

**DOKUZ EYLÜL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**PREPARATION AND CHARACTERIZATION OF  
DIFFERENT GRAPHENE BASED-MATERIALS  
AND INVESTIGATION IN GRAPHENE/SILICON  
SCHOTTKY JUNCTION SOLAR CELL**

by  
**Ala Khalaf JEHAD**

**March, 2021**  
**İZMİR**

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AND INVESTIGATION IN GRAPHENE/SILICON  
SCHOTTKY JUNCTION SOLAR CELL**

**A Thesis Submitted to the  
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**by  
Ala Khalaf JEHAD**

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**İZMİR**

## Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**PREPARATION AND CHARACTERIZATION OF DIFFERENT GRAPHENE BASED-MATERIALS AND INVESTIGATION IN GRAPHENE/SILICON SCHOTTKY JUNCTION SOLAR CELL**” completed by **ALA KHALAF JEHAD** under supervision of **PROF. DR. KEMAL KOCABAŞ** and **ASSOC.PROF. DR. METİN YURDDAŞKAL** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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# **PREPARATION AND CHARACTERIZATION OF DIFFERENT GRAPHENE BASED-MATERIALS AND INVESTIGATION IN GRAPHENE/SILICON SCHOTTKY JUNCTION SOLAR CELL**

## **ABSTRACT**

In this thesis, three graphene forms are synthesized using practical and cost-effective methods. Graphene oxide (GO) powder, few-layer graphene flakes (FLG), and monolayer graphene sheet have been synthesized by modified Hummers' method, electrochemical exfoliation (EE) method, and chemical vapor deposition method (CVD), respectively. Pure GO with lateral size of 4-80  $\mu\text{m}$  was successfully synthesized. High-quality FLG were synthesized by EE method followed by sonication in DMF and rapid microwave (MW) treatment. Raman spectra confirms the formation of few-layer graphene in the final product. High quality mono-layer graphene sheet was on the copper foil was confirmed by Raman Spectroscopy measurements with  $I_{2D}/I_G = 2.05$  and low defect density of  $I_D/I_G = 0.14$ .

Graphene based photovoltaic device has been investigated, where CVD graphene sheet with n-type silicon in order to fabricate graphene/silicon (G/Si) Schottky junction solar cell with top-window structure and active area of  $0.11\text{ cm}^2$ . The effect of moderate and high-doped n-Si were investigated for making Schottky device. The effect of etching time of  $\text{SiO}_2$ , thermal annealing to graphene, and p-doping graphene were also examined. Annealing treatment showed a noteworthy reduction in the PMMA residue, while, graphene p-doping with nitric acid vapors and GO dispersion showed an enhancement in graphene's work function. The best obtained power conversion efficiency (PCE) was found around 3.2% in Pristine graphene/moderate n-Si, and 2.24% in p-G/highly n-Si Schottky junction solar cell after thermal annealing and doping with synthesized GO.

**Keywords:** Graphene material, electrochemical exfoliation, graphene based Schottky junction solar cell, thermal annealing, doping

# FARKLI GRAFEN ESASLI MALZEMELERİN HAZIRLANMASI VE KARAKTERİZASYONU VE GRAFEN/SİLİSYUM SCHOTTKY EKLEMLİ GÜNEŞ HÜCRESİNİN İNCELENMESİ

## ÖZ

Bu tezde, kolay ve uygun maliyetli yöntemler kullanılarak grafenin üç formu sentezlenmiştir. Grafen oksit (GO) tozu modifiye edilmiş Hummers yöntemiyle, birkaç katmanlı grafen pulları (FLG) sonikasyon ve mikrodalga'nın yanı sıra elektrokimyasal eksfoliasyon yöntemiyle ve tek katmanlı grafen levha da kimyasal buhar biriktirme yöntemiyle (CVD) üretilmişlerdir. Düzlemsel boyutu 4-80  $\mu\text{m}$  olan saf grafen oksit başarıyla üretilmiştir. Yüksek kaliteli FLG pulları elektrokimyasal eksfoliasyon (EE) yöntemiyle başarıyla sentezlendi, ardından DMF'de sonikasyon ve hızlı mikrodalga (MW) işlemi yapıldı. Raman spektrumları, nihai üründe birkaç katmanlı grafen oluşumunu doğrulamaktadır. Yüksek kaliteli tek katmanlı grafen levha, geçiş metali olan bakır folyo üzerine CVD yöntemi ile sentezlendiği Raman spektroskopisindeki  $I_{2D}/I_G = 2,05$  ve düşük kusur yoğunluğu  $I_D/I_G = 0,14$  ile teyit edilmiştir.

Grafen esaslı fotovoltaiik cihaz incelenmiştir, üst görünüş yapısında aktif alanı 0,11  $\text{cm}^2$  olan grafen levha olan grafen/silisyum (G/Si) Schottky cihazını üretmek için CVD'de üretilen grafen ve n-tipi silikon altlıklar kullanılmıştır. Schottky cihazını elde etmek için orta ve yüksek katkılı n tipi silisyumun etkisi de araştırılmıştır. Ayrıca,  $\text{SiO}_2$ 'nin dağlanma süresi ile grafenin ve p tipi katkılı grafenin ısı tavlama sürecinin etkisi de incelenmiştir. Tavlama işlemi, PMMA kalıntısında kayda değer bir azalma gösterirken, nitrik asit buharları ve GO dispersiyonu ile p-katkılı grafen, grafenin çalışma fonksiyonunda bir artış göstermiştir. En iyi elde edilen güç dönüşüm verimliliği (PCE), termal tavlama ve sentezlenmiş GO ile katkılanmadan sonra saf grafen/orta katkılı n-Si'de % 3,2 ve p-katkılı grafen/yüksek katkılı n-Si Schottky eklemli güneş hücresinde yaklaşık % 2,24 bulunmuştur.

**Anahtar Kelimeler:** Grafen malzemesi, elektrokimyasal eksfoliasyon, grafen esaslı Schottky eklemli güneş pili, termal tavlama, doplama

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# **CHAPTER ONE**

## **INTRODUCTION**

### **1.1 Background**

Graphene has emerged among the academic society in such a captivating way, since the first isolation of graphene sheet in 2005 as the first 2D material discovered, researchers in academics and industry have dedicated much time to discover more about this wonder material. The sheet of one-atom thick of hexagonal geometry structure of carbon atoms has superior properties, it is highly conductive to electric and heat, transparent, very strong material, flexible and still helium atom cannot penetrate it. Graphene has different species, and can be produced in many methods. All these extraordinary properties of graphene have opened a new horizon in both nanotechnology and industry areas, whereas graphene has been used in electronics branch in order to design longer-lasting batteries, sensors and high-speed transistors, in the energy harvesting applications in order to make more efficient solar cells, in the coating composites to prevent surface corrosion, in the distillation process of non-fresh water, and in the biological applications.

### **1.2 Objective of the Study**

The aim of this study is to synthesis graphene material and employ it in a photovoltaic device. Accordingly, this research can be divided into two parts; the first part is dealing with graphene synthesis methods, where three different graphene materials have been synthesized; graphene oxide powder, few-layer graphene flakes, and mono-layer graphene sheet. Whilst, the second part is dealing with employing the synthesized graphene in a simple photovoltaic device which is graphene/silicon (G/Si) Schottky junction solar cell. Plain and cost-effective methods were used in order to produce good quality and stable graphene by modified Hummers' method, electrochemical exfoliation (EE) method, and chemical vapor deposition (CVD) method. Later, the preferable graphene was chosen to make the photovoltaic device, whereas CVD graphene was chosen to make the Schottky junction with silicon along with GO powder was used later as a p-dopants to graphene sheet. G/Si Schottky

junction solar cell with a top-window design has been fabricated without using the photolithography system.

### **1.3 Organization of the Thesis**

This thesis is of seven chapters deals with two main parts which are synthesis different graphene material and employing it the photovoltaic application. Chapter 2 provides a comprehensive view on the history of the discovering graphene, literature background, graphene species, properties of graphene, and sorts of graphene applications. Chapter 3 provides detailed theories about the construction of Schottky junction between semiconductor and metal as well as graphene. Chapter 4 highlights and describes the experimental methodologies used to produce graphene materials, the fabrication steps used to design the graphene/silicon junction with annealing and doping process and lastly the characterization tools used in this study according to the quality of graphene and the type of the solar cell. Chapter 5 deals with results of all synthesis graphene materials, where graphene oxide, reduced graphene oxide, few-layer graphene and mono-layer graphene have been examined throughout many characterization techniques. Chapter 6 underlines the results of the fabricated G/n-Si Schottky junction solar cell and the critical issues we have faced during optimizing the solar cell performance, it also discusses how PMMA residue can affect the cell main parameters which significantly impacts of not having a good Ohmic contact. Chapter 7 concludes and sums up the major findings, results, and suggestions to some potential future work when G/Si junction is made.

## CHAPTER TWO

### GRAPHENE: INTRODUCTION, SYNTHESIS METHODS, PROPERTIES, AND APPLICATIONS

#### 2.1 The Inception of Graphene

As stated by International Union of Pure and Applied Chemistry (IUPAC), graphene is a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size (Fitzer et al., 1995). Pristine graphene is a single layer of carbon atoms tightly bound into a two-dimensional hexagonal crystal lattice consists of  $sp^2$  hybridization of carbon atoms (Brownson & Banks, 2010). The packed layers of graphene (G) together called graphite (Gr) which is considered as a parent of graphene. Graphene sheets in graphite are separated by 0.335 nm distance and aligned on top of each other by weak van der Waals forces (Geim & Kim, 2008). Graphite, diamond, amorphous carbon, and nanocarbon are major allotropes forms of carbon, each allotrope has a distinctive electronic structure of carbon atoms that allow to build up  $sp^3$ ,  $sp^2$ , and  $sp$  hybridization networks (Georgakilas, 2014).

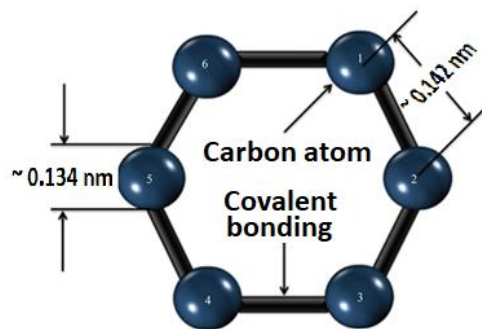


Figure 2.1 Typical structure of graphene

Carbon atoms share the same basic structural arrangement in graphite, fullerenes and graphene, where six carbon atoms are tightly bound in hexagonal lattice with ~0.142 nm separation distance (Geim & Kim, 2008) as shown in Figure 2.1. On the other hand, graphene is considered as the basic building block for graphitic materials

of all other dimensionalities shown in Figure 2.2. Planar sheet of graphene can be wrapped up into 0D fullerenes ( $C_{60}$ ), rolled into 1D carbon nanotubes (CNT) or stacked into 3D graphite (Brownson & Banks, 2014). It is noteworthy to mention that a single sheet of pristine graphene is considered as a graphene nanosheet (GNS) which implies a large, scalable graphene sheet of ‘quasi-infinite size’.

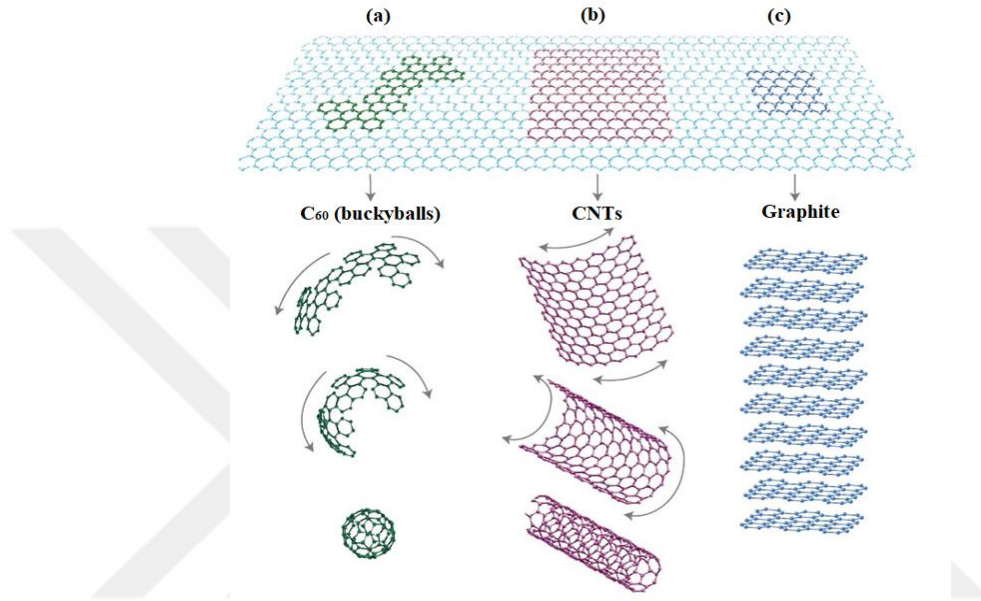


Figure 2.2 Schematic representation of graphitic materials of graphene, (a) fullerene ( $C_{60}$ ), (b) carbon nanotubes (CNTs), (c) graphite (adopted from Geim & Novoselov, 2010)

## 2.2 Brief History of Graphene

Graphene came into the scientific perspective in such a captivating way. The accurate theoretical history of graphene has begun in 1947 when Philip Wallace introduced his pioneering paper regard the electronic behavior of graphite that eventually led to the discovery of graphene (Wallace, 1947). The name of graphene has been coined in 1986 when Boehm *et al.* reported their observations of the existence of graphene (Boehm et al., 1986). The term “Graphene” was used to designate the individual carbon layers in graphite intercalation compounds. Earlier in 1962, Boehm *et al.* found that the chemical reduction dispersions of graphene oxide (rGO) in alkaline media such as hydrazine and hydrogen sulfate contained a lamellar carbon with small amounts of hydrogen and oxygen (Boehm et al., 1962). Moreover, the electrical

conductivity of these layers were found significantly less than the one in graphene (Park & Ruoff, 2009). However, graphene did not manifest until 2005 when two scientists from Manchester university, Andre Geim and Konstantin Novoselov could isolate a sheet of ‘pristine’ graphene for the first time using simple tools; pencil, paper and sticky tape (Novoselov, et al., 2005). In 2010, the Nobel Prize in Physics was awarded jointly to Geim and Novoselov for the discovery of the first two-dimensional crystalline material graphene (Brownson & Banks, 2014).

Thus, this technique was copied worldwide as a protocol to produce graphene sheets in large area. Dreyer *et al.* have represented in detail the history, preparation and characterization of graphene (Dreyer et al., 2010) shown in Figure 2.3.

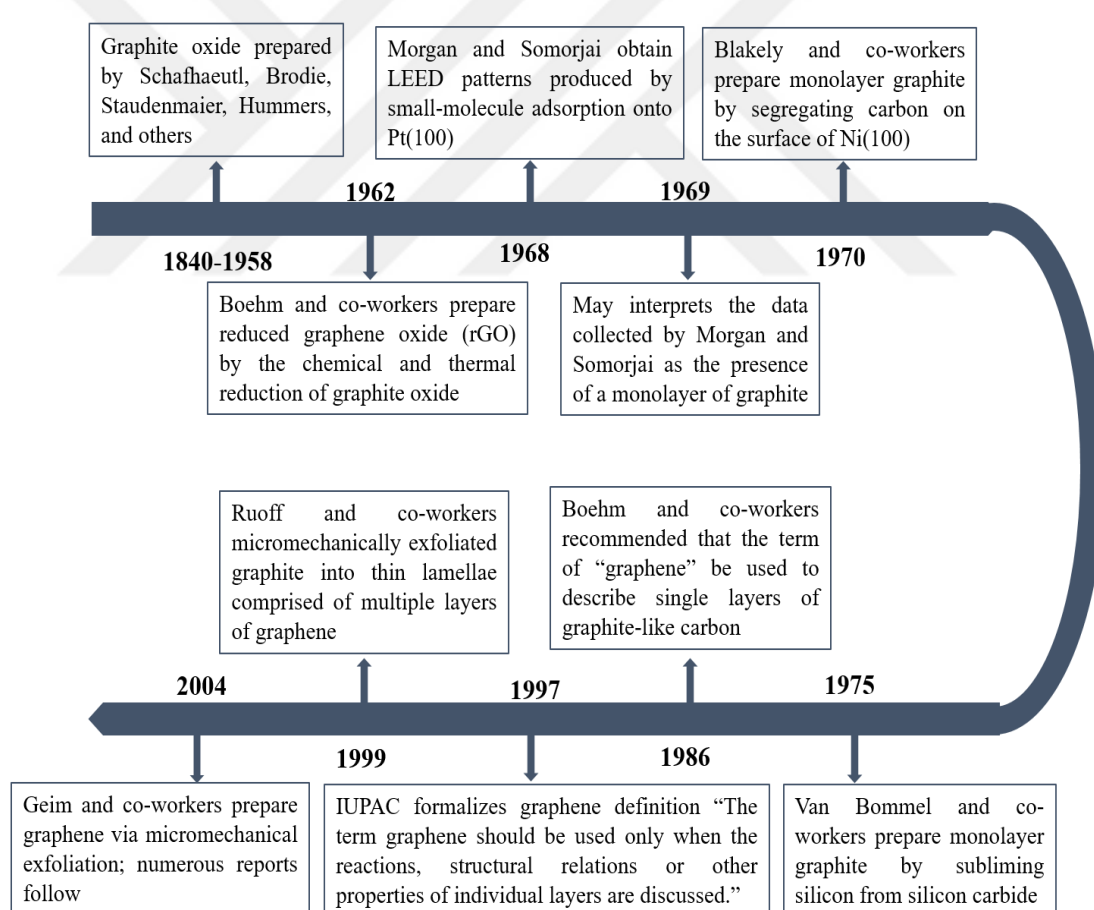


Figure 2.3 A timeline of selected events in the history of preparation, isolation and characterization of graphene (reproduced and adapted from Brownson & Banks, 2014; Dreyer et al., 2010)

### 2.3 Graphene Forms

Graphene exists in different forms, each used for specific purposes:

- CVD graphene (monolayer or bilayer) synthesis by chemical vapor deposition (CVD).
- Graphene oxide (GO) and reduced graphene oxide (rGO) synthesis by oxidation Modified Hummer's method.
- Graphene nanoplates (GNPs) or nanosheets synthesis by chemical exfoliation method.
- Graphene quantum dots (GQD) is a graphene flake with size less than 100 nm.
- Graphene foam is a 3D structure of graphene (GF) synthesis by CVD.
- Graphene aerogel is an aerogel made of graphene layers separated by carbon nanotubes.

### 2.4 Graphene Synthesis Methods

Since the pioneering paper of discovering graphene in 2005, imagination of many scientists around the world has been captured by the astonishing properties of graphene. Thus, many methods have been testified regarding graphene production (Berger et al., 2006; Li et al., 2009; Liu & Yan, 2009; Stankovich et al., 2006; Sutter et al., 2008). Graphene has been synthesized in various techniques and on different substrates, each fabricating or extracting technique depends on the desired type, size, quality, and purity of graphene material. Generally, graphene can be produced by two main approaches, top-down and bottom-up, see Figure 2.4.

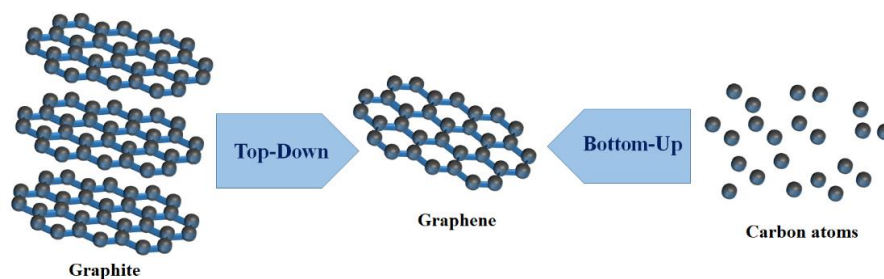


Figure 2.4 Two different approaches to produce graphene

### 2.4.1 Top-Down Approach

This approach suggests producing graphene by exfoliating or peeling up of the bulk graphite in order to break down the van der Waals forces between stacked graphite layers (d-spacing). Bulk graphite has been used as a starting material in the manner to exfoliate it to obtain different graphene-based materials, such as single layer, few-layer, or multi-layer of graphene, graphene oxide, or reduced graphene oxide sheets. Three different methods may include for top-down approach, micromechanical exfoliation, liquid phase exfoliation, and oxidation method (Hummer's Method). Top-down approaches are preferred in terms of scalable, low-cost and high production yield of GNS.

#### 2.4.1.1 Micromechanical Exfoliation (Mechanical Cleavage)

Micromechanical cleavage and so-called the scotch tape method, which shows how graphene was first isolated (Novoselov, et al., 2005). Simply, by using an adhesive tape that performs the exfoliation process by cleaving apart of graphite layers as shown in Figure 2.5, where graphite can be simply exfoliated using an adhesive tape (Zheng & Kim, 2015a).

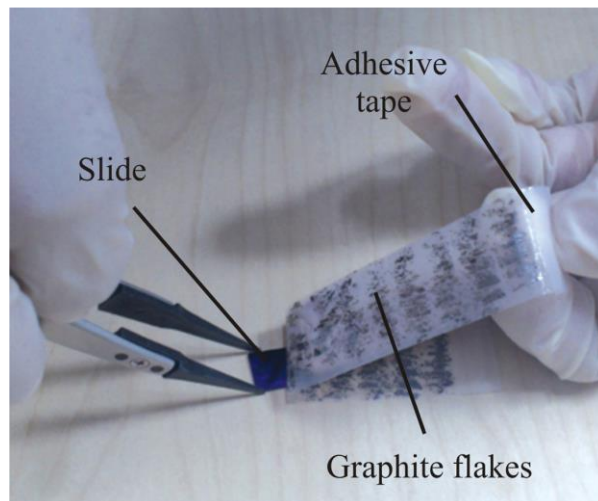


Figure 2.5 Scotch tape' procedure, reported by Novoselov and Geim in 2004, picture adapted from (Noorden, 2012)

Repeating this for few times is adequate to obtain a mono-layer of graphene flakes. Later, graphene flakes can be transferred gently onto a cleaned substrate to examine it with microscope. Produced graphene sheets by this method have high crystal quality and low defects (Sinclair et al., 2019) besides that the effective separation can be done without damaging the individual sheets and preventing of re-agglomeration. However, this method is preferred only for laboratory due to its low production yield (Mahato et al., 2015; Ranjbartoreh et al., 2011).

#### *2.4.1.2 Liquid Phase Exfoliation method (LPE)*

Liquid phase exfoliation (LPE) method (Hernandez et al., 2008; Lotya et al., 2009) is considered as a principle method of producing 2D materials such as graphene in large quantities and in a cost-effective way. This method includes three steps. Preparation of graphite dispersion with a suitable solvent, which can be organic solvent, ionic liquid, or water surfactant. The exfoliation technique may include electrochemical, sonication, or mechanical. Lastly, washing and purifying the exfoliated graphene dispersion. By intercalation of bigger molecules (guest species) between graphite sheets in the dispersion, the inter-planar spacing in graphite becomes easier to separate. LPE methods include direct LPE (Park & Ruoff, 2009), graphite intercalation compound (Melezhyk & Tkachev, 2014), and electrochemical exfoliation (Su et al., 2011; Yang et al., 2015; Yang et al., 2019). Produced graphene by this method might consist single-, few-, and multi- layers of graphene nanosheets (GNS), with some impurities and structural defects.

#### *2.4.1.3 Oxidation (Hummer's Method)*

In this method, oxidizing graphite is the first step, then exfoliation graphite oxide to graphene oxide (GO) followed by chemical or thermal (Stankovich et al., 2007). Oxidation process increases the d-spacing hence weakens the interaction between stacked graphene sheets. Currently, modified Hummer's method is considered as a common route towards the production of graphene nanosheets (GNS) by this approach (Patil et al., 2015; Yu et al., 2015). The major advantages of modified Hummer's method are the stability of both GO and rGO as well as controlling the amount of functional groups such as epoxy, hydroxyl and carboxyl in the obtained graphene

sheets. However, the lateral size of rGO sheets are found in the range of several hundred nanometers to several micrometers which is appropriate for mass production applications such as coating, conductive ink paste, energy storage application.

### 2.4.2 Bottom-up Approach

In this approach, carbon molecules from different sources are considered as the building blocks. Graphene is performed by molecular growth of carbon atoms and this could be either by chemical vapor deposition (CVD) or epitaxial grown on a substrate. Figure 2.6 illustrates graphene synthesis methods quality with prices.

#### 2.4.2.1 Epitaxial Growth

Graphene can be epitaxial grown on various crystalline surfaces like as silicon carbide (SiC) by heating the surface of silicon carbide to high temperatures under vacuum (Allen et al., 2010; Sutter, 2009). At  $\sim 1300^\circ\text{C}$ , silicon atoms sublime while carbon atoms enrich the surface to form graphene. Graphene layers can be obtained directly on a semiconductor or semi-insulator substrate. In this method, at least three bilayers of SiC are necessary to set free enough carbon atoms needed to form a single layer of graphene (Yu et al., 2011).

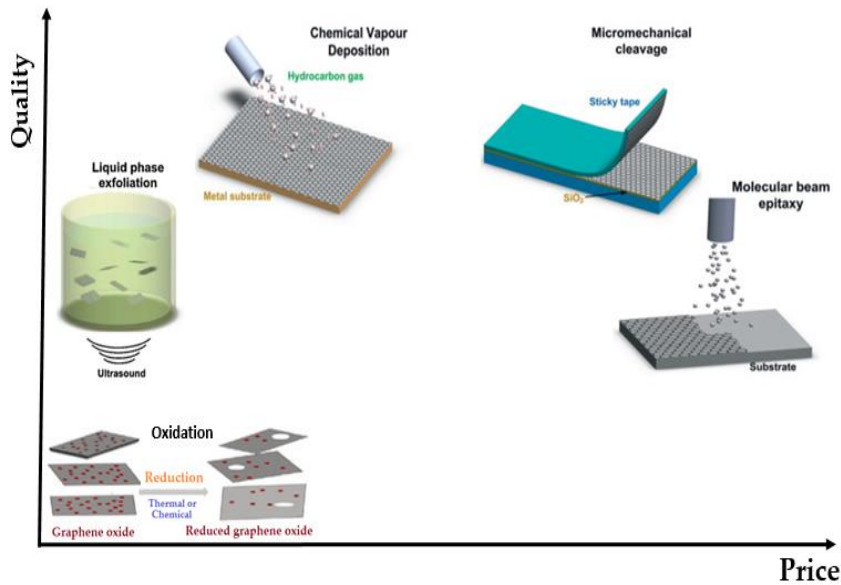


Figure 2.6 Mass production graphene methods, quality and price

This method offers the possibility to avoid transferring of free standing high quality nanostructured graphene with large area to the desired substrate. Graphene on SiC has been used in electronic devices, such as field effect transistors, radio frequency transistors, integrated circuits, and sensors. Disadvantages of this method is high production cost beside producing graphene in small grain size and different thicknesses (30 nm-200 nm) which caused by applying high temperatures.

#### *2.4.2.2 Chemical Vapor Deposition (CVD)*

Chemical vapor deposition (CVD) method is a preferable method to produce high quality graphene layer/s. Where graphene is deposited on transition metal films that endure high temperatures such as copper, nickel or iron foils as a catalyst substrate and by introducing a hydrocarbon gas such as methane, carbon atoms can nucleate to form graphene. Cu foil is preferred as a catalyst substrate due to low solubility of carbon atoms on it as well as the well-controlled number of the graphene layers (Murakami et al., 2015).

CVD method is considered as one of the most promising methods to produce high crystal quality and large-area (few centimeter scale) graphene sheets, besides the possibility of tuned graphene chemically basically by changing gas source (Park et al., 2010). After growth process, produced graphene onto the catalyst substrate is required to protect first by spin-coating of a resist polymer before etching the catalyst film with an appropriate acid. Later, transferring graphene to a desired substrate which might cause contamination, defects, or wrinkles to the graphene layer (Regan et al., 2010).

## **2.5 The Extraordinary Properties of Graphene**

Graphene is one of the most attractive carbon nanostructures with exceptional mechanical, optical, thermal, and electrical properties. Scientists and researchers in academics and industry have been fascinated about it. It is a very light material at the same time very strong and flexible, an excellent heat and electric conductor, and yet helium atom cannot penetrate it.

### 2.5.1 The Electronic Structure of Graphene

Graphene is a two-dimensional hexagonal lattice structure consisting of  $sp^2$  hybridized carbon atoms shown in Figure 1.7 a. Each carbon atom has six electrons distributed in the atomic orbitals as  $1s^2 2s^2 2p^2$ . The two electrons in the  $1s^2$  orbital are strongly bonded, while the four remaining  $2s$ ,  $2p_x$ ,  $2p_y$  and  $2p_z$  are the valence electrons. The  $2s$ ,  $2p_x$  and  $2p_y$  orbitals combine/hybridize to form three planar orbitals covalent bonds so-called  $\sigma$ -bonds, each having one electron combine with its three neighbors. Whereas, the  $p_z$  orbital so-called  $\pi$ -bond is oriented out of plane of carbon atoms and do not contribute to the hybridization as shown in Figure 1.7 b.

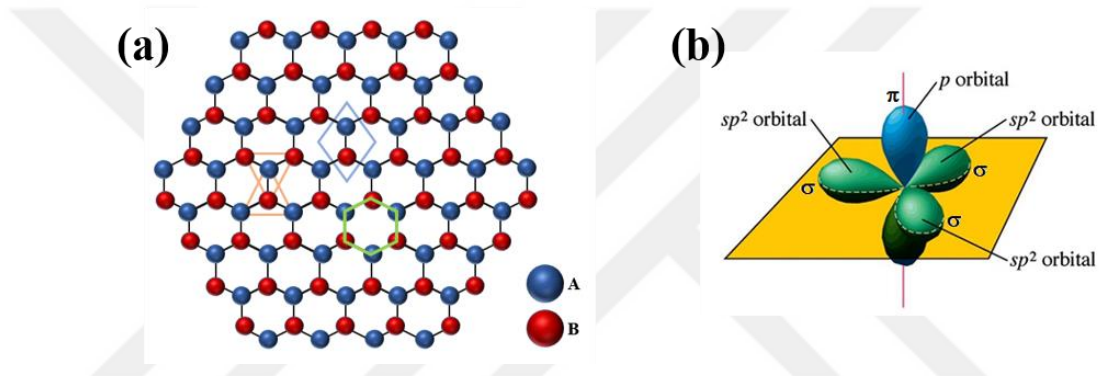


Figure 2.7 (a) Graphene hexagonal lattice with representation of unit cell, (b) The  $sp^2$  hybridization orbitals of graphene (reproduced and adopted from Bao, 2011)

The  $\sigma$ -bonds are responsible for the mechanical stability of the carbon sheet, while  $p_z$  orbitals (overlap to form a band of filled  $\pi$  orbitals (valence band) and a band of empty  $\pi^*$  orbitals (conduction band)) are responsible for conduction phenomena in graphene (Soldano et al., 2010). Graphene hexagonal lattice can be interpreted as a two interleaving triangular sub-lattices showed in Figure 2.7 a, each with centered atom. The unit cell can be represented as a hexagonal, rhombus or two triangle sub-lattices containing of two atoms and it remains unchanged under a rotation of  $120^\circ$  around any atom (Soldano et al., 2010). Where each lattice consists of only A and B carbon sites.

### 2.5.2 Mechanical Properties

Graphene is considered as the strongest, thinnest and lightest material ever discovered. In 2008, Lee *et al.* were able to measure the elastic properties and the strength of free-standing monolayer pristine graphene membrane by nanoindentation in an atomic force microscope (AFM) (Lee et al., 2008). Graphene sheets were suspended on the top of small holes (1.5, 1, 0.5  $\mu\text{m}$  diameter) of  $\text{SiO}_2/\text{Si}$  substrate. The results showed that breaking strength (tensile stress) of a defect-free graphene sheet is 42 N/m. Later in 2013, Lee *et al.* utilized the transmission electron microscopy (TEM) with nanoindentation to examine the mechanical properties of CVD graphene (Lee et al., 2013). The study concluded that the elastic stiffness of CVD graphene is matched with the pristine graphene. In addition, graphene sheet consists of well-stitched grain boundaries that can maintain ultrahigh strength and even stronger than previously measured values (Huang et al., 2011; Tsen et al., 2012), which is in agreement with the maximum values predicted in simulations. The flexibility and stretch ability of graphene reached up to 20% of its initial length (Yu et al., 2017).

Based on the model of atomic-scale ab initio density functional theory (Van Lier et al., 2000), graphene has been found to be 7 times harder than diamond and 300 times stronger than a stainless steel of the same thickness (Lee et al., 2008). The Young's modulus of graphene sheet has been found around 1 TPa and a fracture strength of 130 GPa.



Figure 2.8 Bright-field TEM image of a suspended graphene membrane. Adapted from (Meyer et al., 2007)

A study by Meyer *et al.*, reported a free suspended of single graphene sheet on a micro-fabricated scaffold in vacuum have been tested by transmission electron microscopy (TEM). The results showed that graphene sheets are not perfectly flat and in fact they exhibit some roughness and deformation within the scale of 1 nm as shown in Figure 2.8 (Meyer et al., 2007).

### **2.5.3 Optical Properties**

Transparent graphene has exceptional optical properties, where mono-layer graphene absorbs only 2.3% of the incident light and transmits around 97.7% (Lindvall, 2012; Nair et al., 2008). Figure 2.9a shows mono- and bi- layer of graphene cover a hole of 50 nm partially. Therefore, bilayer graphene absorbs 4.6% and for five-layers about 11.5% (Fan et al., 2012).

The transparency of a single layer graphene decreases linearly as the number of layers' increases. Since it is not easy to observe the single layer of graphene due to its high transparency, graphene layer is usually transferred on silicon substrate coated with 300 nm of SiO<sub>2</sub> which is considered as the minimum thickness makes graphene visible.

Thus, it is possible to distinguish the number of graphene layers due to the color shift of graphene layers onto a SiO<sub>2</sub>/Si (Blake et al., 2007). Nair *et al.* reported in their study in 2007 (Blake et al., 2007; Nair et al., 2008) that the visibility of graphene on SiO<sub>2</sub>/Si depends on both thickness of the oxide layer and the wavelength of the light (Nair et al., 2008).

However, when graphene nonosheets are dispersed in organic solvents the liquid shows a gray color and becomes darker as the amount of graphene increases. Graphene possess zero band gap energy so there will not be any optical losses which makes preferable for photovoltaic applications (Suhail, 2019) such as transparent flexible electrodes in touch screens (Bae et al., 2010), organic light emitting diodes (Han et al., 2012), and solar cells (Wang et al., 2009).

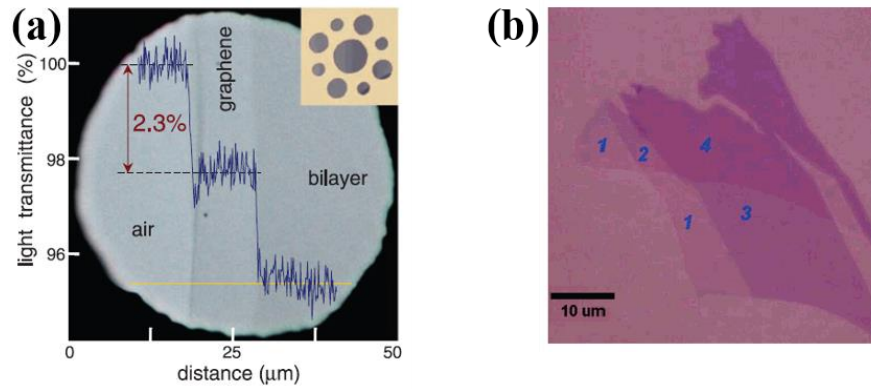


Figure 2.9 (a) mono- and bi- layer of graphene cover a hole of 50 mm partially (adopted from Nair et al., 2008). (b) Optical image of graphene sheets with mono-, bi, tri-, quad- layers on a 285 nm thick SiO<sub>2</sub>/Si substrate (adopted from Ni et al., 2007)

#### 2.5.4 Thermal Properties

Pursuing to find an excellent heat conductor material became a necessity for the next generations of integrated circuits, optoelectronic and advanced electronics. The thermal conductivity ( $k$ ) depends on the structured scale and it differs from nano- to bulk due to the increasing of phonon-boundary scattering (Chen et al., 2001) or changing in phonon dispersion (Balandin & Wang, 1998). 2D sheet of graphene material consists over 100-fold anisotropy of heat flow between the in-plane and out-of-plane directions. High in-plane thermal conductivity is due to  $sp^2$  bonding among carbon atoms, while out-of-plane thermal conductivity is limited by weak van der Waals coupling (Pop et al., 2012). Thus, it is easy to say that the thermal conductivity of graphene is controlled by both phonon transport (diffusive conduction) at high temperature and ballistic conduction at low temperature (Zhu et al., 2010).

In 2008, Balandin *et al.* examined the thermal conductivity of a suspended single-layer graphene experimentally for the first time with a confocal micro-Raman spectroscopy assisted (Balandin et al., 2008). Graphene's thermal conductivity was found around 5300 W/m.K at room temperature. The thermal conductivity was measured based on the dependence of the Raman G band frequency on the excitation laser power, where Raman spectrometer acts as a thermometer to measure the local temperature rise in graphene that responds to the Raman laser heating (Yan et al.,

2015). Figure 2.10 shows the schematic view of the thermal conductivity measurements of graphene sheet.

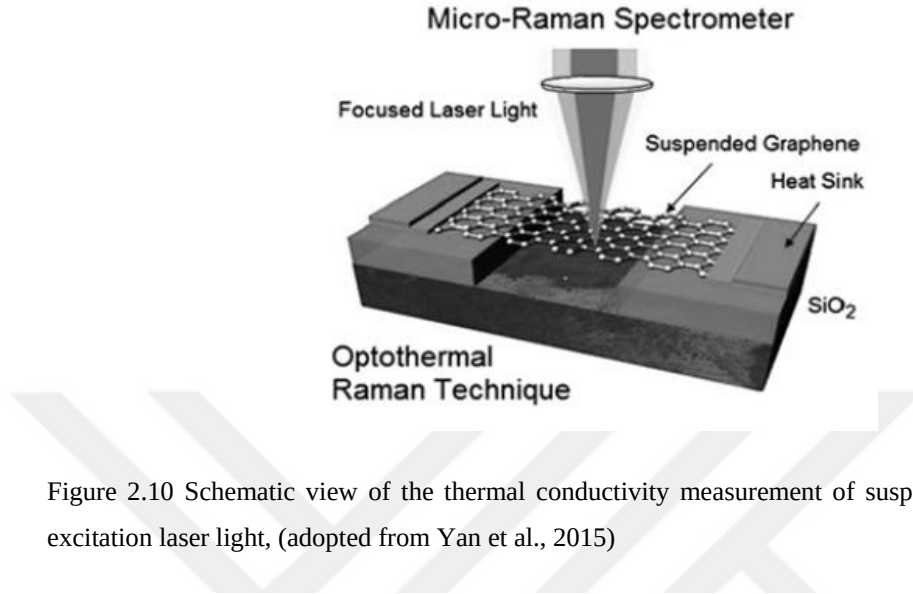


Figure 2.10 Schematic view of the thermal conductivity measurement of suspended graphene and excitation laser light, (adopted from Yan et al., 2015)

In Yan *et al.* study, the intrinsic thermal conductivity of graphene was reported as the dominated by the phonons near the room temperature (Yan et al., 2015). It also showed that few-layer graphene (FLG) heat spreaders can lower the hot-spot temperature during device operation which is demanded to improve the performance of the electronic devices. Same approach (micro-Raman spectroscopy) was used in Cai *et al.* study but CVD with Cu- assisted mono-layer graphene was suspended over a circular hole. The thermal conductivity of monolayer graphene sheets was found around  $\sim 2500$  W/mK,  $\sim 1400$  W/mK at 350 K and 500 K respectively (Cai et al., 2010).

### 2.5.5 Electrical Properties

Graphene has a unique band structure, where carbon atoms are arranged in a hexagonal lattice in 2D (xy) plane. Each carbon atom is  $1.42 \text{ \AA}$  away from its three neighbors ( $\sigma$  bonds) Figure 2.1. The fourth bond ( $\pi$ -bond) is perpendicular on the plane (z direction) and responsible for graphene electronic properties. The band structure is defined by the relation between the energy and momentum of electrons using a tight-binding approximation (Wallace, 1947). In the case of high crystal quality graphene sheet, electrons are moving in two dimensions and able to travel to sub-micrometer

distances without scattering in a phenomenon known as ballistic transport (Meyer et al., 2007). As graphene is a semimetal with a zero band gap, its conduction and valence bands meet at single point so-called Dirac points. There are six of Dirac points locations in momentum space at the Brillouin zone corner which are classified into two sets. Each set is not equivalent to the other labeled as K and K' (Cooper et al., 2012).

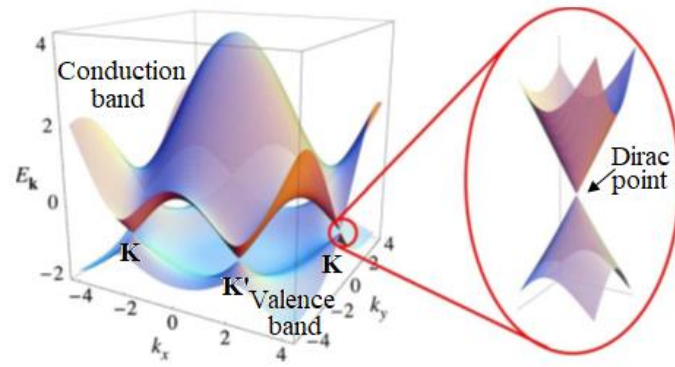


Figure 2.11 The band structure of graphene (adopted from Castro Neto et al., 2009)

Those two bands meet each other and produce a conical-shaped valley “cones” (Lau et al., 2012; Soldano et al., 2010) of graphene band structure. Figure 2.11 shows a plot of the energy versus momentum dispersion relation of graphene. The charge carriers in a perfect structure graphene sheet have very small effective mass, thus their mobility reach up to  $200,000 \text{ cm}^2/\text{V.s}$  at  $10^{12} \text{ cm}^{-2}$  carrier density (Du et al., 2008; Morozov et al., 2008; Novoselov, et al., 2005). In 2008, Du *et al.* reported that even at low temperature graphene’s mobility reach to  $200,000 \text{ cm}^2/\text{V.s}$  at carrier density of  $5 \times 10^9 \text{ cm}^{-2}$ .

The study also showed that the conductivity of suspended graphene on an insulating substrate depends on the temperature and could reach to ballistic state at  $\sim 4\text{K}$ . While, at higher temperature than  $100 \text{ K}$ , carriers noticed to begin long range of thermally induced scattering (Du et al., 2008). However, in Novoselov *et al.* and Morozov *et al.* studies (Morozov et al., 2008; Novoselov, et al., 2005), graphene carrier mobility reported as almost independent around temperature between  $10\text{-}100 \text{ K}$  which suggests that the dominant scattering mechanism is defect scattering.

## 2.6 Applications of Graphene

Since the isolation of graphene for the first time in 2005 by simply “Scotch Tape”, a great number of scientists dedicate their time to discover more about this wonder material. The academic publications rise up to 40 publications per day in 2013 due to the enormous interest in graphene (Randviir et al., 2014) and was about to 35,000 publications by the end of 2017 (Mohan et al., 2018). Graphene is a promised candidate in many potential applications depending on its type and required property. However, it can be employed in longer-lasting batteries (Zhao et al., 2011), high-speed transistors (Liao et al., 2010), more efficient solar cells (Miao et al., 2012; Wang et al., 2013), corrosion prevention (Prasai et al., 2012), circuit boards (Hyun et al., 2013), and medicinal technologies (Bonanni & Pumera, 2011).

### 2.6.1 Electronics

The unique atomic arrangement of carbon atoms in graphene as well as the atomic thickness of graphene eases the movement of electrons throughout the sheet, where they can travel for long distances before scattering. These properties opened a new scope of flexible and stretchable electronic devices, high speed electronics, transistors, superconductors, and data storage.

A study by Li *et al.* reported the fabrication of flexible and lightweight of lithium ion battery (LIB) by utilizing graphene foam (3D graphene) network (Li et al., 2012). The battery showed a good electrical conductivity, flexibility and high capacity. Another study by Hu *et al.* showed that using of defect-introduced graphene on the anode surface can provide pathways in LIB in order to enhance its capacity performance with shorter recharge time (Hu et al., 2016).

Graphene has a large surface area of  $2,600\text{ m}^2$  for each gram of graphene. This has found to considerably improve cathode electrochemical performance of the transistor (Kucinskis et al., 2013). In 2017, Liu *et al.* reported a development of a transparent stretchable conductive electrodes in graphene-based stretchable transistor made of graphene scrolls in (mono-, bi, and tri-) structures (Liu et al., 2017). Graphene is a

semimetal with zero band gap material which limits the achievable on–off switching in transistor. Even though, graphene has the potential to enable ballistic transistors (electrons avoid collisions) at room temperature. Various techniques have been used to accomplish graphene band gap. First graphene field-effect transistors (FETs) have already been demonstrated (Novoselov et al., 2004). It has been also tuned to 0.25 eV by applying voltage to a dual-gate of bilayer graphene field-effect transistor (FET) at room temperature (Zhang et al., 2009). The 400 meV bandgap of patterned graphene nanoribbons with a specific width have also been produced (Han et al., 2007; Li et al., 2008) and resulted high mobility degradation.

### 2.6.2 Sensors

Graphene's nanostructure, excellent electrical and thermal conductivities with large surface area makes it a good choice to detect individual molecules even at atomic scale by simply measuring the voltage changes in the presence of an analyte. The changing in voltage provides a determinate response of molecules to be detected. The defects in graphene's structure also offers a good surface adsorption for molecules to be detected. However, graphene whether in quantum dots, nanoparticle, oxide, or composite has been used in various sensor applications such as gas, chemical, temperature, optical, and biosensors (Aslam et al., 2019; Davaji et al., 2017; Deng et al., 2014; Jeong et al., 2015; Schedin et al., 2007).

In a study by Schedin *et al.*, it was reported the fabrication of a micrometer-size sensor made from exfoliated few-layer graphene (Schedin et al., 2007). The sensor was able to detect individual NO<sub>2</sub> gas molecule in vacuum environment. The study also showed that the electron acceptors and electron donors can be distinguished by their resistivity changes. It decreased with increasing of hole concentration (electron acceptors) and increased with increasing of electron concentration (electron donors). Another study by Jeong *et al.* reported the fabrication of highly stretchable up to 70% and sensitive strain up to 10,000 stretching cycles sensor made from a composite of fragmentized 3D graphene foam (FGF) and polydimethylsiloxane (PDMS) (Jeong et al., 2015). The study also showed that this sensor could be used in wearable bio-

sensors, where the positive bio-signals of the attached body were recognized such as wrist pulse, bending of elbows and fingers.

Moreover, the high sensitivity of graphene oxide to the adsorption of gas molecules makes it a good choice for gas sensing application. In 2009, a PhD work by Kayhan revealed a high-performance of gas sensor based on reduced graphene oxide (GO) sheets dispersed onto gold electrode (Kayhan, 2013). The partial thermal reduction of GO sheets was achieved throughout multi-annealing steps has showed a p-type semiconducting behavior. This behavior has exhibited a responsivity to low-concentration of NO<sub>2</sub> and NH<sub>3</sub> gases in ambient conditions.

### ***2.6.3 Energy Harvesting and Storage***

To keep up with the human civilization developments, scientists around the world are facing challenges to find a replacement source of energy to enable them giving up using the conventional nonrenewable sources of energy. Looking for a clean and renewable energy became a necessity, including hydrogen-based fuel cells, lithium batteries, supercapacitors, and solar cells. Graphene has become an attractive material to use in energy storage applications due to its high electrical conductivity and high surface area.

#### ***2.6.3.1 Hydrogen storage***

Several studies about using graphene for hydrogen storage have been reported. A study by Liu *et al.* highlighted a simple electrostatic assembly method to synthesis 3D hierarchically porous graphene with nickel nanoparticles (3DHPG-Ni) with the assistance of poly-methyl methacrylate (PMMA) (Yurong Liu et al., 2018). The nanocomposite structure showed a high specific surface area, large pore volume and higher hydrogen storage capacities at different temperatures. The study showed the possibility to improve the storage capacity by disrupting stacked graphene layers to increase the surface area.

### 2.6.3.2 Supercapacitors

Graphene is often suggested as an alternative candidate of existing carbon and polymer supercapacitors due to its high surface area. Graphene as a supercapacitors material was established first in 2008 by Stoller *et al.*, where electrode of graphene was synthesized by chemically modified method (Stoller *et al.*, 2008). The capacitance of the double layer capacitor showed dependency on the flexible graphene sheet instead of the porous structure of the activated carbon. The capacitor also showed a high electrical conductivity with specific capacitances of 135 F/g in aqueous and 99 F/g in organic electrolytes. Later, Wang *et al.* reported the fabrication of graphene materials supercapacitor using hydrazine gas-based as a reduction reagent of graphene oxide and the specific capacitance was found of 205 F/g at room temperature (Wang *et al.*, 2009).

Graphene nanosheets have been also used in the composition of graphene nanosheet/carbon nanotube/polyaniline (GNS/CNT/PANI) of an electrode for supercapacitor, where the composite synthesized via situ polymerization as Yan *et al.* study reported, graphene nanosheets were used as a support material which provides both high conductivity and mechanically strength (Yan *et al.*, 2010). The specific capacitance shows 1035 F/g with excellent cycle stability. Another study by Bai *et al.* reported a high capacitance supercapacitor using the electrode composite of reduced graphene oxide/carbon nanotubes/Nickel oxide (rGO/CNTs/NiO) (Bai *et al.*, 2014). The fabricated composite shows high electrical conductivity and electrochemical performance with the specific capacitance of 1180 F/g.

### 2.6.3.3 Solar cells

High optical transparency, high carrier mobility beside mechanical strength of graphene makes it an ideal material for photovoltaic (PV) applications. The ultrahigh optical transmittance of single layer graphene (~97.7%) allows a wide range of wavelengths from ultraviolet to far infrared to pass through the cell as well as fabricate the cell with more flexibility and more efficient as well as providing a high heat dissipation (Das *et al.*, 2014). The zero bandgap of graphene can be tuned by surface chemical modifications to employ it in various energy-harvesting applications.

Graphene has become a strong candidate as transparent conducting electrodes, flexible optoelectronics, and energy harvesting devices. In conventional transparent conducting electrodes, indium tin oxide (ITO) has been widely used that contains toxic indium and has a rare brittle nature as well as its high production cost (Patel & Tyagi, 2015).

To date, graphene has been employed different functions in PV applications (Behura et al., 2019). It has been used as a transparent conducting film in amorphous silicon (Altuntepe et al., 2020; Vaianella et al., 2015) that improved the cell efficiency by 8% and in the indium gallium nitride solar cells (Shim et al., 2011). Graphene has been used as an active light-harvesting material in silicon (Si) heterojunction solar cells, Fan *et al.* reported a Schottky junction of graphene on silicon nanowire solar cell with energy conversion efficiencies of up to 2.86% (Fan et al., 2011). However, Song *et al.* study reported higher efficiency up to 12.4% by controlling the thickness of the oxide layer between graphene and silicon (Song et al., 2015).

Graphene materials have been used as counter cathode electrodes as alternatives of Pt electrode for dye sensitized solar cells (DSSCs) (Kavan et al., 2011; Seo et al., 2013) due to its unique hybridization structure, high conductivity, and the ability to dope with metals, metal oxides, and polymers. A study by Dao *et al.* reported utilizing of reduced graphene oxide (rGO) besides with Pt nanoparticles to produce counter electrode of DSSCs (Dao et al., 2013). The cell showed a long-term stability and excellent energy conversion efficiency up to 8.56%.

Graphene has been also used as a photo-anode electrode in, organic, and quantum dot solar cells (Cao et al., 2016; Park et al., 2015; Wang et al., 2009) where the electrodes are required to be highly transparent and conductive. Park *et al.* recorded high power conversion efficiency of polymer solar cells (PSCs) on polyethylene naphthalate substrates based on graphene anode- and cathode reached to 6.1% and 7.1% respectively (Park et al., 2015). However, the cell has also showed some degree of bending under some conditions. Another study by Wang *et al.* reported using CVD few-layer graphene films as an anode in organic solar cells (OSCs) (Wang et al., 2009) along with pyrene buanoic acid succidymidyl ester. The study reported an improvement in the power conversion efficiency of the cell by 55%. One more study

by Cao *et al.* reported the synthesis of graphene/Zn-Ti (mixed metal oxides) MMO nanocomposite acting as an electrode of CdS in quantum dot solar cell (QDs), where the cell showed significant increases in the surface-absorbed and decreases in the charge transfer resistance with power conversing efficiency of 37.5% (Cao et al., 2016).

Graphene oxide and its derivatives have been also used as qualified hole-transporting materials (HTM) for hybrid organic–inorganic perovskite solar cells (Capasso et al., 2016; Niu et al., 2017; Stratakis et al., 2014). A study published by Niu *et al.* reported a high HTM with high mobility and transmittance using GO-doped PEDOT:PSS in perovskite solar cells films which improved the cell efficiency to 14.2% (Niu et al., 2017). The study also showed that adding graphene oxide led to reduce the charge recombination and improve both separation and collection of carriers. Another study reported by Yang *et al.* investigated the optimum thickness of GO prepared by modified Hummer method to use as a hole transporting material in perovskite solar cells (Yang et al., 2017). The cell achieved high power conversion efficiency up to 16.5% and showed excellent stability photocurrent even after 2,000 hours.

#### **2.6.4 Composites and Coatings**

Graphene's remarkable mechanical strength and low weight makes it a required material for different purposes such as body structured composites, anti-corrosion, super-hydrophobic coatings, and radiation shielding protection (Chen et al., 2013; Hashemi et al., 2018; Pourhashem et al., 2017; Wang et al., 2017). A study by Chen *et al.* reported a lightweight and flexible composite of graphene/poly(dimethyl siloxane) (PDMS) foam with density of only 0.06 g/cm<sup>3</sup> and stability electromagnetic interference (EMI) shielding of 500 dB.cm<sup>3</sup>/g under mechanical distortion (Chen et al., 2013). Another study published by Yu *et al.*, reported a preparation of a polymer-graphene hybrid coating, where two single layers of CVD graphene were sandwiched by three layers of polyvinyl butyral (P-G-P) (Yu et al., 2018). The composite provides for the first time a long-term corrosion protection coating for up to 120 days. Graphene has super-hydrophobic property which can be used beside the anti-corrosion. A study

published in 2017 by Wang *et al.* presented a super-hydrophobic coating prepared by a combination of electrochemically exfoliated graphene and PDMS (Wang et al., 2017). The coating showed an excellent self-cleaning, anti-corrosion, and resistivity to water-impact properties.

Graphene also showed the possibility to be used as an X-Ray radiation shielding. Hashemi *et al.* reported the using of graphene oxide prepared by Hummers method to fabricate GO-Pb<sub>3</sub>O<sub>4</sub> composite via the vacuum shock technique at different filler loadings and thicknesses (Hashemi et al., 2018). The results showed high rate of shielding against X-ray radiation.

### **2.6.5 Membranes**

Perfect graphene sheet (defect-free) with atomic thickness is entirely impermeable to all gases and liquids (Bunch et al., 2008). Graphene membrane considered as the world's thinnest balloon with one atom thickness. Several studies examined the detection limit of monolayer graphene sheet which is found to be  $10^5$ - $10^6$  atoms per second. No gas can penetrate graphene membrane size of micrometer. A new study published in 2020 by Sun *et al.* reported that defect-free graphene membrane is impermeable with a very high accuracy than previous experiments. The results showed that only few helium atoms could penetrate in one hour, where all other gases could not except hydrogen molecule (Sun et al., 2020). Another study by Seo *et al.* reported a CVD graphene membrane with centimeter-scale has been used as an active layer in membrane distillation (MD) technique (Seo et al., 2018). Graphene membrane showed high amount of water flow and good elimination of salt ions as well as long stability.

A simulation study published by Cohen-Tanugi and Grossman showed that a nano-pores monolayer graphene membrane is able to block NaCl salt ions from water depending on the pore size, chemical functionalization, and the applied pressure (Cohen-Tanugi & Grossman, 2012). However, the existence of pores or defect in graphene membrane can act as a selective barrier to allow some molecules and ban others. This property has been used in gas filtration, water purification, and separation of organic solvent from water.

### **2.6.6 Biomedical Application**

Graphene's high surface area and high carrier mobility have been paving a new way in biomedical technologies. Graphene materials have been used as a platform for drug delivery and imaging, sensor and bioanalytical device, photodynamic therapy, antimicrobials, and tissue engineering (Cheng et al., 2017). Using of graphene in biosensing applications includes two technologies; a probe molecule onto graphene sheet that interacts with the analyte, and the label-free to measure the electrical signals changes. For example, graphene biosensors for thrombin can offer the diagnosis and monitor the chronic from acute pathological conditions (Bitounis et al., 2013).

Graphene materials have been suggested for drug delivery due to its high surface area and biocompatibility (Reina et al., 2017). A remarkably result has been announced by Russier *et al.* about the ability of few layer graphene sheet dispersion to kill monocytes and exhibit no toxic nor activated immunocompetent cells.

## CHAPTER THREE

### GRAPHENE/SEMICONDUCTOR SCHOTTKY JUNCTION SOLAR CELL

#### 3.1 Introduction

When a metal and semiconductor are brought together, two types of junction may form depending on the work functions of both the semiconductor ( $\Phi_{\text{semi}}$ ) and the metal ( $\Phi_{\text{m}}$ ). If  $\Phi_{\text{m}} > \Phi_{\text{semi}}$ , the junction is Schottky (rectifying), and if  $\Phi_{\text{m}} < \Phi_{\text{semi}}$  the junction is the Ohmic (non-rectifying). Thus, Schottky junction is referred to an interface between a metal and semiconductor that provides an abrupt potential difference due to the difference between the metal Fermi level and the conduction band of the semiconductor. This metal-semiconductor junction creates a potential energy barrier or depletion layer known as a Schottky barrier, where the electrons have to overcome this barrier to flow across the device.

#### 3.2 The Physics Behind Schottky Junction

There are two types of Schottky junctions, rectifying when metal brought into contact with low doping concentration semiconductor, and non-rectifying with high doping concentration semiconductor (Ohmic junction). The Schottky barrier (depletion layer) is formed only in the rectifying case, and its width increases as the doping concentration increase. Figure 3.1 shows the formation of Schottky junction, where metal and n-type semiconductor are brought into contact. Once the junction is formed, electrons in the semiconductors close to the junction interface will move toward metal side as shown in Figure 3.1a.

After reaching the equilibrium level a depleted region is formed at the interface called depletion layer, where the accumulation of positive ions at the semiconductor side and negative ions at the metal side interface as shown in Figure 3.1b, thus no more charge carriers can reach the metal. Due to the accumulation of different charge ions, an internal electric field is established inside the depletion layer as shown in Figure 3.1c.

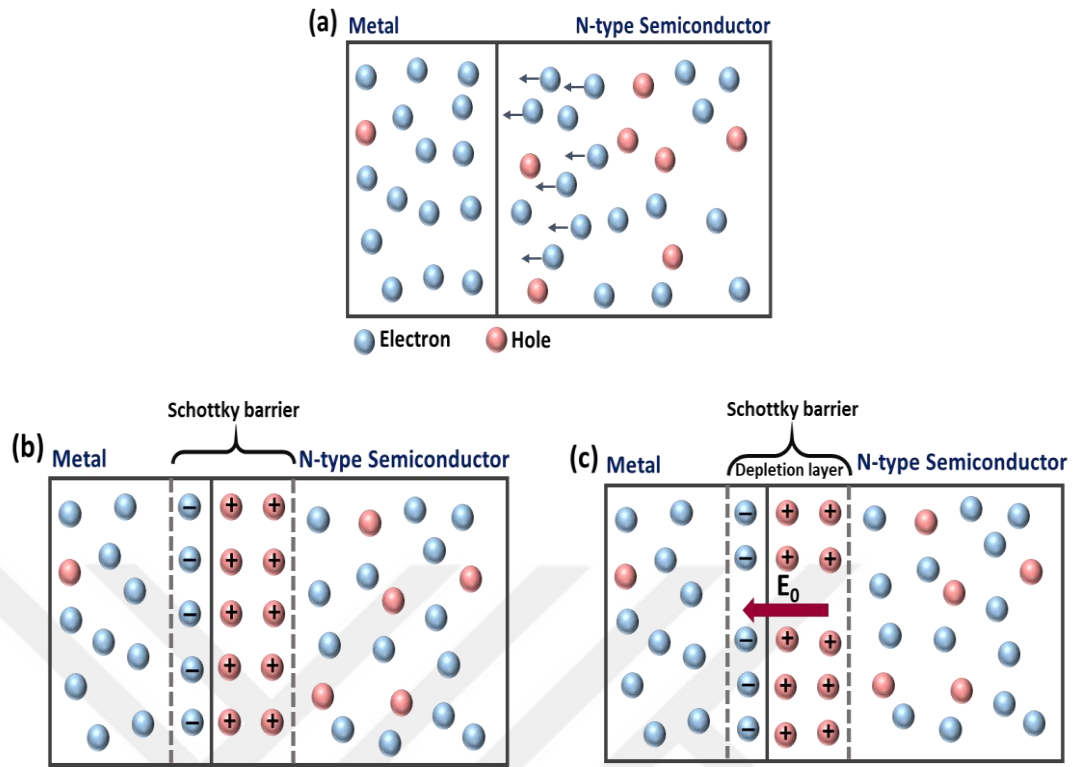


Figure 3.1 Schottky junction between metal and n-type semiconductor, (a) the formation of Schottky junction. (b) equilibrium state when accumulation of positive and negative ions at the depletion layer, (c) internal electric field in the depletion layer

In the case of Schottky junction, electrons in the semiconductor have high potential energy than the electrons in the metal, thus semiconductors' electrons can tunnel into the metal looking for lower empty levels so they will accumulate close to the metal surface. Once these electrons tunnel toward the metal, they leave behind a depletion region of width  $W$  which is depleted of free charge carriers. The width of this region depends on the type of the metal and the doping concentration of the semiconductor (Kasap, 2006). Figure 3.2 shows the energy band diagram of Schottky junction before and after making contact, where  $V_0$  is the vacuum level, the energy level when electron moves free outside the material.  $\Phi$  is the work function which is defined as the energy required for electron to move to vacuum level given by  $\Phi = V_0 - E_F$ , and  $E_F$  is the Fermi level, see Figure 3.2a.

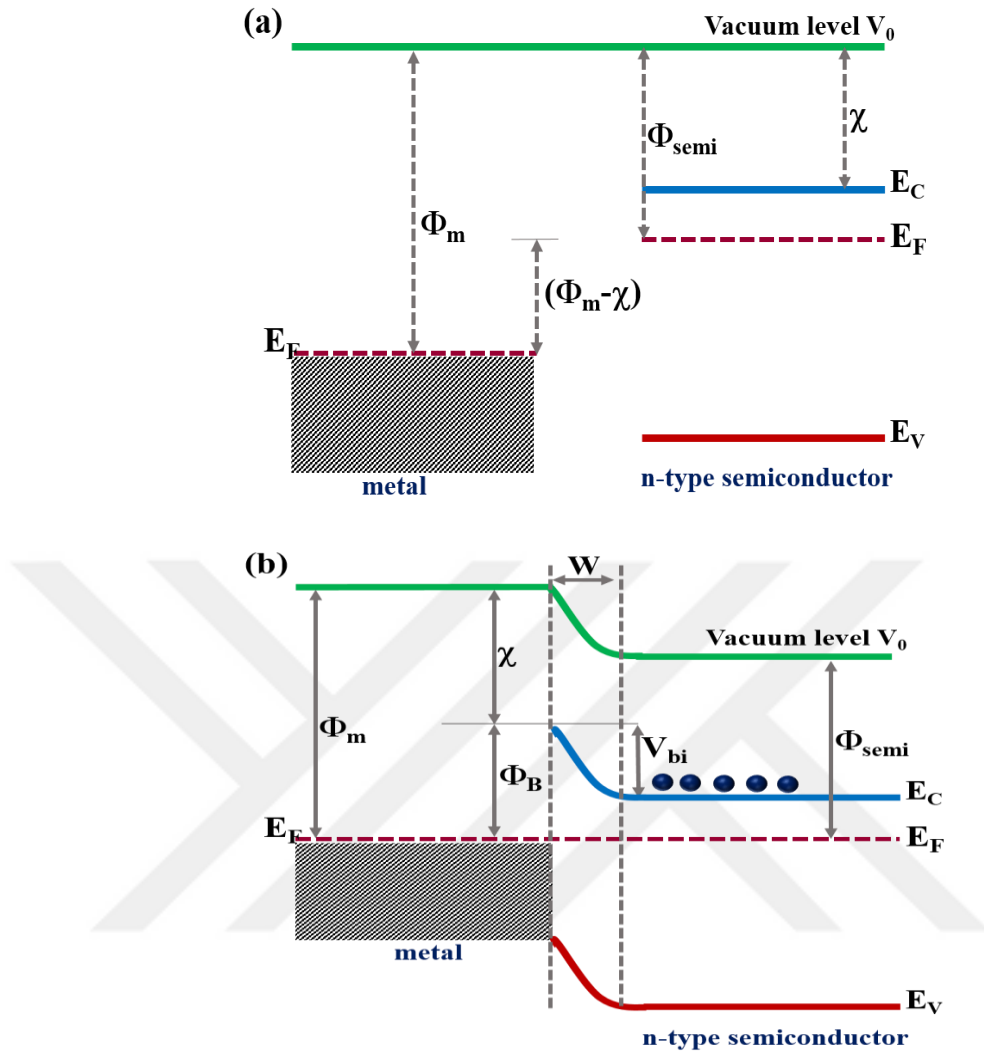


Figure 3.2 Energy band diagram of Schottky junction between metal and n-type semiconductor when  $\Phi_m > \Phi_{\text{semi}}$ , (a) before contact, (b) after contact

When Schottky junction formed, Fermi levels of metal and semiconductor must be aligned. This will lead to the band bending with maintain the continuity of vacuum level as shown in Figure 3.2b. The resulted potential barrier for metals' electrons toward semiconductor is called the Schottky barrier height  $\Phi_B$ , where  $\Phi_B = \Phi_m - \chi = eV_{bi} + (E_C - E_F)$ , where  $V_{bi}$  is the built-in potential which is defined as the difference between the work functions of metal and semiconductor as shown in Figure 3.2b.  $\chi$  is electron affinity, the difference between the vacuum level and the conduction band edge. As  $V_{bi}$  established within the depletion layer due to the movement of electrons

in semiconductor toward metal, an electric field  $E_0$  will establish until reach the equilibrium level where no more electrons can attain the metal surface.

Two types of biased Schottky junction when external potential is applied, where the Fermi levels no longer line up. Forward bias; when negative terminal is connected with n-type semiconductor, electrons in semiconductor will move to the metal as majority carriers and form a drift current. Once applied voltage increases, the depletion width decreases and become thinner. Reverse bias; when positive terminal is connected with n-type semiconductor, more excited electrons in metal, but higher barrier toward the semiconductor which will result in a widen depletion region. Thus, the current flow will stop except a small amount of leakage current when reverse biased increased and this might cause device damage.

### **3.3 Electrons Movement Through Schottky Junction**

Schottky junction is formed between metal and semiconductor when the potential barrier height is more than  $\sim 0.40$  eV (Dharmadasa, 2018) therefore, electrons flow from the semiconductor toward the metal due to the higher Fermi level in semiconductor material. Consequently, the Fermi level will bend upwards/downwards depending on the semiconductor concentration type. This will lead to establish an internal electric field within the depletion region at the metal/semiconductor interface. Three possible movements of electrons in the case of forward biased Schottky junction as follows,

- Thermionic emission, when electrons in semiconductor are able to cross the barrier potential toward the metal in the case of moderate doping.
- Quantum tunneling, when electrons are able to reach metal side by tunneling the barrier in the case of heavy doping.
- Carriers recombination within the depletion layer or within semiconductor material because of the hole injection (Ojo et al., 2019).

### 3.4 Schottky Junction Solar Cell

Due to the formation of internal electric field  $E_0$  inside the depletion layer, the junction can be employed as a photovoltaic device as well as a photodetector. When photons shine on a very thin metal ( $\sim 10$  nm) deposited on an n-type semiconductor, metal/semiconductor Schottky junction is formed.

As it is known, only photons with greater energy than semiconductor band gap  $E_g$  are able to release the valence electron, thus the electron-hole pair is generated, as shown in Figure 3.3a. The electric field in the junction region works on separating the electron-hole pairs by drifting the electrons toward the semiconductor and holes toward the metal.

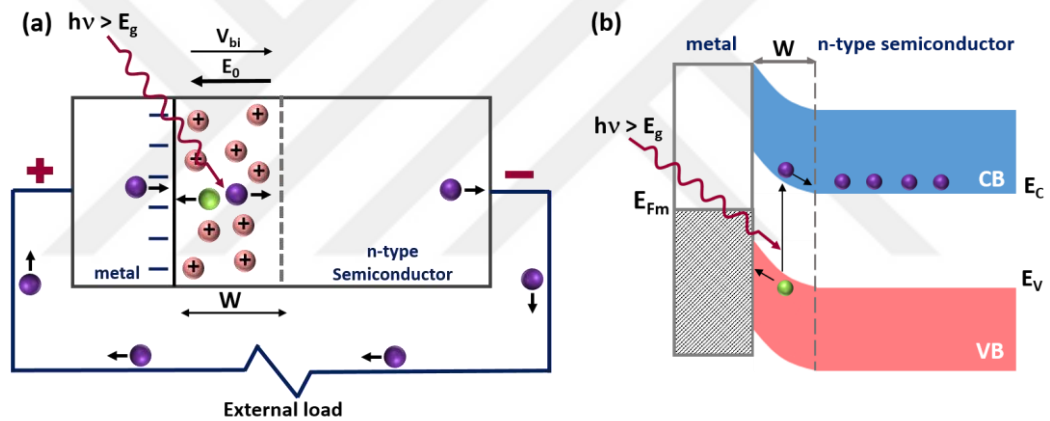


Figure 3.3 The Principle of the Schottky junction solar cell (adopted from Kasap, 2006)

As electron reaches the semiconductor conduction band in order to decrease its potential energy, the region negativity is increased. Similarly, the photogenerated hole will roll down to reach the surface of metal to recombine with an electron, thus the region negativity is decreased, see Figure 3.3b. In the case of Schottky junction with n-type semiconductor, the metal acts as the anode and the n-type semiconductor acts as the cathode.

### 3.5 Graphene-based Schottky junction solar cells

In Schottky junction solar cells, one metal is used as a current collector which must be a good conductor. Graphene has large surface area, high mobility of electrons and holes, and almost zero bandgap which makes it an ideal metal in Schottky junctions. The advantages of using graphene in such cells offer both the cost-effective and the flexibility compared with other electrodes such as ITO and FTO. Various semiconductors have been used with graphene in order to make Schottky junction such as n-Si planer, silicon pillar, CdS nanowire, CdS nanobelt, and CdSe nanobelt (Ye et al., 2010; Ye & Dai, 2012; Zhang et al., 2011).

The study by Ye et al. developed a feasible and scalable graphene patterning method using electron-beam followed by a lift-off process in order to obtain high accurate alignment of graphene sheet in micro-scale patterns. Novel CdSe nanobelt (NB)/graphene Schottky junction solar cell was fabricated without etching and using difficult processes. The cell showed an excellent photovoltaic behavior, with power conversion efficiency of 1.25%, 0.51 V of open-circuit voltage of 0.51 V, and 5.75 mA/cm<sup>2</sup> of short-circuit current density (Ye et al., 2011).

Another study by Jie et al. reported using mono- and bi- graphene layer to fabricate G/n-GaAs Schottky junction solar cell. Whereas in the case of bi-layer graphene sheet, the cell showed an open-circuit voltage of 0.65 V, a short-circuit current density of 10.03 mA/cm<sup>2</sup>, and a power conversion efficiency of 1.95%. the study concluded that, the cell performance parameters are similar to those of other pristine graphene/semiconductor junction-based devices (Jie et al., 2013). Since our study is concerned about graphene with n-Si, the next section is focused on G/n-Si Schottky junction solar cells.

### 3.6 Graphene/Si Schottky Junction

Since the isolation of graphene for the first time in 2005, researches related to graphene have become a vital topic in nanotechnologies. When graphene layer covers

the entire surface of Si substrate, Schottky junction is formed considering built-in field for charge separation.

Graphene has been used as a transparent electrode and active layer in Schottky junctions for the first time in 2010 (Li et al., 2010) when Li *et al.* reported the fabrication of G/Si Schottky junction, whereas CVD graphene was transferred on 1cm<sup>2</sup> of n-type Si substrate, phosphor doped 10<sup>15</sup> cm<sup>-3</sup> coated with 300nm of patterned SiO<sub>2</sub>. The cell showed 0.42–0.48 V, 4–6.5 mA.cm<sup>-2</sup>, 45–56%, and 1–1.7% of open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), fill factor (FF), and power conversion efficiency ( $\eta$ ) respectively for 0.5 cm<sup>2</sup> window of active area. In 2013, a detailed report published by Lin *et al.*, discussed two essential parameters that affect the performance of G/Si solar cells: the work function of graphene and semiconductor and the number of graphene layers in the cell. As graphene's work function increases, the electric field increases therefore, the ability of junction to collect more electron-hole generated pairs is enhanced (Lin et al., 2013). Another study discussed the transmittance of the cell as well as the affection on the sheet resistance due to the number of graphene layers (Li et al., 2015).

Later, many strategies have been used to enhance the graphene/Si Schottky junction solar cells, where the power conversion efficiency has been raised up to 15.6% from 1.65% within 5 years. Table 3.1 shows the advancement of selected studies of graphene/Si Schottky junction solar cells at illumination intensity of 100mW/cm<sup>2</sup> from 2010 to 2015.

The rapid increasing in the cell efficiencies resulted due to working on the following parameters. Textured silicon substrates, where number of studies suggested employing porous silicon, silicon nanowires instead of planar silicon to provide larger surface area besides using the anti-reflection coating for light harvesting. Surface modification of graphene, where doping graphene and/or multi-layered graphene have been proved to increase the work function and the conductivity in graphene. Passivation techniques of the interface between graphene and silicon will be detailed in the next section.

### 3.6.1 Textured Silicon Substrate for Light Trapping

Nanostructured semiconductors has been used in G/Si Schottky junctions to reduce the sunlight reflection by trapping it within the layer in order to enhance the generation rate, such as nanowires (Xie et al., 2011), microholes (Xie, et al., 2013), and nanopillars (Feng et al., 2012). A study published by Fan *et al.* reported the fabrication of chloride doped G/SiNW Schottky junction that shows low reflectance and high absorption of light with power conversion efficiency of 2.86% (Fan et al., 2011). Thus, using silicon nanowire (SiNW) structure in graphene/Si was proved to enhance the light trapping compared to planar Si structure.

Another study by Feng *et al.* reported higher powder conversion efficiency reach to 2.9% when CVD graphene film was transferred onto a silicon-pillar-array substrate of 0.09 cm<sup>2</sup> to fabricate a Schottky junction solar cell (Feng et al., 2012). Pillar array with height of 200 nm has been used instead of planar silicon and has proved to reduce the reflectance and enhance the absorption of light. The study also suggested doping graphene with HNO<sub>3</sub> to enhance the efficiency to 4.35%. The study group also introduced Poly(3,4-ethylenedioxythiophene) polystyrenesulfonic acid (PEDOT-PSS) coated on graphene/silicon pillar array in order to improve the cell performance due to its high conductivity.

A comprehensive study in 2013 published by Zhang *et al.* reported the fabricating of two types of graphene/Si nanoarray Schottky junction solar cells (Zhang et al., 2013). G/Si nanowire and G/Si nanohole Schottky junction were introduced with high power conversion efficiency reach to 8.71% and 10.30% respectively with an excellent stability when a thin conducting polymer poly(3-hexylthiophene) (P3HT) was inserted as the electron blocking layer. Those high efficiencies were obtained by controlling the number of graphene layers and the type of graphene doping as well as choosing an appropriate surface passivation.

Table 3.1 Graphene/n-Si Schottky junction solar cells from selective studies

| Solar cell structure                                                                    | PCE (%) | Active area (cm <sup>2</sup> ) | J <sub>sc</sub> (mA/cm <sup>2</sup> ) | V <sub>oc</sub> (V) | FF (%) | Year |
|-----------------------------------------------------------------------------------------|---------|--------------------------------|---------------------------------------|---------------------|--------|------|
| G/n-Si (Xinming Li et al., 2010)                                                        | 1.65    | 0.1                            | 6.50                                  | 0.480               | 56     | 2010 |
| SOCl <sub>2</sub> -doped G/n-SiNW (Xie et al., 2011)                                    | 2.86    | 0.28                           | 11.24                                 | 0.503               | 50     | 2011 |
| TFSA-doped G/n-Si (Miao et al., 2012)                                                   | 8.6     | 0.09                           | 25.30                                 | 0.540               | 63     | 2012 |
| Acid-doped G/P3HT/n-Si (Xie, Zhang, Wu, et al., 2013)                                   | 10.56   | 0.04                           | 32.83                                 | 0.480               | 67     | 2013 |
| TiO <sub>2</sub> /Acid-doped G/n-Si (Shi et al., 2013)                                  | 14.5    | 0.047                          | 32.70                                 | 0.612               | 72     | 2013 |
| TiO <sub>2</sub> /Acid-doped G/GO/n-Si (Jiao et al., 2014)                              | 12.3    | 0.09                           | 37.40                                 | 0.570               | 57     | 2014 |
| TiO <sub>2</sub> /AuCl <sub>3</sub> -doped G/SiO <sub>2</sub> /n-Si (Song et al., 2015) | 15.6    | 0.11                           | 36.70                                 | 0.595               | 72     | 2015 |

### 3.6.2 Graphene's Doping and using multi- layer graphene

The maximum power conversion efficiency of pristine graphene/Si Schottky junction solar cells were reached to 5–6.5% in 2014. However, using pristine graphene limits the electrical conductivity of graphene and the built-in field at the interface. Thus, several techniques have been used to tunable its work function, p-type chemical doping has been done with acids (Jiao et al., 2014; Xie et al., 2011), polymers (Miao et al., 2012) boron (Li et al., 2012) and so on, could improve the performance of solar cells.

In another study published by Miao *et al.* in 2012, chemically doped CVD graphene with bis-(trifluoromethanesulfonyl) amide (TFSA) was transferred onto n-type silicon substrate (Miao et al., 2012). Doping process has improved the cell efficiency 3-5 times to reach to 8.6%. This modification has increased graphene carrier density by reducing their sheet resistance by 70%, thus increase the built-in potential  $V_{bi}$ .

Another study by Li *et al.*, investigated the effect of the number of graphene layers in G/Si Schottky junction solar cells. 1-6 of CVD graphene layers have been examined under light illumination of range from 400–940 nm wavelengths (Li et al., 2014). The study showed that the number of graphene layers displays a crucial role to determine the cell efficiency, where the open-circuit voltage increases with the increasing of number of layers as well as the short-circuit current and the efficiency until 4 layers of graphene. The transmission rate decreased with 5 or more graphene layers, hence the study suggested that the 4-layer graphene is the most favorable material to obtain high efficiency Schottky junction solar cells.

### **3.6.3 Passivation the Graphene/Silicon interface**

Using doped graphene in Schottky junction with silicon has improved the efficiency to reach to 10–12.4%. Still, these efficiencies are limited by low barrier height at the interface. Several studies investigated how to increase the barrier height (Jiao et al., 2014; Xie et al., 2013; Yang et al., 2014). When the junction formed between graphene and Si, holes accumulate at the surface of Si and might either travel toward graphene by tunneling or recombine with electrons at Si surface. A study by Xie *et al.*, suggested inserting a thin layer at the interface between graphene and silicon, where an optimum thickness of 10 nm of P3HT organic layer has been introduced as electron blocking layer which helped to reduce the charge carriers recombination with enhanced efficiency of 9.70% (Xie et al., 2013).

Many studies were concerned about using an anti-reflection coating to improve the cell performance (Lancellotti et al., 2016; Shi et al., 2013). A study published by Shi *et al.* suggested using  $\text{TiO}_2$  as a colloidal anti-reflection coating in G/Si Schottky junction solar cell (Shi et al., 2013). After transferring doped monolayer CVD

graphene by  $\text{HNO}_3$  onto Si substrate, about 56 nm of  $\text{TiO}_2$  was spin-coated. The results showed a significant enhancement in short-circuit current and power conversion efficiency up to 14.5% as well as long stability.

Thus, the cell performance can become more efficient through the combining of number of graphene layers and an appropriate of anti-reflection coating in G/Si Schottky junction solar cells. A study published by Lancellotti *et al.* reported the fabrication G/n-Si Schottky junction solar cell, where few-layer of CVD doped graphene with  $\text{HNO}_3$  were transferred onto n-type Si substrate and later coated with double layer of magnesium fluoride/zinc sulfide ( $\text{MgF}_2/\text{ZnS}$ ) antireflection coating (DARC). The results showed a significant enhancement in graphene work function due to doping process and reducing the reflection of sun light by DARC led to higher power conversion efficiency of 8.54% (Lancellotti *et al.*, 2016).

Another study published by Song *et al.* investigated the impact of inserting a native silicon oxide layer at the junction interface in G/n-Si Schottky junction solar cells (Song *et al.*, 2015). Where p-doped CVD graphene by  $\text{AuCl}_3$  was transferred on the top of silicon substrate coated with  $\sim 15 \text{ \AA}$  of native silicon oxide. The cell efficiency was found around 10% before using the anti-reflection coating. Furthermore, cell efficiency was enhanced to 12.4% when a thin native oxide of  $\sim 9 \text{ \AA}$  was regrown before transferring doped-graphene layer with applying  $\text{TiO}_2$  as an anti-reflection coating. Chemical doping raises the graphene work function and the regrowth of native oxide enhances the recombination over the tunneling. The best efficiency has been reported in the study was 15.6% when both doped graphene was used as well as  $15 \text{ \AA}$  of native oxide and anti-reflection coating. The study also shows that when the thickness of the native oxide layer is larger than  $15 \text{ \AA}$ , the kink in IV curve will be more observable.

## **CHAPTER FOUR**

### **DESIGN AND METHODOLOGY**

#### **4.1 Introduction to our Experimental Work**

In our study, graphene has been successfully synthesized in three different forms and three different techniques. From graphite (Gr) powder as a starting material, reduced graphene oxide (rGO) and few-layer graphene flakes (~5 layers) have been chemically produced. While monolayer graphene sheet was prepared by CVD furnace with the assistance of copper foil. Section 4.2 is concerned about our experiment work which are used to produce graphene materials in three detailed subsections. In section 4.3, the procedures used to fabricate G/Si Schottky junction solar cells are detailed. While, section 4.4 illustrates the characterization tools used to examine the produced graphene.

#### **4.2 Synthesis Methods**

Different graphene materials have been synthesized using modified Hummers' method, electrochemical exfoliation with microwave assisted, and chemical vapor deposition method to produce graphene oxide, reduced graphene oxide, few-layer graphene flakes in different exfoliated degrees, and monolayer graphene sheet.

##### ***4.2.1 Reduced Graphene Oxide (rGO) by Hummers' Method***

Hummers' method is considered as one of the most widespread adopted method to synthesis graphene oxide from pure graphite powder (Gr) as a starting material by increasing the interlayer spacing between packed graphite sheets. Where graphene oxide can be obtained by introducing a strong oxidizing agents to the graphite acid dispersion. The oxidation of graphite was used for the first time in 1859, when Brodie oxidized graphite dispersion by inserting potassium chlorate (Brodie, 1859). After that, in 1898 Staudenmaier developed Brodie's method by adding sulfuric acid ( $H_2SO_4$ ) to the graphite dispersion.

Almost 100 years after Brodie's method, Hummers and Offeman demonstrated another oxidation method called Hummers' method (Hummers & Offeman, 1958). Where Sodium nitrate ( $\text{NaNO}_3$ ) and Potassium permanganate ( $\text{KMnO}_4$ ) were used beside sulfuric acid to oxidize graphite. Several modifications have been utilized to improve the production of GO (Alam et al., 2017; Chen et al., 2013; Marcano et al., 2010; Yu et al., 2016). Produced GO by this method has been used in large scale production as graphitic films, fillers, component of the cathode of lithium batteries, and conductive graphitic material. In spite of that, using Hummers' method to produce GO resulted in some toxic gases (Marcano et al., 2010).

#### 4.2.1.1 First Step: Synthesis of Graphene Oxide from Graphite

Table 4.1 illustrates chemicals used in this method. For oxidation process of graphite powder, 100 ml of  $\text{H}_2\text{SO}_4$  was placed in an ice bath, then 4 g of graphite powder (Figure 4.1a) with particle size 100-250  $\mu\text{m}$  was introduced and stirred for 40 minutes as shown in Figure 4.1b. Later, 12 g of  $\text{KMnO}_4$  was introduced little by little with keeping the dispersion temperature less than  $20^\circ\text{C}$  with stirring for 3 hours.

Table 4.1 Chemical materials with quantities used in synthesizing of GO

| Material                       | Quantity | Function                      |
|--------------------------------|----------|-------------------------------|
| Graphite powder                | 4 g      | Starting material             |
| $\text{H}_2\text{SO}_4$        | 100 ml   | catalyzer                     |
| $\text{KMnO}_4$                | 12 g     | oxidizer                      |
| $\text{H}_2\text{O}_2$         | 20 ml    | To stop the chemical reaction |
| $\text{HCl}$                   | 100 ml   | Metal contamination removal   |
| $\text{H}_6\text{N}_2\text{O}$ | 0.5 ml   | Reduction reagent             |

Subsequently, 200 ml of distilled (DI) water was added dropwise to the dispersion with keeping the temperature less than  $50^\circ\text{C}$ , the color of the dispersion will turn from black to yellowish brown as shown in Figure 4.1c approves the formation of graphene oxide. After 30 minutes, 400 ml of DI water was added instantly to finish the oxidation process and stirred for 1 hour. Eventually, 20 ml of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) was

dropped to accomplish the chemical reaction as well as eliminate any excess of  $\text{KMnO}_4$  and stirred for 10 minutes.

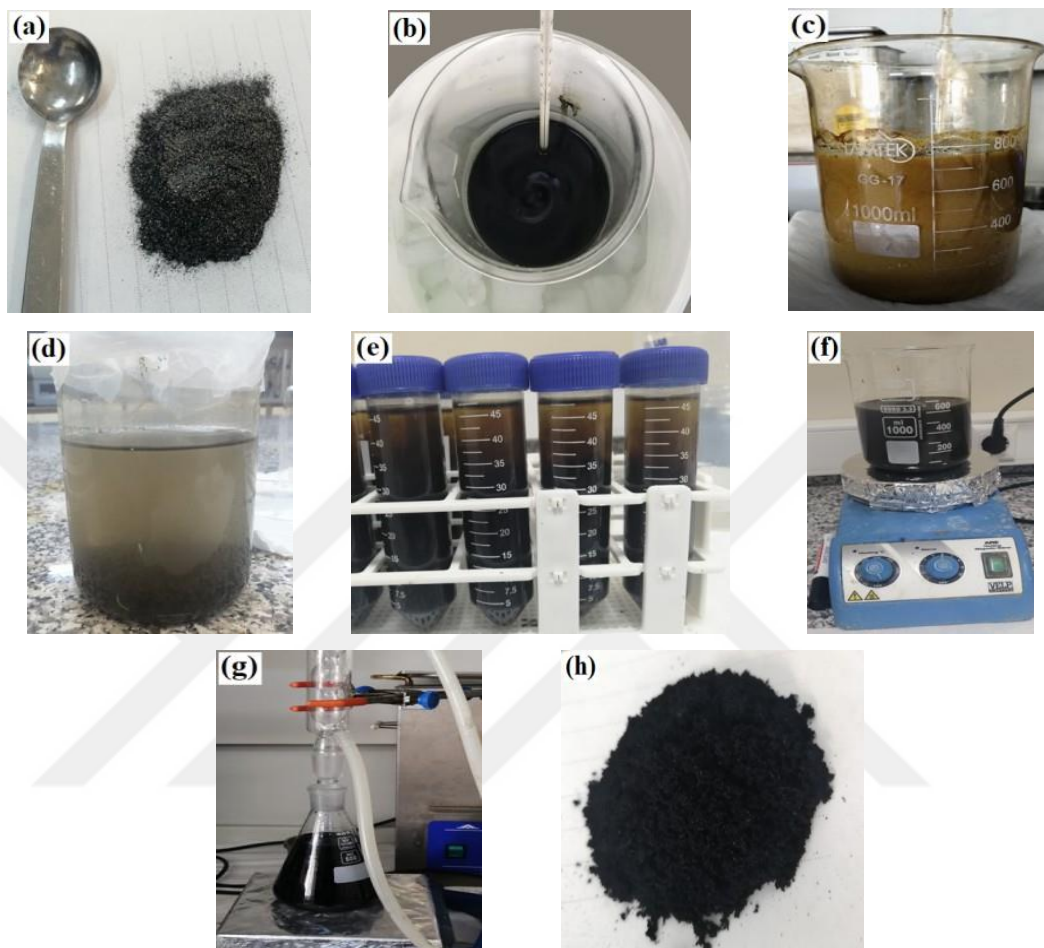


Figure 4.1 Experimental setup of modified Hummers' method. (a) Pure graphite powder. (b) Dispersion of graphite with  $\text{H}_2\text{SO}_4$  and  $\text{KMnO}_4$  in ice bath. (c) yellowish brown of graphite dispersion when chemical reaction end. (d) Graphene oxide before purification processes. (e) GO dispersion in centrifuge tubes during purification processes. (g) Reflux setup for reduction process. (h) Reduced graphene oxide powder (Personal archive, 2019)

#### 4.2.1.2 Second Step: Purifying and Washing Graphene Oxide Dispersion

The next day purifying process of GO dispersion was started, where GO dispersion was precipitated at the bottom of the beaker as shown in Figure 4.1d. in order to remove acid residue and metal impurities of GO dispersion, 100 ml of hydrochloric acid (HCl) was added with 900 ml of DI water to the dispersion. Then the dispersion

was distributed to the centrifuge tubes as shown in Figure 4.1 e and centrifuged for several times at 6000 rpm for 15 minutes.

After that, the purifying process was made 7 times at 6000 rpm for 15 min with only DI water in order to collect the exfoliate GO flakes and leave at tube bottom the multi-layer GO. The dispersion viscosity was noticed to increase after each purifying step. Eventually, the collected purified dispersion was left it to dry on a hotplate at 70°C during a night, see Figure 4.1f.

#### *4.2.1.3 Third step: Reduction of Graphene oxide (rGO)*

For reduction process, 1.5 g of dried GO powder we obtained from previous step was added to 500 ml of DI water. The dispersion was placed in Reflux condenser as shown in Figure 4.1g with a proper stirring, and 0.5 ml of Hydrazine Hydrate ( $\text{H}_6\text{N}_2\text{O}$ ) was added, and the whole dispersion was placed onto a hotplate at 80°C with stirring at 400 rpm during a night. The next day the reflux setup was removed, and the dispersion was washed 3 times with DI water in centrifuged at 3000 rpm for 15 minutes, and left to dry overnight. Figure 4.1h shows the obtained rGO powder throughout our experiment, the GO powder shows a dark black color with a fluffy form.

#### ***4.2.2 Few-layer Graphene Sheets (FLG) by Electrochemical Exfoliation, Sonication with Microwave-assisted***

Electrochemical exfoliation of synthesis graphene is considered as a green method to produce high-quality graphene on large scale. Produced graphene sheets by this method tend to have high lateral size and high electrical conductivity with low defect concentration (Bose et al., 2014). The effectiveness of this method can be shortened as follows: when electrolysis is applied, hydroxyl and oxygen are produced. The oxidation at the graphite anode will open up between graphite sheets therefore, the intercalation of electrolytic molecules can penetrate through these spaces at the graphite anode to exfoliate graphite stacked sheets.

The studies on electrochemical exfoliation of graphite have reported the producing of single layer graphene (Singh et al., 2012) and hundred nanometers thickness graphene flakes (Hathcock et al., 1995) with the presence of oxygen functional groups at a ratio of 7.3-30% wt. (Parvez et al., 2014; You et al., 2011). The oxidation process can be performed as an anodic oxidation, cathodic reduction, or mixtures of both (Morales et al., 2011; Su et al., 2011). Still, there is no agreement about the amount of voltage that has to be applied, where some studies reported using around 2 V (Kakaei, 2013) and others used about 15 V (Texter, 2014) as well as the exfoliation time which may take 5 minutes to 14 hours (Hofmann et al., 2015).

In our work, few-layer graphene sheets (~5 layers) have been synthesized throughout simple techniques. The preparation procedures have started with electrochemical exfoliation using two different electrolytes, sodium sulfate solution ( $\text{Na}_2\text{SO}_4$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The obtained electrochemical exfoliated graphene powders were given names depending on used electrolyte, EE1 for sodium sulfate, and EE2 for sulfuric acid. Later, pure natural graphite (NGr), EE1, and EE2 powders were sonicated in Dimethylformamide (DMF). The final step was to expose the obtained powders to microwave irradiation. Table 4.2 shows materials were used in these experiments.

#### *4.2.2.1 First step: Electrochemical Exfoliation of Graphite*

In this part, two circular shape of graphite electrodes (30 mm diameter, 2mm thickness) as shown in Figure 4.2a were made, each by pressing 4 g of pure graphite powder using hydraulic press. Two separate experiments were set to exfoliate graphite electrodes with different electrolytes. Two electrochemical cells were prepared with a constant voltage 10 V to initiate the graphene expansion. 0.1 M of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  solutions were prepared separately to make two electrochemical cells for EE1 and EE2 respectively as shown in Figure 4.2b. Aluminum (Al) electrode was used as a cathode while graphite electrode was connected to the anode (working electrode). After applying voltage, the exfoliation process was initiated and black bubbles were gradually appeared on the surface due to exfoliation process which took around one hour to complete the reaction as shown in Figure 4.2c.

Table 4. 2 Chemical materials with quantities used in synthesizing of FLG

| Material                        | Quantity |
|---------------------------------|----------|
| Graphite powder                 | 12 g     |
| Na <sub>2</sub> SO <sub>4</sub> | 11.36 g  |
| H <sub>2</sub> SO <sub>4</sub>  | 4.26 ml  |
| DMF                             | 300-350  |

Later, the two obtained dispersions EE1 and EE2 were placed to sonication bath for 2 hours in order to enhance the obtaining low-layer graphene sheets. Next day, the purification processes have been carried out with centrifugation system, where each dispersion was purified with DI water 3 times and centrifuged at 4000 rpm for 15 min as shown in Figure 4.2 d. Finally, the purified dispersions were left to dry in furnace at 80°C overnight.

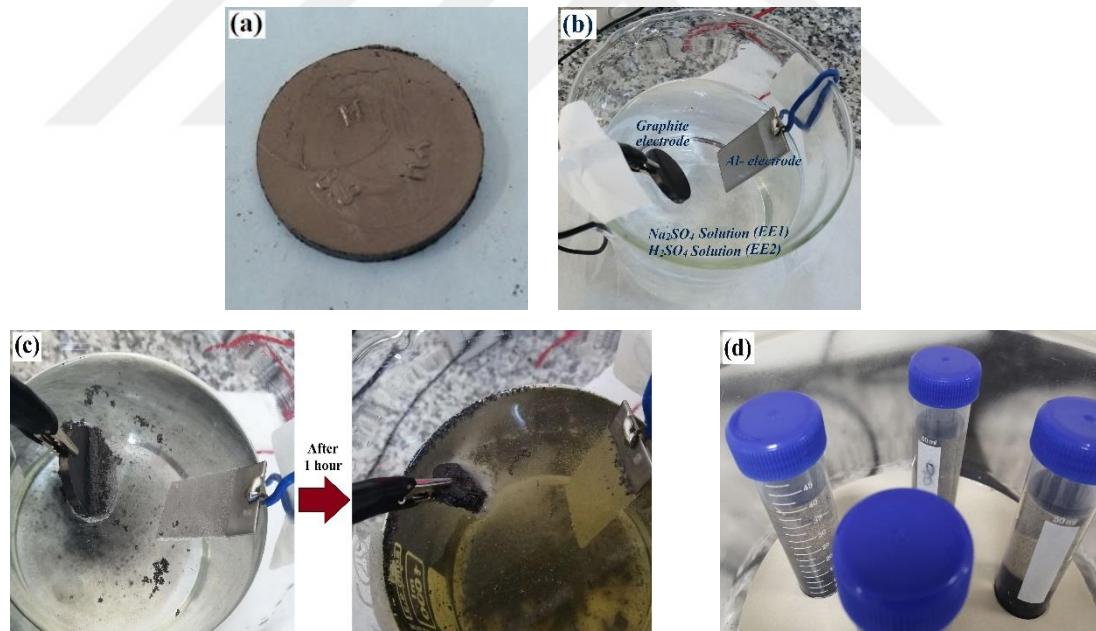


Figure 4.2 Experimental setup of synthesis low-layer graphene sheets by electrochemical exfoliation method. (a) Graphite electrode (pressed graphite powder). (b) Electrochemical cell setup for both EE1 and EE2 experiments. (c) Exfoliation process throughout one hour. (d) Purifying the obtained dispersions in centrifuge tubes (Personal archive, 2019)

#### 4.2.2.2 Second step: Sonication of EE1 and EE2 powders in DMF

Obtained EE1 and EE2 with NGr powders as shown in Figure 4.3a were used to prepare three dispersions in 3 mg/ml of Dimethylformamide (DMF). Dispersions were placed into a sonication bath for 1 hour, see Figure 4.3b. After sonication, the dispersions showed a grayish layer floating on the surface as shown in Figure 4.3c which indicates the obtaining of few-layer graphene flakes. Later, the obtained dark dispersions were purified carefully with DI water for 5 times by centrifuging at 4000 rpm for 15 min in order to dispose large flakes as shown in Figure 4.3d and then were left to dry at 80 °C overnight.

#### 4.2.2.3 Third step: Microwave irradiation

The obtained powders from previous step exhibited significant defects as well as oxygen functional groups. Thus, in order to synthesis few-layer graphene sheets, microwave irradiation was applied.

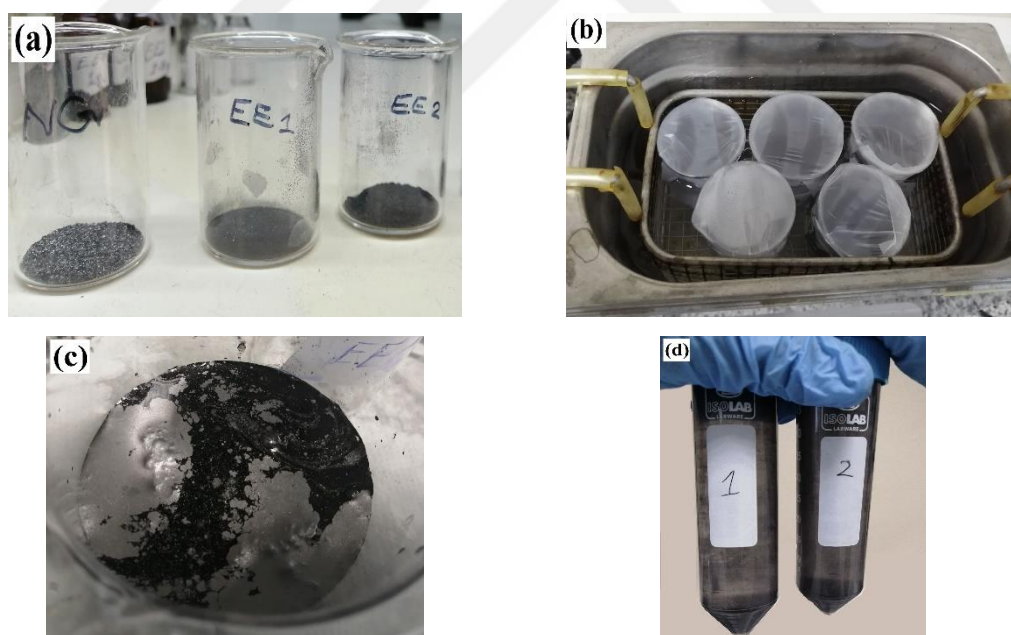


Figure 4.3 Experimental setup of sonication graphite powders in DMF. (a) NGr, EE1, and EE2 used powders. (b) DMF Dispersions in sonication bath. (c) Graphite dispersion after sonication process. (d) Purifying the obtained dispersions in centrifuge tubes (Personal archive, 2019)

Same volume of the three powders in ceramic crucibles were placed into the microwave furnace at 800 W for 30 s. Eventually, the resulted powders showed expanded structures as well as higher roughness corresponded to a higher surface area (Bose et al., 2014).

#### ***4.2.3 Mono-layer Graphene Sheet (G) by Chemical Vapor Deposition Method***

The basic role of synthesis graphene by CVD method is mostly performed by nucleation of carbon atoms directly on a transition metal. Graphene synthesized by CVD method possesses high transparency, mechanical stability as well as high carrier mobility. Thus, graphene is grown by the decomposition of carbon atoms come out of precursor hydrocarbon gas at high temperatures in order to provide a source of carbon atoms and subsequently rearrange them in  $sp^2$  graphene form. It has been reported that copper is considered as the most suitable catalysts for synthesis high-quality graphene due to its low affinity to carbon beside its ability to stabilize carbon atoms on the surface (Mattevi et al., 2011). Moreover, pre-treatment (annealing) of the transition metal catalysts is a preferred step in order to obtain large graphene domains on the top of the transition metal (Brownson & Banks, 2014). In our work, CVD graphene has been synthesis with Cu foil assisted. Figure 4.4 shows the three steps of CVD graphene growth.

##### ***4.2.3.1 First step: Annealing Treatment of Copper Foil***

Annealing treatment was applied first onto  $2 \times 2 \text{ cm}^2$  of commercially copper foil (99.99% purity) of 80  $\mu\text{m}$  thick shown in Figure 4.4a, in order to eliminate the native copper oxide layer as well as to enlarge the Cu grains size before synthesis process. Copper foil was placed at the middle of CVD furnace as shown in Figure 4.4d of a standard 2-inch quartz tube and gradually annealed at 1070  $^{\circ}\text{C}$  in the flowing of  $\text{H}_2$  and Ar both at 100 sccm for 2 h under ambient pressure then was left for cooling down. Later, Cu foil was chemical-mechanically polished with diluted Iron chloride ( $\text{FeCl}_3$ ) as shown in Figure 4.4b for few times using laboratory tissue then washed with DI water.

#### 4.2.3.2 Second step: Synthesis of Monolayer Graphene

Polished Cu foil was placed again to CVD furnace and then synthesis of graphene begun, where Cu foils with area of  $2 \times 2 \text{ cm}^2$  was gradually heated up to  $1070^\circ\text{C}$  in 56 min in a flow of  $\text{H}_2$  at 60 sccm and Ar at 1000 sccm for 40 min, then 10 sccm of methane gas ( $\text{CH}_4$ ) was introduced for 90 s all under ambient pressure, then chamber was left to cool down to room temperature in few minutes while  $\text{H}_2$  and Ar were flowing on. Thus, graphene sheet has been grown onto the Cu foil as shown in Figure 4.4c ready for transferring step.

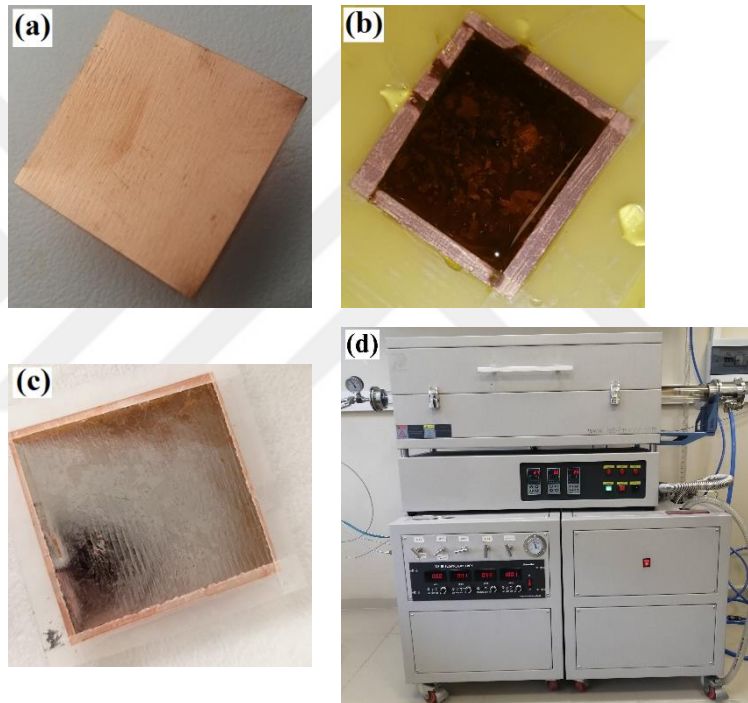


Figure 4.4 Synthesis of CVD graphene with assisted of Cu foil. (a)  $2 \times 2 \text{ cm}^2$  of Cu foil ( $80 \text{ }\mu\text{m}$ ) before annealing treatment. (b) Cu foil after annealing ready for chemical-mechanical polishing by  $\text{FeCl}_3$  with visible grain size. (c) Graphene synthesized on Cu foil. (d) The CVD system used in this work (Personal archive, 2020)

#### 4.2.3.3 Third step: Transfer of mono-layer graphene

In order to protect the grown graphene onto Cu foil before transferring process onto a desired substrate, G/Cu was first spin-coated with 2% of PMMA (as a supporting membrane) at 3000 rpm for 1 min which will have an approximately 90 nm thickness

(Suhail, 2019), then placed on a hotplate at 180°C for 1 min in order to dry PMMA. In CVD process, graphene can grow on both sides of the Cu foil thence, after protecting one side (front side) of grown graphene with PMMA, the PMMA/G/Cu/G was floated in 10% of nitric acid ( $\text{HNO}_3$ ) for 15 min and then transferred to DI water to remove the  $\text{HNO}_3$  residue.

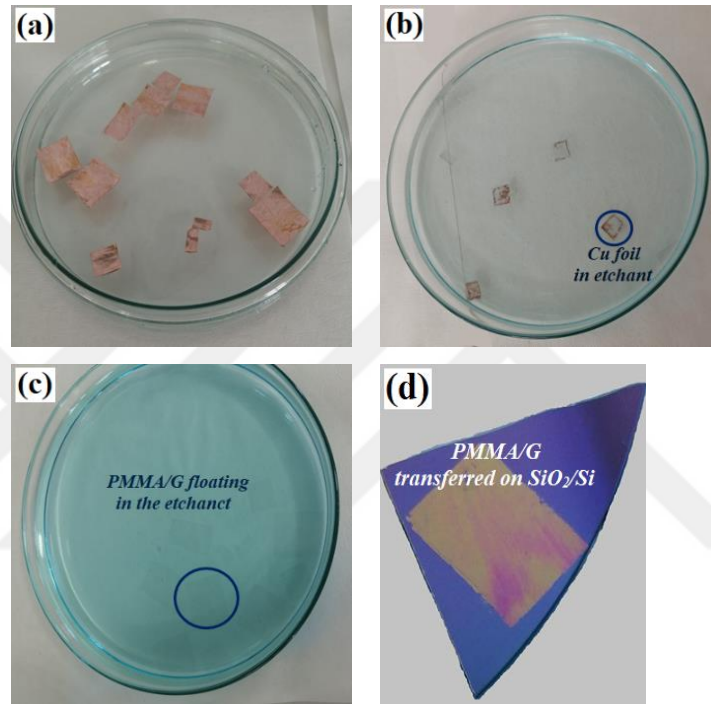


Figure 4.5 Etching and transferring processes of CVD graphene. (a) spin-coated G/Cu with PMMA floating in ammonium persulfate solution. (b) Etching of Cu foil with time. (c) Cu foil was fully etched and PMMA/G floated visibly on the surface. (d) PMMA/G layer wet transferred on the top of  $\text{SiO}_2/\text{Si}$  substrate (Personal archive, 2020)

Later, the suspended PMMA/G/Cu film was floated in 0.1 M of ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) in order to etch the Cu substrate for around 13 hours. Moreover, ammonium persulfate is suggested as a preferred Cu etchant due to its reduction of the nucleation sites number as well as larger surface area and smoother graphene sheet than  $\text{FeCl}_3$  and  $\text{HNO}_3$  etchants (Ibrahim et al., 2017). After etching Cu foil, the transparent PMMA/G layer was seen visibly floating and were transferred carefully using  $\text{SiO}_2/\text{Si}$  substrate to a rinse bath of DI water 3 times each of 20 min before last transfer onto a desired substrate.

### 4.3 Fabrication of graphene/silicon Schottky junction solar cell

Four types of graphene materials have been successfully synthesized; GO, rGO, FLG, and monolayer graphene sheet. In order to fabricate a photovoltaic device, CVD graphene has been chosen to act as an active layer in G/Si Schottky junction solar cell. In addition to a dispersion of our synthesized GO, it has been used as a p-dopant as well as an anti-reflection coating in our solar cell.

Graphene/n-Si Schottky junction solar cells with a top-window structure have been fabricated using simple techniques without photolithography system. In our study, silicon wafer (100) orientation, n-type (phosphorus doped), 500 $\mu$ m thickness coated with 300nm SiO<sub>2</sub> on the polished side with resistivity of 0.04  $\Omega$ cm<sup>-1</sup> was used in order to fabricate G/Si solar cell. Back- and front metal contacts were achieved by thermal evaporation system using Cr, Ag, and Au, while monolayer graphene sheet was synthesized by CVD method.

#### 4.3.1 Silicon substrate cleaning route

Silicon wafer was cut to Si substrates of 1 $\times$ 1 cm<sup>2</sup> as shown in Figure 4.6a and then were prepared for cleaning steps. General cleaning was first performed by immersing Si substrates in hot acetone (55°C) for 10 min followed by methanol for 5 min. Particle removal was achieved by Radio Corporation of America (RCA) steps with 5:1:1 solution of DI water: NH<sub>4</sub>OH: H<sub>2</sub>O<sub>2</sub> where first DI water and ammonium hydroxide were heated up to 70°C then hydrogen peroxide was introduced, then Si substrates were soaked after 2 min and left for 15 min. Metal contamination removal was performed by sonication Si substrates in 6:1:1 of DI water: HCl: H<sub>2</sub>O<sub>2</sub> at 70°C in sonication bath for 5 min as shown in Figure 4.6b. After each cleaning step, silicon substrates were washed with running DI water for 3 min and then dried with blowing of nitrogen gas (N). Later, native SiO<sub>2</sub> (300 nm) was etched by dipping Si substrates in 2% of HF for 30 s followed by rinsing in DI-water for 2 min and dried with N, fully etching of SiO<sub>2</sub> can be predicted by checking the hydrophobic of silicon surface as shown in Figure 4.6c.

### 4.3.2 Thermal Evaporation Technique

Thermal evaporation system has been used to deposit back- and front- contacts. Two stainless steel shadow masks have been designed to deposit back- and front- metal contacts, where shadow mask with open window of  $0.64 \text{ cm}^2$  as shown in Figure 4.6d was used to deposit 5/150 nm of Cr/Ag as a back metal contact and another shadow mask with an open frame of 1.5 mm width and covered of  $0.11 \text{ cm}^2$  in the middle for graphene active area was designed.

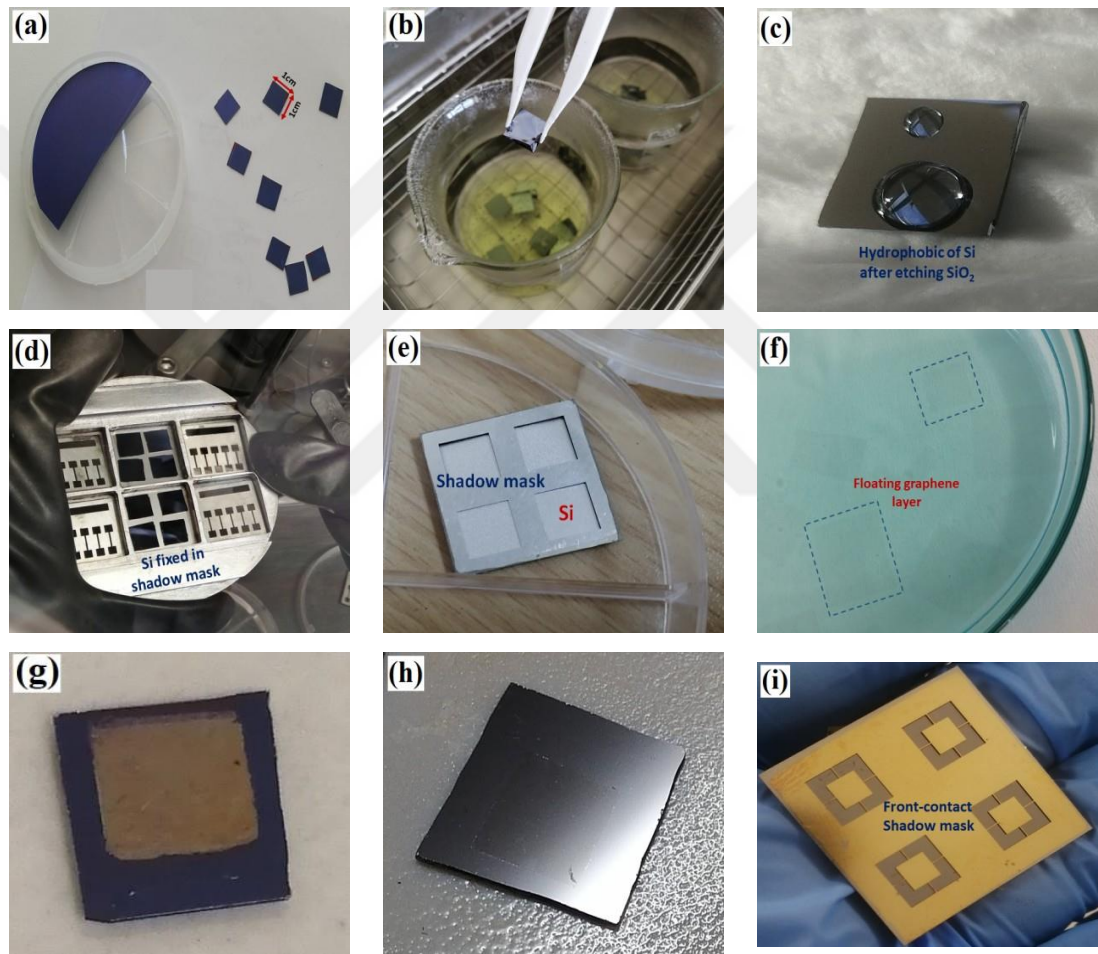


Figure 4.6 Graphene/silicon Schottky junction solar cell fabrication steps (a) cleaving the Si wafer with desired dimensions. (b) clean Si substrates through different steps. (c) hydrophobic of Si substrate after etching SiO<sub>2</sub> layer. (d) aligning Si substrates onto shadow mask for back- contact thermal evaporation. (e) back metal contact evaporated throughout the shadow mask. (f) PMMA/G floating in Cu etchant solvent. (g) transferring PMMA/G onto Si substrate. (h) G/Si after removing PMMA with acetone. (i) depositing the front metal contact throughout the other shadow mask (Personal archive, 2020-2021)

Evaporation process is performed by tuning the applied power between two terminals of a tungsten boats holder containing Chromium (Cr) and silver (Ag) in the case of back contact and chromium (Cr) and gold (Au) in the case of front contact, all depositions were done under vacuum at  $6 \times 10^{-6}$  Torr. When metals reach to melting point, the metal vapor will deposit on the surface substrate. Back- contact were deposited before transfer graphene sheet, where 5/150 nm of Cr/Ag were evaporated throughout the shadow mask, see Figure 4.6e. However, front contact (A frame of Cr/Au of 1.5 mm width) was evaporated after transferring graphene, where 5/50 nm of Cr/Au was deposited. Chromium was used as an adhesion layer and Au was used in order to provide small contact resistance to graphene layers (Xu et al., 2016).

#### ***4.3.3 Wet transfer process of CVD-graphene***

Synthesis graphene sheet by CVD method was explained in details in section 4.2.3, where produced graphene was protected by PMMA coating before etching Cu foil in 0.1 M of ammonium persulfate and washed in DI water for 3 times before transferring PMMA/G onto a desired substrate. However, in our study PMMA/G was transferred directly on the top of n-type silicon substrate (with back- contact formed) while floating in DI water as shown in Figure 4.6f in order to make G/Si Schottky junction. Consequently, the samples were left to dry in a vacuum for 3h before removing PMMA process. Dried PMMA/G/Si showed in Figure 4.6g was placed onto a hot plate at 220 °C for 10 min in order to allow graphene sheet to re-flat after transferring in wet medium and then left to cool down. Thereafter, the PMMA layer was removed by immersing PMMA/G/Si in hot acetone at 50 °C for 30 min followed by isopropyl alcohol (IPA) for 10 min and DI water for 5 min followed by drying in vacuum for another 3h, after this step graphene sheet cannot be observed easily on the top of Si substrate as shown in Figure 4.6h.

#### ***4.3.4 Thermal Annealing and Doping of Graphene***

Before deposition the front metal frame, G/Si samples were placed for thermal annealing in CVD furnace at 350°C with 100 sccm of H<sub>2</sub> and Ar for 2 hours. Thermal annealing step is used to extra remove the PMMA residue in graphene sheet as well as

attain a smoother graphene sheet. Many studies reported that PMMA is merely etched by hot acetone that caused a rough surface in transferred graphene sheet which eventually decreased the cell performance (Wu et al., 2013; Song et al., 2015). Chen *et al.* reported that PMMA residue can be seen as an “island” of 10 nm height in AFM microscope (Chen et al., 2016). Since the melting point of PMMA is  $\sim 130$ - $140^{\circ}\text{C}$  thus, at high temperatures ( $350^{\circ}\text{C}$ ) PMMA melts into nanoparticle-liked and leaves the graphene surface smoother with a flowing of  $\text{H}_2$  and Ar.

As graphene is a 2D atomic thickness with near-zero energy gap and work function of  $\sim 4.7$  eV. In order to enhance graphene’s work function, p-doping can significantly increase the electrical conductivity. Nitric acid ( $\text{HNO}_3$ ) has been used as a p-dopants to graphene (Chen et al., 2016; Lancellotti et al., 2014; Yavuz, 2018). When graphene sheet is doped by  $\text{HNO}_3$  in order to make p-doped layer onto n-Si substrate in Schottky junction, this can be seen as pulling electrons from graphene side toward silicon as well as creating holes toward graphene. In our study, after pre-step thermal annealing to remove PMMA residue, G/n-Si was p-doped with two dopants separately; nitric acid and graphene oxide. The cell was exposing to 65% of  $\text{HNO}_3$  vapor for 30 s, and 3mg/ml of GO dispersion with DI water was spin coated on the graphene surface.

#### **4.3.5 Graphene on Silicon Schottky Junction Solar Cell**

After thermal annealing and doping processes, front metal contact was deposited using thermal evaporation system, where 5/50 nm of Cr/Au has been deposited on the top of a graphene sheet. As we were not able to use the photolithography system, a shadow mask mentioned in section 4.3.2 with a frame of 1.5 mm width was designed. The frame as shown is constructed of four pieces with  $100\ \mu\text{m}$  interspacing (gaps), see Figure 4.6i.

After deposition of the front contact, these gaps were connected using silver paste. Eventually, thin Cu wires were used to form the external circuit of the solar cell in order to examine the current-voltage characteristics.

#### **4.4 Characterization Techniques**

Four different graphene materials have been successfully synthesized. Graphene oxide (GO), reduced graphene oxide (rGO) powder, few-layer graphene flakes (FLG), and mono-layer graphene sheet (G) by modified Hummers' method, electrochemical exfoliation method, and chemical vapor deposition method respectively. Produced graphene materials have been characterized using Raman spectroscopy, X-ray diffractometer (XRD), Scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR). Moreover, the smoothness of graphene sheet produced by CVD technique has been characterized using Atomic force microscopy the its sheet resistance was measured by with Hall effect measurements.

##### **4.4.1 Raman Spectroscopy**

Raman spectroscopy is considered as a powerful tool to examine the number of layers and the quality of the obtained graphene sheets as well as the presence of any functional groups in the sample. In our study, Raman spectroscopy characteristics have been performed by RENISHAW Raman microscope (10-100X objective lenses), with laser monochromatic light at 532nm with scan range of 1100 to 3000  $\text{cm}^{-1}$  at room temperature.

Basically, a specific spot on the sample's surface (graphene) is illuminated with a monochromatic laser beam which interacted in an inelastic way with the molecules of graphene. This interaction resulted in changing the photon's frequency thus, when the molecules absorb the incident photon will form a unique electromagnetic radiation spectrum. This spectrum will be collected by lens and sent to a monochromator. Thus, molecular structure, defect density, and the thickness layer ratios can be obtained from the changes in wavelengths or wave numbers in the scattered spectrum (Schrader, 2008).

##### **4.4.2 Fourier Transform Infrared Spectroscopy (FTIR)**

Fourier transform infrared (FTIR) spectroscopy is a tool utilized to identify and describe the different functional groups in chemical structures of powder material. When infrared is applied to the sample, material's molecules will absorb infrared light

at different wavelengths thus, determines the material's molecular composition and structure. In this study, FTIR Spectroscopy characteristic was performed on Thermo scientific NICOLET iS10, with spectrum range of 500-4000  $\text{cm}^{-1}$ .

#### **4.4.3 X-Ray Powder Diffraction**

X-ray powder diffraction is a tool used to investigate and identify the phase changing in material as well as to determine the interlayer spacing between graphene sheets. XRD is considered as the main technique for graphene structural characterization, where XRD patterns can provide three types of structural information: the number of graphene/graphene oxide layers, the interlayer distance, and the size of graphene crystallites. In our study, X-ray diffraction was performed by Cu-X-ray source with scanning range ( $2\theta = 5^\circ\text{--}80^\circ$ ), THERMO Scientific ARL X'TRA.

#### **4.4.4 Scanning Electron Microscopy (SEM)**

Scanning Electron Microscopy (SEM) is a powerful magnification tool utilized to perceive information about the morphology and surface microstructure of graphene materials. In this study SEM images were collected by SEM (COXEM EM-30 Plus) with magnification rate 500- 10k $\times$  at 20KV in order to represent a high resolution surface morphology.

#### **4.4.5 Atomic Force Microscopy (AFM)**

Atomic force microscopy is a powerful tool used to examine the topography structure and smoothness of graphene sheet at nanoscale before and after annealing treatments which were observed using AFM. Transferred graphene sheet onto Si substrate coated with 300 nm of  $\text{SiO}_2$  and were examined before and after annealing step (350 $^\circ\text{C}$  for 2 hours in 100sccm of  $\text{Ar}/\text{H}_2$ ). In this study, AFM measurements were performed by NANOSURE, EASYSCAN 2 in order to characterize graphene sheet morphology.

#### 4.4.6 Current density - Voltage (J-V) characteristics of solar cell

To evaluate the solar cell performance, current density-voltage curve under illumination is obtained. When sun light is shines on the solar cell, the dark J-V curve is shifts down to the fourth J-V quadrant which means that the power is extracted from the device, see Figure 4.7.

Four main parameters are used to analyze the cell performance; open circuit voltage ( $V_{oc}$ ), short circuit current ( $I_{sc}$ ), fill factor (FF), and power conversion efficiency ( $\eta$ ). The output current of a solar cell is given by:

$$I = I_L - I_0 \left[ \exp \left( \frac{eV}{nKT} \right) \right] \quad (4.1)$$

Where  $I_L$  is the photogenerated current,  $I_0$  is the saturation dark current,  $e$  is the electronic charge,  $n$  is the ideality factor, and  $K$  is the Boltzmann's constant.

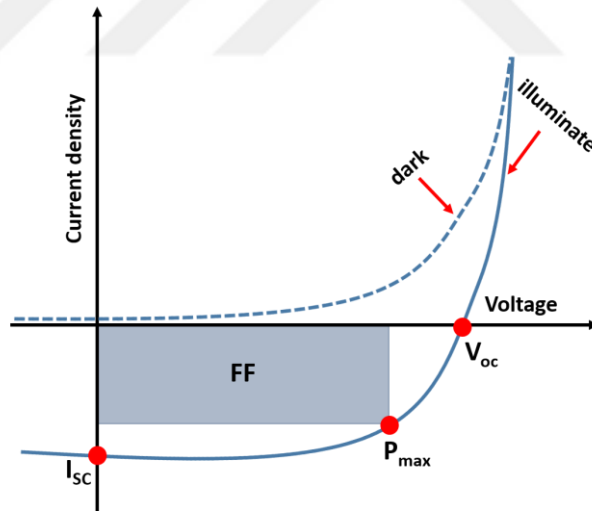


Figure 4.7 Typical J-V characteristics of a solar cell in dark and under illumination

From Figure 4.7, short circuit current ( $I_{sc}$ ) is the largest current can be extracted from the solar cell when the voltage across is zero. The value of this current depends on the active area of the cell, incident light photons, and the charge carrier collection probability at the junction. It is noteworthy to mention that at short circuit condition  $I_L = I_{sc}$ . The open circuit voltage ( $V_{oc}$ ) is defined as the largest voltage can be provided

in the cell when there is no current. The open circuit voltage depends on the photogenerated current beside the saturation dark current and it is given from equation 4.1 by setting  $I = 0$  as;

$$V_{oc} = \frac{nKT}{e} \ln \left( \frac{I_L}{I_0} + 1 \right) \quad (4.2)$$

At  $V_{oc}$  and  $J_{sc}$  points, the power of the solar cell is zero, therefore the fill factor term (FF) is introduced to determine the maximum current and voltage at maximum power point shown in Figure 4.7. FF measures the preferable squareness of the J-V curve, given by;

$$FF = \frac{P_{max}}{V_{oc} \times I_{sc}} \quad (4.3)$$

Finally, the power conversion efficiency ( $\eta$ ) of the solar cell is defined by the ratio of output energy from the cell to the input incident energy given by sunlight. At standard conditions, the input power is  $100 \text{ mW/cm}^2$ .

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}} \quad (4.4)$$

J-V characterization of fabricated G/Si Schottky junction solar cells were performed with a Keithley 2400 source meter at the incident power of  $100 \text{ mW/cm}^2$  illumination (AM 1.5 G) in air at room temperature.

## CHAPTER FIVE

### RESULTS AND DISCUSSION OF SYNTHESIZED GRAPHENE MATERIALS

#### 5.1 Raman Spectra Analysis

Three main features in Raman spectra of graphene and bulk graphite materials are the so-called D, G, and 2D bands, which locate at around  $1350\text{ cm}^{-1}$ ,  $1580\text{ cm}^{-1}$ , and  $2700\text{ cm}^{-1}$ , respectively. These peaks are used to analyze the structure of graphene by specifying two ratios: defect density ratio ( $I_D/I_G$ ) and thickness layer ratio ( $I_{2D}/I_G$ ).

The D band is known as a defective band that represents the first-order scattering of  $sp^3$  hybridized carbon atoms, which appears due to breathing modes of  $sp^2$  atoms (Castiglioni et al., 2001; Ferrari & Robertson, 2000). The high intensity in D band refers to the significant number of defects in the graphene sheet, whilst G band represents the stretching vibration of  $sp^2$  hybridized carbon bonds and affords the testimony number of graphene layers. However, the third band 2D represents the second order of D band, which is also considered as the second most prominent band observed in graphite samples (Vidano et al., 1981). The position of 2D band changes according to the number of graphene layers. The band is sharp in single graphene layer and becomes wider in bilayer graphene. While in few-layer graphene form, the position of 2D peak becomes wider and shifts to higher wavenumbers with appearance of a second shoulder towards low wavenumbers. According to the literatures, few-layer graphene form is considered to be around five layers (Ferrari, 2007; Georgakilas, 2014). A study by Ferrari *et al.*, reported that only the thickness layer ratio and the position of the G peak are not enough to determine the number of graphene layers (Ferrari et al., 2006). Other studies (Graf et al., 2007; Gupta et al., 2006) suggested that the shape of 2D band remarkably identifies the number of layers.

### 5.1.1 Raman Spectra of NGr, GO, and rGO Powders

Figure 5.1 shows Raman spectra for our starting material natural graphite (Gr), and synthesized graphene oxide (GO) and reduced graphene oxide (rGO) within the range of 1100–3000  $\text{cm}^{-1}$ . The G peak was recognized at 1582  $\text{cm}^{-1}$  which represents the typical  $\text{sp}^2$  hybridization of carbon materials while, D band was observed at 1348  $\text{cm}^{-1}$  which represents the structural defects and impurities on the flake's surface. The defect density ratio was found 0.11 in the starting material (before oxidation) and increased as defects increased, see Table 5.1. The 2D peak was found at 2718 and the thickness layer ratio was 0.44 for graphite –the starting material- before any chemical treatments.

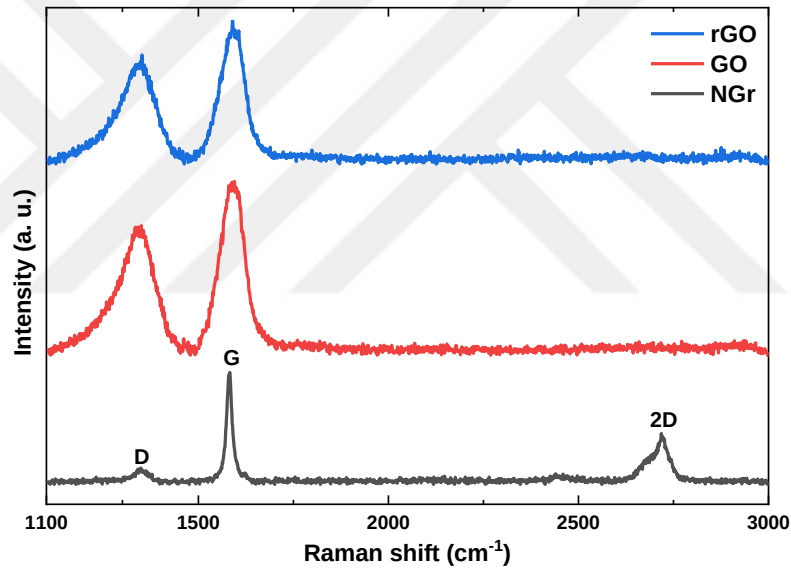


Figure 5.1 Raman spectra of NGr and synthesized GO and rGO

Table 5.1 Raman defect ratio data of NGr and synthesized GO, and rGO

| Sample | $R_{\text{shift}}$ | $I_D$ | $R_{\text{shift}}$ | $I_G$ | $I_D/I_G$ |
|--------|--------------------|-------|--------------------|-------|-----------|
| NGr    | 1348               | 142   | 1582               | 1344  | 0.11      |
| GO     | 1349               | 3647  | 1580               | 3711  | 0.98      |
| rGO    | 1351               | 2900  | 1590               | 3014  | 0.96      |

For GO and rGO, it was seen that the D peaks in GO and rGO are significantly strong which indicates the presence of lattice deformations of graphene planes (Chen et al., 2013) and the defect ratio has increased from 0.11 in natural graphite to 0.98 for graphene oxide which indicates that the use of chemicals has introduced more defects to the obtained sample, see Table 5.1. The defect density was slightly decreased in the final product to 0.96 after reduction process, which means reduction in the oxygen functional group. While 2D peak for both GO and rGO was found broad, low intense and shifted to higher wavenumber around  $2771\text{ cm}^{-1}$  in GO spectra that confirms the obtaining of multi-layer GO powder with the presence of oxygen functional groups which inhibits graphene layer to stack (Dresselhaus et al., 2010; Thakur & Karak, 2012). It has been reported that, higher intensity in D peak in rGO indicates more exfoliated graphene compared with GO (Hidayah et al., 2017).

#### **5.1.2 Raman Spectra of Few-layer Graphene of NGr, EE1, and EE2**

Figure 5.2 shows Raman spectra of electrochemical exfoliated graphene powders EE1 and EE2 as the first step in order to produce few-layer graphene sheets with the spectrum of NGr as the starting material. As can be seen in the Figure 5.2 and from Table 5.2, when electrochemically exfoliation was applied to the graphite electrodes in 0.1 M of  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  solutions separately, the defect ratio was increased from 0.11 in the starting material NGr to 0.34 and 0.38 in EE1 and EE2 respectively which indicates the presence of oxygen as well as the deformation in the produced graphene structure (Ferrari & Robertson, 2000). While the thickness layer ratio was increased from 0.44 in the starting material to 0.45 and 0.52 in EE1 and EE2 respectively. The enhancement in the ratio indicates the improvement in exfoliation graphene sheets. Defect density gave better results when  $\text{H}_2\text{SO}_4$  solution was used as an electrolytic in the case of (EE2). The resulted graphene still considered as low-layer exfoliated graphene (Akbar et al., 2015; Geim, 2009).

Only electrochemical exfoliation was not sufficient to produce few-layer graphene sheets, thus the resulted powder was used to prepare a 3 mg/ml of Dimethylformamide (DMF) dispersion that placed in sonication bath for 1 hour followed by rapid

microwave irradiation (MW) for 30 s. Figure 5.3 shows Raman spectra throughout sonication in DMF and exposing to MW.

In Figure 5.3a, Raman spectra of NGr as a starting material (black curve), after sonication in DMF (red curve), and after microwave irradiation (blue curve) are displayed. As can be seen, a significant increase in both D and 2D peaks after sonication in DMF, while G peak intensity showed a slight decrease.

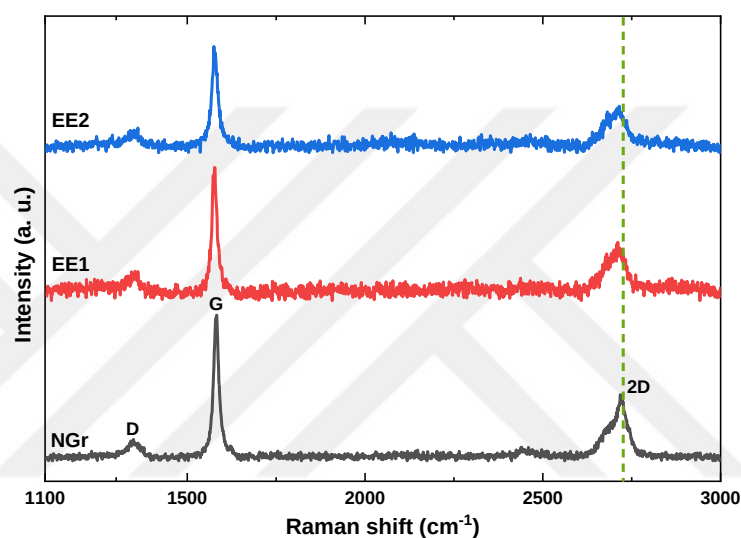


Figure 5.2 Raman spectra electrochemical exfoliated graphene sheets EE1 and EE2 with the starting material NGr

From Table 5.2, the thickness layer ratio was enhanced to  $I_{2D}/I_G = 0.68$  after treating with DMF which proves a successful exfoliation and increasing in the inter-planar spacing between graphene sheets. The defect density was found  $I_D/I_G = 0.59$  which is acceptable due to the intercalation of a strong exfoliated reagent molecules of DMF which affected the structure lattice and caused deformations in graphitic layer structure (Afanasov et al., 2010; Gu et al., 2009).

To overcome this, one effective and quick technique was used in this work by irradiating the obtained powder after sonication with microwaves for 30 s. Microwaves can be absorbed very easily in carbon materials (Menéndez et al., 2010), in other words

microwaves penetrate the substrate molecules and generate heat internally. Thus, it is a useful technique to reduce the oxygen as well as the defect ratio, whereas after applying MW for 30 s, the defect ratio was decreased to 0.46 and thickness layer ratio was slightly enhanced to 0.69. Therefore, irradiation of microwaves works as an oxidation–reduction agent for the graphene as well as enhancing the exfoliation of graphene sheets. The same effect was obtained when electrochemical exfoliated powder was used instead of natural graphite.

Table 5.2 Raman data of synthesized graphene materials in electrochemical exfoliation, sonication in DMF and microwave irradiated with defect density and thickness layer ratios

| Sample            | R <sub>shift</sub> | I <sub>D</sub> | R <sub>shift</sub> | I <sub>G</sub> | R <sub>shift</sub> | I <sub>2D</sub> | I <sub>D</sub> /I <sub>G</sub> | I <sub>2D</sub> /I <sub>G</sub> |
|-------------------|--------------------|----------------|--------------------|----------------|--------------------|-----------------|--------------------------------|---------------------------------|
| <b>NGr</b>        | 1348               | 141.7          | 1582               | 1344           | 2718               | 584.8           | 0.11                           | 0.44                            |
| <b>NGr+DMF</b>    | 1358               | 844            | 1579               | 1443           | 2719               | 977             | 0.59                           | 0.68                            |
| <b>NGr+DMF+MW</b> | 1350               | 1130           | 1580               | 2438           | 2717               | 1689            | 0.46                           | 0.69                            |
| <b>EE1</b>        | 1349               | 683.7          | 1577               | 2030           | 2716               | 909.7           | 0.34                           | 0.45                            |
| <b>EE1+DMF</b>    | 1346               | 1346           | 1580               | 2539           | 2716               | 1637            | 0.53                           | 0.65                            |
| <b>EE1+DMF+MW</b> | 1344               | 934            | 1580               | 2238           | 2717               | 1432            | 0.42                           | 0.64                            |
| <b>EE2</b>        | 1352               | 702            | 1577               | 1844           | 2716               | 960.8           | 0.38                           | 0.52                            |
| <b>EE2+DMF</b>    | 1325               | 1640           | 1581               | 2981           | 2722               | 2113            | 0.55                           | 0.71                            |
| <b>EE2+DMF+MW</b> | 1373               | 3427           | 1579               | 4946           | 2712               | 3829            | 0.7                            | 0.77                            |

In Figure 5.3b, Raman spectra demonstrated the effective extra exfoliation to graphene after sonication in DMF of EE1 with defect density of  $I_D/I_G = 0.53$  and thickness layer ratio of  $I_{2D}/I_G = 0.65$  which is less than the case of natural graphite but with less defects in the produced graphene structure. When microwave was applied, defect ratio decreased to 0.42 and the thickness layer ratio slightly decreased to 0.64 which again approved the successful expansion of graphene flakes and minimize the defects.

Figure 5.3c shows the Raman spectra of EE2 sample throughout sonication in DMF and MW. Significant increase in the D, G, and 2D peaks with intense increase in G peak when sonication in DMF was applied for 1 hour.

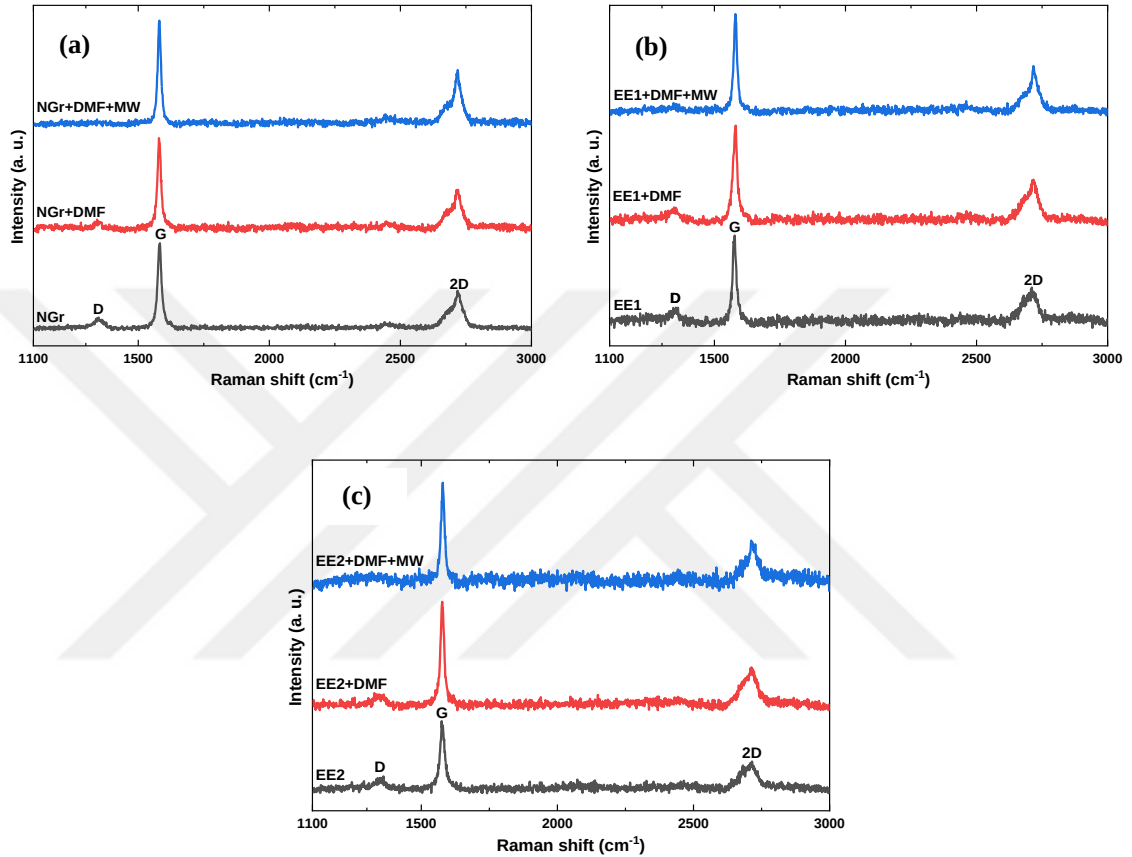


Figure 5.3 Raman spectra after sonication in DMF for NGr, EE1 and EE2

Therefore, defect density ratio was increased to  $I_D/I_G = 0.55$  after sonication in DMF and more to 0.70 after microwave irradiation. While, the thickness layer ratio exhibited a significant high values to  $I_{2D}/I_G = 0.71$  after DMF sonication. This value has been more increased after applying microwave irradiation for 30 s and reached to  $I_{2D}/I_G = 0.77$  which belonged to obtaining few-layer graphene sheets with about  $\sim 5$  layers (Georgakilas, 2014) in the final product. Figure 5.4 shows the statistical histograms for both  $I_D/I_G$  and  $I_{2D}/I_G$  ratios of NGr, EE1, and EE2 throughout the exfoliation processes.

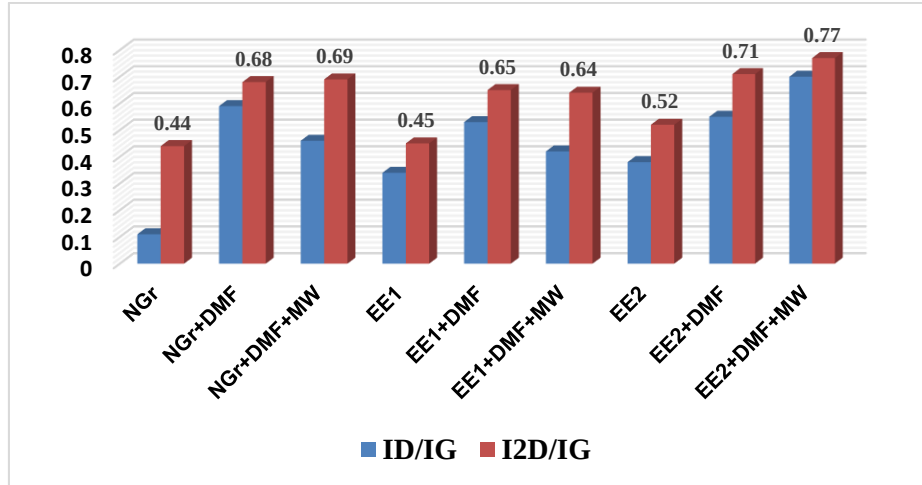


Figure 5.4 Statistical histograms of the defect density and thickness layer ratios for second synthesis method (EE → DMF → MW)

### 5.1.3 Raman spectrum of monolayer CVD graphene

Figure 5.5 shows Raman spectra of the graphene sheet synthesized by chemical vapor deposition (CVD) method before and after annealing treatment. The three key peaks D, G, and 2D were found around  $1349\text{ cm}^{-1}$ ,  $1588\text{ cm}^{-1}$ , and  $2686\text{ cm}^{-1}$  respectively. From Table 5.3, before annealing treatment (purple line), the defect density ratio was found  $I_D/I_G = 0.14$ , while the thickness layer ratio was  $I_{2D}/I_G = 2.04$  that is considered as monolayer graphene (Cançado et al., 2008). The D peak refers to defects in graphene sheet that might be the presence of oxygen functional groups of deformation in graphene structure as well as the residue of PMMA in graphene sheet.

The typical G peak exists between  $1580\text{--}1630\text{ cm}^{-1}$  and it is quite sensitive to the doping level in graphene (Tivanov et al., 2016), whereas shifting in this peak could provide more details about the number of graphene sheet. While 2D peak is the most powerful peak in graphene structure that can provide the quality of graphene, and was found at  $2686\text{ cm}^{-1}$ .

In order to reduce the PMMA residue in graphene sheet, annealing treatment was applied, where transferred graphene on silicon substrate was placed in CVD furnace at  $350^\circ\text{C}$  for 2 hours at 100 sccm of Ar/H<sub>2</sub>. The data showed in Table 5.3 and from

Figure 5.5 (red line). The D, G, and 2D peaks were found at  $1362\text{ cm}^{-1}$ ,  $1585\text{ cm}^{-1}$  and  $2699\text{ cm}^{-1}$  respectively. The defect density was  $I_D/I_G = 0.16$  and the thickness layer ratio was decreased to  $I_{2D}/I_G = 1.49$ . The shifting in 2D position toward higher energies declares that the annealing process caused a p-doping in graphene sheet which is in an agreement with other studies (Chen et al., 2016; Choi et al., 2014; Lin et al., 2012).

Table 5.3 Raman data of CVD synthesized monolayer graphene sheet before and after annealing

| Monolayer G      | $R_{\text{shift}}$ | $I_D$ | $R_{\text{shift}}$ | $I_G$ | $R_{\text{shift}}$ | $I_{2D}$ | $I_D/I_G$ | $I_{2D}/I_G$ |
|------------------|--------------------|-------|--------------------|-------|--------------------|----------|-----------|--------------|
| Before annealing | 1349               | 758.6 | 1588               | 5623  | 2686               | 11,500   | 0.135     | 2.049        |
| After annealing  | 1362               | 750.3 | 1585               | 4547  | 2699               | 6782     | 0.165     | 1.492        |

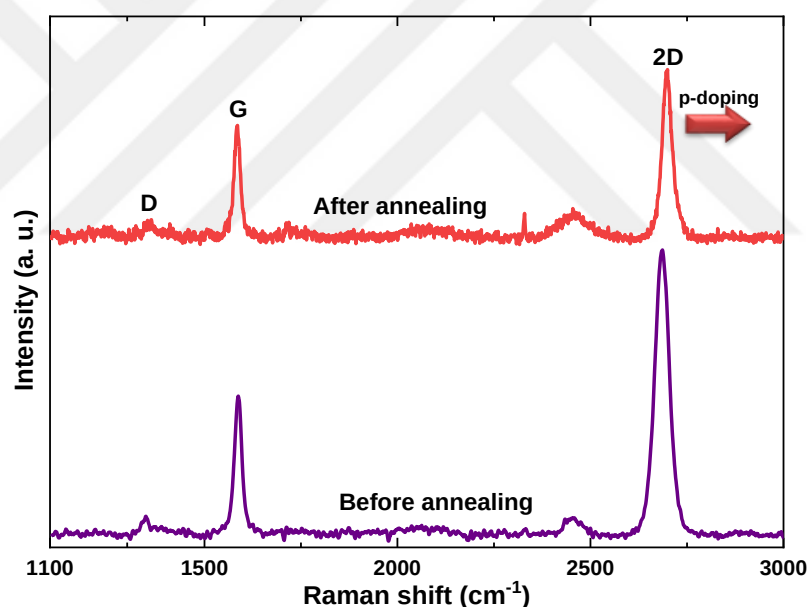


Figure 5.5 Raman spectrum of monolayer CVD graphene sheet before and after annealing

## 5.2 Fourier Transform Infrared Spectroscopy (FTIR)

### 5.2.1 FTIR of NGr, GO, and rGO Powders

The obtained FTIR spectra of NGr, GO, and rGO are shown in Figure 5.6. there was no significant peak observed in NGr powder (black line) except the C=C=C allene stretching band around  $1900\text{--}2000\text{ cm}^{-1}$ . FTIR spectrum of GO (red line) shows a wide

band O-H stretching vibration band at 3000–3600  $\text{cm}^{-1}$  caused by the presence of hydroxyl group, a C=O stretching carboxyl at 1744-1670  $\text{cm}^{-1}$ , and C-O stretching epoxy group at 1332  $\text{cm}^{-1}$  both indicate the presence of oxygen-functional groups.

The presence of hydroxyl group, carboxyl group and epoxy group vibrations indicate the successful synthesis of graphene oxide (Cheng et al., 2019). Another significant absorption peak was found at 1639  $\text{cm}^{-1}$  belonging to the in-plane vibrations of aromatic C=C.

After reduction process, the rGO FTIR spectrum (blue line) showed a significant decrease in O-H band proving that the hydroxyl group has completely removed and the characteristic absorption peaks of both C=O and C-O bands became broad and less intense indicating a successful reduction of oxygen-functional group on the surface using hydrazine (Cao & Zhang, 2015; Peng et al., 2013; Rao et al., 2018). However, some residual oxygen sorts remain in the material.

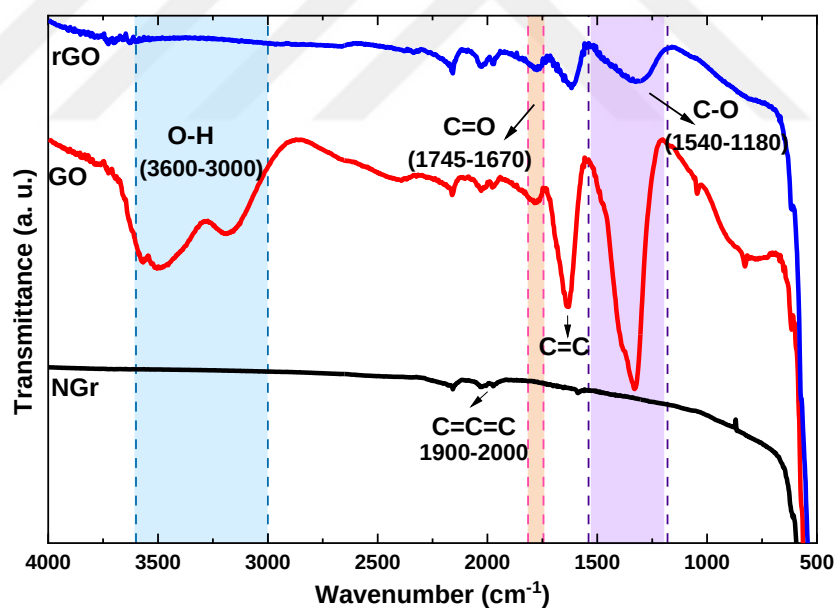


Figure 5.6 FTIR spectra of NGr, prepared GO, and rGO by modified Hummers' method

### 5.2.2 FTIR of Few-layer Graphene Sheets of NGr, EE1, and EE2

Figure 5.7 shows FTIR spectra for natural graphite powder, and two exfoliated graphene powder obtained by electrochemical exfoliation method in  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  solutions are EE1 and EE2 respectively, discussed in section 4.2.2.1.

After sonication in DMF, a strong oxygen functional group C=O stretching band was observed around  $1745\text{--}1696\text{ cm}^{-1}$  that decreased significantly after applying microwave irradiation. In the case of the starting material NGr (black line), no significant peaks of any functional group were observed, except some weak bands which may appear due to adsorption of water molecules.

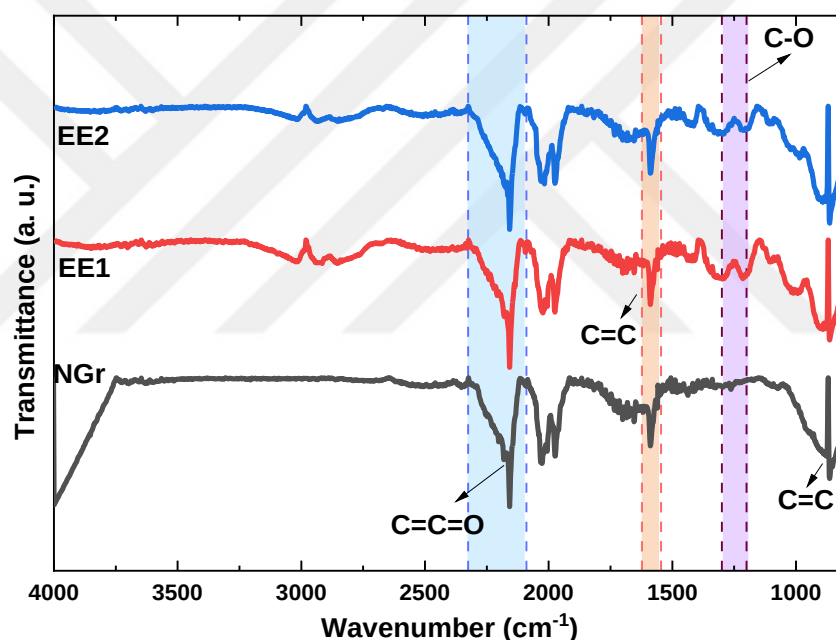


Figure 5.7 FTIR spectra of NGr, electrochemical exfoliated powders EE1 and EE2

While, in the electrochemically exfoliated powders EE1 and EE2, the characteristic FTIR absorption peaks shows the presence of some functional groups including medium alkene C=C stretching band at  $1585\text{ cm}^{-1}$ , C=C bending band at  $863\text{ cm}^{-1}$ , and weak C–O stretching vibration band were found around  $1214\text{--}1305\text{ cm}^{-1}$ . Moreover, other peaks were slightly appeared in the exfoliated powder due to the intercalation of acid molecules throughout producing processes (Liu et al., 2013; Shengtao et al.,

2011). The obtained powders were low-layer graphene sheets thus, in order to obtain few-layer graphene sheets, simple and quick techniques were used as follow.

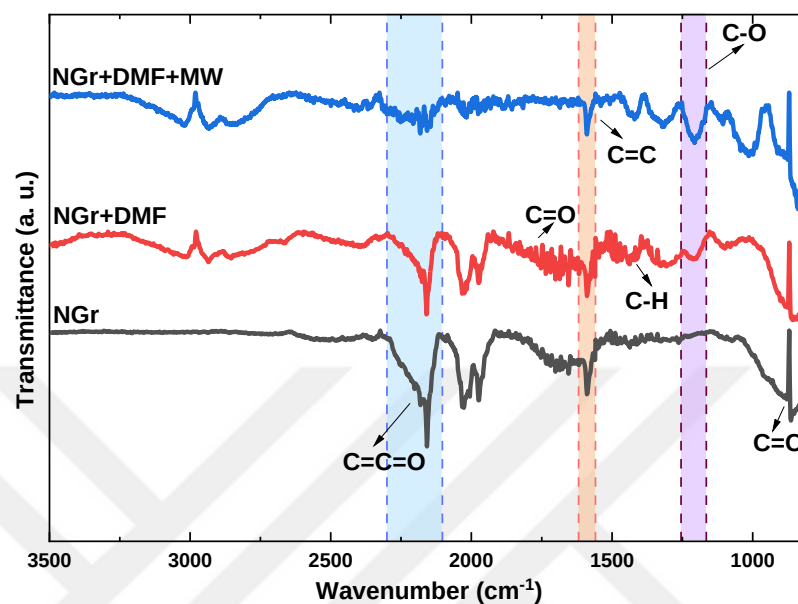


Figure 5.8 FTIR spectra of NGr, NGr+DMF, and NGr+DMF+MW

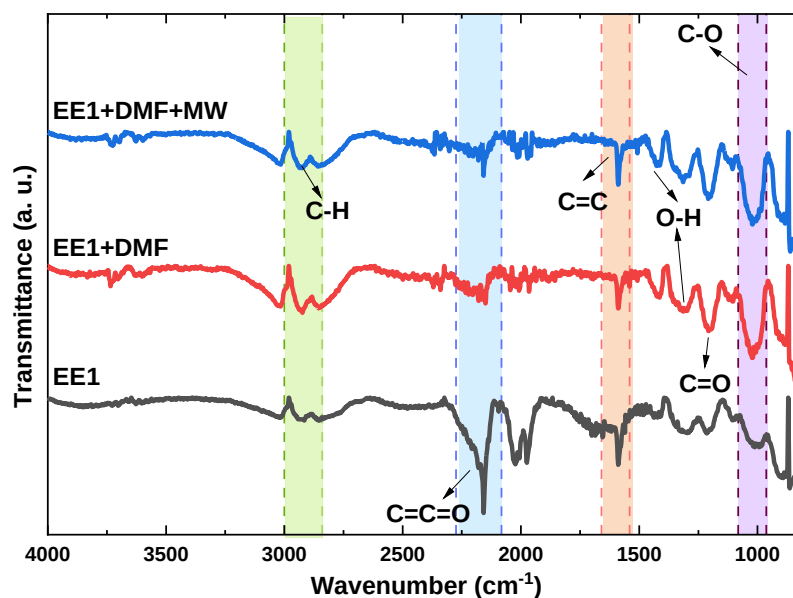


Figure 5.9 FTIR spectra of EE1, EE1+DMF, and EE1+DMF+MW

NGr, EE1, and EE2 powders were separately used to prepare 3 mg/ml of Dimethylformamide (DMF) and placed in sonication bath for 1 hour. Later, the powders have been produced were irradiated with microwaves (MW) for 30 s. In Figure 5.8, FTIR spectra of NGr powder before sonication, after DMF sonication, and after MW irradiation were displayed. In NGr spectrum, two absorption peaks were revealed including stretching C=C=O band and alkene C=C band at  $2157\text{ cm}^{-1}$  and  $865\text{ cm}^{-1}$  respectively. When the same technique was applied to EE1, FITR spectra shows in Figure 5.9 three absorption peaks; stretching C-H band at around  $2948\text{ cm}^{-1}$ , bending O-H bands at  $1426\text{ cm}^{-1}$  and  $1316\text{ cm}^{-1}$ , and oxygen functional groups C=O at  $1208\text{ cm}^{-1}$  and stretching C-O band at  $1030\text{ cm}^{-1}$ .

Withal EE2 material, Figure 5.10 shows FTIR spectra throughout sonication and microwave irradiation. The characteristic FTIR absorption peaks show the presence of stretching C-H band at  $2930\text{ cm}^{-1}$ , bending O-H band at  $1416\text{ cm}^{-1}$  and  $1305\text{ cm}^{-1}$ , and strong stretching band of C-O at  $1028\text{ cm}^{-1}$  in the obtained few-layer graphene flakes.

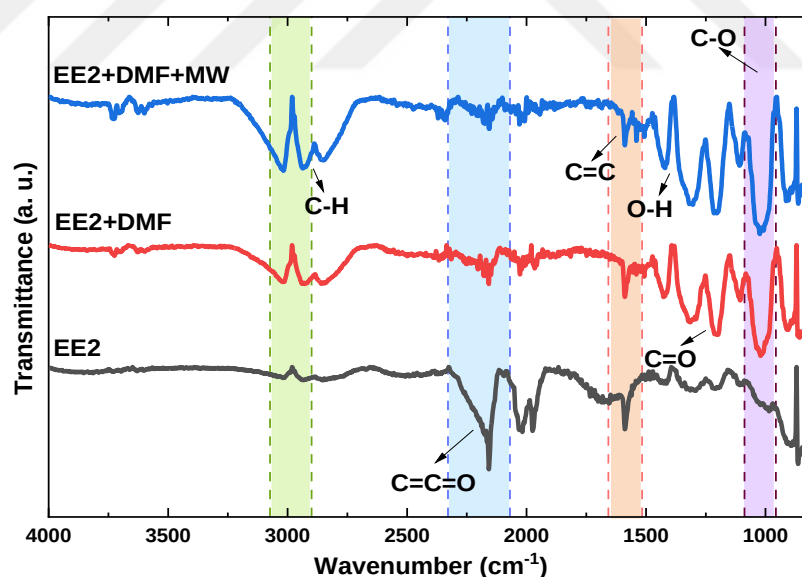


Figure 5.10 FTIR spectra of EE2, EE2+DMF, and EE2+DMF+MW

### 5.3 X-Ray Diffraction

#### 5.3.1 XRD of NGr, GO, and rGO Powders

Figure 5.11 shows the X-ray diffraction spectra of natural graphite (NGr), graphene oxide (GO), and reduced graphene oxide (rGO) powders synthesized by modified Hummer's method. The XRD pattern of NGr (black line) shows a very sharp and intense two peaks at  $2\theta = 26.42^\circ$  and  $2\theta = 54.6^\circ$  which are related to the carbon essential reflection peaks (002) and (004) respectively (Kun et al., 2011). The diffraction peak at  $2\theta = 26.42^\circ$  is confirmed the presence of well-arranged layer structure of carbon with d-spacing of 0.337 nm (Yang et al., 2015).

While XRD pattern of GO (red line) exhibits an intense diffraction peak at  $2\theta = 12.48^\circ$  which is related to the (001) GO crystalline plane corresponding to d-spacing of 0.8 nm and this increment is due to the intercalation of oxygen functional groups between carbon basal planes.

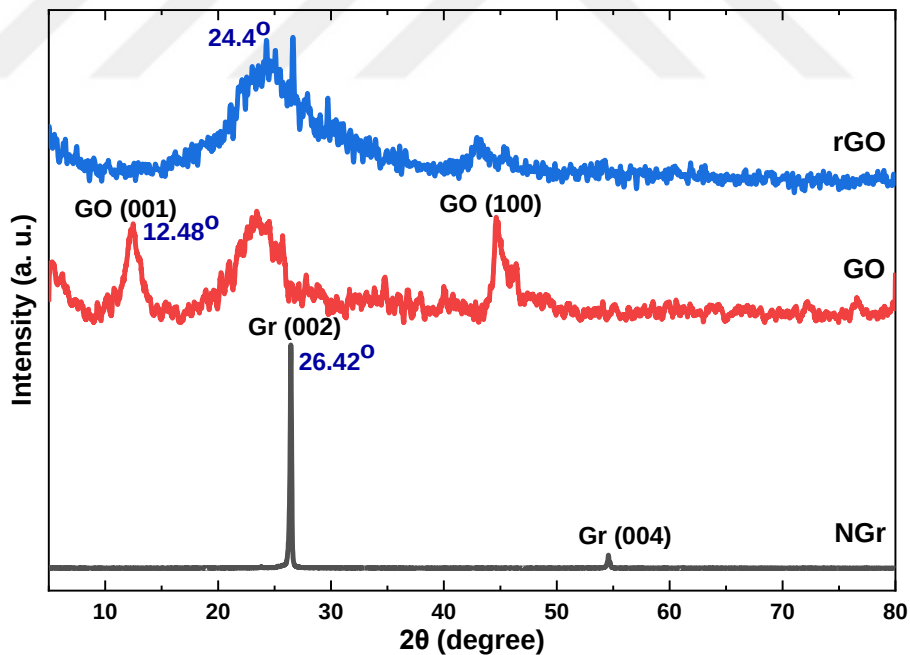


Figure 5.11 XRD patterns of NGr, GO, and rGO

This high intensity in GO pattern indicates the presence of high amount of water molecules/oxygen functional groups (Rao et al., 2018). No observed carbon peak at

26.4° in the GO material is an indication of the effective oxidation process with no unconverted graphite. The other diffraction peak at  $2\theta = 42.3^\circ$  of (001) orientation in GO pattern is interpreted as the incomplete oxidation material caused by the turbostratic band of disordered carbon materials (Cao & Zhang, 2015; Hidayah et al., 2017). After reduction process, the XRD pattern of rGO (blue curve) exhibits a new broad peak at  $2\theta = 24.24^\circ$  of (002) corresponding to d-spacing of  $\sim 0.4$  nm, while the peak at  $12.48^\circ$  was completely disappeared which clearly proves that the oxygen function groups were significantly reduced and rGO has produced (Cao & Zhang, 2015; Hidayah et al., 2017). The decreasing in d-spacing is a confirmation of a significant structural changes before and after reduction process (Jabbar et al., 2017).

### **5.3.2 XRD of Few-layer Graphene Sheets of NGr, EE1, and EE2**

In the second synthesis method; electrochemical exfoliation, sonication in DMF, and microwave irradiation were applied in order to produce few-layer graphene sheets. The XRD patterns for all obtained samples showed that all peak positions had the two symmetry peaks at  $26.4^\circ$  and  $54.6^\circ$  which are related to the carbon essential reflection crystalline (002) and (004) orientation respectively as well as an indication of existing pure graphene in the final products (Kun et al., 2011). The peak position of XRD patterns of graphite and two electrochemical exfoliated powders did not change and only the peak intensity has weakened from graphite to electrochemically exfoliated graphene sheets. In contrast, the diffraction peak position was significantly changed in the first synthesis method (modified Hummers') which was caused by the presence of oxygen functional groups in the final product.

On the other hand, peak positions ( $2\theta$ ) in all patterns have slightly changed during synthesis processes between  $26.4^\circ$  and  $26.6^\circ$ , while the significant change was in the peak intensities. The significant decrease in peak intensity was shown from the starting material (graphite) to the final product (graphene). This massively dropping in the peak intensity of obtained graphene compared to graphite peak intensity is related to reduction in the number of graphene layers which confirms the successful exfoliation and obtaining of few-layer graphene sheets in the final product (Carrasco et al., 2014; Hadi et al., 2018; Liu et al., 2020).

Figure 5.12 shows the XRD patterns of natural graphite powder (NGr) and the two electrochemically exfoliated graphene powders EE1 and EE2. The diffraction peaks have showed a slight change during synthesis process from  $26.44^\circ$  in the starting material NGr to  $26.47^\circ$  in the electrochemically exfoliated graphene and a significant decrease in the peak intensities in the final graphene product, see Table 5.4.

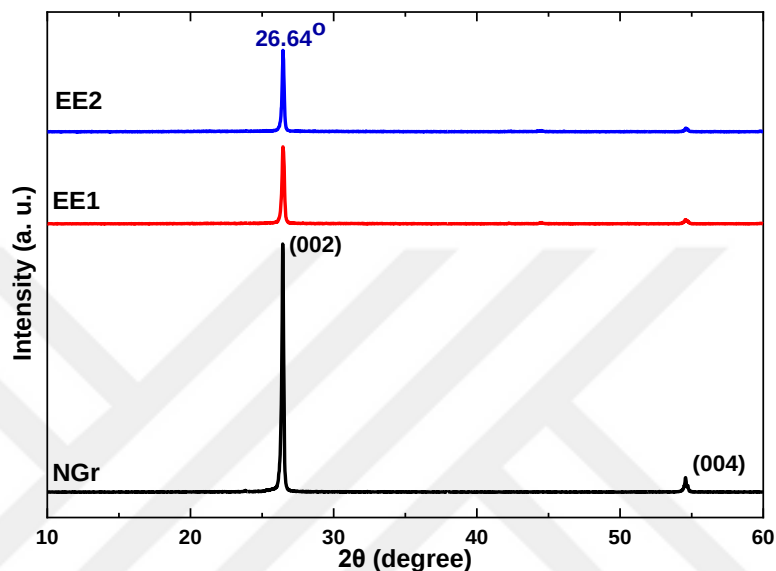


Figure 5.12 XRD patterns of NGr, electrochemical exfoliated powders EE1 and EE2

Figure 4.13 shows the XRD patterns of NGr powder during exfoliation processes by sonication in DMF for 1 hour and microwave irradiation for 30 s. As can be seen, all specimens have the same intense diffraction peaks around  $2\theta = 26.44^\circ$  and  $2\theta = 54.6^\circ$  which are related to the carbon essential reflection (002) and (004) orientation respectively.

Moreover, no other diffraction peak was observed in XRD patterns which indicates that no oxygen or any other functional groups are present in the final product (Badri et al., 2017). The intense peak position of (002) was slightly shifted from starting material (NGr) to  $26.63^\circ$  after sonication in DMF for 1 h and to  $2\theta = 26.56^\circ$  after microwave irradiation. The shifting in peak position is an indication of obtained high crystalline structure of graphene sheets (Cheng et al., 2017). However, the peak intensity exhibited a significant decrease throughout the synthesis process, whereas it decreased

from 24,350 in the starting material (NGr) to 5222 after sonication in DMF then reached to 3977 after microwave irradiation.

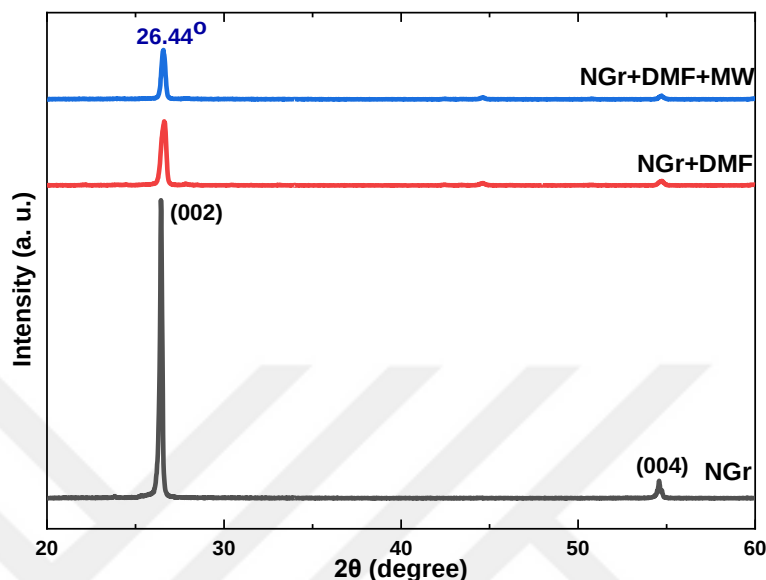


Figure 5.13 XRD patterns of NGr as a starting material, after sonication, and after microwave irradiation

The more the peak intensity decreases the more the graphene layers decrease in the final product. This result signifies that the lower peak intensity, the higher exfoliation amount of packing dense graphite layers (Valapa et al., 2015). This result is compatible with Raman results, where the increase in thickness layer ratio to 0.69 is an indication of obtaining few-layer graphene sheets. It was found that the interlayer spacing ( $d$ ) in all obtained samples was between 3.34 and 3.37 Å which refers to the distance between carbon atom planes. The position of the diffraction peak can be used to determine the interlayer distance, see Table 5.4. It has been reported that, when  $d$ -spacing is equal to 3.34 nm, the product is considered as a multi-layer graphene sheet, while at  $d \geq 3.35$  nm (larger interlayer distance) the product is few-layer graphene sheets (Coroş et al., 2016). Additionally, the full peak width of the diffraction peak at half-maximum height (FWHM) increased from starting material to the final product after sonication in DMF and microwave irradiation which emphasizes the enhancement of amorphous nature in produced graphene sheets (Graf et al., 2007). Figure 5.14 shows XRD patterns of electrochemical exfoliation graphene EE1 during

synthesis methods. The sharp intense diffraction peak of (002) was found around  $2\theta = 26.47^\circ$  indicating that the basal carbon crystal layer does not experience any change after molecules' intercalation throughout the sonication in DMF.

Table 5.4 The XRD patterns' data of NGr powder and all synthesis graphene materials

| SAMPLE     | Diffraction peak of (002) |           |                            |           |
|------------|---------------------------|-----------|----------------------------|-----------|
|            | Peak Position (deg)       | Intensity | d-spacing ( $\text{\AA}$ ) | FWHM (nm) |
| NGr        | 26.44                     | 24350     | 3.37                       | 0.17      |
| NGr+DMF    | 26.63                     | 5222      | 3.34                       | 0.33      |
| NGr+DMF+MW | 26.56                     | 3977      | 3.35                       | 0.36      |
| EE1        | 26.47                     | 7498      | 3.36                       | 0.21      |
| EE1+DMF    | 26.50                     | 5489      | 3.36                       | 0.21      |
| EE1+DMF+MW | 26.52                     | 2694      | 3.36                       | 0.26      |
| EE2        | 26.47                     | 7757      | 3.36                       | 0.25      |
| EE2+DMF    | 26.48                     | 6428      | 3.36                       | 0.26      |
| EE2+DMF+MW | 26.56                     | 3505      | 3.35                       | 0.18      |

However, the diffraction peak intensity was considerably decreased from 7498 in the starting material EE1 to 5489 after sonication in DMF for 1 hour and reached to 2694 after microwave irradiation which indicates the lowering of graphene layer (increasing the inter-layer spacing) in the final product and successful exfoliation (Valapa et al., 2015). The d-spacing was found around 3.36 nm which is considered as a few-layer form of graphene sheets (Coroş et al., 2016).

Figure 5.15 shows XRD patterns of the electrochemical exfoliation graphene EE2 during synthesis processes. The diffraction peaks in all products exhibited almost the same diffraction peak as graphite, the unique and sharp characteristic peak is around  $2\theta = 26.47^\circ$  of carbon (002), which indicates the retaining of carbon structure. The narrowness of the (002) peak is increased with the increasing number of graphitic layers per each crystalline (Prolongo et al., 2014). All peak positions have showed a slight change throughout synthesis processes around this value, which corresponds to

the characteristic graphene diffraction peak. The only significant change in patterns was in the peak intensity, where it has been weakened from graphite to final graphene product whereas the size of graphene sheet became smaller when graphite was exfoliated to graphene (Wang & Zhang, 2019).

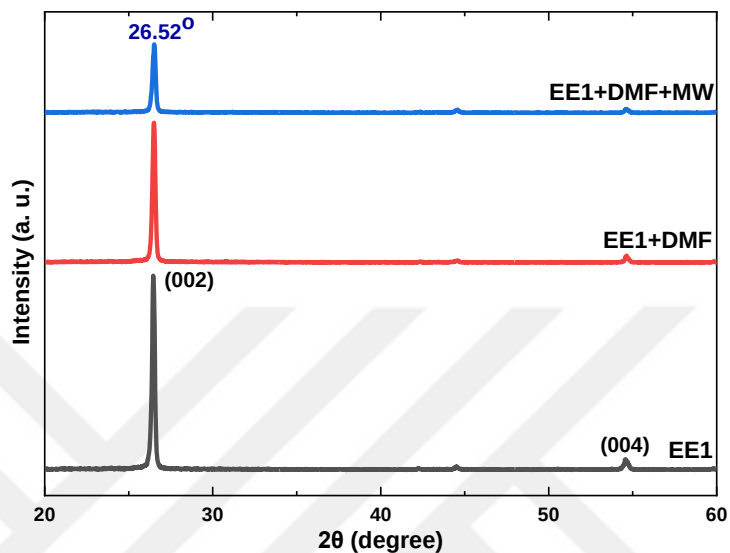


Figure 5.14 XRD patterns of EE1 as a starting material, after sonication, and after microwave irradiation

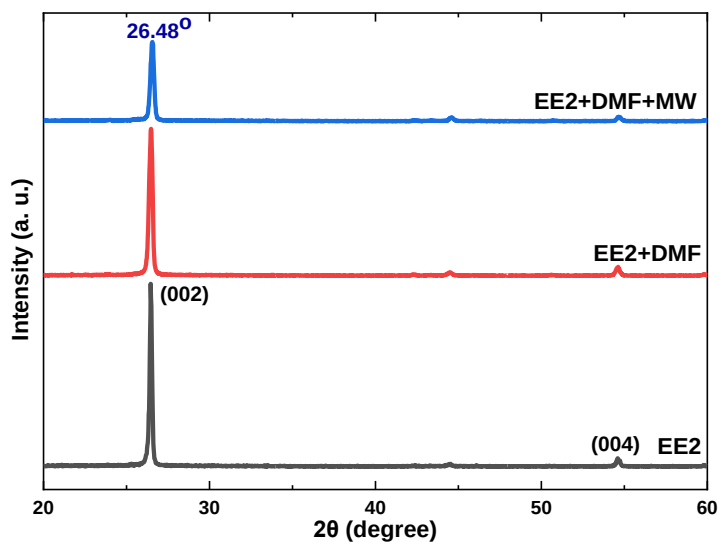


Figure 5.15 XRD patterns of EE2 as a starting material, after sonication, and after microwave irradiation

However, the diffraction peak intensity was decreased from 7757 in EE2 to 6428 after sonication in DMF for 1 hour and reached to 3505 after microwave irradiation

for 30 s. This indicated that electrochemically exfoliated graphene powders have adequately exfoliated to few-layer graphene sheets form simply be sonication in DMF followed by quick microwave irradiation. Figure 5.16 shows the decrease in the diffraction peak intensity of all samples throughout synthesis methods to obtain few-layer graphene sheets.

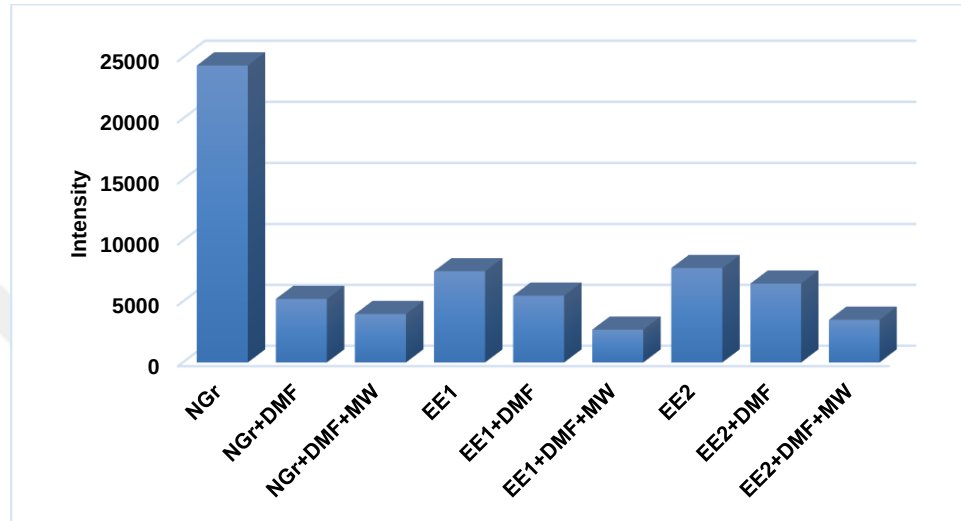


Figure 5.16 The decrement in diffraction peak intensities according to XRD data

## 5.4 Scanning Electron Microscopy (SEM)

### 5.4.1 SEM Images of NGr, GO, and rGO Powders

Figures 5.17 show the morphology of natural graphite (NGr) - a starting material for both synthesis methods-, graphene oxide (GO), and reduced graphene oxide powders synthesized by modified Hummers' method. Figure 5.17a shows a highly magnified SEM image of NGr surface morphology at magnification of 5000x, where graphite particles are in the platelet-like crystalline form of carbon (Loryuenyong et al., 2013). Therewith, SEM image of NGr shows the aggregation and agglomeration at the flat surfaces of ordered stacked carbon sheets with lateral size between 40-200  $\mu\text{m}$ . On the other hand, SEM image of GO synthesized by a modified Hummers' method in Figure 5.17b shows the exfoliated GO flakes with small wrinkles and folded at the edges with lateral size of 4-40 $\mu\text{m}$  which is indicated the successful oxidation (Dubey et al., 2015).

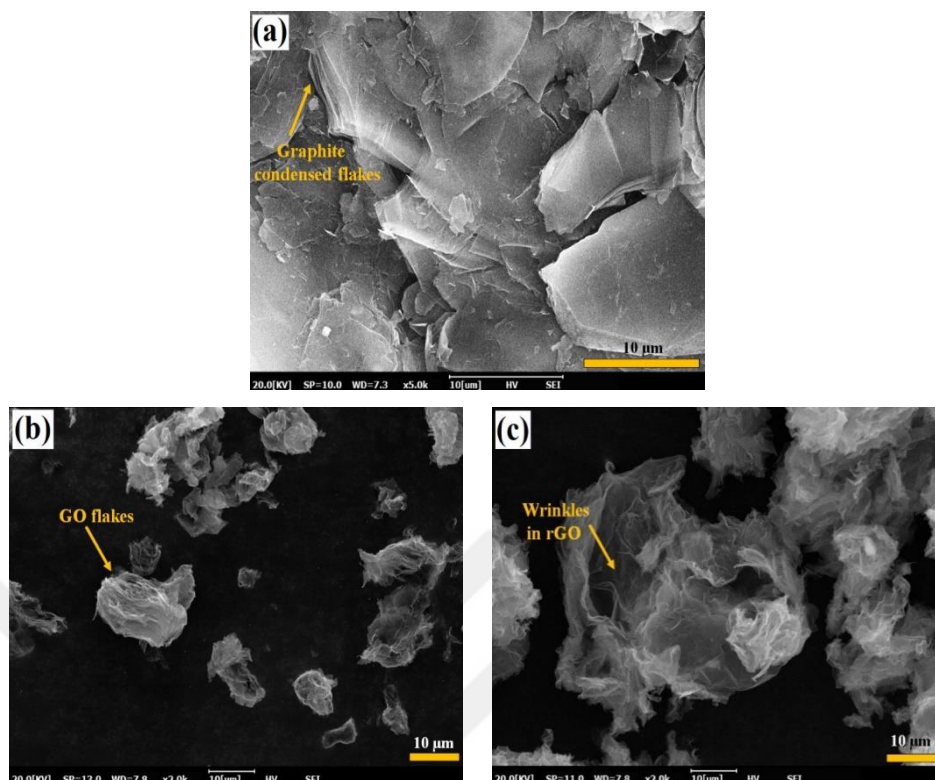


Figure 5.17 SEM images of (a) NGr, (b) GO, and (c) rGO

The sheet-like structure of synthesized GO has clearly showed a lamellar layer structure at the edges of each flake caused by the formation of oxygen groups (Park et al., 2012). The GO sheets were found thicker at the edges, this caused by the introduction of the oxygen functional groups which are present at the edges of GO (Alam et al., 2017).

Figure 5.17c shows the SEM image of rGO which showed much smoother than the case of graphene oxide. Lamellar and wrinkle structure are also observed in SEM image with less degree due to the chemical reduction process by hydrazine that exhibits well exfoliated flakes of rGO with lateral size of 10-80  $\mu\text{m}$ . The rGO sheets were observed very thin and transparent with folds in surface structure which represents the morphology of few layer rGO structure (Cao & Zhang, 2015; Saleem et al., 2018).

#### 5.4.2 SEM Images of Few-layer Graphene Sheets of NGr, EE1, and EE2

In the second synthesis method; electrochemical exfoliation, sonication in DMF, and microwave irradiation have been used in order to produce few-layer graphene sheets. SEM images showed few- to multi- chemically exfoliated graphene layers which can be readily distinguished by opacity in SEM images.

SEM image in Figure 5.18a shows the morphology of NGr after sonication in 3 mg/ml of Dimethylformamide (DMF) for 1 hour. The image shows the actual size of exfoliated crumpled graphite flakes which randomly overlapped with each other (Gu et al., 2009). Sonication in DMF led to effective expansion in graphite layer, yet some of them are still not fully expanded. However, the lateral size of obtained graphene sheets have been lowered after exfoliation process to 4-40  $\mu\text{m}$  which attributed to breaking graphite flakes from their defect points or related to exfoliation mechanism. It has been reported that in order to obtain a complete exfoliation with relatively large graphite sheets, low and sustain energy is needed to be applied during sonication (Hadi et al., 2018). After applying microwave for 30 s to the sonicated powder, SEM image shows higher degree of exfoliated graphene sheets with almost no wrinkles with lateral size of 10-50 $\mu\text{m}$ , see Figure 5.18b.

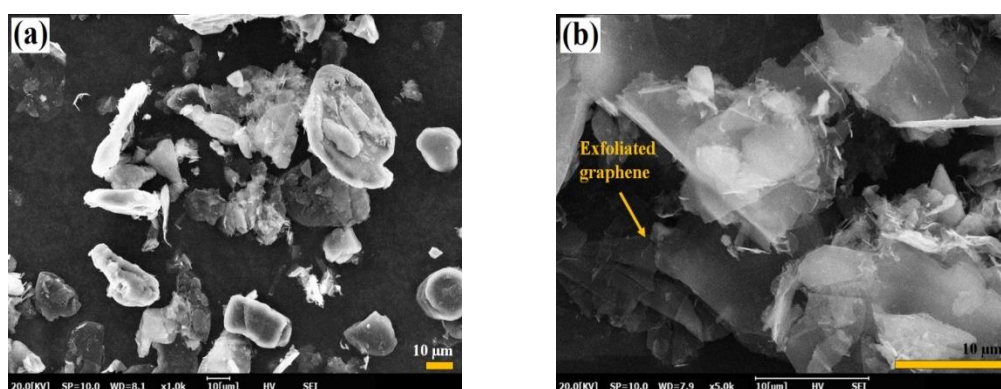


Figure 5.18 SEM images of (a) NGr+DMF, (b) NGr+DMF+MW

The same procedure was applied to the exfoliated graphene powder EE1 and EE2 in order to obtain few-layer graphene sheets. Figure 5.19a shows the morphology of the electrochemically exfoliated graphene EE1 as a starting material before sonication in DMF. Where the morphology shows stacked of expanded graphene layers on the

top of each other with partially presence of aggregation and less wrinkles on the surface with lateral size of 20-100 $\mu\text{m}$ . When sonication was applied in DMF for 1 hour, the morphology showed less aggregated and more interlayer spacing between graphene sheets Figure 5.19b.

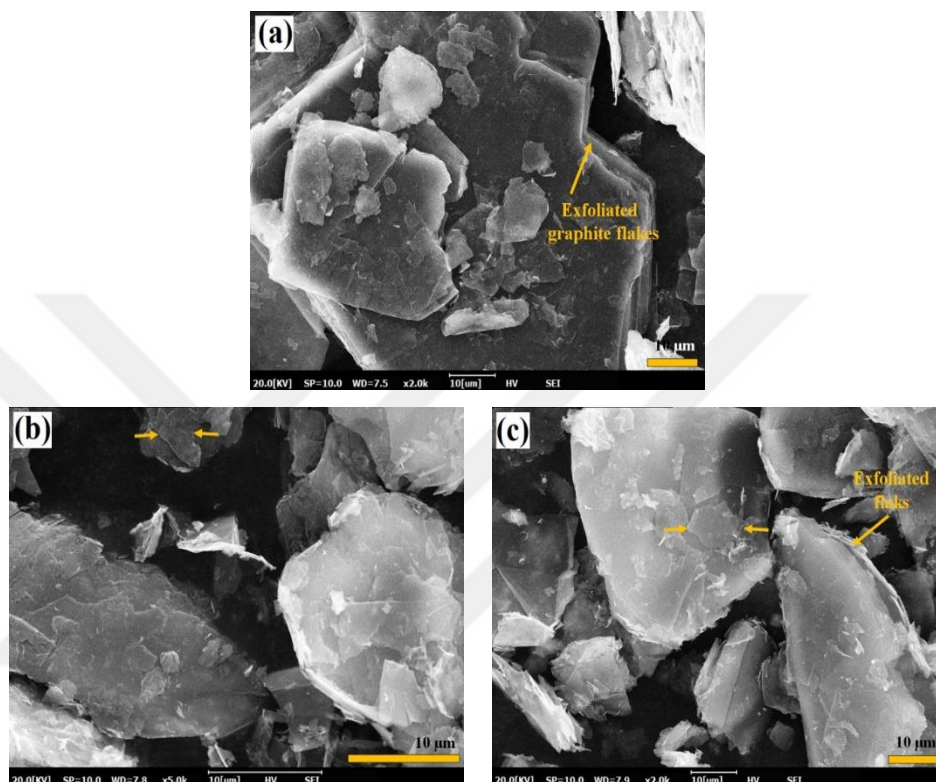


Figure 5.19 SEM images of (a) EE1, (b) EE1+DMF, and (c) EE1+DMF+MW

However, the lateral size of sheets has decreased due to sonication and DMF molecules intercalation, where 30% of graphene sheets were found with lateral size of 70  $\mu\text{m}$  and about 70% with  $\sim 20\mu\text{m}$ . The intercalation of DMF molecules between low-layer exfoliated graphene sheets has increased the interlayer spacing that made the exfoliation process easier. When MW was applied, graphene sheets showed more exfoliated sheets as paper-like structure and less wrinkles that guaranteed the intrinsic properties of graphene (Hadi et al., 2018), with lateral size of 10-80  $\mu\text{m}$ , see Figure 5.19c. This confirms that graphite is a good microwave absorbent (Xian et al., 2014; Liu et al., 2015) thus, we suggest that when microwave irradiation came after sonication in DMF, the obtained graphene sheets are few-layer sheets (Jehad et al., 2020).

Figure 5.20 shows SEM images of electrochemically exfoliated graphene material EE2 throughout the two processes; sonication in DMF for 1 hour and microwave irradiation for 30s. In Figure 5.20a, SEM image on EE2 as a starting material shows flatter and smoother surface of stacked graphene sheets with lateral size of the majority flakes of 70 $\mu$ m.

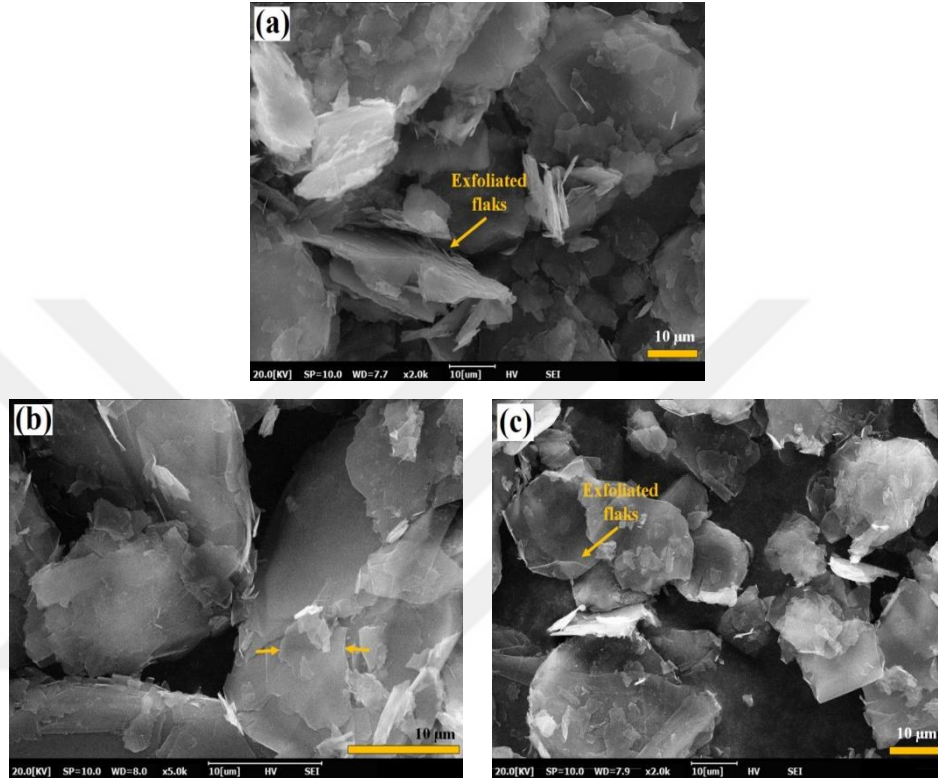


Figure 5.20 SEM images of (a) EE2, (b) EE2+DMF, and (c) EE2+DMF+MW

While, SEM image shows more increment in the interlayer spacing with well-defined edges of graphene sheets after sonication in DMF. Simultaneously, the obtained graphene sheets have become thinner with smaller lateral size of 20 $\mu$ m which approves effective expansion by DMF, see Figure 5.20b. Eventually, after applying microwaves for 30 s, SEM image in Figure 5.20c shows exfoliated graphene sheets with a lamellar structure and lateral size of 70–25 $\mu$ m which is considered as a large lateral size (Boeva et al., 2014; Zhang et al., 2018).

### 5.4.3 SEM images of CVD graphene on Cu foil and on Si substrate

Figure 5.21 shows the morphology of graphene sheet synthesized by chemical vapor deposition method on copper foil in (a) and after transferring onto Si substrate and reduction processes of PMMA in (b). The graphene growth process was performed in atmospheric CVD furnace, where Cu foil was gradually heated up to 1070°C in 56 min in a flow of 60/1000 sccm of H<sub>2</sub>/Ar for 40 min after reaching 1070°C, then 10 sccm of methane gas (CH<sub>4</sub>) was introduced for 90 s, after that chamber was processed to fast cooling to room temperature in few minutes.

In Figure 5.21a, SEM image confirms the growth of smooth surface and continuous graphene sheet on copper foil by presenting some wrinkles on the surface caused by the difference in thermal expansion coefficients of copper and graphene (Li et al., 2009; Li et al., 2015). Graphene domain size can be controlled by growth time in order to obtain an entirely homogeneous graphene layer.

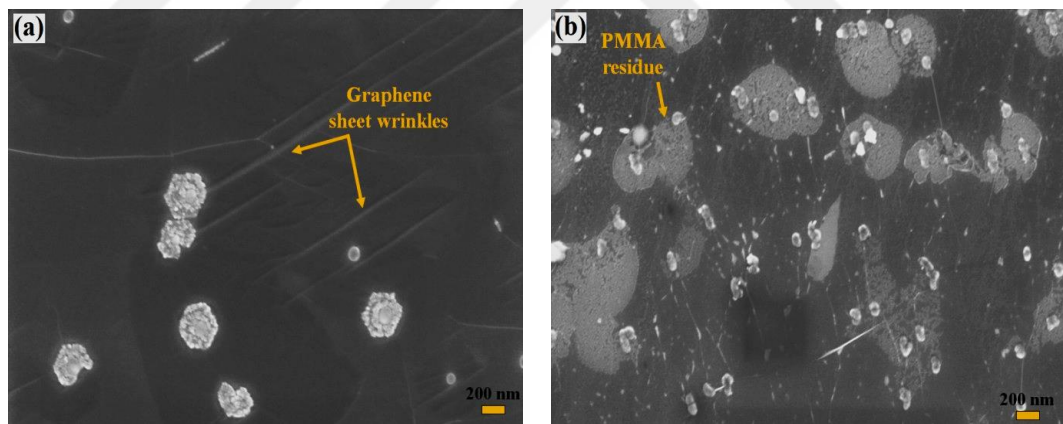


Figure 5.21 SEM images of grown graphene sheet on (a) copper foil before PMMA coating, (b) After transfer to Si substrate and reducing PMMA with acetone and annealing treatment

As mentioned in section 4.2.3, graphene on copper foil was protected by PMMA coating at 2000rpm for 60 s, then was baked on hot plate at 180 for 1 min before placed in Cu etchant. Later, the floating PMMA/G layer was washed before transferred to Si substrate and left to dry in vacuum. The polymer layer (PMMA) was removed by soaking PMMA/G/Si in hot acetone 50°C for 30 min followed by IPA and DI water. Still PMMA residue was found in the G sheet. Therefore, the samples were placed in

CVD furnace at 350°C for 2 hours at 100 sccm of Ar/H<sub>2</sub> in order to eliminate PMMA. Figure 5.21b shows the SEM image of transferred graphene sheet onto Si substrate after eliminating PMMA residue. The image confirms a full coverage of a continuous graphene sheet and significantly reduction in PMMA that will be discussed in the next chapter. Still, small amount of PMMA islands were found on the G surface. Some studies suggested applying deep UV (DUV) treatment to graphene sheets in order to effectively remove of the PMMA residue (Suhail et al., 2018).



## CHAPTER SIX

### RESULTS AND DISCUSSION OF FABRICATED G/SI SCHOTTKY JUNCTION SOLAR CELL

#### 6.1 Configuration of our fabricated solar cell device

In this chapter, our fabricated G/n-Si Schottky junction solar cell with a top window structure and an active area of  $0.11 \text{ cm}^2$  has been investigated without using photolithography technique. A schematic view of the fabrication processes is demonstrated in Figure 6.1, where the cleaning of silicon substrate was applied after cleaving the wafer and etching the native oxide (300 nm of  $\text{SiO}_2$ ) followed by deposition of the back side of silicon (unpolished side) with 5/150 nm of Cr/Ag using thermal evaporation system as shown in Figure 6.1a.

High-quality mono-layer graphene sheet was synthesized using CVD furnace at  $1070^\circ\text{C}$ . After graphene growing process, the catalyzer substrate (Cu foil) was processed to fast cooling to room temperature in few minutes in order to precipitate carbon atoms to form monolayer graphene sheet on the substrate (Zheng & Kim, 2015b).

Wet transfer process was used to transfer graphene sheet to the silicon substrate which is supported by coating PMMA layer as shown in Figure 6.1b, which is eventually eliminated by using hot acetone, isopropyl alcohol, DI water, and annealing treatment at  $350^\circ\text{C}$  for 2 hours in the flowing of 100 sccm of  $\text{Ar}/\text{H}_2$  in CVD furnace. Finally, a metal front contact frame of 5/50 of Cr/Au was deposited using thermal evaporation system and the final solar cell forms as shown in Figure 6.1c.

Figure 6.2 shows the configuration of our G/n-Si Schottky junction solar cell, where (a) demonstrates the fabricated cell after deposition of the front contact, as we mentioned before in our study we were not able to use photolithography technique that is why the front metal contact was designed to thermal evaporated of Cr/Au through four pieces of a square ring of 1.5 mm width separated by  $100 \mu\text{m}$ . After deposition of front contact on the top of G/Si, these small gaps were filled a silver paste and the final touch was using a thin Cu wires to form a circuit.

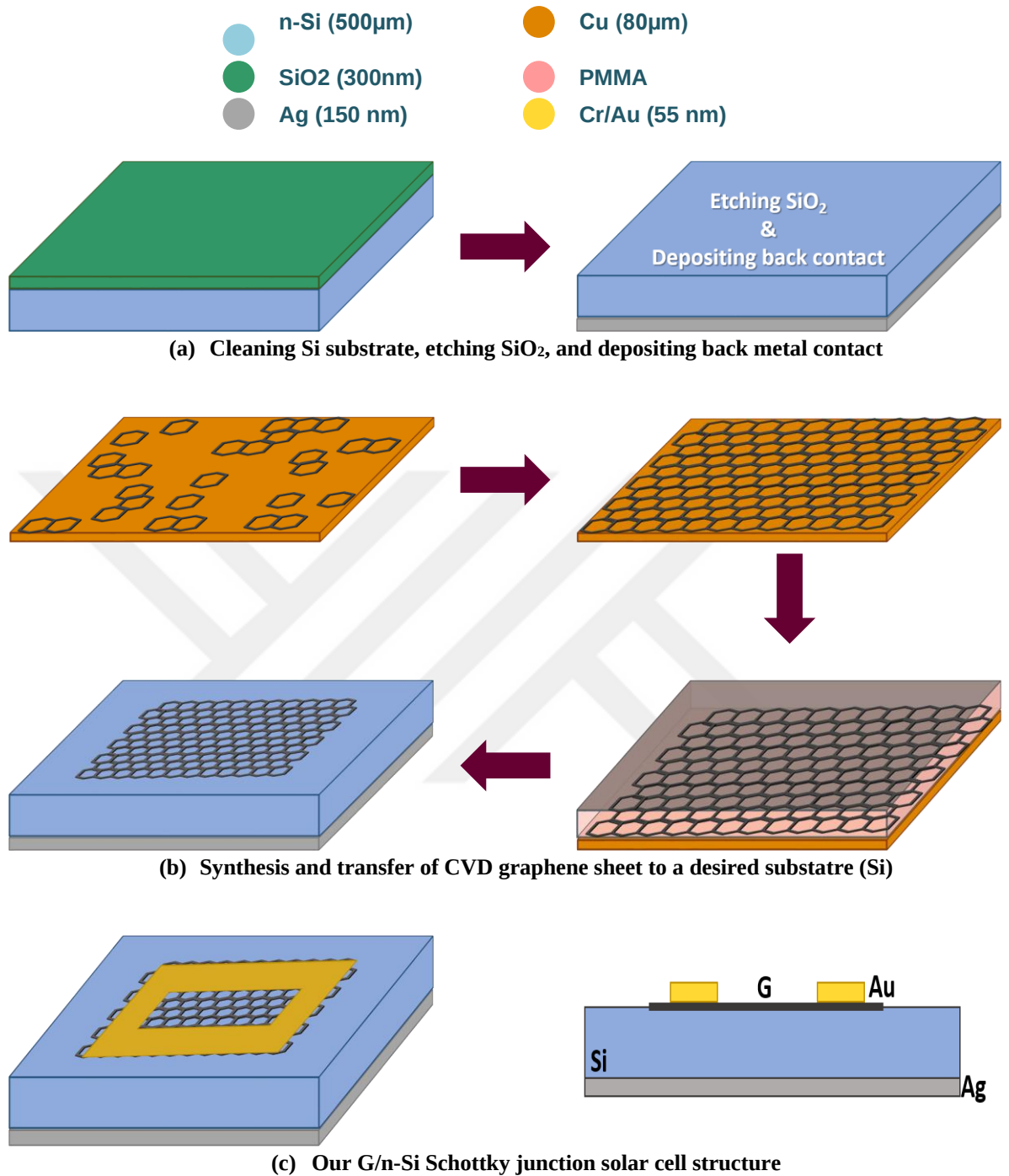


Figure 6.1 A schematic representation of fabrication G/Si Schottky solar cell (a) Etching native oxide by 2% HF for 30 s, then depositing back metal contact. (b) Synthesis CVD graphene from nucleation to growing the monolayer sheet, coated with PMMA, then wet transfer of graphene. (c) After etching PMMA, annealing and doping processes to graphene sheet before depositing front contact

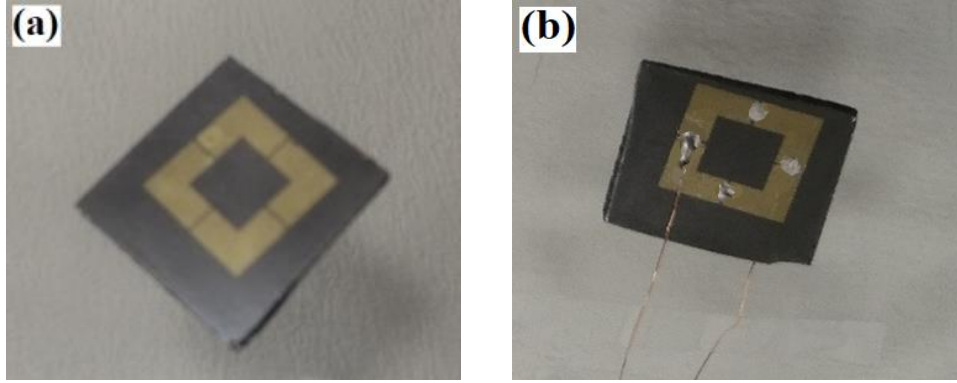


Figure 6.2 Fabricated G/n-Si Schottky junction solar cell (Personal archive, 2021)

## 6.2 Doping graphene with p-dopants

In order to enhance the graphene work function as well as to increase the Schottky barrier height and the build-in potential showed in Figure 6.3, graphene sheet was separately doped with different p-dopants; nitric acid vapor and GO dispersion. The p-doping is performed by pulling electrons from graphene sheet which generates p-doping to graphene, while n-doping can be seen as donation electrons to graphene which generates an n-doping. Theoretically, p-doping will increase the work function of graphene ( $\phi_G$ ) while n-doping would reduce it. Thus, modifying graphene work function by chemical doping is important to design the Schottky barrier height (SBH). As graphene work function is  $\phi_G \sim 4.47$  eV, thus any material with larger work function is considered as a p-type dopant such as graphene oxide  $\phi_{GO} \sim 5.3$  eV, Gold  $\phi_{Au} \sim 5.4$  eV, and Nickel oxide  $\phi_{NiO} \sim 5.4$  eV-6 eV.

In the case of  $HNO_3$ , after annealing treatment, the assembled cell was hold downward on the graphene side and exposed to the vapor of nitric acid (65%) for 30 s. While in the case of doped by GO, 3mg/ml of synthesized GO dispersion with DI water was spin coated on the graphene side at 2000 rpm for 1 min. doping graphene with GO has served two functions; as p-dopant for graphene to increase its work function and as anti-reflection coating, moreover GO has proven an effective stability of the solar cell performance.

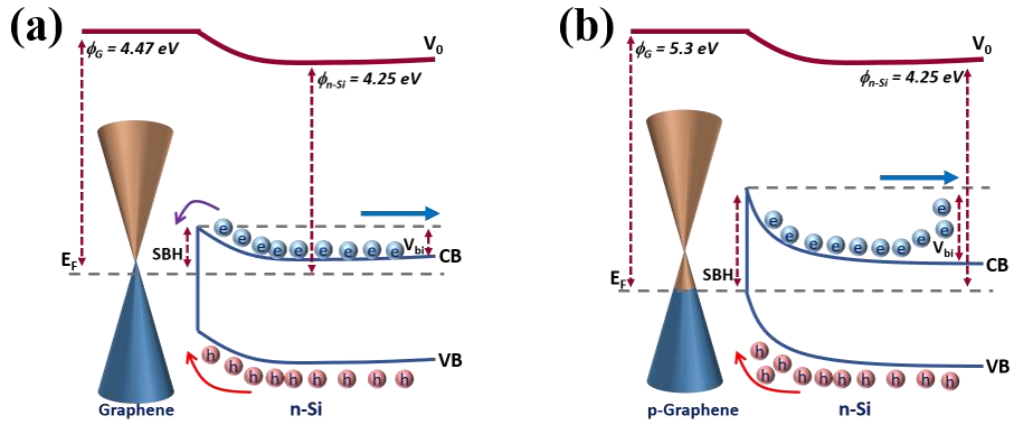


Figure 6.3 Energy band diagram of G/n-Si Schottky junction solar cell. (a) with pristine graphene, (b) with p-doped graphene

### 6.3 Raman Spectroscopy of graphene sheet after doping

Figure 6.4 shows Raman spectra of two different p-doped graphene. An exposure to nitric acid (65%) vapors for 30 s and spin coated on 3mg/ml of GO dispersion. The three key features of graphene Raman spectra in both cases. Where D peak was found around  $1444\text{ cm}^{-1}$ , while G, and 2D were found around  $1581\text{ cm}^{-1}$  and  $2697\text{ cm}^{-1}$ , respectively in the case of doping graphene sheet with GO dispersion. By comparison of Raman data of doped graphene in Table 6.1 with Raman data of synthesized graphene before doping illustrated in Table 5.3, a significant increase in 2D peak position from  $2686\text{--}2697\text{ cm}^{-1}$  after doping process which confirms a successful p-doping graphene with defect density of  $I_D/I_G = 0.54$ , and the high D peak is an indication of the presence of oxygen functional groups came from GO.

While in the case of doping graphene with  $\text{HNO}_3$  vapor, the D, G, and 2D peaks were observed clearly around  $1349\text{ cm}^{-1}$ ,  $1587\text{ cm}^{-1}$ , and  $2695\text{ cm}^{-1}$  respectively with very low defect density of  $I_D/I_G = 0.15$ . the decreasing in the thickness layer ratio in the doping graphene samples indicates the presence of few-layer in the final graphene structure (Das et al., 2008). The shifting in 2D peak after doping graphene with GO and  $\text{HNO}_3$  is a confirmation of successful doping (Lancellotti et al., 2014).

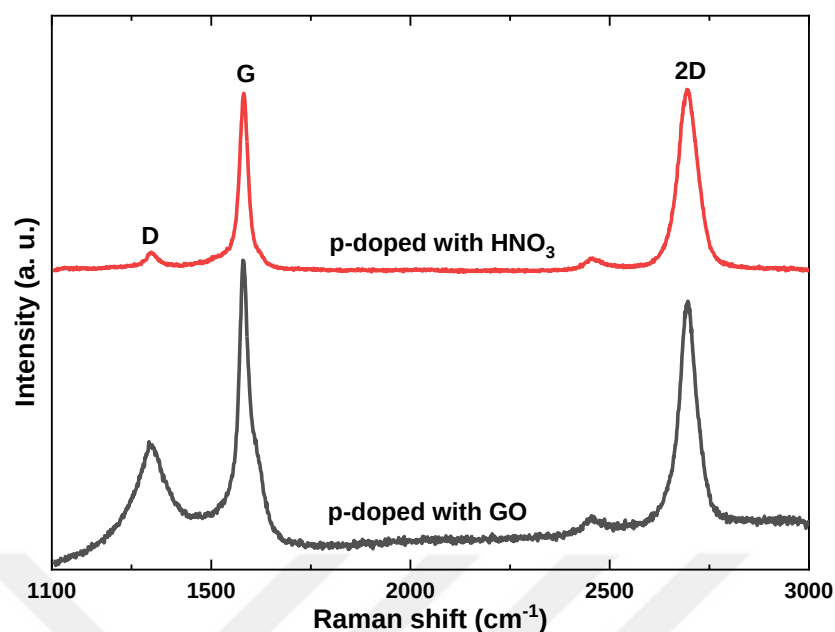


Figure 6.4 Raman spectrum of p-doped graphene sheet with HNO<sub>3</sub> and GO

Table 6.1 Raman data of doped graphene sheet with GO and HNO<sub>3</sub>

| p-doped G             | R <sub>shift</sub> | I <sub>D</sub> | R <sub>shift</sub> | I <sub>G</sub> | R <sub>shift</sub> | I <sub>2D</sub> | I <sub>D</sub> /I <sub>G</sub> | I <sub>2D</sub> /I <sub>G</sub> |
|-----------------------|--------------------|----------------|--------------------|----------------|--------------------|-----------------|--------------------------------|---------------------------------|
| with GO               | 1344               | 6838           | 1581               | 12760          | 2697               | 11450           | 0.54                           | 0.90                            |
| With HNO <sub>3</sub> | 1349               | 919.6          | 1582               | 6087           | 2695               | 6132            | 0.15                           | 1.01                            |

#### 6.4 SEM image of cross section of the solar cell

Figure 6.5 shows cross-sectional scanning electron microscopy (SEM) image of our fabricated solar cell reveals a smooth layer with the average thickness of 54.7 nm (typically, 5+50 nm of Cr + Au respectively) was deposited successfully on the front surface of the n-Si (black area). SEM image shows a good adhesion between silicon and the metal front surface whereas the annealed graphene layer is just under the gold frame.

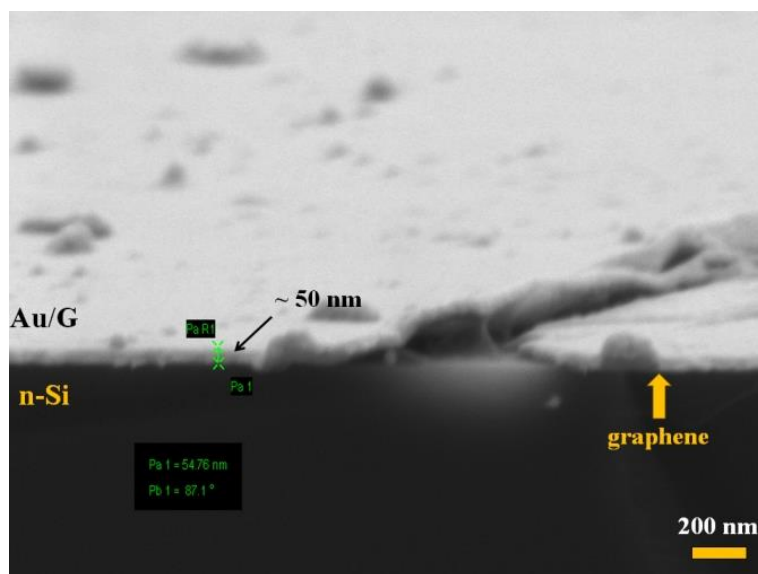


Figure 6.5 Cross-section in front side of the cell, confirms the thickness of the front metal contact

## 6.5 Atomic Force Microscopy (AFM)

The presence of PMMA molecules was verified to inhibit the essential properties of graphene (Zhuang et al., 2020). Using only hot acetone in order to remove the supported PMMA layer throughout the transferring of graphene sheet has been reported as an insufficient way. However, annealing treatment process has been suggested as an effective way to eliminate the PMMA molecules with an appropriate configurations of annealing temperature, time, and the atmosphere conditions.

In this study annealing treatment has been applied to eliminate the PMMA residue. Atomic force microscopy (AFM) has been employed to examine the surface morphology of transferred graphene sheet on SiO<sub>2</sub>/Si substrate before and after annealing treatment.

From Figure 6.6a, AFM image showed an abundant of PMMA “islands” on the surface before annealing. With the purpose of eliminating PMMA residue, transferred graphene on Si substrate were placed to atmospheric CVD furnace and annealed to 350°C for 2 hours with flowing of 100 sccm of Ar/H<sub>2</sub>. Later, AFM was employed again in order to check the smoothness of the graphene surface, see Figure 6.6b. By comparison, annealing treatment has worked effectively and the density of PMMA residue was decreased about 75% of the original sample. Besides being a significant

reduction of PMMA, the height of PMMA “islands” were noteworthy decreased. At high temperature  $\sim 350$  °C, PMMA particles were melted and left graphene surface smoother.

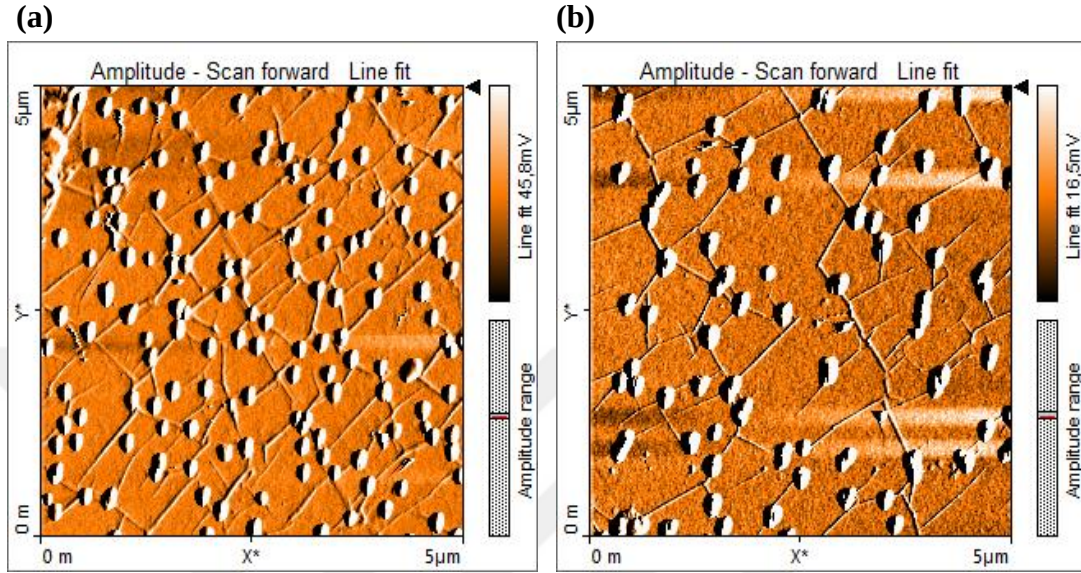


Figure 6.6 AFM images of graphene sheet transferred onto SiO<sub>2</sub>/Si substrate (a) before annealing, (b) after annealing to 350 °C for 2 hours

## 6.6 Current density-voltage (J-V) characteristics

In this section, two different ways have been used in order to understand the mechanism carriers' movement in G/Si Schottky junction. The first part is investigating the etchant time required to eliminate the silicon oxide layer coated on silicon substrate, while the second part is dealing with the effect of annealing treatment and doping graphene sheet with p-type dopants.

In this part, etching time of 2% HF to eliminate the silicon oxide layer was investigated, where two types of n-type silicon substrates were used, highly doped silicon with  $N_D = 10^{19} \text{ cm}^{-3}$  coated with 300 nm SiO<sub>2</sub> and moderate doped silicon with  $N_D = 10^{17} \text{ cm}^{-3}$  coated with 100 nm SiO<sub>2</sub>. The fabricating process was similar in both cases, only etching time of oxide layer has been tested by 30, 90, 120 s of etching time was selected in order to investigate the effect of etching the oxide layer.

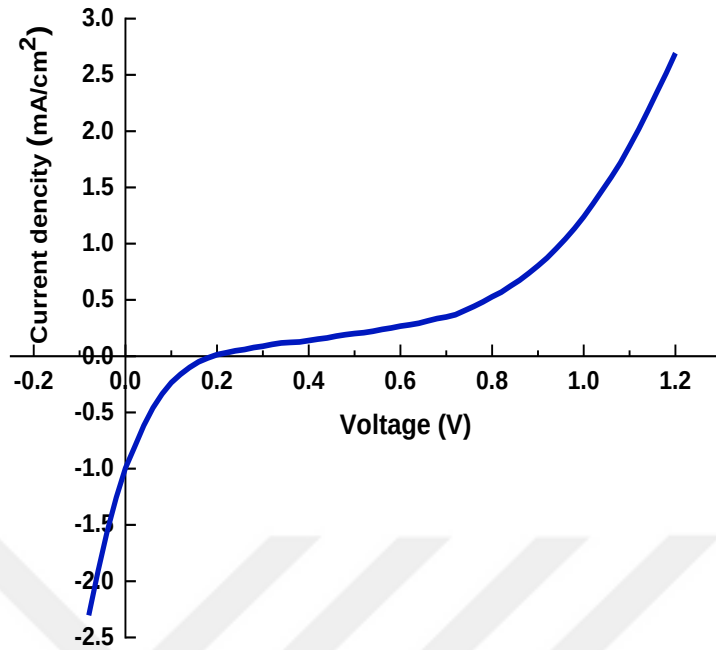


Figure 6.7 Obtained current density- Voltage (IV) characteristics

As can be seen from Table 6.2, for the first sample of moderate doping concentration with (100 nm thickness of SiO<sub>2</sub>), both short circuit current and open circuit voltage increased when the substrate was left in etchant for longer time of 2 min, however the fill factor showed 62% and the best obtained efficiency is 1.02%.

Table 6.2 Solar cell parameters with different etchant time to two different types of silicon

| Sample name<br>G/n-Si                                                          | SiO <sub>2</sub><br>Thickness (nm) | Etched in 2%<br>HF for (s) | J <sub>sc</sub><br>(mA/cm <sup>2</sup> ) | V <sub>oc</sub><br>(mV) | FF (%) | PCE (%) |
|--------------------------------------------------------------------------------|------------------------------------|----------------------------|------------------------------------------|-------------------------|--------|---------|
| <b>Moderate doped Si</b><br>N <sub>D</sub> = 10 <sup>17</sup> cm <sup>-3</sup> | 100                                | 120                        | 3.01                                     | 260                     | 39     | 3.20    |
|                                                                                |                                    | 90                         | 3.06                                     | 260                     | 16     | 1.27    |
|                                                                                |                                    | 30                         | 2.70                                     | 160                     | 24     | 1.05    |
| <b>Highly doped Si</b><br>N <sub>D</sub> = 10 <sup>19</sup> cm <sup>-3</sup>   | 500                                | 120                        | 1.64                                     | 250                     | 12     | 0.50    |
|                                                                                |                                    | 90                         | 1.00                                     | 180                     | 18     | 0.32    |
|                                                                                |                                    | 30                         | 0.04                                     | 250                     | 29     | 0.07    |

The same procedures were applied to the highly doped Si coated with 300 nm of SiO<sub>2</sub> showed enhancement in the obtained current as the etchant time increased. Still, the efficiencies did not reach 1%, as shown in Figure 6.7. None the less, typical diode IV characteristic was observed with a low percentage of being a solar cell device under illumination condition. Many reasons might be behind these poor results, a considered amount of SiO<sub>2</sub> thickness, the quality of graphene sheet as well as the feature of junction between silicon and graphene, and high sheet resistance of graphene sheet was discussed in the previous section.

The other factor we suspect about it was examining the Ohmic junction at the back contact, as we mentioned, the thermal vapor deposition system was used to evaporate 5/150 nm of Cr/Ag. Where recently, Scotch tape has been utilized to peel off the deposited metal layer and examined by EDS-SEM microscopy. The peeling process was very easy with tape and a grey-yellowish color was observed as shown in Figure 6.8a, we suspect that CrO<sub>2</sub> has deposited instead of Cr during evaporation process which might be a significant issue not to release higher current and voltage.

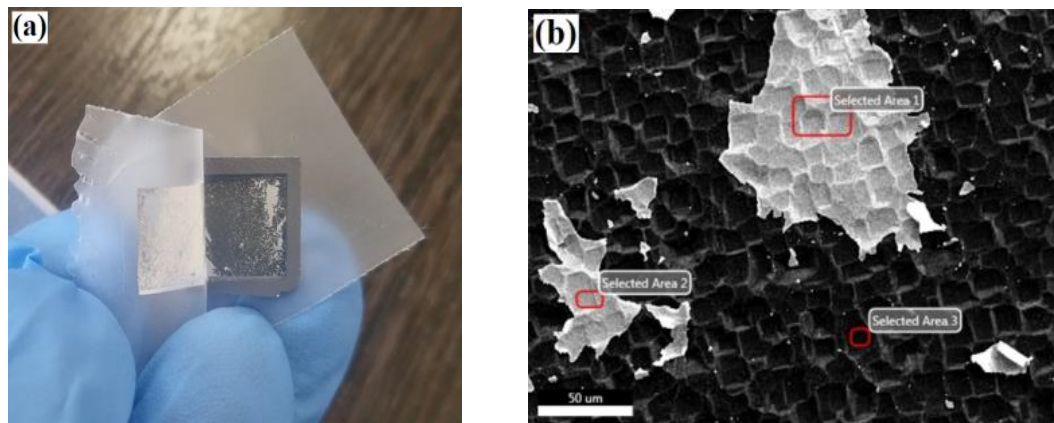


Figure 6.8 The back side of silicon substrate after depositing metal contact. (a) Peeled easily with a Scotch tape (Personal archive, 2021), (b) EDS-SEM image of selected area

Finally, EDS results observed a significant amount of oxygen in the back contact even more than Cr ratio in EDS test of the back metal contact shown in Figure 6.8b, where the image shows the structure of the back side of silicon, bright area is the

unpeeled deposited silver and the dark area is related to peeled area (selected area 3). The obtained data from EDS text is shown in Table 6.3. Moreover, the concentration of oxygen was 3 times more than the Cr concentration. In our experiment, the thermal evaporation process was done under vacuum of  $5 \times 10^{-16}$  Torr, and nevertheless we had a considered amount of oxygen which might be present inside the glovebox and contaminated internal surfaces.

Table 6.3 EDS test results data of after removing the back contact of silicon by Scotch tape

| <b>Element</b> | <b>Weight %</b> | <b>Atomic %</b> | <b>Net Int.</b> | <b>K ratio</b> |
|----------------|-----------------|-----------------|-----------------|----------------|
| <b>O K</b>     | 9.77            | 16.08           | 551.85          | 0.0328         |
| <b>Si K</b>    | 88.65           | 83.12           | 14448.49        | 0.8553         |
| <b>Cr K</b>    | 1.58            | 0.80            | 57.36           | 0.0133         |

On the other hand, the second part of investigation the IV characteristic parameters are related by the effect of doping graphene sheet by  $\text{HNO}_3$  and GO. We used the highly doped Si substrate to fabricate G/n-Si Schottky junction solar cells and the cell were tested at four stages before and after annealing treatment that discussed in section 4.3.4 in order to remove PMMA residue that confirmed to disturb IV curve by producing s-shape (Adhikari et al., 2018; Suhail et al., 2018), after doping with  $\text{HNO}_3$ , and after doping with GO as showing Figure 6.9. After annealing treatment, an effective reduction in PMMA residue was approved from AFM images explained in section 6.5, where about 75% of PMMA molecules was successfully eliminated which led to enhance the conversion power efficiency from 0.68% to 1.8% with higher short circuit current density of  $2.07 \text{ mA/cm}^2$  and 300 mV of open circuit voltage, while the fill factor was only 19% due to appearing of s-kink in IV curve that related to many factor together.

To achieve more efficiency, graphene sheet was chemically p-doped with two dopants separately with nitric acid ( $\text{HNO}_3$ ) and our synthesized graphene oxide (GO). For the first dopant, the fabricated cell was held downwards and the graphene surface exposed to (65%) of  $\text{HNO}_3$  vapor for 30 s before depositing the front metal frame.

While in the case of GO doping, the fabricated cell was spin-coated with 3mg/ml of GO dispersion with DI water and baking process was not applied after doping.

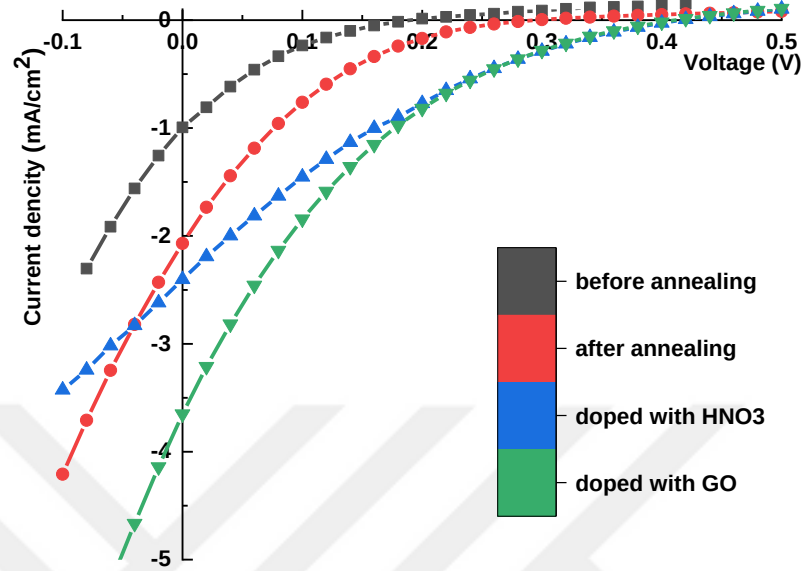


Figure 6.9 Current density- Voltage (IV) curve of highly doped cell before and after annealing treatment, and doped with HNO<sub>3</sub> and GO

Doping graphene sheet with p-dopants attribute to increase the work function of graphene that will increase the Schottky barrier between graphene and silicon and eventually will lead to increase the built-in potential. The other factor is decreasing graphene sheet resistance which leads to a decreasing in the series resistance ( $R_s$ ) which has a direct relation with the photogenerated current in the solar cell and the percentage of FF. Furthermore, the vapor of HNO<sub>3</sub> is expected to recover the junction homogeneity at the interface between graphene and silicon (Cui et al., 2013; Lancellotti et al., 2016).

Table 6.4 Solar cell parameters before and after annealing and doping

| Sample name<br>G/n-Si       | $J_{sc}$<br>(mA/cm <sup>2</sup> ) | $V_{oc}$<br>(mV) | FF (%) | PCE (%) |
|-----------------------------|-----------------------------------|------------------|--------|---------|
| Before annealing            | 1.03                              | 250              | 26     | 0.68    |
| After annealing             | 2.07                              | 300              | 19     | 1.80    |
| Doped with HNO <sub>3</sub> | 2.40                              | 420              | 28     | 1.92    |
| Doped with GO               | 3.65                              | 420              | 14     | 2.24    |

The obtained IV characterization data illustrated in Table 6.4, after doping with nitric acid and graphene oxide as a p-dopants. The results show that a significant enhance was obtained in open circuit voltage after doping process, where it found around 420 mV after being 250 before annealing. The effect of short circuit current density observed after doping from 1.03 mA/cm<sup>2</sup> before annealing to 2.4 mA/cm<sup>2</sup> when graphene doped with nitric acid and further to 3.65 mA/cm<sup>2</sup> after doping with GO. While the fill factor (FF) showed larger percentage of 28% in the case of nitric acid doping then the power conversion efficiency enhanced from 0.68% before annealing to 2.24% after doping with graphene oxide. Consequently, by comparison, the cell treated with GO showed a higher efficiency but suffer from the poor fill factor. In addition, the efficiency of the cell treated with HNO<sub>3</sub> decreased significantly over several days, while the cell treated with GO showed more stability.

## CHAPTER SEVEN

### CONCLUSION AND RECOMMENDATIONS

#### 7.1 Conclusions

As a conclusion of this study, graphene is synthesized in three different forms. Reduced graphene oxide was obtained after the reduction process of graphene oxide synthesized by Hummer's method. We produced pure graphene oxide powder with size particle of 4-80  $\mu\text{m}$  which was later used as p-dopant to CVD graphene. Few-layer graphene (FLG) flakes with high-quality have been successfully synthesized throughout electrochemical exfoliation (EE) followed by sonication in DMF and microwave irradiation (MW). Using DMF to sonicate the exfoliated powder was proven as a stronger exfoliation reagent, especially when followed by MW. Raman spectroscopy analysis indicate the formation of few-layer graphene, and the XRD analysis also confirmed this by the significant reduction in (002) peak intensity of carbon. High quality mono-layer graphene sheet was synthesized with copper foil assisted using chemical vapor deposition (CVD) method, where Raman result showed the thickness layer ratio of  $I_{2D}/I_G = 2.05$  with low defect density of  $I_D/I_G = 0.14$  before annealing treatment, and  $I_{2D}/I_G = 1.49$  after annealing with defect density of  $I_D/I_G = 0.16$ . The continuity of graphene sheet was proved by the wrinkles on the graphene surface on the top of copper foil before etching treatment.

Graphene/silicon Schottky junction solar cell with a top-window structure has been fabricated. Two different n-type silicon substrates were used; highly doped and moderate doped with different thicknesses of  $\text{SiO}_2$ , etching time was investigated as well as the effect of annealing graphene sheet before making the front metal contact was also examined. The annealing treatment was used for reducing PMMA residue which causes to degradation of cell performance. In order to enhance graphene work function, two p-dopants were tested which are nitric acid vapor and synthesized GO dispersion. The IV characteristics of the graphene/silicon solar cells were recorded under standard conditions (AM 1.5,  $100 \text{ W/cm}^2$ ) during optimization steps before and after thermal annealing, chemical doping. The cells with highly doped silicon showed poor efficiency which might be caused by the poor back Ohmic contact or a considered

remaining of SiO<sub>2</sub> layer. For cells with pristine graphene and moderate Si ( $N_D = 10^{17}\text{cm}^{-3}$ ), the power conversion efficiency (PCE) showed 3.2 % with 3.01 mA/cm<sup>2</sup> short circuit current density while the high-doped Si cells showed PCE of 0.5% when SiO<sub>2</sub> layer was etched for 120s in the case of pristine graphene. As a result, the best obtained PCE was 3.2% in the case of moderate n-type silicon without any treatment, while in the case of high-doped n-type silicon, the best PCE was 2.24% after thermal annealing step and doping with synthesized GO. Thus, we can say that dealing with high-doped silicon substrate is more complicated. Still, an extensive research is needed to understand the mechanisms of charge carriers in graphene sheet as well as the nature of graphene/silicon interface.

## 7.2 Future Work and Recommendations

In order to optimize the G/Si Schottky junction solar cell, many challenges need to be overcome such as finding a new design that helps to enlarge the active area of the cell ( $>0.11\text{cm}^2$ ). Studies have reported that, when graphene sheet become larger than 0.11 the junction quality will degrade. Reduction PMMA residue using other techniques in addition to annealing treatment whereas the PMMA residue causes charge recombination that led to reduce the PCE. Enhancing the Schottky barrier and the conductivity of graphene by doping with an appropriate material that could maintain the cell stability. Reducing the large sheet resistance of graphene sheet in order to enhance the Fill factor and PCE.

Furthermore, using multi-graphene layers instead of a monolayer is an option in order to enhance the cell performance. Texturing silicon substrates (porous silicon, silicon nanowires in order to provide a larger surface area. Using an anti-reflection coating such as TiO<sub>2</sub> or SiO<sub>2</sub> could enhance the cell efficiency.

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## APPENDICES

### Appendix 1: LIST OF EQUATIONS

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## Appendix 2: ACRONYMS AND ABBREVIATIONS

$\chi$ : Affinity

$\eta$ : Efficiency

$\phi$ : Work function

AFM: Atomic force microscopy

C<sub>60</sub>: fullerenes

CNT: carbon nanotube

CVD: Chemical vapor deposition

DARC: Double layer anti-reflection coating

DMF: Dimethylformamide

DSSCs: Dye sensitized Solar cells

e: Charge electron

E<sub>0</sub>: Internal electric field

E<sub>c</sub>: Conduction energy

EE1: Electrochemical exfoliated graphene in Sodium sulfate

EE2: Electrochemical exfoliated graphene in Sulfuric acid

E<sub>F</sub>: Fermi level

E<sub>g</sub>: Energy band gap

EMI: electromagnetic interference

FET: Field effect transistor

FF: Fill factor

FGF: Fragmentized graphene foam

FLG: Few-layer graphene sheets

FTIR: Fourier-transform infrared spectroscopy

FTO: Fluorine doped Tin Oxide

FWHM: Full Width at Half Maximum

G: Graphene

GF: Graphene foam

GNP: Graphene nanoplate

GNS: Graphene nanosheet

GQD: Graphene quantum dot

Gr: Graphite  
HTM: Hole-transporting material  
IPA: Isopropyl alcohol  
 $I_{sc}$ : Short circuit current  
ITO: Indium Tin Oxide  
IUPAC: International Union of Pure and Applied Chemistry  
IV: Current-voltage characteristic curve  
k: Thermal conductivity  
K: Boltzmann's constant  
 $I_0$ : Saturation current density  
 $I_L$ : Generated photocurrent  
LIB: Lithium ion battery  
LPE: Liquid phase exfoliation  
MD: Membrane distillation technique  
MW: Microwave  
n: Ideality factor  
NGr: Natural graphite powder  
OSCs: Organic solar cells  
PCE: Powder Conversion Efficiency  
PDMS: Polydimethylsiloxane  
PMMA: Poly-methyl methacrylate  
PV: Photovoltaic  
RCA: Radio Corporation of America  
rGO: reduced graphene oxide  
 $R_s$ : Series resistance  
 $R_{sh}$ : Sheet resistance  
SEM: Scanning electron microscopy  
Si: Silicon  
SiNW: Silicon nanowire  
SiO<sub>2</sub>: Silicon dioxide  
T: Temperature  
TEM: Transmission electron microscopy

$V_0$ : Vacuum level energy  
 $V_{bi}$ : Build-in potential  
 $V_E$ : Valence energy  
 $V_{oc}$ : Open circuit voltage  
 $W$ : Depletion width  
XRD: X-ray diffractometer



### **Appendix 3: PUBLICATION AND PRESENTATIONS**

#### ***Journal Publications***

Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “A comparative study for producing few-layer graphene sheets via electrochemical and microwave-assisted exfoliation from graphite powder,” *Journal of Materials Science: Materials in Electronics*, vol. 31, 2020, pp. 7022–7034.

#### ***Conference Papers***

- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “Production and Application of CVD Graphene in Solar Cells,” 6th International Student Symposium Conference Proceedings, Dec. 5-6, 2020,
- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “Investigation in Graphene/Silicon-based Schottky Junction Solar Cell,” 4th International Students Science Congress Proceedings, Sep. 18-19, 2020, ISBN: 978-605-81050-6-5, pp. 310-314.
- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “Producing the graphene/p-silicon Schottky junction solar cell and investigation the effect of multi-layer graphene in this cell,” 36th Turkish physical society international physics congress, Sep. 1-5, 2020,
- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “A Feasible Technique to Prepare Few-layered Graphene Sheets from Pencil Lead Graphite,” 5th International Student Symposium Conference Proceedings, Dec. 6-8, 2019, ISBN: 978-975-8738-55-72178, pp. 75-88.
- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “A practical method to synthesis few-layered graphene sheets via electrochemical with microwave assisted exfoliation,” 35th Turkish physical society international physics congress, AIP Conference Proceedings, Sep. 4-8, 2019, 2178, 030009, pp. 1-4.
- Ala K. JEHAD, Kemal KOCABAŞ, Metin YURDDAŞKAL, “Preparation and Characterization of Graphene Synthesized by Different Methods,” 3rd

International Students Science Congress Proceedings, May 4-5, 2019, E-ISBN: 978-605-81050-1-0, pp. 556-563.

- Ala K. JEHAD, Ibrahim HAMMAMU, “Calculating the Efficiency of Silicon Solar Cell,” 2nd International Students Science Congress Proceedings, May 4-5, 2018, pp. 245-249.
- Ala K. JEHAD, Ibrahim HAMMAMU, Ibrahim, “Computer simulation on solving Poisson’s equation for the silicon solar cell,” 1st International Conference on Electrical and Computer Engineering ICECE Conference Proceedings, Mar. 26-28, 2013, pp. 1-4.

