THE IMPACT OF ADSORBATES ON THE OPTOELECTRONIC PROPERTIES OF GRAPHENE/SILICON BASED SCHOTTKY BARRIER PHOTODIODES

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by Nusret ŞAHAN

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Dedicated to My Mother

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ABSTRACT

THE IMPACT OF ADSORBATES ON THE OPTOELECTRONIC PROPERTIES OF GRAPHENE/SILICON BASED SCHOTTKY BARRIER PHOTODIODES

The aim of this study is to investigate the effect of atmospheric adsorbates on the electronic and optoelectronic properties of graphene/n-type Silicon (Gr/n-Si) based Schottky barrier photodiodes. Wavelength resolved photocurrent spectroscopy and transient photocurrent spectroscopy measurements conducted under high-vacuum conditions revealed that the adsorbates cause hole doping in graphene and hence increase the zerobias Schottky barrier height of the Gr/n-Si heterojunction from 0.71 to 0.78 eV. Adsorbate induced increment in the barrier height promotes the separation of photo-excited charge carriers at the depletion region of the heterojunction and leads to an improvement in the maximum spectral response (e.g., from 0.39 to 0.46 AW⁻¹) and response speed of the Gr/n-Si photodiode in the near-infrared region. The experimentally obtained results are expected to give an insight into the adsorbate induced variations in the rectification and photo-response characters of the heterojunctions of graphene and other 2D materials with different semiconductors.

ÖZET

ADSORBATLARIN GRAFEN/SİLİKON BAZLI SCHOTTKY BARİYER FOTODİYOTLARININ OPTOELEKTRONİK ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİ

Bu çalışmanın amacı, atmosferik adsorbatların grafen/n-tipi Silikon (Gr/n-Si) bazlı Schottky bariyer fotodiyotlarının elektronik ve optoelektronik özelliklerine etkisini araştırmaktır. Yüksek vakum koşulları altında yapılan dalga boyu çözümlemeli fotoakım spektroskopisi ve geçici fotoakım spektroskopi ölçümleri, adsorbatların grafende boşluk katkısına neden olduğunu ve dolayısıyla Gr/n-Si heteroyapısının sıfır beslem Schottky bariyer yüksekliğini 0.71'den 0.78 eV'ye yükselttiğini ortaya çıkardı. Bariyer yüksekliğinde adsorbatla indüklenen artışın, heteroyapının tükenme bölgesinde foto uyarımlı yük taşıyı-cıların ayrılmasını teşvik eder ve yakın kızılötesi bölgede Gr/n-Si fotodiyotun maksimum spektral tepkisinde (0.39'dan 0.46 AW⁻¹'a) ve tepki hızında bir iyileşmeye yol açtığı bulunmuştur. Deneysel olarak elde edilen sonuçların grafen ve diğer 2D materyallerin farklı yarı iletkenlerle oluşturduğu heteroyapılarının düzeltmesinde ve foto-tepki karakterlerindeki adsorbat kaynaklı varyasyonları anlaması beklenmektedir.

TABLE OF CONTENTS

LIST OF FIGURES	viii
LIST OF TABLES	xiii
LIST OF SYMBOLS	xiv
LIST OF ABBREVIATIONS	xvi
CHAPTER 1. INTRODUCTION	1
1.1. What is Graphene?	1
1.1.1. Structural Properties of Graphene	1
1.1.2. Electrical Properties of Graphene	4
1.1.3. Optical Properties of Graphene	6
1.2. Schottky Barrier Photodiodes	6
1.3. Graphene-based Schottky Barrier Photodiodes	11
CHAPTER 2. EXPERIMENTAL DETAILS	14
2.1. Thermal Evaporation System	14
2.1.1. Deposition of Interfacial Oxide and Metallic Electrodes	16
2.2. Growth and Transfer of CVD Graphene	17
2.3. Raman Spectroscopy Measurements	20
2.4. Wire Bonding System	25
2.5. Photocurrent Spectroscopy	26
CHAPTER 3. CHARACTERIZATION OF GRAPHENE/SILICON	
PHOTODIODE	29
3.1. Raman Characterization	29
3.2. Electronic Characterization	30
3.3. Optoelectronic Characterization	34

3.3.1. I-V measurements under light illumination	34		
3.3.2. Spectral Response measurements	35		
3.3.3. Time-dependent Photocurrent Measurements	37		
CHAPTER 4. THE EFFECT OF ADSORBATES ON THE RECTIFICATION OF			
GRAPHENE/SILICON HETEROJUNCTION	40		
4.1. Comparison of the Electronic Properties of Graphene/n-Si			
Photodiode Before and After UV illumination	40		
4.2. Optoelectronic Properties of Graphene/n-Si Photodiode Before			
and After UV illumination	42		
4.2.1. I-V measurements under light illumination	42		
4.2.2. Spectral Response Measurements	44		
4.2.3. Time-dependent Photocurrent Measurements	46		
4.3. Impact of Adsorbates on Characteristics of Graphene/n-Si			
Photodiode	48		
CHAPTER 5. CONCLUSION			
REFERENCES	52		

LIST OF FIGURES

<u>Figure</u> <u>Page</u>
Figure 1.1 (a) Two different types of carbon atoms, named as A and B in a honeycomb
lattice, the shaded region shows the primitive unit cell. (b) In-plane bonds,
(c) out of plane bonds, (d) two different orientations of carbon atoms (Dash
et al., 2014)2
Figure 1.2 (a) The real and (b) the reciprocal space structure of graphene. The grey
(blue) shaded region is the primitive unit cell (Brillouin zone) in the real
(reciprocal) space. δ_1 , δ_2 and δ_3 are the nearest-neighbor vectors. The carbon
atoms are represented by blue (green) circles in the real (reciprocal) space
and, the unit vectors are represented by \mathbf{a}_1 and \mathbf{a}_2 (\mathbf{b}_1 and \mathbf{b}_2) in the real
(reciprocal) space (Raj and Eapen, 2019)
Figure 1.3 The energy dispersion variations of graphene (Li et al., 2019). The six
corners of the first Brillouin zone involve two types of inequivalent points.
These are K and K' which are named the Dirac points (Castro Neto and
Guinea, 2009). K and K' are $\frac{2\pi}{3a}\left(1,\frac{1}{\sqrt{3}}\right)$ and $\frac{2\pi}{3a}\left(1,-\frac{1}{\sqrt{3}}\right)$, respectively (Neto
et al., 2009)
Figure 1.4 Fermi levels of (a) undoped, (b) hole-doped and (c) electron-doped
graphene (Giubileo and Di Bartolomeo, 2017)5
Figure 1.5 The optical transmittance of graphene for visible and NIR regimes (Nair et
al., 2008; Zhu et al., 2014)
Figure 1.6 Simplified construction of Schottky diodes7
Figure 1.7 Energy-band diagrams of metal-semiconductor contacts. Metal and n-type
semiconductor (a) not in contact (b) in contact and (c) in contact under
equilibrium while work function of metal is higher than work function of
semiconductor. These schematics reprinted from Zhang and Yates Jr (2012).
Figure 1.8 Charge flow mechanisms under forward bias. (1), (2), (3), (4) and (5) are
thermionic emission, quantum tunneling, recombination, diffusion of

Figure 1.9	Energy bang diagram at (a) forward and (b) reverse bias (Colinge and
	Colinge, 2005)10
Figure 1.10	(a) A schematic representation (Lv et al., 2013) (b) Current Density versus
	Voltage culve (c) Current Density versus Voltage culve in logarithmic
	scale (d) Current Density versus Voltage culve in logarithmic scale in
	forward bias of a typical graphene/n-Si Schottky barrier photodiode
	(Kalita et al., 2013)
Figure 1.1	1 Graphene/semiconductor junction energy bands adjustment and
	modulation of Φ_B at (a) zero, (b) reverse and (c) forward bias in contact
	under equilibrium (Di Bartolomeo et al., 2018)
Figure 1.12	2 Photodetection mechanism in a graphene/semiconductor junction. hv' is
	the energy of incident light to the surface of graphene and hv is the energy
	of absorbed light at the graphene/semiconductor interface (Di Bartolomeo
	et al., 2018)
Figure 2.1	Schematic representation of a typical Thermal Evaporation System (Hardy,
	2013)
Figure 2.2	(a) Sample holder. (b) Hard mask for SiO ₂ deposition. (c) Hard mask for
	Cr/Au deposition15
Figure 2.3	Device preparation procedures16
Figure 2.4	The schematic of device structures of Gr/Si Schottky diodes (a) Nanovak
	NVTH-350 Thermal Evaporation System including Edwards RV8
	Turbomolecular Pump, Inficon VG401 Pressure Gauge, Ordel PC771
	Temperature Gauge, SQM-160 Rate/Thickness Monitor, Pot Switch, 12V
	- 200A Sequential/Co-evaporation Thermal Evaporation Sources, Diener
	Electronic SS 304 Vacuum Chamber and CW-5000 Industrial Chiller in
	QDL. (b) Inside of the vacuum chamber (1) Radiative heater, (2) Quartz
	crystal monitor, (3) sample holder, (4) Four crucibles (left-top: SiO ₂ , right-
	top: Al, left-bottom: Cr, right-bottom: Au) 17
Figure 2.5	Schematic representation of CVD set-up used for graphene production
	(Miao et al., 2011)
Figure 2.6	Growth steps of graphene for CVD method: (1) heating, (2) annealing, (3)
	growth, (4) cooling

- Figure 2.9 Schematic representation of Raman spectroscopy (Hung et al., 2013).......24
- Figure 2.10 The molecular energy diagrams of various scatterings and absorptions.....25
- Figure 2.12 Raman Spectroscopy Setup in Quantum Nanophotonics and Quantum Optics Laboratory in Physics Department of İzmir Institute of Technology.

<u>Figure</u>

Page

Figure 3.1 (a) Optical image and (b) the schematic of the fabricated Gr/n-Si
photodiode. (c) A typical single-point Raman spectrum taken on the
graphene electrode shown in (a). Inset is the large area (35 x 35 μ m ²)
integrated 2D band intensity micro-Raman map of the graphene electrode
on n-Si
Figure 3.2 (a) I-V characteristics of Gr/n-Si photodiode in dark ambient. (b) I-V
characteristics of our sample in the semi-logarithmic scale
Figure 3.3 Current vs. dV/dIn(I) plot
Figure 3.4 Current vs. H(I) plot
Figure 3.5 Voltage vs. In I plot under 905 nm light illumination
Figure 3.6 Power dependent V_{oc} and I_{sc} plots
Figure 3.7 The spectral response of Gr/n-Si photodiode. Maximum spectral response
was found at 905 nm as indicated with the dashed line
Figure 3.8 Wavelength-dependent, D^* and NEP plots of our Gr/n-Si photodiode 35
Figure 3.9 Large scale on-off measurement of Gr/n-Si photodiode. The measured
photocurrents were normalized with the maximum values
Figure 3.10 Zoom scale on-off measurement. The measured photocurrents were
normalized with the maximum values
Figure 4.1 (a) I-V curves of the fabricated Gr/n-Si photodiode in dark, measured under
high vacuum before and after UV light illumination. (b) The semi-
logarithmic scale I-V curves of the photodetector which were used to
extract the ideality factors and the zero-bias Schottky barrier heights BUV
and AUV illumination. (c) Current vs. dV/dIn(I) plot and (d) Current vs.
H(I) plot BUV illumination. (e) Current vs. dV/dIn(I) plot and (f) Current
vs. H(I) plot AUV illumination
Figure 4.2 Voltage vs. In I plot under 905 nm wavelength light, AUV illumination and
5 x 10 ⁻⁵ of vacuum level
Figure 4.3 Power-dependent (a) V_{oc} and (b) I_{sc} plots for each of the I-V curves BUV
and AUV illumination
Figure 4.4 Wavelength resolved spectral response of the Gr/n-Si photodiode measured
at zero-bias ($V_b = 0 V$) BUV and AUV illumination. The maximum
spectral response of the sample observed at 905 nm wavelength44

<u>Figure</u> <u>Page</u>
Figure 4.5 Wavelength-dependent (a) D^* and (b) NEP plots of our Gr/n-Si photodiode
BUV and AUV illumination
Figure 4.6 Large scale on-off measurement of Gr/n-Si photodiode AUV illumination.
The measured photocurrents were normalized with the maximum values46
Figure 4.7 Transient photocurrent spectroscopy of Gr/n-Si photodetector BUV and
AUV illumination. The measurements were acquired at zero-bias ($V_b = 0$
V) and under 905 nm wavelength light. The measured photocurrents were
normalized with the maximum values
Figure 4.8 (a) and (b) schematic illustrations of the cross-sectional side views of the
Gr/n-Si photodetector depicting the UV driven desorption of atmospheric
adsorbates from graphene electrode into vacuum and corresponding
charge transfer process. Schematic illustrations of the energy band
diagram for the Gr/n-Si heterojunction (c) BUV and (d) AUV illumination.

LIST OF TABLES

<u>Table</u>		Page
Table 1.1	The values of electrical conductivity (σ), resistivity (ρ) and band gap of	
	graphene and other selected 2D materials.	. 5
Table 2.1	Growth parameters for CVD graphene.	. 19
Table 3.1	Comparison of our Gr/n-Si and the other Gr/n-Si photodiodes' elec-	
	tronic and optoelectronic properties.	. 39
Table 4.1	The performances of the Gr/n-Si photodiode BUV and AUV illumina-	
	tion	. 50

LIST OF SYMBOLS

η	Ideality factor
Φ_B	Schottky barrier height
I_{2D}	2D Intensity of graphene on Raman
I_D	D Intensity of graphene on Raman
I_G	G Intensity of graphene on Raman
е	Elementary charge
k	Boltzman constant
Т	Temperature
R_s	Series resistance
I_0	Saturation current
A	Effective junction area
A^*	Richardson constant
χ	Affinity of n-Si
W_{Gr}	Work function of graphene
${ m E}_{F}^{Gr}$	Fermi level of graphene
V_{oc}	Open-circuit voltage
I_{sc}	Short-circuit current
I_p	Photocurrent
I_d	Dark current
V_b	Bias voltage
D^*	Specific detectivity
R	Spectral response
λ	Wavelength
v	Frequency
t_r	Rise time
t_d	Decay time
α	Fine structure constant
μ_e	Electron mobility
μ_h	Hole mobility
σ	Electrical conductivity

n	Concentration of electrons
p	Concentration of holes
v_d	Electron drift velocity
n_d	Charge Carrier Concentration
\hbar	Plank Constant
v_F	Fermi velocity of graphene
$I_{S \to M}$	Flow current from semiconductor to metal
$I_{M \to S}$	Flow current from metal to semiconductor
$FeCl_3$	Iron Chloride
HCl	Hydrochloric Acid

LIST OF ABBREVIATIONS

Gr	Graphene
n-Si	n-type Silicon
AUV	After Ultraviolet
AT	Annealing Time
BUV	Before Ultraviolet
CVD	Chemical Vapour Deposition
DI	Deionized Water
GT	Growth Time
IPA	Isopropanol Alcohol
NEP	Noise-Equivalent Power
NIR	Near-Infrared
PCB	Printed Circuit Board
PR	Photoresist
PVD	Physical Vapour Deposition
QDL	Quantum Device Laboratory
QTH	Quartz Tungsten Halogen
RT	Ramp Time
TE	Thermionic Emission
TMP	Turbomolecular Pump
UV	Ultraviolet

CHAPTER 1

INTRODUCTION

1.1. What is Graphene?

1.1.1. Structural Properties of Graphene

Graphene is a two-dimensional (2D) (Gupta et al., 2015) and single atom thick material (Geim and Novoselov, 2010; Service, 2009; Singh et al., 2011) which is arranged carbon atoms (Alvial-Palavicino and Konrad, 2019) in a honeycomb structure (Allen et al., 2010; Behera and Mukhopadhyay, 2012; Wang et al., 2013). The bond length between each carbon atoms is 0.14 nm (Yazyev and Helm, 2007) and the atomic thickness of graphene is 0.34 nm (Nemes-Incze et al., 2008). Carbon atoms have sp² hybridization and form three covalent bonds by the hybridization of 2s orbital (De Andres et al., 2008). The strong sigma (σ) bonded p_x and p_y in the plane produce to a stable hexagonal structure and, the angle between the $2p_x$ and $2p_y$ orbits is 120° . Partially filled and weak π bonded p_z orbitals provide the electron conduction and are perpendicular to the plane (Giubileo and Di Bartolomeo, 2017). Moreover, graphene layers have randomly distributed sp³ hybridization. (He et al., 2014; Phuc et al., 2018; Zhang et al., 2011). The geometric and atomic structure of graphene is shown in Figure 1.1. In Figure 1.1 (a) the dark and the light circles represent carbon atoms at two different sites named respectively as A and B, the shaded region indicates the unit cell. Figure 1.1 (b) shows the sp² hybridized orbitals of carbon atoms symmetrically distributed in the molecular plane at angles of 120° forming three σ -bonds with those of the three nearest neighbors. In Figure 1.1 (c) the orbitals of the remaining electrons distributed perpendicular to the molecular plane form π -bonds with those of one of the nearest neighbor, assigning four bonds to each carbon atoms. In Figure 1.1 (d) two different orientations of the arrangement of carbon atoms at lattice sites A and B, the honeycomb lattice can be viewed as two



interpenetrating triangular lattices of A and B carbon atoms (Dash et al., 2014).

Figure 1.1. (a) Two different types of carbon atoms, named as A and B in a honeycomb lattice, the shaded region shows the primitive unit cell. (b) In-plane bonds, (c) out of plane bonds, (d) two different orientations of carbon atoms (Dash et al., 2014).

Position vector of each carbon atom on the periodic lattice of Real space (see Figure 1.2 (a)) can be determined by $\overrightarrow{R} = m\overrightarrow{a_1} + n\overrightarrow{a_2}$ (Suzuki et al., 2017), where m and n are integers, $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ are the unit vectors in real space which are calculated by Equation 1.1 (Mina et al., 2012; Moon and Koshino, 2013).

$$\overrightarrow{a_1} = a\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right), \qquad \overrightarrow{a_2} = a\left(\frac{\sqrt{3}}{2}, \frac{-1}{2}\right).$$
 (1.1)

where *a* is the lattice constant which is approximately 0.24 nm for graphene (Dresselhaus et al., 1998; Podaru, 2011). The nearest-neighbor vectors $(\delta_1, \delta_2 \text{ and } \delta_3)$ are determined as $\overrightarrow{\delta_1} = a/2(\sqrt{3}, -1)$, $\overrightarrow{\delta_2} = a/2(-\sqrt{3}, -1)$ and $\overrightarrow{\delta_3} = a(0, 1)$. In addition, $\overrightarrow{b_1}$ and $\overrightarrow{b_2}$ are the unit vectors in reciprocal space of graphene (see Figure 1.2 (b)) which are calculated by Equation 1.3 (Jiang et al., 2009; Marconcini and Macucci, 2007).

$$\vec{b}_{1} = 2\pi \frac{\vec{a}_{2} \times \vec{z}_{0}}{\vec{a}_{1} \cdot (\vec{a}_{2} \times \vec{z}_{0})} = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}}, 1\right),$$

$$\vec{b}_{2} = 2\pi \frac{\vec{z}_{0} \times \vec{a}_{1}}{\vec{a}_{2} \cdot (\vec{z}_{0} \times \vec{a}_{1})} = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}}, -1\right).$$
(1.2)

where $\overrightarrow{z_0}$ is the unit vector along the z-axis.



Figure 1.2. (a) The real and (b) the reciprocal space structure of graphene. The grey (blue) shaded region is the primitive unit cell (Brillouin zone) in the real (reciprocal) space. δ_1 , δ_2 and δ_3 are the nearest-neighbor vectors. The carbon atoms are represented by blue (green) circles in the real (reciprocal) space and, the unit vectors are represented by \mathbf{a}_1 and \mathbf{a}_2 (\mathbf{b}_1 and \mathbf{b}_2) in the real (reciprocal) space (Raj and Eapen, 2019).

Graphene has an electronic band structure with a completely filled valence band and empty conduction band which crosses linearly at the Dirac point (Ihn et al., 2010). Its electronic band structure can be calculated by the nearest-neighbor and next-nearestneighbor tight-binding approximation (Giubileo and Di Bartolomeo, 2017; Kundu, 2011; Wright et al., 2009). The energy bands of graphene are shown in Figure 1.3 (Castro Neto and Guinea, 2009).



Figure 1.3. The energy dispersion variations of graphene (Li et al., 2019). The six corners of the first Brillouin zone involve two types of inequivalent points. These are K and K' which are named the Dirac points (Castro Neto and Guinea, 2009). K and K' are $\frac{2\pi}{3a}\left(1, \frac{1}{\sqrt{3}}\right)$ and $\frac{2\pi}{3a}\left(1, -\frac{1}{\sqrt{3}}\right)$, respectively (Neto et al., 2009).

1.1.2. Electrical Properties of Graphene

In graphene, each carbon atom is connected to 3 neighbor carbon atoms on the two dimensional plane, leaving 1 electron freely available in the third dimension for electronic conduction. This situation leads to high electrical conductivity for graphene (Chen et al., 2008; Rao et al., 2009). The electrical conductivity (σ) of graphene is calculated by $\sigma = e(n\mu_e + p\mu_h)$, where *e* is the elementary charge, *n* is the concentration of electrons, μ_e is the electron mobility, *p* is the concentration of holes and μ_h is the hole mobility (Kittel and McEuen, 1976). Table 1.1 shows that the values of electrical conductivity (σ), resistivity (ρ) and band gap of graphene and other selected 2D materials and, indicates that graphene is a better conductor than other selected 2D materials.

	$\sigma \rho$		Band gap	References
	$(ohm^{-1}cm^{-1})$	(ohm.cm)	(eV)	
Gr	$0.96 imes10^6$	1.04×10^{-6}	0	Chyada et al.
$2H-MoS_2$	0.03	33.3	1.6	El-Mahalawy and Evans
$2H-WSe_2$	6	0.16	1.3	El-Mahalawy and Evans
Bi_2S_3	$4.15 imes 10^{-7}$	$2.40 imes 10^6$	1.3 - 1.45	Mane et al.
As_2Te_3	$5 imes 10^{-5}$	$2 imes 10^4$	0.2 - 0.3	Hrubỳ and Stourac
HfS_2	3×10^{-3}	333	2	Xu et al.

Table 1.1. The values of electrical conductivity (σ), resistivity (ρ) and band gap of graphene and other selected 2D materials.

Graphene is doped n-type (p-type) by increasing the concentration of electrons (holes) on its surface (Dong et al., 2009). When graphene is doped n-type (p-type), Fermi level of graphene shifts upwards (downwards) from Dirac point (Giovannetti et al., 2008). Fermi level of graphene is computed by using $E_F = \hbar v_F \sqrt{\pi n_d}$, where \hbar is plank constant (6.58 × 10⁻¹⁶ eV), v_F is Fermi velocity of graphene (10⁶ m/s), n_d is charge carrier concentration (Di Bartolomeo et al., 2015). Figure 1.4 indicates Fermi levels of undoped, hole-doped and electron-doped graphene.



Figure 1.4. Fermi levels of (a) undoped, (b) hole-doped and (c) electron-doped graphene (Giubileo and Di Bartolomeo, 2017).

1.1.3. Optical Properties of Graphene

Graphene's linear band structure, zero band-gap and strong interaction of Dirac Fermions with electromagnetic radiation lead to unique optical properties (Kavitha and Jaiswal, 2016). Interband and intraband transitions dictate the optical absorption and transmittance of graphene (Kavitha and Jaiswal, 2016). In visible and near-infrared (NIR) region, the optical transmittance of graphene is calculated as $\sim 97\%$ by using the Fresnel equation (shown in Equation 1.3) (Pang et al., 2011).

$$T = (1 + 0.5n\alpha)^{-2} \approx 1 - n\alpha \tag{1.3}$$

where α is the fine structure constant, $\alpha = e^2/\hbar c = 1/137$. Figure 1.5 shows the transmittance of graphene in visible and NIR region. The absorption is calculated as 2.3% from $A = 1 - T = \pi \alpha$ (Lu et al., 2015; Ponraj et al., 2016). The reflectance of graphene was reported smaller than 0.1% of the incident light in the visible region (Nair et al., 2008; Pang et al., 2011).



Figure 1.5. The optical transmittance of graphene for visible and NIR regimes (Nair et al., 2008; Zhu et al., 2014).

1.2. Schottky Barrier Photodiodes



Figure 1.6. Simplified construction of Schottky diodes.

Schottky diodes are historically the first fabricated diodes. A Schottky diode is created by the rectifying behaviour between the metal and the semiconductor (Sheng et al., 2002), where the electric current only forms from the majority carriers (AL-Oqla et al., 2018). Simplified construction of Schottky diodes was shown in Figure 1.6. The properties of the rectifying contact resemble a one-sided abrupt PN junction diode (Colinge and Colinge, 2005). F. Braun discovered the rectifying behavior of metal-semiconductor diodes in 1874 (Braun, 1875). Schottky and Mott declared the effect of rectifying in 1938 (Mott and Littleton, 1938) and this model was improved by Bethe in 1942 to become the thermionic emission model which correctly explains the electrical behavior (Bethe, 1991).

Let consider a metal and an n-type semiconductor that work function of the metal is higher than that of the n-type semiconductor. If the metal and the n-type semiconductor is allowed to be junction with each other, the charge transfers from the semiconductor to the metal. Thus, thermal equilibrium is formed in one system. Subsequently, the Fermi levels on both sides are equalized. Figure 1.7 shows the energy band diagrams of a metal and an n-type semiconductor.



Figure 1.7. Energy-band diagrams of metal-semiconductor contacts. Metal and n-type semiconductor (a) not in contact (b) in contact and (c) in contact under equilibrium while work function of metal is higher than work function of semiconductor. These schematics reprinted from Zhang and Yates Jr (2012).

The work function is defined as the energy difference between the vacuum level and the Fermi level. It is calculated with the formula of $q\phi_m$ for metals and $q\chi + q\phi_n$ for semiconductors, where $q\chi$ is electron affinity and $q\phi_n$ is the energy difference between the energy of electrons in the conduction band and the Fermi level. The difference between metal's and semiconductor's work function $(\phi_m - (\chi + \phi_n))$ gives contact potential. In addition, the barrier height is calculated by Equation 1.4.

$$q\Phi_B = q(\phi_m - \chi) \tag{1.4}$$

Charge flow is described in five parts in which thermionic emission (TE) over the barrier (1), quantum tunneling through the barrier (2), recombination in the depletion region (3), diffusion of carriers across the depletion region (4) and (5) under forward bias (shown in Figure 1.8). In Schottky diodes, the dominant effect of charge flow is due to the TE at room temperature.



Figure 1.8. Charge flow mechanisms under forward bias. (1), (2), (3), (4) and (5) are thermionic emission, quantum tunneling, recombination, diffusion of electrons and diffusion of holes, respectively (Dönmez, 2019).

TE releases electrons on the surface due to thermal energy. When adequate thermal energy is provided, charge carriers exceed the potential barrier from metal to semiconductor or vice versa. This can be occurred by thermionic emission in Schottky contacts. The Fermi level of metal and semiconductor changes at thermal equilibrium. The applied voltage does not affect the barrier height on the metal side. This barrier height can be controlled by the applied voltage on the semiconductor side. If this voltage is forward bias, it decreases, and if it is a reverse bias, at that time the barrier height increases as shown in Figure 1.9. The current increases from the semiconductor to the metal when the



Figure 1.9. Energy bang diagram at (a) forward and (b) reverse bias (Colinge and Colinge, 2005).

forward bias is applied. If the applied voltage is reverse bias, the current decreases. In Schottky diodes, this situation is realized by the majority carriers. The flow current from semiconductor to metal and vice versa is described by Equation 1.5 and 1.6, respectively.

$$I_{S \to M} = A^* T^2 exp\left(-\frac{q\Phi_B}{kT}\right) exp\left(\frac{qV_i}{\eta kT}\right)$$
(1.5)

$$I_{M\to S} = -A^* T^2 exp\left(-\frac{q\Phi_B}{kT}\right) \tag{1.6}$$

where A^* is Richardson constant. η is ideality factor. According to Equation 1.5 and 1.6,

total current is written as (Cheung and Cheung, 1986; Di Bartolomeo et al., 2018)

$$I = I_{S \to M} - I_{M \to S}$$

= $A^*T^2 exp\left(-\frac{q\Phi_B}{kT}\right) \left[exp\left(\frac{qV_i}{\eta kT}\right) - 1\right]$ (1.7)
= $I_0\left[exp\left(\frac{qV_i}{\eta kT}\right) - 1\right].$

1.3. Graphene-based Schottky Barrier Photodiodes



Figure 1.10. (a) A schematic representation (Lv et al., 2013) (b) Current Density versus Voltage culve (c) Current Density versus Voltage culve in logarithmic scale (d) Current Density versus Voltage culve in logarithmic scale in forward bias of a typical graphene/n-Si Schottky barrier photodiode (Kalita et al., 2013).

The graphene/semiconductor junction has an intense research activity due to a variety of phenomena that allow it to be both easy to manufacture and study. It provides an opportunity to research the physics of 2D semi-metal and 3D semiconductor junction. (Di Bartolomeo, 2016). Figure 1.10 (a) shows a typical graphene/n-Si Schottky photodiode and, Figure 1.10 (b), (c) and (d) indicates electrical characteristics of the graphene/n-Si Schottky photodiode. Also, the graphene/semiconductor junction shows rectifying I-V characteristics (see Figure 1.10 (b)) like metal/semiconductor Schottky diodes. This feature is demonstrated using various substrates such as Si, GaAs, SiC, ZnO, Ge, MoS₂ and GaN in literature (Tongay et al., 2012; Yang et al., 2017; Zhang et al., 2014). Figure 1.10 indicates that schematic and electrical characteristics a typical Gr/n-Si Schottky photodiode.

Tongay et al. also remarked that the Fermi level of graphene is shifting during charge transfer at the graphene/semiconductor interface (Tongay et al., 2012). The tunable Fermi level of graphene influences Schottky barrier height (Φ_B). Φ_B is increased (decreased) at the forward (reverse) bias.



Figure 1.11. Graphene/semiconductor junction energy bands adjustment and modulation of Φ_B at (a) zero, (b) reverse and (c) forward bias in contact under equilibrium. (Di Bartolomeo et al., 2018).

Figure 1.11 shows the energy bands adjustment of graphene/semiconductor junction. The graphene/semiconductor junction is more advantageous than the other metal/ semiconductor junction (Di Bartolomeo et al., 2018). The use of graphene electrodes has advantages over other Schottky electrodes because of the build-up of optically active built-in potential over regions just beneath the electrode, without substantial loss of light absorption by the metal grid. (Lee et al., 2018). Although most of the incident light is converted to photocharge into semiconductor, the absorbance in graphene enables detection of photons with semiconductor sub-bandgap energy through internal photoemission over the Schottky barrier (Riazimehr et al., 2015). Photocharges injected over the Schottky barrier (see Figure 1.12), under high reverse bias, can be accelerated by the electric field in the depletion region of the diode and cause avalanche multiplication by scattering with the Si lattice, thus enabling internal gain (Di Bartolomeo et al., 2018).



Figure 1.12. Photodetection mechanism in a graphene/semiconductor junction. $h\nu'$ is the energy of incident light to the surface of graphene and $h\nu$ is the energy of absorbed light at the graphene/semiconductor interface (Di Bartolomeo et al., 2018).

In this thesis work, we have investigated the effect of adsorbates on electronic and optoelectronic characteristics of graphene/n-Si Schottky barrier photodiode. Firstly, we have measured electronic and optoelectronic characteristics of Gr/n-Si Schottky barrier photodiode on atmospheric ambient. Then we repeated the same measurements invacuum after 15 minutes of 254 nm UV illumination. UV illumination removed adsorbates on the surface of Gr/n-Si Schottky barrier photodiode. In this way, it was clarified how the effect of adsorbates the electronic and optoelectronic properties of Gr/n-Si Schottky barrier photodiode.

CHAPTER 2

EXPERIMENTAL DETAILS

2.1. Thermal Evaporation System

Thermal evaporator is a physical vapour deposition (PVD) technique to deposit pure materials on to the surface of substrates. Deposited materials which are called thin films are in the range of angstrom to micron thick. The materials evaporated in TE can be atomic scale elements including both metals and non-metal or organic molecules. Basically, the vapor of material cloud is produced by heating a solid material under a high vacuum in the chamber reaching a pressure level of $10^{-5} - 10^{-9}$ mbar. When molecules are vaporized inside the vacuum chamber, they reach from the source to the substrate and it forms a thin film on the substrate. Schematic representation of a thermal evaporator system is shown Figure 2.1.



Figure 2.1. Schematic representation of a typical Thermal Evaporation System (Hardy, 2013).

For our experiments, a sample holder and hard masks were designed to evaporate metallic electrodes in suitable geometries by the former master and doctoral students in Quantum Device Laboratory (QDL). By getting use of AutoCAD, we designed sample holder and hard masks and the fabrication of them was done by Sparks Technologies Turkey with a laser cutting machine with a precision of 5 μ m. We usually use 10 × 10 mm² samples. In this study, the sample holder has 32 cells, each 10.1 × 10.1 mm² (Figure 2.2 (a)).There are two 300 μ m thick, stainless steel with 9.5 × 9.5 mm² sized cells and 10.1 × 10.1 mm² sized cells. Combining these different sized of holders helps to protect the samples from falling. Holders were fabricated with a precision of 10 μ m. The dimension of the stainless steel hard masks (Figure 2.2 (b) & 2.2 (c)) were 10 × 10 × 0.15 mm³ (L × W × H).



Figure 2.2. (a) Sample holder. (b) Hard mask for SiO₂ deposition. (c) Hard mask for Cr/Au deposition.

2.1.1. Deposition of Interfacial Oxide and Metallic Electrodes

SiO₂ was used between graphene and n-Si as an isolation layer, and Cr/Au as metallic electrodes were deposited to get contacts. Firstly, the n-Si substrate kept in the HF solution for about 5 seconds to get rid of the accumulated native oxide on the substrate just before starting the deposition processes. Afterwards, hard masks were placed on the cells of the sample holder. With this, $10 \times 10 \text{ mm}^2$ polished n-Si substrates were put on the hard masks. Then, the sample holder was loaded into the chamber of the thermal evaporator. The system was waited overnight, until when the pressure level reaches 10^{-7} mbar. In the next step, 400 nm SiO_2 was deposited on the n-Si substrates. When this process is over, the temperature of the chamber increased from 40 °C to 106 °C. We waited until the temperature reaches room temperature to avoid cracks on the samples causing by the thermal difference. When the room temperature was achieved, the system was ventilated with N₂ gas. Then it was prepared for Cr/Au deposition. 4 nm Cr and 80 nm Au were deposited on the SiO₂/Si substrate, respectively. The purpose of Cr deposition is to make Au atoms to stick on the n-Si and SiO_2 . The reason of Au deposition is to provide good electrical conductivity. After all the deposition processes, the samples became ready for the graphene transfer process. All the deposition procedures (shown in Figure 2.3) were conducted with Nanovak NVTH-350 thermal evaporator system in QDL (see Figure 2.4).



Figure 2.3. Device preparation procedures.



Figure 2.4. (a) Nanovak NVTH-350 Thermal Evaporation System including Edwards RV8 Turbomolecular Pump, Inficon VG401 Pressure Gauge, Ordel PC771 Temperature Gauge, SQM-160 Rate/Thickness Monitor, Pot Switch, 12V
200A Sequential/Co-evaporation Thermal Evaporation Sources, Diener Electronic SS 304 Vacuum Chamber and CW-5000 Industrial Chiller in QDL. (b) Inside of the vacuum chamber (1) Radiative heater, (2) Quartz crystal monitor, (3) sample holder, (4) Four crucibles (left-top: SiO₂, righttop: Al, left-bottom: Cr, right-bottom: Au).

2.2. Growth and Transfer of CVD Graphene

Chemical vapour deposition (CVD) is simply defined as the production of a solid compound through the chemical reaction of activated gas reactants. Carbon-rich gasses such as methane and ethane react on transition metal films such as copper (Cu)⁶⁸, nickel (Ni)⁶⁹, and platinum (Pt)⁷⁰ at different temperatures (400 °C - 1000 °C) (Li et al., 2011). Carbon atoms break up on these films as a result of this reaction and form graphene layers. The schematic representation of the CVD method is given in Figure 2.5.



Figure 2.5. Schematic representation of CVD set-up used for graphene production (Miao et al., 2011).

It is possible to synthesize single crystal graphene layers by using the CVD method (Li et al., 2009). In the films synthesized by this method, the grain size of graphene are larger than those obtained by other methods. Since the substrates are metals, which is used in this method, they dissolve in acid solutions. Therefore, synthesized graphene films can be easily transferred onto other substrates. Graphene production by CVD method generally tracks the following steps:

Heating Step (1) : In a controlled atmosphere, the catalyst-substrates and gases are heated up to the pre-treatment temperature.

Annealing Step (2) : Catalyst surface is reduced while maintaining temperature and gas atmosphere. This process is the first chemical reaction of the whole process. Ar and H_2 performed to clean catalyst surface and to change surface morphology of the metal which includes particle size, roughness, and crystal distribution. The vaporization of metal is avoided.

Growth Step (3) : Process that involves the addition of new precursor and growth of graphene on catalyst substrate.

Cooling Step (4) : After the graphene growth reactor is cooled at an appropriate atmosphere. The atmosphere is generally the same as in the annealing or growth step until the reactor temperature is below 200 °C to prevent oxidation of the uncoated catalytic surface and the reaction of the graphene with oxygen containing groups then reactor chamber is filled with inert gasses until the atmospheric pressure is reached and then it is opened.



Figure 2.6. Growth steps of graphene for CVD method: (1) heating, (2) annealing, (3) growth, (4) cooling.

In our work, Cu foil (25 μ m thick, 99.8 purity, Alfa Aesar) was placed on a quartz plate as catalyst-substrate material. Then it was inserted through the tube of the CVD furnace (see Figure 2.7 (a)). In the first step, Cu foil was heated up to 1000 °C under an H₂ (20 sccm) + Ar (1000 sccm) gas mixture during ramp time (RT, 33 minutes) as seen in Figure 2.6. Then, Cu foil was annealed for an hour. After annealing time (AT, 1 hour), CH₄ (10 sccm) was sent through the quartz tube during growth time (GT, 2 minutes) in order to form graphene. After that, the sample was left self-cooling from 1000 °C to room temperature under a gas mixture of H₂ (20 sccm) and Ar (1000 sccm) in the tube. The growth parameters for single layer graphene given in Table 2.1 and, temperature control and time-dependent gas flow control softwares for single layer graphene growth was shown in Figure 2.7 (b) and (c).

Table 2.1. Growth parameters for CVD graphene.

Temp. (°C)	H_2 (sccm)	Ar (sccm)	CH ₄ (sccm)	RT (min)	AT (min)	GT (min)
1000	20	1000	5	33	59	2



Figure 2.7. (a) CVD furnace including a quartz tube, a thermocouple, a heater, and flowmeters. (b) Temperature control software designed in LabVIEW. (c) Time-Dependent gas flow control software designed in LabVIEW.

In order to protect the graphene layer against possible damage during the transfer process, Microposit S1813 Photoresist (PR) was used as a supporting layer. PR was dropped onto the Graphene/Cu template by using the drop-casting method. Then, it was baked at 70 °C overnight. Cu foil was etched into 0.2 M Iron Chloride ($FeCl_3$) solution. After completely removing Cu foil, deionized water and 33% diluted Hydrochloric Acid (HCl) solution were used to get rid of $FeCl_3$ residues. PR/Graphene was transferred onto the clean SiO₂/n-Si substrate after N₂ drying. In order to provide better adhesion of the graphene layer to the surface of the substrate, it was baked at 90 °C for about 5 min. After that, the sample was dipped into acetone twice in order to solve PR and leave graphene alone on the SiO₂/n-Si substrate. Then, Isopropanol Alcohol (IPA) was used to remove acetone residues from the substrate. Finally, deionized water (DI) was used to clean IPA residues from the substrate (see Figure 2.8). The number of graphene layers transferred on the substrate was determined by Raman spectroscopy measurements which will be discussed in the following section.


Figure 2.8. Schematic representation of the graphene transfer on substrate.

2.3. Raman Spectroscopy Measurements

Raman spectroscopy is an effective spectroscopic technique typically used to determine the vibrational modes of molecules, although rotational and other low-frequency modes of systems may also be observed. Raman spectroscopy is commonly used to provide a structural fingerprint by which material can be identified. A schematic representation of the Raman spectroscopy is shown in Figure 2.9.



Figure 2.9. Schematic representation of Raman spectroscopy (Hung et al., 2013).

When a monochromatic beam of light is sent to the matter, it interacts with electrons in molecules. The interacted light beam can be absorbed, emitted, or scattered by electrons. The electron excites into the virtual energy state. Then, an electron comes back to vibrational energy state. When this situation happens, the photon scatters. There are two types of scattering. One of them is elastic scattering. If the energy of the used photon to excite the electron in the ground state and the energy of the scattered photon as the electron returns to the ground state are the same, it is known as the elastic scattering. Rayleigh scattering is an example of elastic scattering. The other one is the inelastic scattering. If the energy of the utilized photon to excite the electron in the ground state and the energy of the scattered photon as the electron goes back to the ground state are not equal, it is dubbed inelastic scattering. Anti-stokes and Stokes scattering are examples of inelastic scattering. Figure 2.10 shows the molecular energy diagrams of various scatterings and absorptions.



Figure 2.10. The molecular energy diagrams of various scatterings and absorptions.

In this thesis, the Raman spectroscopy set-up shown in Figure 2.12 was used to specify the number of the graphene layers. It is examined three main peaks in graphene. These are D peak, G peak and, 2D peak. Figure 2.11 contains the Raman spectra of graphene with different layer numbers. D peak gives information about sp³ bond revealing the amount of disorder. G peak corresponds to the C - C reaching of sp² bond. Finally, 2D peak is the second-order D peak.

For the graphene layer D peak, G peak and, 2D peak are resolved at the wavenumbers of ~ 1350 cm⁻¹, ~ 1580 cm⁻¹ and, ~ 2700 cm⁻¹ (Ferrari et al., 2006). The number of graphene layers is determined in accordance with the ratio I_G/I_{2D} . If the ratio I_G/I_{2D} corresponds to 1/2, graphene is single layer, Provided that the ratio I_G/I_{2D} equals 1, graphene is bilayer. If the ratio I_G/I_{2D} is greater than 1, graphene is either a few layer or multilayer. Moreover, Information about the amount of defect is given the I_D/I_G ratio of graphene. The ideal ratio of the I_D/I_G is ranged between 0.025 and 0.3 (Reina et al., 2009).



Figure 2.11. Raman spectra of different graphene layers (Liu et al., 2013).

Raman spectroscopy measurements were done in the Nanophotonics and Quantum Optics Laboratory in the Physics Department of İzmir Institute of Technology (See Figure 2.12). Raman signals were observed with 100x microscope objective, using an Ar^+ ion laser beam which has a scan range between 1000 - 3100 cm⁻¹ and 532 nm laser excitation.



Figure 2.12. Raman Spectroscopy Setup in Quantum Nanophotonics and Quantum Optics Laboratory in Physics Department of İzmir Institute of Technology.

2.4. Wire Bonding System

After the number of layers of transferred CVD graphene on the sample was determined, the wire bonding system shown in Figure 2.13 was used to get electrical contacts for the optoelectronic measurements. Firstly, 6-pin sockets were soldered to the copper paths of the Printed Circuit Board (PCB). In the next step, the fabricated photodiode was stuck on PCB with the aid of double-sided tape to prevent the movement of the sample. Thereafter, the predetermined gold contacts of the photodiode were soldered to the copper paths of PCB with 80 μ m copper wires and used indium wire solder as a solder material. Indium wire solder is a useful material to solder gold contacts with copper paths. Indium wire solder melts at 157 °C. Due to this property, gold contacts are not damaged. Lastly, connections were checked with Fluke 28-II TRMS Industrial Multimeter with IP67 Rating. Figure 2.13 illustrates the used devices for soldering in our lab (QDL).



Figure 2.13. (a) Wire bonding system including Sony ExwaveHAD Color Video Camera, Olympus U-CMAD3 Camera Adapter, Olympus U-CMAD3/U-TVIX-2 Mount Microscope Camera Adapter, Olympus WHS10X-H/22 Microscope Eye Piece, Olympus SZX9 Stereo Zoom Microscope, Sunline 852D⁺SMD Rework Station, Emsan Enamelled Insulated Copper wire, and Zeiss KL 1500 LCD Cold Light Source. (b) Our fabricated photodetector (c) Fluke 28-II TRMS Industrial Multimeter with IP67 Rating.

2.5. Photocurrent Spectroscopy

Photocurrent spectroscopy is a versatile characterization technique to investigate the optoelectronic properties of semiconductors and photosensitive devices capable of light absorption (Fry et al., 2000). A schematic representation of the photocurrent spectroscopy (Figure 2.14 (a)) and time-dependent photocurrent spectroscopy (Figure 2.14 (b)) are shown in Figure 2.14.



Figure 2.14. Schematic representations of (a) the photocurrent spectroscopy and (b) time-dependent photocurrent spectroscopy setups in QDL.

First of all, broadband spectrum (320 - 1100 nm) light is sent to a focusing lens assembly by a quartz halogen lamp. In this step, the incident light is focused on one direction. The focused light is sent to a monochromator to separate it into the desired wavelength. Then, the transmitted light is passed through the light-sensitive device. After that, the photocurrent is generated by the light-sensitive device and can be measured by using amperemeter. This is a fundamental principle of the photocurrent spectroscopy.

In this study, the electronic and optoelectronic characterizations were done using a rack unit comprising Keithley 2400 Sourcemeter as voltage and current sources, Keithley 6485 Picoamperemeter to the current measurements (photocurrent and darkcurrent), Keithley 2182 Nanovoltmeter for the precise voltage measurements, a Pfeiffer High Cube Turbomolecular Pump (TMP) for the high vacuum studies, GW-Instek power supply to use as a voltage source, respectively. Under ambient conditions and 10^{-5} mbar vacuum level, power-dependent transient photocurrent and wavelength-dependent photoresponsivity measurements were performed by the photocurrent spectroscopy set-up including an Osram 24V-250W quartz tungsten halogen (QTH) lamp as a light source, a Newport Focusing Assembly for focusing a collimated light, Oriel Cornerstone high-resolution monochromator for procuring monochromatic light, Oceans Optics flame spectrometer for adjusting the precise gaussian peak of the wavelength of light, and a 5 K - 300 K closed-loop cryostat for protection from environmental factors. The power output calibration of the QTH lamp was done by using Thorlabs FDS10X10 Si photodiode. On-off measurements were done by the time-dependent photocurrent spectroscopy set-up including a Thorlabs AMP102 Transimpedance Amplifier, a Thorlabs DC2200 High Power LED Controller and a Rigol MSO5204 Digital Oscilloscope. The electronic/optoelectronic unit and photocurrent spectroscopy set-up in QDL was shown in Figure 2.15 (a), (b) and (c).



Figure 2.15. (a) The Electronic and Optoelectronic unit including Keithley 2400 Sourcemeter Units, Keithley 6485 Picoammeter, Keithley 2182 Nanovoltmeter, Rigol MSO5204 Digital Oscilloscope ,GW-Instek power supply, Orial Instruments 68831 300W Radiometric Power Supply, Thorlabs AMP102 Transimpedance Amplifier, Thorlabs DC2200 High Power LED Controller, and Thorlabs COP4-B Collimation Adapter (b) Photocurrent spectroscopy set-up including Osram 24V-250W quartz tungsten halogen, Newport Focusing Assembly, Oriel Cornerstone high-resolution monochromator, Oceans Optics flame spectrometry, a 5 K to 300 K closed loop cryostat, Pfeiffer High Cube TMP, and Thorlabs FDS10X10 Si photodiode in QDL. (c) Fabricated Photodiode placed onto cryostat's sample holder.

CHAPTER 3

CHARACTERIZATION OF GRAPHENE/SILICON PHOTODIODE

3.1. Raman Characterization

In this section, Gr/n-Si Schottky barrier photodiode was fabricated and, its optical image and the schematic representation were shown in Figure 3.1 (a) and (b), respectively. The thickness of the transferred graphene was determined by single-point Raman spectroscopy measurements on randomly chosen spots of the sample surface. In all the measurements, graphene related D, G, and 2D peaks were well resolved as shown in Figure 3.1 (c). The strong G peak and weak D peak indicate good graphitic quality, and the large 2D to G peak intensity ratio ($I_{2D}/I_G > 2$) confirms the single-layer thickness of the graphene layer (Lin et al., 2015). The thickness uniformity of graphene electrode on the n-Si side of the substrate is verified by micro-Raman mapping of the 2D peak intensity in a randomly selected area as shown at the inset of Figure 3.1 (c). The micro-Raman map was acquired in a spectral range between 2600 and 2800 cm^{-1} and the data is recorded for a laser excitation wavelength of 532 nm by raster scanning mode with a precision twodimensional stage having 1 μ m step size. From the obtained Raman map, the average 2D peak intensity variation $\sigma(I_{2D})$ was calculated to be only about 6 % suggesting a homogeneous coverage of the single-layer graphene electrode throughout the active junction area. It should be mentioned that such a small variation in the 2D peak intensity may arise from unintentional weak fluctuations of the laser power during the scanning process. D peak, G peak and, 2D peak was found at \sim 1370.2 cm⁻¹, \sim 1584.9 cm⁻¹ and \sim 2712.9 cm⁻¹ for graphene, respectively.



Figure 3.1. (a) Optical image and (b) the schematic of the fabricated Gr/n-Si photodiode. (c) A typical single-point Raman spectrum taken on the graphene electrode shown in (a). Inset is the large area $(35 \times 35 \ \mu m^2)$ integrated 2D band intensity micro-Raman map of the graphene electrode on n-Si.

3.2. Electronic Characterization

I-V measurements are one of the significant experimental methods to understand the electronic characteristics of a photodiode. Figure 3.2 (a) displays the fabricated graphene/n-Si Schottky photodiode characteristic at the reverse and forward bias. This characteristic is called the rectifying behavior. The I-V characteristics of our sample was also shown in the semi-logarithmic scale in Figure 3.2 (b). The I-V measurement shown in Figure 3.2 was done between the bias voltage range -0.25 and 0.25 V in dark ambient. From the semi-logarithmic scale I-V plot the dark current of our device was determined as in 1.20 nA. In literature, the dark current of a typical Gr/n-Si photodiode was reported as 9.50 nA (Wang et al., 2020) and 9.30 nA (Li et al., 2016).



Figure 3.2. (a) I-V characteristics of Gr/n-Si photodiode in dark ambient. (b) I-V characteristics of our sample in the semi-logarithmic scale.

The ideality factor (η) is an essential parameter to control the electronic performance of a diode Dalapati et al. (2014). It is a measure of how similar a diode is to an ideal diode. Inhomogeneity between graphene and semiconductor brings about nonideality. The value of η is 1 for an ideal photodiode. It is found by multiplying the intercept (lined region in Figure 3.3) of linear region of the dV/dIn(I) vs I plot (shown in Figure 3.3) with q/kT. In addition, according to the Cheung's method, η can be calculated using Equation 3.1,

$$\eta = \frac{e}{kT} \left(\frac{dV}{d\ln I} - R_s I_0 \right) \tag{3.1}$$

where e, k, R_s and T are the elementary charge (1.602×10⁻¹⁹C), Boltzmann constant (1.38×10⁻²³ m²kg s⁻²K⁻¹), series resistance and the temperature, respectively. In this study, η of our device was extracted as 1.25. η values in the literature range between 1.60 and 33.50. (Chen et al., 2011; Miao et al., 2012). When η value in this study is compared with the literature, it is observed that the value is consistent.



Figure 3.3. Current vs. dV/dIn(I) plot.

Schottky barrier height (Φ_B) is a potential energy barrier for the electrons at a

metal-semiconductor interface and can be calculated by dividing the intercept of the H(I) vs. Current plot (shown in Figure 3.4) with η (Cheung and Cheung, 1986). Theoretically, Φ_B is calculated by the in Equation 3.2,

$$H(I) = V - \eta \frac{kT}{e} \ln\left(\frac{I_0}{AA^*T^2}\right) = IR_s + \eta \Phi_B$$
(3.2)

where A is the effective junction area (for this study $A = 0.15 \text{ cm}^2$), A^* is the Richardson constant (~112 Acm⁻²K² for n-Si) from the measured forward I-V plot in the darkness (Wang et al., 2020). In this study, the value of Φ_B was determined as 0.78 eV. In the literature, Φ_B values ranges between 0.41 and 0.86 eV (Chen et al., 2011; Parui et al., 2014; Tongay et al., 2012).



Figure 3.4. Current vs. H(I) plot.

After calculating Φ_B , the work function of the graphene (W_{Gr}) can be determined according to the Schottky-Mott relation, as shown in Equation 3.3,

$$W_{Gr} = \Phi_B + \chi \tag{3.3}$$

where χ is the affinity of n-Si (Har-Lavan et al., 2012). Using Equation 3.3 the W_{Gr} in our sample was determined as 4.83 eV, which is higher than the one reported in the literature (Giovannetti et al., 2008).

3.3. Optoelectronic Characterization

3.3.1. I-V measurements under light illumination

The I-V measurements of our sample were conducted under the influence of 905 nm wavelength light with different powers ranging between 2 - 20 μ W. And the obtained results were plotted in the semi-logarithmic scale in Figure 3.5.



Figure 3.5. Voltage vs. In I plot under 905 nm light illumination.

For each of the I-V curves shown in Figure 3.5, the voltage read at the minimum current and the current at zero bias correspond to open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}), respectively. As seen in Figure 3.6, although I_{sc} exhibits a clear linear

responce to the incident light, V_{oc} increases non-linearity and converges to a saturation level above 0.12 V as the light power exceeds 20 μ W. The non-linear behaviour of V_{oc} is typical for the photodiodes operating in photovoltaic mode and can be explained in terms of the Schockley model written as Equation 3.4,

$$V_{oc} \approx \eta \frac{kT}{e} \ln \left(\frac{I_p}{I_0} + 1 \right) \approx \eta \frac{kT}{e} \ln \left(\frac{I_p}{I_0} \right)$$
(3.4)

where η , T, k, e, I_p and I_0 are ideality factor, temperature, Boltzmann constant (1.38×10⁻²³ m²kgs⁻²K⁻¹), elementary charge (1.602×10⁻¹⁹C), photocurrent and the saturation current, respectively. From the slope of I_{sc} - P line, the spectral response of our sample was determined to be 0.41 A W⁻¹ at 905 nm wavelength light. The wavelength dependent spectral response of our sample is discussed in the next section.



Figure 3.6. Power dependent V_{oc} and I_{sc} plots.

3.3.2. Spectral Response measurements

The spectral response or photoresponsivity (R) is one of the most important parameters for the light detection limit of a photodiode and can be determined using Equation 3.5,

$$R(\lambda) = \frac{I_p - I_d}{P(\lambda)}$$
(3.5)

where I_p , I_d and $P(\lambda)$ are photocurrent, dark current and incident light power, respectively. The R of our sample were measured at zero-bias (V_b = 0 V) as a function of the λ of incident light varied in the spectral range between 550 and 1050 nm and the obtained results are plotted in Figure 3.7.



Figure 3.7. The spectral response of Gr/n-Si photodiode. Maximum spectral response was found at 905 nm as indicated with the dashed line.

The measurements showed that the maximum R of the photodiode appearing at the peak wavelength of 905 nm is 0.46 A W⁻¹. The spectral response of our sample is consistent with those single layer Gr/n-Si devices reported in literature. The comparison has been done in Table 3.1. The specific detectivity (D^*) is one of the figures of merit for a photodiode and the capability of a photodiode to detect weak light signals (Zhang et al., 2018) can be written as Equation 3.6,

$$D^* = \frac{A^{\frac{1}{2}}R}{\sqrt{2eI_d}} \tag{3.6}$$

where A is the effective junction area of the photodiode, R is the spectral responsivity at a specific wavelength e is the elementary charge and I_d is the dark current.

Noise equivalent power (NEP) describes the incident power required to obtain a signal to noise ratio of 1 at a bandwidth of 1 Hz. The NEP can be obtained by using the Flicker noise (1/f), shot noise and thermal noise of a device and this gives information about the minimum detectable signal of the photodetector (Aydın et al., 2018; Ni et al., 2017) and can be written as, $NEP = A^{\frac{1}{2}}/D^*$.



Figure 3.8. Wavelength-dependent, D* and NEP plots of our Gr/n-Si photodiode.

Using the spectral response values acquired under light illumination, Wavelength dependent, (D^{*}) and NEP were calculated and the obtained results were plotted as shown in Figure 3.8. (D^{*}) and NEP was calculated as 9.20×10^{12} Jones and 0.42 fW Hz^{-1/2} at peak wavelength of 905 nm, respectively.

3.3.3. Time-dependent Photocurrent Measurements

Laser-induced charge carrier formation and the consequent separation of these charges at the graphene-semiconductor interface result in photocurrent creation. When light is incident to the interface between graphene and the semiconductor, the photoexcited electron-hole pairs are formed and accelerated in the reverse direction by the internal electric field (Liu et al., 2017). Thereby an observable photocurrent is generated. This photocurrent can be measured in different ways. In this section, time-dependent photoresponse of the photodetector by on/off switching under zero-bias was measured. Normalized time-dependent photo-response of our Gr/n-Si photodiode under 905 nm wavelength light at a frequency of 5 kHz and room temperature (300 K) was plotted in Figure 3.9. Time-dependent photo-response of our sample by on/off switching were shown at large (Figure 3.9) and zoom (Figure 3.10) scales. The rise time (t_r) is defined as the range that



Figure 3.9. Large scale on-off measurement of Gr/n-Si photodiode. The measured photocurrents were normalized with the maximum values.

photocurrent rises from 10 % to 90 % of its maximum and, the decay time (t_d) is defined similarly. From the obtained transient photocurrent measurement data, the t_r of our sample was determined to be 13.3 μ s and the t_d was measured as 20.5 μ s. In (Li et al., 2016)' work t_r and t_d are were reported as 0.32 ms and 0.75 ms, respectively. In order to determine the performance of our Gr/n-Si photodiode, all the obtained photodiode parameters were compared with those of reported in literature. The comparison was summarized in Table 3.1.



Figure 3.10. Zoom scale on-off measurement. The measured photocurrents were normalized with the maximum values.

R	Φ_B	W_{Gr}	η	t _r	t_d	Reference	
$(A W^{-1})$	(eV)	(eV)		(µs)	(μs)		
0.46	0.78	4.83	1.25	13.3	20.5	this work	
0.51	0.76	4.81	-	130	135	(Periyanagounder et al., 2018)	
$1.8 imes 10^{-4}$	-	-	-	$3 imes 10^5$	17×10^5	(Sun et al., 2012)	
0.029	-	-	-	~ 100	~ 100	(Lv et al., 2013)	
0.43	0.80	4.85	-	1200	3000	(An et al., 2013)	
-	0.44	4.49	1.87	-	-	(Kalita et al., 2013)	
_	0.83	4.88	2.53	-	-	(Parui et al., 2014)	

Table 3.1. Comparison of our Gr/n-Si and the other Gr/n-Si photodiodes' electronic and optoelectronic properties.

CHAPTER 4

THE EFFECT OF ADSORBATES ON THE RECTIFICATION OF GRAPHENE/SILICON HETEROJUNCTION

4.1. Comparison of the Electronic Properties of Graphene/n-Si Photodiode Before and After UV illumination

Electronic measurements of the fabricated Gr/n-Si Schottky photodiode was done at the reverse and forward bias (voltage range is -0.25 and 0.25 V) in dark ambient under a vacuum level of 5×10^{-5} mbar before and after ultraviolet (BUV and AUV) light illumination. The UV irradiation wavelength was specifically selected to be 254 nm since it is energetically sufficient enough to remove the adsorbates such as O₂ and H₂O from the graphene layer. It should be mentioned that the dark current of our device was determined as 1.20 nA in Chapter 3. AUV light illumination, the dark current value decreased to 1.04 nA. Accordingly, the Schottky barrier height decreased from 0.78 eV to 0.71 eV. The ideality factor also increased from 1.25 to 1.39. I-V measurements and semi-logarithmic I-V measurements of the fabricated Gr/n-Si Schottky photodiode before and after UV illumination was shown in Figure 4.1 (a) and (b). In addition, Figure 4.1 (c) and (d) shows Current vs. dV/dIn(I) and Current vs. H(I) plots before UV (BUV) illumination, respectively. Figure 4.1 (e) and (f) shows Current vs. dV/dIn(I) and Current vs. H(I) plots.



Figure 4.1. (a) I-V curves of the fabricated Gr/n-Si photodiode in dark, measured under high vacuum before and after UV light illumination. (b) The semilogarithmic scale I-V curves of the photodetector which were used to extract the ideality factors and the zero-bias Schottky barrier heights BUV and AUV illumination. (c) Current vs. dV/dIn(I) plot and (d) Current vs. H(I) plot BUV illumination. (e) Current vs. dV/dIn(I) plot and (f) Current vs. H(I) plot AUV illumination.

4.2. Optoelectronic Properties of Graphene/n-Si Photodiode Before and After UV illumination

4.2.1. I-V measurements under light illumination

In addition to the ambient conditions in the Chapter 3, I-V measurements of our sample were conducted under the vacuum level of 5×10^{-5} mbar and 15 min. UV illumination and the obtained results were plotted in Figure 4.2. For each of the I-V curves, V_{oc} and I_{sc} are plotted and shown in Figure 4.3 (a) and (b). From the slope of I_{sc} - P line the spectral response of our device was determined as 0.36 A W⁻¹ at 905 nm light AUV illumination.



Figure 4.2. Voltage vs. In I plot under 905 nm wavelength light, AUV illumination and 5×10^{-5} of vacuum level.



Figure 4.3. Power-dependent (a) V_{oc} and (b) I_{sc} plots for each of the I-V curves BUV and AUV illumination.

(a)

4.2.2. Spectral Response Measurements

The R of our sample was also measured before and after UV light illumination at zero-bias ($V_b = 0$ V) as a function of the λ of incident light varied in the spectral range between 550 and 1050 nm and the obtained results are plotted in Figure 4.4. The measurements showed that the maximum R of the sample appearing at the peak wavelength of 905 nm is decreased from 0.46 A W⁻¹ to 0.39 A W⁻¹ after UV illumination. The calculations showed that W_{Gr} reduced from 4.83 eV to 4.76 eV AUV light illumination.



Figure 4.4. Wavelength resolved spectral response of the Gr/n-Si photodiode measured at zero-bias ($V_b = 0$ V) BUV and AUV illumination. The maximum spectral response of the sample observed at 905 nm wavelength.

The D * and NEP values were plotted using the R values shown in Figure 4.5 (a) and (b), respectively. The calculations showed that the detection limit of the Gr/n-Si photodiode is reduced from 9.2×10^{12} Jones to 3.1×10^{12} Jones AUV light illumination. At the same time, the calculations showed that the NEP value of Gr/n-Si photodiode is increased from 0.42 to 0.46 fW Hz^{-1/2} at 905 nm light AUV light illumination.



Figure 4.5. Wavelength-dependent (a) D* and (b) NEP plots of our Gr/n-Si photodiode BUV and AUV illumination.

4.2.3. Time-dependent Photocurrent Measurements

Time-dependent photo-response of the our Gr/n-Si photodiode by on/off switching under zero-bias was also measured at a frequency of 5 kHz under a vacuum level of 5×10^{-5} mbar and room temperature (300 K). Time-dependent photo-response of our sample by on/off switching AUV at large scale were shown in Figure 4.6. In addition, normalized time-dependent photo-response of our Gr/n-Si photodiode under 905 nm wavelength light were compared in Figure 4.7 for before and after UV light illumination. t_r was defined as the range that photocurrent rises from 10 % to 90 % of its maximum and t_d was defined similarly. From the obtained transient photocurrent measurement data, t_r values of our sample are determined to be 13.3 μ s and 19.7 μ s before and after UV illumination, respectively. In addition, t_d values of our sample are measured as 20.5 μ s and 22.1 μ s before and after UV illumination, respectively. These results show that the response speed of Gr/n-Si photodidode is higher (lower) before (after) removing the adsorbates from graphene electrode.



Figure 4.6. Large scale on-off measurement of Gr/n-Si photodiode AUV illumination. The measured photocurrents were normalized with the maximum values.



Figure 4.7. Transient photocurrent spectroscopy of Gr/n-Si photodetector BUV and AUV illumination. The measurements were acquired at zero-bias ($V_b = 0$ V) and under 905 nm wavelength light. The measured photocurrents were normalized with the maximum values.

4.3. Impact of Adsorbates on Characteristics of Graphene/n-Si Photodiode

The illustrations in Figure 4.8 display the adsorption/desorption induced modification in the charge carrier dynamics of our sample and give an insight into the effect of charge transfer between the adsorbates and graphene electrode on the rectification character of the Gr/n-Si heterojunction. It is known from the literature that graphene grown by CVD has strong p-type conductivity due to unintentional hole doping with chemicals used in the growth and transfer processes (Melios et al., 2018; Suk et al., 2013). When graphene and n-Si get in contact, a Schottky junction with a depletion region and Φ_B are formed at the Gr/n-Si interface due to the difference between the Fermi levels of graphene and of Si. The electrons in n-Si are injected to graphene electrode until the Fermi level of graphene aligns with that of Si across the junction and thermodynamic equilibrium is established. However, when the molecules such as O₂ and H₂O are adsorbed on the graphene electrode, they behave like electron trapping surface states and lead to a hole doping as schematically depicted in Figure 4.8 (a) (Di Bartolomeo et al., 2015). Upon UV light illumination, the adsorbates are desorbed into the vacuum and the electrons trapped by these adsorbates are released back to the graphene electrode (Figure 4.8 (b)). Electrons injected to graphene decrease the hole carrier density and therefore shift its Fermi level towards lower energy levels close to the Dirac point (K) as displayed in Figure 4.8 (d). Such a shift in graphene's Fermi level (E_F^{Gr}) decreases the W_{Gr} and hence the zero-bias Φ_B of Gr/n-Si heterojunction. As a consequence of low Φ_B the built-in potential and the effective electric field at the heterojunction are reduced as well. These changes in the Gr/n-Si heterojunction partially hinder the efficient separation of photo-generated charge carriers in the depletion region and thus lower both the photocurrent and spectral response of the device under light illumination.



Figure 4.8. (a) and (b) schematic illustrations of the cross-sectional side views of the Gr/n-Si photodetector depicting the UV driven desorption of atmospheric adsorbates from graphene electrode into vacuum and corresponding charge transfer process. Schematic illustrations of the energy band diagram for the Gr/n-Si heterojunction (c) BUV and (d) AUV illumination. The photodiode characteristics of our sample were compared in Table 4.1 for before and after UV treatment.

	Φ_B	R	D *	NEP	\mathbf{t}_r	\mathfrak{t}_d
	(eV)	$(A W^{-1})$	$(10^{12} \times \text{Jones})$	$(fW Hz^{-1/2})$	(μs)	(µs)
BUV	0.78	0.46	9.2	0.42	13.3	20.5
AUV	0.71	0.39	3.1	0.46	19.7	22.1

Table 4.1. The performances of the Gr/n-Si photodiode BUV and AUV illumination.

CHAPTER 5

CONCLUSION

In this thesis, in the first part of the experiments, Gr/n-Si Schottky barrier photodiode was fabricated and its electronic/optoelectronic properties were investigated. Maximum spectral response, ideality factor, NEP, specific detectivity, Schottky barrier height, rise time and decay time of Gr/n-Si Schottky barrier photodiode were found as 0.46 A W^{-1} , 1.25, 0.42 fW Hz^{-1/2}, 9.2 10¹² × Jones, 0.78 eV, 13.3 μ s and 20.5 μ s, respectively. Also, the work function of graphene was calculated as 4.83 eV.

Subsequently, electronic and optoelectronic properties of Gr/n-Si Schottky barrier photodiode were investigated in-vacuum after 15 minutes of UV illumination. Maximum spectral response, ideality factor, NEP, specific detectivity, Schottky barrier height, rise time and decay time of Gr/n-Si Schottky barrier photodiode were found as 0.39 A W⁻¹, 1.39, 0.46 fW Hz^{-1/2}, 3.1 10¹² × Jones, 0.71 eV, 19.7 μ s and 22.1 μ s, respectively. Also, the work function of graphene was calculated as 4.76 eV.

Consequently, we have experimentally investigated the impact of atmospheric adsorbates on the electronic and optoelectronic properties of Gr/n-Si Schottky barrier photodiodes. In-vacuum optoelectronic measurements showed that the adsorbates stuck on graphene electrode in air lead to hole doping as they trap the free electrons in graphene layer. Adsorbate induced hole doping shifts the Fermi level of graphene towards higher energy levels away from its Dirac point and therefore increases the zero-bias Schottky barrier height and the built-in potential at the Gr/n-Si heterojunction. As a consequence, both the electronic and optoelectronic properties of the Gr/n-Si photodiode are improved. The obtained results presented in this study can be used to interpret the adsorbate induced variations in the photo-response characteristics of the heterojunctions of graphene and other 2D materials with different semiconductors.

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