RECTIFYING EFFECT FROM PROTOTYPE DNA-SCHOTTKY DIODE

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ABSTRACT

In recent years, deoxyribonucleic acid (DNA) has been a targeted field of research due to its various properties and easy availability. Research findings have highlighted the semiconducting ability of the DNA molecule. However, proper understanding of its functionalities and properties, especially in the form of DNA film is inadequate. In this research, DNA thin films were prepared using the Langmuir-Blodgett (LB) method in the development of an Indium-Tin Oxide (ITO)/DNA/Aluminium (Al) Schottky diode. The thin film was analysed using structural and imaging techniques such as Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM). The film produced demonstrated a uniformly repeating pattern. The prototype sensor was then subjected to electrical characterisation involving acquisition of current-voltage (I-V) graphs, which suggested rectifying behaviour of the DNA molecule. Further studies of electrical behaviour revealed that electric field alignment improves electrical conductivity with a potential barrier of 0.796 eV for non-aligned films and 0.780 eV for aligned films. Significant improvements on measured ideality factor and series resistance post electric field alignment have also been observed. The results obtained suggest an exciting opportunity to achieve functional semiconductor properties for future research on fabrication of efficient and low-cost hybrid electronic devices based on DNA.

ABSTRAK

Beberapa tahun kebelakangan ini, asid deoksiribonukleik (DNA) merupakan bidang penyelidikan yang disasarkan kerana ciri-ciri yang amat menarik dan kesenangan untuk didapati. Hasil penyelidikan telah menghuraikan keupayaan molekul DNA sebagai suatu semikonduktor. Walaubagaimanapun, pemahaman yang terperinci tentang fungsi and ciri-ciri DNA, terutamanya dalam bentuk filem DNA adalah tidak mencukupi. Dalam penyelidikan ini, filem nipis DNA telah disediakan dengan kaedah Langmuir-Blodgett (LB) untuk digunakan sebagai diod Schottky indium besi oxida (ITO)/DNA/Aluminium (Al). Filem nipis ini telah dianalisa dengan teknik pengimejan struktur seperti Atomic Force Microscopy (AFM) dan Field Emission Scanning Electron Microscopy (FESEM). Filem yang dibentuk menunjukkan corak yang seragam. Seterusnya, prototaip peranti ini telah dianalisa dengan kajian elektrik untuk mendapatkan graf arus-voltan (I-V) yang mencadangkan ciri rektifikasi dalam molekul DNA. Pengajian yang lebih mendalam dalam ciri kekonduksian telah mendedahkan penjajaran dalam medan elektrik boleh meningkatkan ciri kekonduksian dengan potensi rintangan untuk filem yang tidak dijajarkan didapati adalah 0.796 eV dan filem yang telah dijajarkan adalah 0.780 eV. Peningkatan yang ketara untuk ciri-ciri diod selepas dijajarkan dalam medan elektrik juga boleh dikesan. Hasil penyelidikan yang diperolehi telah mencadangkan peluang baik untuk penghasilan semikonduktor berfungsi direkai dengan peranti elektronik hybrid yang menggunakan DNA sebagai bahan binaan yang cekap dan berkos rendah.

Last but not least, no one else has been more supportive than my family members and friends from various walks throughout my whole journey especially during difficult times. I am forever in debt to my parents, Mr. Chan Yet Wah and Mdm. Pang Sook Ching for their love and care towards me. To my close friends, Mr. Gregory Thien, Mr. Daryl Tan, Mr. Ban Fook Yun, Dr. Ho Wai Loon, Mr. Choo Shi Jin, Mr. Chan Yi Shin, Ms. Nicole Yew and Ms. Ng Peck Yee, thank you for morally supporting me all this time and now you can stop making fun of me as I have completed this Masters research.

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LIST OF ABBREVIATIONS

AFM   :   Atomic Force Microscopy

DNA   :   Deoxyribonucleic Acid

FESEM   :   Field Emission Scanning Electron Microscopy

FTIR   :   Fourier Transform Infrared

ITO   :   Indium-Tin Oxide

LB   :   Langmuir-Blodgett

LED   :   Light Emitting Diode

LEEPS   :   Low-Energy Electron Point Source

PCR   :   Polymerase Chain Reaction

SMU   :   Source Measurement Unit

TBE   :   Tris-Borate EDTA

UV-VIS   :   Ultra-Violet Visible

LIST OF APPENDICES

CHAPTER 1 :   INTRODUCTION

1.1   General Introduction

Research interest towards biomaterials has been rapidly increasing with various groups around the world exploring the feasibility of biomaterials replacing conventional electronics in the future world. Terminologies such as green technology or renewable technology have emerged as the goals of humankind in the 21st century as the awareness towards sustainable science continues to expand. Of all the various kinds of biomaterials which exist in the current biosphere, deoxyribonucleic acid (DNA) is the most well-known and often referenced in various contexts including non-scientific sources such as movies and media.

To the general public, the mention of DNA brings up thoughts of forensic science, genetic or biological information, or in more recent times-cloning of organisms. Those are some of the examples of the biological applications of DNA. On the other hand, DNA research has also been carried out in biology labs as biological sensors for the detection of diseases and infections.

Should we apply a more multidisciplinary approach to study the applications of DNA, an interesting proposition surface- *"What would happen if we were to use the DNA molecule as an electric conductor?"* An interesting new field of science coined "DNA electronics", which is basically using the DNA molecule as a substitute for the conventional electronic materials is formed. DNA electronics is a cross-disciplinary research which applies the knowledge of both the biological structure of DNA and the physical understanding of electric circuits and currents. Hence the term biophysics which also includes other types of cross-disciplinary research involving biology and physics.

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DNA electronics is currently at its birth stage of research where many people are still unaware of its existence and its applications. As we progress along the course of this dissertation, various prior research works, understanding of the DNA molecule, current conduction theories and applications of DNA electronics will be explained in detail to shed light in this new and exciting field of research which will undoubtedly shape the future of the electronics industry and humankind.

1.2   Background and Scope

The idea of this research was initiated by the simple thought of passing electric current through DNA molecules and studying the behaviour of these molecules while conducting electricity. Many queries surfaced such as the current conduction mechanism and the parameters which influences the conductivity of the molecule. Without a doubt, there are two main areas of focus in this research, which is the DNA and the rectification or diode-like behaviour of the electric conduction.

The biological applications of DNA are widely known due to the glamorisation in the media industry. However, as mentioned in the earlier section, DNA can also be used in the field of DNA electronics, which opens a whole new area of exciting research and study. Conventional electronics are mainly made up of semiconductor or metal materials which are non-renewable and will eventually become scarce in the future. We foresee that biomaterials such as DNA which are readily available and in infinite supply will one day be used as a replacement for conventional circuits.
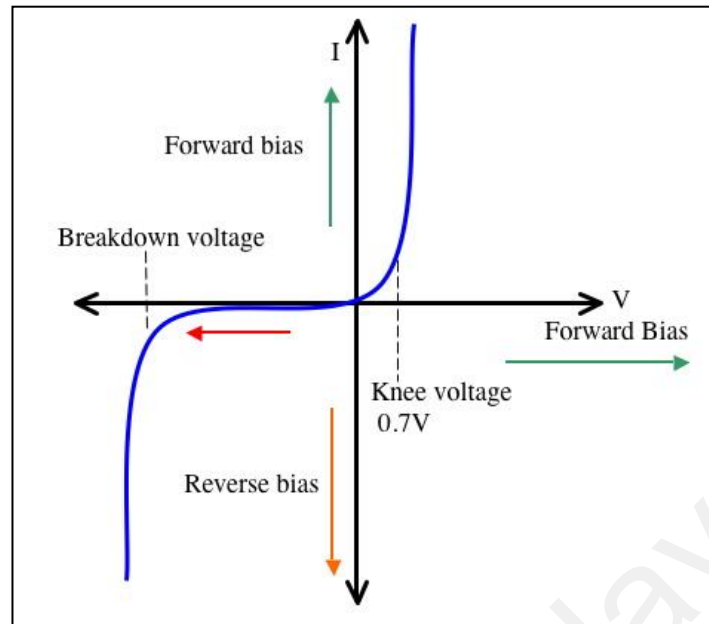
Figure 1.1: The rectifying behaviour of conventional diodes which only allow current to flow in one direction (O'Hanlon, 2000).

Diodes are electronic devices which allows current to flow in one direction only. Common current-voltage (I-V) graphs of diodes depict an exponential growth in the current with a small increase in the voltage, also known as a rectification behaviour. When connected in a way where the diode allows current to flow, the diode is said to be forward-biased and on the other hand, it is known as reverse-biased when it restricts current flow. **Figure 1.1** above illustrates the I-V graph of a conventional semiconductor diode, with the common diode parameters such as knee voltage and breakdown voltage included in the diagram. The most well-known form of diodes, the light-emitting diode (LED) are found in numerous uses and has proven to be extremely suitable to replace the aging technology of fluorescent lamps due to its efficiency of electric conduction.

In this work, we utilise the DNA molecules as a wafer to create a metal-DNA-metal device and study the effect of electric current conduction across it. Previous works have indicated that DNA has rectifying properties. By sandwiching the DNA with a metal, we are able to create a form of diode known as the Schottky diode. This DNA-Schottky

diode is a novel technology with potential applications ranging from biosensors to DNA detection devices.

1.3 Research Motivations

Whether DNA is a conductor, insulator, semiconductor or even superconductor has been a major topic of argument for different groups of scientists with varying results. In 1998, Braun et al., 1998 used a 12-16 μm long DNA molecule as a template for conducting silver wire connected to two gold electrodes. Later in 1999, Fink and Schönenberger reported that DNA molecules transport electric current just as good as an efficient semiconductor (Fink & Schönenberger, 1999). A paper published in 2000 by Porath et al., 2000 shows that the DNA molecules exhibit large band gap semiconductor behaviours. In the same year De Pablo et al., 2000 through experimentation and also calculation, suggests that DNA is an insulator, with minimum DNA resistance of 10^{16} Ω per molecule. Kasumov et al., 2001 published a paper showing that at temperatures below 1K, a proximity-induced superconductivity was observed (Kasumov et al., 2001). This result provides another argument on the conductivity of DNA.

Nevertheless, in 2004, Armitage et al., 2004 demonstrated that conduction of the DNA strand varies with humidity, implying that the conductivity is due to water molecules, instead of electrons. Similarly, Zhang et al., 2002 supported this result with their observation when the DNA was removed of salt and water that clings to it, it becomes an insulator with resistivity of >10^6 Ωcm. Moreover, further experiments done by Otsuka et al., 2002 and Ha et al., 2002 showed that the conductivity / resistivity of the DNA samples is dependent on the relative humidity of the chamber.

DNA-Schottky diodes are electronic devices fabricated using DNA as a substitute for the semiconductor material Silicon. Prior research done by Güllü and his team has

indicated that DNA-Schottky diodes portray rectifying behaviour and DNA has properties of semiconductor-like material (Ö Güllü et al., 2008). However, proper understanding of the fundamental properties of DNA conductivity is yet to be fully explored.

There are several models proposed to explain the conduction of DNA molecules including charge hopping mechanism or tunnelling mechanism. Roh et al., 2003 concluded that the dominant conduction mechanism in DNA is ionic conduction via proton transfer (Roh et al., 2003). However, DNA molecule's short-range conductivity can also be attributed to the tunnelling effect, which grows impossible at longer distances (Berlin et al., 2000).

The current work will look into the possibility of developing a prototype DNA-Schottky diode based on the ITO/DNA/Al structure. Thorough characterisation studies will be done to optimise the working conditions of this prototype device. Through this current work, investigation of the optimum parameters of the DNA-Schottky diode will shed light to the understanding of the electrical conductivity of DNA.

1.4   Objectives of Research

The objectives of this research work are as follows:

1) To fabricate a prototype DNA-Schottky diode

2) To study and analyse the composition of the DNA-Schottky diode using spectroscopic, morphology and characterisation techniques

3) To conduct I-V characterisation of the DNA-Schottky diode

4) To obtain optimal parameters for the working conditions of the DNA-Schottky diode fabricated in this work

1.5   Structure of Dissertation

The general overview of the structure of the dissertation in various chapters is presented as below.

Chapter 2. Literature Review

This chapter starts with the general introduction of the DNA and its discovery in the 18th century and subsequently the unravelling of the DNA double helix structure in the infamous paper published in 1953. In the same breathe, the structures of the DNA molecule is studied in this chapter as the groundwork for the understanding on the later chapters. The latter part of the chapter focuses on DNA electronics, where prior research on DNA conductivity, theories and DNA-Schottky are explained. Finally, the chapter concludes with the applications and importance of the current work.

Chapter 3. Experimental Methods

This chapter discussed the experimental methods involved in this project which includes the extraction of the DNA and the preparation of the materials. Also, the characterisation techniques to study the properties of the DNA-Schottky diodes were described. Finally, the detailed methods and techniques employed for electrical measurements of the DNA-Schottky diodes were presented.

Chapter 4. Results and Discussion

The obtained characterisations results and the corresponding discussions to understand it's structural and properties of the samples were documented in this chapter. Then, the results of the electrical measurement was explained in detail. At the end, an analysis of the electrical measurement was done to further understand the factors influencing the current conduction mechanisms of the DNA molecule.

Chapter 5. Conclusions and Future Works

In this final chapter, an overall summary of the findings of this work is concluded and presented. Further to that, suggestions for future works utilising DNA-Schottky diodes were provided at the end of this chapter.

CHAPTER 2 :   LITERATURE REVIEW

2.1   Overview

This chapter is divided into five sections. The first section covers the general introduction of the DNA molecule, from the initial discoveries of the molecule to the forming of the structure. The second section explains the various structures and forms of DNA and its constituents. Subsequently, a detailed explanation of DNA electronics and prior works done in the field is provided. Next, a complete section of this chapter is provided to explain the various forms of DNA-Schottky diodes and its potential uses as previous works has indicated. Finally, the various applications of DNA electronics and its relation to the work done in this study is discussed.

2.2   Introduction to DNA

DNA is a molecule well-known for the genetic functions of every organism and its hereditary information, which is passed down from parent to child. As often portrayed in media and movies, the applications of DNA in the field of forensic sciences has been well acknowledged. The DNA molecule is so well known that in fact, it would be suffice to say that every science museum or gallery in the world would not be complete without featuring the double helix model (**Figure 2.1**) of the DNA molecule.
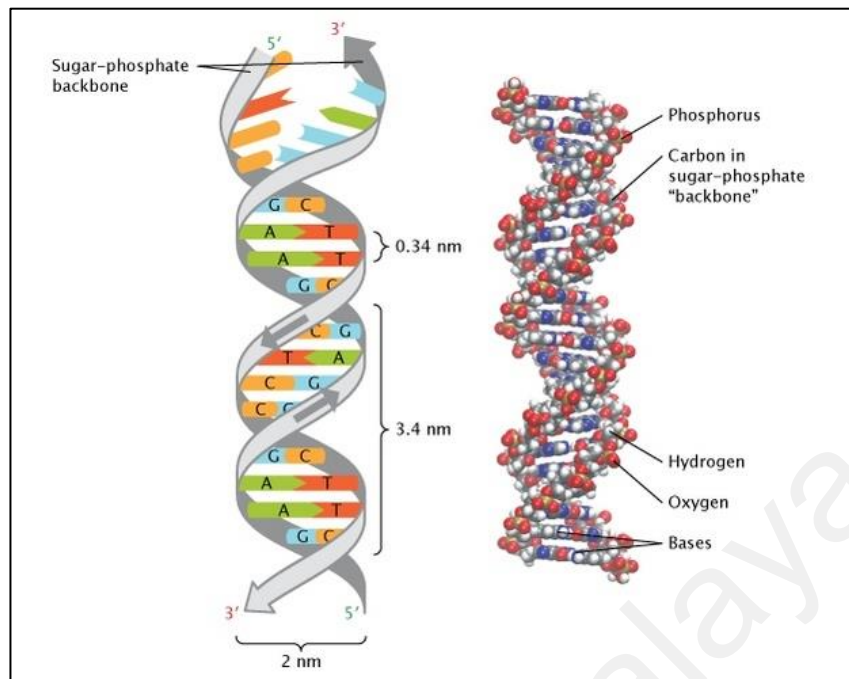
Figure 2.1: The double helix model of DNA (Pray, 2008).

However, the identification and understanding of the molecule was not a single discovery by an individual but yet a collective learning of the molecule over the years to achieve what we understand of the molecule today. The DNA double helix model Nobel Prize award in 1962 stands out as the most notable discovery, but yet it would have been impossible without the prior discoveries and contributions of other researchers.

2.2.1 Initial Discoveries

The first observation on DNA was by biochemist Johannes Friedrich Miescher in 1869 who discovered a new matter extracted from the cell nucleus that he named *nuclein*, which is what we know today as nucleic acids (Zon, 2015). He made this discovery in the laboratory of Felix Hoppe-Seyler, who was one of the pioneers of physiological chemistry then. According to the book "Friedrich Miescher & the Story of Nucleic Acid" (Tracy, 2006), in Miescher's own words,

"I had set myself the task of elucidating the constitution of lymphoid cells. I was captivated by the thought of tracking down the basic prerequisites of cellular life on the simplest and most independent form of animal cell."

"I was faced with the task of determining, as completely as possible, the chemical building blocks whose diversity and arrangement determines the structure of the cell. For this purpose pus is one of the best materials."

The method he used was isolating the white blood cells made readily available from pus from fresh surgical bandages in the local surgical clinic. Eventually, Miescher had managed to produce a precipitate of DNA which he named *nuclein*.

"...I could obtain precipitates that could not be dissolved either in water, acetic acid, very dilute hydrochloric acid, or in solutions of sodium chloride, and which thus could not belong to any of the hitherto known proteins."

By studying the composition of the precipitate, Miescher tried to investigate the elements in *nuclein* and he discovered that there were large amounts phosphorus in addition to other elements such as carbon, oxygen, hydrogen and nitrogen. Although his work was completed in 1869, it was only in 1871 that his manuscript titled "*Ueber die chemische Zusammensetzung der Eiterzellen*" (Miescher-Rüsch, 1871) which was German for "On the Chemical Composition of the Pus Cells" was published as Hoppe-Seyler was sceptical of the results and opted to repeat the experiments himself.

At that time, Miescher had guessed that this material has a fundamental role in hereditary due to its presence in other cells. He intuited that his discovery of this new substance will be of equal importance to proteins. At the concluding remarks of his publication, he wrote:

"This is how far I have come based on the material at my disposal. It is obvious that elementary analyses apart, a number of simple and obvious experiments are missing,

which would likely give essential information on the relationship between nuclein and the other hitherto known groups [of molecules]. I myself will, as soon as possible, report further news. However, I believe that the given results, albeit fragmentary, are significant enough to invite others, in particular chemists, to further investigate the matter. Knowledge of the relationship between nuclear substances, proteins and other closest conversion products will gradually help to lift the veil which still utterly conceals inner processes of cell growth."

2.2.2 Subsequent Contributions to DNA Research

Prior to the discovery of the double helix structure, two notable findings paved the way to understand this elusive molecule. Previously, it was believed that proteins served the function of carrying genetic information. The connection between nucleic acid and genes was not discovered for a long time after Miescher's work until the contribution of Oswald Theodore Avery Jr. in 1944 (Avery et al., 1944).

In the paper published, Oswald Avery together with his co-workers Colin Macleod and Maclyn McCarty designed an experiment known as the Avery–MacLeod–McCarty experiment to report that DNA was the substance that causes bacterial transformation. In the experiment, they had managed to transfer the ability that cause diseases from across bacterial strains. On top of that, it was discovered that the previously harmless bacteria could pass the new trait to the next generation. The substance moved which carried the genetic information was nucleic acids, which led Avery and his colleagues to suggest that DNA, rather than proteins are the hereditary material of the bacteria and possibly other biological organisms. As they concluded in their 1944 paper:

"If the results of the present study on the chemical nature of the transforming principle are confirmed, the nucleic acids must be regarded as possessing biological specificity the chemical basis of which is as yet undetermined."

Upon reading Oswald Avery's research on the gene, Erwin Chargaff, an American scientist furthered this research by discovering two rules which helped to shed light on the DNA structure. Chargaff wrote the following in the Preface to a grammar of biology: A hundred years of nucleic acid research (Chargaff, 1971), where he referred to Avery's finding as a stimulation for his research:

"I saw before me in dark contours the beginning of a grammar of biology.... Avery gave us the first text of a new language, or rather he showed us where to look for it. I resolved to search for this text."

By that time, scientists knew that the DNA molecule was made up of four bases or components, adenine (A), thymine (T), guanine (G) and cytosine (C). However, the components were organised so simply that many people thought the proteins and not the DNA carried the genes, even after Avery's publication. Erwin Chargaff had used techniques such as paper chromatography and ultra violet spectroscopy to measure the precise amount of bases in a DNA sample.

In 1950, Chargaff published his works (Chargaff, 1950) consisting of two findings. Firstly, he found a pattern where the number of adenine would match the number of thymine and guanine would equal cytosine. Furthermore, he observed that the number of guanine/cytosine and adenine/thymine varied among different species but remained the same for the same species; which laid the grounds of what we know now that DNA sequences are variable and species specific. This is now known as Chargaff's rules studied by biological students around the world.

2.2.3 Discovery of the Double Helix Model

Almost a century after the discovery of *nuclein* by Miescher, the Nobel Prize in Physiology or Medicine was awarded to James Dewey Watson, Francis Harry Compton Crick and Maurice Hugh Frederick Wilkins in 1962 "for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material" (Nobel Prize, 2014).

The pursuit to understand and unravel the structure of the DNA molecule was intensified in the late 1940s by three separate groups (Oregon State University Libraries, 2015). Maurice Wilkins and Rosalind Franklin in Kings College London, Linus Pauling in California Institute of Technology and the American PhD student James Watson with Francis Crick in University of Cambridge were all working intensively on the DNA structure at the same time with each group vying to be the first to suggest a proper structure for the DNA molecule.

Wilkins and Franklin were using X-ray crystallography which is a technique to determine the three-dimensional structure by studying the X-ray diffraction patterns to study DNA. Using the images of the formed X-ray patterns, Rosalind Franklin had an idea where maybe the DNA molecule was coiled into a helical shape, however she had no supporting proofs to that claim.

Other the other side of the world, Pauling was eager to solve the mystery of the DNA shape. In early 1953, he published a paper "Proposed Structure for the Nucleic Acids" (Pauling & Corey, 1953) suggesting a triple-helical structure for DNA as seen in **Figure 2.2**. However, there was a major error as he placed the phosphate groups in the inside of the structure. Watson and Crick has previously advanced that structure a year prior to that but was rejected on chemical and physical grounds as Chargaff's observation of

equal number of A-T and G-C bases would not be able to be applied. In the race to be the first, Pauling had erred.
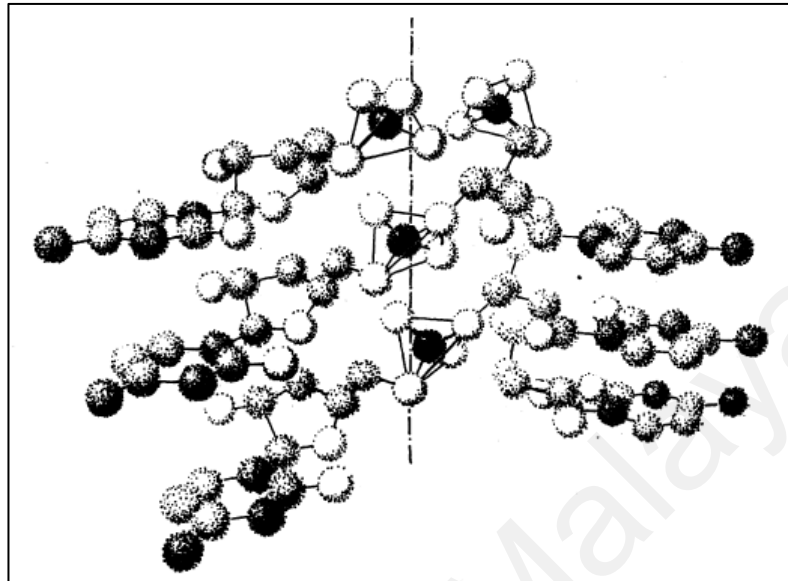
Figure 2.2: The incorrect model of the Pauling-Corey structure of DNA as published in the paper (Pauling & Corey, 1953).

In the Cavendish Laboratory, Watson and Crick opted for a model building approach to crack this mystery. They had an idea where the structure of the molecule had to be able to replicate during cell division to allow genetic information to pass to new cells. In 1952, Chargaff went to Cavendish for a visit. Although the meeting wasn't a success and both parties disliked each other, Chargaff told the two all he knew about the molecule at the time (Hunter, 2000).

With the publication by Pauling, it spurred Watson and Crick to greater determinations to come out with their own model of DNA. By a stroke of fate, during a visit to King's College, Maurice Wilkins showed James Watson "Photograph 51" (**Figure 2.3**), an unpublished X-ray pattern of B form of DNA obtained from results of Rosalind Franklin and Raymond Gosling, her PhD student working on the same project. Previous works had used the A form of the DNA molecule, which had less water and the image was hard to analyse. In Photograph 51, the helical structure of molecule could

be seen clearly. With much excitement, Watson raced back to Cavendish to share this latest development to Crick.
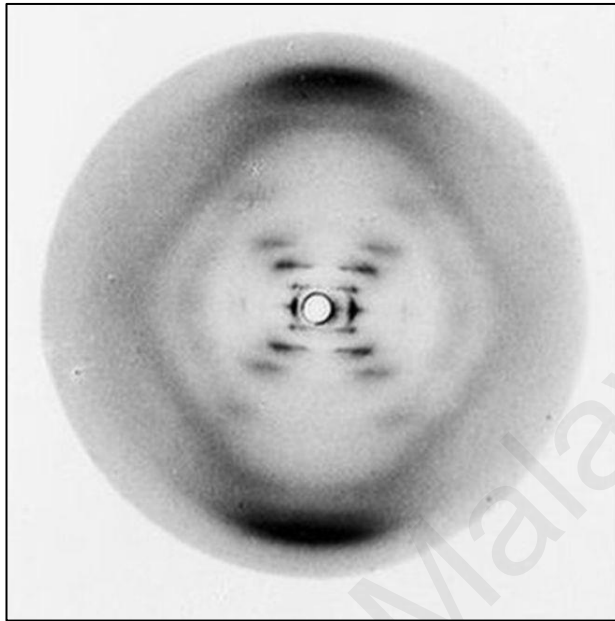
Figure 2.3: Photograph 51 as pictured by Rosalind Franklin and Raymond Gosling (LeMieux, 2016).

Using cardboard cut-outs of the bases, Watson was trying to fit them in a helical model reveal by the X-ray pattern of Photograph 51. From the X-ray data, they knew that the DNA must consist of two anti-parallel chains and the backbone had to be outside but they did not know how to make use of the Chargaff's findings of the bases. During an interview with Watson (Conova, 2003), he shared:

"Francis kept telling me there's Chargaff's pairs; would they pair to each other? But I didn't like Chargaff, ever since I had met him a year before. I thought: I don't want to use his data in finding the structure. Boy, it was really stupid. But I couldn't help, you know, just switching around on the table to see that adenine and thymine had formed a very nice base pair and guanine and cytosine formed one identical in shape, and I thought you can build a double helix with adenine and thymine and guanine and cytosine base pairs."
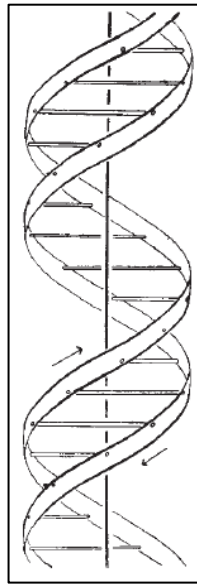
Figure 2.4: Structure of DNA proposed by Watson and Crick in Nature (Watson & Crick, 1953).

The final clue for the structure came with another visitor, American chemist Jerry Donohue who pointed out hydrogen bonding to allow A to pair with T and G with C (Watson, 2012). All this information allowed the double helical structure of the DNA, where two strands had the bases on the inside paired up, with the phosphate backbone on the outside.

On April 25, 1953, Watson and Crick published their structure of DNA in Nature where the double helix structure (**Figure 2.4**) was unveiled to the world for the first time (Watson & Crick, 1953). In the same issue, Wilkins published the X-ray pattern of the DNA structure (Wilkins et al., 1953). Watson and Crick also hinted in the Nature paper that the suggested structure allowed for the function of gene replication which was proved right in experiments years later. As they wrote at the end of the Nature paper:

"It has not escaped our notice that the specific pairing we have postulated immediately suggests a possible copying mechanism for the genetic material"

Watson et al., 1962 went on to win the Nobel Prize in 1962. At that time, Franklin had passed away 4 years earlier due to ovarian cancer, suspected as a result of the extended exposure to radioactive materials used in the X-ray imaging technique. As the Nobel Prize is not awarded posthumously, Rosalind Franklin was not rewarded in the race to discovery of DNA structure; however her contributions was made abundantly clear by Watson and Crick, who's discovery of the DNA structure would not been made possible without the X-ray pattern she discovered.

2.3   Structure of the DNA Molecule
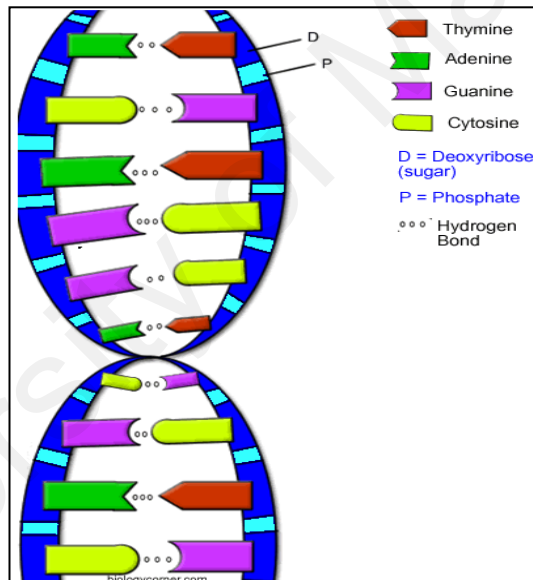
Figure 2.5: Structure of DNA depicting the four bases, phosphate backbone and the hydrogen bond between the bases (Biologycorner.com, 2001).

The most common form of DNA structure as depicted in the 1953 paper is a double helix structure which consists of two strands. Looking into the double helix structure (**Figure 2.5**), the DNA is actually made up of molecules known as nucleotides (Calladine et al., 2004). Each nucleotide contained a phosphate group, a sugar group and a nitrogen base. There are 4 types of nitrogen bases, which are adenine (A), thymine (T), guanine (G) and cytosine (C). The arrangement of these bases is what determines

the DNA's genetic code. This order, also referred as DNA sequence forms the genes, which tells the cells how to produce protein.
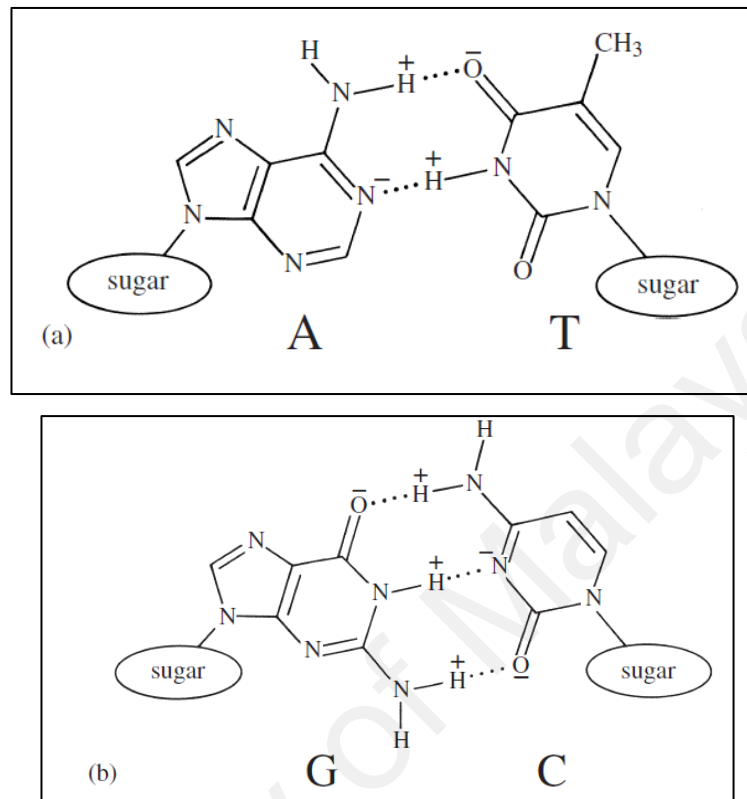
Figure 2.6: (a) Adenine-thymine base pair with two hydrogen bonding and (b) Guanine-cytosine base pair with three hydrogen bonding (Calladine et al., 2004).

The nucleotides are attached together to form two long strands which are spiral to create a structure called a double helix. Sometimes drawn in the form of a ladder, the phosphate and sugar are the sides and the bases are the rungs of the ladder forming a base pair. The nitrogen bases are complementary, which is either an adenine-thymine pair (**Figure 2.6 (a)**), which is form by a two-hydrogen bond, or a cytosine-guanine pair (**Figure 2.6 (b)**), which is a three-hydrogen bond. In that way, the base pairing is hence restricted.
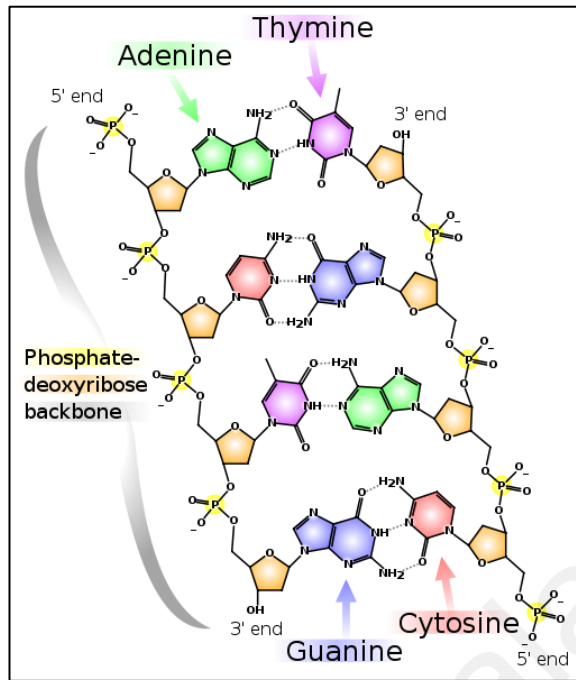
Figure 2.7: Structure of DNA with the bases as rungs and the chemical bonding (Biologycorner.com, 2001).

As seen in **Figure 2.7**, the DNA molecule is made up of two strands which are anti-parallel. The strands are label 5' and 3' indicating the directionality of the strands. The numbers 5' and 3' refers to the carbon number of the DNA backbone. In nucleic acids, 3' refer to the 3rd carbon in the sugar ribose or deoxyribose linked to the hydroxyl group and the 5' refer to the 5th carbon linked to the phosphate group.
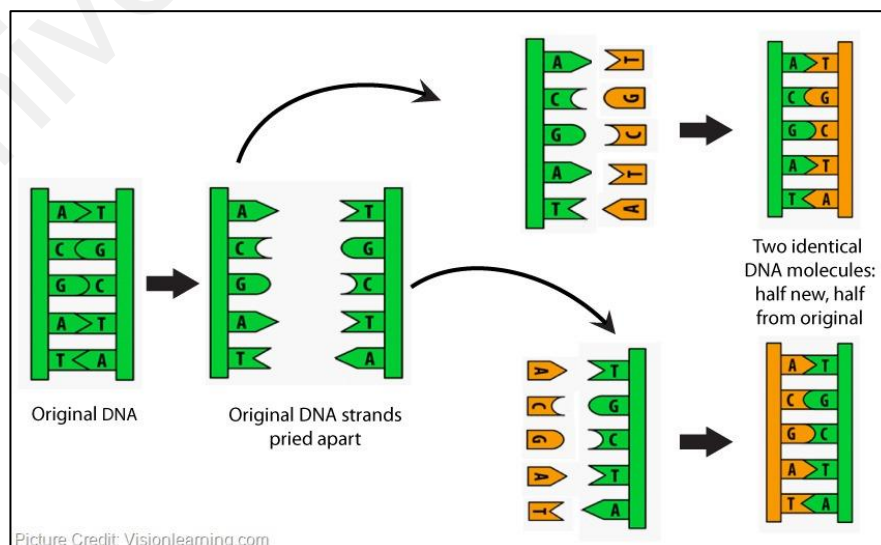
Figure 2.8: Schematic diagram of PCR process (Lents, 2010).

The base pairing restriction plays an important role when DNA is being replicated. The helical structure will be unzipped to form two long stretches of single strand DNA (Alberts et al., 2002). Each half will be used as a template for a new complementary strand. The cells will then arrange corresponding free bases into the single strand and after this process, two exact copies of the original DNA molecule are produced. This method is used in biological labs in a process known as polymerase chain reaction (PCR) as illustrated in **Figure 2.8**.

Figure 2.9: From left to right: A-DNA, B-DNA and Z-DNA (Carr, 2010).

DNA in its most common form of helix is known as the B-DNA. However, there are other forms of DNA namely A-DNA and Z-DNA. **Figure 2.9** shows the varying structures of A-, B- and Z-DNA. The structure of a DNA molecule depends on its environment (Calladine et al., 2004). In aqueous environments, including the majority of DNA in a cell, B-DNA is the most common structure. The A-DNA structure dominates in dehydrated samples and is similar to the double-stranded RNA and DNA/RNA hybrids. Z-DNA is a rare structure found in DNA bound to certain proteins (Calladine et al., 2004).

2.4 DNA Electronics

2.4.1 Conductivity in DNA

The possibility of electrical conductivity in DNA was first put forward in 1962 by Eley and Spivey not long after Watson and Crick's discovery of the DNA model (Eley & Spivey, 1962). At that period, fundamental questions regarding the mechanisms, charge behaviour and dynamics could not be pursued by researchers as DNA was difficult to obtain and synthetic DNA was not available yet. Early suggestions was that DNA could be a conductor due to the formation of the π-band across the different bases, but there was no substantiated data or results. Measuring electrical conductivity on the DNA molecule at that time was just a floating idea, without much means of possible thorough investigation.

In the early 1990s, the idea of DNA electronics started to be pursued with more vigour. Murphy et al., 1993 suggested that the electron transfer across DNA was responsible for the fluorescence quenching of an excited molecule but many had different opinions on the matter. Since early investigations, researchers have looked at electronic properties of the DNA and have found that it behaves as a conductor, semiconductor, or insulator with various contradicting results.

Contradictions in DNA electronics have been attributed to the large phase space where DNA can be prepared and DNA electronics can be investigated. Experimental conditions and attributes of the DNA used not limited to base sequence, base length, orientation, temperature, counterions, electrode and so on could affect its conducing properties (Di Ventra & Zwolak, 2004). Other difficulties include the complex aperiodic system of the DNA molecule. As a result, even though progress has been made in this aspect, the DNA transport properties are still in question.

Despite the many contradictions of electron transfer in DNA, the self-assembly properties of DNA is being used to create novel and unique nanoscale devices. Braun and team has successfully created a silver wire made using DNA as a template (Braun et al., 1998) whereas Winfree and his group (Winfree et al., 1998) has built various forms of DNA structures including 2 dimensional Holliday junctions arrays using the self-assembly nature of the DNA molecules. These structures suggest possible applications of DNA electronics including bio-transistors, biosensors, and even complex circuits made up of DNA.

2.4.2 Prior Works

The first direct measurement of the conducting properties of DNA was done by Fink and Schonenberger in 1999 (Fink & Schönenberger, 1999). It was found that DNA was a good conductor, where the I-V results represent resistance comparable to polymer conductors. This experiment was conducted in vacuum to eliminate other possible conducting factors, and a low-energy electron point source (LEEPS) microscope was used to image the DNA. A tungsten tip was used to apply a bias across the DNA and the measured resistance for a 600 nm portion of DNA was 2.5 MΩ. However, other works has suggested that the LEEPS imaging had contaminated the DNA and as such resulting in the conducting behaviour observed.

Majority of other researchers however has found out that DNA resembles a large band gap semiconductor. By measuring the conductivity of poly(G)-poly(C) DNA, Porath et al. (Porath et al., 2000) discovered that the DNA oligomer did not conduct charge for biases below 1 V at room temperature, a similar characteristics of a semiconductor with a large bandgap. Similarly, Watanabe's team (Watanabe et al,

2001) reported semiconducting behaviour of a double-strand DNA measured using an AFM with a carbon nanotube tip and a two-probe "nanotweezer".

On the other hand, De Pablo et al., 2000 performed measurements on the resistance of λ-DNA by depositing DNA on a mica surface with a gold electrode. A gold-covered AFM tip was used as a second contact. At different distances from the electrode, a lower resistivity limit of 10^4 Ω cm was found for the DNA molecule. This suggest that λ-DNA is an insulator, directly contradicting the previous results by Fink and Schonenberger. De Pablo suggest that the dispute can be due to the effect of the contamination from the low-energy electron beam used to image the DNA rope by Fink and Schonenberger which was proven when DNA samples resistivity was greatly reduced after irradiation.

Storm et al., 2001 measured the conductivity of single DNA molecules and bundles of DNA molecules. Results indicated that while measured in ambient conditions, a lower resistance limit of 10 TΩ is found for 10 mixed-sequences, 1.5 µm long DNA molecules in parallel on a SiO_2 surface. There have been suggestions that compression caused by the depositing of DNA on surfaces changes its electronic structure. In this case, DNA height was at 0.5 nm, suggesting that compression induced by the surface decreased the conductivity.

Besides semiconducting and insulating behaviour of DNA, Kasumov et al. reported proximity-induced superconductivity in DNA (Kasumov et al., 2001). Rhenium/carbon electrodes were deposited on a mica surface and a flow of 16 µm long λ-DNA solution parallel to the electrodes was introduced. The overall resistance of the structure decreased from 1 GΩ without any DNA molecules to a few kΩ after deposition. Three different samples of varying lengths were obtained and the effect of temperature to resistance was studied. All samples increased resistance as temperature decreased, but

samples of 10 DNA chains (DNA1) and 40 DNA chains (DNA2) decreased resistance below the superconducting transition of electrodes. Application of magnetic field increases resistance at temperatures close to superconducting transition, which is observed for proximity-induced superconductivity. Although inconclusive, results showed that proximity-induced superconductivity can be realized in DNA and thermal hopping is an unlikely mechanism of charge transport in λ-DNA as resistance does not increase directly with a decrease in temperature.

While the effect of ionic contamination to the DNA conductivity is well studied and noted by various researchers, other factors do influence the conductivity of DNA molecule. Lee et al., 2002 studied the effect of humidity and oxygen on the DNA molecule. Results revealed that trapped oxygen has been found to dope poly(G)-poly(C) DNA with holes and increased the conductivity. When poly(G)-poly(C) DNA was exposed to pure oxygen gas instead of air, the conductance of the DNA increased by more than 100 times. Alternatively when poly(T)-poly(A) DNA was placed in the similar condition, conductance of the DNA decreased. This results support initial findings that G-C DNA is a p-type conductor and A-T is an n-type conductor.

2.4.3 DNA Charge Transport Mechanisms

Over the past several years, many charge transport mechanisms have been proposed. This is not startling as there were various differing experimental results. Nevertheless, three main possible mechanisms for charge transport were suggested as the main processes: thermal hopping, sequential tunnelling and coherent tunnelling. The schematic of the processes are illustrated as in **Figure 2.10**.
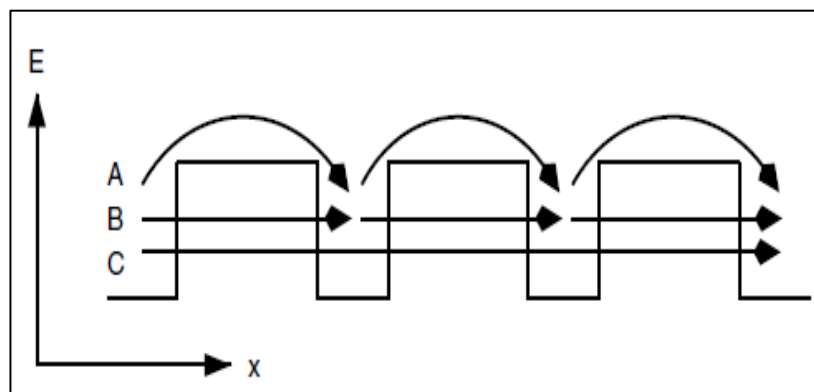
Figure 2.10: Schematic of three possible mechanisms of charge transfer in DNA (Di Ventra & Zwolak, 2004).

Thermal hopping refers to the process where charges thermally hop from base to base as per example A. However, the thermal energy required for this process is quite large. Charges could also tunnel from one site to another, as depicted in example B. After each tunnelling process, the coherence of the charge wavefunction is lost through dephasing processes such as scattering. Alternatively, as per example C, charges can tunnel through the whole length of a DNA. However, this mechanism depends heavily on the distance or the length of the DNA molecule.

As the charge transport over large distances by a single tunnelling step is unlikely and the high thermal energy required for thermal hopping, most researchers argue that sequential tunnelling is the most likely mechanism of charge transport in DNA. In this mechanism, holes have been studied as the likely charge carrier. Of the four bases, the G base is the most favourable site for hole locations due to the order of ionisation potential.

2.5 DNA-Schottky Diodes

Schottky diodes, also known as hot carrier diodes were named after German physicist Walter H. Schottky. It is made up of a metal-semiconductor junction which

creates the Schottky barrier (Mishra & Singh, 2007). Common metals used in conventional Schottky diodes are usually molybdenum, platinum, chromium or tungsten whereas the semiconductor would normally be n-type silicon. In contrast, DNA-Schottky diodes are made up of DNA as the semiconductor, and common metals used in prior works include Al and gold. In our work, the semiconductor material was the DNA isolated from *Mimosa pudica* whereas the metal was Al.

The study on DNA-Schottky diodes is a relatively new area. Nonetheless, there has been previous works done on the study of DNA-Schottky diodes with varying setups and its vast applications such as sensors in various fields including thermal, optical, radiation and magnetic are well documented (Al-Ta'ii et al., 2016; Ö Güllü & Türüt, 2011; Gupta et al., 2011; Khatir et al., 2012). These works explain the complexities and contributes to the understanding of DNA-Schottky diodes.

Güllü and his team are one of the pioneers in the subject of DNA-Schottky diodes with works as early as 2008. In one of the work published (Ö Güllü et al., 2008), an Al/DNA/p-Si Schottky device was fabricated using the self-drying method of the DNA solvent. Electrical measurements of the Schottky device had demonstrated rectifying effects and DNA has properties of semiconductor-like material with a wide band gap of 4.12 eV and resistivity of 1.6×10^{10} V cm representing p-type conductivity.

Various other works performed by Güllü and his team were published in the subsequent years with varying device setups and research outcomes. These includes an Al/DNA/p-InP type device which had a remarkable ideality factor of 1.26 (Ömer Güllü et al., 2008) and an Ag/DNA/p-InP type device with an ideality factor of 1.087 (Ö Güllü et al., 2012). Güllü et al. also studied the changes in electronic properties of Al/DNA/p-Si sandwich devices in regards to the temperature (Ö Güllü & Türüt, 2011). Results had indicated that ideality factor n and the barrier heights varied with a change of

temperature from 200-300 K, suggesting the suitability of the DNA-Schottky diodes as a temperature sensor.

Electrical characterisation of DNA-Schottky diodes were carried out by various groups throughout the years utilising different set-ups. All the works indicated rectifying behaviour of the device. Sönmezoğlu et al., 2010 had fabricated an Au/DNA/n-Si/Au set-up which had a typical ideality factor of 1.22. Meanwhile Okur et al., 2009 discussed the effect of thickness and coverage of DNA film on the electrical characterisation and interface properties of Au/DNA/n-Si Schottky diodes. The thickness and coverage rate of the DNA layer significantly affects the electrical properties of the Au/DNA/n-Si organic-on-inorganic structures. Al-Ghamdi et al., 2012 studied DNA based sensor and compared the electronic performance of DNA/Si junction with SiO_2/Si junction. The ideality factor for the DNA/Si junction is lower at 1.82 as compared to 3.31 for the SiO_2/Si junction.

Aside from the application of DNA-Schottky diodes as a temperature sensor, Gupta et al., 2011 had demonstrated in their work that an Ag/DNA/p-Si/Al diode can be used as an optical sensor. The photoresponse of the diode was measured with varying frequencies. At lower frequencies, the capacitance of the diodes was found to increase as an effect of the change in interfacial states. It was also observed that the series resistance of the diode is decreased with increasing light intensity and increased with decreasing frequency under constant light intensity.

DNA-Schottky diodes have also demonstrated its ability to behave as a magnetic and radiation sensor by prior works done. In 2012, Khatir et al., 2012 had studied the effect of magnetic field on Au/DNA/Au Schottky diodes and results indicated a decrease in conductivity with increase of magnetic field strength, suggesting a potential application as a magnetic sensor. More recently, Al-Ta'ii et al., 2016 studied the effect of alpha

particle radiation on an Au/DNA/ITO device. Barrier heights from I-V measurements were calculated from 0.7284 eV for non-radiated samples which increased to 0.7883 eV in 0.036 Gy of alpha radiation. Based on the results, the authors suggested that the Au/DNA/ITO Schottky junction sensor may be utilised as a sensitive alpha particle detector.

2.6 Applications of DNA Electronics and Importance of This Work

DNA electronics has come a long way since the first direct measurement of electrical measurement by Fink and Schonenberger. The great multitudes of the applications of DNA-Schottky diodes have been previously mentioned in the earlier sections including sensor applications and DNA detection devices. However, those are just the mere surface of the potential in DNA electronics.

In the field of nanotechnologies, DNA has been envisioned as a nanoelectronic device. This could be in the form of a DNA chip, where possible functions include DNA sequencing, disease screening, and gene expression analysis. With enough research in this field, DNA sequencing potentially can evolve from the conventional biological method of using florescent dyes to an electronical read out of the DNA sequence. This will allow a faster and more efficient sequence analysis of the DNA molecule. The feasibility of this work has already been confirmed by the publication by Periasamy et al., 2016 where electronic profiles were used to identify different mushroom species.

Aside from the applications of using the DNA as a chip, DNA can also be used as a support for fabricating conducting wires (Periasamy et al., 2015; Vengadesh et al., 2015). These template, using the phosphate backbone of the DNA molecule, attaches

metals on the backbone creating an extremely thin wire which could be use in nano-circuits and nanoscale electronic devices.

The other unique ability of the DNA molecule, the self-assembly property, allows DNA molecules to be manipulated to build complex nanowire geometrical arrangements. Complex nanostructures can be built with small molecules which could have numerous applications in the medical field. In fact, several devices have been constructed using this method including the first single-DNA field-effect transistor (Yoo et al., 2001). As the research in DNA electronics expands, more DNA based molecular electronic devices will be common.

Despite the numerous applications of DNA electronics detailed above, it is unfitting to limit the potential applications of such devices as with each passing day new technologies are developed. As of today, numerous research groups are studying DNA in its applications as Schottky diodes with much vigour due to its great potential. Then again, DNA electronics is still in its birth stage of research and many other applications may have yet to be discovered.

With the work done in this study, further knowledge can be contributed to this field of research especially in regards to the conductivity of the DNA molecule. DNA thin films, especially in the form of LB films are not widely researched and its properties in electrical conductivity are not explored. Furthermore, this work studies the effect of electric field alignment to the DNA molecule which contributes to the understanding of the multiple parameters that affects DNA conductivity, assisting in the fundamental research of DNA electronics.

CHAPTER 3 : EXPERIMENTAL METHODS

3.1 Overview

In this chapter, the experimental methods are explained in four sections. In the first section, the preparation of the materials, namely the DNA extraction process and the procurement of the materials needed to produce the DNA-Schottky diode is detailed. In the second section, the fabrication of the DNA-Schottky diode using the LB method is described. Next, the characterisation techniques presented in the following section explains the various forms of sample analysis used in this study. Finally, the last section depicts the techniques employed during the electrical measurement of the DNA-Schottky diode and the devices used.

3.2 Materials and Methods

3.2.1 Materials Preparation

The Plant Genomic DNA Mini Kit was purchased from Yeastern Biotech, Taiwan. The Tris-Borate-EDTA (TBE) buffer solution was purchased from Bioneer Corp, South Korea. The ITO-coated glass was purchased from KINTEC, Hong Kong while the Al wire was purchased from Diamond, Malaysia. Deionized water was obtained using an in-house available Barnstead (Nanopure II) water deionizing system.

While there are many methods of obtaining DNA molecule including procuring the molecules directly, the DNA molecule in this work was extracted from plant leaves using a genomic DNA kit. The plant used was the *Mimosa pudica* plant (**Figure 3.1**) which is more commonly known as the sensitive plant. DNA kits are commonly available in the market and are ideal for use for DNA extraction protocols. In the

process of DNA extraction, the five main steps were tissue dissociation, lysis, DNA binding, washing and DNA elution as seen in **Figure 3.2**.

Figure 3.1: The *Mimosa pudica* plant (Leonard, 2012).

3.2.2 Extraction of DNA
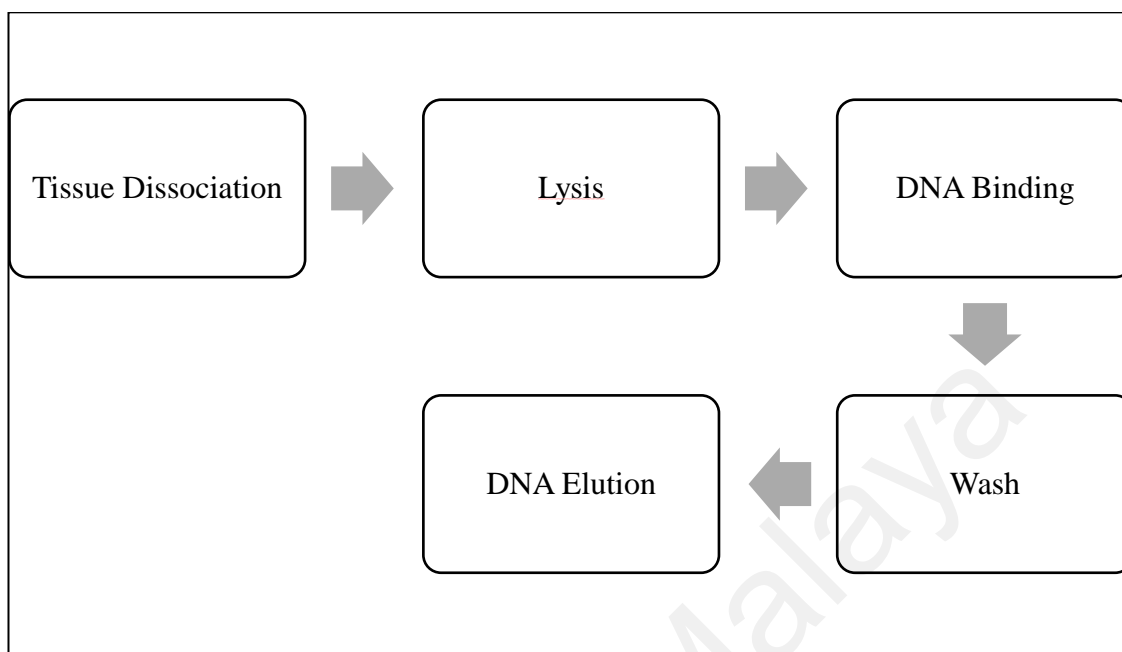
Figure 3.2: Five main steps of DNA extraction process.

In the tissue dissociation process of DNA extraction, 100.0 mg of leaves from the plant was weighed and grinded into fine powder to break up the leaves. This process sheared the cell walls and membranes and increases the surface area so the DNA molecules can be properly extracted from the leaves.

On the second step of DNA extraction that was the lysis process, the plant cells were broken open to expose the DNA within the cell. This was achieved by adding 400 µl of GP1 buffer (**Figure 3.3**) and 5 µl of proteinase provided in the DNA kit and mixing it by using a vortex. The solution was then incubated at 60 °C for 10 minutes to allow the buffer and proteinase to remove the proteins from the plant cells. Following that, 100 µl of GP2 buffer was added and the sample was incubated on ice for 3 minutes to deactivate the proteinase. Finally, the sample was filtered off with a filter column and centrifuge for 1 minute at 1000 x g to remove impurities and the clear lysate was stored.

Figure 3.3: Mixing of buffer solutions to break down the plant cells.

In the DNA binding process, 750 µl of GP3 buffer mixed with isopropanol was added into the clear lysate. The sample was then centrifuged twice at 16000 x g for 2 minutes each with the column matrix. This process was to enhance and influence the binding of nucleic acids to the column matrix. The column matrix contained a silica resin that selectively binds the DNA on to it. When centrifuged with the buffer solution, only the DNA will bind with the column matrix which was used to elute the DNA in the following steps.

Prior to DNA elution, the column matrix was washed with 600 µl wash buffer mixed with ethanol and centrifuged at 16000 x g for 30 seconds. The wash step served to remove all the impurities in the column matrix such as polysaccharides, residual protein and salts. Following that, the column matrix was centrifuged at 16000 x g for 3 minutes to dry it and removed all ethanol prior to DNA elution to ensure the end DNA solution did not contain ethanol as it could cause the nucleic acids not able to rehydrate fully.
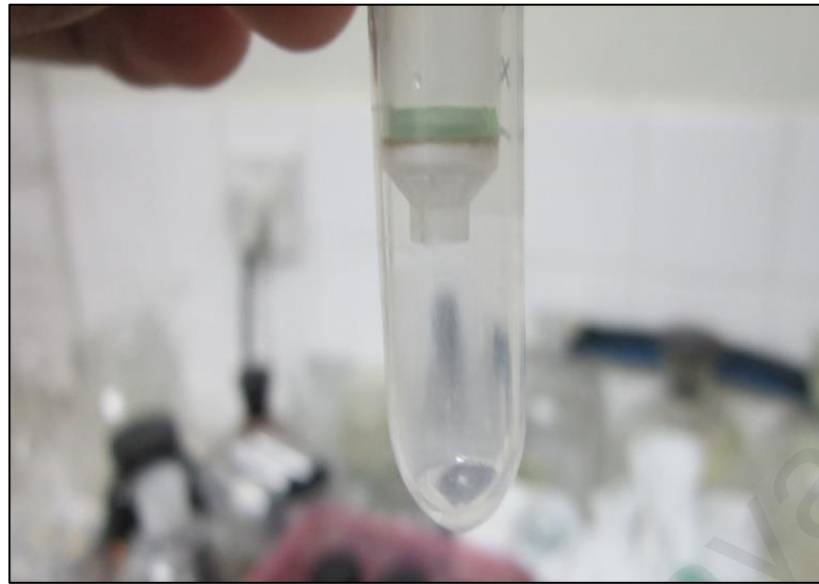
Figure 3.4: Final elution to extract DNA solution from column matrix.

In the final step of the DNA extraction, the pure DNA was released from the column matrix by adding 200 µl elution buffer to the column matrix as seen in **Figure 3.4**. The buffer was left to stand for 3-5 minutes to allow absorption of the buffer to the matrix before centrifuging it at 16000 x g for 30 seconds. Extracted DNA from the *Mimosa pudica* plant was stored at a -20 °C freezer to avoid degradation prior to use.

Nanodrop and UV-Vis spectrophotometric analysis were performed to check on the DNA purity. The OD260/OD280 ratio is a ratio to determine the purity of the nucleic acids. A ratio of around 1.8 is generally accepted as pure DNA (Wilfinger et al., 1997).

3.3 DNA-Schottky Diode Fabrication
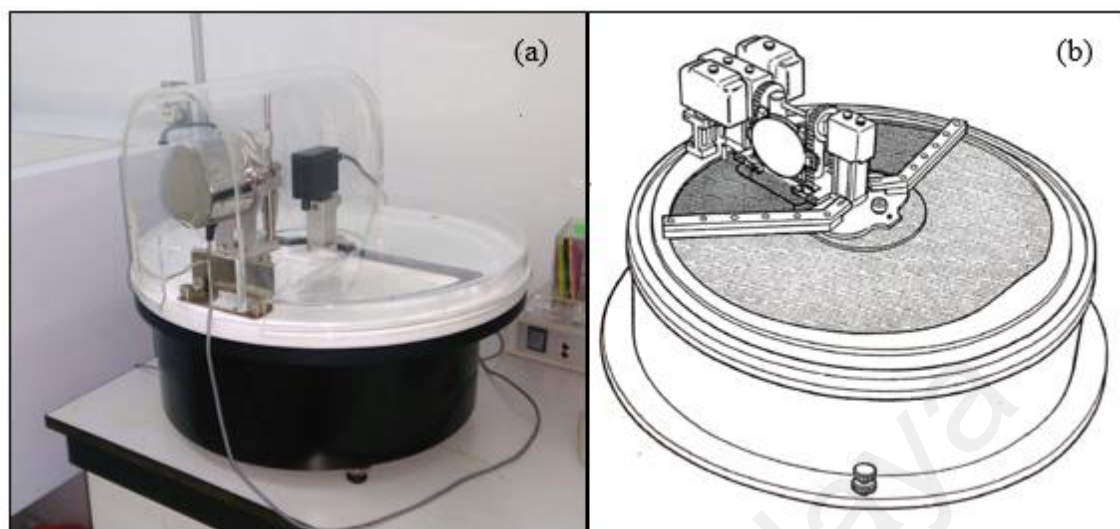
Figure 3.5: (a) NIMA LB trough (Model 2200) used for this work and (b) its schematic diagram (Martin & Szablewski, 2002).

DNA film deposition was achieved using two methods. Firstly, a round-type NIMA LB trough (Model 2200) from NIMA Technology, UK as seen in **Figure 3.5** was used to perform the LB method of depositing thin film. A total of 500 µL of purified DNA was used. The experimental area was maintained at a 1K clean room. TBE buffer was used as a subphase for the first time in LB experiment due to the fact that this enables DNA molecules to almost completely float on the TBE surface. Conventional subphase material such as deionized water does not allow this as a result of DNA being significantly hydrophilic. A filter paper to the scale of (1.0×2.2) cm was placed at the hook of tensiometer to monitor the surface pressure. After the trough was filled with TBE buffer, the pressure sensor was zeroed and left for 2 hours. A compression barrier speed (12 cm^2/minute) without DNA was done to ensure there is no crystallization of the subphase that may affect the isotherm graph. The DNA sample was then applied drop by drop by using micro-syringe, allowing about a minute between drops to enable molecular dispersion and to avoid molecular aggregation. After that, the pressure sensor

was zeroed again and the system was left for a further 2 hours to stabilise it. The monolayer was then compressed at a slow barrier speed (12 cm^2/minute).
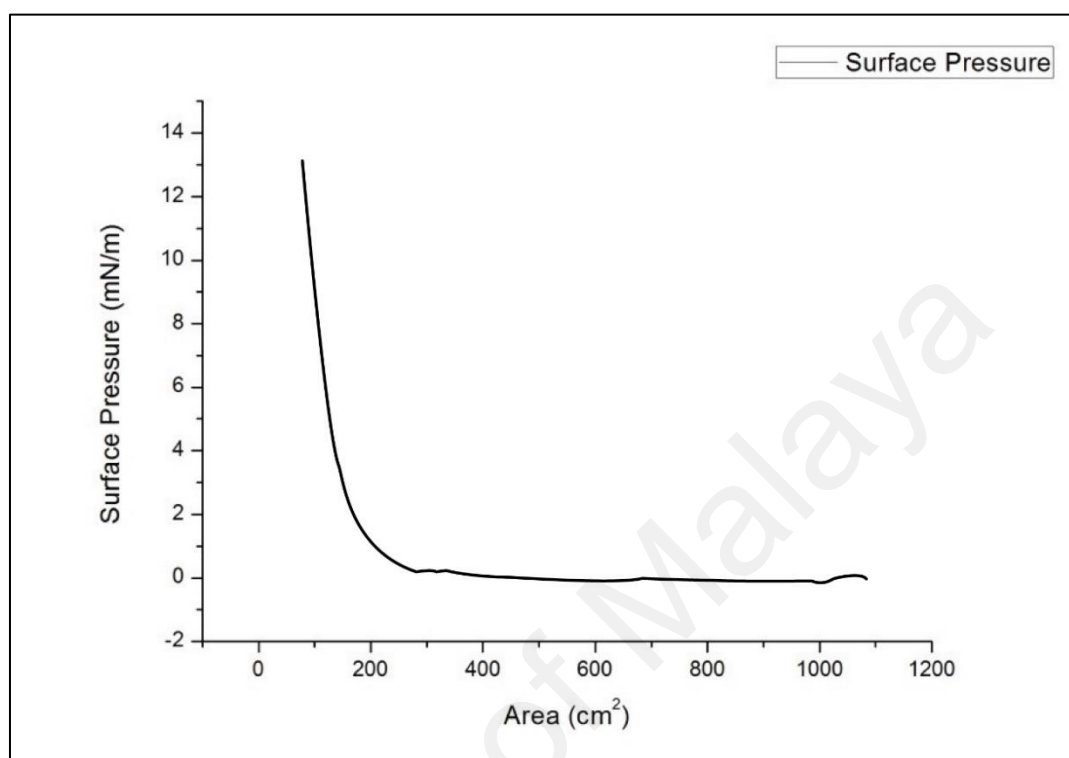
Figure 3.6: Isotherm graph of DNA solution produced by LB method.

An isotherm graph as seen in **Figure 3.6** was monitored during compression to the target pressure. As the surface area is decreased, the surface pressure gradually increases. The target pressure for dipping for our study was found to be at 10 mN/m. At this target pressure, the molecules are aligned neatly in a monolayer formation. If the surface area decreases further, the molecules will eventually collapse and overlap onto other molecules. Different substrates such as ITO, glass, and quartz with dimensions of (2.5 x 2.5) cm were vertically dipped at a speed of 15 mm/minute. The DNA sample was then transferred onto the different substrates during the dipping process.

An alternative method of producing the DNA film was conducted by using a drop cast method. A total of 10 µl of the DNA solution was diluted in deionized water with a weight ratio of 1:100. Using a micro syringe, the solution was cast on the ITO-coated

glass substrate and allowed to air-dry overnight. This method was used to study the effect of electric field alignment on the conductivity of the DNA molecules. The sample was dried under two conditions, without the presence of electric field and under presence of electric field which the effects of electric field alignment was studied. Both forms of DNA thin films electrical circuit was completed by attaching an Al foil as a counter electrode atop the DNA forming an ITO/DNA/Al Schottky diode. All electrical measurements were performed in triplicates and the average was calculated.

3.4 Characterisation Techniques

3.4.1 UV-Vis Spectroscopy

UV-Vis Spectroscopy is a method of characterisation where a beam of varying wavelength ranging from the ultraviolet to the visible light spectrum passes through a sample solution and the absorbance of the sample across the wavelength is measured. The UV-Vis spectroscopy works on the principle of Beer-Lambert Law (Spectronic, 2012), which states that:

$$A = log_{10} \frac{I_o}{I} = \varepsilon c L \qquad (3.1)$$

where A is the measured absorbance, I_o is the intensity of the incident light, I is the transmitted intensity, ε is the molar absorptivity constant (L mol^{-1} cm^{-1}), c is the concentration of the sample (mol L^{-1}), and L is the path length through the sample (cm). In this study, all UV-Vis analysis was obtained using a Thermo-Fisher Scientific Evolution™ 300 UV-Vis Spectrometer as shown in **Figure 3.7**. Scan range was from 200 to 600 nm with intervals of 1 nm. Samples used in the UV-Vis analysis was DNA solution diluted with deionized water and using deionized water as a reference.
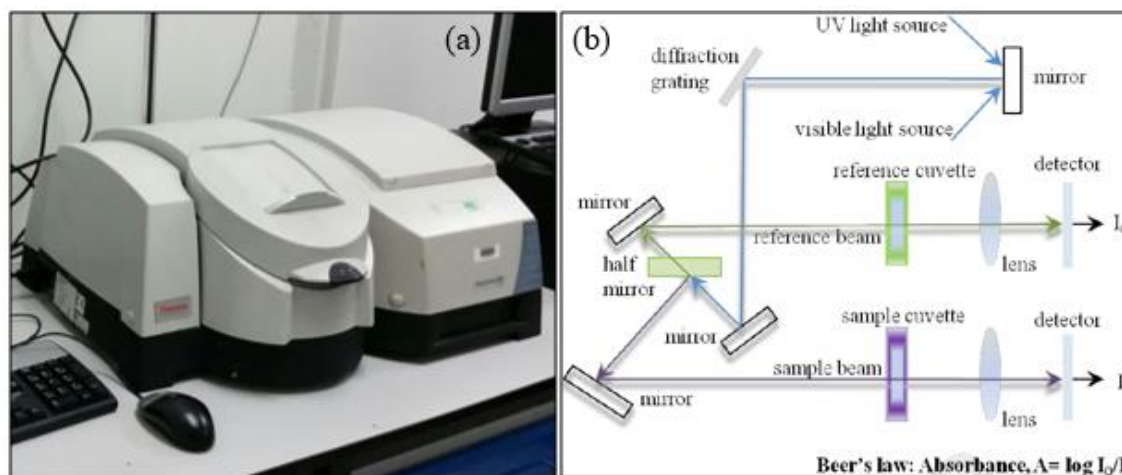
Figure 3.7: (a) Thermo-Fisher Scientific Evolution™ 300 UV-Vis Spectrometer used in this work and (b) its schematic diagram (Palchoudhury et al., 2016).

3.4.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) Spectroscopy works on the principle of passing a spectrum of infrared radiation with varying wavelengths through a sample (Griffiths & De Haseth, 2007). Within the spectrum, some of the radiations will be absorbed by the sample, resulting in a spectrum of absorbance and transmittance. This absorbance of the spectrum is due to the molecular vibrations of the bonds. When the infrared signal is passed through the sample, specific vibration states is known to absorb certain wavelength signal, causing a dip in the spectrum. By comparing the spectrum with a known database, we can identify the bonds in the sample, and from which we can determine the sample composition. For this study, we used the Thermo Scientific Nicolet iS 10 as shown in **Figure 3.8** to carry out this part of the project. The scan mode of the spectrometer was set as transmittance mode and the scan range wavenumber is varied from 850 to 4000 cm^{-1}.
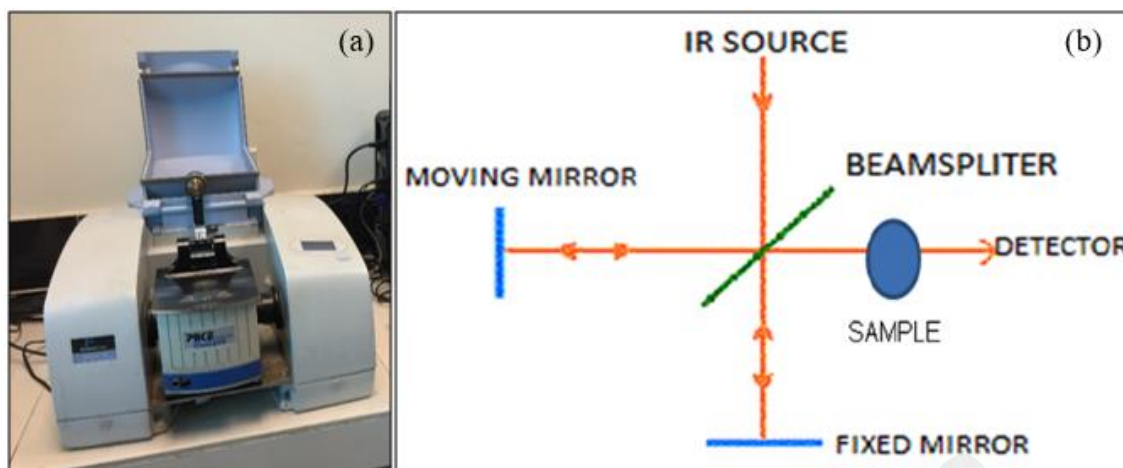
Figure 3.8: (a) Thermo Scientific Nicolet iS 10 Spectrometer used in this work and (b) its schematic diagram (Kumar et al., 2015).

3.4.3 Field Emission Scanning Electron Microscopy

In order to understand the morphology and structural composition of a sample, the FESEM characterisation is used. FESEM focuses a beam of electron on samples which causes an interaction on the targeting atoms and electron. Emitted signals from the sample can be collected to obtain the surface structure. From the electron beam, secondary electrons will be produced by the surface structure and these secondary electrons will be processed and captured into an electronic signal and transferred to an imaging monitor. Morphological properties of samples in this work were obtained using a Quanta FEG 450 FESEM (**Figure 3.9**) with an acceleration voltage of 1 kV. By analysing the images obtained, the structural characteristics of the sample can be described.
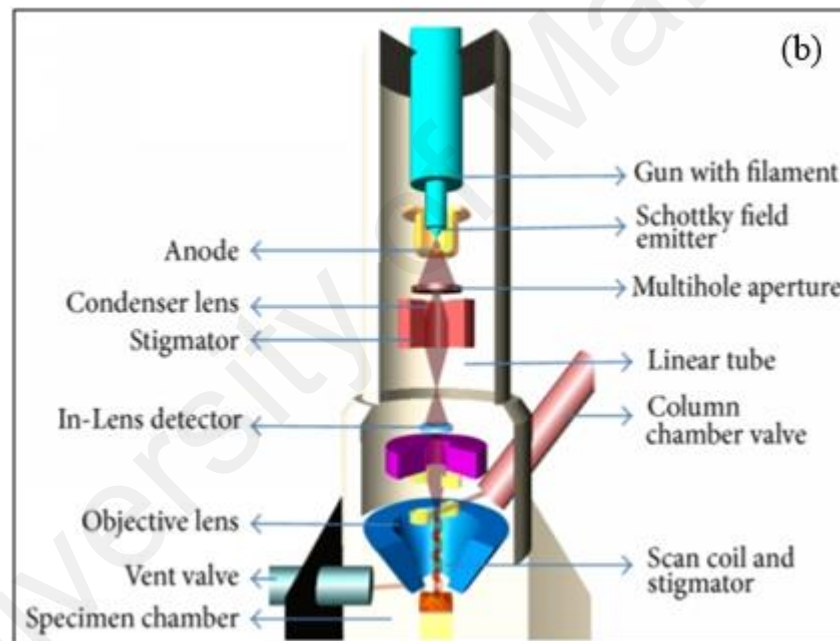
Figure 3.9: (a) Quanta FEG 450 FESEM used in this work and (b) its schematic diagram (Jusman et al., 2014).

3.4.4 Atomic Force Microscopy

AFM analysis was used to further study the surface morphology of a sample. A reading of the surface was recorded when a fine tip ranging in nanometre dimensions passed on the surface of the sample. This reading captures the surface profile of the scanned area, and also the depth of the sample and displayed the result on a graphical

and image format. AFM analysis of this work was performed using an Ambios Q Scope AFM machine as shown in **Figure 3.10**.
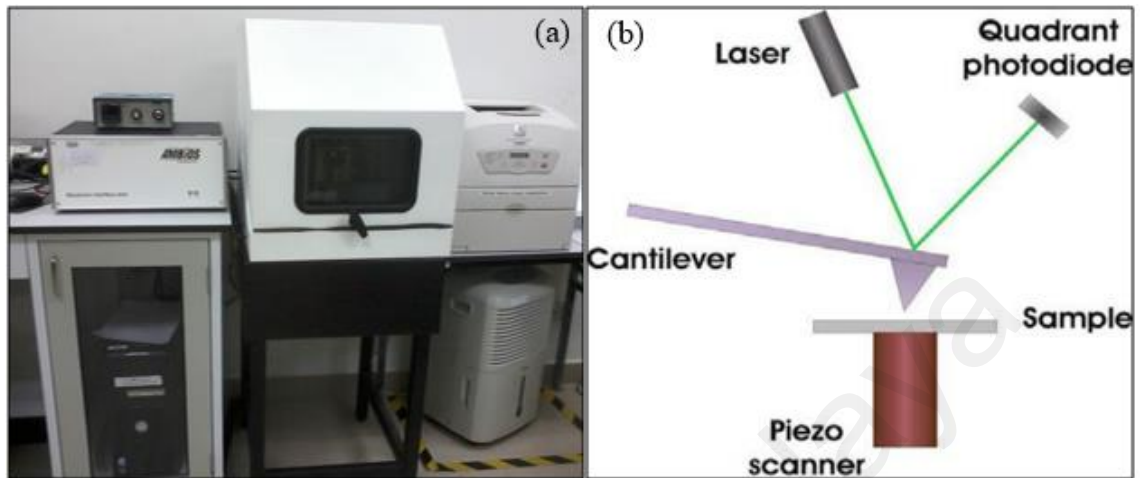
Figure 3.10: (a) Ambios AFM machine used in this work and (b) its schematic diagram (Amin, 2012).

3.5   Electrical Characterisation

3.5.1 Electrical Measurement

Electrical measurement is a method of measuring the current flow across a sample while applying a potential difference between two electrodes. An experiment schematic diagram for I-V measurement is shown as per **Figure 3.11**. While there are many methods to do this measurement, one of the most common and efficient method is by using modern electronic devices such as Source Measurement Unit (SMU) or electrometers. These devices allow the simultaneous measurement of the current passing through the sample while providing voltage source.
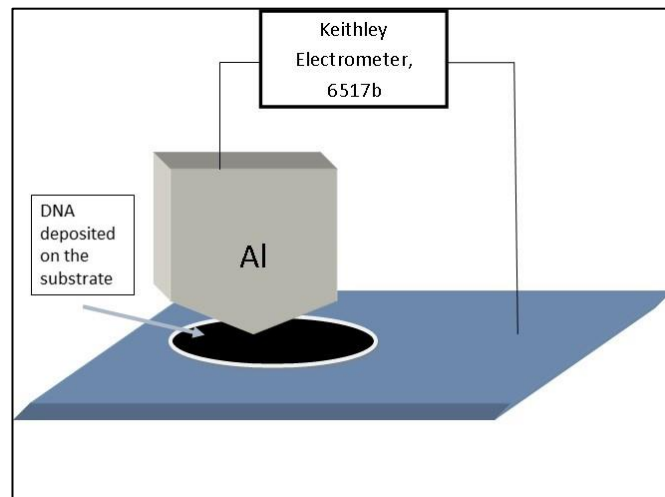
Figure 3.11: Experimental schematic diagram for I-V measurement.

Furthermore, these devices can be connected to a personal computer and by using LabVIEW program; the measurement can be automated and performed completely on the personal computer. LabVIEW is a graphical programming program developed by National Instruments, USA which allows automated measurement that is able to connect with many modern lab devices (El-Hajjar et al., 2012). By using a block diagram and input panel, users are able to define automated measurement parameters for various forms of measurement not only limited to electrical. The following section will describe the user panel and block diagram which was self-developed for this study.
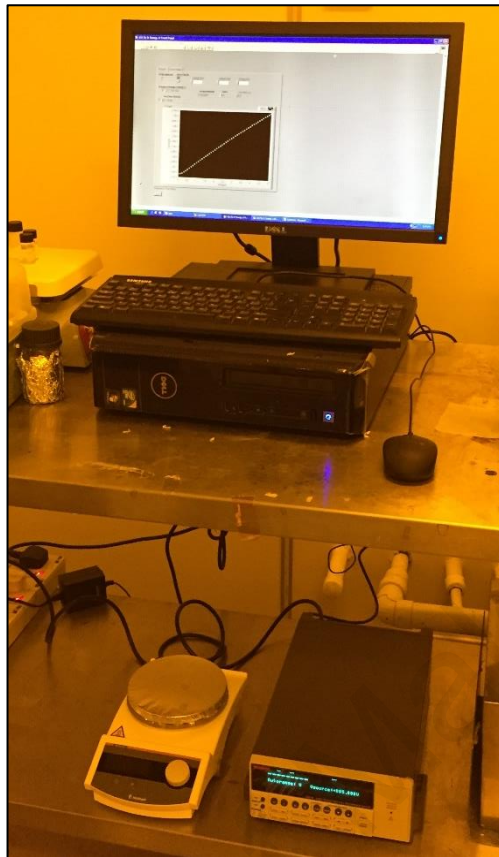
Figure 3.12: Electrical measurement set-up with Keithley 6517b electrometer and Dell Vostro 230 personal computing system used in this work.

In this work, the electrical measurement process was done using a Keithley 6517b electrometer while connected to a Dell Vostro 230 personal computer system as seen in **Figure 3.12**. The version of LabVIEW used was LabVIEW 7.0. The entire electrical measurement process was carried out in a 10k clean room to minimize risk of sample contamination.

3.5.2 LabVIEW Design

The simultaneous measurement of current with increasing step voltage was attained with the assistance of LabVIEW to obtain the I-V graph of the DNA-Schottky diode. All LabVIEW program are called virtual instruments, or "VI" which is the method the LabVIEW circuit speaks to the measuring instrument. For this work, the LabVIEW VI was self-designed using learning resources from the internet and training manuals. In

the following sections, the working principle of the LabVIEW program and circuit design will be described.

While connected with the Keithley 6517b electrometer, the LabVIEW program just needs the user to select the start/end voltage and the step voltage for the measurement and other parameters to start the measurement. The LabVIEW program will then instruct the electrometer to begin measuring the current across the sample while slowly increasing the voltage step as per predefined voltage step amount. While this measurement is in progress, the data from the electrometer will pass to the LabVIEW program to be stored. An onscreen I-V graph is also available for quick viewing of results of measurement. Once the voltage has increased to equal the end voltage, the measurement will stop and the user will be prompted to save the data.

LabVIEW VI is made up of two windows, the front panel and the block diagram. Front panel is the user interface area for the VI where the user can enter or edit necessary parameters for measurement. **Figure 3.13** below depicts the front panel of the VI which was designed to obtain I-V measurements of the DNA-Schottky diode. The Voltage Start, Voltage Step and Voltage End area can be entered manually by the user which determines the start voltage, step voltage and end voltage. Other customisable areas of the front panel include the V-source range for higher voltages, function to change voltage supply from direct current to alternating current, and loop delay to adjust the speed of the voltage step increment.

While the front panel of the VI is where user interface takes place, the block diagram is where the actual programming and communication of the device happens. Any input in the front panel will be passed to the block diagram which processes the input depending on how the VI is scripted. A VI which instructs a device to measure the current while increasing voltages by predetermined steps may seem straightforward, but

the block diagram can be complex and lengthy to build as the device needs to be able to understand how or what the user wants to measure. **Figure 3.14** shows the block diagram of the self-designed VI for this study.

The working principle of the block diagram is by placing the voltage step and voltage end input in a loop. When the program starts, the value of the voltage start will be fed into the Keithley 6517b electrometer which will change the voltage source and measure the current. Once that is done, the measured current and voltage source will be tabled and presented in a x-y Graph. The voltage value is then re-entered into the loop which will add the specific voltage step value. The new voltage value will be compared to the end voltage. If the new voltage is lower than the end voltage, it will be fed to the electrometer which will change the voltage value accordingly and repeat the previous steps.

As the measurement continues the block diagram will re-loop the measurement each time comparing the new voltage value with the end voltage value. If the new voltage value is higher or equals to the end voltage, the command will ask the device to stop the measurement. Within the loop is a loop delay that specifies the time taken for each loop which is the time taken for each voltage step.
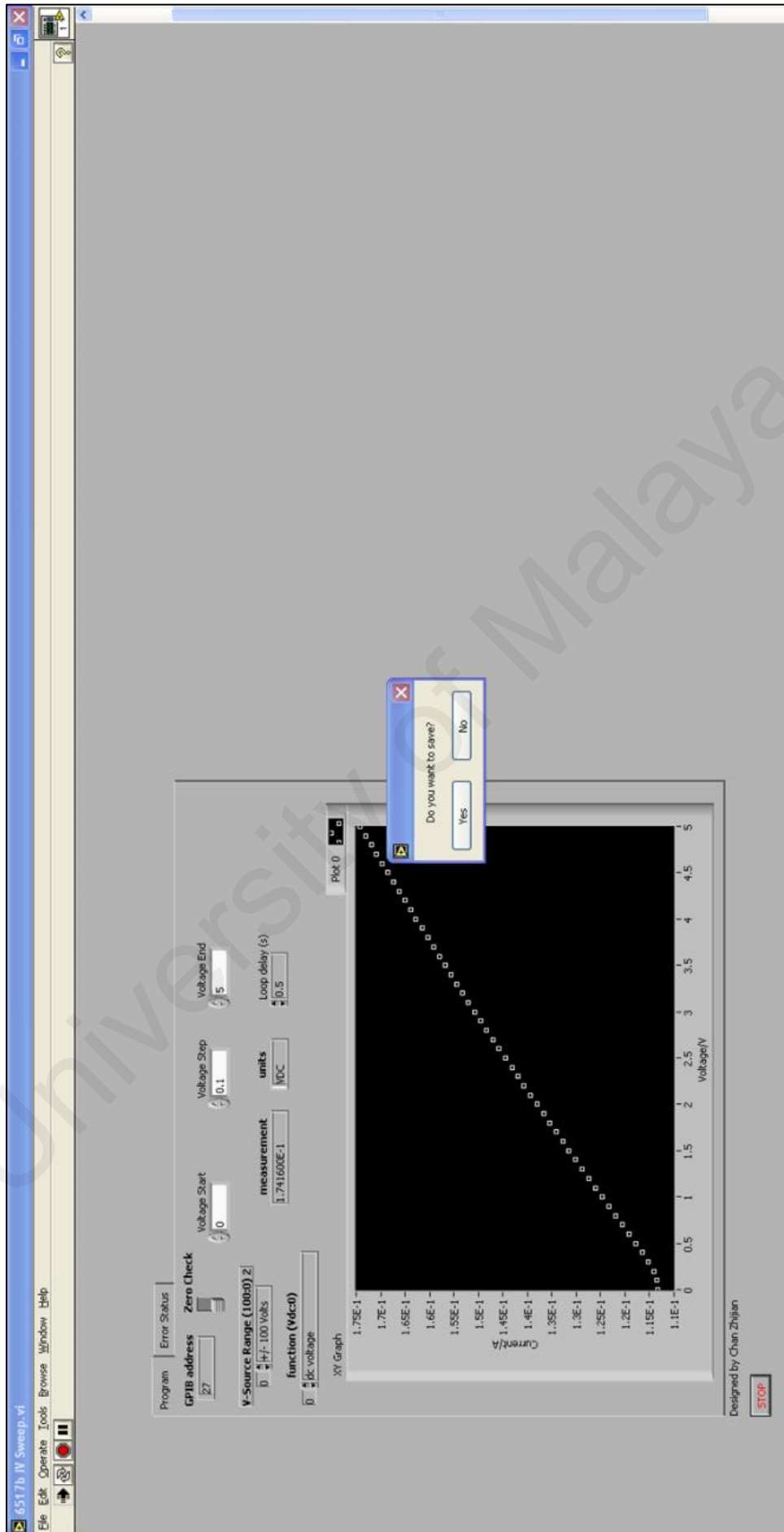
Figure 3.13: Front panel of the self-developed VI used in the electrical measurement.
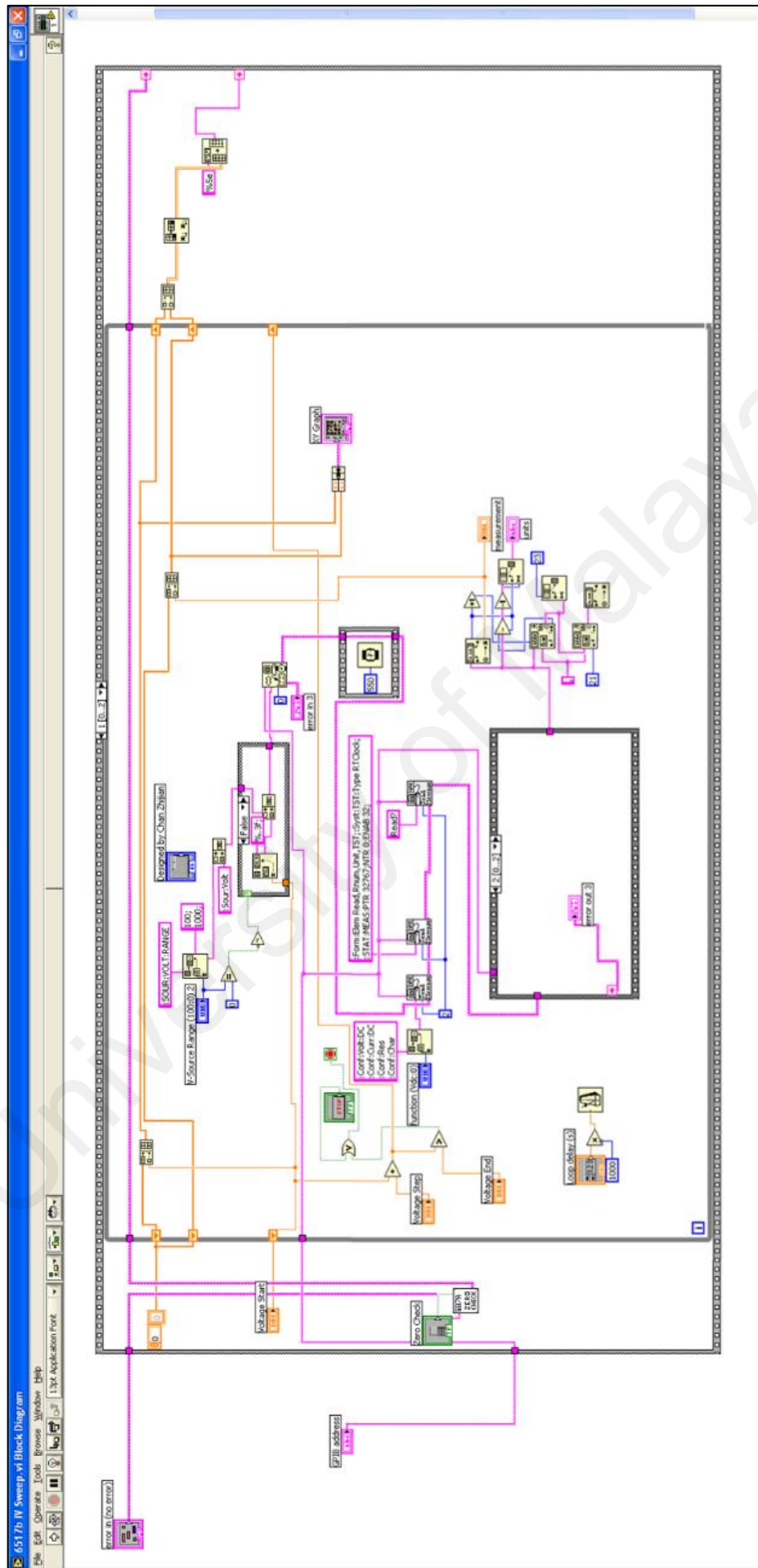
Figure 3.14: Block diagram of the self-developed VI used in the electrical measurement.

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CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Overview

In this chapter, the results and discussion are presented in three different sections. The first section includes the characterisations of the as-prepared samples by using UV-Vis Spectroscopy, FTIR, FESEM and AFM. The different characterisations allow a clear understanding on the structural and morphological composition of the formed DNA film. The second section explains the electrical measurement in the form of I-V graphs obtained from the ITO/DNA/Al device. In the final section, an analysis of the electrical measurement is presented by obtaining the diode parameters such as barrier height, ideality factor and series resistance. The results denote that rectifying behaviour of the DNA molecule is able to be produced from the I-V graphs. Further investigation revealed that the alignment of the DNA film with the assistance of electric field improves the electrical conductivity of the DNA molecule suggesting the conductivity of the DNA strands depends on the orientation, which is likely to be related to the rectification behaviour.

4.2 Characterizations

4.2.1 UV-Vis Spectroscopy

The OD260/OD280 ratio of the extracted DNA obtained from the Nanodrop spectrometer was 1.9 and the concentration of the solution was at 74.1 ng/µl. By analysing the DNA solution diluted with deionized water, the UV-Vis analysis on the sample showed a maximum absorbance at 260 nm as seen in **Figure 4.1**. This corresponds to the maximum absorbance value of DNA as reported in a previous study by Tataurov et al., 2008. Due to the nature of the sample being diluted with deionized

water, the absorbance of the UV light at 260 nm was reduced. Higher absorbance can be obtained if the concentration of the extracted DNA was higher, however it is not required for this study as this characterisation is purely to determine the presence of DNA. The absence of other peaks in the graph also indicated that there were no foreign objects or contaminants in the sample.
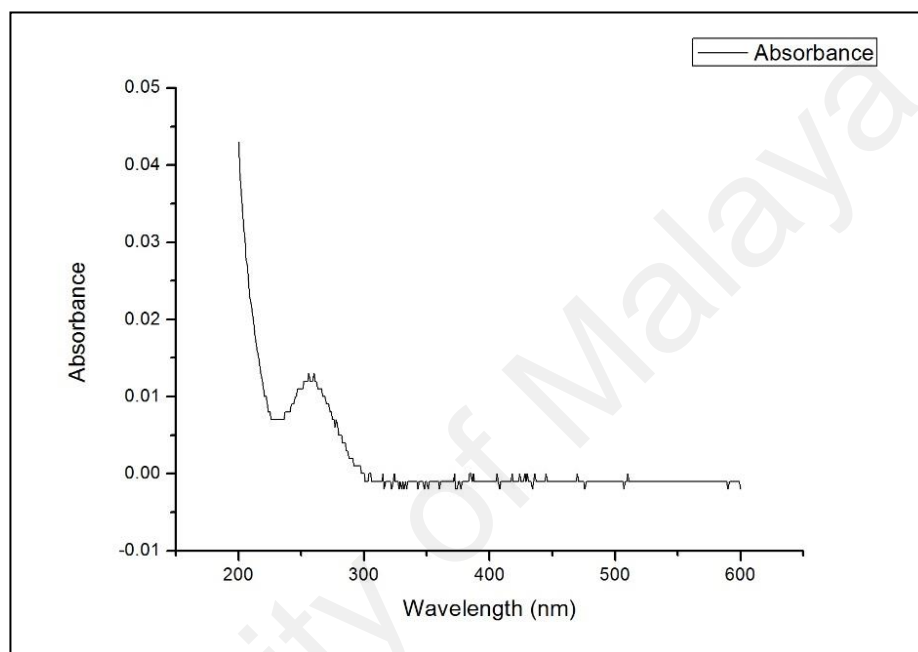
Figure 4.1: UV-Vis analysis of DNA.

4.2.2 Fourier Transform Infrared Spectroscopy

FTIR is a simple method of identifying the composition of a sample by detecting the wavenumber that the infrared signal absorbed due to the vibrational modes of specific bonds. Spectrums can be displayed in the form of absorbance or transmittance as both measurements are inversely proportionate. For this work, the IR spectrum was displayed in the transmittance mode.
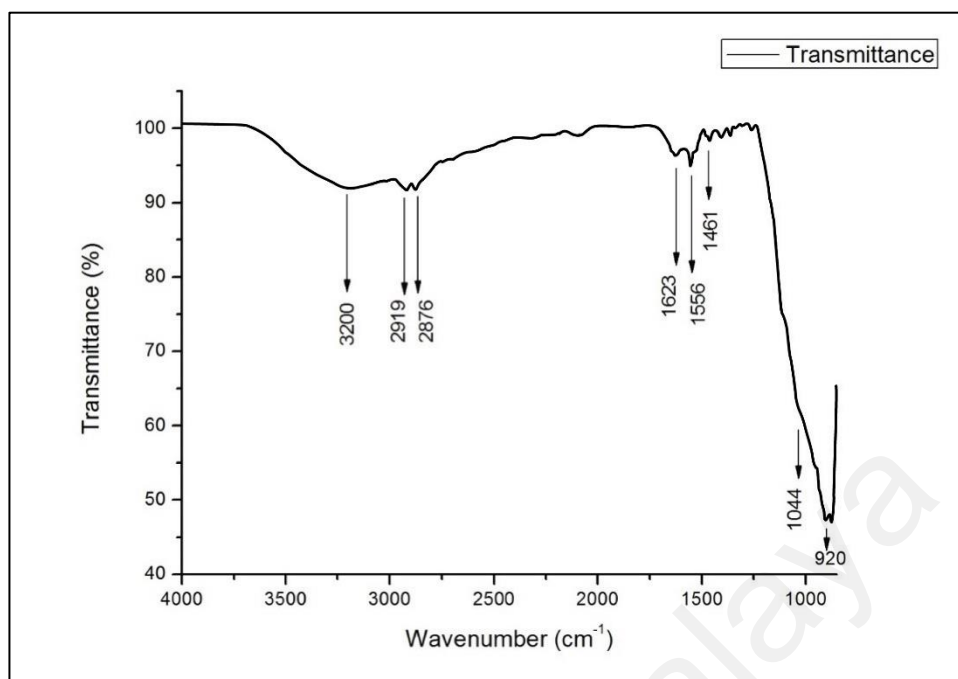
Figure 4.2: FTIR spectrum of the DNA sample extracted.

Several peaks are observed from the spectrum of DNA as labelled in the **Figure 4.2**. By comparing results obtained with other published papers (Ahmed et al., 2009; Stuart & Ando, 1997; Taillandier & Liquier, 1992), certain bonds identifiable in the sample corresponds to the presence of DNA. The peaks around 3200 and 2900 cm^{-1} are mainly due to the NH stretching vibrations of proteins and CH stretching vibrations of lipids (Ahmed et al., 2009). Peaks observed at 1623 and 1556 cm^{-1} are attributed to the C=O stretching and NH bending modes of the peptide linkage of the proteins whereas the peak at 1461 cm^{-1} is due to the CH bending modes of the molecule (Ahmed et al., 2009).

DNA absorption bands occur in the region of 1375-875 cm^{-1} of the infrared spectra. As due to the extraction of the DNA is not limited to a single form, the infrared spectrum produced was a combination of various forms of DNA. In the spectrum produced, two peaks were observed in the range, a shoulder peak at 1044 cm^{-1} and a peak at 920 cm^{-1}. The peak at 1044 cm^{-1} is attributed to the antisymmetric and symmetric vibrations of the PO$_2^-$ groups of the DNA and could be a result from the

backbone of the B form of DNA. On the other hand, the peak at 920 cm^{-1} reflects the phosphate-sugar backbone of Z-DNA (Ahmed et al., 2009).

4.2.3 Field Emission Scanning Electron Microscopy

Using the LB method, extracted DNA was deposited onto ITO coated glass and allowed to air-dry in a 1K clean room. To investigate the formation of the DNA film and to determine the uniformity of the film, the FESEM and AFM techniques were used. **Figure 4.3** depicts the FESEM image of the DNA film at a magnification of 1000x. The DNA film formed on the surface of the ITO depends on the ability of the LB technique. As explained in section 3.3, the isotherm graph of the extracted DNA allowed the determination of the optimum dipping pressure, which resulted in the uniform film of the DNA. The boundaries of the film and substrate were uneven and not in a straight line most probably due to the different lengths and sizes of DNA molecule in the sample. As the DNA extraction kit used was genomic DNA, extracted DNA can vary in base lengths and structures. This is the reason for non-perfect uniformity achieved in this sample.
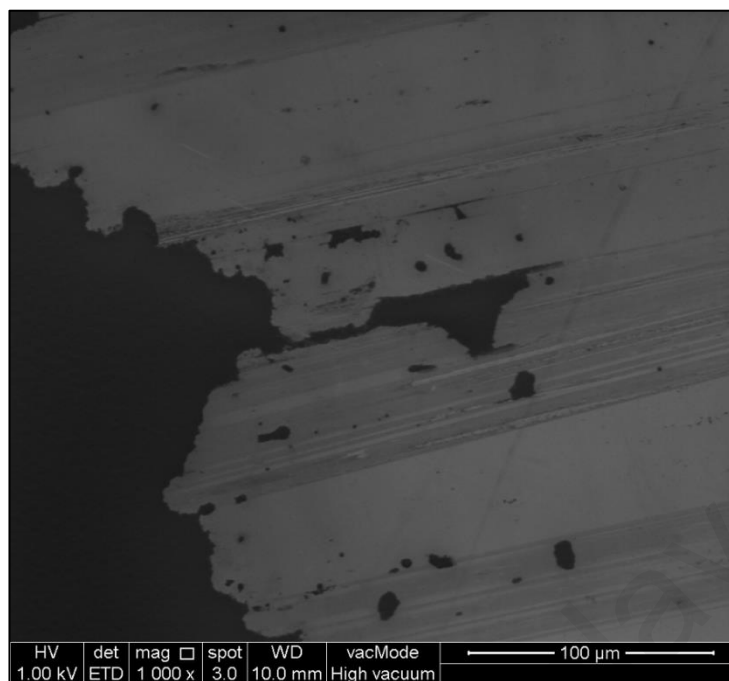
Figure 4.3: FESEM image of DNA film using LB method at 1000× magnification.
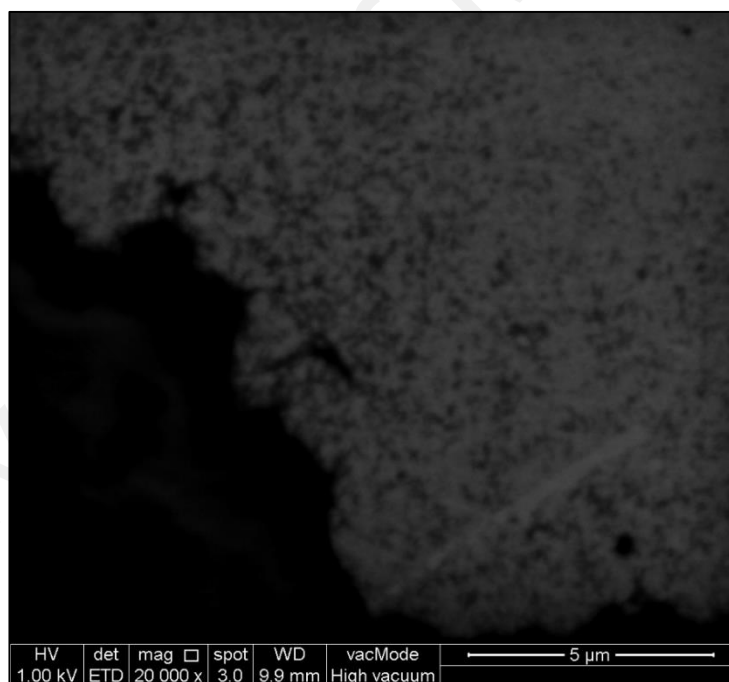
Figure 4.4: FESEM image of DNA film using LB method at 20000× magnification.

Further magnification of 20000x on a selected area of the sample (**Figure 4.4**) reveals neatly packed DNA strands on the sample, forming a neat layer of film. This neatly packed formation of thin film can only be obtained using the LB film deposition technique.

4.2.4 Atomic Force Microscopy

Further investigation of the DNA film is done using the AFM technique. LB film deposition achieved a uniform pattern of DNA film as shown in the AFM image in **Figures 4.5** and **4.6**. This corresponds with the FESEM result in the previous sections which depicts neatly packed DNA strands on the surface of the substrate. The benefit of AFM over FESEM is by using AFM technique, a 3D image can be displayed which allows investigation on the film thickness.
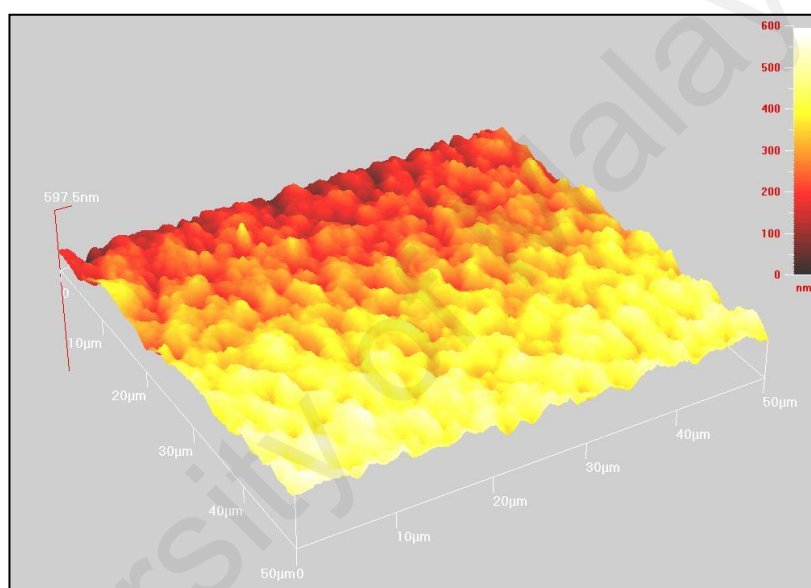
Figure 4.5: AFM imaging of DNA LB film with the surface profile of the film.

The height of the DNA film varies from 200 to 600 nm as seen in **Figure 4.5** where the area below is thicker compared to the area above. This may be due to the dipping process of the LB technique where the ITO was dipped vertically, and the effect of gravity takes place causing the lower area to be accumulated with the DNA strands, becoming slightly thicker. Additionally, the different sizes and lengths of DNA molecules that are deposited on the ITO substrate contributed to this effect as the DNA solution used was genomic DNA.
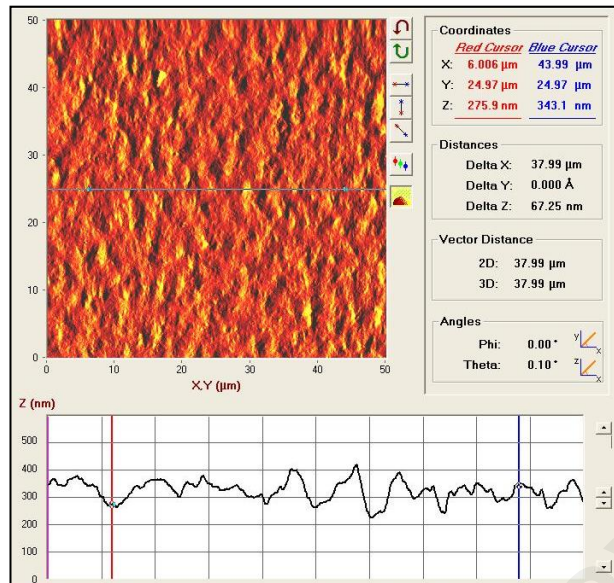
Figure 4.6: AFM imaging of DNA LB film with the dimension analysis of the film.

A dimensional analysis carried out horizontally across the film as seen in **Figure 4.6** further agrees with the FESEM observation of a uniform, repeating pattern of DNA film deposited on the ITO. The height of the film does not vary much horizontally and peaks and troughs reflect the corresponding DNA strands and space between strands.

4.3   Electrical Measurement

For this work, DNA-Schottky diodes was formed by attaching an Al electrode on the DNA film while the circuit is completed. Two forms of DNA film was produced, a thin film made using the LB technique and the other film created using a drop-cast technique. Electrical measurements done using the Keithley electrometer for both devices revealed rectifying behaviour of the ITO/DNA/Al Schottky diode.
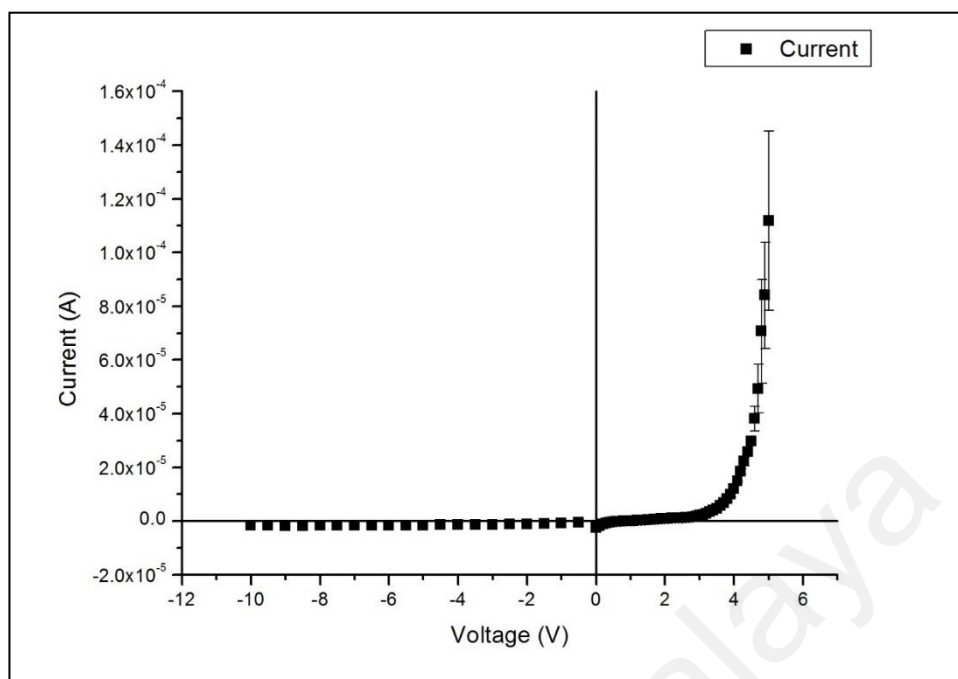
Figure 4.7: I-V curve for ITO/DNA/Al device fabricated using the LB technique.

Figure 4.7 above describes the I-V curve for ITO/DNA/Al Schottky diode in forward and reverse bias. Forward biased voltage was measured from 0 - 5 V in voltage steps of 0.1 V whereas reverse biased voltage was measured from 0 to -10 V in steps of 0.5 V. In forward bias, the conductivity of the DNA strands was very minimal at lower voltages. Specific to the type of DNA strands used, the strands become conducting at the threshold voltage of 4 V, and the current increases exponentially with increasing voltage thereafter. It can be observed that as the voltage increases, the error in the current increases as well. This may be attributed to the inability of the molecule to properly conduct electricity at larger voltages.

In the reverse bias, the current flow across the DNA strands was very close to zero, as similar to conventional electronic diodes. This was observed even as the voltage was increased to -10 V across the electrodes. The results obtained suggested that DNA-Schottky diode could be formed using the ITO/DNA/Al arrangements.

4.4 Investigation of Parameters Influencing Electrical Measurement

To investigate parameters which could influence the conductivity of the DNA molecule, the drop cast technique of creating the DNA film was used. The DNA solution was cast on the ITO-coated glass substrate and allowed to dry overnight. By using the similar setup (ITO/DNA/Al) for the Schottky diode, the I-V measurements were obtained. Subsequently, the sample was wetted with a few drops of deionised water and dried under the presence of an electric field of 120 Vm^{-1}. The idea of this research was to investigate the influence of electric field alignment to the conductivity of the DNA molecules. The results of this study has been published previously (Chan et al., 2015).
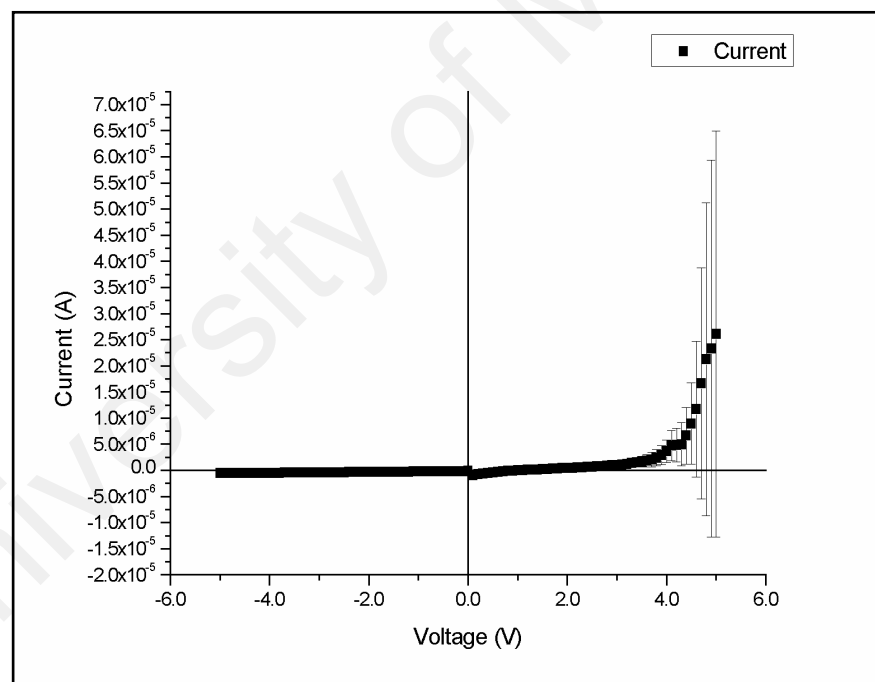
Figure 4.8: I–V curve obtained for the ITO/DNA/Al device without DNA alignment.
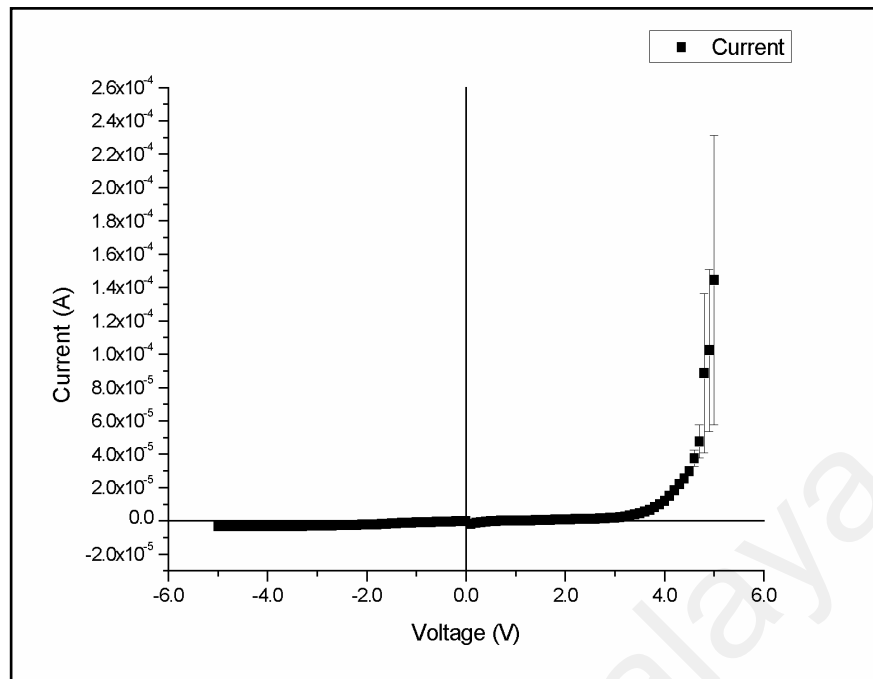
Figure 4.9: I–V curve obtained for the ITO/DNA/Al device after electric field assisted alignment of DNA strands.

I-V measurements for both samples are as shown in **Figures 4.8** and **4.9**. The former figure shows the I-V curve for the sample dried without the presence of electric field whereas the latter shows the I-V curve for the sample dried in the presence of electric field. Both results were also plotted on the same graph (**Figure 4.10**) for easier comparison.

By comparing the I-V curves for both samples, it was easily observed that the sample dried in the presence of electric field exhibits better rectification. The rectification behaviour was more pronounced and the maximum current obtained was also higher as compared to the sample without electric field alignment. Furthermore, the error margin becomes smaller as the DNA strands are more aligned, contributing to a better net flow of current.
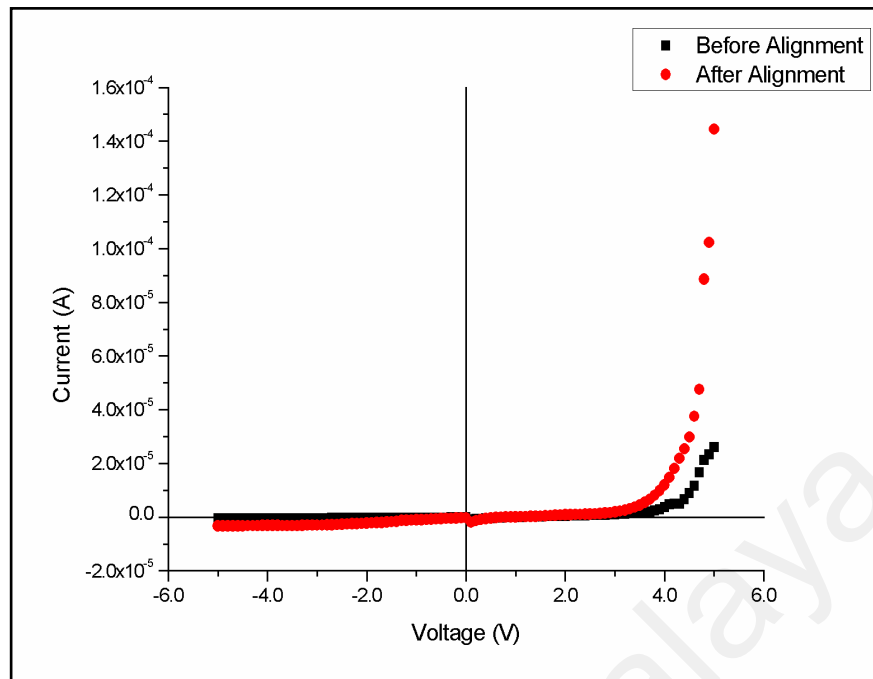
Figure 4.10: Combined I–V curves for the ITO/DNA/Al device.

An alternative method of comparing the conductivity prior and after electric field alignment is to calculate the rectification ratio of the I-V curves. The rectification ratios for the samples dried in the presence and absence of electric field was found to be 44.1 and 50.3 at ± 5 V, respectively. A plot of rectification ratio against the voltage is shown in **Figure 4.11**. Rectification ratio is the ratio of the forward current to the reverse current at the particular voltage. The lower rectification ratio for the electric field aligned sample is due to the lower current in the reverse bias direction after electric field alignment, which suggests improved current conduction in both directions.
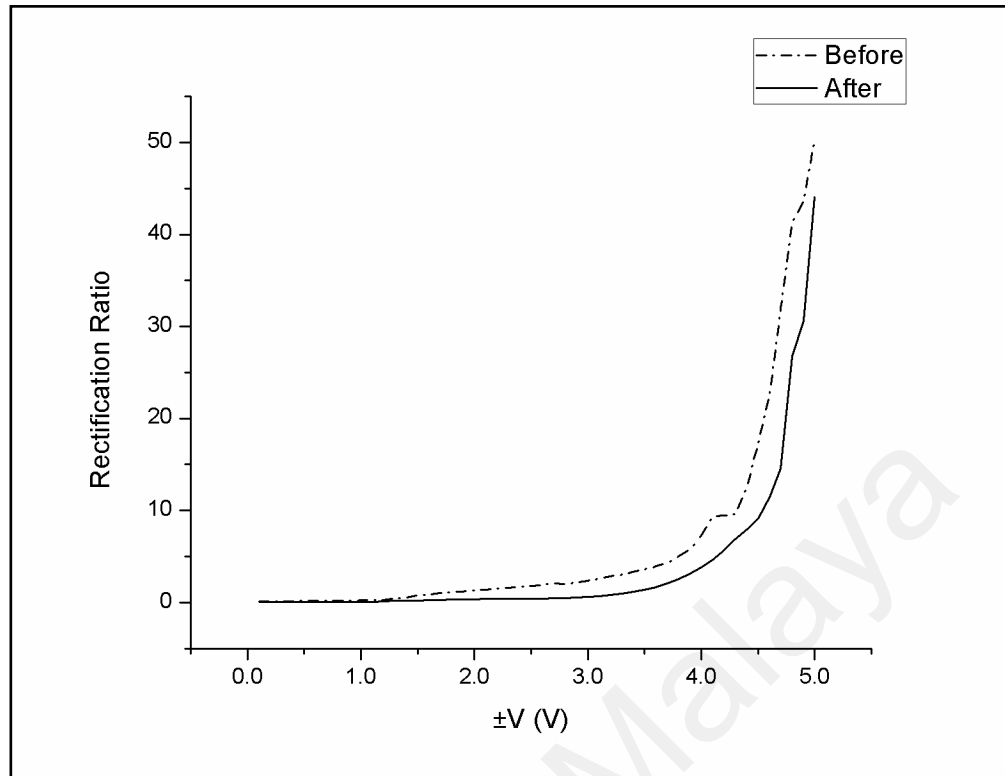
Figure 4.11: Rectification ratios vs the voltage.

By using the I-V curves, the main parameters of a diode such as the series resistance, ideality factor and barrier height can be calculated. Based on the thermionic emission theory (Rhoderick & Williams, 1988), the current in the Schottky barrier diodes can be expressed as:

$$I = I_0 \exp\left(\frac{qv}{nkT}\right)\left[1 - \exp\left(-\frac{qv}{nkT}\right)\right] \qquad (4.1)$$

where I_0 is the reverse saturation current and can be expressed as:

$$I_0 = AA^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \qquad (4.2)$$

where V is the applied voltage, A is the effective diode area (3×10^{-5} m^2), A^* is the effective Richardson constant (110.079 Acm^{-2}K^{-2}) (Khatir et al., 2012), ϕ_b is the barrier height, n is known as the ideality factor, k is the Boltzmann constant and T is the temperature. The value of the ideality factor n is calculated from the slope of the linear region of the forward bias of the I-V curve with current plotted on the logarithmic scale with the following equation:

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$$n = \frac{q}{kT}\left(\frac{dV}{d(\ln I)}\right) \tag{4.3}$$

The combined forward and reverse biased I-V curves with current plotted on the logarithmic scale are shown in **Figure 4.12**.
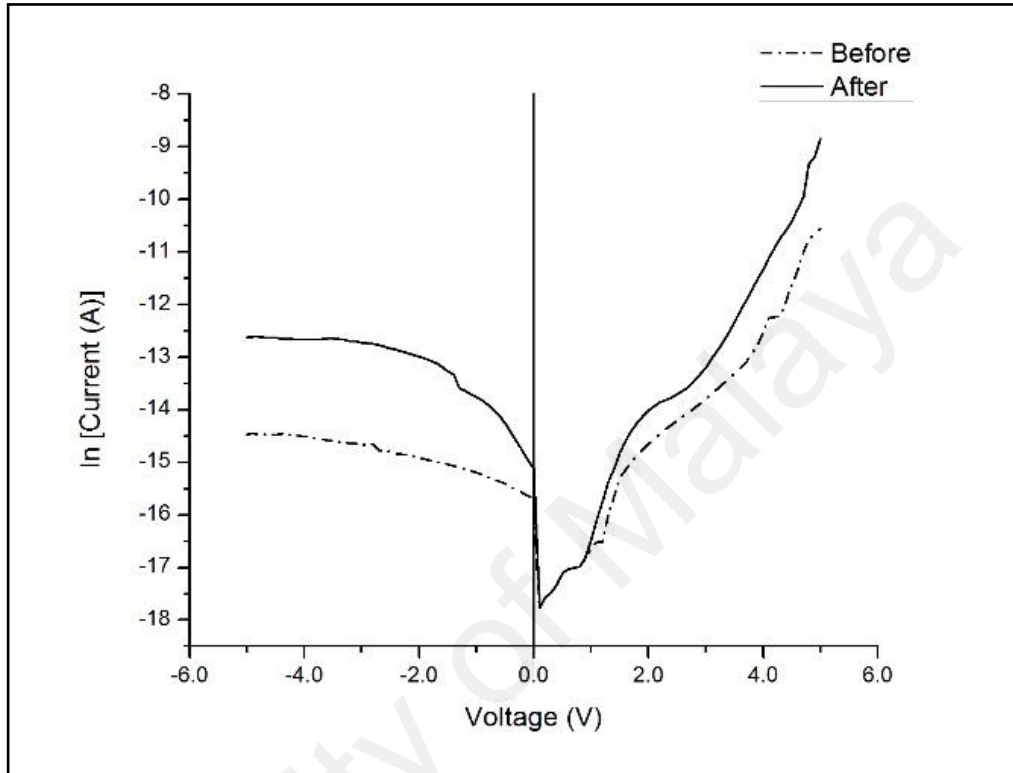
Figure 4.12: Current (on the logarithmic scale) vs voltage.

Using the equations (1), (2) and (3) above, the calculated values for barrier height, series resistance and ideality factor are listed in **Table 4.1**. The diode parameter values were compared for samples in the presence and absence of electric field.

Table 4.1: Diode parameters before and after the electric field assisted alignment.

Samples	Barrier height, [eV]	Series resistance [kΩ]	Ideality factor, n
Without alignment	0.796	191.5	15.0
With alignment	0.780	34.6	11.9

Ideality factor describes how close the diode performs compared to an ideal diode. For an ideal diode, the value of n will be 1. The higher value of n in this device may be due to the irregular thickness in the DNA film or the formation of oxide layer in the interface (Cetinkara et al., 2003; Karataş & Türüt, 2004). The forward bias I-V characteristics are linear in the semi-log scale at lower voltages but deviate from the linear behaviour at higher voltages. This deviation in the I-V curve is due to the effect of series resistance. If the effect of the series resistance is less, the nonlinearity will be less (Turut et al., 1995). Barrier height describes the contact potential barrier at the interface of the DNA and Al. A higher barrier height will limit the flow of charge carriers in the device. Large values of ϕ_b are related to non-uniform junctions at the interfaces (Schmitsdorf et al., 1997).

Comparing the values of barrier height, series resistance and ideality factor, it can be observed that the diode parameters have improved upon placing under electric field. This property leads us to suggest that the current conduction of the DNA strand depends on the orientation of the strand, which may relate to the rectifying behaviour or uni-directional current flow in the strands.

CHAPTER 5 : CONCLUSIONS AND FUTURE WORKS

5.1 Summary of Findings

The work reported in this dissertation involves some novel research work pertaining to DNA electronics currently being carried out intensively in our laboratory. The findings generally highlights preliminary but crucial data towards the fabrication of prototype DNA-specific Schottky diodes with potential applications in pathology, diagnostics and a host of other medical and biological relevance. The research work was therefore designed with the following objectives:

1) To fabricate a prototype DNA-Schottky diode

2) To study and analyse the composition of the DNA-Schottky diode using spectroscopic, morphology and characterisation techniques

3) To conduct I-V characterisation of the DNA-Schottky diode

4) To obtain optimal parameters for the working conditions of the DNA-Schottky diode fabricated in this work

1) To fabricate a prototype DNA-Schottky diode

A prototype DNA-Schottky diode in the form of an ITO/DNA/Al structure was successfully developed in house by using two methods, the LB thin film deposition and the drop cast method. DNA extraction from *Mimosa pudica* was also carried out to the complement the research work.

2) **To study and analyse the composition of the DNA-Schottky diode using spectroscopic, morphology and characterisation techniques**

Spectroscopic techniques used for characterisation of DNA were UV-Vis and FTIR spectroscopy. Both methods obtained results confirming the presence of DNA in the sample.

FESEM technique was applied to the DNA film produced using the LB method and revealed a uniform and neatly packed structure of DNA strands, which could only be achieved using the method used. Magnified images of 1000x and 20000x revealed the minimal spacing between molecules which also corresponds to the AFM results.

AFM obtained results in agreeable to the images obtained by the FESEM method revealing neat, uniform and repeating structures of the film produced using the LB technique. Film thickness was found to vary from 200 to 600 nm due to the genomic DNA which contains various lengths and sizes.

3) **To conduct I-V characterisation of the DNA-Schottky diode**

I-V characterisation of ITO/DNA/Al Schottky diode was successfully obtained using a Keithley 6517b electrometer. In order to simplify I-V measurements, a LabVIEW VI was built in-house connecting the electrometer to a personal computer. I-V curve obtained from ITO/DNA/Al Schottky diode exhibits rectifying behaviour agreeable to literature in section 2.5.

4) **To obtain optimal parameters for the working conditions of the DNA-Schottky diode fabricated in this work**

Investigation of the I-V curve for electric field aligned and non-electric field aligned DNA film was performed. Results revealed that electric field alignment assist in

improving the conductivity of the DNA molecule, which suggested that orientation of DNA strands affect the conductivity.

5.2   Future Works

DNA electronics is only at its birth stage with emerging technologies allowing better, quicker and more advanced sensing capabilities previously thought impossible. Upon completion of this dissertation, fabrication of DNA-Schottky diodes are well documented (Chan et al., 2015) and can be used for potential electronic devices. However, further research and study must be done to achieve optimum working conditions of DNA-Schottky diodes.

The study of DNA-Schottky diodes has potential to change how the world works by evolving conventional biological methods to a multidisciplinary method of semiconductor based DNA analysis. With more research into this field, in the near future, it is believed we could transfer lab-based DNA analysis into portable fully electronic technologies which will change the fields of taxonomy, forensics, pathology and others.

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LIST OF PUBLICATIONS AND CONFERENCE

1. **Chan, Z.**, Ahgilan, A., Sabaratnam, V., Tan, Y. S., & Periasamy, V. (2015). Rectification of DNA films self-assembled in the presence of electric field. *Applied Physics Express (APEX)*, *8*(4), 047002.

2. Vengadesh, P., Ciniciato, G. P. M. K., **Zhijian, C.**, Musoddiq, M., Fisher, A. C., & Yunus, K. (2015). Capillary force assisted fabrication of DNA templated silver wires. *RSC Advances*, *5*(11), 8163-8166.

3. **Chan, Z.**, Ahgilan, A., Musoddiq, M., Sabaratnam, V., & Periasamy, V. (2013, Apr). Electrical Characterisation of Self-Assembled DNA film on ITO. Paper presented at the International Conference on Functional Materials & Devices, Penang, Malaysia.

LIST OF AWARDS

1. Vengadesh P., **Chan Z.**, Tan Y.S., Vikineswary S. DNA Based Rectifying Device For Applications In Hybrid Electronics. *International Innovation, Design and Articulation 2013 (i-IDeA 2013),* Silver Medal.

2. Ng F.L., Muhammad M.B.J., Siti A.B.I., Vengadesh P., Phang S.M., **Chan Z.**, Adrian C.F., Kamran Y. Novel Reduced Graphene Oxide (rGO) Based Algae-Fuel Cell (AFC) For Generation Of Electricity From Photosynthesis. *International Innovation, Design and Articulation 2014 (i-IDeA 2014),* Bronze Medal.

3. Phang S.M., Vengadesh P., Ng F.L., Muhammad M.B.J., **Chan Z.**, Siti A.B.I., Kamran Y., Adrian C.F. Novel Reduced Graphene Oxide (rGO) Based Algae-Fuel Cell (AFC) For Generation Of Electricity From Photosynthesis. *BioInnovation Awards 2014,* Silver Award.

APPENDIX A - PUBLICATIONS

Rectification of DNA films self-assembled in the presence of electric field

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We report rectification phenomena in electric field induced self-assembled thin films of DNA that were employed in the development of an ITO/DNA/Al sensor. The prototype sensor was subjected to electrical characterization involving the acquisition of current–voltage graphs. Electric field aligned DNA films exhibited reduced potential barrier of 0.780 eV while the potential barrier for non-aligned films was 0.796 eV. Similar reduction was also observed for the measured ideality factor and series resistance. This enhanced rectification following electric field induced self-assembly of DNA films may prove beneficial for generating accurate and rapid response in DNA-based devices.
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olecular electronics has attracted significant attention during the past two decades. Amongst the biomaterials of interest, DNA has attracted most attention owing to its low cost and wide availability. Various groups have published numerous reports regarding the usage of DNA as rectifiers and sensors. However, proper understanding of its functionality and properties, especially when the DNA molecules are assembled into films, remains incomplete. As such, charge transfer mechanisms in DNA molecules are being exhaustively investigated, because this phenomenon provides insights on various biological processes and cell repair mechanisms. Semiconductor characteristics of DNA were first reported in 2000 when Porath et al. demonstrated large band gap semiconductor behavior, while Lintao, Hitoshi and Tomoji demonstrated similar properties of DNA on a mica surface.[1,2] Various other groups[3–7] have also reported rectification in DNA using various modifications and parameters. More recently, one research group investigated the current density–voltage characteristics of an Ag/DNA/p-InP device and reported rectification in this device.[8] Meanwhile, Wang et al.[9] illustrated DNA utilization as a template for fabricating nanowires exhibiting rectification. Finally, Gupta et al.[10] used spin-coating technique for constructing an Ag/DNA/p-Si/Al device with photodiode properties.

The double helix structure of DNA is composed of two strands of DNA wound around each other. The strands are composed of repeating sugar and phosphate groups attached to the bases. DNA strands accommodate four bases: guanine (G), cytosine (C), adenine (A) and thymine (T). These bases are the building blocks of the genetic code. In a double-stranded DNA, every two bases on the opposing strands are coupled by hydrogen bonds. The unique characteristic of these bonds is that adenine can only pair with thymine, while guanine can only pair with cytosine.[11] Previous works[12] have determined that holes (positive charges) are more stable on G–C pairs compared with A–T pairs. It has also been found that the energy difference between the pairs is large compared with the thermal energy of charge carriers, resulting in charge localization on G–C pairs.[12] In addition, energy levels in A–T pairs are higher, acting as a barrier. Various conduction mechanisms have been suggested for describing the electrical properties of DNA molecules, including hopping and tunneling.[1,13,14] The former phenomenon describes a mechanism similar to the conventional semiconductor electronics where charges "hop" from a G–C pair to an A–T pair. The latter phenomenon is similar to the quantum tunneling between potential barriers, which only happens at relatively short distances. These explanations provide a simple picture of charge transfer mechanism in DNA molecules. However, a proper understanding of the actual process remains incomplete. To date, little research has addressed the phenomena occurring in thin films of DNA, which is an important and promising field of study. In addition, another interesting property of DNA, the self-assembly ability,[2] allows for manufacturing low cost and high precision nanostructured materials.

Here, we demonstrate rectification in a self-assembled thin film of DNA on an indium tin oxide (ITO) coated glass with Al as a counter electrode. The DNA film exhibits a comparatively low threshold voltage in the forward bias orientation. Applying the Schottky's rule and the current–voltage ($I–V$) curve, the potential barrier between DNA and Al was 0.780 eV when the sample was dried in the presence of electric field. Without the electric field alignment, the calculated value was 0.796 eV. Field emission scanning electron microscopy (FESEM) images confirmed the formation of highly aligned DNA film on the substrate's surface. These results are likely to assist in developing DNA sensors and detectors for biomedical applications.

DNA molecules were extracted from *Mimosa pudica* by using a genomic DNA mini-plant kit from Yeastern Biotech. UV spectrophotometric analysis indicated that OD260/OD280 was 1.9 and the DNA concentration was 74.1 ng/µL. The ITO-coated glass was purchased from KINTEC, while the Al wire was purchased from Diamond. Deionized water was obtained using an in-house available Barnstead (Nanopure II) water deionizing system.

The DNA solution was diluted in deionized water with a weight ratio of 1 : 100. Using a micro syringe, the solution was cast on the ITO-coated glass substrate and allowed to air-dry overnight. The circuit was completed by attaching an Al foil as a counter electrode atop the DNA. After obtaining the $I–V$ measurements, the sample was wetted using a few drops of deionized water and dried in the presence of electric field ($120 \, \mathrm{V \, m^{-1}}$) that was utilized for aligning the DNA strands parallel to the field lines. The electric field helped to hold the molecules in place during the drying process. Owing to their electrodynamic characteristics, the DNA strands realigned and dispersed, as shown in Fig. 3. The same measurements

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Capillary force assisted fabrication of DNA templated silver wires

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We demonstrate for the first time the formation of micron scale conductive silver (Ag) wires induced by capillary forces through scribed micro-cuts on a deoxyribonucleic acid–silver nanoparticle (DNA–AgNPs) film. The "writing" flexibility based on the physical rearrangement of the particles may prove to be prominent towards the fabrication of conductive wires.

Deoxyribonucleic acid or DNA has in the last few decades been increasingly studied as a smart electronic material with highly complementary base pair specificity.[1,2] Fuelled by "technological aggravations" caused by predictions of Moore's Law, DNA electronics promises nano-scaled dimensions of tuneable electronic properties. The main interest lies in the fact that DNA molecular constituents enable specific bindings with metallic nanoparticles allowing flexible nano-templating abilities. Not surprising, DNA assisted metallic wire deposition has been studied for its potential use in electronics by various groups.[1,2] DNA was chosen primarily for its self-assembly and selective metallic templating properties. It has been reported that metals evenly distribute along the phosphate backbone of DNA.[3,4] These properties in turn can be utilized to selectively bind inorganic materials such as silver (Ag) along the DNA strands. The last two decades showed much progress in these aspects,[5] yet the challenge still remains to establish a flexible, practical and cost effective methodology.

In 1997, Deegan et al.[6] observed higher particulate concentrates at the edge of a drying drop as a result of evaporation influenced capillary forces. This phenomenon, known as the coffee-ring effect, involves movement of particles from the interior of the drop towards the edge. Particles are also redistributed back to the interior by means of the Marangoni effect.[7] By addition of surfactants, which drastically reduces the

surface tension of the droplet, this effect could be drastically reduced.[7] In this communication, we employed these capillary forces to displace DNA strands templated with Ag nanoparticles (NPs) along a micro-cut, which acts as the edge through where evaporation occurs. Continuous evaporation towards the edge results in the metal loaded DNA molecules to aggregate and form long micro-wires on both sides of the edges. As demonstrated by Deegan et al. in their coffee ring experiment, migration of the molecules is influenced by the outward flow within the droplet containing the molecules, which is driven by the evaporation induced solvent loss through the cut edges. According to them, this is further determined by the geometrical constraint of the boundary of the shape of the DNA–AgNPs droplet.

Fabrication of the proposed silver microwires involves three major stages; self-assembly of DNA–AgNPs suspension, scribing process and material rearrangement. A silicon (Si) wafer (single side polished, ⟨100⟩, n-type, undoped) with a dimension of 2.0 inch × 0.5 mm bought from Sigma, UK was used as a substrate for the microwire formation. The sample used in this work was used only once and fresh from the supplier, as such no further cleaning was necessary. Indium tin oxide (ITO) (KINTEC, Hong Kong) slides for the Field Emission Scanning Electron Microscope (FESEM) imaging meanwhile was first sonicated for 15 minutes in detergent. The slides were then rinsed with deionized water, followed by acetone, isopropyl alcohol and deionized water. Finally, the slides were purged with nitrogen gas prior to usage. An aliquot of 0.5 mL of deionized water (18.2 MΩ cm) was mixed with the vial containing lyophilized pBR322 DNA (MW 2.9 × 10^6 Da) from Escherichia coli RR1 (Sigma, UK). 400.0 μL of this DNA solution was mixed with 400.0 μL of AgNPs dispersion (10 nm particle size, 0.02 mg mL⁻¹, Sigma, UK) in aqueous buffer and sodium citrate as stabilizer. The solution was then incubated overnight to allow metallic silver aggregates to bind to the DNA molecules. A micropipette was then used to displace 50.0 μL of the DNA–AgNPs solution onto the silicon wafer. 15 minutes later a drop of ethanol (10.0 μL) was applied onto the droplet

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