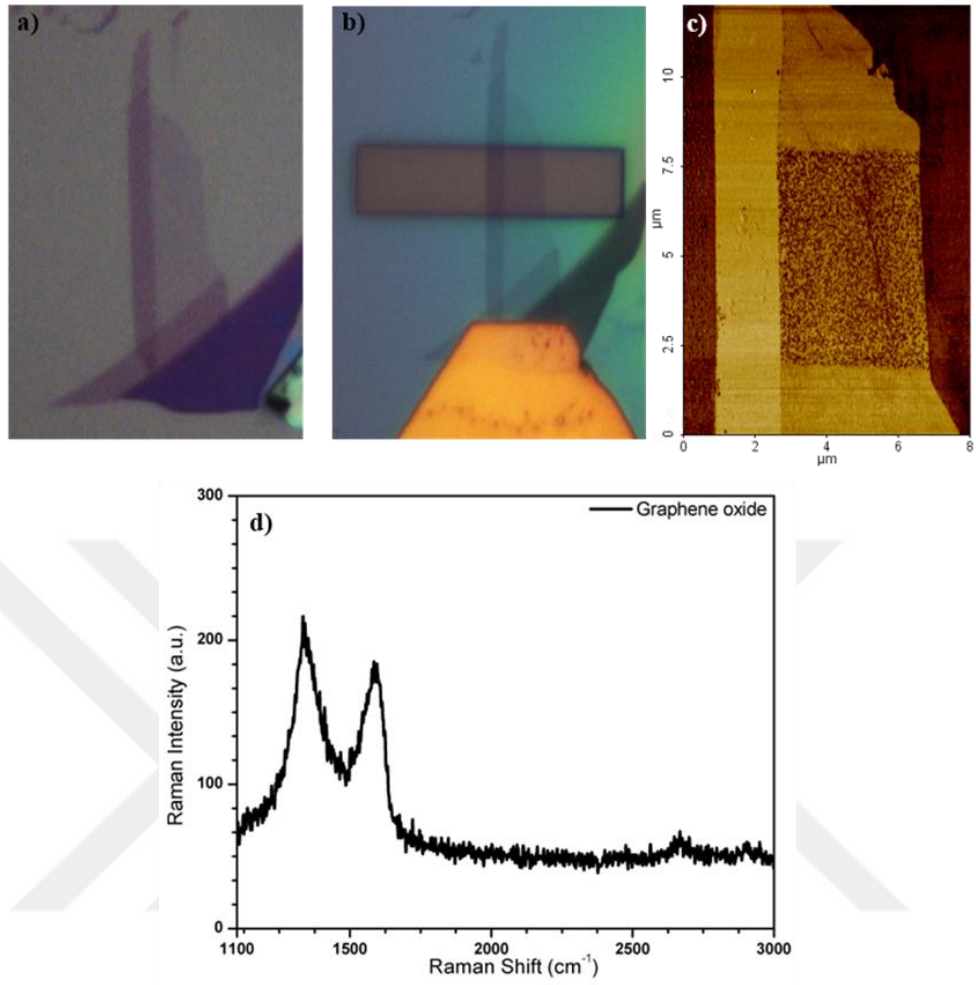


Figure 3.8: Optical image **a)** before oxidation process **b)** after lithography **c)** Lateral force image **d)** Raman spectrum after 15 minutes of oxidation.

As it is seen from the Raman analysis, the D peak is very intensive and sharp due to the total formation of graphene oxide on graphene homogenously. In addition, since graphene was oxidized, the intensity of the 2D band at approximately 2700 cm^{-1} decreased dramatically.

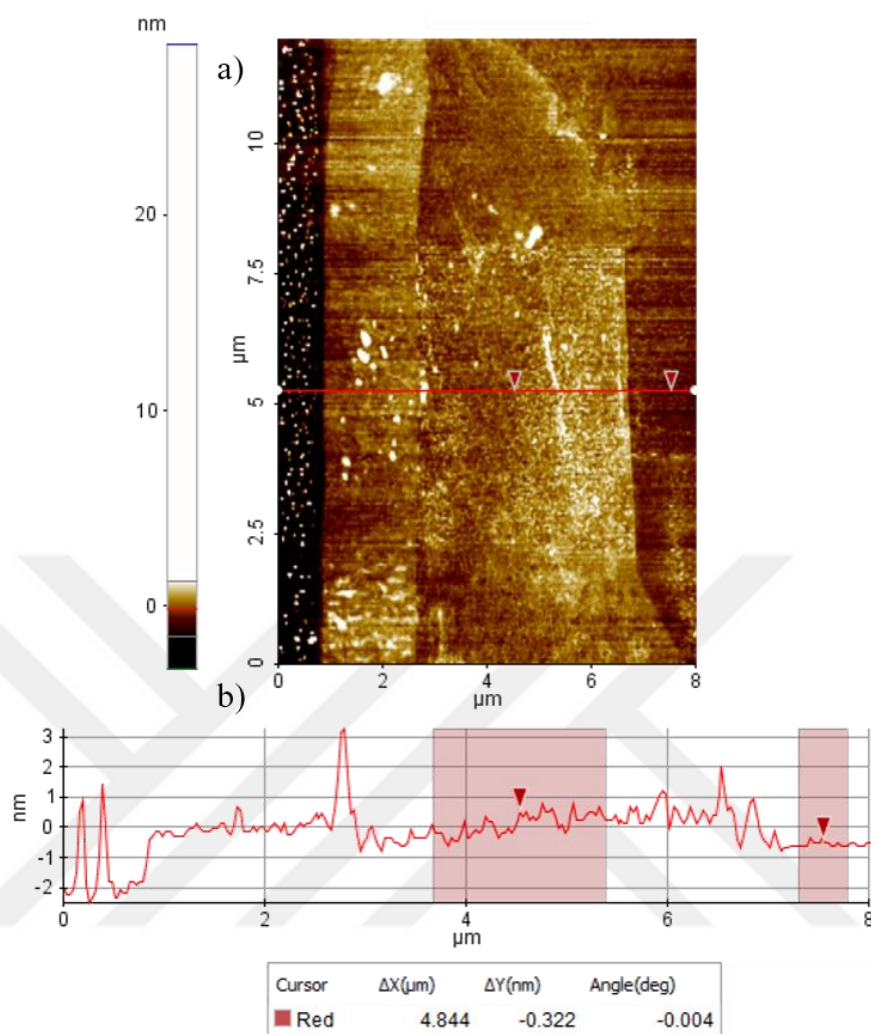


Figure 3.9: a) The topography image of the hybrid structure b) the height profile of the surface.

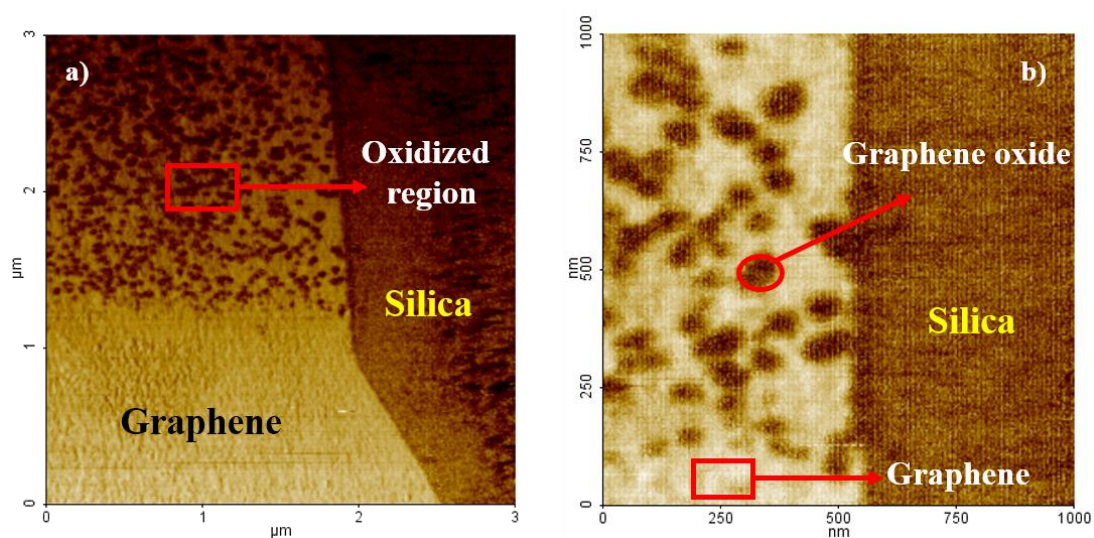


Figure 3.10: a) LFM image of the sample in $3 \times 3 \mu\text{m}$ scan size b) LFM image of the graphene oxide nano-islands with high resolution.

By looking at the topography image illustrated in the Figure 3.9, the difference between the oxidized and unoxidized parts is enough to discern. The height profile taken over the surface is plotted in Figure 3.9b. Oxidized region has a higher surface than the unoxidized part. Exposed region, not coated with PMMA, includes single layer and triple layer graphene regions. The left part of the sample is triple layer. In the LFM image, light color indicates the graphene parts and dark indicates the graphene oxide parts (see Figure 3.10a). The detailed scanning with a high resolution and low scanning rate, another LFM image was taken shown in the Figure 3.10b. Here, the graphene oxide nano domains which has a size of ~ 50 nm were observed. Single layer part was oxidized but the triple was not which is coherent with our previous studies.

Another single layer graphene sample was covered with PMMA and a circular pattern was formed by e-beam lithography shown in the Figure 3.11a and b. This sample was also immersed into the oxidative solution for 15 minutes and it was cleaned with distilled water. To remove the PMMA, the sample was steeped in an acetone bath and cleaned with chloroform in order to elude PMMA residuals from the graphene surface (see Figure 3.11c). Raman spectra shows very strong D peak on the region which was exposed to the oxidative solution in Figure 3.12. On the other hand, the region which was passivated with the PMMA resist does not exhibit any change about defect. As it is understood from the Figure 3.12 that the D peak has arisen after the oxidation process. And it was observed only at the non-covered region. This claims that the rest of surface does not include any defect peak. It shows that PMMA protect the single layer graphene from the oxidative solution.

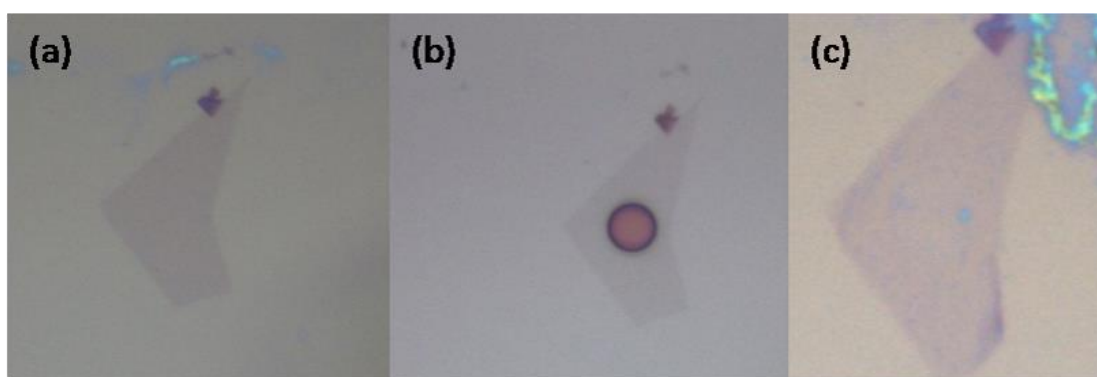


Figure 3.11: a) Optical image of the single layer graphene b) after lithography c) after 15 min oxidation.

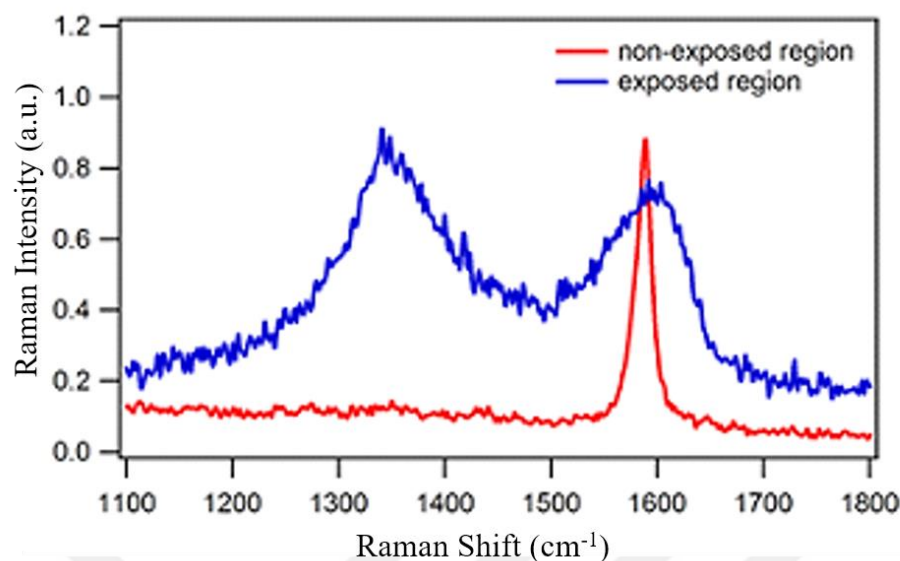


Figure 3.12: Micro-Raman spectroscopy measurements taken from the exposed and non-exposed graphene region after the oxidation process.

With the results of the Raman spectra of the corresponding regions, it was proven that the oxidation process has been successful for obtaining the graphene oxide. In addition to the Raman spectroscopy, AFM and LFM images testify the procedure and give satisfactory information about it such as frictional property of the material (Figure 3.12). For the purpose of height measurement, the topography image was taken with a force applied to the tip of 5 nN in contact mode. The image resolution was set to 256×256 pxl and the scanning rate was kept 1 Hz. It is clearly seen that the PMMA residual was not removed after the oxidation and cleaning procedure with chloroform. As it is understood from the image the dark brown regions are the silica surface and the brightest features screen the residue of the resist. Another observation is that the contrast between the silica and the unmasked region which is oxidized graphene is similar.

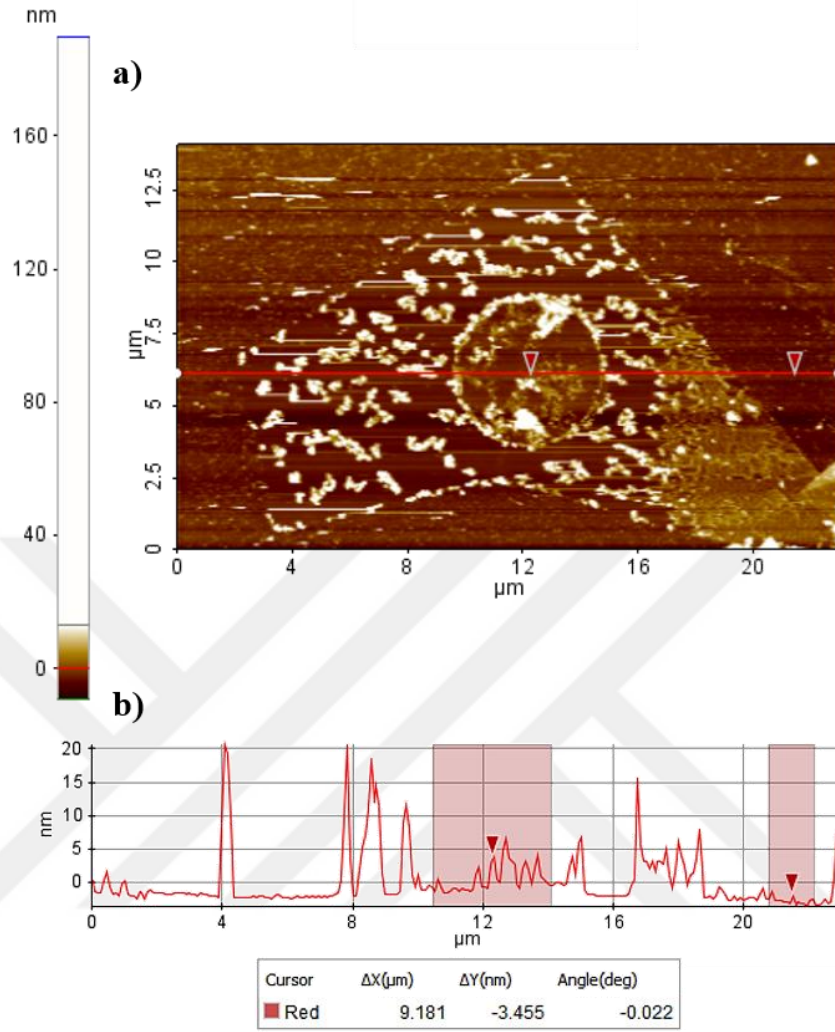


Figure 3.13: **a)** The topography image of the sample after 15 minutes oxidation process **b)** the height profile with respect to the line indicated with cursors.

The height profile states that the oxidized graphene part is approximately 3.5 nm higher than the silica surface. In the middle of the hole the light brown parts were the graphene oxide regions. Since there is no considerable resist residue on the lower right part of the flake, it is very easy to recognize the graphene surface by the help of contrast.

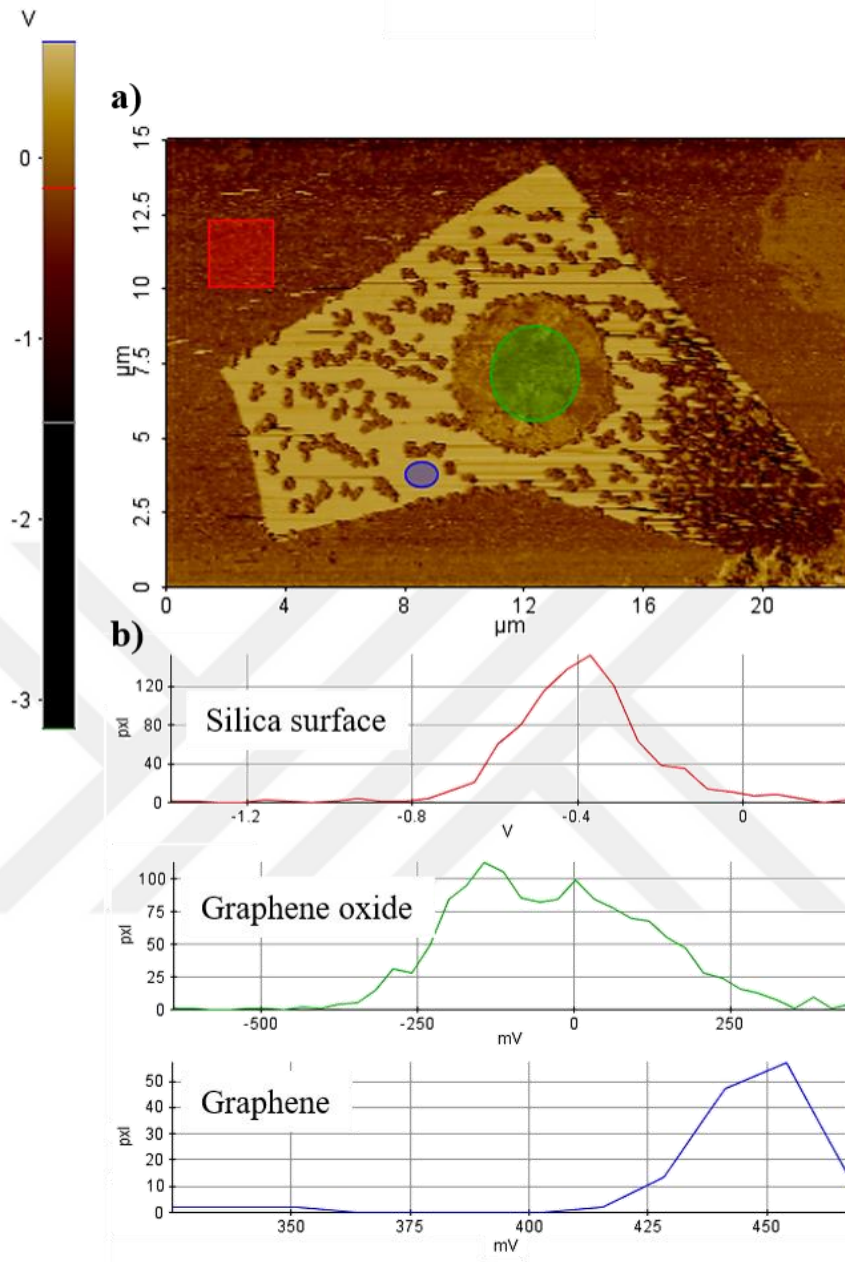


Figure 3.14: a) LFM image of the sample after the oxidation process **b)** the region histograms for graphene, graphene oxide and the silica surfaces.

Generally, LFM images give the best contrast because of the frictional force exerted on the tip by the scanned surface. Using this property, we can separate the boundaries between the different surfaces facilely. In figure 3.13a, three different region was chosen for the surface analysis. The average roughness of the corresponding surfaces were calculated by the each histograms and listed below. For the surface roughness, there are also another calculation types as indicated in Table 3.1. But, to make a comparison on the structural analysis of the surfaces, we used average roughness values depicted with R_a .

Table 2.1: The list of the parameters related to the surface roughness of the corresponding region.

Region	Min(V)	Max(V)	Mid(V)	Mean(V)	Rpv(V)	Rq(V)	Ra(V)	Rz(V)	Rsk	Rku
Red	-1.384	0.250	-0.567	-0.422	1.633	0.168	0.123	1.287	0.167	6.142
Green	-0.641	0.441	-0.100	-0.049	1.081	0.154	0.126	0.923	-0.247	2.892
Blue	0.325	0.467	0.396	0.438	0.142	0.020	0.011	0.064	3.518	18.663
R-G	-0.743	-0.191	-0.467	-0.373	0.552	0.014	-0.003	0.365	0.413	3.249
R-B	-1.709	-0.217	-0.963	-0.860	1.491	0.148	0.112	1.223	-3.351	-12.522
G-B	-0.966	-0.026	-0.496	-0.487	0.939	0.134	0.115	0.859	-3.764	-15.771

The selected region in red square is the silica surface which has an average surface roughness as 0,123 V in terms of the distortion on the tip by the surface. The green circle remarks the oxidized region which was unmasked lithographically and has a similar roughness to the silica with the value of 0,126 V. Unlike silica and graphene oxide surfaces, the unoxidized graphene regions brings about lower frictional forces on the scanned tip. The small blue circle indicates the single layer graphene surface with an average roughness of 0,011 V. When these three different surfaces are compared with each other, the graphene surface roughness is nearly 11 times smaller than the silica and graphene oxide. When the R_q values which is the root-mean-squared roughness are examined, graphene oxide has approximately 8 times higher surface roughness than the graphene one. By observing the different roughness calculation types, one can get different numbers but; the unchanged reality is that the graphene gets rough as it is oxidized with our wet chemistry processes and more lubricious compared to the graphene oxide. This result was expected and proved with the AFM and LFM measurements.

3.1.3. AFM analysis for the hybrid GFETs

The same structural analysis has been also done on the graphene samples which was tailored with e-beam lithography techniques to manufacture a graphene/graphene oxide hybrid FET device. For this purpose, prepared hybrid structure was investigated by AFM and LFM with a high image resolution and low scanning rate in order to reveal the structural properties in depth. Figure 3.15 demonstrates the stages of the manufacturing the hybrid device with the optical microscope images taken during the process.

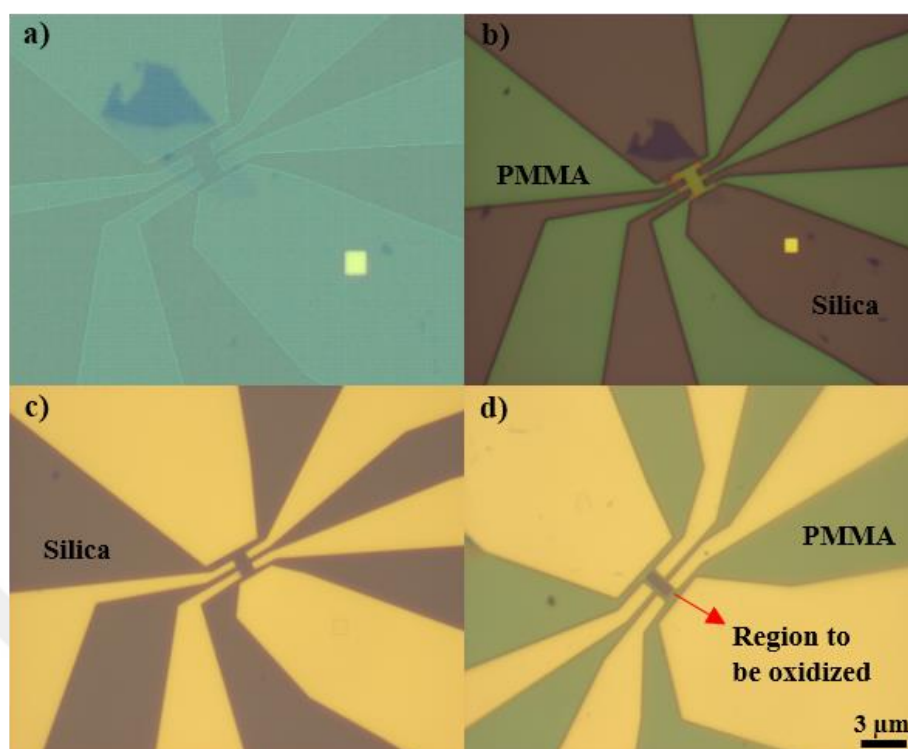


Figure 3.15: Optical image of the desired pattern on graphene **a)** before the e-beam lithography **b)** after the development of the contact lines **c)** after the metal deposition **d)** after the second e-beam lithography for opening a space on the graphene surface.

The structural properties of S5 were deduced by AFM analysis after the confirmation of the oxidation on graphene by Raman spectroscopy. The topography and lateral force images were taken in contact mode of AFM simultaneously. In order to reveal the oxidized regions on graphene surface with a high resolution image, the scan rate was set to 0.4 Hz. The force applied by the tip to the surface was kept of 4 nN. Images were saved in a 1024×1024 pixels data width and height. In Figure 18, a 3D topographic image of S5 is presented. The scale bar indicates the lowest height as brown, the highest one as white. During the oxidation process, the functional groups bonded to the surface so the height of the oxidized regions are plotted in white color. Conversely, the unoxidized parts of graphene is depicted with brown color. The height measurements of the structures on graphene surface was evaluated by a line profile analysis. The difference in height between the oxidized and the unoxidized region is about 2.3 nm by taking the average height in the selected range account.

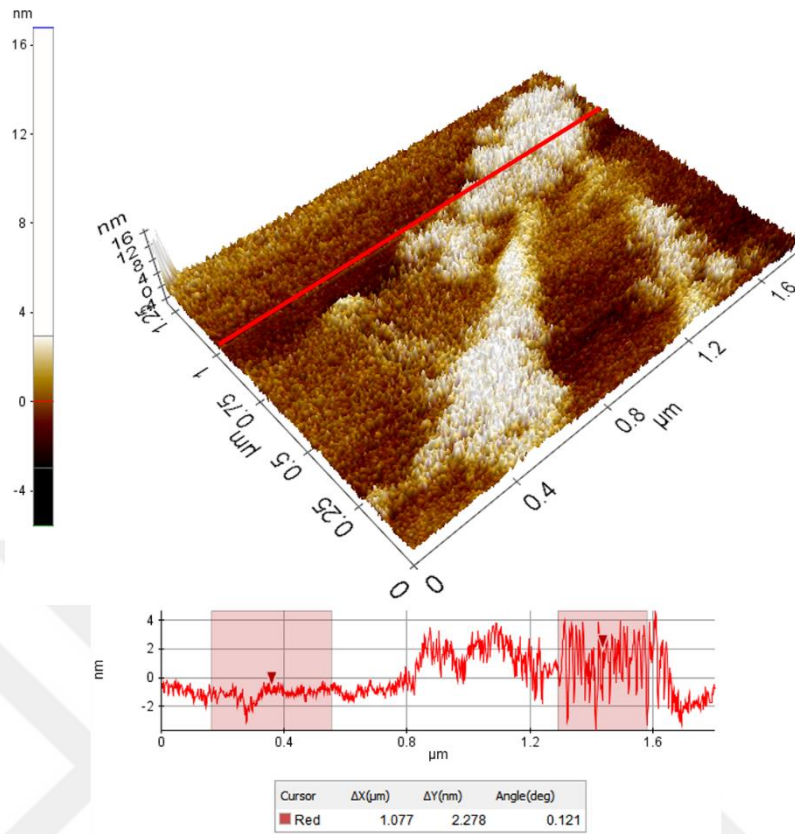


Figure 3.16: The topography image of the oxidized sample in a high resolution 3D image with a line profile analysis.

This analysis was calculated on the basis of the red line drawn on the image. In addition to these, the surface roughness of both graphene and graphene oxide was calculated. In the view of Figure 3.17, three different shaded areas in color of red, green and blue are selected for the estimation of the roughness. The red and green circles are on the oxidized (graphene oxide) regions and the blue one is on unoxidized (graphene) region. The amount of each surface roughness is calculated according to the acquired histogram. The results of each surface roughness are illustrated under the topography image which includes three types of calculation methods. They are R_{pv} (peak to valley), R_q (root mean square) and R_a (average) in turn. In our study, R_a was chosen to highlight the amount of roughness in order for comparison. In the red and green region, the average surface roughness was calculated as 1.431 and 1.427 nm successively. However, the blue region exhibited an average surface roughness of 0.568 nm. From this point of view, it can be said that the region of graphene oxide is approximately 2.5 times rougher than the region of graphene.

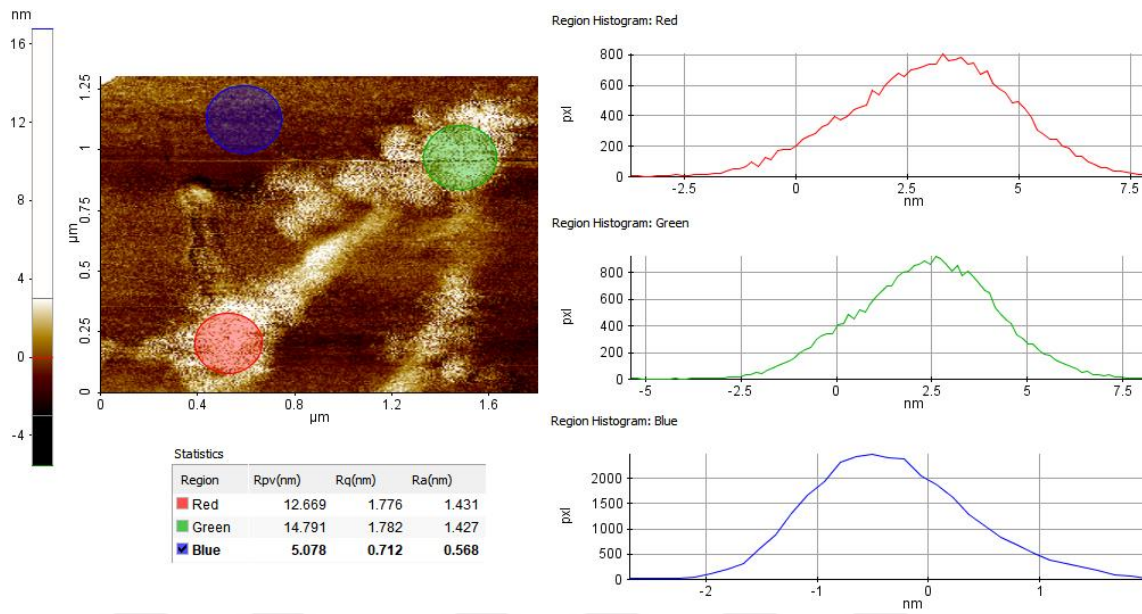


Figure 3.17: The analysis of surface roughness for graphene and graphene oxide via topography image.

On the other hand, a similar analysis was done on lateral force images. Lateral force microscopy generally gives better contrast and sharpness rather than topography. Furthermore, the plotted images are in accordance with the frictional force between the tip and the surface. Therefore; a quantitative analysis that is related to the side to side twisting of the cantilever by torque can be done additionally. Figure 20 shows the lateral force images of S5 in different scan sizes with a resolution of 2048 pixels. The scanned area in lateral force images is identical to that of the topography images. With the help of the lateral force microscopy the oxidized parts are completely observable. The dark brown spots are the oxidized graphene parts where the light brown region is the whole graphene surface. Figure 20.a presents the total part of the graphene surface between the four contacts. Figure 20.b is a closer lateral force image of the graphene oxide structures. Both figures represent a hybrid structure of graphene/graphene oxide together. In addition, similar to the analysis of the topography image above, three different parts on the device were specified as graphene and graphene oxide. The red and green areas are the graphene oxide parts where the blue square is the unoxidized graphene surface. The frictional force on

the tip arising from the surface was obtained in terms of the volts measured on the photodetector.

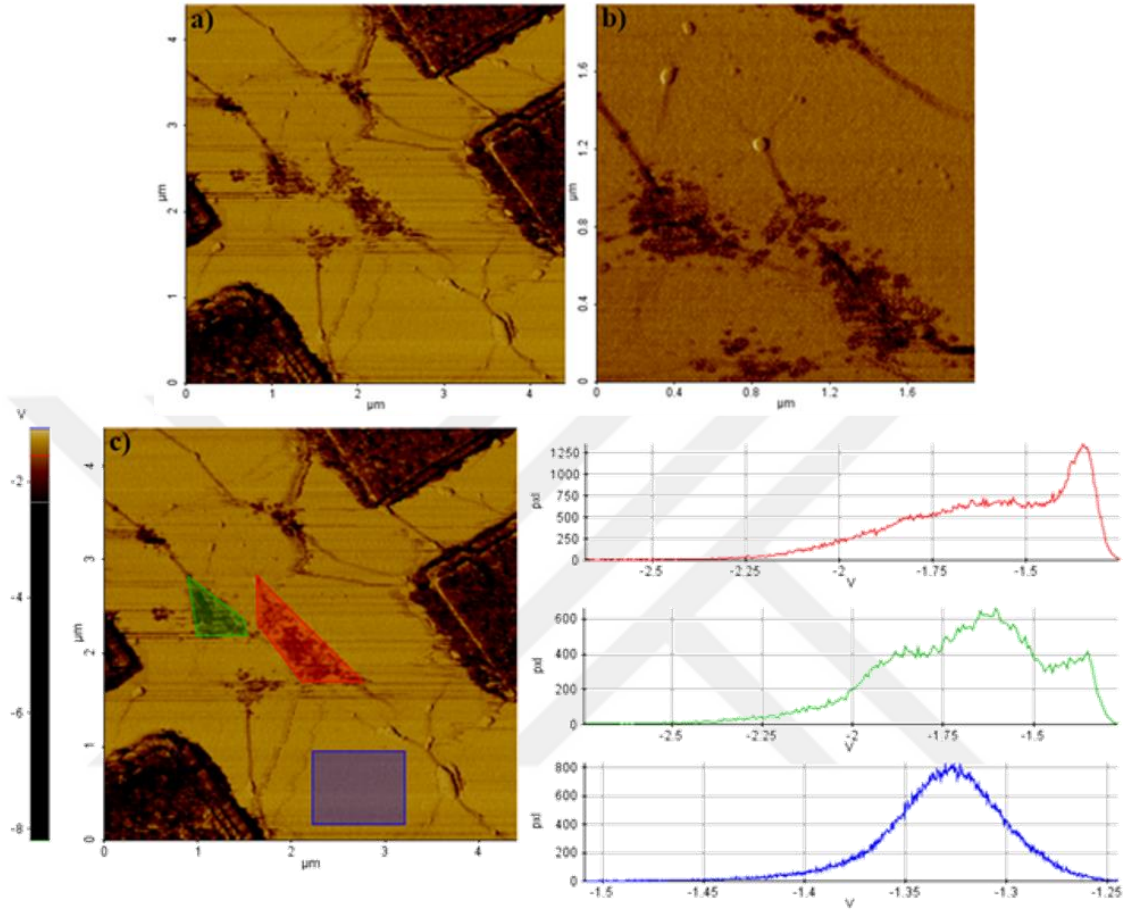


Figure 3.18: Lateral force image of **a)** graphene/graphene oxide hybrid structure at $4.4 \times 4.4 \mu\text{m}$ scan size **b)** at $1.95 \times 1.95 \mu\text{m}$ scan size **c)** the structural investigation of the hybrid structure.

Due to the illustrated histograms of the shaded geometries, the average frictional force was determined for each one. As a result of it, it is obviously said that the friction of the graphene oxide is much more than the graphene. In other words, the friction is 8 times higher in graphene oxide than the graphene surface. This result also states the both formation of the graphene oxide and the structural property of the hybrid device as a consequence of the oxidation.

3.2. OPTICAL PROPERTIES OF HYBRID DEVICES

For the optical characterization of the graphene samples and the hybrid devices, we used Raman, UV-VIS and FT-IR spectroscopy. The measurements in Raman spectroscopy were carried out for all the graphene samples which prepared by scotch tape method. In order to facilitate the UV-VIS and FT-IR spectroscopy, we had to prepare graphene samples by wet chemical synthesis method for the sampling due to the ability of the characterization systems. For this purpose, we have obtained graphene oxide colloidal suspensions and used for the UV-VIS and FT-IR analyses.

During this thesis, Raman spectroscopy have a place in first determination and characterization of the graphene and hybrid devices. In addition, Raman mapping was used to investigate the behaviour of the graphene surface before and after the oxidation process.

3.2.1. Raman spectroscopy analyses of graphene

When graphene samples are prepared, a Raman spectrum are first taken to check whether it is single layer or not. Due to the graphene has a Raman fingerprint, it is very easy to obtain. In Figure 3.19, a Raman spectra were given which is taken from the single and double layer graphene. As it is easily seen from the Figure 3.19a, there is an apparent difference between the single and double layer graphene. The G peak which arises from about 1550 cm^{-1} is sharp and narrow with an intensity lower than the 2D peak which takes place at approximately 2700 cm^{-1} . As the number of graphene layers increase, the G peak intensity is increasing. However on graphite, the G peak intensity is weaker due to the lack of interference effect. On the other side, 2D peak shape changes as the number of layer increases and these changes are attributed to the changes in the band structure. Raman spectra taken from the graphene are used as an effective tool in determining the number of layers. We have been using this technique since the beginning of our work to determine the thickness of few-layer graphene specimens. Although the Raman peak shapes for samples up to three layers can be clearly and easily used for determining the thickness of the layer, the spectra given in the literature for the thicknesses on it do not cover all thicknesses [89]. Since we sometimes need to specify the number of layers in thicker samples during our work, it has become necessary to create a library for ourselves. By comparing the Raman spectra taken from various samples and the contrasts in the photographs of these samples, it has been determined how the sample spectra of the samples changed from streak to stroma. In this way, spectra that can be used to reliably determine thickness up to eight layers

have been determined. In contrast to the literature, changes in the Raman spectra were observed in thicker than ten layers, but since the thickness of these samples can not be reliably determined from the contrasts in the photographs, the thicknesses corresponding to these spectra have not been determined precisely for the time being. The thicknesses of up to eight layers can be determined using the shape of the 2D peak in the Raman spectra given in Figure 3.19. During our study, we noticed that the 2D peak shapes of the four layer and six layer samples are quite similar, but the peak width is slightly larger in the six layer samples and can be distinguished from the others. There is another important band at $\sim 1350\text{ cm}^{-1}$ that describes the crystal quality of the graphene is called as D peak. If graphene has not any defect, dislocations or mismatch in its crystal structure, D peak is not observed in Raman spectrum. As it is seen below, all graphene samples we have prepared are high crystalline quality.

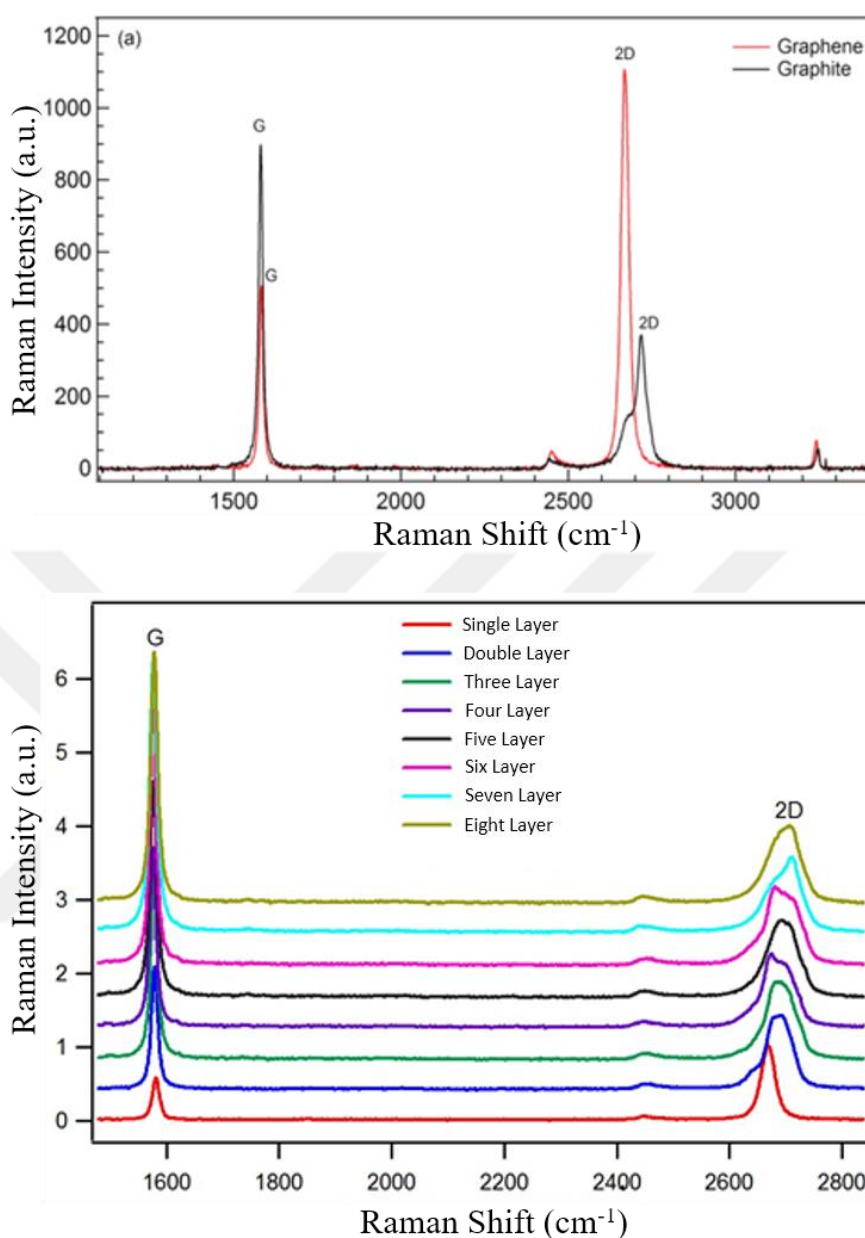


Figure 3.19: a) Raman spectra of graphene and graphite b) Raman spectra of graphene in layers.

During our research we have observed that tape residues on the sample substrate which sometimes lead to contamination problems. Work has been done to clean these tape stains to avoid these problems. In these studies, firstly samples were tried to be cleaned at room temperature and then at high temperature (50 °C) only in acetone or by sonication in an ultrasound bath. However, in the case of low temperature and holding conditions, it was concluded that the band stains were not cleaned as much as the ultrasonic process and that the graphene and graphite specimens were observed to be damaged or damaged from the surface and thus it was an inadequate method for cleaning the band stains. As an alternative cleaning

method, samples were annealed in a continuous flow of argon and hydrogen atmosphere and at a temperature of 250°C. Subsequent to this treatment it was observed that the residuals were removed from the surface very successfully. Although the band stains are cleaned, the process also causes changes in the graphene specimens. The Raman measurements plotted in Figure 3.20, show that the post-annealing makes the signal intensity of the 2D peak decreases with respect to the G peak, and also shows a significant shift in the positions of both peaks. Observation of the lack of D peak indicates that the crystal structure is still steady. The shift in Raman peaks are usually linked to, for example, impurity contribution. Here, too, we think that graphene were subjected to a strong contribution during or after the cleaning process, for example in the atmosphere. Furthermore, it is strongly possible that the morphology of the graphene changes due to the expansion and shrinkage of the substrate during the annealing.

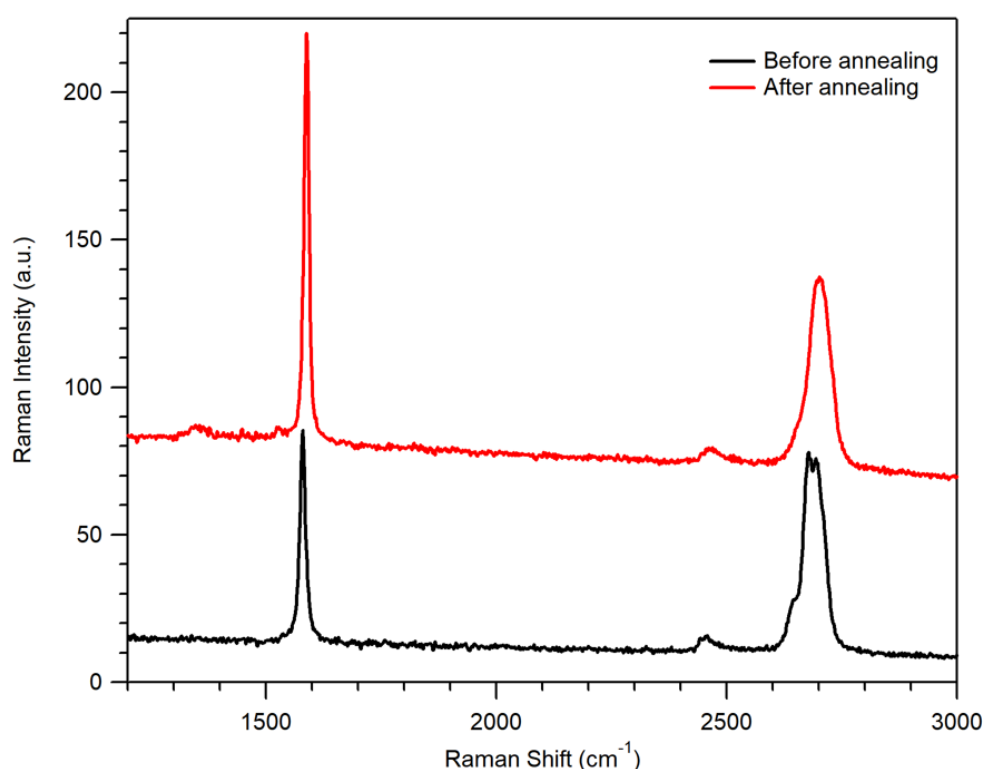


Figure 3.20: The effect of annealing on Raman spectrum of the single layer graphene.

3.2.2. Raman spectroscopy analyses of graphene oxide

In order to optimize the process of graphene oxidation, Raman spectroscopy has played a key role. To prove the oxidation of graphene, the D peak must be observed in the spectrum. For this purpose, we have prepared graphene oxide samples and took Raman spectrum right after. In

Figure 3.21, an example of Raman spectrum of graphene oxide is drawn. After 20 minutes oxidation the Raman spectrum shows the difference between

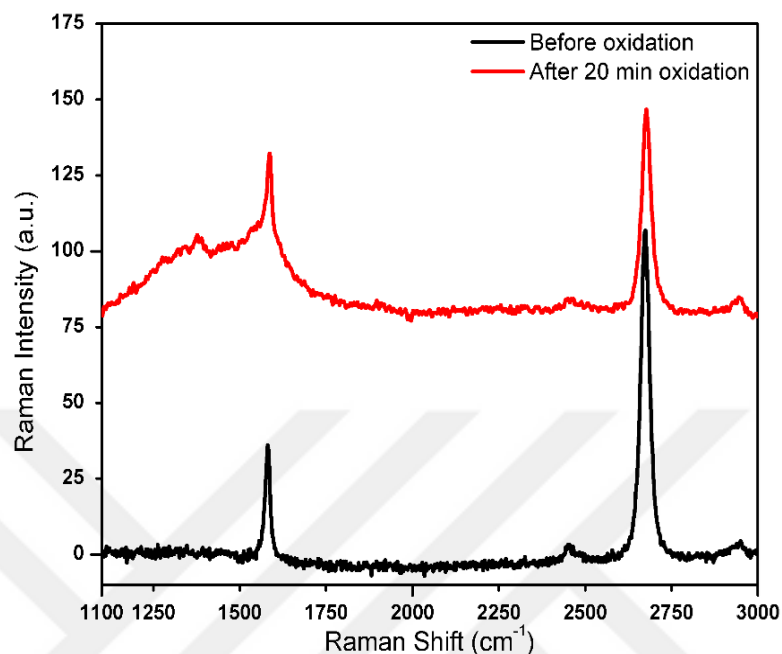


Figure 3.21: The Raman spectra of graphene and graphene oxide.

the graphene and graphene oxide with the D peak shoulder on G band at $\sim 1350 \text{ cm}^{-1}$ Raman shift. This is the indication of the graphene's oxidation. Also, it was observed that the total oxidation occurs when the time is chosen longer than 15 minutes and the space on graphene surface encloses the whole graphene flake due to the oxidation starts from the edges and proceed through the inner parts of graphene. For the hybrid structures, the oxidation takes longer time because of the reason that the spaces patterned on graphene surface was not enough to be oxidized due to the capillary effect. According to our estimation of the experiments, the frame size should be minimum $5 \mu\text{m}$ and circulate the graphene edges. It was also demonstrated for a device which has a frame size smaller than $5 \mu\text{m}$ and does not surround the part of edges. The oxidation mechanism was exhibited in a different case. Figure 3.21 presents both optical image of the frame on graphene device which is the part to be oxidized and the Raman spectra taken from that part to check the reaction occurred or not.

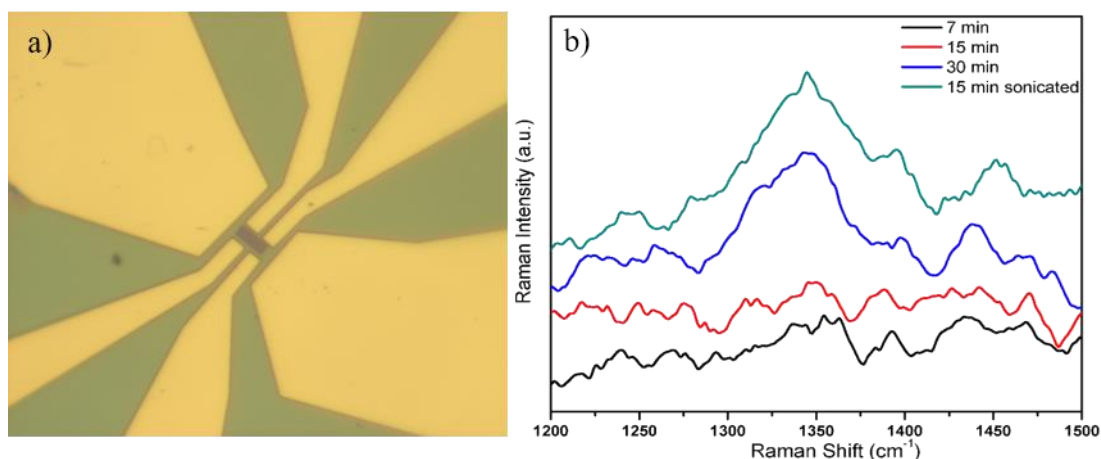


Figure 3.22: a) Optical image of the device with the space which was opened lithographically before the oxidation b) Raman spectra taken from the space after the oxidation.

As the Raman spectra shows that 7 minutes oxidation time was not enough for this sample. An additional 8 minutes chemical treatment was also ineffective. At the end of 30 minutes, the D peak has arisen. On the other hand, in the view of the smaller frame size and capillary effect the sonication treatment has been tried and the result was successful.

3.2.3. FT-IR spectroscopy of graphene oxide

We have also synthesized colloidal suspension of graphene oxide by a modified Hummers' method. It is possible to obtain the amount of oxidation qualitatively by FT-IR spectroscopy analysis. The functional groups bonded on graphene flakes have a special bands on FT-IR spectrum. Since graphene oxide consists of hydroxyl, carbonyl and carboxyl groups, the formation of graphene oxide can be easily controlled by a FT-IR analysis. For this purpose we have taken a FT-IR spectrum from the graphene oxide suspension which is presented in Figure 3.23. As it is seen that our results are compatible to the literature of graphene oxide analysis by FT-IR which indicates the bands corresponding to the hydroxyl and carbonyl groups at 3400 cm⁻¹ and 1624 cm⁻¹. Moreover, as the amount of oxidation increases the intensity of these bands increases. The corresponding bands of graphene oxide are 1732 cm⁻¹ (C=O), 3000–3600 cm⁻¹ (OH), ~1700 cm⁻¹ (COOH) and 1000 – 1400 cm⁻¹ (COC/COH) vibrations.

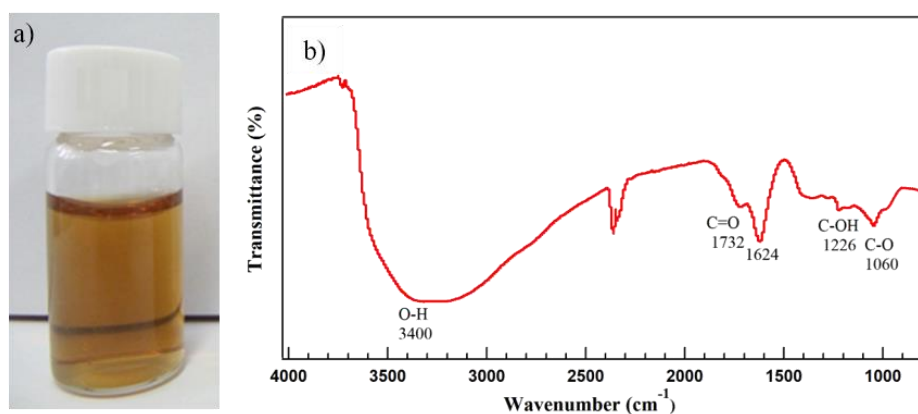


Figure 3.23: a) Graphene oxide suspension b) FT-IR spectrum of graphene oxide.

3.2.4. UV-VIS spectroscopy of graphene oxide

In addition to the FT-IR analysis, UV-vis spectroscopy was also carried out to prove that the prepared samples are graphene oxide or not. In Figure 3.24, a UV-VIS spectrum taken from the graphene oxide suspension is exhibited. A well suited result to the literature is also obtained in this analysis where a peak which arises from 230 nm related to the $\pi - \pi^*$ transitions of the aromatic C-C band and a shoulder at about 300 nm correspond to the $n - \pi^*$ transition of the C=O bond transition.

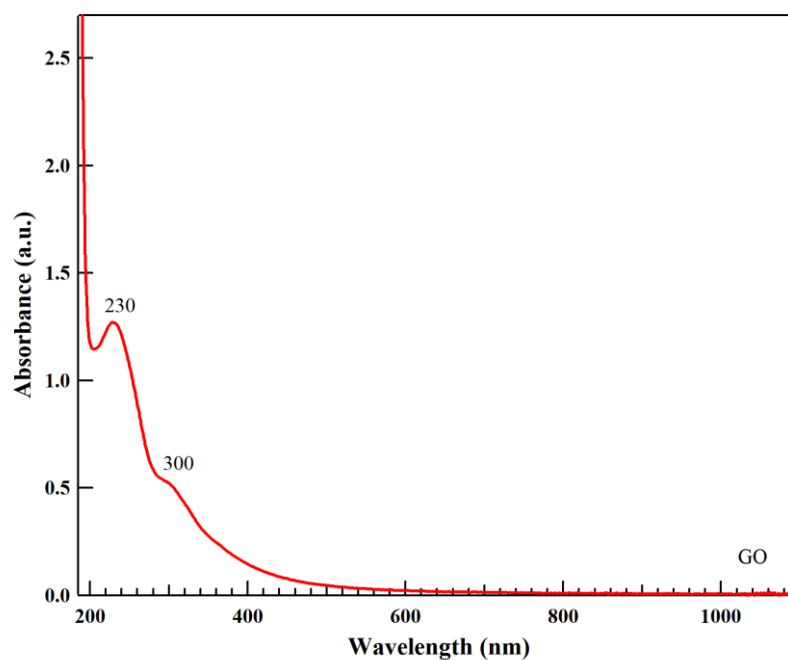


Figure 3.24: The UV-VIS spectrum of graphene oxide.

3.3. ELECTRICAL PROPERTIES OF HYBRID DEVICES

We tried to fabricate a FET device from single layer graphene (SLG) flake on SiO₂/Si wafer which was going to be used in preparing the graphene/graphene oxide hybrid structure. For this purpose, we prepared many graphene samples to manufacture hybrid devices but; most of them did not present the expected behavior of the graphene electronic structure due to the short circuit or other technical problems. During the electrical measurements it is very challenging to obtain a graphene device that works properly because of the long and demanding experimental processes. The critical hindrances are often the contact resistance and short circuits of the contact pads with the substrate (Silicon part). Another difficulty encountered is during the liftoff process, graphene may get harmed or removed from the surface completely. In addition to these, big ripples might appear on the graphene surface that affect the impurity amount around that region. In our recently published work we have established a relationship between the oxidation rate with the local doping level in graphene [88]. These problems can arise from the e-beam lithography and metal deposition processes. For example, if a metal, sharp-edged tweezer is used in handling the substrate, it might scratch the silica surface deep enough such that, a short circuit will occur between the contact pads and the conductive silicon beneath the insulating SiO₂ layer of the substrate if contact metals are deposited on these scratches. During the electrical measurements, the excess current may also damage the graphene or the contacts. Especially, any static electric discharges from the surrounding to the device may result in permanent damage. To protect the sample, electrical grounding of the experimenter is a first step before performing the electrical measurements.

The instrument used as the current source should be operated with a proper voltage compliance value to ensure that the current passing from the circuit does not exceed 1 μ A. The compliance voltage can be easily determined by taking the contact resistances into account. To check the operation of the device, first each contact is checked for shortage to the substrate. If there is no short circuit, the conductivity or resistivity of graphene is measured via 4-wire method. Afterwards, FET measurements are done to measure the gate voltage corresponding to zero charge doping of the graphene device. These measurement techniques are depicted in Figure 3.25.

Due to the electronic structure of graphene, its resistivity varies with the applied back-gate voltage. As the gate voltage is swept from the negative values to positive, the resistivity first increases to a maximum value (peak point) and then decreases. Six graphene devices have been fabricated at Sabancı University Nanotechnology Research and Application Center. One device contained bilayer graphene while the others were made from SLG flakes. Flakes were produced by scotch tape method. The contact designs were built with e-beam lithography (EBL) technique. The metal deposition was performed by thermal evaporation. Each device has been intended to be used for preparation of hybrid structures but; due to the experimental problems, only two devices survived all analysis without getting damaged (S5 and S6). These devices labeled as S1, S2, S3, S4, S5 and S6 respectively are listed in Table 3.2.

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Sample name	# Layer	Length (μm)
S1	Single layer	22
S2	Single layer	16
S3	Single layer	27
S4	Single layer	14
S5	Single layer	18
S6	Double layer	11

Sample name	# Layer	Length (μm)
S1	Single layer	22
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S4	Single layer	14
S5	Single layer	18
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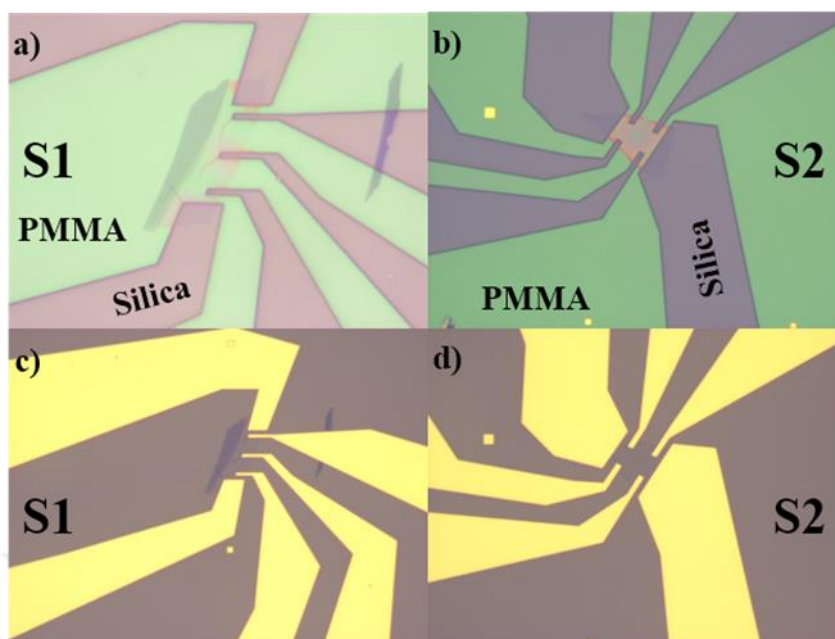


Figure 3.26: Optical images of **a)** S1 **b)** S2 after lithography process at 100X magnification **c)** and **d)** Optical images of S1 and S2 after metal deposition and liftoff processes at 50X magnification.

S1 and S2 were the first devices that were investigated under the probe station for electrical measurements. In Figure 2 and 3, the optical images of S1 and S2 are shown before and after the EBL and liftoff processes at different magnifications.

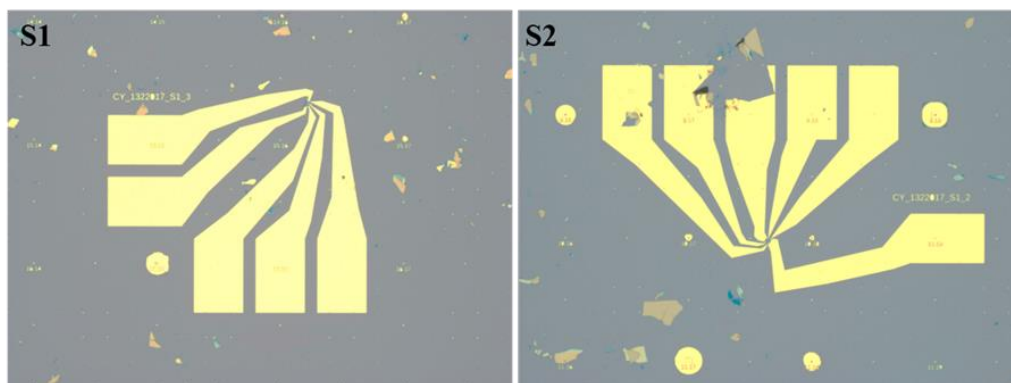


Figure 3.27: Optical images of S1 and S2 before electrical measurements at 5X magnification.

The electrical properties of S1 and S2 were investigated by a probe station (Keithley 4200-SCS) using 4-wire method with 4 individual probes. Prior to the electrical measurements, Raman spectra were collected from S1 and S2. As shown in Figure 3.28, the G band ($\sim 1600\text{ cm}^{-1}$) and 2D (2700 cm^{-1}) band peaks correspond to that of a single layer graphene; confirming that both samples are monolayer graphene. Absence of D peak ($\sim 1300\text{ cm}^{-1}$) indicates that both S1 and S2 are of high crystalline quality.

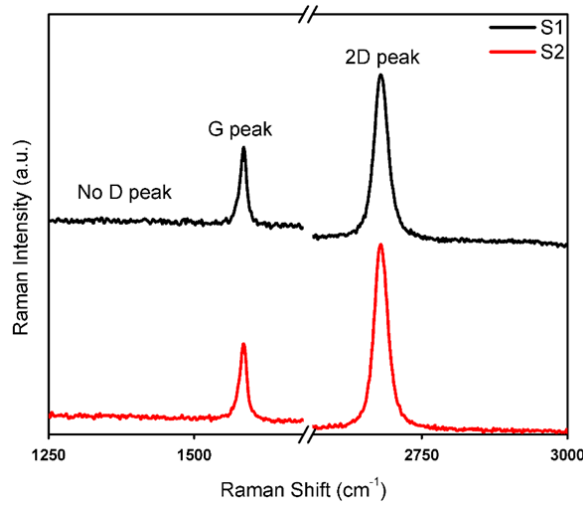


Figure 3.28: Raman spectra of S1 and S2 devices before making electrical measurements.

We expect the Raman spectrum to be different after the oxidation treatment during the preparation of graphene/graphene oxide hybrid structure. This is due to carboxyl, hydroxyl and carbonyl groups bonding to the graphene surface and inducing defects on its crystal structure. Before the transformation of S1 to the hybrid device, electrical properties were investigated and exhibited in Figure 3.29.

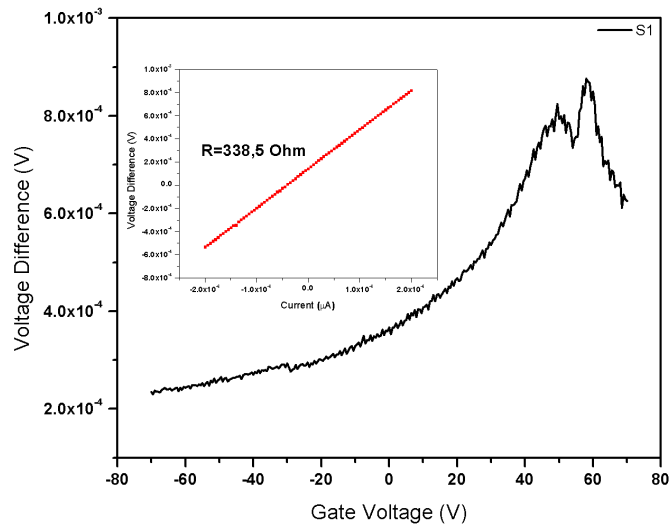


Figure 3.29: The electrical measurements of S1 before the oxidation.

With 4-wire connections the sheet resistance of graphene has been calculated as 338,5 Ohm. In FET measurement, zero charge doping was attained at approximately 55 Volts (V). These results shows that for zero back gate voltage S1 was p-type. The reason for the p-type doping

is usually the PMMA (Polymethyl methacrylate) resist residues on the surface after the e-beam lithography process. To get rid of PMMA residues S1 was annealed on a hot plate at 120 °C for 10 minutes and shortly after, the electrical measurements were repeated (Figure 3.30). There has been an improvement in the signal to noise ratio. It would not be wrong to say that better contacts to graphene is the main reason for this improvement. The cleaner surface reduced the sheet resistance to 9,4 Ohm (inset of Figure 3.30). In addition, the position of the charge neutrality point shifted to 33,5 V. In order to check the stability of this shift, the measurement was repeated 30 minutes later.

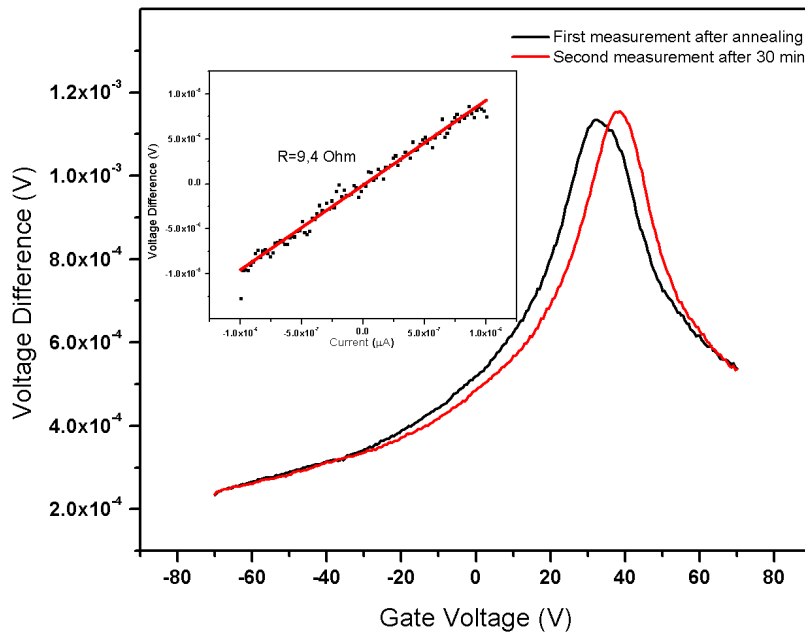


Figure 3.30: FET measurement shortly after annealing and 30 minutes later.

If the annealing makes the device stable on charge transport, Dirac voltage should not fluctuate by the time. But; as shown in Figure 3.30, there is a little shift back to the higher voltages of 38.5 V. Since annealing in air changed the charge doping transiently, Dirac point and the resistance drifts over time. For further study, an annealing process in Ar atmosphere can be tried for a persistent cleaning and stability. In air, the surface becomes very sensitive to the moisture right after annealing. AFMs may be a better choice. In our experiments we observed that any contaminants or residues on the surface of graphene can be cleaned as the AFM tip scans over the surface in the contact mode. However, this requires precise control of applied force so that the sample is not damaged. This was discussed in the AFM section in detail. S1

and S2 burnt out by the static electrical discharges while measuring and testing the devices. Thereby, we could not use S1 and S2 for hybrid subsequent experiments. Below are the optical images of S1 and S2 after the devices are damaged.

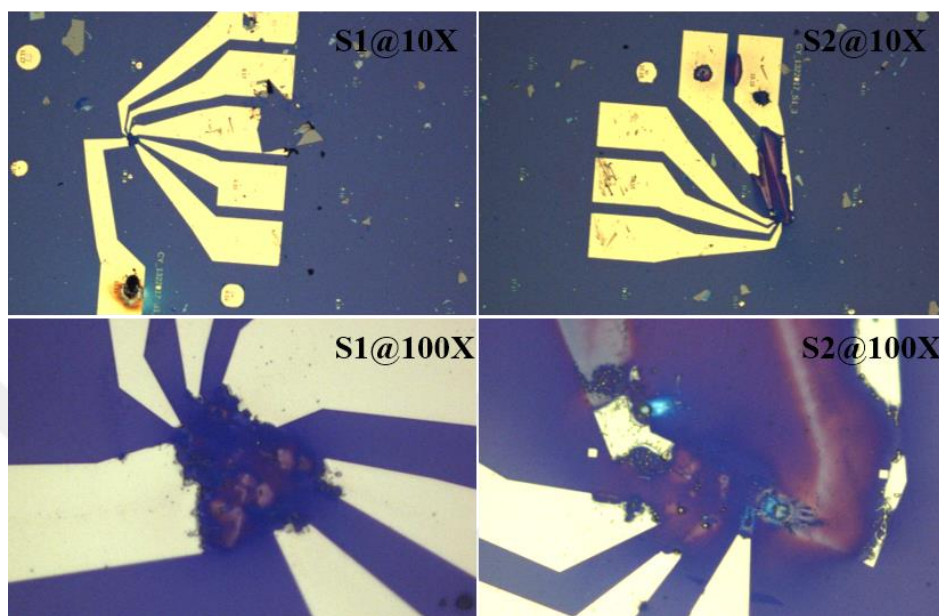


Figure 3.31: The optical images of the effect of static electric discharges on S1 and S2.

After S1 and S2, S3 was manufactured and tested under probe station for electrical measurements. Due to the problems mentioned above device did not allow the desired current to pass through it. All the contacts have been examined in different combinations but; device did not perform properly. The reason could be the high contact resistance and, the low compliance voltage. Here the compliance voltage range is generally between 0.02-0.03 V for all graphene devices. To pass a current of $1\ \mu\text{A}$ through graphene, the compliance voltage was increased up to 1 – 2 V but we did not see any significant conductance. So this sample could not be used for hybrid device but was used to test to find the proper duration for oxidation. Figure 3.32 shows the lithography and liftoff procedures of S3 below.

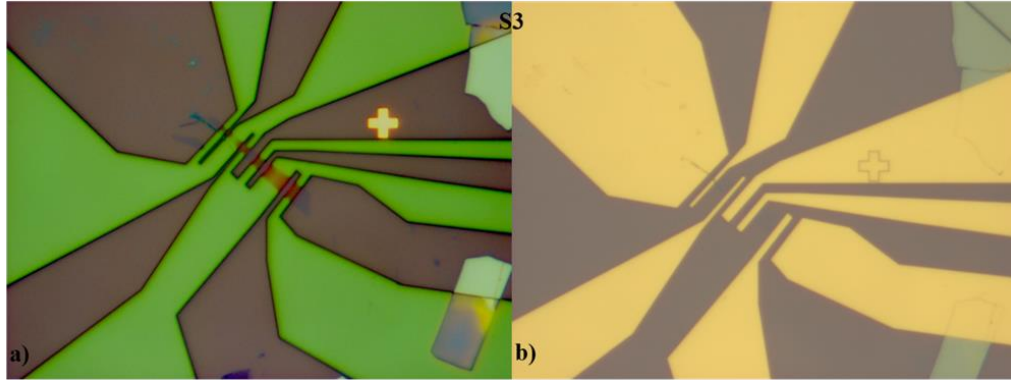


Figure 3.32: a) Optical image of S3 after e-beam lithography at 100X b) after metal deposition and liftoff.

S4, S5 and S6 were fabricated after these problems and they were also tested under probe station to check the contacts and the sheet resistances and the charge neutrality points were determined before the oxidation steps.

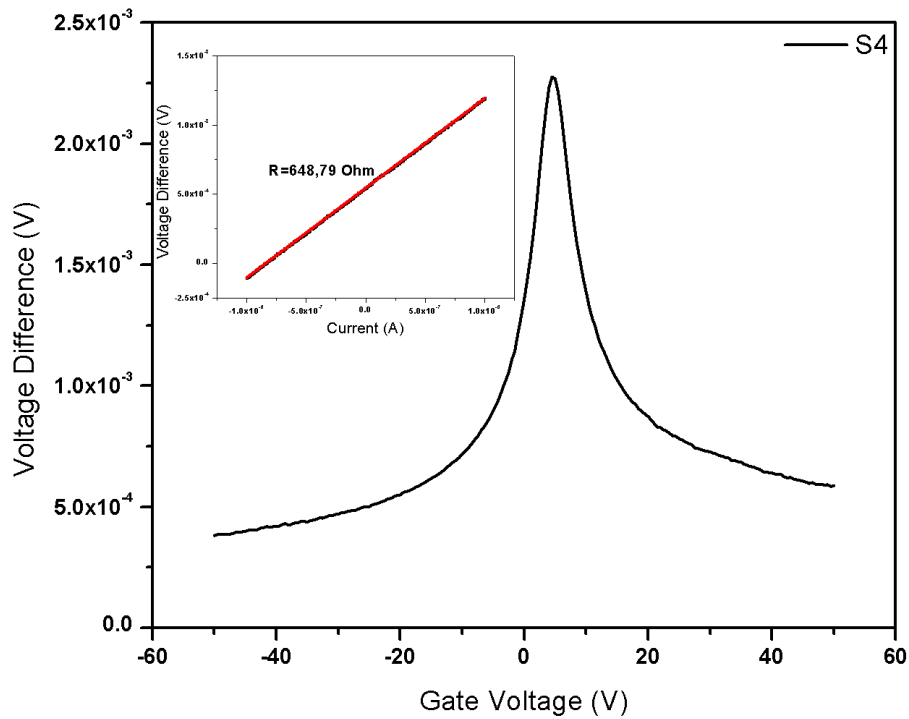


Figure 3.33: The electrical measurements of S4 before the oxidation.

S4 was the best sample among the other graphene devices because of its Dirac voltage value of 4.5 V which was very close to 0 V (Figure 3.33). It is the fact that S4 was unaffected by fabrication processes and had a very clean surface than the others. The sheet resistance of S4

was measured as 648.79 Ohm. S4 was kept aside for making hybrid device because it had the best electrical and structural properties among the others. After perfecting the experimental techniques using the other devices, S4 would be used for the best results. So, S5 and S6 were also tested under probe station after S4 and the measurements are shown in Figure 3.34.

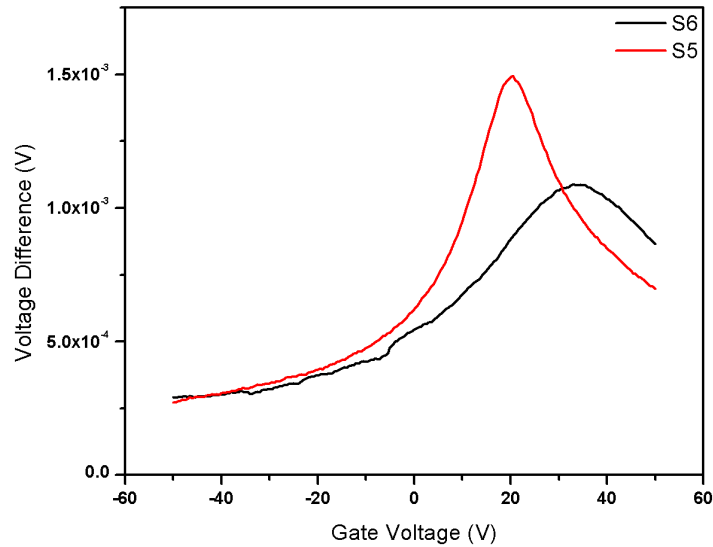


Figure 3.34: A comparison of S5 (single layer graphene) and S6 (double layer graphene) by FET measurement before oxidation.

Clearly, there is a big difference in the shapes of Dirac curves between S5 and S6 and the voltage values of the peaks are 20.5 and 34.75 V respectively. Due to the crystal structure of double layer graphene (S6), the increase in resistance is not so big as in single one. Resistance change in S5 reaches up to 1.5×10^3 Ohm from 272 ohm. On the other hand, the resistance of S6 varies between 291.49 and 1.09×10^3 Ohms. These curves were obtained right after they were built so these curves are very important to compare the results after oxidation process. In addition to voltage difference versus gate voltage plot, resistance and resistivity versus gate voltage graph was obtained for S5 and S6 to compare the single and double layer graphene (Figure 3.35). Since 1 μ A current was passed through the graphene flakes, the resistance versus gate voltage graph has the same characteristic behaviour with the voltage difference versus gate voltage. The variation in resistance values can be easily extracted from the graph shown in the Figure 3.35a.

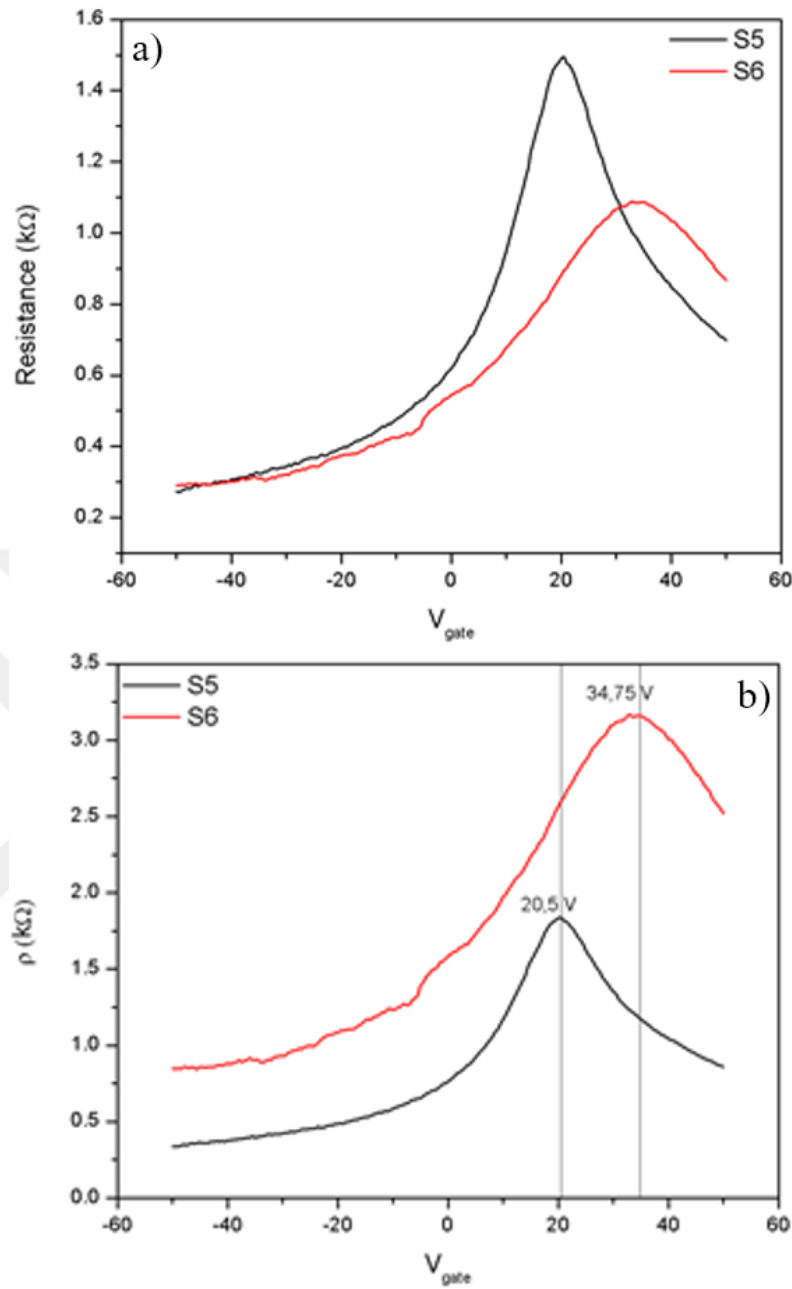


Figure 3.35: a) Resistance vs gate voltage **b)** resistivity vs gate voltage of S5 and S6 before the oxidation.

It is also seen that the resistivities of single layer and double layer graphene are the distinctive feature for them. The resistivity of single layer graphene is 335.65Ω at the gate voltage of 50 V and $1.84 k\Omega$ at Dirac voltage where it takes the highest value due to the charge carrier density is lowest. On the other hand, in double layer graphene, the resistivity changes from 847.96Ω to $3.17 k\Omega$. Moreover, S6 could not be used for further characterization related to the oxidation process to make a hybrid structure of double layer graphene because of the technical problems.

The only sample that was oxidized and investigated by electrical measurements for revealing the hybrid properties was S5. For the purpose of such kind of analysis, a comparison of the resistivity measurement with respect to the gate voltage for S5 is presented before and after the oxidation process in Figure 3.36. It seems that the charge neutrality point shifts from the voltage value of 20.5 V to the 5V.

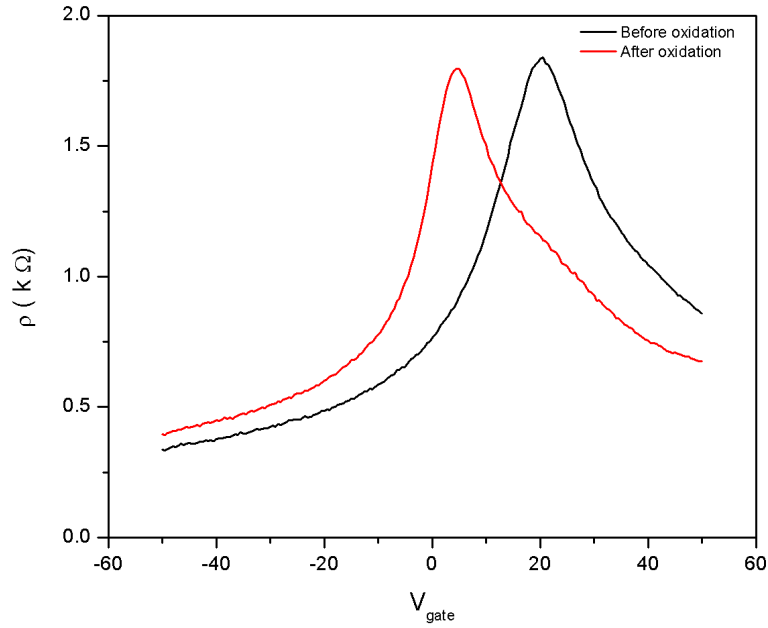


Figure 3.36: Charge neutrality points of S5 before and after the oxidation at room temperature.

This variation in the Dirac voltage claims that S5 was p-type doped with the effect of oxidation where the functional groups were bonded to the surface of the graphene flake. Another analysis can be done on the graph of the mobility versus charge carrier density which is shown in Figure 3.37. The mobility (μ) calculation was done using the Drude formula as followed;

$$\mu = \frac{\sigma}{en} \quad (3.6)$$

Here, the σ is the electrical conductivity of measured sample which is directly proportional to the length and width of the graphene flake. And, e is the elementary charge of electron. The n is the charge carrier density which is tuned by the gate voltage. Since graphene is on an insulating layer (silica), a relation can be regarded as follows;

$$n = \alpha(V_g - V_{CNP}) \quad (3.7)$$

where α refers to a relation with the gate capacitance written in equation below;

$$n = \frac{\varepsilon_0 \varepsilon_r V_g}{te} \quad (3.8)$$

where ε_0 is the vacuum dielectric constant, ε_r is the relative dielectric permittivity of the silica and t is the thickness of silica. Upon these formulas, it can be said that the resistance of the graphene gets its highest value when the Fermi level is taken place at the Dirac point where the carrier density of states is lowest but not zero. During the electrical measurements Dirac point can be obtained by determining the V_{CNP} (charge neutrality point). By applying a gate voltage, Fermi level can be tuned via electron or hole accumulation. This is the ambipolar effect of graphene.

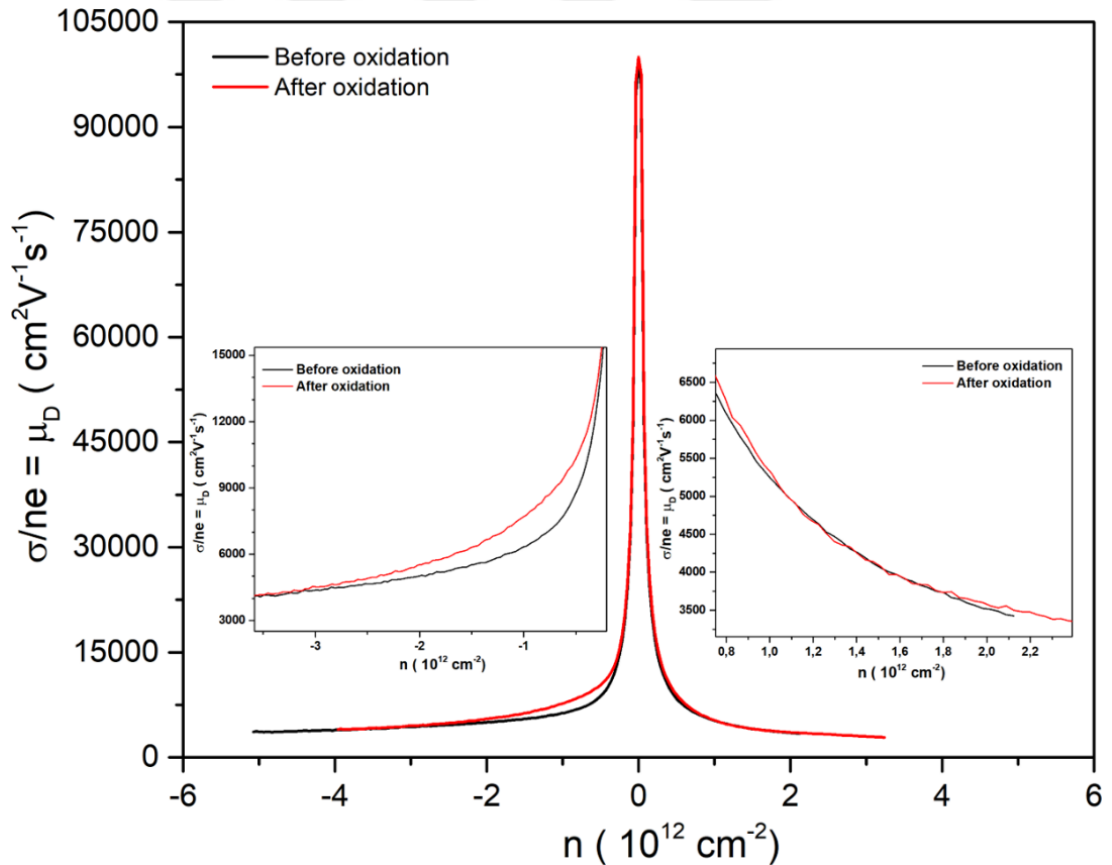


Figure 3.37: Mobility values for electrons and holes before and after the oxidation of S5.

To assess the electrical behavior of the hybrid structure, FET measurements at different temperatures (varying from the room temperature up to 140 °C) were carried out. The heating

operation was done under probe station using a special hot plate system with a heat controller unit. In order to be sure about the surface temperature accurately, an infrared laser thermometer was used. Figure 3.38 provides the variation of the Dirac voltage of S5 with respect to the increasing temperature.

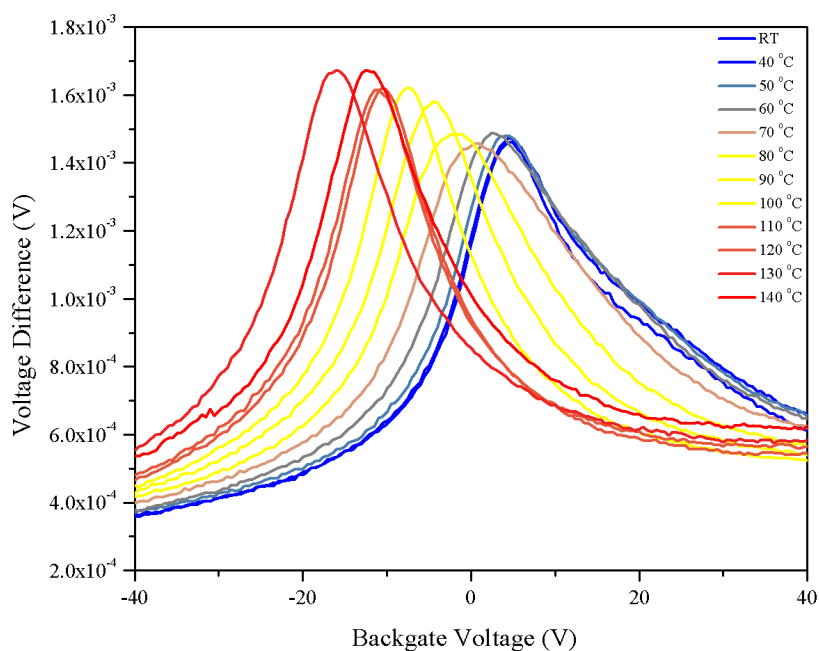


Figure 3.38: The plots of voltage difference versus gate voltage of S5 with temperature gradient.

From the graph above we can see that the Dirac voltage shifts to the negative voltages as the temperature increases from the room temperature. After 130 °C it shifts back to the negative direction of the gate voltage. This temperature value can be a turning point of the reduction since the functional groups volatilized from the surface by heat. The relation between the temperature and charge neutrality point is plotted in Figure 3.39. Since the electronic behaviour of graphene is easily changed with different doping mechanisms, the alteration of the Dirac voltage can be attributed to the variations in the structural properties where the graphene oxide parts start to reduce to the graphene. We expected to see the effect of the reduction of graphene oxide when the temperature is enough to make the functional groups to evaporate from the surface. In the view of Dirac voltage characteristics, it can be said that as the temperature increases the scattering rate increases too. As a result, the resistance of the hybrid structure also increases.

The effect of the temperature on hybrid device presents that it was p-type up to 130°C. After this temperature, it was n-type. This change can be attributed to the small amount of reduction of the graphene oxide parts. The experiments was carried out

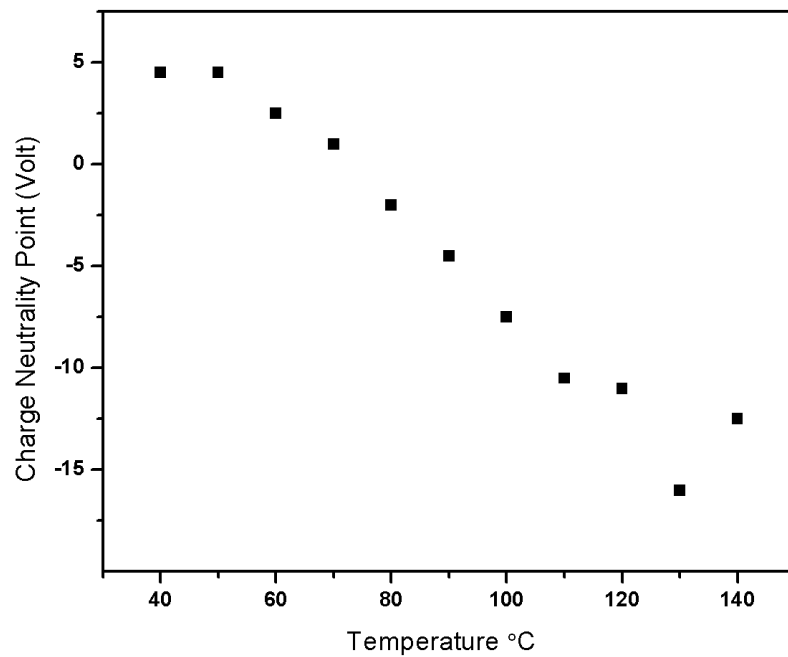


Figure 3.39: Charge neutrality point vs temperature graph of hybrid device.

at temperatures till to 140 °C since the golden contact pads and lines could start to melt. Additionally, to see how the electron mobility changes as the temperature increases a plot of mobility vs temperature is drawn in Figure 3.40.

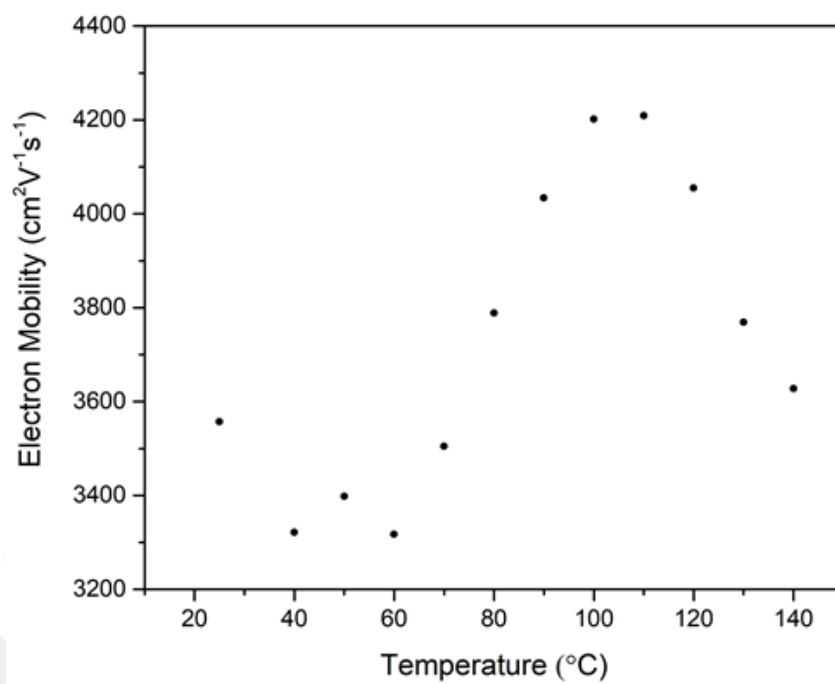


Figure 3.40: The deviation of electron mobility of hybrid device via temperature.

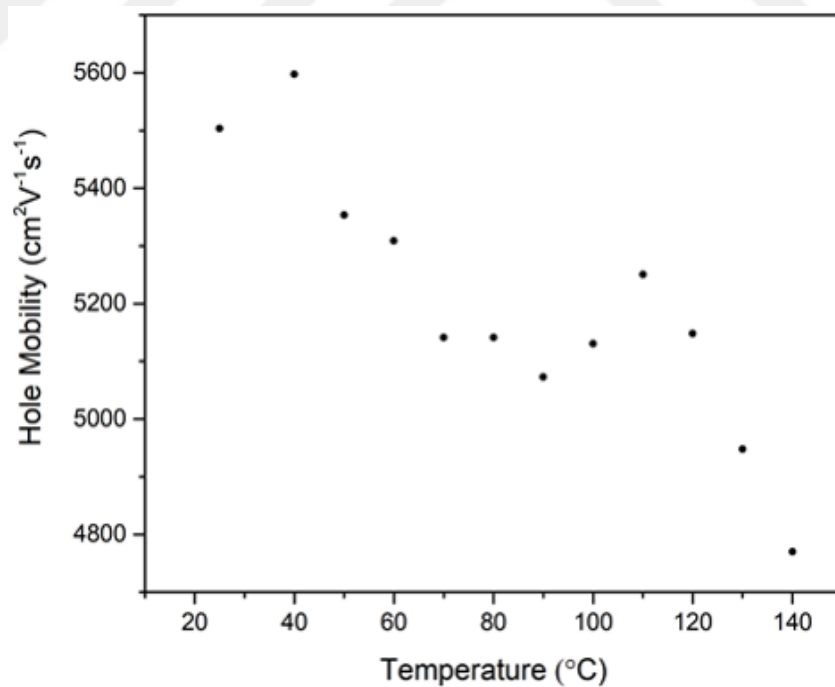


Figure 3.41: The deviation of hole mobility of hybrid device via temperature.

4. DISCUSSION

Unlike graphene and graphene oxide structures found in the literature, our aim was to produce a hybrid material that is consist of both of them in together. For this purpose, graphene samples were obtained on insulating substrate by scotch tape method. It was checked by the Raman spectroscopy whether the prepared samples are one atom thick or not. The determined graphene layers were formed by lithographic methods and spaces were formed on them. These openings were created to oxidize a certain section of the graphene. The samples which had been stored for 15 min in the specific chemical solution were completely oxidized. In the meantime, experiments have shown that oxidation of the graphene is difficult, depending on whether or not the edge regions are within the openings. In addition to this, according to the results of the Raman mapping, locally substrate and contamination-induced dopings was found on the surface of the graphene. This type of contribution has been the subject of discussion in the literature. After we obtained similar results in the literature on the results of the investigations we made, we realized that the zones where oxidation began were the doped parts. Detailed information about this study is available in our publication [88].

In the structural analysis it has been shown that graphene oxide has a more surface roughness than graphene. This result is expected and it has been found that when the average surface roughness values are taken into account, graphene oxide has almost the same surface roughness as silica. Another structural analysis for the nanomechanical properties of graphene, we prepared suspended graphene samples using a perforated substrate. To achieve this, the silica surface was first patterned by optical lithography then etched with a hydroflouric acid mixture in an ultrasound bath for 5 minutes. Without using the sonication the etch process was not successful. The spring constant of the suspended graphene was found as 0,3 N/m. These observation is consistent with the results of the studies in literature. Moreover, it was possible to calculate the surface tension of the suspended graphene as 0,264 N/m. For Young's modulus calculation we needed to break the suspended graphene under AFM tip but we did not try this mesaurement. According to the force-distance curves the elastic modulus of the suspended graphene may be extracted due to the similar studies in the literature. In AFM and LFM analysis, we observed that LFM images gives the best contrast for differentiating the graphene and graphene oxide parts. Since the frictional force exerted on the tip by the graphene oxide is larger than the graphene surface, one can easily differentiate different phases of the surface.

According to the line profile taken over the oxidized surface, it was seen that the oxidized part is higher than the non-oxidized part (~ 2 or 3 nm). To prove the oxidized graphene parts that are insulating I-AFM was carried out. Due to the tip scanned over the surface in contact mode the region which is not conductive did not allow the current to pass. As a result of the scanning, a topographic image which shows the current ways on the surface was obtained. Using the software of the AFM (XEI), both LFM and I-AFM images were stacked on together and it was shown that the estimated graphene oxide parts seems as insulating. So we have proved the formation of graphene oxide on the surface with the AFM analysis in addition to the Raman analysis.

In the optical analysis, graphene oxide was investigated with Raman, UV-VIS and FT-IR spectroscopy. The expected result in the dispersive Raman spectroscopy for graphene oxide was the D peak which arisen at 1350 cm^{-1} . D peak formation refers to the defects on the surface which the oxidation process caused. The bonded functional groups are determined with the FT-IR spectroscopy in line with the literature. We also compared the UV-VIS measurements of the graphene oxide from the literature and observed that our results were compatible with them.

We have prepared more than 30 devices during all the PhD studies but most of them were employed for the know how of graphene device caharacterization. One of the most common error to hold the graphene device without electrically grounding yourself completely. The static caharges on the body can rapidly destroy the device. Another problem for preparing hybrid device is to sonicate the sample with solution for longer time than it is needed. As a result of that photoresist can not stand on anymore. As shown in the Figure 4.1, while preparing the S4 for oxidation, the optimal time which was adjusted by the test sample did not succeed in oxidizing. The short duration in ultrasound bath did also not change the situation. So, we decided to sonicate the sample in the ultrasound bath for a long time to be oxidized. However, this long treatment affected the sample unfavorably.

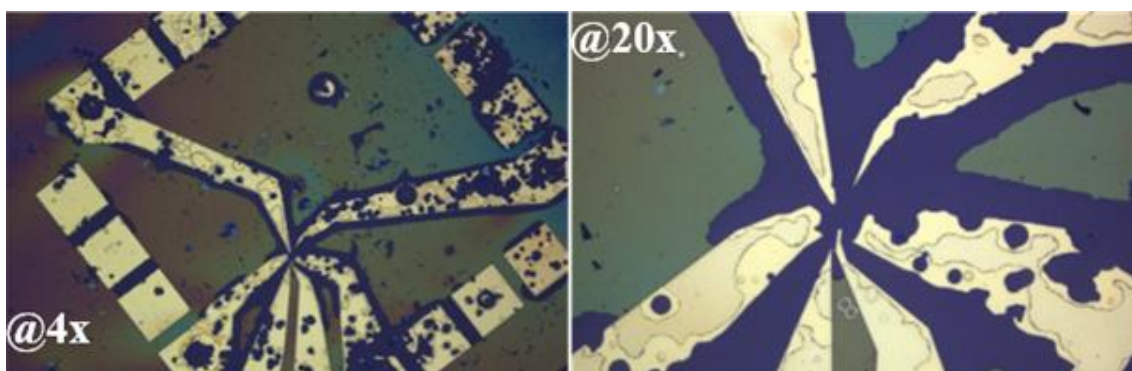


Figure 4.1: The breakdown of S4 by an excessive ultrasound treatment.

For the electrical measurements of the hybrid samples, graphene field effect transistor built at the first step then using the second lithography process hybrid structures were formed via wet chemistry. This enabled us to compare the electrical behaviour of pure graphene flake with a hybrid one. All remarkable and precise measurements were done on semiconducting analyzer system allied with a probe station and air vibration isolation table. In FET measurement, the Dirac voltage is the key parameter which states the doping type of the sample. And the PMMA residuals or other contaminations on graphene generally affect the Dirac point by shifting to the positive voltages in addition to the substrate effect. On the other hand, to make a reliable comparison of the graphene FET and hybrid FET devices, samples should be decontaminated by passing current through it or annealing on hot plate. Observations on annealing method present that the it is not a persistent way to get rid of the contamination. But, annealing in H_2 at an elevated temperatures provide an effective cleaning which we used for our graphene samples. In the view of this aspect, S4 might be the cleanest sample among the others having a very low Dirac voltage of 4.5 V at ambient conditions. But due to the problems mentioned above it was not possible to make a hybrid device from it. S5 was the other working FET device which has a Dirac point of 20.5 V before the oxidation process and 5 V after the oxidaiton. It can be said that the formation of graphene oxide on graphene makes it hole doped according to the shift of the Dirac voltage to the negative part. To investigate the transport properties of the samples, the electron and hole mobility was calculated for a charge carrier density of $2 \times 10^{12} \text{ cm}^{-2}$ before and after the oxidation process of graphene FET. The electron mobility of the graphene FET was found as $3511.52 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ where the hole mobility was $4989.45 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. The electron mobility of the graphene/graphene oxide hybrid FET was $3557.18 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ where the hole mobility was $5503.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. As it is

seen both electron and hole mobility of the device has increased after the oxidation due to the impurity doping increased.



5. CONCLUSION AND RECOMMENDATIONS

During this thesis study, approximately 300 graphene samples have been prepared by scotch tape method and scanned under optical microscope with naked eye. And nearly 30 of these samples were patterned lithographically to produce graphene/graphene oxide hybrid but most of them were broken due to the different problems during the analysis. It seems that the most practical and low cost production method is the exfoliation one among the others since high crystalline single layer graphene flakes with no defects is obtained. For making graphene/graphene oxide hybrid structure, the wet chemistry is used via a modified Hummers' method which provides to oxidize the flakes with harsh acidic treatment.

When compared with other graphene oxide studies from the literature, graphene oxide thin films and the hybrid form produced within the scope of this study, a new method emerges as an antagonism. Oxides can be made at different ratios depending on the purpose for which they are obtained. Moreover, other composites can be attached to the hydroxyl side epoxy groups present in graphene oxides. Thus, instead of the usual graphene layer we can use, there will be thin films that can be functionalized and can work for certain purposes for example sensor applications.

We proved that it is possible to prepare graphene/graphene oxide hybrid structures through wet chemistry and lithography techniques. Moreover, we examined the surface of these structures with AFM and LFM by providing also the I- AFM to show the difference between the insulating graphene oxide and the conducting graphene parts. We have also proven the graphene oxide structures by Raman spectroscopy. The distinctive Raman fingerprint of the graphene oxide has played a significant role to be determined. FT-IR and Uv-vis analysis were also compatible with the examples of the literature.

Through analyzing the electrical properties of the hybrid structures, the diffused mobility of the charge carriers were calculated by Drude formula. But other approximation methods such as residual transport analysis can be done for a further analysis to differentiate the impurity doping effect on the hybrid devices.

REFERENCES

- [1]. Geim, A.K. and K.S. Novoselov, 2007, The rise of graphene, *Nat Mater.*, p. 183-91.
- [2]. Wallace, P.R., 1947, The Band Theory of Graphite, *Physical Review*, 71(9): p. 622-634.
- [3]. Novoselov, K.S., et al., 2004, Electric Field Effect in Atomically Thin Carbon Films, *Science*, 306(5696): p. 666-669.
- [4]. Hass, J., W.A. de Heer, and E.H. Conrad, 2008, The growth and morphology of epitaxial multilayer graphene, *Journal of Physics-Condensed Matter*, 20(32): p. 27.
- [5]. Yu, Q.K., et al., 2008, Graphene segregated on Ni surfaces and transferred to insulators. *Applied Physics Letters*, 93(11): p. 3.
- [6]. Zhan, N., et al., 2011, Layer-by-layer synthesis of large-area graphene films by thermal cracker enhanced gas source molecular beam epitaxy, *Carbon*, 49(6): p. 2046-2052.
- [7]. Zhang, Y.B., et al., 2005, Experimental observation of the quantum Hall effect and Berry's phase in graphene, *Nature*, 438(7065): p. 201-204.
- [8]. Bolotin, K.I., et al., 2008, Ultrahigh electron mobility in suspended graphene. *Solid State Communications*, 146(9-10): p. 351-355.
- [9]. Du, X., et al., 2008, Approaching ballistic transport in suspended graphene, *Nat Nanotechnol*, 3(8): p. 491-5.
- [10]. Norimatsu, W. and M. Kusunoki, 2014, Growth of graphene from SiC{0001} surfaces and its mechanisms, *Semiconductor Science and Technology*, 29(6).
- [11]. Ritter, K.A. and J.W. Lyding, 2009, The influence of edge structure on the electronic properties of graphene quantum dots and nanoribbons, *Nature Materials*, 8(3): p. 235-242.
- [12]. Gilje, S., et al., 2007, A chemical route to graphene for device applications, *Nano Letters*, 7(11): p. 3394-3398.
- [13]. Elias, D.C., et al., 2009, Control of graphene's properties by reversible hydrogenation: evidence for graphane, *Science*, 323(5914): p. 610-3.
- [14]. Robinson, J.T., et al., 2010, Properties of Fluorinated Graphene Films, *Nano Letters*, 10(8): p. 3001-3005.
- [15]. Eda, G., G. Fanchini, and M. Chhowalla, 2008, Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, *Nat Nanotechnol*, 3(5): p. 270-4.
- [16]. Becerril, H.A., et al., 2008, Evaluation of solution-processed reduced graphene oxide films as transparent conductors, *ACS Nano*, 2(3): p. 463-70.
- [17]. Gomez-Navarro, C., et al., 2007, Electronic transport properties of individual chemically reduced graphene oxide sheets, *Nano Letters*, 7(11): p. 3499-3503.
- [18]. Hummers, W.S. and R.E. Offeman, 1958, Preparation of Graphitic Oxide, *Journal of the American Chemical Society*, 80(6): p. 1339-1339.
- [19]. McClure, J.W., 1956, Diamagnetism of Graphite, *Physical Review*, 104(3): p. 666-671.

- [20]. Slonczewski, J.C. and P.R. Weiss, 1958, Band Structure of Graphite, *Physical Review*, 109(2): p. 272-279.
- [21]. Boyle, W.S. and P. Nozières, 1958, Band Structure and Infrared Absorption of Graphite, *Physical Review*, 111(3): p. 782-785.
- [22]. Spry, W.J. and P.M. Scherer, 1960, de Haas-van Alphen Effect in Graphite between 3 and 85 Kilogauss, *Physical Review*, 120(3): p. 826-829.
- [23]. Soule, D.E., J.W. McClure, and L.B. Smith, 1964, Study of the Shubnikov-de Haas Effect. Determination of the Fermi Surfaces in Graphite, *Physical Review*, 134(2A): p. A453-A470.
- [24]. Williamson, S.J., S. Foner, and M.S. Dresselhaus, 1965, de Haas-van Alphen Effect in Pyrolytic and Single-Crystal Graphite, *Physical Review*, 140(4A): p. A1429-A1447.
- [25]. Dillon, R.O., I.L. Spain, and J.W. McClure, 1977, Electronic energy band parameters of graphite and their dependence on pressure, temperature and acceptor concentration, *Journal of Physics and Chemistry of Solids*, 38(6): p. 635-645.
- [26]. Schroeder, P.R., M.S. Dresselhaus, and A. Javan, 1968, Location of Electron and Hole Carriers in Graphite from Laser Magnetoreflexion Data, *Physical Review Letters*, 20(23): p. 1292-1295.
- [27]. Chang, H. and H. Wu, 2013, Graphene-based nanocomposites: preparation, functionalization, and energy and environmental applications, *Energy & Environmental Science*, 6(12): p. 3483.
- [28]. Yavari, F., 2012, *Graphene nano-devices and nano-composites for structural, thermal and sensing applications* Thesis (PhD), Rensselaer Polytechnic Institute.
- [29]. Zhang, Y., et al., 2012, Improving the photocatalytic performance of graphene-TiO₂ nanocomposites via a combined strategy of decreasing defects of graphene and increasing interfacial contact, *Phys Chem Chem Phys*, 14(25): p. 9167-75.
- [30]. Shen, J., et al., 2012, Graphene quantum dots: emergent nanolights for bioimaging, sensors, catalysis and photovoltaic devices, *Chem Commun (Camb)*, 48(31): p. 3686-99.
- [31]. Singh, A.K., 2014, *Tunable graphene chem-fet and graphene heterojunction chemi-diode sensors*, Thesis (PhD), University of South Carolina.
- [32]. Novoselov, K.S., et al., 2005, Two-dimensional atomic crystals *Proc Natl Acad Sci U S A*, 102(30): p. 10451-3.
- [33]. Babichev, A.V., et al., 2012, Electroluminescence of GaP $\times$ N y As $1 - x - y$ nanoheterostructures through a transparent electrode made of CVD graphene, *Semiconductors*, 46(6): p. 796-800.
- [34]. Shetu, S.S., 2014, *Influence of defects in epitaxial graphene towards material growth and device performances*, Thesis (PhD), University of South Carolina.
- [35]. Park, S. and R.S. Ruoff, 2009, Chemical methods for the production of graphenes, *Nat Nanotechnol*, 4(4): p. 217-24.
- [36]. Li, D., et al., 2008, Processable aqueous dispersions of graphene nanosheets, *Nat Nanotechnol*, 3(2): p. 101-5.

- [37]. Hernandez, Y., et al., 2008, High-yield production of graphene by liquid-phase exfoliation of graphite, *Nat Nanotechnol*, 3(9): p. 563-8.
- [38]. Stankovich, S., et al., 2007, Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide, *Carbon*, 45(7): p. 1558-1565.
- [39]. Stankovich, S., et al., 2006, Stable aqueous dispersions of graphitic nanoplatelets via the reduction of exfoliated graphite oxide in the presence of poly(sodium 4-styrenesulfonate), *J. Mater. Chem.*, 16(2): p. 155-158.
- [40]. Balandin, A.A., et al., 2008, Superior thermal conductivity of single-layer graphene, *Nano Lett*, 8(3): p. 902-7.
- [41]. Das Sarma, S., et al., 2011, Electronic transport in two-dimensional graphene, *Reviews of Modern Physics*, 83(2): p. 407-470.
- [42]. Katsnelson, M.I., K.S. Novoselov, and A.K. Geim, 2006, Chiral tunnelling and the Klein paradox in graphene, *Nature Physics*, 2(9): p. 620-625.
- [43]. Stander, N., B. Huard, and D. Goldhaber-Gordon, 2009, Evidence for Klein Tunneling in Graphene p-n Junctions, *Physical Review Letters*, 102(2).
- [44]. Young, A.F. and P. Kim, 2009, Quantum interference and Klein tunnelling in graphene heterojunctions, *Nature Physics*, 5(3): p. 222-226.
- [45]. Wirtz, L. and A. Rubio, 2004, The phonon dispersion of graphite revisited, *Solid State Communications*, 131(3-4): p. 141-152.
- [46]. Cooper, D.R., et al., 2012, Experimental Review of Graphene, *ISRN Condensed Matter Physics*, p. 1-56.
- [47]. Mingo, N. and D.A. Broido, 2005, Carbon nanotube ballistic thermal conductance and its limits, *Physical Review Letters*, 95(9): p. 4.
- [48]. Nika, D.L., et al., 2009, Phonon thermal conduction in graphene: Role of Umklapp and edge roughness scattering, *Physical Review B*, 79(15): p. 12.
- [49]. Munoz, E., J.X. Lu, and B.I. Yakobson, 2010, Ballistic Thermal Conductance of Graphene Ribbons, *Nano Letters*, 10(5): p. 1652-1656.
- [50]. Jeong, C., S. Datta, and M. Lundstrom, 2011, Full dispersion versus Debye model evaluation of lattice thermal conductivity with a Landauer approach, *Journal of Applied Physics*, 109(7): p. 8.
- [51]. Pop, E., V. Varshney, and A.K. Roy, 2012, Thermal properties of graphene: Fundamentals and applications, *MRS Bulletin*, 37(12): p. 1273-1281.
- [52]. Geim, A.K., 2009, Graphene: Status and Prospects, *Science*, 324(5934): p. 1530-1534.
- [53]. Novoselov, K.S., et al., 2005, Two-dimensional gas of massless Dirac fermions in graphene, *Nature*, 438(7065): p. 197-200.
- [54]. Emtsev, K.V., et al., 2009, Towards wafer-size graphene layers by atmospheric pressure graphitization of silicon carbide, *Nature Materials*, 8(3): p. 203-207.
- [55]. Kim, K.S., et al., 2009, Large-scale pattern growth of graphene films for stretchable transparent electrodes, *Nature*, 457(7230): p. 706-710.

- [56]. Bae, S., et al., 2010, Roll-to-roll production of 30-inch graphene films for transparent electrodes, *Nature Nanotechnology*, 5(8): p. 574-578.
- [57]. Li, X.S., et al., 2010, Graphene Films with Large Domain Size by a Two-Step Chemical Vapor Deposition Process, *Nano Letters*, 10(11): p. 4328-4334.
- [58]. Berger, C., et al., 2004, Ultrathin epitaxial graphite: 2D electron gas properties and a route toward graphene-based nanoelectronics, *Journal of Physical Chemistry B*, 108(52): p. 19912-19916.
- [59]. Juang, Z.Y., et al., 2009, Synthesis of graphene on silicon carbide substrates at low temperature, *Carbon*, 47(8): p. 2026-2031.
- [60]. Unarunotai, S., et al., 2009, Transfer of graphene layers grown on SiC wafers to other substrates and their integration into field effect transistors, *Applied Physics Letters*, 95(20): p. 202101.
- [61]. Reina, A., et al., 2009, Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition, *Nano Letters*, 9(1): p. 30-35.
- [62]. Li, X., et al., 2009, Large-area synthesis of high-quality and uniform graphene films on copper foils, *Science*, 324(5932): p. 1312-4.
- [63]. Stankovich, S., et al., 2006, Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets, *Carbon*, 44(15): p. 3342-3347.
- [64]. Gomez-Navarro, C., et al., 2010, Atomic Structure of Reduced Graphene Oxide, *Nano Letters*, 10(4): p. 1144-1148.
- [65]. Bagri, A., et al., 2010, Structural evolution during the reduction of chemically derived graphene oxide, *Nature Chemistry*, 2(7): p. 581-587.
- [66]. Brodie, B.C., 1860, *Ann. Chim. Phys.*, 59: p. 466.
- [67]. Staudenmaier, L., Ber. Deut. 1898, *Chem. Ges.*, 31: p. 1481.
- [68]. Wang, H.-W., et al., 2010, Facile solvothermal synthesis of a graphene nanosheet–bismuth oxide composite and its electrochemical characteristics, *Electrochimica Acta*, 55(28): p. 8974-8980.
- [69]. Marcano, D.C., et al., 2010, Improved Synthesis of Graphene Oxide, *Acs Nano*, 4(8): p. 4806-4814.
- [70]. Zhu, Y., D.K. James, and J.M. Tour, 2012, New Routes to Graphene, Graphene Oxide and Their Related Applications, *Advanced Materials*, 24(36): p. 4924-4955.
- [71]. Dikin, D.A., et al., 2007, Preparation and characterization of graphene oxide paper, *Nature*, 448(7152): p. 457-460.
- [72]. Vandsburger, L., et al., 2009, Stabilized aqueous dispersion of multi-walled carbon nanotubes obtained by RF glow-discharge treatment, *Journal of Nanoparticle Research*, 11(7): p. 1817-1822.
- [73]. Masubuchi, S., et al., 2009, Fabrication of graphene nanoribbon by local anodic oxidation lithography using atomic force microscope, *Applied Physics Letters*, 94(8): p. 082107.
- [74]. Giesbers, A.J.M., et al., 2008, Nanolithography and manipulation of graphene using an atomic force microscope, *Solid State Communications*, 147(9-10): p. 366-369.

- [75]. Biró, L.P. and P. Lambin, 2010, Nanopatterning of graphene with crystallographic orientation control, *Carbon*, 48(10): p. 2677-2689.
- [76]. Young-Soo Choi, X.W., and Dong-Weon Lee, 2014, Selective nano-patterning of graphene using a heated atomic force microscope tip, *Review of Scientific Instruments*, 85: p.045002
- [77]. Weng, L.S., et al., 2008, Atomic force microscope local oxidation nanolithography of graphene, *Applied Physics Letters*, 93(9): p. 3.
- [78]. Choi, Y.S., X. Wu, and D.W. Lee, 2014, Selective nano-patterning of graphene using a heated atomic force microscope tip, *Rev Sci Instrum*, 85(4): p. 045002.
- [79]. Puddy, R.K., C.J. Chua, and M.R. Buitelaar, 2013, Transport spectroscopy of a graphene quantum dot fabricated by atomic force microscope nanolithography, *Applied Physics Letters*, 103(18): p. 4.
- [80]. Neubeck, S., et al., 2010, Scanning probe lithography on graphene, *Physica Status Solidi B-Basic Solid State Physics*, 247(11-12): p. 2904-2908.
- [81]. Lu, G., et al., 2010, Nanolithography of single-layer graphene oxide films by atomic force microscopy, *Langmuir*, 26(9): p. 6164-6.
- [82]. Mate, C.M., et al., 1987, Atomic-scale friction of a tungsten tip on a graphite surface, *Phys Rev Lett*, 59(17): p. 1942-1945.
- [83]. Erlandsson, R., et al., 1988, Atomic Scale Friction between the Muscovite Mica Cleavage Plane and a Tungsten Tip, *Journal of Chemical Physics*, 89(8): p. 5190-5193.
- [84]. Tanizawa, K. and K. Yamamoto, 2004, Measuring Apparatus of Membrane Tension and Its Characteristics, *Theoretical and Applied Mechanics Japan*, 53: p. 75-82.
- [85]. Lee, C., et al., 2008, Measurement of the elastic properties and intrinsic strength of monolayer graphene, *Science*, 321(5887): p. 385-388.
- [86]. Burnham, N.A. and R.J. Colton, 1989, Measuring the Nanomechanical Properties and Surface Forces of Materials Using an Atomic Force Microscope, *Journal of Vacuum Science & Technology a-Vacuum Surfaces and Films*, 7(4): p. 2906-2913.
- [87]. Burnham, N.A., et al., 1990, Probing the surface forces of monolayer films with an atomic-force microscope, *Phys Rev Lett*, 64(16): p. 1931-1934.
- [88]. Yazici, E., S. Yanik, and M.B. Yilmaz, 2017, Graphene oxide nano-domain formation via wet chemical oxidation of graphene, *Carbon*, 111: p. 822-827.
- [89]. Ferrari, A.C., 2007, Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects, *Solid State Communications*, 143(1-2): p. 47-57.

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Yazıcı E., Yanık S., Yılmaz M.B., (2017). Graphene oxide nano domain formation via wet chemical oxidation of graphene. <i>Carbon</i> , 111, 822-827., Doi: 10.1016/j.carbon.2016.10.062.	

- Yanık S., Yanık C., Yıldırım S., Yılmaz M.B. (2017). The investigation of electrical and mechanical properties of graphene/graphene oxide hybrid structures. *Türk Fizik Derneği 33. Uluslararası Fizik Kongresi*, 33 (Oral presentation)
- Bakış Y., Yanık S., Gülegül Z., Özsoy K., Şimşek Ç. (2016). Fabrication of Nanostructures on Highly Doped Si Substrate for Various Applications using E-Beam Lithography and Reactive Ion Etching. *12th Nanoscience and Nanotechnology Conference* (Oral presentation)
- Bakış Y., Yanık S., Gülegül Z., Şimşek Ç., Özsoy K. (2016). Fabrication of Organic Thin Film Transistor With Lateral Si SiO₂ Channel Gate. *12th Nanoscience and Nanotechnology Conference* (Oral presentation)
- Yılmaz M. B., Yanık S., Yazıcı E. (2016). Wet Chemical Oxidation of Single Layer Graphene A Microscopic Study. *12th Nanoscience and Nanotechnology Conference* (Oral presentation)
- Şeker İ., Yanık S., Karakız M. (2015). Characterization of Au capped Si Nanowhiskers by XRD SEM and Semiconducting Analysis. *International Semiconductor Science and Technology Conference* (Oral presentation)
- Şeker İ., Ünal B., Bakış Y., Karakız M.B., Yanık S. (2014). Influence of Layer Design and Growth Conditions on the Structural Optical and Electrical Properties of Epitaxial SiGe Quantum Dots. *European Conference on Surface Science* (Oral presentation)
- Yazıcı E., Develioğlu Z.R., Yanık S., Yılmaz M.B. (2013). Investigation of Early Stages of Graphite Oxide Formation via Modified Hummers Method. *9th Nanoscience and Nanotechnology Conference* (Oral presentation)
- Yanık S., Yazıcı E., Yılmaz M.B., Gölcük K. (2011). A Raman and AFM Study of Exfoliated Graphene on SiO₂ and Mica. *7th Nanoscience and Nanotechnology Conference* (Oral presentation)

Projects and Awards

- Awareness of Nanotechnology Building from 7 to 70, TÜBİTAK 4004, *Instructor*, 01/09/2013 - 01/05/2014
- Preparation and Characterization of Graphene on SiO₂ and Mica Surfaces by micromechanical exfoliation, University Funding, *Researcher*, 01/01/2010 - 01/01/2011
- Preparation and Characterization of graphene/graphene oxide hybrid structures, TÜBİTAK 3501, *Scholarship*, 01/07/2011 - 01/01/2014
- A unique lamb wave device design that controls the piezoelectric film tension, providing an adjustable phase using an analog voltage, TÜBİTAK 3501, *Scholarship*, 15/12/2017 – continuing

PhD scholar for priority areas by TUBITAK 2211-D, 2014

