DEANSHIP OF GRADUATE STUDIES

AL-QUDS UNIVERSITY

# Molecularly Modified Schottky Diodes with Different Conjugation Degree of Organic Molecules

Tamara Samir Sliman Diek

M.Sc. Thesis

Jerusalem-Palestine 1441 / 2020

# Molecularly Modified Schottky Diodes with Different Conjugation Degree of Organic Molecules

Prepared by: Tamara Samir Sliman Diek

B.Sc. Mathematics (Bethlehem University) (Bethlehem)

Supervisor: Dr: Jamal Ghabboun, Bethlehem University

Co-Supervisor: Dr. Husain Alsamamra, Al-Quds University

A thesis submitted in partial fulfillment of requirements for the degree of master of physics department –Al-Quds University

1441/2020

**Al-Quds University**

**Deanship of Graduate Studies**

**Physics Department**

**Thesis approval**

## Molecularly Modified Schottky Diodes with Different Conjugation Degree of Organic Molecules

**Prepared by: Tamara Samir Sliman Diek**

**Registration No.: 21612583**

**Supervisor: Dr. Jamal Ghabboun, Bethlehem University**

**Co-Supervisor: Dr. Husain Alsamamra, Al-Quds University**

Master thesis submitted and accepted, Date: 2 / 6/2020

The names and signatures of the examining committee members as follows:

Head of Committee: Dr. Jamal Ghabboun Signature:

Co-Supervisor: Dr. Husain Alsamamra Signature:

Internal Examiner: Prof. Musa Abutier Signature:

External Examiner: Dr. Ishaq Musa Signature:

Jerusalem-Palestine 1441 / 2020

# Dedication

Every challenging work needs self-efforts as well as guidance of elders especially those who were very close to our hearts.

My humble effort I dedicate to my sweet and loving

Husband

And

Parents

Whose affection, love, encouragement and prays of day and night make me able to get such success and honor,

Along with all hard working and respected teachers

## Declaration

I certify that this thesis submitted for the degree of master is the result of my own research based on the results found by myself. Materials of works found by other researchers are mentioned by references, except where otherwise acknowledged, and that this thesis, neither in whole nor in part, has been previously submitted for any degree to any other university or institution.

The work was done under the supervision of Dr. Jamal Ghabboun and Dr.Husain Alsamamra

Name: Tamara Samir Sliman Diek

Signed: Tamara

Date: 2 / 6 / 2020

# Acknowledgement

First of all, I am grateful to the Almighty God for establishing me to complete this thesis.

I wish to express my sincere thanks to my supervisor Dr. Jamal Ghabboun who introduced me to the topic, for helping me through all stages of my Master Thesis and for giving me the chance to use all available and purchased equipment and materials in the physics laboratory at Bethlehem University.

I am also very pleased to express my sincere gratitude to my supervisor Dr. Husain Alsamamra for his supervision, guidance and insightful suggestions.

I am also thankful to the employees at the physics and Chemistry laboratories at Bethlehem University in particular Eng. Nader Adawi, Mr. Ahmad Atiyah and Tanas Khoury. Many thanks go to Mrs. Maryam Haroun from the Nano Lab Research Laboratory at Al-Quds University. I am extremely grateful to them for their assistant in using their labs.

I take this opportunity to record my sincere thanks to all the faculty members of the Department of Graduated Studies in Physics for their help and encouragement.

Finally, I am also grateful to my brother Samer for his help, my husband, children, and my family for their unceasing encouragement and support**.**

## **الملخص**

قد تكون الجزيئات الوظيفية والذريّة وحدة البناء الأساسية للأجهزة الإلكترونية المستقبلية. ومع ذلك، يتطلب دمجها في الدوائر تطوير طرق جديدة للتحكم في التداخل بين الجزيئات والأقطاب الكهربائية. في مشروعي، سأجري توصيفًا سطحيًا وكهربائيًا لإظهار أنه يمكن تحقيق تعديل في ارتفاع الحاجز في Schottky Diode باستخدام طبقات جزيئية ثنائية القطب مع درجات مختلفة في الترافق في جهاز معدني / جزيء / أشباه الموصلات. باستخدام الذهب والفضة كمعادن، السيليكون و الغاليوم أرسانايد كأشباه موصلات، PEDOTوحمض السيناميك كجزيئات مترافقة ، و PVA كجزيء غير مترافق.

سيتم مناقشة تأثير التعديل الجزيئي في واجهة جهاز معدني / أشباه الموصلات من خلال تحليل المعاملات مثل ارتفاع الحاجز وعامل المثالية. سيتم وضع الجزيئات على سطح أشباه الموصلات باستخدام جهازspin coating ، متبوعًا بعملية تبخر المعادن لتشكيل Schottky diode. سيتم تنفيذ التوصيف الكهربائي بشكل رئيسي من خلال قياسات الجهد-التيار. علاوة على ذلك ، سيتم تمييز سطح أشباه الموصلات المعدلة جزيئيًا لدراسة الموصلية لجهاز المعدن / الجزيء / أشباه الموصلات على تضاريس الجزيء المترسب على أشباه الموصلات.

تمت دراسة تأثير الجزيئات على الموصلية باستخدام قياسات الجهد-التيار وارتفاع حاجز Schottky diode. بالنسبة لعينات الـ Si-Ag ، خفضت الجزيئات المترافقة وغير المترافقة من الموصلية. أما بالنسبة لـ Si-Au ، زادت الجزيئات المترافقة من الموصلية لكن الجزيء غير المترافق قللت من الموصلية. في حين أن عينات الـ GaAs-Ag، زادت كل من الجزيئات المترافقة وغير المترافقة من الموصلية. و أخيرل بالنسبة لـ GaAs-Au ، قلل الجزيء المترافق من الموصلية لكن الجزيء غير المترافق زاد من الموصلية.

علاوة على ذلك ، تمت دراسة تأثير درجة الحرارة على الموصلية باستخدام قياسات الجهد-التيار. بالنسبة لـ Si-Ag ، فإن زيادة درجة الحرارة زادت من الموصلية. أما بالنسبة لـ Si-cin-Ag ، تؤدي زيادة درجة الحرارة إلى زيادة الموصلية في البداية ثم تبدأ في الانخفاض. في خين أنه بالنسبة لـ Si-PEDOT-Au ، أدت زيادة درجة الحرارة إلى انخفاض الموصلية. بالنسبة لـ Si-PVA-Ag ، أدت زيادة درجة الحرارة إلى زيادة الموصلية في البداية ثم بدأت في الانخفاض. أما بالنسبة لـ GaAs-Ag ، أدت زيادة درجة الحرارة إلى انخفاض الموصلية وأصبح الجهد في التأثير العكسي. بالنسبة لـ GaAs-Au ، أدت زيادة درجة الحرارة إلى زيادة الموصلية في البداية ثم بدأت في الانخفاض وأصبح الجهد في التأثير العكسي. بالنسبة لـ GaAs-cin-Ag ، فإن زيادة درجة الحرارة زادت من الموصلية في البداية ثم بدأت تنخفض وأصبح الجهد في التأثير العكسي. أما بالنسبة لـ GaAs-PVA-Ag ، أدت زيادة درجة الحرارة إلى زيادة الموصلية في البداية ، ثم بدأت في الانخفاض وأصبح الجهد في التأثير العكسي. و أخيرا بالنسبة لـ GaAs-Au ، أدت زيادة درجة الحرارة إلى زيادة الموصلية في البداية ثم بدأت في الانخفاض.

بالإضافة إلى ذلك ، تمت دراسة تأثير زيادة سماكة جزيء حمض السيناميك على Si-cinnamic acid-Ag ، و تبين أن زيادة السماكة في هذه الحالة تزيد من الموصلية.

# Abstract

Functional and atomically precise molecules may be the primary building block of future electronic devises. However, integrating them into circuits requires developing new ways to control the interference between molecules and electrodes. In my project, I will conduct surface and electrical characterization to show that systematic Schottky barrier height modulation can be achieved using dipolar molecular layers with different conjugation degrees in a metal/molecule/semiconductor device. Using Ag and Au as metal, Si and GaAs as semiconductors, PEDOT and cinnamic acid as conjugated molecules, and PVA as non-conjugated molecule.

The effect of molecular modification at the interface of a metal/semiconductor device will be discussed through parameters analysis such as barrier height and ideality factor. Molecules will be deposited on the surface of a semiconductor using spin coating, followed by metal evaporation to form the Schottky diode. Electrical characterization will be mainly carried out through current-voltage measurements. Furthermore, molecularly modified surface of semiconductor will be characterized to study the dependence of the conductivity behavior of the metal/molecule/semiconductor device on the topography of the deposited molecule on the semiconductor**.**

The effect of molecules on the conductivity have been studied using the current-voltage measurements and the Schottky barrier height. For Si-Ag, the conjugated and non-conjugated molecules decreased the conductivity. For Si-Au, conjugated molecules increased the conductivity but the non-conjugated molecule decreased the conductivity. For GaAs-Ag, both conjugated and non-conjugated molecules increased the conductivity. For GaAs-Au, the conjugated molecule decreased the conductivity but the non-conjugated molecule increased the conductivity.

Moreover, the effect of temperature on the conductivity have been studied using the current-voltage measurements. For Si-Ag, increasing the temperature increased the conductivity. For Si-cin-Ag, increasing the temperature increased the conductivity at first then it started to decrease. For the Si-PEDOT-Au, increasing the temperature decreased the conductivity. For the Si-PVA-Ag, increasing the temperature increased the conductivity at first then it started to decrease. For GaAs-Ag, increased the temperature decreased the conductivity and the voltage became in the reverse bias. For the GaAs-Au, increasing the temperature increased the conductivity at first then it started to decrease and the voltage became in the reverse bias. For the GaAs-cin-Ag, increasing the temperature increased the conductivity at first then it started to decrease and the voltage became in the reverse bias. For the GaAs-PVA-Ag, increasing the temperature increased the conductivity at first, then it started to decrease and the voltage became in the reverse bias. For the GaAs-Au, increasing the temperature increased the conductivity at first then it started to decrease.

In addition, the effect of increasing the thickness of cinnamic acid molecule on Si-cinnamic acid-Ag have been studied, and concluded that increasing the thickness in this case increased the conductivity.

**List of contents:**

Acknowledgement ---------------------------------------------------------------------------------------- III

ملخص ------------------------------------------------------------------------------------------------------- VI

Abstract ---------------------------------------------------------------------------------------------------- V

List of abbreviations and symbols --------------------------------------------------------------------- VIII

List of figures ---------------------------------------------------------------------------------------------- X

List of tables ----------------------------------------------------------------------------------------------- XI

Chapter 1: **Introduction ----------------------------------------------------------------------------------- 1**

1.1 Molecular Electronics ------------------------------------------------------------------------------ 1

1.2 Charge Transport in Molecular Junction ------------------------------------------------------- 2

1.3 Uses of Molecular Electronics --------------------------------------------------------------------- 2

1.4 Diodes ------------------------------------------------------------------------------------------------- 3

1.5 PN-Junction ------------------------------------------------------------------------------------------ 4

1.6 Schottky Diodes -------------------------------------------------------------------------------------- 5

1.7 Molecular Schottky Doides ------------------------------------------------------------------------ 11

Chapter 2: **Theory ---------------------------------------------------------------------------------------- 12**

2.1 IV – Characteristics of Schottky Diodes -------------------------------------------------------- 12

2.2 Motion of Electrons through Metal-Molecule-Semiconductor Interference ----------------- 13

2.3 Measurements of current voltage (IV)-Characteristics of Schottky Diodes ------------------ 14

Chapter 3: Experimental: **Modification of Molecular Schottky Diodes with different conjugated degree of organic molecules ------------------------------------------------------------- 15**

3.1 Semiconductor Etching ---------------------------------------------------------------------------- 15

3.2 Spin Coating for Molecular Deposition --------------------------------------------------------- 17

3.3 Metal Deposition ----------------------------------------------------------------------------------- 21

3.4 Current-Voltage Characteristics ----------------------------------------------------------------- 23

Chapter 4: **Result and Discussion ------------------------------------------------------------------- 27**

4.1 IV-Characteristics at Room Temperature ------------------------------------------------------- 27

4.2 IV-effect of temperature on IV-Characteristics ------------------------------------------------ 32

4.3 IV-effect of molecule thickness on IV-Characteristics --------------------------------------- 33

4.4 Barrier height and Ideality Factor results ------------------------------------------------------- 41

Chapter 5: **Conclusion ---------------------------------------------------------------------------- 44**

**References ------------------------------------------------------------------------------------------- 45**

## List of Abbreviations and Symbols

| | |
|---|---|
| IC | Integrated Circuit |
| AC | Alternating Current |
| DC | Direct Current |
| $E_f$ | fermi level |
| $E_{\circ}$ | vacuum level |
| IV | Current-Voltage |
| RF | Radio Frequency |
| SBH | Schottky Barrier Height |
| M-M-S | Metal-Molecule-Semiconductor interference |
| HOMO | Highest Occupied Molecular Orbital |
| LUMO | Lowest Unoccupied Molecular Orbital |
| cin | Cinnamic acid |
| PVA | Poly (vinyl alcohol) |
| PEDOT | Poly (3,4-Ethylenedioxythiophene) |
| I | Current |
| $I_{\circ}$ | reverse saturation current |
| q | Electron charge |
| V | voltage |
| n | Ideality Factor |
| K | Boltzmann constant |
| T | Temperature |
| A | Area of the effective diode |
| A* | effective Richardson constant |
| $\Phi_b$ | Zero bias barrier height |
| $H_2O_2$ | Hydrogen peroxide |
| $Br_2$ | Bromine |

| | |
|---|---|
| $HNO_3$ | Nitric acid |
| NaOCL | Sodium Hypochlorite |
| $NH_4OH$ | Ammonium Hydroxide |
| NaOH | Sodium Hydroxide |
| $H_2SO_4$ | Sulfuric Acid |
| HCl | Hydrogen Chloride |
| HF | Hydrogen Floride |
| $CH_3COOH$ | Acetic Acid |
| Si | Silicon |
| GaAs | Gallium Arsenide |
| $CH_3OH$ | Methanol |
| $H_2O$ | water |

## List of figures

Figure 1.1: Subfield and subarea of molecular electronics ------------------------------------------ 1

Figure 1.2: Tunneling and hopping charge transport in molecular junction ----------------------- 2

Figure 1.3: The current-voltage characteristics of diode -------------------------------------------- 3

Figure 1.4: PN junction diode ---------------------------------------------------------------------- 4

Figure 1.5 a: Effect of applied voltage on a PN junction with forward bias ---------------------- 5

Figure 1.5 b: Effect of applied voltage on a PN junction with reverse bias ----------------------- 5

Figure 1.6: Representation of PN junction diode ------------------------------------------------- 5

Figure 1.7: Schottky diode and Schottky diode symbol -------------------------------------------- 6

Figure 1.8: Energy bands of Schottky diode ------------------------------------------------------- 6

Figure 1.9: Depletoin region in Schottky diode ---------------------------------------------------- 7

Figure 1.10: Band diagram of metal-semiconductor junction at zero bias ------------------------- 8

Figure 1.11: Forward biased Schottky diode ------------------------------------------------------ 9

Figure 1.12: Band diagram of metal-semiconductor junction at forward bias --------------------- 9

Figure 1.13: Reverse biased Schottky diode ------------------------------------------------------ 10

Figure 1.14: Band diagram of metal-semiconductor junction at reverse bias --------------------- 11

Figure 2.1: IV-Characteristics of Schottky diode -------------------------------------------------- 12

Figure 2.2: Energy level diagram of molecular Schottky diode ---------------------------------- 13

Figure 3.1: Si samples ---------------------------------------------------------------------------- 16

Figure 3.2: Si etching ----------------------------------------------------------------------------- 16

Figure 3.3: Stages of spin coating process ------------------------------------------------------- 17

Figure 3.4: Build in spin coater ------------------------------------------------------------------ 19

Figure 3.5: Molecule shape of PEDOT: PSS ------------------------------------------------------ 19

Figure 3.6: molecule shape of cinnamic acid ----------------------------------------------------- 20

Figure 3.7 a: cinnamic acid ---------------------------------------------------------------------- 20

Figure 3.7 b: cinnamic acid dissolved in water --------------------------------------------------- 20

Figure 3.8 a: molecule shape of PVA ------------------------------------------------------------ 21

Figure 3.8 b: PVA -------------------------------------------------------------------------------- 21

Figure 3.9: PVA dissolved in water ------------------------------------------------------------------- 21
Figure 3.10: The thermal evaporator ---------------------------------------------------------------- 22
Figure 3.11: The thermal evaporator during metal deposition process ---------------------------- 22
Figure 3.12: Set up for IV-Characteristics ----------------------------------------------------------- 23
Figure 3.13: During taking the IV-measurements for a sample ------------------------------------ 24
Figure 4.1: IV-curves of M-S interference ------------------------------------------------------------ 27
Figure 4.2: IV-curves of Si-Ag, Si-cin-Ag and Si-PVA-Ag --------------------------------------- 28
Figure 4.3: IV-curves of Si-Au, Si-PEDOT-Au, Si-cin-Au and Si-PVA-Au --------------------- 29
Figure 4.4: IV-curves of GaAs-Ag, GaAs-cin-Ag and GaAs-PVA-Ag --------------------------- 30
Figure 4.5: IV-curves of GaAs-Au, GaAs-cin-Au and GaAs-PVA-Au --------------------------- 31
Figure 4.6: IV-curves of Si-cin-Ag when increasing the molecule thickness -------------------- 32
Figure 4.7: IV-curves of Si-Ag with different temperature ---------------------------------------- 33
Figure 4.8: IV-curves of Si-cin-Ag with different temperature ------------------------------------ 34
Figure 4.9: IV-curves of Si-PEDOT-Au with different temperature ------------------------------ 35
Figure 4.10: IV-curves of Si-PVA-Ag with different temperature -------------------------------- 36
Figure 4.11: IV-curves of GaAs-Ag with different temperature ----------------------------------- 37
Figure 4.12: IV-curves of GaAs-Au with different temperature ----------------------------------- 38
Figure 4.13: IV-curves of GaAs-cin-Ag with different temperature ------------------------------ 39
Figure 4.14: IV-curves of GaAs-PVA-Ag with different temperature ---------------------------- 40
Figure 4.15: IV-curves of GaAs-PVA-Au with different temperature ---------------------------- 41
Figure 4.16: IV-curve of Si-Ag Schottky diode ------------------------------------------------------ 42
Figure 4.17: ln I vs V of Si-Ag Schottky diode ------------------------------------------------------ 42

## List of tables

Table 3.1: list of samples, etching method and molecule deposition steps ---------------------- 24
Table 4.1: The values of the SBH, n and $I_\circ$ for the Schottky diode ------------------------------- 43

# Chapter 1:Introduction

## 1.1 Molecular Electronics:

Molecular electronics is the use of molecules as basis for electronic devices, such as transistors, diodes, memories and switches. It deals with the building structure of electrons and it can be used to create complex fabrications of integrated circuits. In 1974, Mark Ratner published the first theory about transportation through a single molecule, and then several studies were devoted to molecular transport. There were some interesting ideas and observations, including unusual transport behaviors and possible mechanisms for new devices[1]. Later on, the development of the scanning tunneling microscope (STM) and later the atomic force microscope (AFM) gave an important advance in molecular electronics, since these tools could be used to save the property of molecular scale, and to measure the conductivity of single molecule. In late 1990s, Mark Reed came up with the first significant work to measure single molecule transport[2]. He helped to understand how measurements could be made and provided insights about the transport properties of different molecules.

Molecular electronics devises are classified into three categories :(Figure 1.1)

1. Molecular optoelectronics.
2. Molecular conductance Junction.
3. Molecular magnets, Ferro electronics, Actuators clastics.

I will limit my work on Molecular conductance junction and exactly on diodes. So what are diodes?

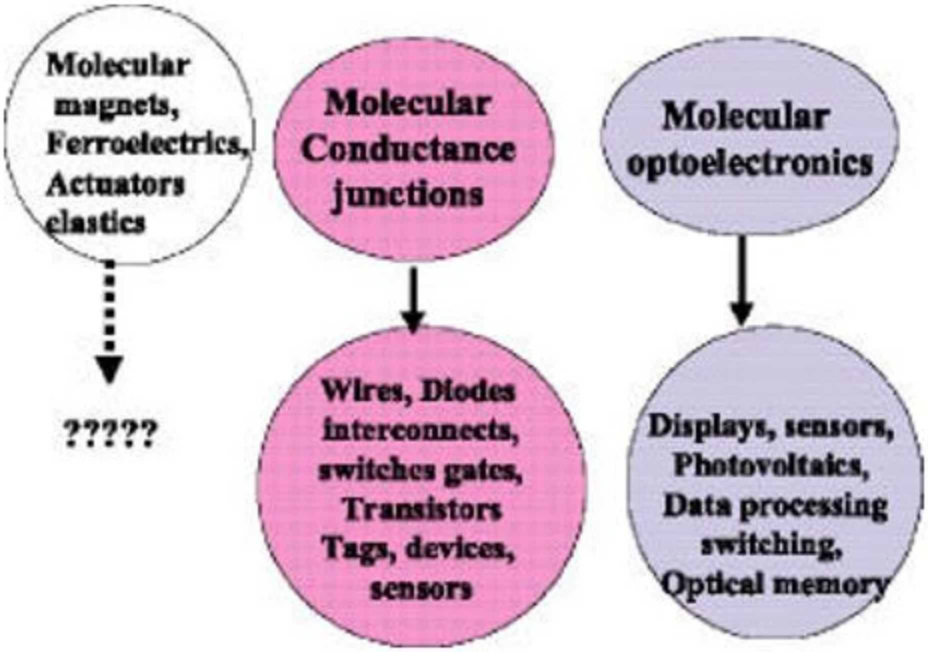


Figure 1.1: Subfield and subarea of molecular electronics[3]

## 1.2 Charge transport mechanisms in molecular junction:

There are two mechanisms for the charge transport in molecular junction, tunneling and hopping as shown in figure 1.2. In the tunneling, the electrons tunnel coherently through energy barrier of the molecule by having enough energy to pass through [4]. We can analyze tunneling I-V for molecule junction using Landauer formula with single electronic state, so the tunneling transport is related to the transport properties to the transmission and reflection properties. In addition, it is temperature independent and its conductance decreases exponentially with molecular length. Whereas, in the hopping mechanism when the charge transferred from electrode to molecule, it interacts with the environment of the molecule and its vibrations and it gets relaxed and trapped on the molecule temporarily and then hopes to the next site by thermal excitation until received by the other electrode. In this mechanism, the charge transfer from one electrode to the redox active state and then to the other electrode so that the redox active state switch between reduction and oxidation state continuously. Moreover, it is temperature dependent and its conductance decreases linearly with molecular length. Therefore, the interaction of the charge with the molecule and the dielectric environment both controls the mechanism of charge transport.

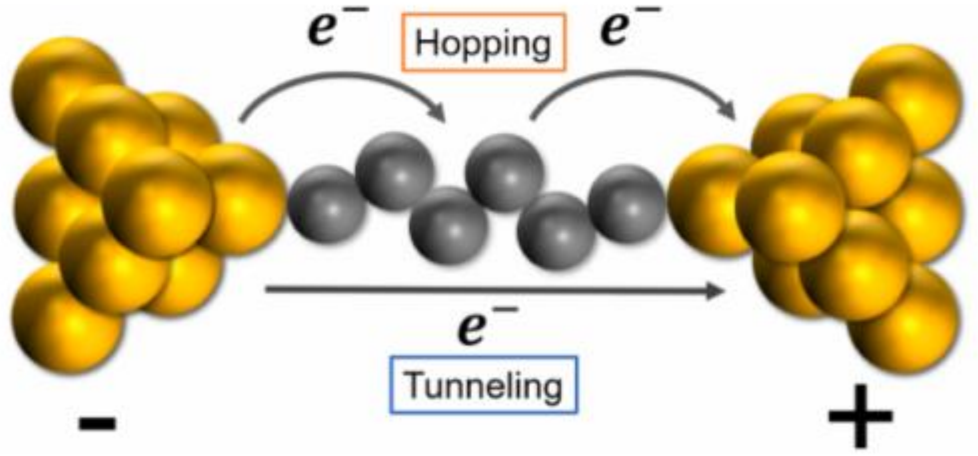


Figure 1.2: Tunneling and Hopping charge transport in molecular junction [4].

## 1.3 Uses of molecular electronics:

There are many uses for molecular electronics, there are used in transistors which are the most important component of an integrated circuit as they act as a switch with the applied voltage. Also in diodes, which is an important component of integrated Circuits (IC), and are used in the smooth running of the transistors. It is also used in wires, where molecular wires are compounds that are proposed to be used in molecular electronics and optoelectronics devices to replace the metal and silicon-based wires in semiconductor devices. Moreover, it is used in capacitors that offers high power density and long cyclability.

## 1.4 Diodes:

Diodes are electrical devices consisting of two electrodes, the anode and the cathode, which tend to conduct electric current in one direction only, it uses P-N junction. Diodes are used to protect circuit by limiting the voltage and for non-linear mixing of two voltages such as amplitude modulation; they are used as voltage rectifiers, which turns AC into DC, and as voltage multiplier such as double input voltage. Figure 1.3 shows the Current-Voltage characteristics of a diode. When the anode voltage is greater than the cathode voltage, then the diode is forward biased. Therefore, it conducts current strongly, the voltage drop across it, is independent of diode current, and the effective resistance is small. Otherwise, if the anode voltage is smaller than the cathode voltage, then the diode is reverse biased. Hence, it conducts current very weakly, diode's current is almost independent of voltage until break down, and the effective resistance is very large.

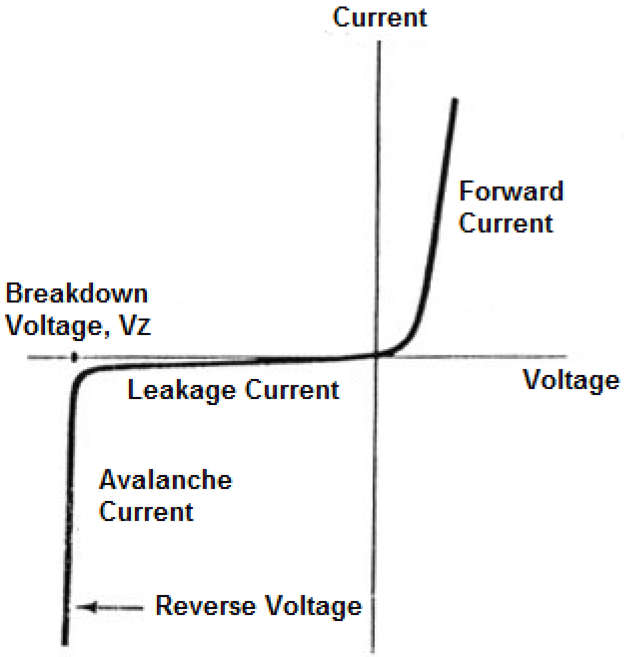


Figure 1.3: The current-voltage characteristics of a diode. [18]

There are many techniques to make a diode; using semiconductors with doped impurities, in order to make a special purpose diode that perform many functions. For example, Zener diodes are used to regulate voltage, avalanche diodes are used to protect circuit from high voltage surges, and there are many other diodes.

Thus, there are many semiconductor diodes: Avalanche diodes, constant current diodes, crystal diodes, tunnel diodes, Gunn diodes, light emitting diodes, laser diodes, thermal diodes, pin diodes, photo diodes, junction diodes, and many more. However, in most cases the basic format for the diode is much the same. The diode contains a PN junction, which provides the basic functionality for the device.

## 1.5 PN-Junction:

It is formed from a semiconductor piece with one end P type and the other end N type as shown in Figure 1.4. Both ends have different characteristics. One end has an excess of electrons while the other has an excess of holes. When the two areas meet, the electrons in the N-type end will fill the holes in the P-type end and there are no free holes or electrons at the interface. Thus there will be an area with depleted charge, and is called a depletion region.

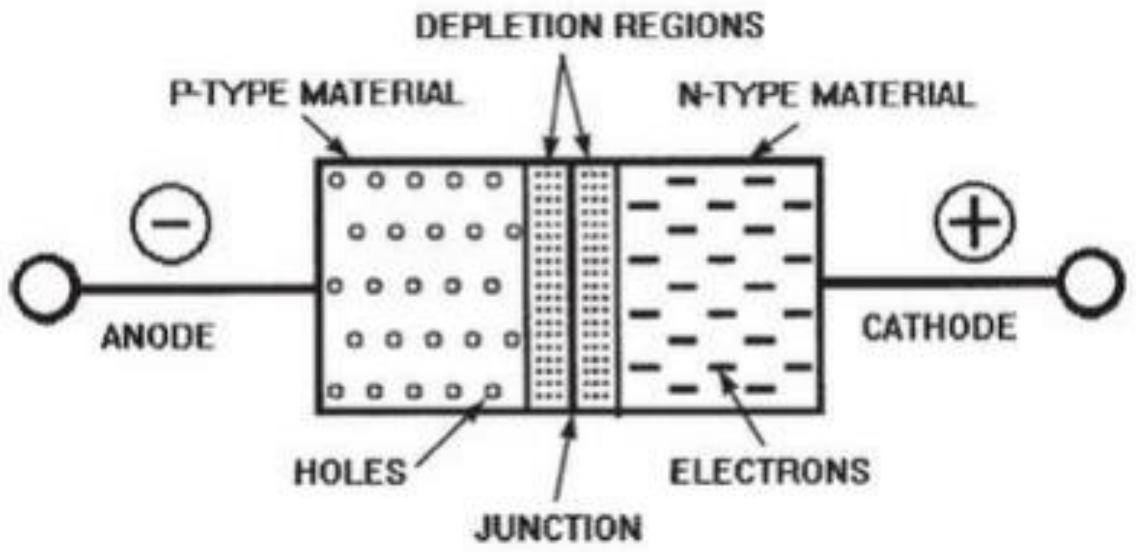
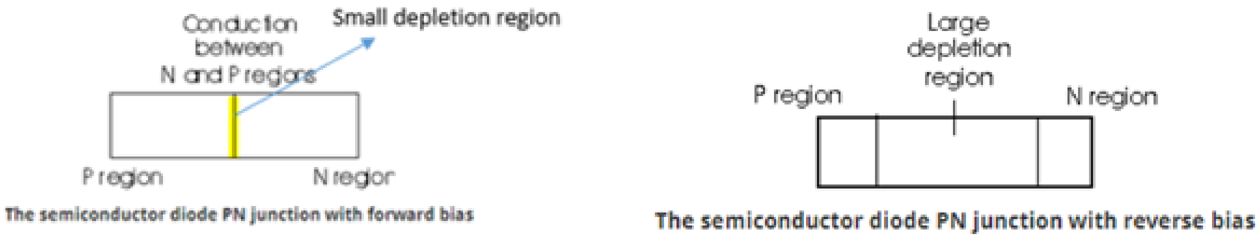


Figure 1.4: PN junction diode [18]

The depletion region is very thin; however, the current cannot always flow in the normal way, which is affected in case that the voltage that is applied to the junction. In Figure 1.4, If the voltage is applied such that the P type area becomes positive and the N type becomes negative, holes are attracted towards the negative voltage and electrons move towards the positive voltage and thus jump the depletion layer, the depletion region decreases (Figure 1.5A). Even though the holes and electrons are moving in opposite directions, they carry opposite charges and as a result, they represent a current flow in the same direction. However, if the voltage is applied in the opposite sense no current flows. That's because the holes and electrons are attracted from the junction itself and the depletion region increases in width (Figure 1.5B).



(a) (b)

Figure 1.5. Effect of applied voltage on a PN junction with (a) Forward bias and (b) Reverse bias. [18]

The PN-junction forms a semiconductor device called *PN junction diode (Figure 1.6)*. Where the P region acts as the anode and the N region acts as the cathode. We can apply an external voltage, making two types of biases, forward biased and reverse biased.

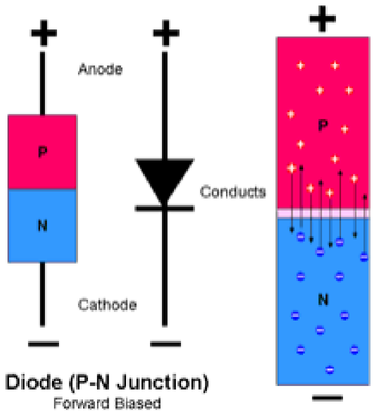


Figure 1.6. Representation of a PN junction diode [18].

## 1.6 Schottky Diodes:

It is a type of junction diodes, but a metal replaces the P-type semiconductor as in Figure 1.7. Thus, the Schottky diode is a metal – semiconductor junction diode, the metal acts as the anode and the semiconductor acts as the cathode. They are widely used in radio frequency applications as a mixer or detector diode, or in power applications as a rectifier.

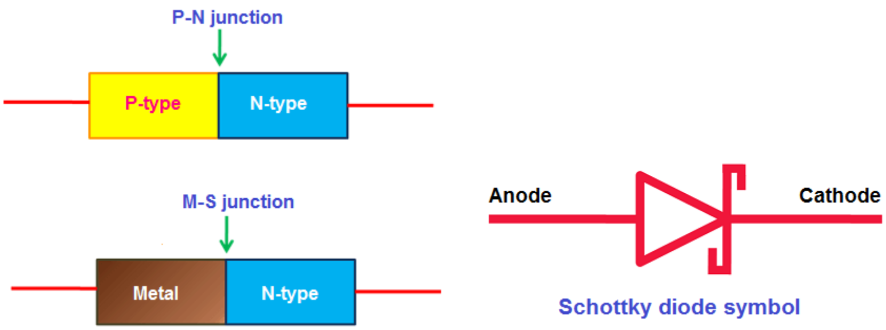


Figure 1.7: schottky diode and schottky diode symbol [18]

The junction between metal and semiconductor creates a depletion layer called Schottky barrier, the value of the barrier height depends on the combination of the metal and the semiconductor. The electrons must overcome this depletion layer to flow across the diode.

Schottky diodes are more useful than the ordinary PN junction diodes, because it switch on and off faster, produces less unwanted noise, making them very useful in high speed switching power circuits. Moreover, Schottky diodes have much higher current density making the forward drops lower, resulting those diodes to be ideal for using in power rectification applications. Although, the voltage drop for silicon diodes is 0.6-0.7V, where the voltage drop for Schottky diodes is faster with 0.2-0.3V. Thus, it consumes less voltage to turn on. However, it has the same voltage drop as Germanium diodes, but it is more useful because the switching speed of Germanium diodes is very low compared to Schottky diodes.

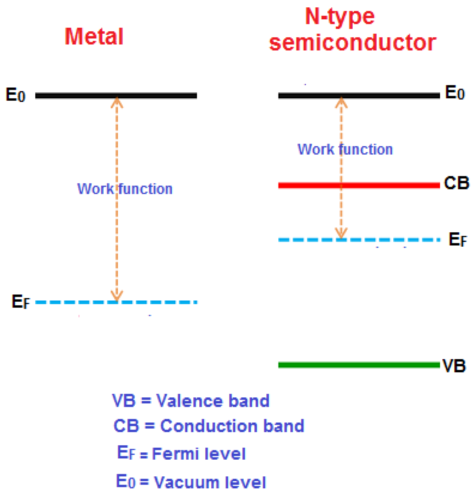


Figure 1.8: energy bands for Schottky diode [19]

As shown in Figure 1.8, the energy levels of the semiconductor and metal are different; the fermi level of the semiconductor is above the fermi level of the metal. Moreover, the work function, which is the energy needed to move an electron from fermi level ($E_f$) to vacuum level ($E_0$), of the metal is greater than that of the semiconductor, and this difference in the work function is defined as the built-in-voltage. Therefore, the electron in the semiconductor has high potential energy than that in the metal. So, what happens when the metal and the semiconductor are joined (at zero bias)?

## Zero Bias:

When we join the metal with the semiconductor, the free electrons of the conduction band in the semiconductor will cross the junction and to be added to the atoms in the metal. Thus, the atoms at the metal side gains extra electron, where the atoms at the semiconductor loses electrons. As a result, positive ions are created in the semiconductor junction and negative ions are created in the metal junction, see Figure 1.9. These negative and positive ions are the depletion region. However, the width of the free electrons moving in the metal is very thin compared to that in the semiconductor, thus the built-in-voltage is primary presented in the semiconductor. Hence, the built-in-voltage is the barrier seen by the conduction band electrons of the semiconductor when trying to move to the metal. Therefore, to overcome this barrier the free electrons need energy greater than the built-in-voltage.

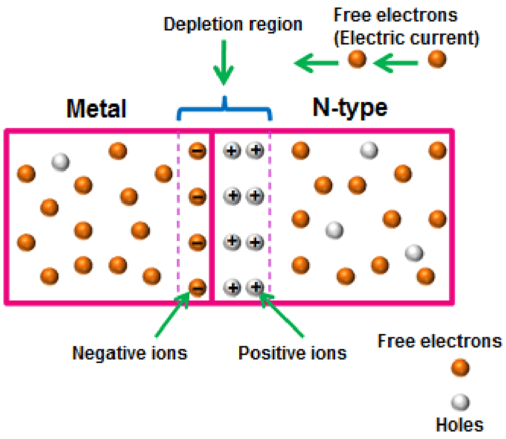


Figure 1.9: depletion region in Schottky diode [19]

For the energy bands, when the metal and the semiconductor are in contact, the fermi energies of them do not change right away. First, the electrons start moving from the semiconductor to the metal reducing the electron concentration in the semiconductor, and a positive charge stays behind. This charge creates a negative field and lowers the band edges of the semiconductor as in Figure 1.10, energy bands are said to be bent. Electrons flows into the metal until reaching a thermal equilibrium between the diffusion of the electrons from the semiconductor to the metal and the drift of the electrons caused by the field created by the ionized impurity atoms. Therefore, the fermi energies of the metal and the semiconductor will align.

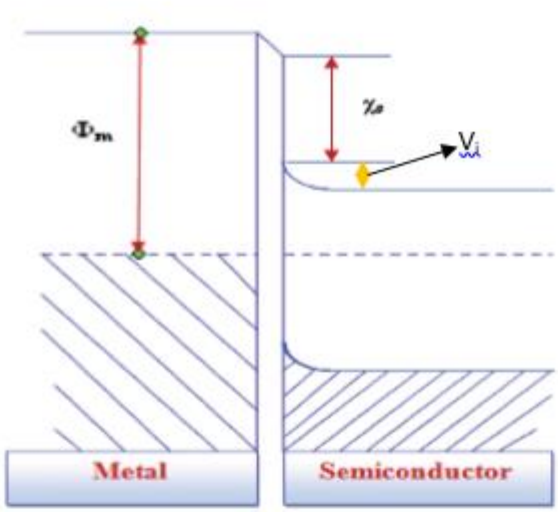


Figure 1.10: energy band diagram of metal-semiconductor junction at zero bias.

**Forward Bias:**

If we connect the positive terminal of the battery to the metal and the negative terminal to the semiconductor, then the Schottky diode is forward biased. When we apply forward bias voltage to the Shottky diode, the free electrons cannot cross the depletion region unless the voltage is greater than 0.2V (voltage drop of a Schottky diode) and electric current will start flowing. If the applied voltage is continuously increased, the depletion region becomes very thin and finally disappears. The effect is shown in Figure 1.11.

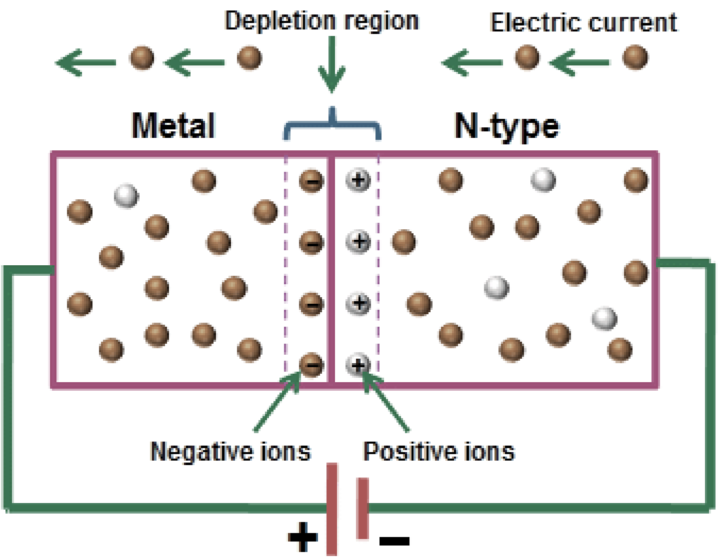


Figure 1.11: Forward biased Schottky diode. [19]

For the energy bands, applying forward bias will result to move more electrons toward the metal. Thus, the fermi energy of the metal will be lowered with respect to the fermi energy of the semiconductor, and there will be a smaller potential drop across the semiconductor. Therefore, there will be a positive current through the junction at a voltage comparable to the built-in potential, see Figure 1.12.

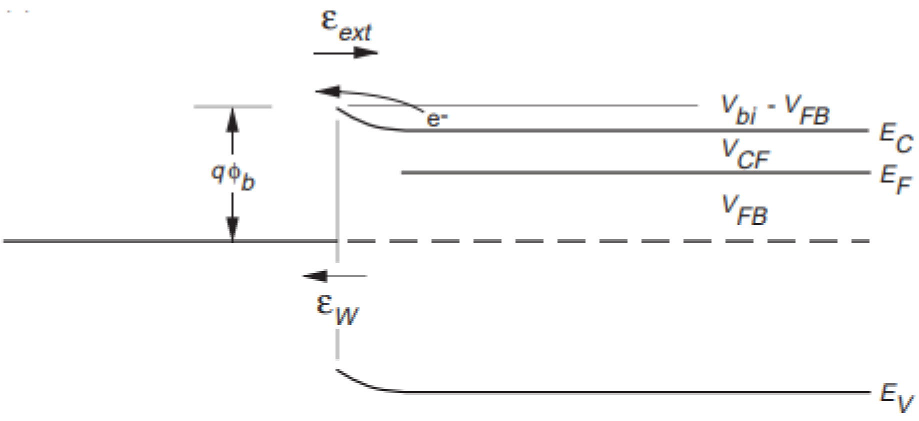


Figure 1.12: energy band diagram of metal-semiconductor junction at forward bias

## Reverse Bias:

However, if the negative terminal of the battery is connected to the metal and the positive terminal is connected to the semiconductor as in Figure 1.13, the Schottky diode is reversed biased. Thus, the depletion width increases and the electric current stops flowing, but a small leakage current flows due to the thermally excited electrons in metal. However, if the reverse bias voltage is largely increased, a sudden rise in electric current takes place. This sudden rise in electric current causes depletion region to break down which may permanently damage the device.

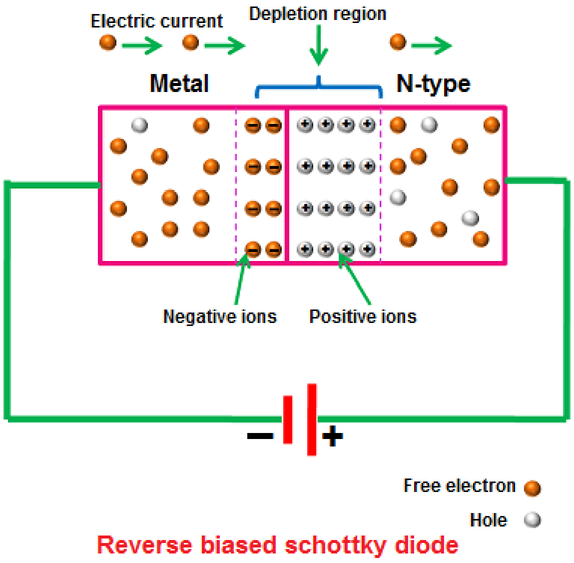


Figure 1.13: Reverse biased Schottky diode [19]

For the energy bands shown in Figure 1.14, applying a reverse bias limits the flow of electrons due to the barrier. Also, the fermi energy of the metal is raised with respect to the fermi energy of the semiconductor, and the potential across the semiconductor increases. Therefore, the depletion region and the electric field at the interface increase. Thus, the metal-semiconductor junction with positive barrier behaves as rectifying and there is almost no current.

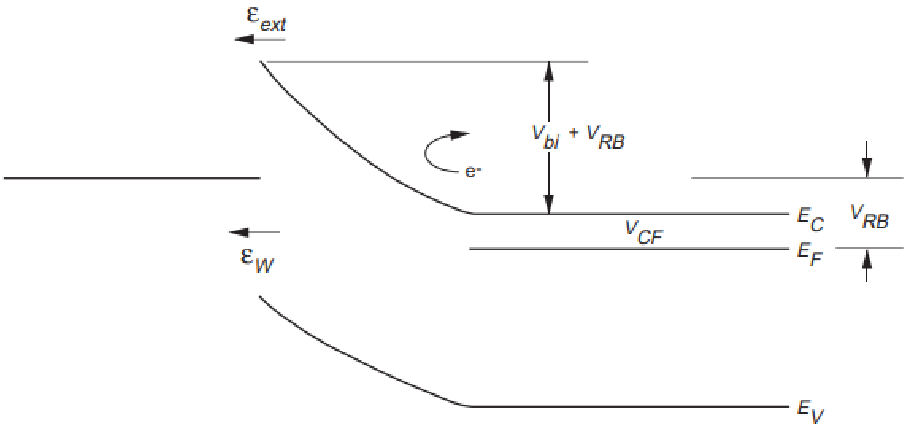


Figure 1.14: energy band diagram of metal-semiconductor junction at reverse bias.

One of the main advantages of using Schottky diode over a regular diode is its low forward voltage drop (low turn on voltage). Also it offers low junction capacitance, fast reverse recovery time and high current density. Moreover, it has high efficiency and operates at high frequency.

Molecular schottky diode can be used in different applications. It can be used as general-purpose rectifiers, in radio frequency (RF) applications and in power supplies. Also, it can be used to detect signals and in logic circuirts.

## 1.7 Molecular Schottky Diodes:

Molecular Schottky diode is a semiconductor – molecule – metal junction. Molecular Schotttky diodes is one of the major research target in the field of molecular electronics. In such devices, the molecular layer modulates electronic properties due both to molecular electronic effects and to its electrostatic influence on the substrate. It has been demonstrated that dipolar molecular layers deposited on semiconductor surfaces can modulate the surface potential in a controlled manner. [10]

# Chapter 2: Molecular Schottcky Diodes

## 2.1 IV- Characteristic of Schottky Diodes:

The characterization of Schottky diode is a common technique used to gain a better understanding of the performance of the device. One of the main reason for taking IV-measurements is to characterize the threshold voltage, and it can show the device response. Figure 2.1 shows the IV-curve of a Schottky diode, the vertical line represent the current flow (dependent variable), and the horizontal line represents the voltage applied across the Schottky diode (independent variable). The forward current rises exponentially, and the forward voltage drop is between 0.2V and 0.3V.

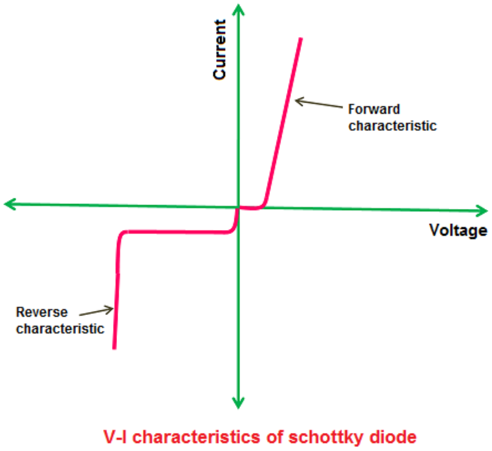


Figure 2.1: IV-Characteristics of Schottky diode. [20]

**Parameters:**

1. Forward voltage drop: is the voltage drop across the diode when it is forward conduction.
2. Reverse break down: the amount of reverse bias that will cause a diode to break down and conduct in the reverse direction. The Schottky diode doesn't have a high break down voltage.
3. Capacitance: this parameter is one of the great importance for small signal RF applications.
4. Reverse recovery time: is the time taken to switch the diode from its forward state to the reverse state.
5. Reverse leakage current: is the current when the devise is in the reverse biased.
6. Working temperature.

## 2.2 Motion of electrons through metal-molecule-semiconductor interference:

Figure 2.2, shows schematically the possible energy band diagram of the metal/molecule/semiconductor device for charge transfer. We know that electron passes through the diode when it is forward biased. Thus, when the left electrode is negatively biased relative to the right electrode, electron transfer onto the acceptor becomes possible as soon as the applied field becomes large enough for the Fermi level of the left electrode to overlap the acceptor level. A similar process occurs at the donor end, where electron transfer from the donor to the right electrode becomes possible when the applied voltage is $V > IP - W$ where IP is donor ionization potential and W is the work function of the metal electrode. Motion of electrons from acceptor to donor occurs under the action of the field via tunneling process. When polarity is reversed, donor level should be lowered to the Fermi level of the right electrode and the Fermi level of the left electrode should be lowered below the acceptor level in order to obtain the tunneling through these levels. Therefore, the threshold voltage for this process is high, which explains rectification properties of the molecular diode. In this model, electrons preferentially flowed from acceptor to donor as a result of the two step charge transfer process. The first step is an electron moving from the left electrode to the LUMO of the acceptor unit and an electron moving from the HOMO of the donor unit to the right electrode and the second step is an internal relaxation of the resultant zwitterion (i.e., $A^-$–$D^+$ ) to the ground-state.

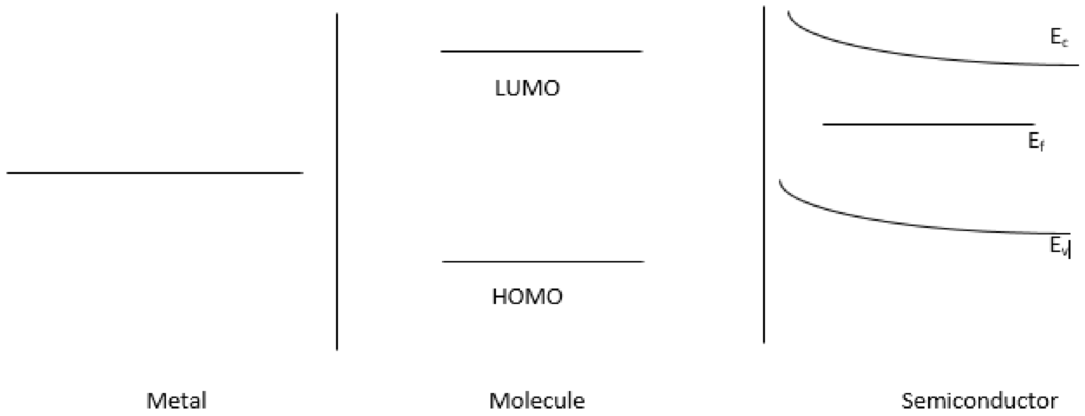


Figure 2.2: energy level diagram of molecular Schottky diode.

## 2.3 Measurements of current voltage (IV)-Characteristics of Schottky Diodes:

Current-Voltage characterization is one of the most common techniques to determine the Schottky barrier height, using the thermionic emission theory. Thus for the Schottky barrier diode, we can express the current as[24]:

$$I = I_{\circ} \exp(\frac{qV}{nKT}) \left(1 - \exp(\frac{-qV}{KT})\right) \qquad \ldots\ldots\ldots (1)$$

If $V > 3KT/q$, it can be expressed as[24]:

$$I = I_{\circ} \exp(\frac{qV}{nKT}) \qquad \ldots\ldots\ldots (2)$$

Where n is the ideality factor, T is the temperature in Kelvin, q is for the electron charge, K is the Boltzmann constant and $I_{\circ}$ is the reverse saturation current and can be written as[24]:

$$I_{\circ} = A\, A^{*}\, T^{2} \exp(\frac{-q\varphi_{b}}{KT}) \qquad \ldots\ldots\ldots (3)$$

Where A is the area of the effective diode, $A^{*}$ is the effective Richardson constant which is equal to 32 A $cm^{-2}$ $K^{-2}$ and $\phi_b$ is the zero bias barrier height and can be expressed as[24]:

$$\phi_b = \frac{KT}{q} \ln(\frac{A\, A^{*} T^{2}}{I_{\circ}}) \qquad \ldots\ldots\ldots (4)$$

To measure the deviation of practical diodes from ideal thermionic emission model we use a parameter called the Ideality Factor and can be expressed as[24]:

$$n = \frac{q}{KT} \left( \frac{\partial V}{\partial (lnI)} \right) \qquad \ldots\ldots\ldots (5)$$

# Chapter 3: Experimental: Modification of molecular schottky diodes with different conjugated degree of organic molecules

In this chapter, we build in a molecular Schottky diode sample with different type of molecules. Firsr, we cleaned the semiconductor samples by etching, then we used the spin coater to deposit the molecule on the semiconductor. Then, we deposit the metal using the thermal evaporator. Finally, we tested our samples and have IV-Characteristics for them using the keithley Instruments and micromanipulators that have been built at Bethlehem University.

## 3.1 Semiconductor Etching:

Etching is the process that is used to remove impurities or selected layers of the semiconductor for the purpose of pattern transfer, wafer polarization, isolation and cleaning. There are two fundamental techniques of etching: wet etching (liquid-based etchants) and dry etching (plasma-based etchants).

**Wet etching** is a chemical process that uses liquid-phase etchant to remove materials from a wafer. Most of etchants consist of an oxidizing agent (like $H_2O_2$, $Br_2$, $AgNO_3|CrO_3$, $HNO_3$, NaOCl), an agent for dissolving the oxides (it may be acid or base like $NH_4OH$, NaOH, $H_2SO_4$, HCl, HF and $H_3PO_4$), and a solvent (it may be water or $CH_3COOH$ to transport reactants and products). [25]

**Dry etching** or plasma etching uses reactive ions in a gas phase to sputter or dissolve the materials. Thus, it uses plasma instead of liquid etchants.[25]

Thus, to clean the semiconductor wafers from any impurities or oxidizing layer I used wet etching. I used two kinds of semiconductors, Si and GaAs wafers.

Steps of Si Etching:

1. Immerse the Si wafers in methanol for 10 min.
2. Immerse in $H_2O_2$ for 15 sec.
3. Immerse in $CH_3OH$:$H_2O$: HF (2%) for 15 sec.
4. Immerse in $H_2O_2$ for 15 sec.
5. Dry it using hot plate for few seconds.

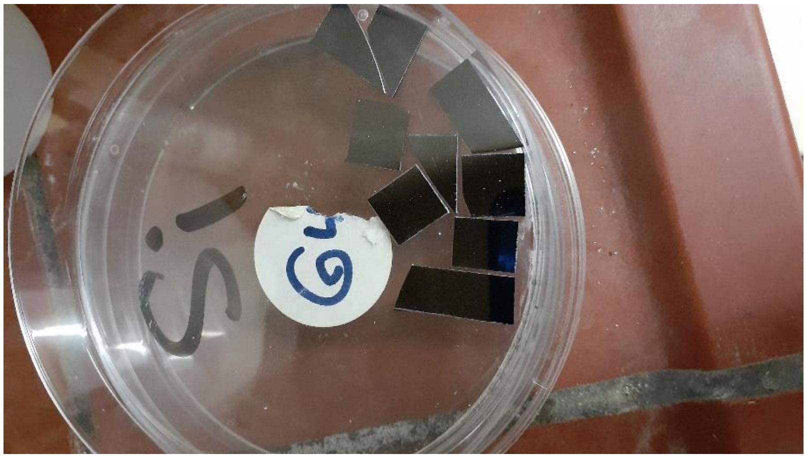


Figure 3.1: Si samples

Figure 3.2: Si Etching

<u>Steps of GaAs Etching:</u>

1. Immerse the GaAs wafers in methanol for 10 min.
2. Immerse in $H_2O_2$ for 15 sec.
3. Immerse in $NH_4OH$: $H_2O$ (1:9) for 15 sec.
4. Immerse in $H_2O_2$ for 15 sec.
5. Dry it using hot plate for few seconds.

### 3.2 Spin Coating for Molecular Deposition:

To deposit the molecule on the semiconductor I used the spin coater device, which is widely used today in the microelectronics industry. Thus, a piece of semiconductor coated with a uniform layer of molecule.

The spin coating process is divided into four stages as shown in the figure 3.3:

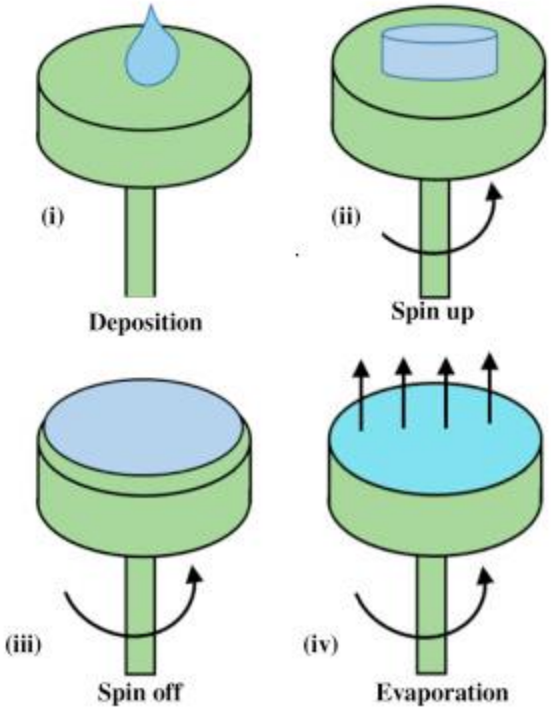


Figure 3.3: Stages of spin coating process [28].

**The first stage is deposition:**

In this stage, the solution fells on a rotating substrate from microsyrings and accelerate the substrate to the desired speed spreading of the solution due to centrifugal force and the height is reduced to critical height. This is the stage of delivering an access of the liquid to be coated to the surface of the substrate [25].

**The second stage is spin up:**

In this stage, the substrate is accelerated to its final desired speed, and fluid is thin enough to balance the rotational accelerations.

**The third stage is stable fluid outflow:**

This stage occurs when the substrate is spinning at a constant rate and the fluid viscous forces dominate fluid thinning behavior. Therefore, due to tension, viscosity, rotation rate there may be a small bead of coating thickness difference around the rim of the final wafer. However, mathematical treatments of the flow behavior show that if the liquid exhibits Newtonian viscosity and if the liquid thickness is initially uniform across the wafer, then the fluid thickness profile at any flowing time will be uniform[27].

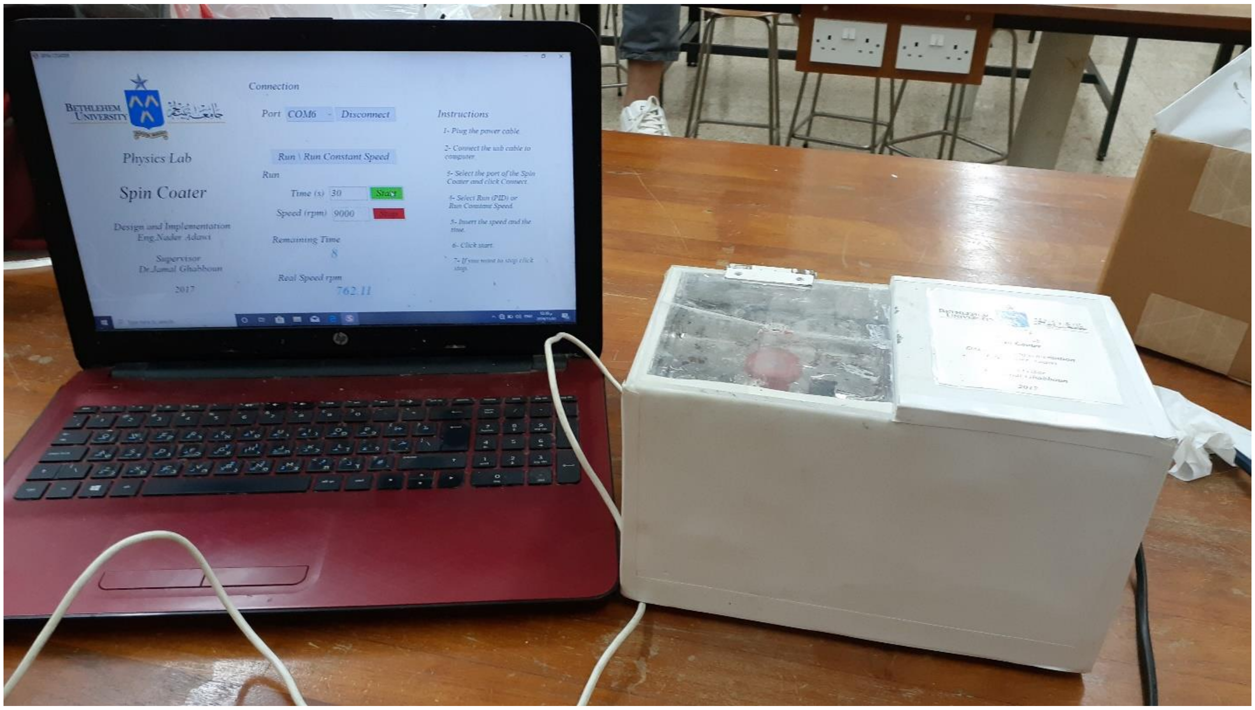
**The fourth stage is evaporation:**

This stage occurs when the substrate is spinning at a constant rate and solvent evaporation dominates the coating thinning behavior.

The rate of evaporation depends on two factors:

1. The difference in partial pressure of each solvent.
2. The bulk of the gas flowing nearby.

I used PEDOT and 27.5mg/ml of Cinnamic acid as conjugated molecules and 5% PVA as non-conjugated molecule. I used 5µl of each molecule to deposit on the semiconductor for 40 sec with 9000 rpm then 20 sec with 6000 rpm for drying the molecule on the semiconductor. One of the samples of the Si I used 10 µl of Cinnamic acid for 60 sec with 9000 rpm then 30 sec with 6000 rpm.



Port COM6

Time (s) 30

Speed (rpm) 9000

Remaining Time 8

Real Speed rpm 762.11

Design and Implementation
Eng.Nader Adawi

Supervisor
Dr.Jamal Ghabboun

2017

1- Plug the power cable.

2- Connect the usb cable to computer.

3- Select the port of the Spin Coater and click Connect.

4- Select Run (PID) or Run Constant Speed.

5- Insert the speed and the time.

6- Click start.

7- If you want to stop click stop.

Figure 3.4: build in spin coater.

### Poly (3, 4 – Ethylenedioxythiophene) (PEDOT):

It is an electrically – conducting conjugated polymer that is highly conducting and demonstrate biocompatibility at the same time. In chemical characterization, it is stable in its oxidized form, insensitive to PH changes, and can form nearly transparent thin films [31].

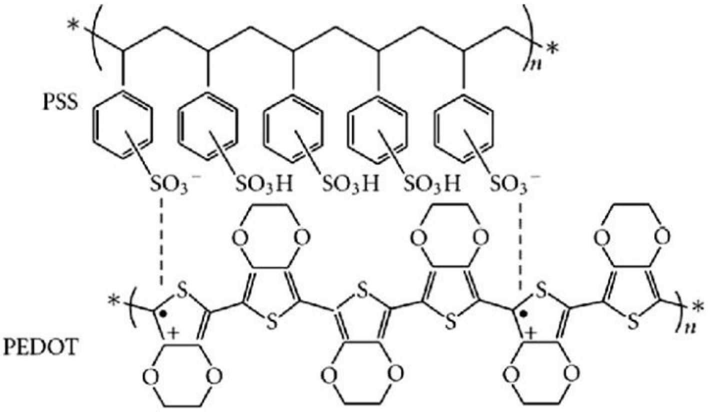


Figure 3.5: molecule shape of PEDOT:PSS[31]

**Cinnamic acid:**

It is a polar organic compound that has the formula $C_6H_5CH{=}CHCOOH$. It is a white crystalline compound and is slightly soluble in water, but very soluble in alcohol (ethanol and methanol).

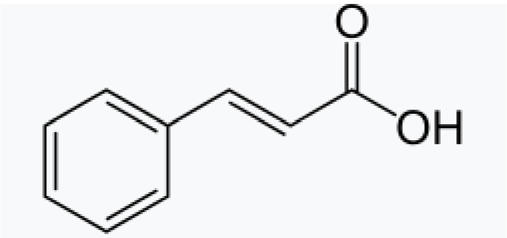


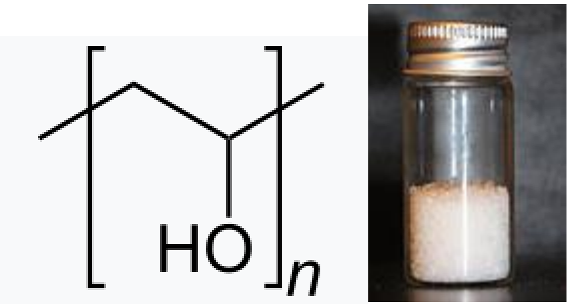
Figure 3.6: molecule shape of cinnamic acid [32].

(a) (b)

Figure 3.7: (a) cinnamic acid, (b) cinnamic acid dissolved in methanol

**Poly (vinyl alcohol):**

PVA is a non-conjugated and a water – soluble synthetic polymer. It has the formula $[CH_2CH(OH)]_n$. It is colorless and odorless.



(a) (b)

Figure 3.8: (a) molecule shape of PVA, (b) PVA [33].

Figure 3.9: PVA dissolved in water.

## 3.3 Metal Deposition:

To build in my molecular Schottky diode I have to deposit the metal on the semiconductor. To do that I used the thermal evaporator to deposit the silver and the gold to my samples. Figure 3.10 shows the thermal evaporator that I used in Bethlehem University.

The thermal evaporator is the simplest equipment to deposit metal on the semiconductor, it uses electric resistance heater to melt the material and raises its vapor pressure to a useful range. This is done in a high vacuum, both to allow the vapor to reach the substrate without reacting with or scattering against other gas phase atoms in the chamber, and reduce the incorporation of impurities from the residual gas in the vacuum chamber. Evaporation occurs when the metal is heated above its melting point in vacuum chamber, then the evaporated atoms travel in straight lines because of the long mean free-path due to the vacuum and deposit on the wafer.

Figure 3.10: The thermal evaporator

Figure 3.11: the thermal evaporator during metal deposition process.

## 3.4 Current – Voltage Characteristics:

An IV measurement is a task to obtain the current vs voltage or resistance characteristics by providing a voltage/current stimulus and measuring current/voltage reaction. It is a basic electric measurement and a fundamental way to discover behavior and characterize devices, such as diodes, memory, transistors, sensors, photovoltaic cells, etc.

Therefore, to test my Schottky diodes I have to do the IV-Characteristics. Therefore, I used the Keithley Instrument and micromanipulators that have been built at the Physics department at Bethlehem University and have been borrowed from the Nano lab at Al-Quds University. Then, I used the hot plate to change the temperature of the diode and I see the effect of temperature on IV-Characteristics.

Figure 3.12: set up for IV-Characteristics.

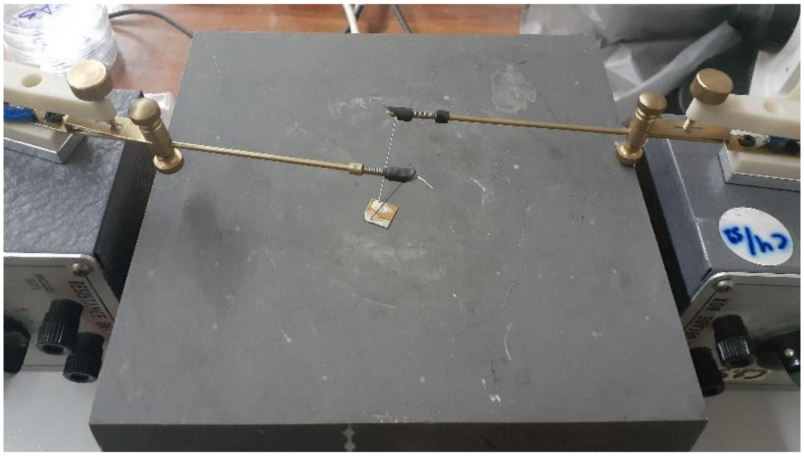


Figure 3.13: during taking the IV-measurements for a sample.

Table 3.1 shows the list of samples of Si and GaAs that I prepared, with the etching method and molecule deposition steps.

Table III.1: list of samples, etching method and molecule deposition steps.

| **Si Samples** | **Etching for Si** | **Deposition of molecule** |
|---|---|---|
| Si-Ag | Rinse in<br>• methanol 10 min<br>• Dionized water 15 sec<br>• HF (2%) 15 sec<br>• De-ionized water 15 sec<br>Dry using hot plate | |
| Si-PEDOT-Ag | The same | 5µl of PEDOT using spin coater with rpm for 40 sec then 6000 rpm for 20sec. |
| Si-cin-Ag | The same | 5µl of cinnamic acid using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| Si-PVA-Ag | The same | 5µl of PVA using spin coater with rpm for 40 sec then 6000 rpm for 20sec. |
| Si-Au | The same | |

| | | |
|---|---|---|
| Si-PEDOT-Au | The same | 5µl of PEDOT using spin coater with rpm for 40 sec then 6000 rpm for 20sec. |
| Si-cin-Au | The same | 5µl of cinnamic acid using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| Si-PVA-Au | The same | 5µl of PVA using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| Si-cin-Ag | The same | 10µl of cinnamic acid using spin coater with 9000 rpm for 60 sec then 6000 rpm for 30sec. |
| **GaAS samples** | **Ethcing of GaAs** | **Deposition of molecule** |
| GaAs-Ag | Rinse in<br>• methanol 10 min<br>• Dionized water 15 sec<br>• $NH_4OH$ : $H_2O$ (1:9) 15 sec<br>• De-ionized water 15 sec<br>Dry using hot plate | |
| GaAs-PEDOT-Ag | The same | 5µl of PEDOT using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| GaAs-cin-Ag | The same | 5µl of cinnamic acid using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| GaAs-PVA-Ag | The same | 5µl of PVA using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| GaAs-Au | The same | |

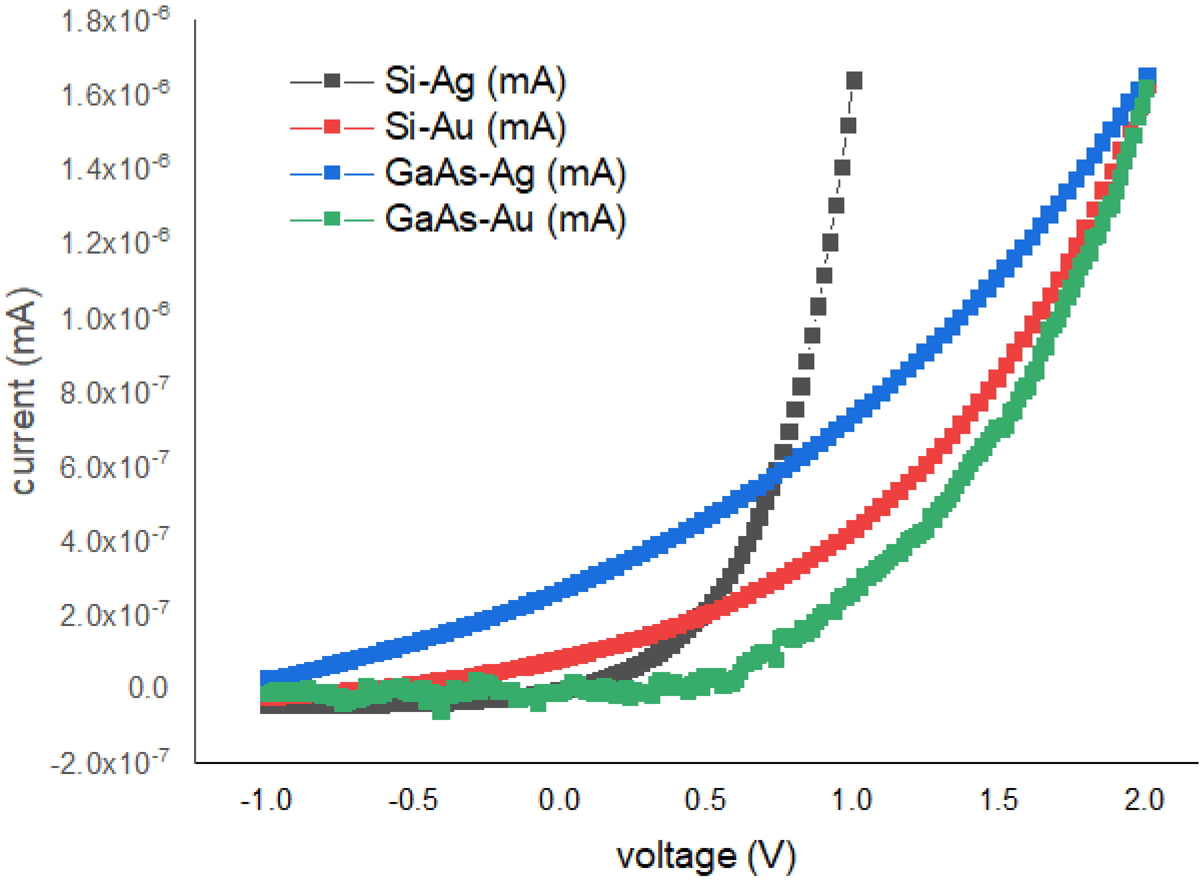
| | | |
|---|---|---|
| GaAs-PEDOT-Au | The same | 5µl of PEDOT using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| GaAs-cin-Au | The same | 5µl of cinnamic acid using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |
| GaAs-PVA-Au | The same | 5µl of PVA using spin coater with 9000 rpm for 40 sec then 6000 rpm for 20sec. |

# Chapter 4: Result and Discussion

In this chapter, we will present the IV- curves that we got form my samples. We used samples consisting of semiconductor and metal, others with conjugated molecules and non-conjugated molecules, and we took the IV-measurements at room temperature and then we changed the temperature and got different IV-curves for these samples. Then we will discuss the barrier height and the ideality factor from these curves.

## 4.1 IV – characteristics at room temperature:

Figure 4.1 represents the IV-Characteristics of the metal-semiconductor interference. From the curve, we can see that Si-Ag has the lowest forward voltage drop than the others, which mean it needs less voltage than the others to produce electrical current. We can organize them from the highest conductivity to the lowest, Si-Ag, GaAs-Ag, Si-Au, and finally GaAs-Au.



Figue 4.1: IV-curves of Metal-Semiconductor interference.

Figure 4.2 repersents the IV-curve of Si-Ag with conjugated molecule(cinnamic acid), and non-conjugated molecules (PVA). From the curves, we can recognise that Si-Ag has the lowest forward voltage drop, then Si-cin-Ag and finally Si-PVA-Ag. So we can conclude that the conjugated molecule (cinnamic acid) is more conducting than the non-conjugated molecule (PVA).

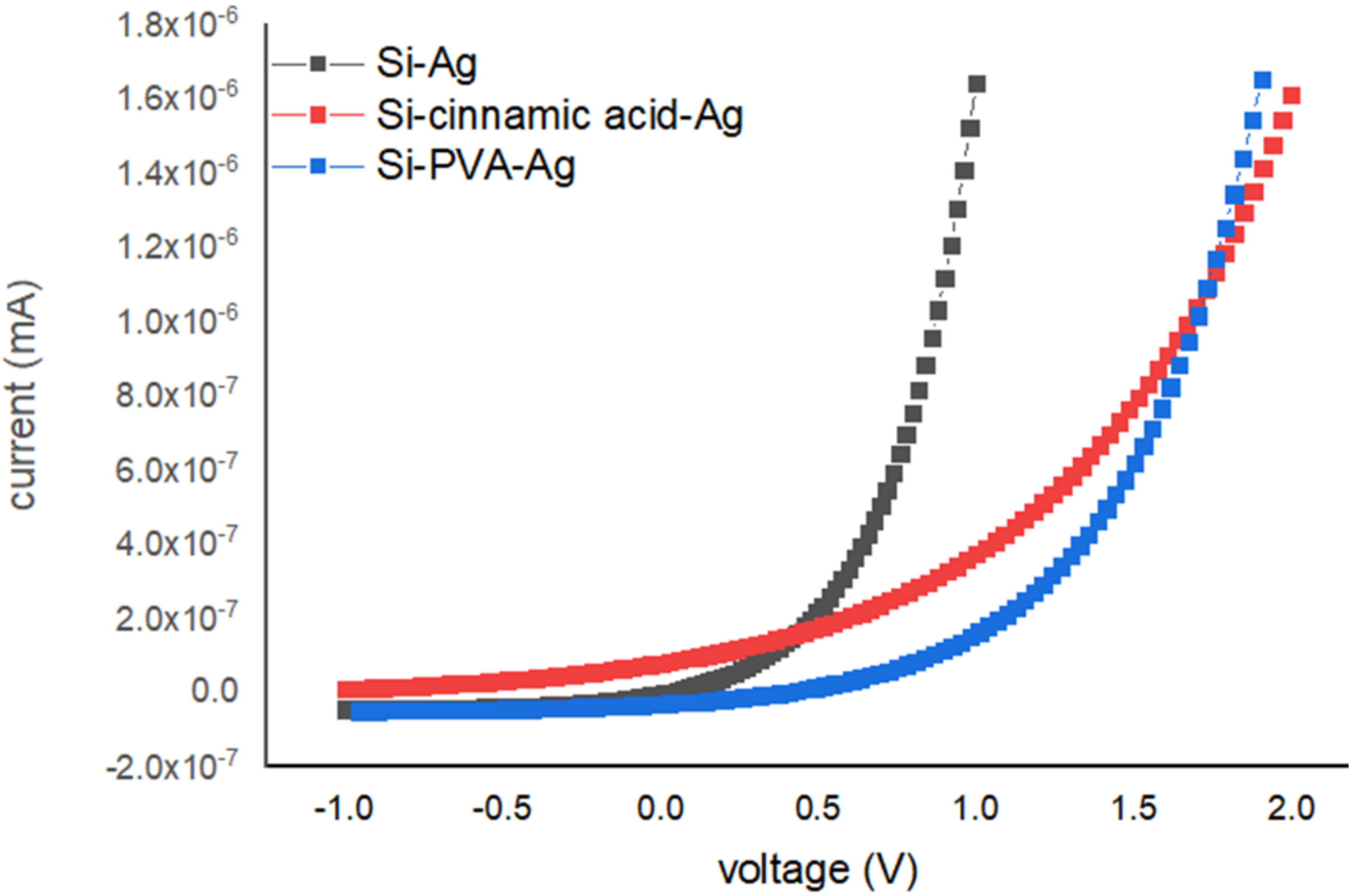


Figure 4.2: IV-curves of Si-Ag, Si-cin-Ag and Si-PVA-Ag.

Figure 4.3 repersents the IV-curve of Si-Au with conjugated molecules (PEDOT and cinnamic acid), and non-conjugated molecules (PVA). From the curves, we can recognise that Si-cin-Au has the lowest forward voltage drop, then Si-PEDOT-Au, then Si-Au and finally Si-PVA-Au. Therefore, the conjugated molecule increases the conductivity of the Si-Au, whereas the non-conjugated molecule decreases the conductivity.

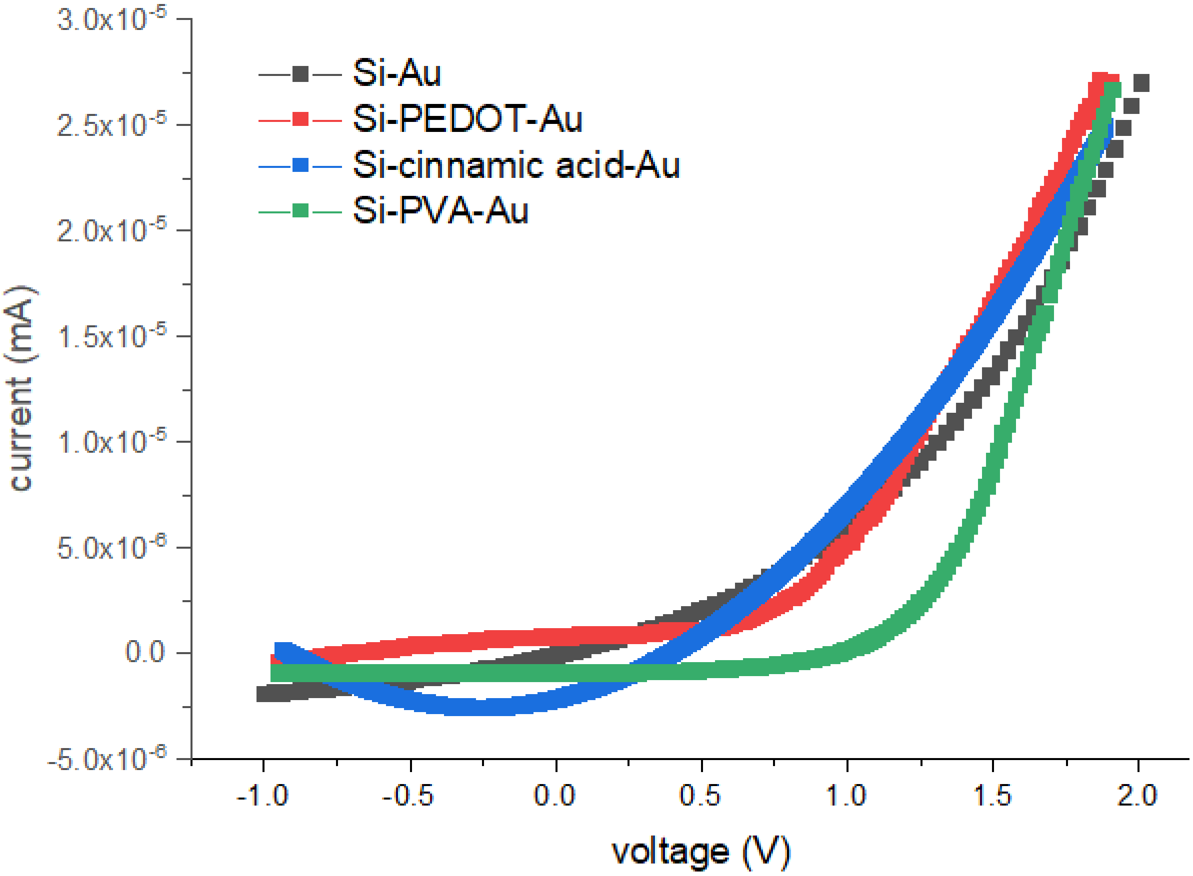


Figure 4.3: IV-curves of Si-Au, Si-PEDOT-Au, Si-cin-Au, and Si-PVA-Au.

Figure 4.4 represents the IV-curves of GaAs-Ag with conjugated molecule (cinnamic acid) and non-conjugated molecule (PVA). From the curve, we can see that GaAs-PVA-Ag has the lowest forward voltage drop, then GaAs-cinnamic acid-Ag, and finally GaAs-Ag. Therefore, the molecules increase the conductivity of the GaAs-Ag.

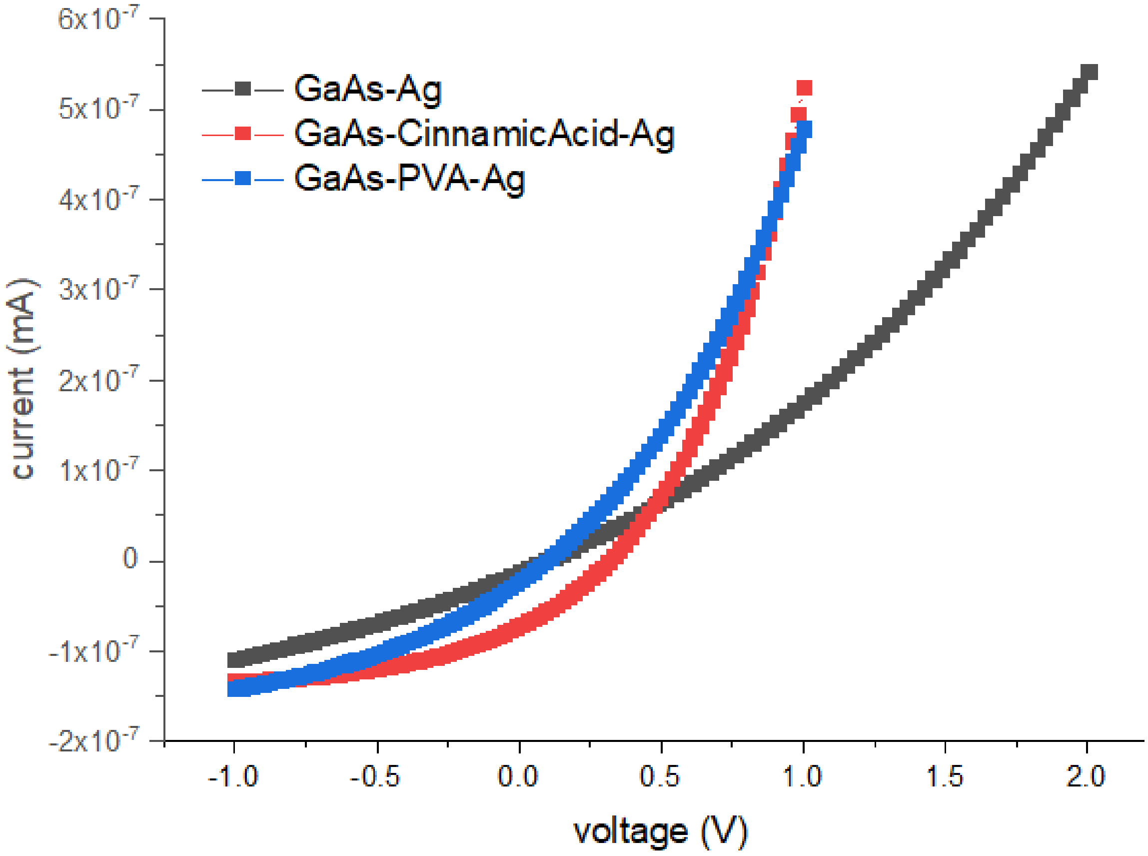


Figure 4.4: IV-curves of GaAs-Ag, GaAs-cin-Ag, and GaAs-PVA-Ag.

Figure 4.5 represents the IV-curves of GaAs-Au with conjugated molecule (cinnamic acid), and non-conjugated molecule (PVA). From the curve we can see that the GaAs-PVA-Au has the lowest forward voltage drop, then GaAs-Au and GaAs-cin-Au. Therefore, the non-conjugated molecule increases the conductivity of GaAs-Au.

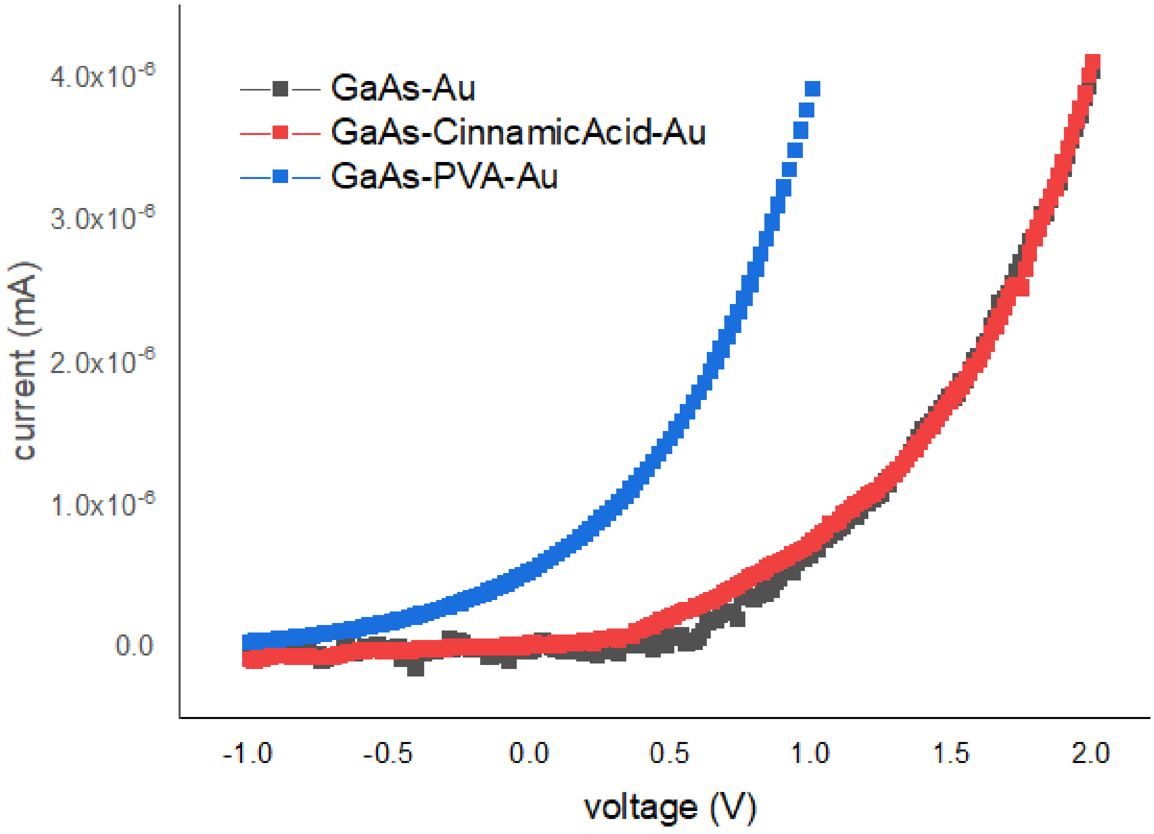


Figure 4.5: IV-curves of GaAs-Au, GaAs-cin-Au, and GaAs-PVA-Au.

## 4.2 IV-effect of molecule thickness on IV-Characteristics:

I also studdied the effect of the molecule thickness on the IV-curve of Si-cin-Ag Schottky diode as shown in figure 4.6. I made two samples, the first one I deposite 10 µL of cinnamic acid and the other I deposite 5 µL of cinnamic acid. Thus the amount of the deposited cinnamic acid should control the thickness with the same conditions of deposition. We can see from the figure that when I inceased the thickness of the cinnamic acid, the forward voltage drop decreased. Thus, increasing the thickness of the molecule in Si-cin-Au Schottky diode increases the conductivity.

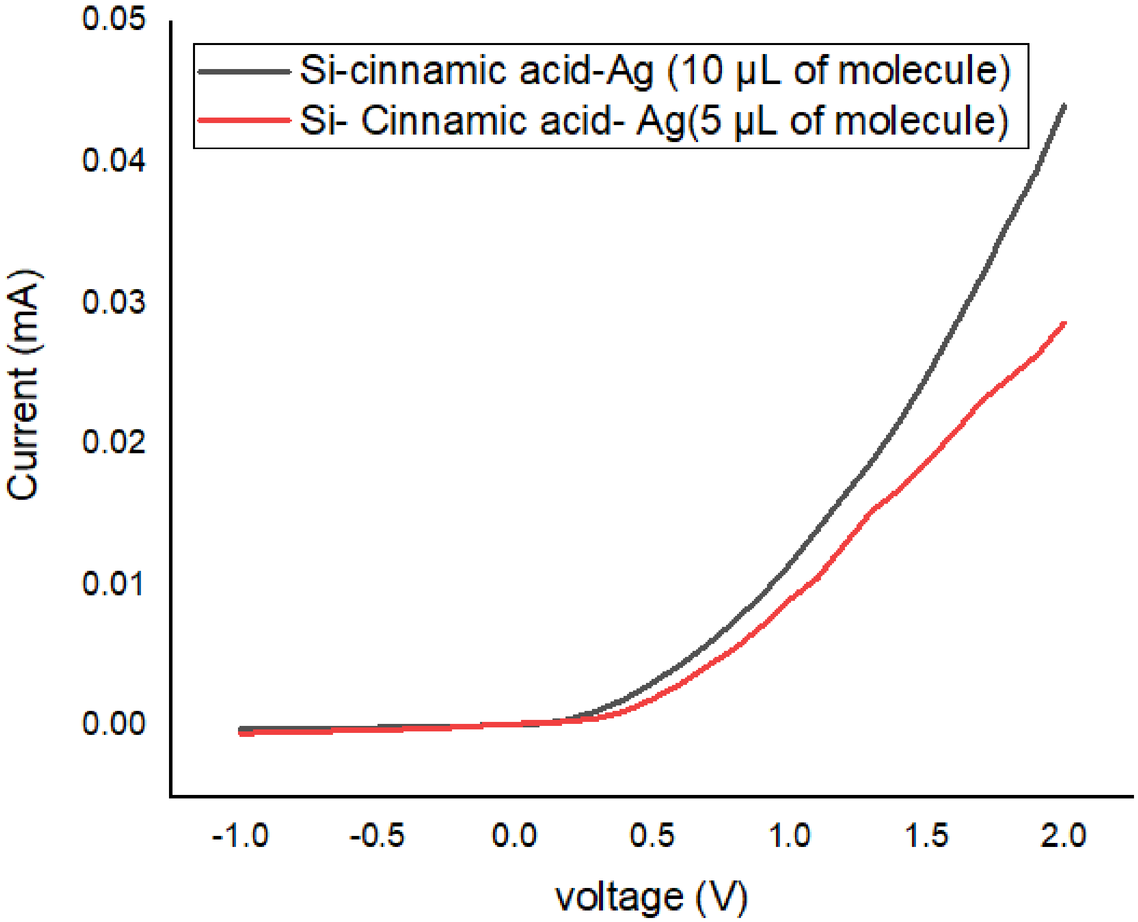


Figure 4.6: IV-curves of Si-cin-Ag when increasing the molecule thickness.

### 4.3 IV – effect of temperature on IV-Characteristics:

In this section, I have studied the effect of temperature on the IV-Characteristics of my samples, and I increased the temperature from 295K to 353K.

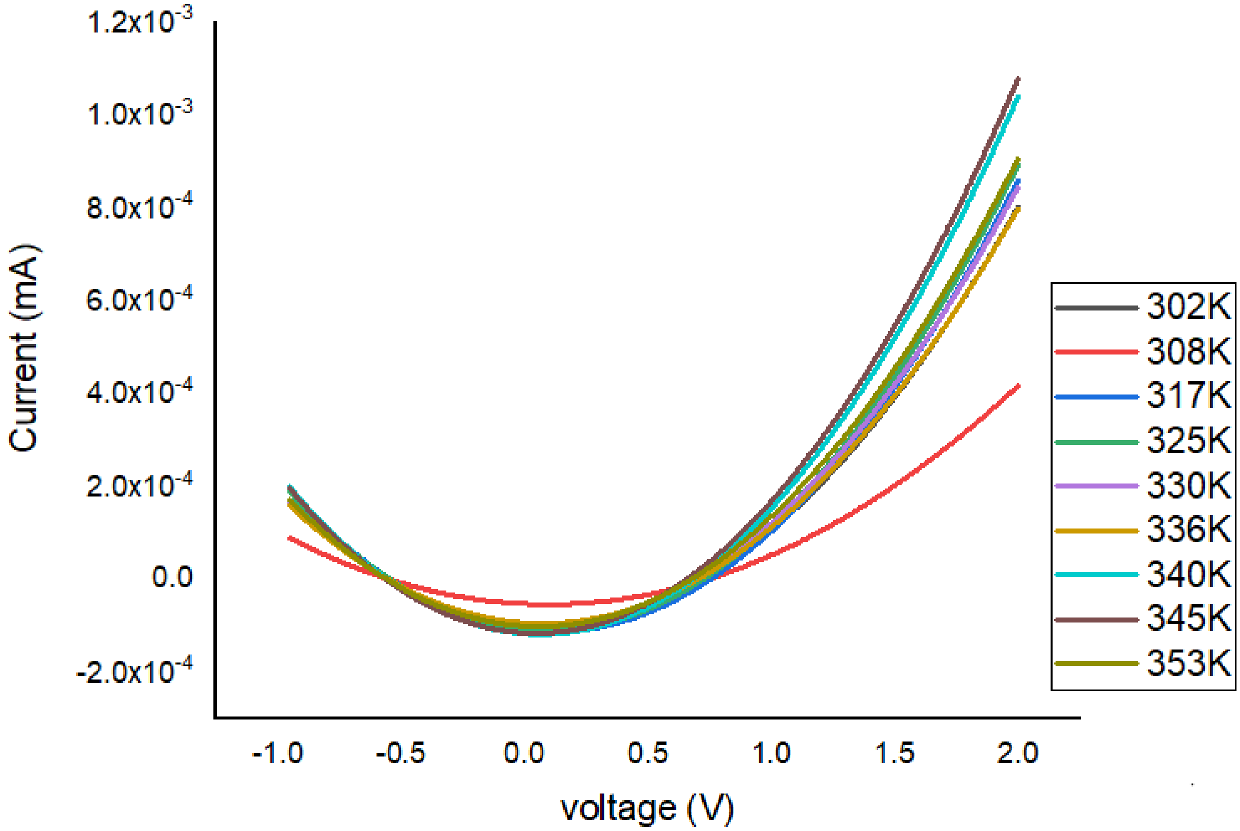


Figure 4.7: IV-curves of Si-Ag with different temperatures.

Figure 4.7 represents the effect of temperature on the IV-Characteristics of Si-Ag. From the curves, we can see that increasing the temperature increases the conductivity until 345K, and then it started to decrease.

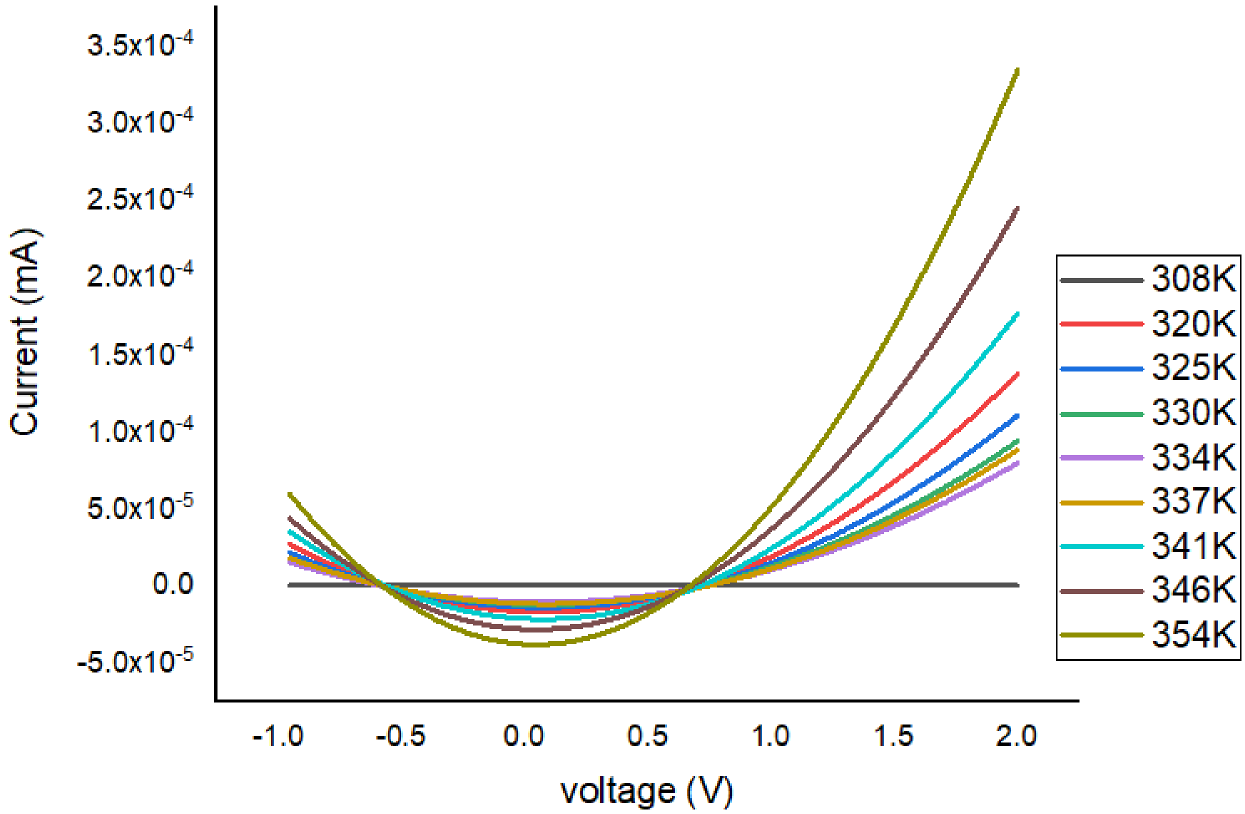


Figure 4.8: IV-curves of Si-cin-Ag with different temperatures.

Figure 4.8 represents the effect of temperature on the IV-Characteristics of Si-cin-Ag. From the curves, we can see that increasing the temperature started to increase the conductivity until 320K, and then it started to decrease until 334K, then it increased.

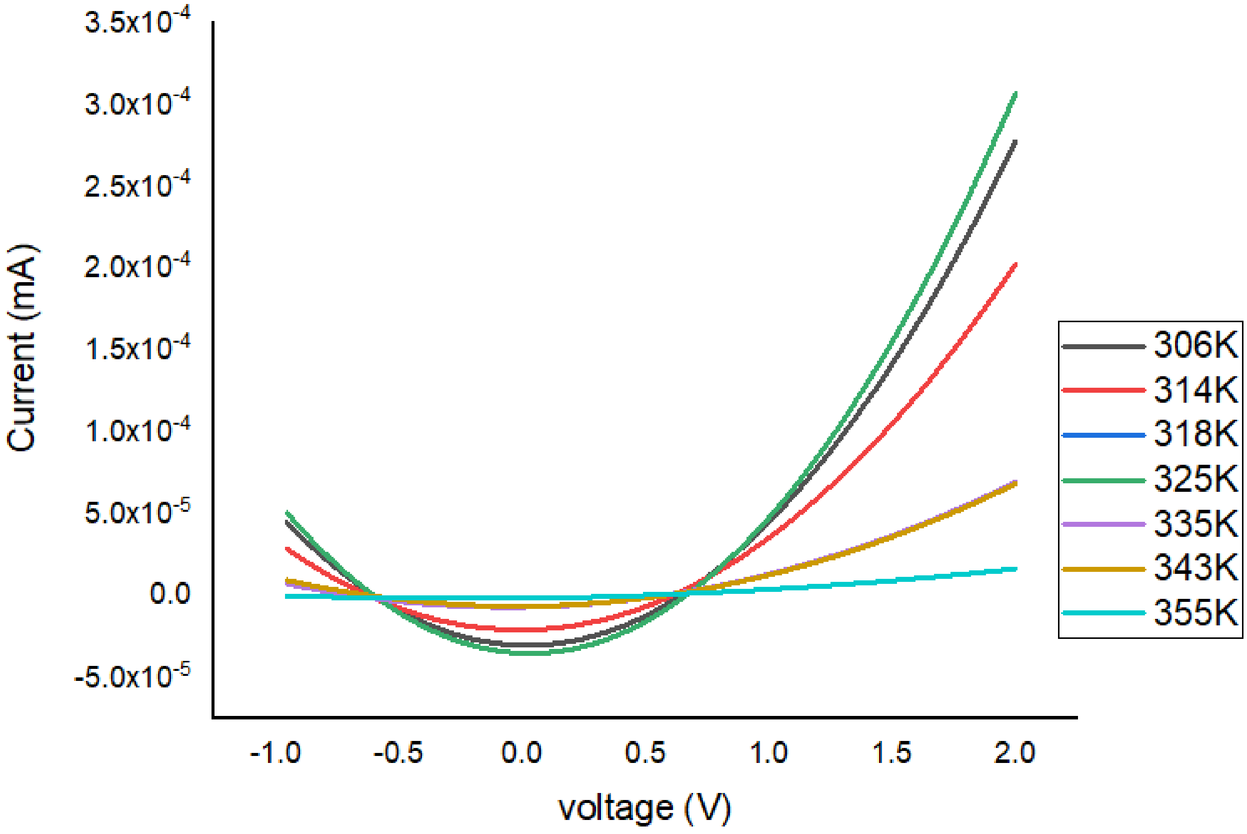


Figure 4.9: IV-curves of Si-PEDOT-Au with different temperatures.

Figure 4.9 represents the effect of temperature on the IV-Characteristics of Si-PEDOT-Au. From the curves, we can see that increasing the temperature decreased the conductivity of the Schottky diode.

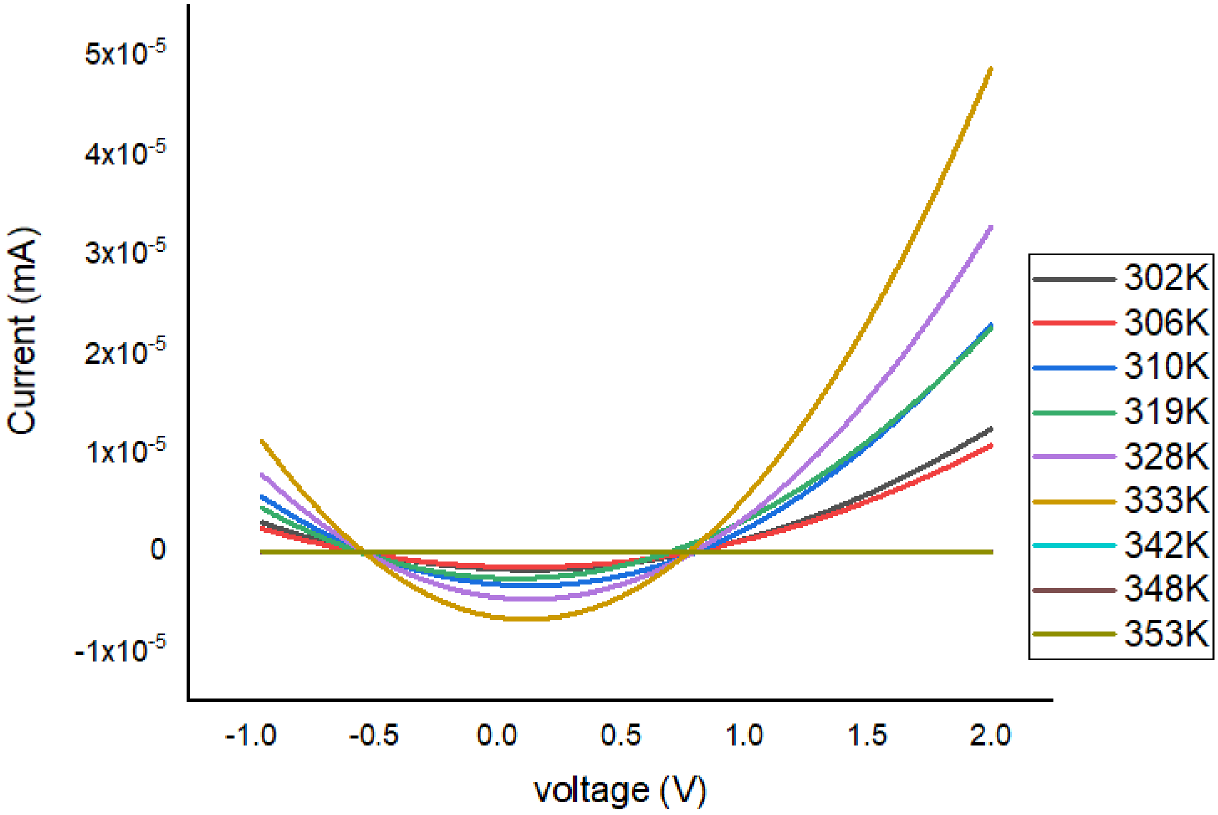


Figure 4.10: IV-curves of Si-PVA-Ag with different temperatures.

Figure 4.10 represents the effect of temperature on the IV-Characteristics of Si-PVA-Ag. From the curves, we can see that increasing the temperature started to increase the conductivity until 333K, and then it decreased.

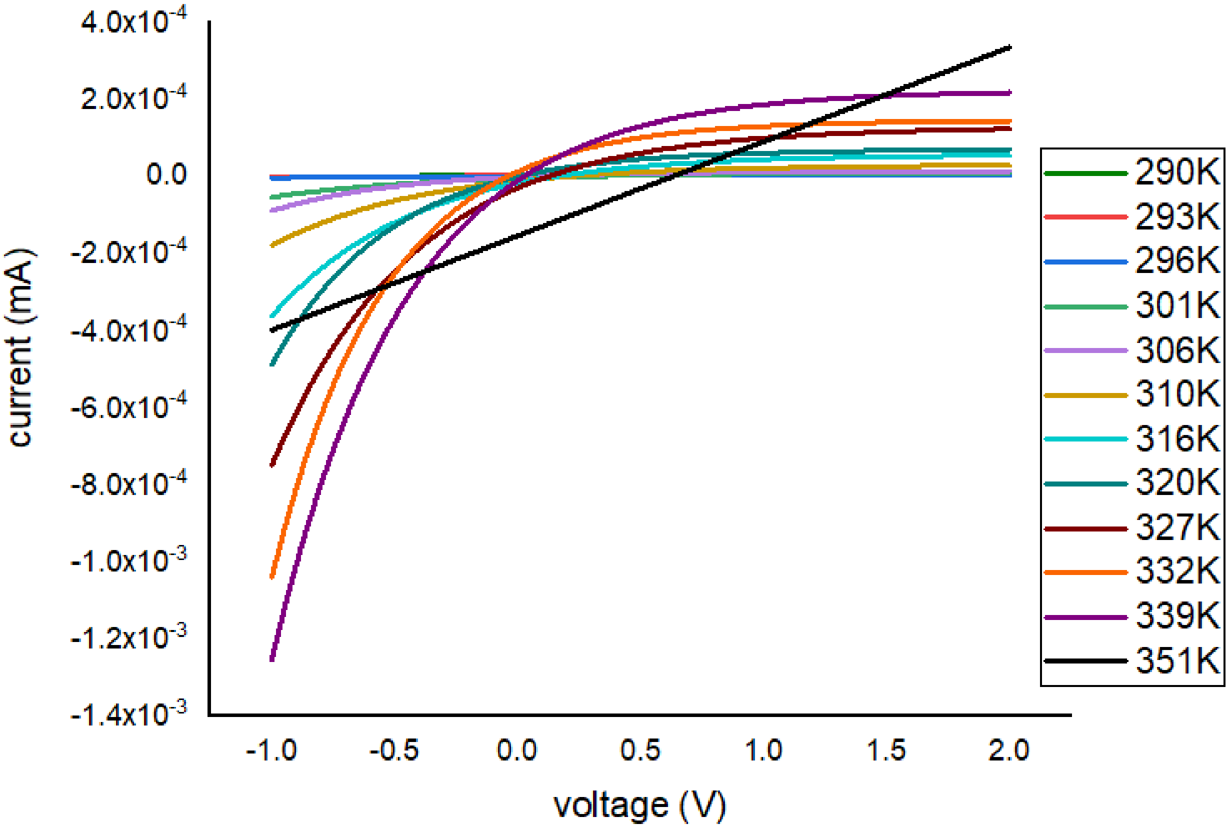


Figure 4.11: IV-curves of GaAs-Ag with different temperatures.

Figure 4.11 represents the effect of temperature on the IV-Characteristics of GaAs-Ag. From the curves, we can see that increasing the temperature decreased the conductivity and it became in the reverse bias.

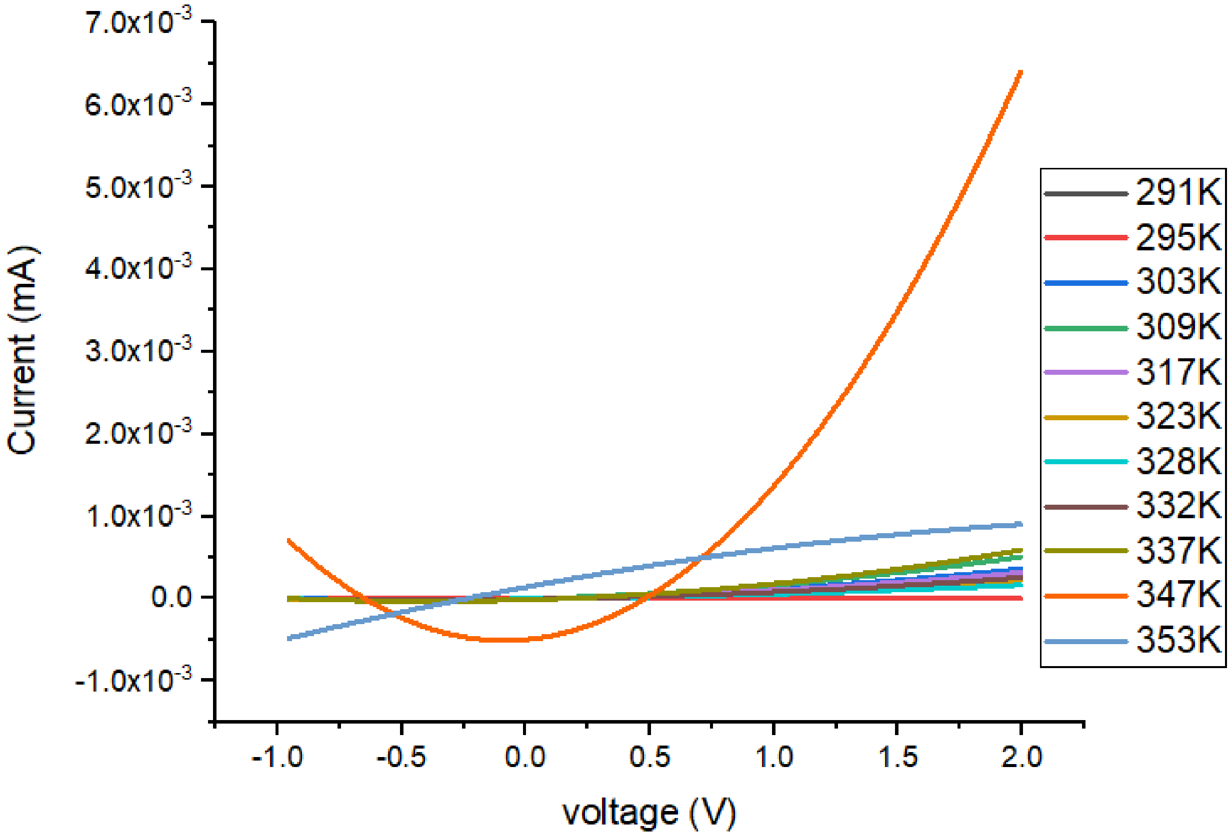


Figure 4.12: IV-curves of GaAs-Au with different temperatures.

Figure 4.12 represents the effect of temperature on the IV-Characteristics of GaAs-Au. From the curves, we can see that increasing the temperature started to increase the conductivity until 347K, and then it decreased and became in the reverse bias. Thus, due to the expanded of the depletion region, it will prevent the current from going through it except for a small current that is called the leakage current. However, the diode has a limited ability to stand with the reverse bias voltage. So, if the applied reverse voltage is too great, it will break down.

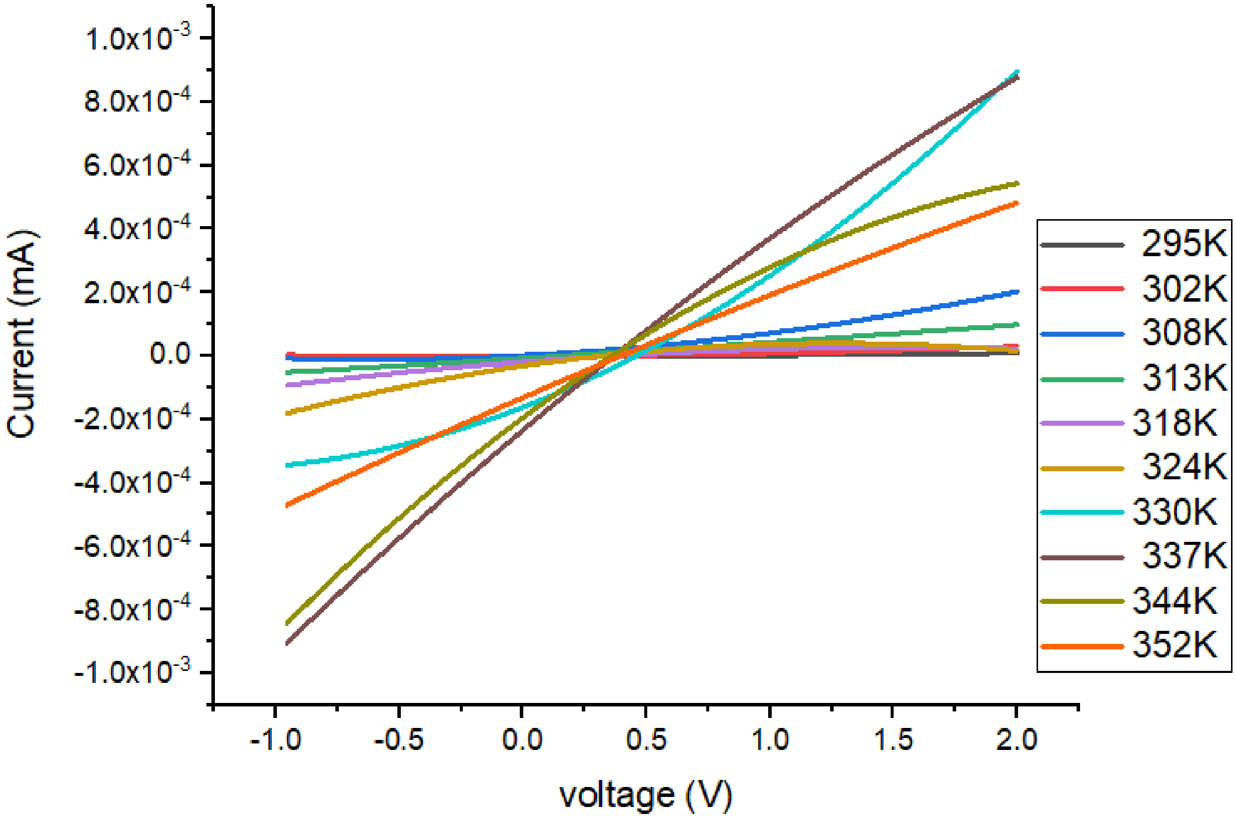


Figure 4.13: IV-curves of GaAs-cin-Ag with different temperatures.

Figure 4.13 represents the effect of temperature on the IV-Characteristics of GaAs-cin-Ag. From the curves, we can see that increasing the temperature started to increase the conductivity until 330K, and then it decreased and became in the reverse bias.

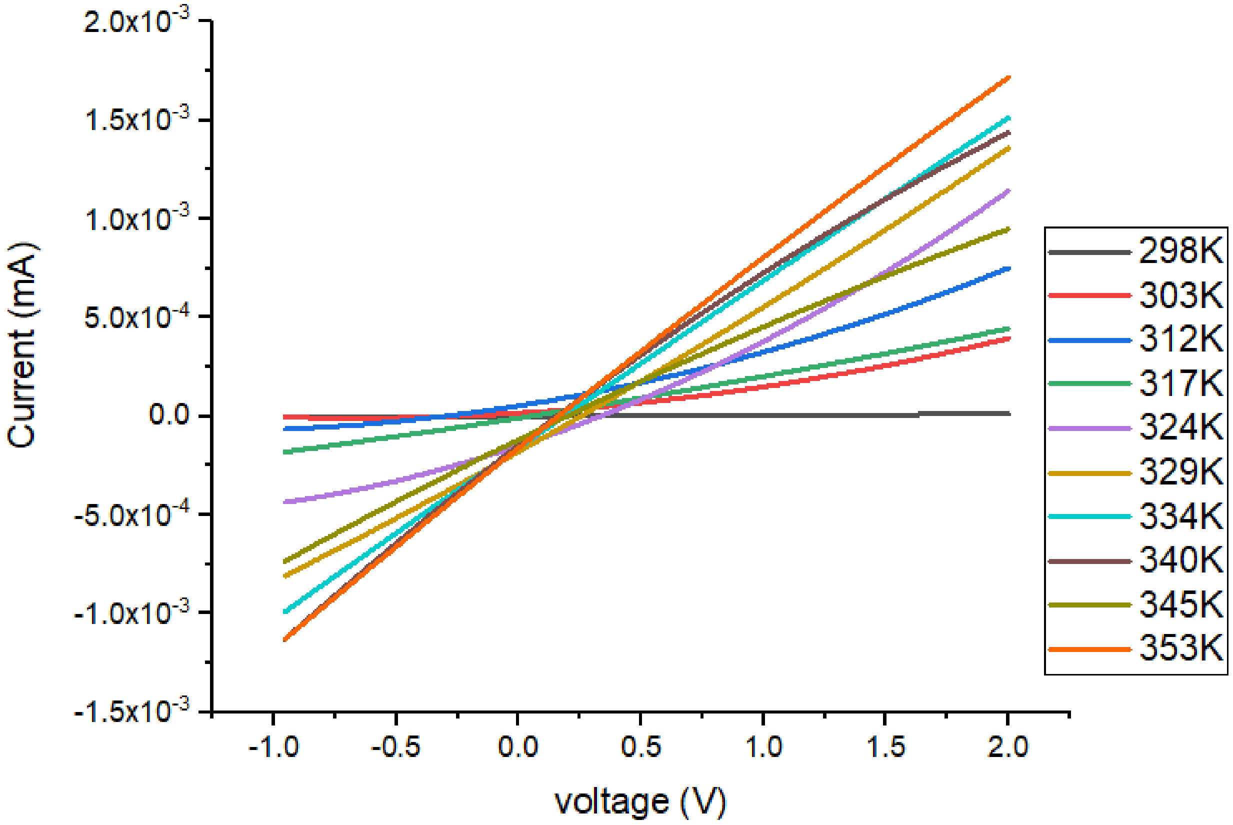


Figure 4.14: IV-curves of GaAs-PVA-Ag with different temperatures.

Figure 4.14 represents the effect of temperature on the IV-Characteristics of GaAs-PVA-Ag. From the curves, we can see that increasing the temperature started to increase the conductivity until 324K, and then it started to decrease and became in the reverse bias.

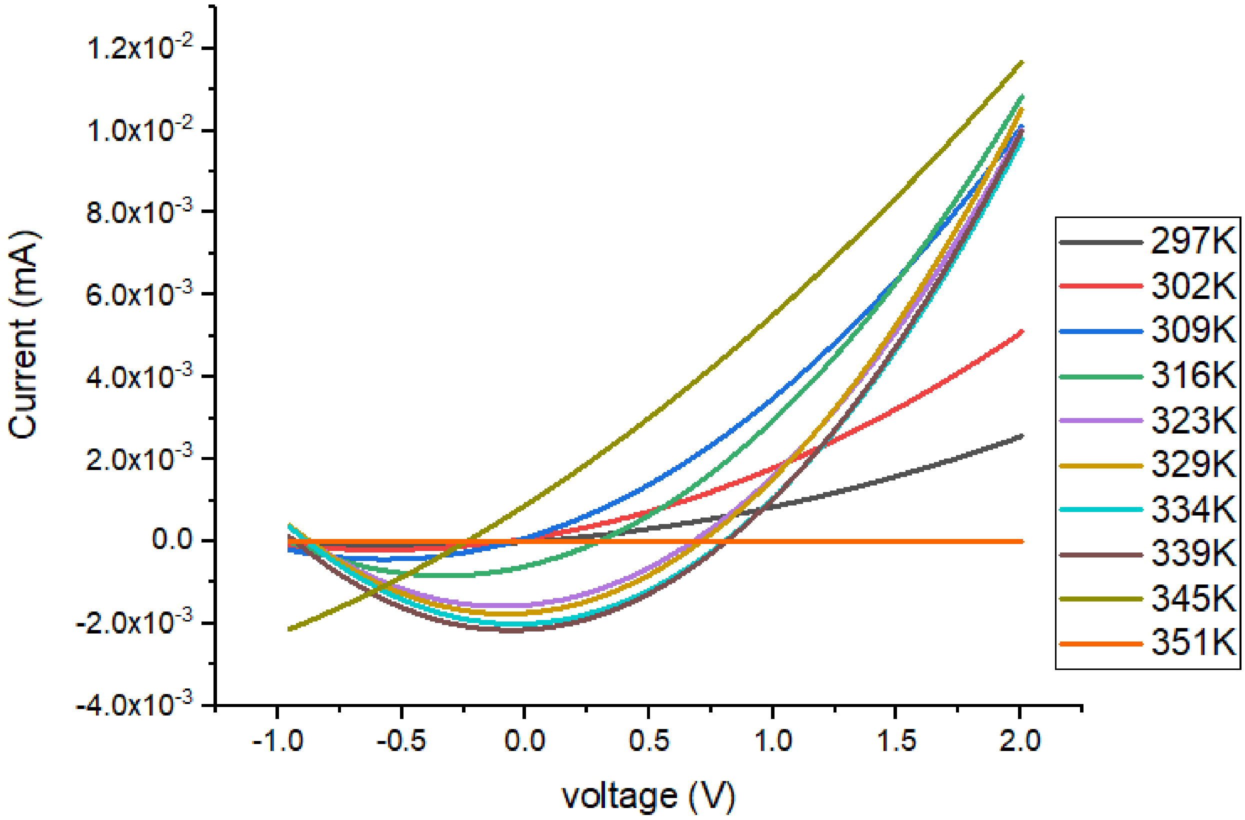


Figure 4.15: IV-curves of GaAs-PVA-Au with different temperatures.

Figure 4.15 represents the effect of temperature on the IV-Characteristics of GaAs-PVA-Au. From the curves, we can see that increasing the temperature started to increase the conductivity until 309K, and then it decreased.

## 4.4 Barrier Height and Ideality Factor:

The Schottky Barrier Height and the Ideality Factor are two important parameters in analyzing the IV-Characteristics of a Schottky diode. The Schottky Barrier height is the potential energy barrier for electrons formed at metal-semiconductor junction, and I obtained it from the extraction of the IV-curve due to equation 4 as in figure 4.16.

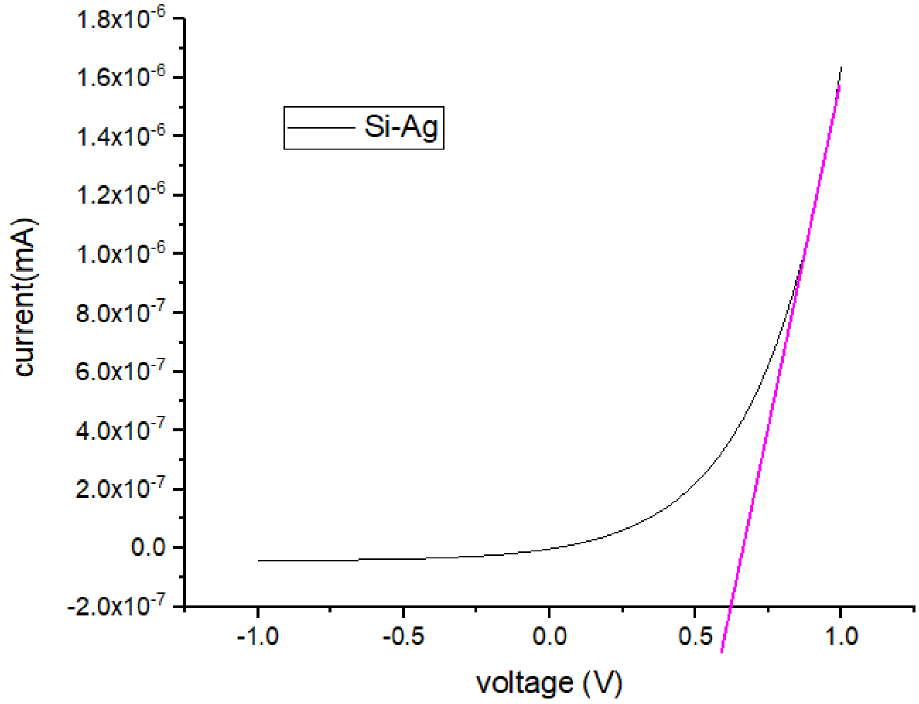


Figure 4.16: IV-curve of Si-Ag Schottky diode.

In figure 4.17, I graph ln I vs V, then I take the slope and the intercept of the forward bias. The intercept indicates the saturation current ($I_o$), and to get the value of the Ideality factor (n) I substitute the slope in eq.5.

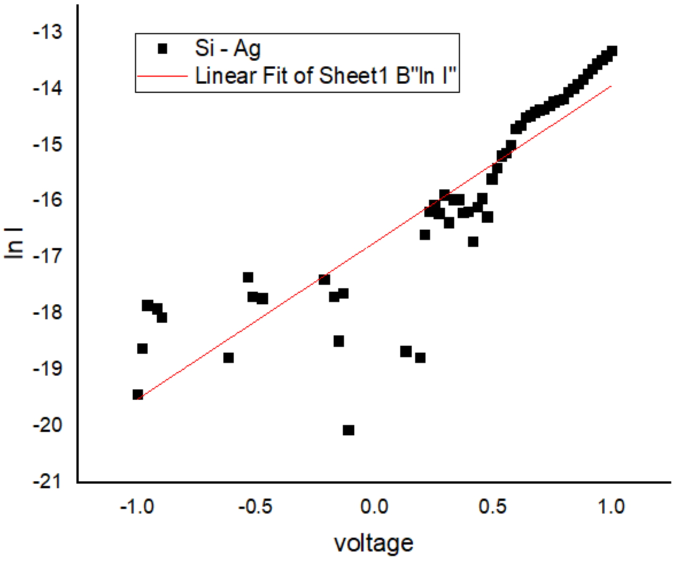


Figure 4.17: ln I – V curve of Si-Ag Schottky diode.

From figure 4.16, I got that the SBH is 0.6 eV. However, from figure 4.17, I got n is 2.79, $I_{\circ}$ is -16.7 mA. I did the same steps for all the samples to get the SBH, $I_{\circ}$ and n as in table 4.1 below.

Table 4.1: The values of the SBH, n And $I_{\circ}$ for the schottky diodes.

| Scottky Diode | SBH from the extraction of IV-Curve (eV) | N | $I_{\circ}$ (mA) |
|---|---|---|---|
| Si-Ag | 0.60±0.039 | 2.79±0.20 | -16.7 |
| Si-cin-Ag | 1.00±0.07 | 3.22±0.10 | -16.6 |
| Si-PVA-Ag | 1.40±0.18 | 3.57±0.097 | -18.6 |
| Si-Au | 1.00±0.18 | 0.08±0.02 | -12.89 |
| Si-PEDOT-Au | 0.75±0.01 | 3.83±0.09 | -16.2 |
| Si-cin-Au | 0.55±0.05 | 3.74±0.16 | -15.1 |
| Si-PVA-Au | 1.20±0.13 | 4.56±0.10 | -16.9 |
| GaAs-Ag | 0.70±0.01 | 1.79±0.08 | -17.6 |
| GaAs-cin-Ag | 0.42±0.09 | 4.05±0.28 | -17.5 |
| GaAs-PVA-Ag | 0.20±0.15 | 4.34±0.26 | -16.9 |
| GaAs-Au | 1.23±0.14 | 2.84±0.09 | -17.6 |
| GaAs-cin-Au | 1.30±0.16 | 7.38±0.23 | -20.6 |
| GaAs-PVA-Au | 0.30±0.12 | 3.07±0.27 | -16.6 |

From table 4.1, in Si-Ag Schottky diode we can see that adding the conjugated and the non-conjugated molecules both increased the SBH, decreased the conductivity, and the ideality factor increased.  For the Si-Au, adding the conjugated molecules decreased the SBH, increased the conductivity, but the non-conjugated molecule increased the SBH, decreased the conductivity. However, the ideality factor increased after adding the molecules. For the GaAs-Ag, adding the conjugated and non-conjugated molecules decreased the SBH, increased the conductivity, and the ideality factor increased. For the GaAs-Au, adding the conjugated molecule increased the SBH, decreased the conductivity, but adding the non-conjugated molecule decreased the SBH, increased the conductivity. However, the ideality factor increased.

# Chapter 5:Conclusion

In this thesis, different Metal-Moleulce-Semiconductor cells have been built and tested. IV-Characteristics have been taken and the parameters Shottky Barrier Height (SBH), saturation current $I_{\circ}$ and (n) have been measured. I used Si and GaAs as semiconductors, Ag and Au as metals, PEDOT and Cinnamic acid as conjugated molecules and PVA as non-conjugated molecules.

For the four basic samples Si-Ag, Si-Au, GaAs-Ag and GaAs-Au, we have seen from the IV-curves that Si-Ag has the lowest forward voltage drop, and GaAs-Au has the highest forward voltage drop.

After adding the molecules to the Schottky diodes, I have studied its effect on the conductivity of the schottky diode. For the Si-Ag Schottky diode, the conjugated and non-conjugated molecules increased the SBH, the forward voltage drop and n. For the Si-Au Schottky diode, the conjugates molecules decreased the SBH, the forward voltage drop and increased n. However, the non-conjugated molecule increased the SBH, the forward voltage drop and n. For the GaAs-Ag Schottky diode, the conjugated and non-conjugated molecules decreased the SBH, forward voltage drop and increased n. For the GaAs-Au Schottky diode, the conjugated molecule increased SBH, forward voltage drop and n. However, the non-conjugated molecule decreased SBH, forward voltage drop and increased n.

In addition, I studied the effect of the thickness on the conductivity. Therefore, I increased the thickness of the cinnamic acid on Si-cin-Ag Schottky diode, and I have realized that increasing the thickness of cinnamic acid molecule decreased the forward voltage drop and increased the conductivity.

Moreover, I studied the effect of temperature on the conductivity of the Schottky diodes. For Si-Ag, increasing the temperature increased the conductivity. For Si-cin-Ag, increasing the temperature increased the conductivity until temperature 320K then after that it decreased. For the Si-PEDOT-Au, increasing the temperature decreased the conductivity. For the Si-PVA-Ag, increasing the temperature increased the conductivity until temperature 333K then after that it decreased. For GaAs-Ag, increasing the temperature decreased the conductivity and the voltage became in the reverse bias. For the GaAs-Au, increasing the temperature increased the conductivity until temperature 347K, then after that, it decreased and the voltage became in the reverse bias. For the GaAs-cin-Ag, increasing the temperature increased the conductivity until temperature 330K, then after that, it decreased and the voltage became in the reverse bias. For the GaAs-PVA-Ag, increasing the temperature increased the conductivity until temperature 324K, then after that, it decreased and the voltage became in the reverse bias. For the GaAs-PVA-Au, increasing the temperature increased the conductivity until temperature 309K, then after that, it decreased.

## References

1. Ratner, M., *A brief history of molecular electronics.* Nat Nanotechnol, 2013. **8**(6): p. 378-81.
2. Amar H.Flood, J.F.S., David W.Steuerman,James R.Heath, *Whence Molecular Electronics?* . sciencemag, 2012: p. 3.
3. Ratner, M.A., *Introducing molecular electronics.* 2002: p. 8.
4. Xianneng Song, Bin Han, Xi Yu, Wenping Hu, *The analysis of charge transport mechanism in molecular junction based on current-voltage characteristics.* Chemical physics 528, 2019.
5. Paven Thomas Mathew, Fengzhou Fang, *Advanced in Molecular Electronics: A Breif Review.* Engineering 4 , 2018: p.760 – 771.

6. NASSAJY, A., *OPTIMIZATION OF ORGANIC SCHOTTKY DIODE CONTACT BY ELECTROCHEMICAL TREATMENT OF ELECTRODES*, in *Electronics and communications engineering*. 2015, Tampere University of Technology. p. 59.

7. Cahen, A.V.a.D., *Chemical Modification of Semiconductor Surfaces for Molecular Electronics* ACS Publications, 2017. **117**.
8. Khakbaz, S.G.a.M., *Measurement of I-V Characteristics of a PtSi/p-Si Schottky Barrier Diode at low Temperatures* World Academy of Science, Engineering and Technology 2011. **5**(9): p. 4.
9. Jang*, M., *Scalability of Schottky barrier metal-oxide-semiconductor transistors* Nano convergence, 2016. **3**: p. 7.
10. Adina Scott, a Chad Risko,2 Nicholas Valley,2 Mark A. Ratner,2 and David B. Janes1 *Molecular modulation of Schottky barrier height in metal-molecule-silicon diodes: Capacitance and simulation results* JOURNAL OF APPLIED PHYSICS 2010. **107**: p. 8.
11. Ghabboun, J., *Making Molecularly Modified Devices: The Impotance of Contact Deposition for Semiconductor/Molecules/Metal Junction Properties*. 2004, Weizmann Institute of Science. p. 131.
12. Ayelet Vilan, A.S., &David Cahen, *Molecular control over Au/GaAs diodes.* Nature, 2000. **404**: p. 3.

13. https://en.wikipedia.org/wiki/Molecular_self-assembly

14. http://academic.brooklyn.cuny.edu/physics/tung/Schottky/measure.htm

15. https://www.physics.ohio-state.edu/~gan/teaching/summer04/Lec5.pdf

16. http://www.chem.ucla.edu/~harding/ec_tutorials/tutorial13.pdf?fbclid=IwAR1Pd0CkxHhsY_2fkMp3lPIWwMKnB7IdkbkQNZ5vgIkAXBUfUPnf4iKOcN0

17. https://whatis.techtarget.com/definition/diode

18. http://www.electronicshub.org/characteristics-and-working-of-p-n-junction-diode/

19. http://www.physics-and-radio-electronics.com/electronic-devices-and-circuits/semiconductor-diodes/schottkydiode.html

20. https://www.radio-electronics.com/info/data/semicond/semiconductor/diodes-theory-basics-tutorial.php

21. http://inside.mines.edu/impl/Modules_5_6_Sample_Report.pdf

22. https://www.electronics-notes.com/articles/electronic_components/diode/schottky-barrier-diode-characteristics-specifications-parameters.php

23. Modoka Iwane, Shintaro Fujii, Manabu Kiguchi, *Molecular Diode Studies Based on a Highly Sensitive Molecular Measurement Technique.* Sensors, 2017,17,956.

24. Somayeh Gholami and Meysam Khakbaz, *Measurement of I-V Characeristics of PtSi/ p-Si Schottky Barrier Diode at low Temperatures.* International Scholarly and Scientific Research of Innovation, 5(9), 2011.

25. Anoop Prakash A B, J. Grace Jency, Manu Mathew, *A Review of Various Etching Techniques used in Micro Fabrication for Real Estate Consumption.* International journal of computer applications(0975-8887), 2013, 26-31.

26. Yue Kuo, *Semiconductor Spin Coating Method.* United state patent (4640846), 1987.

27. Niranjan Sahu, B Parija, S Panigrahi, *Fundemental Understanding and Modeling of Spin Coating Process : A Review.* Indian J. Phys.83(4), 2009, 493-502.

28. https://www.sciencedirect.com/topics/materials-science/spin-coating

29. http://nnfc.cense.iisc.ac.in/equipment/deposition/thermal-evaporator-system

30. http://ww2.che.ufl.edu/unit-ops-lab/experiments/semiconductors/evaporation/Evaporation-theory.pdf

31. Zaxhary A. King, Charles M. shaw, Sarah A. spanninga and David C. Martin, *Structural, chemical and electrochemical characterized of Poly (3, 4 – Ethylenedioxythiophene) (PEDOT) prepared with various counter – ions and heat treatments.* Polymer (52), 2011, 1302-1308.

32. https://en.wikipedia.org/wiki/Cinnamic_acid

33. https://en.wikipedia.org/wiki/Polyvinyl_alcohol

34. Gregory C. Desalvo, Christopher A. Bozada, Jhon L. Ebel, David C. Look and Jhon P. Barrette, *Wet Chemical digital etching of GaAs At room temperature.* J. Electrochem. 143(11), 1996, 3652-3656.

35. Banqiu Wu, Ajay Kumar and Sharma Pamarthy, *High aspect ratio silicon etch: A review.* Electrochimica Acta, 53, 2008, 5509-5516.

36. Tadahiro Ohmi, *Total room temperature wet cleaning for Si substrate surface.* J. Electrochem, 143(9), 1996, 2957-2964.

37. M. Steinert, J. Acker, S. Oswald and K. Wetzig, *Study on the Mechanism of silicon Etching in* $HNO_3$ *– Rich* $HF/HNO_3$ *mixtures.* J. phys. Chem. C, 111, 2007, 2133-2140.

38. Hassan Ghalami Bavil Olyaee, Peter J. S. Foot, and Vincent Montgomery, *Electrical properties and I-V Characteristics of 5,14-dihydro-5,7,12,14-tetraazapentance Doped Schottky Barrier Diode.* J Theor Appl Phys, 9, 2015, 315-319.

39. Somnath Mahato, Debaleen Biswas, Luis G. Gerling, and Cristobal Joaquim Puigdollers, *Analysis of Temperature dependant Current-Voltage and Capacitance-Voltage Characteristics of an Au/* $V_2O_5$*/n-Si Schottky Diode.* AIP ADVANCES, 7, 2017.

40. Demet Korucu, and Abdulmecit Turut, *Temperature Dependance of Schottky Doide Characteristics prepared with Photothography Technique.* International Journal of Electronics, 101(11), 2014, 1595-1606.