

UC Riverside

UC Riverside Electronic Theses and Dissertations

Title

2D-Material-Based Vertical Optoelectronics

Permalink

<https://escholarship.org/uc/item/5x120492>

Author

Deng, Siyu

Publication Date

2016

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA
RIVERSIDE

2D-Material-Based Vertical Optoelectronics

A Thesis submitted in partial satisfaction
of the requirements for the degree of

Master of Science

in

Electrical Engineering

by

Siyu Deng

December 2016

Thesis Committee:

Professor Ming Liu, Chairperson

Professor Nanpeng Yu

Professor Gang Chen

Copyright by
Siyu Deng
2016

The Thesis of Siyu Deng is approved:

Committee Chairperson

University of California, Riverside

Acknowledgments

I want to thank Yangzhi Zhu for fabricating silver nanowires for this work. And I am grateful for productive discussions with Xuezhi Ma and his idea for the PMMA barrier. I also want to thank Qiushi Liu for his help with gold plating process and Mingguang Chen for helpful advice about graphene transfer. Most of all, I would like to express my most sincere gratitude and appreciation for Dr. Ming Liu.

To my parents,

I want to thank you for full support of me pursuing my academic dream.

ABSTRACT OF THE THESIS

2D-Material-Based Vertical Optoelectronics

by

Siyu Deng

Master of Science, Graduate Program in Electrical Engineering
University of California, Riverside, December 2016
Professor Ming Liu, Chairperson

Since graphene has been a popular topic in recent years, we decide to explore its function as a high-efficiency photodetector. As reported, the vertical devices have much stronger ability in photon harvesting than lateral devices [1][2][3][4][5], we choose to make vertical devices. What is new in our design is that we use Ag Nanowires network as one electrode. Ag Nanowires not only can be used as one transparent electrode but also can enhance graphene's absorption of light.

Contents

List of Figures	viii
1 Basic Theories	1
1.1 Photoelectric Effect	1
1.2 Graphene	6
1.3 Plasmon	13
1.4 Device	15
2 Device Fabrication	17
2.1 Graphene	17
2.2 Silver nanowire	21
3 Measurements and Conclusions	24
3.1 Illustration and Conclusion	24
Bibliography	28

List of Figures

1.1	Photoelectric effect	2
1.2	Photoelectric effect with closed circuit	4
1.3	Light current's relationship with light intensity	5
1.4	Graphene Structure	6
1.5	Quote from "BASIC PHOTOPHYSICS"[6]	7
1.6	graphene's band diagram quote from "2D materials: to graphene and beyond" [7]	7
1.7	Band structures of metal and insulator	8
1.8	Band structure of graphene	10
1.9	Device illustration	15
1.10	Silver nanowire mesh on glass	16
2.1	"Schematic of a common setup for chemical vapor deposition of graphene." quote from "Synthesis and biomedical applications of graphene: present and future trends" [8]	17
2.2	Target substrate with a piece of graphene with polymer	19
2.3	Graphene on target substrate	20
2.4	Silver nanowire mesh under 20X microscope	21
2.5	Silver nanowire mesh on glass	22
2.6	PMMA barrier separates the area with and without silver nanowire mesh	23
3.1	Theoretical design and real device	25
3.2	Schematic illustration of the device	26
3.3	Result 1	26
3.4	Result 2	27

Chapter 1

Basic Theories

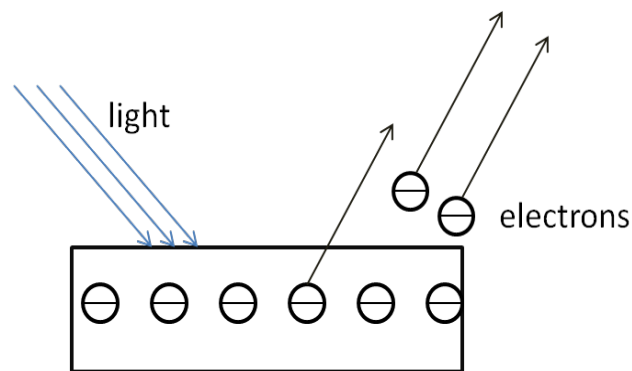
1.1 Photoelectric Effect

In 1887, Heinrich Hertz[9]first noticed the phenomenon that using ultraviolet light illuminated electrodes could create electric sparks more efficiently. In 1905, Albert Einstein correctly explained this phenomenon, photoelectric effect, by quantizing light energy. Albert's theory was quite new at that moment and caused the revolution in quantum theory later. In 1914, Robert Millikan's experiment agreed with Einstein's explanation of the photoelectric effect. In 1921, Albert Einstein was awarded the Nobel Prize in Physics "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect",[10]and in 1923 Millikan was awarded the Nobel Prize for "his work on the elementary charge of electricity and on the photoelectric effect".[11]

One easy way to explain the photoelectric effect is that when the light illuminates the surface of matter, some electrons in the matter will emit from the matter.

According to the corpuscular theory of light, light consists of many photons with discrete energy packages. When one photon hits the surface of a light-sensitive

metal, the photon's energy can be fully absorbed by one electron in the metal. After the electron absorbed the photon's energy, the electron's kinetic energy will increase instantly. If the electron's kinetic energy becomes bigger enough to overcome the nucleus's attraction to the electron, the electron will emit from the metal's surface within 1 ns (nano-second). And this kind of electrons is called photoelectrons which form the photocurrent.



Photoelectric effect

Figure 1.1: Photoelectric effect

The wave property of light is contradictory to the experimental fact. According to the wave property of light, if the incident light carries only a small amount of energy, you will need to shine the metal longer to let the electrons gather enough energy to escape from the surface of the metal, which contradicts to the experimental fact. What's the experimental fact above? The fact is as long as the frequency (f) of the incident light is higher than a certain f_0 , no matter how bright or dim the light intensity is, the photoelectrons will be created instantly within 1ns. So what conditions do we need to meet to let photoelectric effect happen? Only when the wavelength (λ) of the incident light is smaller than a certain wavelength (λ_0), the photoelectric effect could happen.

Or when the incident light frequency $f > f_0$, the photoelectric effect could happen, f_0 is the threshold frequency of the metal. Because the relationship between the wavelength (λ) and frequency (f) is:

$$\lambda = c/f \tag{1.1}$$

c is the speed of light for the equation above. f_0 is determined by the type of metal used. Why is the frequency an important character here? The photons from the light beam have energies proportional to the frequency of the light. According to the Planck–Einstein relation, which associates the photon energy (E) with its wave frequency (f):

$$E = hf \tag{1.2}$$

h is the Planck constant. If one electron within the metal absorbs the energy (E_1) of a photon, and the energy (E_1) is higher than or equal to the work function (Φ) of the metal, then the electron accumulates enough energy, and will escape from the metal, becoming an photoelectron; while if the energy (E_1) is smaller than the work function (Φ) of the metal, then the electron will become a hot electron, interact with other electrons and generate heat. The hot electrons can not escape from the metal.

If you increase the light intensity of the incident light, in the same period, you will excite more electrons. But each excited electron will not gain more energy. In another way, photoelectron's energy has no relationship with light intensity. And one electron must absorb all of the photon's energy (E_1) to use it to overcome the work function (Φ). Otherwise, the energy (E_1) will be released. If the energy (E_1) is bigger than the work function (Φ), then energy (E_2 , where $E_2 = E_1 - \Phi$) will be the electron's kinetic energy after it escaped from the metal.

Work function (Φ) is the minimum κ electron need to become a photoelectron.

Work function (Φ)'s relationship with threshold frequency(f_0) is:

$$\Phi = hf_0 \quad (1.3)$$

After escaped from the metal, the photoelectron's kinetic energy (E_2) is:

$$\kappa = E_2 = hf - \Phi = h(f - f_0) \quad (1.4)$$

In physics, κ must be positive. Thus, the frequency (f) of incident light must be bigger or equal to threshold frequency (f_0), only when the photoelectric effect could happen.

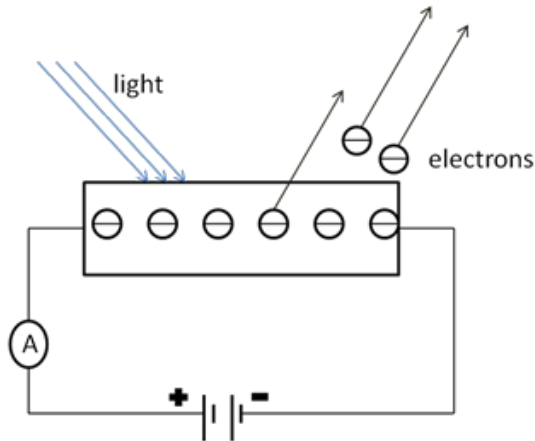


Figure 1.2: Photoelectric effect with closed circuit

As we discussed above, as long as the incident light's frequency (f) is bigger than threshold frequency (f_0), the metal which is being illuminating will have many photoelectrons on its surface instantly, which is the photoelectric effect. When we add one closed circuit and one power source to the metal, the emitted photoelectrons will all move to the anode and form the photocurrent. When remains the light intensity a constant, increase the voltage between anode and cathode will increase the photoelectrons kinetic energy, the photocurrent will become bigger. But the photocurrent is limited by the intensity of the light. The photocurrent has a maximum value which is called

saturation current. Thus, with incident light intensity increasing, the photocurrent will be increasing.[12]

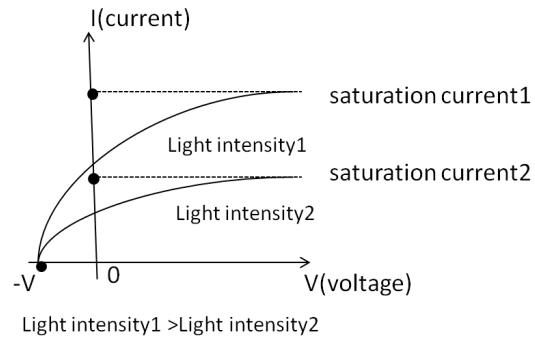


Figure 1.3: Light current's relationship with light intensity

In the end, I want to express my respect and thanks to all the scientists who have devoted their time to photoelectric effect!

1.2 Graphene

Decades ago, scientists got the idea and theory about graphene. But the theory has been developing at a quite slow pace. Until 1962, graphene was first-time observed by scientists under electron microscopes. After approximately 4 decades, in 2004, two talented scientists, Andre Geim and Konstantin Novoselov, in England successfully fabricated and characterized graphene at the University of Manchester.[13] Their success was supported by existing theoretical explanation about graphene's composition, structure, and properties. It was a huge surprise to know that graphene is so easy to fabricate which drew considerable attention to graphene from all researchers around the world. In 2010, Andre Geim and Konstantin Novoselov were awarded Nobel Prize in Physics "for groundbreaking experiments regarding the two-dimensional material graphene." [14]

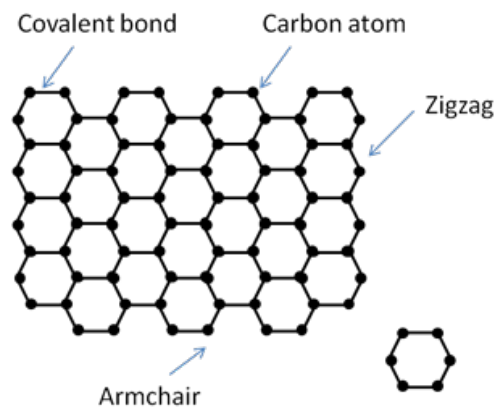


Figure 1.4: Graphene Structure

Graphene is a kind of membrane which formed by sp^2 hybridized carbon atoms which are in the form of the honey-comb lattice. Graphene is a one-atom-thick 2D (two-dimensional) material; its thickness is about 0.335nm. Graphene is also basic structural of all carbon crystals other than diamond, including zero-dimensional Fullerene, one-dimensional carbon nanotube, graphite.

What makes graphene so different? For semiconductors, the point we care the most is the Γ point of a semiconductor. Because at Γ point, conduction band and valence band have the closest distance which is a semiconductor's bandgap. A bandgap determines important properties of semiconductors.

Material	Symbol	Band gap (eV) @ 300K
Silicon	Si	1.11
Selenium	Se	1.74
Germanium	Ge	0.67
Silicon carbide	SiC	2.86
Aluminum phosphide	AlP	2.45
Aluminum arsenide	AlAs	2.16
Aluminum antimonide	AlSb	1.6
Aluminum nitride	AlN	6.3
Diamond	C	5.5
Gallium(III) phosphide	GaP	2.26
Gallium(III) arsenide	GaAs	1.43
Gallium(III) nitride	GaN	3.4
Gallium(III) sulfide	GaS	2.5

Figure 1.5: Quote from “BASIC PHOTOPHYSICS” [6]

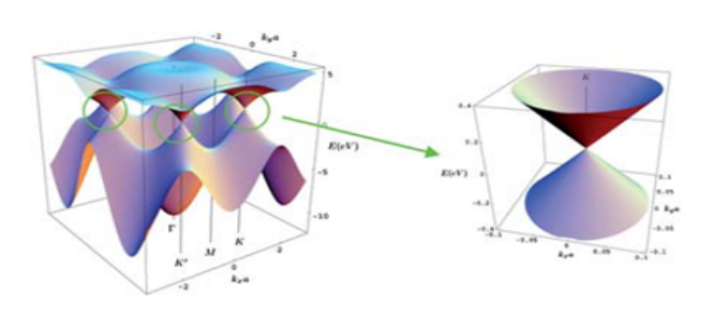


Figure 1.6: graphene's band diagram quote from “2D materials: to graphene and beyond” [7]

Fig.1.5 are the bandgap of some most common semiconductors. Graphene is so unique that it doesn't have a bandgap. Because graphene's conduction band and valence band meet at the Dirac points which showed at Fig.1.6. [15] So graphene's properties are quite new and different from traditional materials.

To understand the Fig.1.7, we need to know Fermi level. Fermi level is the total chemical potential for electrons.[16] At the band structure view, electrons are assumed occupying a series of energy bands which consists of single-particle energy eigenstates ϵ ; the Fermi level is explained as an energy level of an electron. This energy level has a 50% probability to be occupied at thermodynamic equilibrium. Fermi level largely determines the matter's electrical properties.

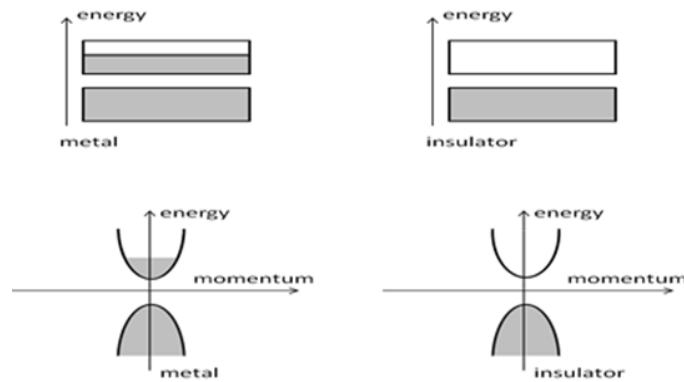


Figure 1.7: Band structures of metal and insulator

At thermodynamic equilibrium, the probability that a state with energy ϵ occupied by an electron is given by the Fermi-Dirac distribution:

$$f(\epsilon) = \frac{1}{e^{\frac{\epsilon-\mu}{kT}} + 1} \quad (1.5)$$

k is Boltzmann's constant, and T is the temperature. If $f(\epsilon)$ is one, that means the state is occupied by electrons; if $f(\epsilon)$ is zero, that means the state is not occupied with electrons, in other words, the state is empty. The value of μ depends on the characteristic of materials. In another explanation, the states below the Fermi level are all filled with electrons. When the electrons in the states absorb energy, they will excite to higher energy states. Higher energy states are far from the nucleus, so electrons in the high energy states are affected less by strong attraction force from the nucleus. Thus, the electrons

in high energy states are easier to be affected by other forces comparing to the electrons in lower energy states, so they are more “active.”

For metals, μ lies in a delocalized band. At Fig.1.7, μ lies in the conduction band. Thus, they have no bandgap. There have many states in conduction band filled with “active” electrons. Electrons can move freely within them under external forces. When applying external voltage, electrons within will all move to one direction and form current. That is why metals also called conductors. For insulators, μ lies in the conduction band as shown in Fig.1.7, all the states below Fermi level are low energy states. Electrons in these states are affected by strong attraction force from the nucleus. So when we apply external forces, the electrons hardly can be affected. And insulator’s bandgap is very big; it takes pretty high energy to active electrons from valence band to conduction band. So, electrons in insulators can not move freely under external forces. When we apply external forces, insulators will not show too many differences. That is why insulators are bad conductors.

So what about graphene? Graphene’s band structure is quite different from other materials. Graphene’s conduction band and valence band meet at the Dirac points. One exciting thing for us is that graphene’s bandgap is tunable. As we know, different bandgap gives materials different properties. So it is quite important and interesting that one material’s bandgap can be tuned. If we mastered tuning graphene’s bandgap, we could use graphene to replace semiconductors in modern electrical devices and produce much more advanced devices. Scientists have been putting a lot of effort into tuning graphene’s bandgap. Now let us discuss the basic theory about tuning graphene’s bandgap. At thermodynamic equilibrium, graphene’s band structure with no doping is shown at the left part of Fig.1.8. We put graphene on a thin insulator membrane which is on a metal substrate and add closed circuit and power source. This structure will

provide electric field we need to tune graphene's bandgap. At the middle part of Fig.1.8, if we apply a positive voltage to graphene, the whole structure will be like a capacitor. As graphene is the anode, more electrons will move to the graphene side; this is like "doping" electrons to graphene. As graphene has more electrons, more states will be filled by electrons.

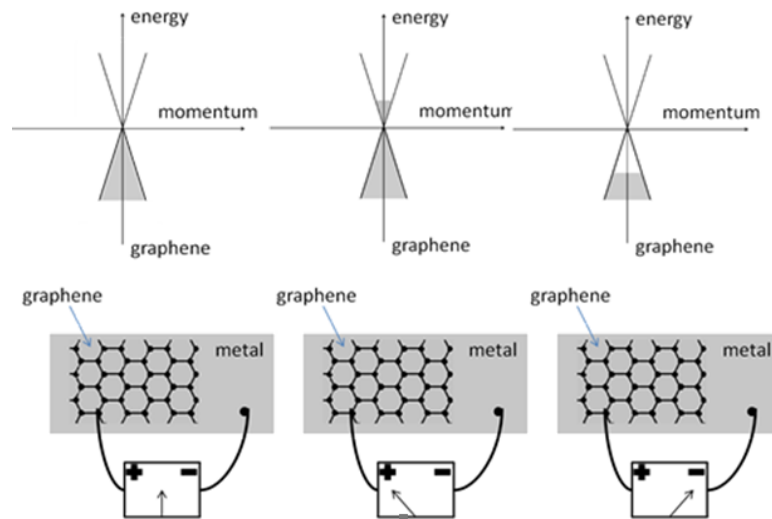


Figure 1.8: Band structure of graphene

It is like the top side cone is being filled up by electrons. So the graphene's Fermi level "goes up" to the conduction band part which means more "active" electrons are in the system. Now, look at the right side of Fig.1.8, if we apply a negative voltage to graphene, the graphene will be the cathode. In the capacitor, more holes will move to the graphene side; this is like "doping" holes to the graphene. As graphene has more holes, fewer states will be filled by electrons. Thus, the graphene's Fermi level "goes down" to the valence part band part, and there will be less "active" electrons in the system. All these only can be done in graphene which makes graphene a high probable alternative of traditional semiconductors. Other than that, graphene has surprisingly high electron mobility even at room temperature; its electron mobility can be larger

than $15000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. [17] In most common semiconductors, holes usually tend to be move slower than electrons, because of the heavier effective mass, but in graphene, the mobility of holes and electrons are very close to each other. Also, the mobility of holes and electrons in graphene affect very little at the temperature from 10K to 100K . [18][19][20] This proves that defect scattering is the dominant scattering mechanism in graphene from 10K to 100K . At room temperature, with a carrier density of 10^{12}cm^{-2} , the mobility of electrons in graphene is limited by graphene's acoustic phonons' scattering which is $200000\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ which are still 10 times of the electrons mobility in copper. [20][21][22] Also, graphene can absorb light from the visible range to infrared plus graphene's fast electron mobility make graphene suitable for very sensitive photodetectors.

Graphene's properties are so interesting and attractive, then how do we get graphene or how do we synthesis graphene? The first method is mechanical exfoliation or called mechanical cleavage. Mechanical exfoliation is use friction between graphene and other materials to get graphene. Graphene got from mechanical exfoliation has fine crystal structure and relative clean from other methods.[23] And this method is easy in theory, but hard to operate. Mechanical exfoliation is the method that Dr. Andre Geim and Konstantin Novoselov used to get graphene. However, this method requires the operators have a lot of experience in doing exfoliation. Even experienced operators have very low yield. Recent years, numbers of industries have put a lot of effort in trying to make mechanical exfoliation industrialize, and some of them have succeeded. They are now using mechanical exfoliation to produce low-cost and high-quality graphene.

The second method is “oxidation-reduction” method. This method needs to use sulfuric acid, nitric acid and so on to combine with potassium permanganate, hydrogen peroxide to oxidize graphite which increases the space in graphite between layer and layer by putting oxide between layer and layer, which gives us graphite oxide. After washing the graphite oxide clean, we need to dry and reduce temperature to get the powder of graphite oxide. Then we use mechanical exfoliation to get graphene oxide. Finally, by using chemical reduction methods, we get graphene. This method is easy to operate, able to have a high yield, but the quality of graphene is relatively low comparing to other methods. Also, this method uses a lot of chemicals which is not environmental friendly. [24] The third method is CVD (Chemical Vapor Deposition). This method is using carbonaceous gas like methane to react with substrates like copper at about 1000 Celsius degree through vapor deposition to get graphene membrane. Chemical vapor deposition is the most effective to produce graphene so far. By using chemical vapor deposition, we can get large-area and high-quality graphene. However, this method is expensive and still need to be perfected. Chemical vapor deposition is the method we chose to fabricate graphene in Dr. Liu’s lab.

1.3 Plasmon

Photons are optical oscillation; phonons are mechanical vibrations and plasmons are plasma oscillation. In the classical view, we can describe plasmons as an oscillation of free electron density. We could use electrostatic shielding to help us understand the concept. If a piece of metal is being put in an electric field. Electrons inside the metal will move to the opposite direction which the electric field points. Until the internal electrical field inside the metal is canceled with the electric field outside the metal. At that moment, we take the metal outside of the electric field, the electrons inside the metal will be only affected by the repulsion force between each other, and attraction force from positive electrical particles. Repeat the process above at the plasma frequency, after a period the energy will be lost because of resistance. Plasmons are a quantization of the oscillation we discussed above.

Plasma was found in 1879 by William Crookes, and in 1928 American scientists Irving Langmuir and Tonks first induced the word plasma into physics. So what is plasma? Plasma is positive and negative ions gas come from atoms, with partial electrons deprived, after ionization. Plasma widely exists in the universe. Plasma exists in the sun, fixed stars and lightning. It takes a percentage of 99% of all the matter existed. And plasma is considered the fourth state of matter other than solid, liquid and gas. Matters consist of molecules, and molecules consist of atoms, and atoms consist of the positive nucleus and negative electrons around the nucleus. When matter is heated to high enough temperature, the electrons around nucleus will overcome the attraction from the nucleus and become free electrons. This process is called ionization. After which, the matter will consist of the positive nucleus and negative free electrons, because of it always close to electric neutrality. This is plasma. Plasma is a kind of good conductor.

Let us talk about surface plasmons next. Surface plasmons are plasmons which are restrained to matters' surfaces. Surface plasmons have the character that they interact with light so strong which will result in a polariton. [25] Surface plasmons' characteristic was discussed in "Surface Plasmons on Smooth and Rough Surfaces and on Gratings" by Raether, Heinz.[26] When we use He-Ne laser generating laser with a wavelength of $632.8nm$, surface plasmons are normally formed by silver or gold, which permittivity's real part is negative, contacts with dielectric like air or silicon dioxide. Surface plasmons always exist at the interface of two different materials, one's permittivity's real part is negative, and its permittivity's absolute value should be less than the other material's permittivity's absolute value which is positive. Otherwise, the light will not be bounded to the surface. Surface plasmons are used in surface-enhanced Raman spectroscopy (SERS). Surface-enhanced Raman spectroscopy is kind of method which can enhance Raman scattering, whose enhancement factor could be surprisingly big to 10¹⁰ to 10¹¹. [27][28][29] Graphene is also kind of material which can have surface plasmons, which was observed by infrared spectroscopy[30] and near-field infrared optical microscopy techniques[31]. With graphene's this character, optical modulators, photodetectors, biosensors could be potential applications of graphene plasmonics.[32] So how do we get surface plasmons at laboratory? When light shines on the surface of metals, the surface plasmons will be created. It can be considered as a connection between photons and electrons. The wavelength of surface plasmons is much lower than the incident light when plasmons spread at the surface of metals. And these plasmons can be processed through the mirror, waveguide, and lens and become optical signal or electrical signal. According to a research group come from Denmark and Switzerland, single nanowire could gather light which gives a light intensity 15 times stronger than normal light intensity.[33]

1.4 Device

This is the design of our device, graphene photodetector. We choose to use the silicon substrate with $300nm$ silicon oxide on it. On the top of silicon oxide, we put a thin layer of $5nm$ chrome, by electron beam physical vapor deposition, to strengthen the gold layer's contact with silicon oxide. On the top of gold layer is mono-layer graphene.

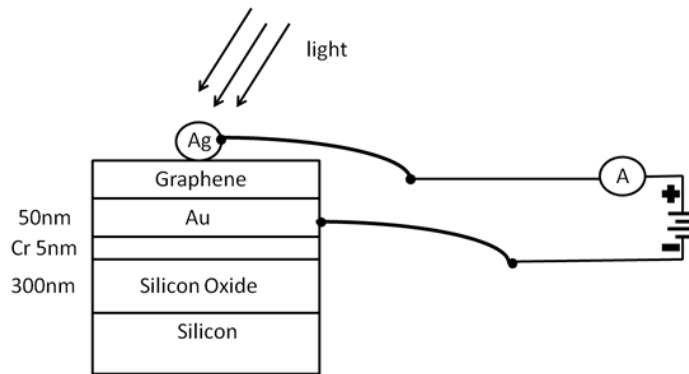


Figure 1.9: Device illustration

And we put silver nanowires onto graphene. Then we will get the metal (silver nanowires)-graphene-metal (gold) structure, which is excellent at light absorption. The silver nanowires we use is about 100 micrometers long and has a radius of $100nm$. In the experiment, we used silver-nanowire mesh instead of single silver nanowire. Because the graphene's area is about $3mm \times 5mm$, it is very big when comparing to silver nanowires. Then we use silver paste to glue copper wires to two electrodes, the gold layer, and the silver nanowire mesh layer. The reason we used silver nanowire mesh as one electrode is that the silver nanowire mesh can be used as a transparent electrode.

As you can see in Figure 10, the silver nanowire mesh has very high light transmittance. The gray dots on the right side of the glass are silver paste dots that we use to connect an ohmmeter to measure the resistance of the silver nanowire mesh.

That is one good part of the silver nanowire mesh transparent electrode. Another part as I mentioned in previous part of the thesis is when light shines on the silver nanowire. Surface plasmons will be created around the silver nanowire surface.

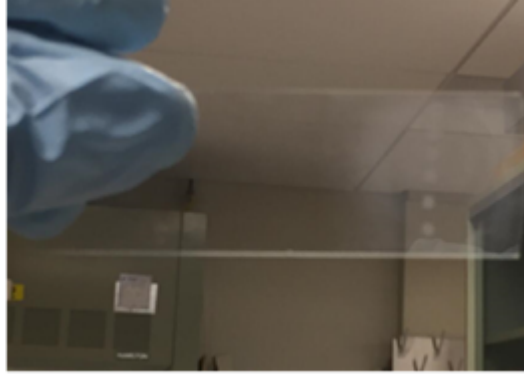


Figure 1.10: Silver nanowire mesh on glass

The surface plasmons will enhance graphene's absorption of light, which is a higher level comparing to traditional metal-graphene-metal photodetectors. Also, the surface plasmons wavelength is much lower than the incident light, which gives the photons higher energy. So the photons have a higher probability to excite the electrons within graphene, which will give more photoelectrons forms higher photocurrent, in other words, a better graphene photodetector.

Chapter 2

Device Fabrication

2.1 Graphene

We use the most common method to fabricate graphene in the laboratory which is chemical vapor deposition (CVD).

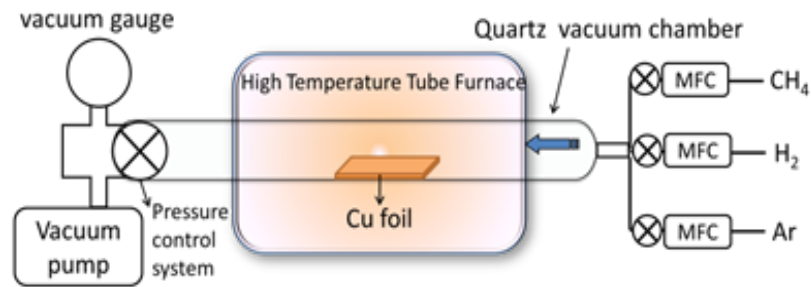


Figure 2.1: “Schematic of a common setup for chemical vapor deposition of graphene.” quote from “Synthesis and biomedical applications of graphene: present and future trends” [8]

The first step is cut copper foil to appropriate area corresponding to the boat which is used to keep the fragile copper foil from bending, or other things may damage the smoothness of the copper foil’s surface. After we got an appropriate area of copper foil, we use a solution mixed with hydrochloric acid, hydrogen peroxide, and water, to

clean the surface of the coil. Then we use water to wash the copper foil for 2 minutes to clean the residues from the solution.

The second step is to put the cleaned copper foil into the chamber of the furnace. And then pump air from the furnace to make the chamber a safe and clean place for the annealing step. After pump air, we let argon and hydrogen gas flow through the chamber at a certain rate while open the furnace and set the heating cycle as 40 minutes heating from room temperature to 1030 Celsius degree. And then is the annealing process which remains the gasses flow and the temperature at 1030 Celsius degree for one hour. After which is the graphene growing process, we let methane flow through the chamber at a certain rate. After one hour we turn off the furnace to let it naturally cool down, until 700 Celsius degree we open cover of the furnace to let the chamber cool down faster. Wait until the temperature decreases to 100 Celsius degrees, we open the furnace and get the copper foil. Both sides of the copper foil have graphene on it. We then watch under the microscope to find the good side of a continuous large area of graphene. This is the last step of growing graphene; we need to transfer graphene to target substrate from copper foil.

The target substrate is silicon with 300nm silicon oxide plating with 5nm chrome and 50nm gold onto the chrome. This process is being done by electron beam physical vapor deposition at UCR's cleanroom.

We want continuous graphene. Otherwise the current will flow through gold to silver nanowire instead of flowing through gold to graphene then silver nanowire, which is the way we want it to be. So a piece of continuous graphene is very crucial to the success of this project.

As the high requirements of the transfer method, I tried many types of transfer method I found in the published papers. Finally, the improved method in "Transfer of

Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes”

helped me at getting the large-area continuous graphene. [34]

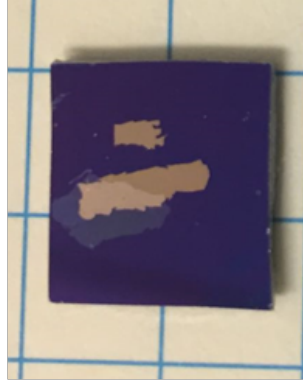


Figure 2.2: Target substrate with a piece of graphene with polymer

As the high requirements of the transfer method, I tried many types of transfer method I found in the published papers. Finally, the improved method in “Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes” helped me at getting the large-area continuous graphene. [34]

The traditional transfer method is first deposited a thin membrane on the good quality graphene side of the copper foil. I used PMMA 4.5 to do the spin coating. And then bake to dry the PMMA. Then I used a plasmonic cleaner to clean the bad quality side graphene. Next, we let PMMA-graphene-copper layer float on a solution mixed with hydrochloric acid, hydrogen peroxide and water to etch the copper away and leave us with the PMMA-graphene layer. To clean the residues come from the chemicals, we use watch glass to change the PMMA-graphene layer in different dishes with clean water for 5 times. Then we put target substrate into the water and slowly moves up until the PMMA-graphene layer lies onto the target substrate. Then we bake the target substrate to strengthen the contact between graphene and target substrate. The last step is to remove PMMA layer by soaking the target substrate into hot acetone for 30

minutes. After which, we finished the traditional transfer process of putting graphene onto the target substrate. However, this old method can hardly give us high-quality graphene, because the transferred graphene is not continuous, and the graphene layer always has big cracks which can not meet the requirements of our experiment. What is new in the paper “Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes” is that before the wash off PMMA process. They will put a second layer of pmma1.5 by drop a droplet and wait until the PMMA naturally becomes dry. The dropped pmma1.5 will dissolve the precoated PMMA. To help better understanding of the reason I quote a sentence from the paper “The redissolution of the PMMA tends to mechanically relax the underlying graphene, leading to a better contact with the substrate.”[34]



Figure 2.3: Graphene on target substrate

Fig.2.3 shows my transfer result. Although the graphene’s surface has some chemical residues, we can see through it; the graphene is perfectly continuous which meets the requirements for graphene for this experiment.

2.2 Silver nanowire

The silver nanowires we use are fabricated by Yangzhi Zhu. The silver nanowires we use are about 100 micrometers long and have a radius of $100nm$.

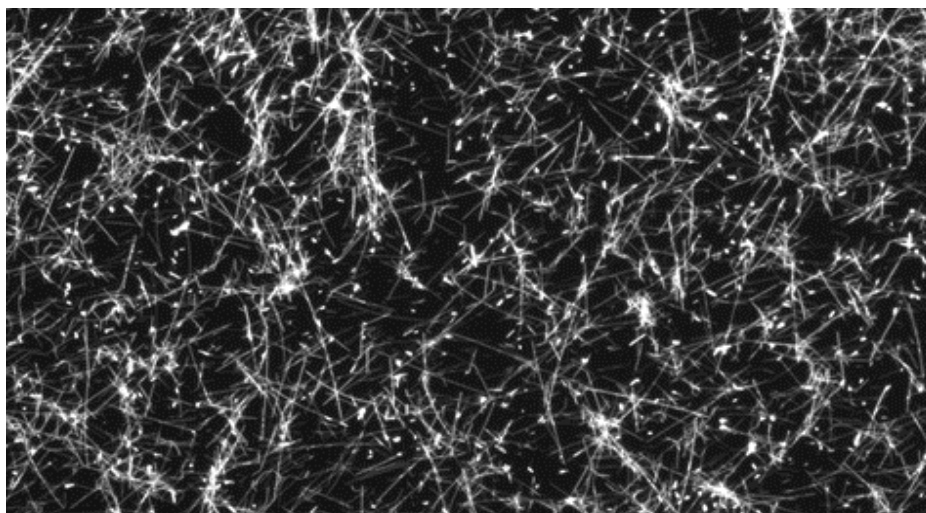


Figure 2.4: Silver nanowire mesh under 20X microscope

At this part, the problem we are facing it is how to put silver nanowire mesh onto graphene without damaging graphene or polluting graphene and make the silver nanowire mesh a perfect transparent electrode. Both silver nano wire and graphene are extremely fragile materials. The formal method to deposit silver nanowire is to spray the solution mixed with ethanol and silver nano wire onto the target substrate.

Yangzhi and I have tried using spray method to deposit silver nanowire for a long time, and we failed. The spraying speed, the distance of target substrate to the nozzle, spray angle, spray directions, and spray time is all variables. We ended either the silver nanowire mesh is too sparse to be conductive, or the silver nanowire mesh is too dense that the light transmissivity is too small that our transparent silver nanowire mesh becomes opaque. Both conditions can not meet the requirement for a transparent electrode. At last, I decided to drop the solution mixed with ethanol and silver nanowire.

I began with low silver nanowire concentration solution and put silver paste(the six gray dots on the glass) on the different depth of color to find out the right concentration solution of the silver nanowire, which can make the silver mesh both transparent and conductive, by measuring its resistance. And make silver nanowire solution's concentration higher each time, trying to find the perfect solution that meets the requirements most closely. In Fig.2.5, the right side of the glass is covered by silver nanowire mesh, which can be distinguished from the depth difference of the color. The silver nanowire mesh in Fig.2.5 is the electrode I found that can meet the transparency and conductive at the same time.



Figure 2.5: Silver nanowire mesh on glass

After solved the above problem, another problem occurred after we deposited the silver nanowire mesh electrode. Because the silver nanowire mesh is dropped on the target substrate, after drops the solution onto the target substrate, the droplet spreads very fast to all directions on the surface of the target substrate, which will connect the two electrodes directly and make the device get shorted. The whole target substrate is about $1\text{cm} \times 1\text{cm}$. So it is extremely hard to control it without damaging another part of the target substrate.

During my discussion with Xuezhi about my project's problem, he came up with a possible solution. It is put a little piece of PDMS onto the substrate which covers partial of the electrode, as the silver nanowire solution spreads easily into the small gap between pads and electrodes, we apply a thin barrier at the edge of PMMA.

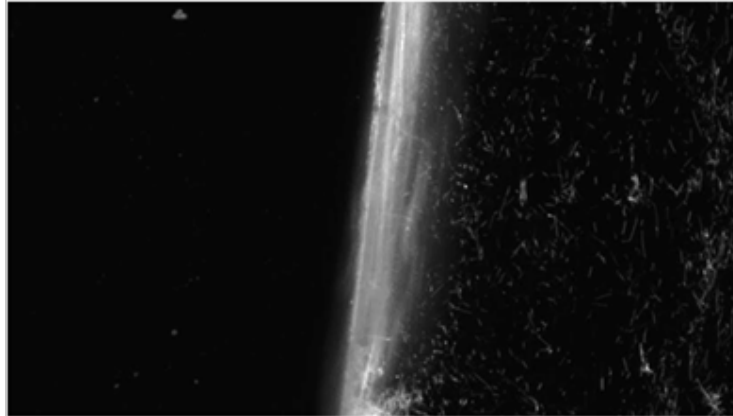


Figure 2.6: PMMA barrier separates the area with and without silver nanowire mesh

After the dropped silver nanowire solution becomes dry, we peel off the PDMS layer. After we had tried it out, it worked, and the problem is solved.

Chapter 3

Measurements and Conclusions

3.1 Illustration and Conclusion

Before the measurement part, it is necessary to briefly illustrate the whole device again. The silicon substrate with $300nm$ silicon oxide on it looks purple. The two rectangles are two golden electrodes of the device. The bigger one has graphene covered partial of it which looks light blue. And the line in Fig.3.2 which separates the substrate represents the PMMA barrier which divides the substrate into the the left part and right part. The left part is covered with PDMS before spraying the silver nanowire, so the right part is covered with silver nanowire mesh, and the left part has no silver nanowire on it. The two orange lines are the copper wires which connect the device to Keithley to measure the current of the device.

So in this way, the current will flow through the bigger golden electrode first and then go through graphene, after graphene the current goes to the silver nanowire mesh, then the current goes through the smaller golden electrode, or begins with the smaller golden electrodes and go through, silver nanowire mesh, graphene, and the bigger golden electrode. It is exactly the route we want the current to go through.

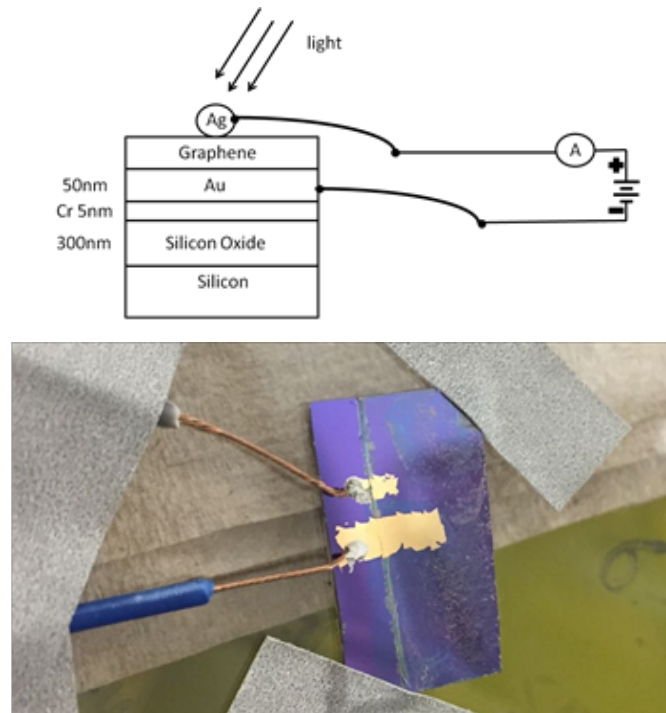


Figure 3.1: Theoretical design and real device

Before measurement, we connect two copper wires from the electrodes to Keithley. And check every connection part to see if the circuit is closed. The resistance between the two electrodes varies in the range from 50Ω to 200Ω , which means the device is functional, and every connection part is in good condition. If the resistance is too high or varies constantly, that is the sign that the copper wire is not glued well to the gold pad by silver paste.

We did the experiment at night, so we can control the light difference by open and turn off the light. In order not to let device affected by the lights from Keithley, we use aluminum foil to cover the whole device when we measure at the dark condition.

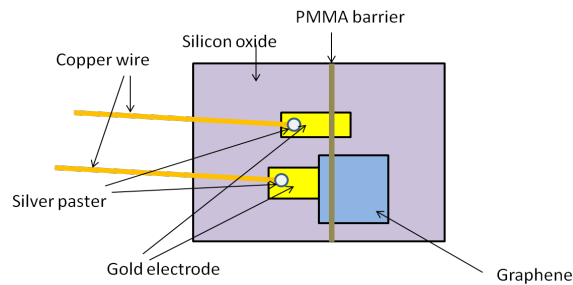


Figure 3.2: Schematic illustration of the device

Because of the effective area on our device, it is much bigger than conventional photodetector. It should be sensitive to the light from the fluorescent lamp, the light intensity in which is much smaller than laser.

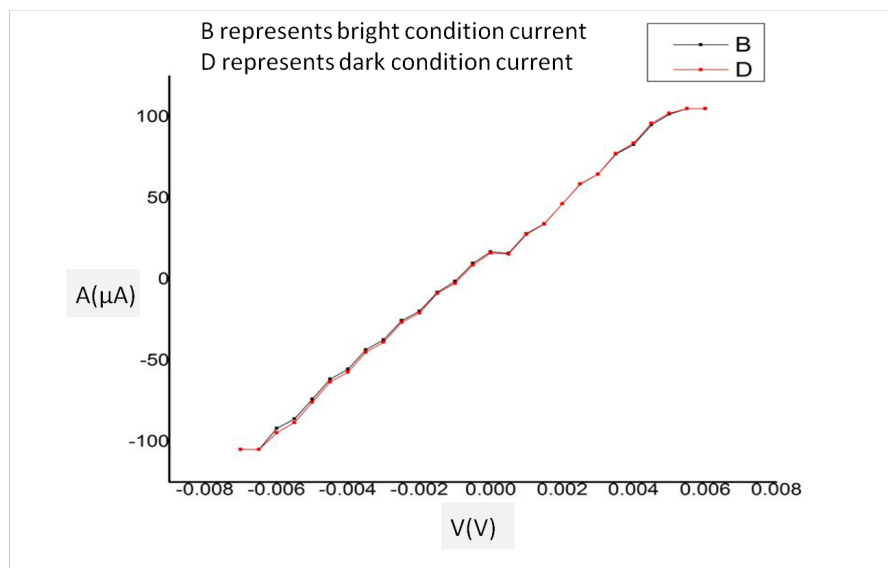


Figure 3.3: Result 1

Due to small differences between each device, devices give different results. In Fig.3.3 and Fig.3.4, the black “B” represents the bright condition with light illuminating;

the red “D” represents dark condition without light illuminating. From the figure, we can get result 2’s dark current and light current has a bigger difference than result 1. But both figures have the same trend which is when the voltage becomes smaller, the difference between light current and dark current becomes bigger; when the voltage becomes bigger, the difference between light current and dark current becomes smaller.

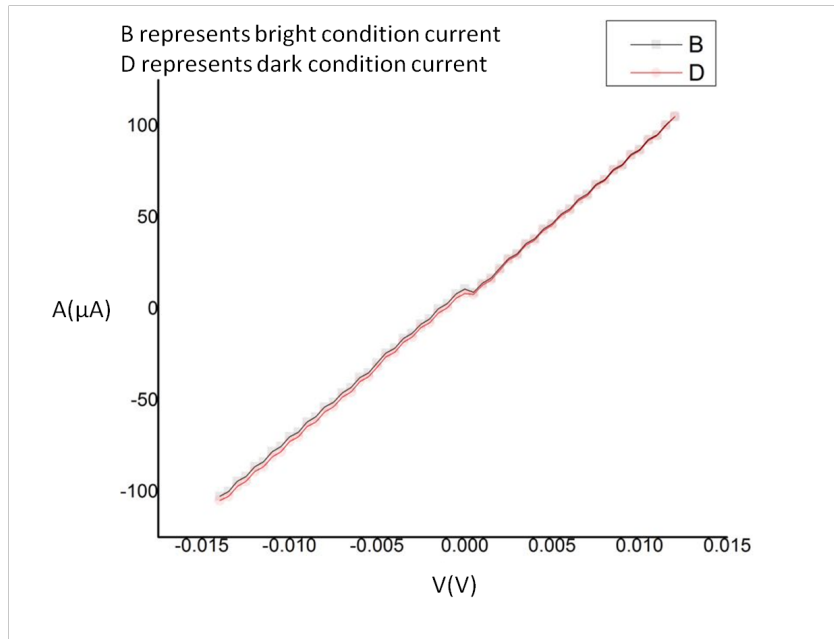


Figure 3.4: Result 2

In summary, we designed a kind of photodetector based on graphene’s features about a large range of light absorption and high electron mobility. And we use silver nanowires as one transparent electrode, which also enhances graphene’s absorption of light, for our vertical optoelectronics. The result we got shows the vertical optoelectronics based on graphene and silver nanowires have great potential to become photodetectors with high sensitivity.

Bibliography

- [1] F. Xia, T. Mueller, Y.-m. Lin, A. Valdes-Garcia, and P. Avouris, “Ultrafast graphene photodetector,” *Nat Nano*, 2009.
- [2] T. Mueller, F. Xia, and P. Avouris, “Graphene photodetectors for high-speed optical communications,” *Nat Photon*, 2010.
- [3] Y. Liu, R. Cheng, L. Liao, H. Zhou, J. Bai, G. Liu, L. Liu, Y. Huang, and X. Duan, “Plasmon resonance enhanced multicolour photodetection by graphene,” *Nature Communications*, 2011.
- [4] T. Echtermeyer, L. Britnell, P. Jasnós, A. Lombardo, R. Gorbachev, A. Grigorenko, A. Geim, A. Ferrari, and K. Novoselov, “Strong plasmonic enhancement of photovoltage in graphene,” *Nature Communications*, 2011.
- [5] D. Sun, G. Aivazian, A. M. Jones, J. S. Ross, W. Yao, D. Cobden, and X. Xu, “Ultrafast hot-carrier-dominated photocurrent in graphene,” *Nat Nano*, 2012.
- [6] A. J. Visser and O. J. Rolinski, “Basic photophysics,” 2014.
- [7] R. Mas-Ballesté, C. Gómez-Navarro, J. Gómez-Herrero, and F. Zamora, “2d materials: to graphene and beyond,” 2010.
- [8] A. Kumar and C. H. Lee, “Synthesis and biomedical applications of graphene: Present and future trends.”
- [9] F. W. Sears, M. W. Zemansky, and H. D. Young, *University Physics*, ser. Addison-Wesley, 1983.
- [10] “The nobel prize in physics 1921,” *Nobel Foundation*.
- [11] “The nobel prize in physics 1923,” *Nobel Foundation*.
- [12] X. Yang, *College Physics*, ser. Huazhong University of Science and Technology press, 2011.
- [13] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” *Science*, 2004.
- [14] “The nobel prize in physics 2010,” *Nobel Foundation*.

- [15] D. R. Cooper, B. D’Anjou, N. Ghattamaneni, B. Harack, M. Hilke, A. Horth, N. Majlis, M. Massicotte, L. Vandsburger, E. Whiteway, and V. Yu, “Experimental review of graphene,” *condensed matter physics*, 2011.
- [16] C. Kittel, *Introduction to Solid State Physics*.
- [17] A. K. Geim and K. S. Novoselov, “The rise of graphene,” *Nat Mater*, 2007.
- [18] A. K. M. S. V. J. D. K. M. I. G. I. V. D. S. V. F. A. A. Novoselov, K. S. and Geim, “Two-dimensional gas of massless dirac fermions in graphene,” *Nature*, 2005.
- [19] S. V. Morozov, K. S. Novoselov, M. I. Katsnelson, F. Schedin, D. C. Elias, J. A. Jaszczak, and A. K. Geim, “Giant intrinsic carrier mobilities in graphene and its bilayer,” *Physical Review Letters*, 2008.
- [20] C. Chen, J. H. and Jang, S. Xiao, M. Ishigami, and M. S. Fuhrer, “Intrinsic and extrinsic performance limits of graphene devices on sio₂,” *Nature Nanotechnology*, 2008.
- [21] N. Akturk, A. and Goldsman, “Electron transport and full-band electron–phonon interactions in graphene,” *Journal of Applied Physics*, 2008.
- [22] F. V. Kusmartsev, W. M. Wu, M. P. Pierpoint, and K. C. Yung, *Application of Graphene within Optoelectronic Devices and Transistors*.
- [23] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, “Fine structure constant defines visual transparency of graphene,” *Science*, 2008.
- [24] R. M. Tromp and J. B. Hannon, “Thermodynamics and kinetics of graphene growth on sic(0001),” *Physical review letters*, 2009.
- [25] S. Zeng, X. Yu, W.-C. Law, Y. Zhang, R. Hu, X.-Q. Dinh, H.-P. Ho, and K.-T. Yong, “Size dependence of au np-enhanced surface plasmon resonance based on differential phase measurement,” *Sensors and Actuators B: Chemical*, 2013.
- [26] H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and Gratings*, 1988.
- [27] E. J. Blackie, E. C. L. Ru, and P. G. Etchegoin, “Single-molecule surface-enhanced raman spectroscopy of nonresonant molecules,” *Journal of the American Chemical Society*, 2009.
- [28] E. C. L. Ru, E. Blackie, M. Meyer, and P. G. Etchegoin, “Surface enhanced raman scattering enhancement factors: A comprehensive study,” *The Journal of Physical Chemistry C*, 2007.
- [29] X. Xu, H. Li, D. Hasan, R. S. Ruoff, A. X. Wang, and D. L. Fan, “Near-field enhanced plasmonic-magnetic bifunctional nanotubes for single cell bioanalysis,” *Advanced Functional Materials*, 2013.
- [30] H. Yan, T. Low, W. Zhu, Y. Wu, M. Freitag, X. Li, F. Guinea, P. Avouris, and F. Xia, “Damping pathways of mid-infrared plasmons in graphene nanostructures,” *Nature Photonics*, 2013.

- [31] Z. Fei, A. S. Rodin, G. O. Andreev, W. Bao, A. S. McLeod, M. Wagner, L. M. Zhang, Z. Zhao, M. Thiemens, G. Dominguez, M. M. Fogler, A. H. C. Neto, C. N. Lau, F. Keilmann, and D. N. Basov, “Gate-tuning of graphene plasmons revealed by infrared nano-imaging,” *Nature*, 2012.
- [32] T. Low and P. Avouris, “Graphene plasmonics for terahertz to mid-infrared applications,” *ACS Nano*, 2014.
- [33] P. Krogstrup, H. I. Jørgensen, M. Heiss, O. Demichel, J. V. Holm, M. Aagesen, J. Nygard, and A. F. i Morral, “Single-nanowire solar cells beyond the shockley-queisser limit,” *Nature Photonics*, 2012.
- [34] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo, and R. S. Ruoff, “Transfer of large-area graphene films for high-performance transparent conductive electrodes,” *Nano letters*, 2009.