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ELECTRICAL PROPERTIES OF THIN NANOCRYSTALLINE DIAMOND BASED SCHOTTKY BARRIER DIODES AND **OTHER TWO-TERMINAL STRUCTURES**

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ELECTRICAL PROPERTIES OF THIN NANOCRYSTALLINE DIAMOND BASED SCHOTTKY BARRIER DIODES AND OTHER TWO TERMINAL STRUCTURES

By

Mitchell Douglas Parr

A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

ELECTRICAL PROPERTIES OF THIN NANOCRYSTALLINE DIAMOND BASED SCHOTTKY BARRIER DIODES AND OTHER TWO-TERMINAL STRUCTURES

By

Mitchell Douglas Parr

Diamond possesses many unique characteristics that make it attractive for a number of applications. Research in electronics has seen the development of diamondbased devices over recent years but they have, for the most part, remained structurally flat. This thesis presents a preliminary study on the fabrication potential of flexible diamond electronics. Undoped nanocrystalline diamond (nanodiamond) films grown from a microwave plasma-enhanced chemical vapor deposition (MPECVD) process ranging from $0.25 - 1.0 \,\mu\text{m}$ in thickness were used in the fabrication of electronic devices and current-voltage characteristics were investigated. Both freestanding nanodiamond films and substrate-mounted films were studied. For the latter, Schottky barrier diodes of a zirconium-nanodiamond-silicon configuration were fabricated from nanodiamond film of varying thickness and rectification ratios up to 1.1×10^4 at ± 80 V were observed. Temperature dependence of both the Schottky junction and field-activated conductivity following a Poole-Frenkel reduction in ionization energy was studied. This thesis also includes a preliminary investigation into the unintentional development of what is speculated to be a nanodiamond/carbon-filament based Schottky barrier diode. Currentvoltage characteristics were studied under varying nanodiamond film thickness and temperature where rectification ratios up to 1.69×10^5 were observed at ± 10 V.

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Chapter 1

Introduction

1.1 Research motivation

Over the past 15 years, diamond has been of increased interest to researchers in chemistry, physics, material science, and engineering due to the unique characteristics that this rare material possesses and the availability of new methods of synthesizing it. One often touted application of diamond is in electronics. Diamond has qualities that make it ideal for high power, high frequency, and high temperature electronic applications such as high breakdown field, high saturation velocity, high thermal conductivity and more [1,2]. Past research has demonstrated the development of diamond-based vacuum tubes, Schottky barrier diodes, field-effect transistors (FET), and other electronic switches [3,4,5]. Perfecting the development of these fundamental devices is crucial for the development of more complex circuits. Though currently only in a preliminary stage, advancements in diamond growth technology through research here at Michigan State University and elsewhere continuously close in on the realization of diamond-based electronics in our everyday life.

As an extension to current research into diamond based electronics, this thesis introduces the idea of flexible diamond based electronics. Thin sheets of diamond film have already been shown to have the capability to conform to curved surfaces and maintain this shape without fracturing or breaking [6]. This thesis presents a preliminary

step in the investigation of electronic devices fabricated from thin diamond films that maintain this degree of flexibility. Doped and undoped polycrystalline and single crystalline diamond on the order of a few micrometers thick have been used in past research for electronic device fabrication; however, diamond and contact thickness may limit or prevent flexibility.

The research presented in this thesis utilized undoped nanocrystalline diamond film (nanodiamond) with grain size on the order of tens to hundreds of nanometers in diameter and film thickness down to a quarter micrometer to aid in flexibility. Simple freestanding nanodiamond based devices behaving as voltage-controlled resistors were fabricated. Pressures up to 15-20 psi were applied to two-terminal devices formed on nanocrystalline membranes. Also, zirconium-nanodiamond-silicon Schottky barrier diode configurations were fabricated with nanodiamond film ranging in film thickness from about 250 - 770 nm. Testing was completed on the Schottky barrier diodes at temperatures of 300 - 425 K to investigate temperature dependence of the Schottky junction and electric field-activated conductivity. The latter follows a Poole-Frenkel reduction in ionization energy associated with Coulombic centers in the nanodiamond. A DC model was developed for these diodes based on device characterization. Also, investigation into the unintentional, but fortuitous, development of a Schottky diode with improved rectification along with a developed DC model and subsequent device characterization for this device is presented in this thesis.

1.2 Thesis organization

This thesis is divided into six main chapters with the next chapter providing background material as an aid to the reader. The reason for interest in diamond, different types of chemical vapor deposition (CVD) diamond, field-activated conductivity, Schottky barrier diodes, previous diamond studies, and flexible diamond are the topics covered in Chapter 2.

Chapter 3 presents the experimental methods used in this research. Several types of contact metals along with a few different sample configurations were considered. These electrical sample configurations along with details on nanocrystalline and ultrananocrystalline diamond film growth, contact metallization, silicon back-etching, current-voltage measurements, and diamond-film thickness measurements are presented in this chapter.

Chapter 4 presents the experimental results of the nanocrystalline diamond based Schottky diodes investigated in this thesis. Current-voltage measurements on these "initial-state" diodes were performed at various temperatures and with varying diamond film thickness and the results are presented in this chapter. Also, this chapter provides results on modified diodes resulting from an unexpected "phase-change" through high voltage/current combinations. Results from current-voltage measurements on these "phase-change" diodes performed at various temperatures and with varying diamond film thickness are presented in the later part of Chapter 4.

Chapter 5 goes through an analysis of the experimental results of Chapter 4 in an attempt to model both the initial-state and phase-change diodes through device

characterization. A proposed DC model along with the investigation and calculation of the barrier height, saturation current, and voltage activated conductivity following a Poole-Frenkel reduction in ionization energy is presented. Also, a DC model for the phase-change diodes and subsequent device characterization giving rise to an estimated barrier height, forward bias and reverse bias resistance, reverse bias activation energy, saturation current, and ideality factor follows in the last section of Chapter 5.

Finally, Chapter 6 follows with a conclusion and recommendations for future research.

Chapter 2

Background

2.1 Introduction

This chapter presents background information to aid the reader in the understanding of this research. The reason for interest in diamond for electronic applications along with the different types of polycrystalline diamond currently being used in the fabrication of electronic devices is presented in the first two sections. Fieldactivated conductivity is discussed along with a short explanation on the construction and operation of Schottky barrier diodes follows in the next two sections. Finally, a discussion on previous diamond Schottky diode research along with a discussion on flexible diamond is presented in the last two sections of this chapter.

2.2 Why diamond for electronics?

Diamond has many properties that make it desirable for use in solid-state electronics such as: wide band gap, high breakdown electric field, high saturation velocity, high hole and electron mobility, and the highest thermal conductivity of any room temperature solid [1,2]. Collectively, these properties make diamond a potentially suitable material for use in high power, high frequency, and high temperature electronic applications. In addition, due to diamond's natural chemical inertness and radiation-hard physical properties, such diamond-based electronics could be realized for applications in extremely harsh environments.

Two figures of merit, Keyes' figure of merit (KFM) and the Johnson figure of merit (JFM), provide an indication of a material's suitability in electronic applications. The KFM addresses the thermal limitations of a material for high-frequency applications [7] and is given by:

$$KFM = \lambda \left[\frac{cv_s}{4\pi\varepsilon_r} \right]^{\frac{1}{2}}$$
 [2.01]

where λ is the thermal conductivity, c is speed of light, v_s is saturation velocity, and ε_r is dielectric constant. The JFM addresses the potential of a material for both high-frequency and high-power applications [8] and is given by:

$$JFM = \left[\frac{E_M v_s}{2\pi}\right]^2$$
[2.02]

where E_M is breakdown field. A large value for KFM or JFM indicates a material to be more suitable than materials of a lesser value.

Both Johnson and Keyes figure of merit calculated for diamond and a few other semiconductors are shown in Table 2.1, along with some electronic properties commonly compared among semiconductor materials. Values for the first six rows in the table are from a variety of sources and are used to calculate the values in the last two rows. Diamond exceeds all other semiconductors in both figure of merits and in the specific case of silicon, diamond is up to several orders of magnitude higher by comparison. Other studies have shown the same trend in comparison with other semiconductors besides those listed in Table 2.1 [2,9,10] with the exception of the JFM calculated for AlN in reference [9]. However, it should be noted that the researchers chose to use a smaller breakdown field [9] in the JFM calculation instead of the maximum used in the table below. A recalculation using the maximum breakdown field present in Table 2.1 produces a relatively larger JFM for diamond.

Property	Si	SiC-4H	GaN	Diamond	Units
E _G	1.12	3.2	3.4	5.5	eV
E _M	0.3	3	5	10	MV / cm
μ_n	1450	900	2000	4500 [11]	cm^2/Vs
λ	1.5	5	1.3	20	W/cmK
v _s	1.0	2.0	2.5	2.7	$10^7 cm/s$
E _r	11.8	10	9.0	5.5	no units
KFM	1.0	5.1	1.57	32	no units
(normalized)					
JFM	1.0	400	1736	8,101	no units
(normalized)					

Table 2.1 Physical properties and figures of merit for common semiconductors

2.3 CVD diamond

Over the years, several different deposition processes have been developed and used by researchers to grow diamond film. All films grown for this study were produced using the microwave plasma-enhanced chemical vapor deposition (MPECVD) process which appears to be one of the more popular alternatives today for creating good quality diamond. Depending on the substrate, both single crystalline or polycrystalline diamond can be grown using this process. For the purpose of this thesis, only polycrystalline films were investigated.

By varying the growth conditions and seeding procedure for diamond films, different polycrystalline diamond film variations are possible using the MPECVD process and are classified as; microcrystalline, nanocrystalline, and ultrananocrystalline diamond (UNCD) as described by Reinhard et al [6]. Microcrystalline diamond film is comprised of a multitude of diamond grains each on the order of a micrometer to several micrometers in diameter bonded together to form a diamond sheet. Nanocrystalline diamond film is similar except it contains diamond grains on the order of tens of nanometers to hundreds of nanometers in diameter. The difference in grain size between these two films is a result in substrate seeding methodology. Depending on nucleation density from different seeding methods, a diamond film with smaller grain sizes (nanocrystalline) results with a higher nucleation versus films with larger grain sizes (microcrystalline) resulting from a smaller nucleation density.

UNCD films require different deposition chemistry all together. The microcrystalline and nanocrystalline diamond films mentioned above are produced from a H_2/CH_4 , with optional oxygen containing, gaseous environment. Excited with plasma, the end result is a diamond film on the surface of the substrate as described by Celii and Butler [12]. However, if an Ar/CH₄, with optional hydrogen containing, gaseous environment is used, a UNCD film is deposited on the substrate surface as described by Gruen [13]. A UNCD film contains grain sizes on the order of a few nanometers to tens of nanometers in diameter. Therefore, by varying the diamond nucleation and deposition

chemistry, the MPECVD process has the potential to produce polycrystalline films ranging in grain sizes from a few nanometers to tens of micrometers.

2.4 Field-activated conductivity

Due to the grain boundaries of polycrystalline diamond, the electrical conductivity can be different from that of single crystalline material. Grain boundary effects give rise to electron transport phenomena that have the potential to dominate the electrical conductivity within the material under specific conditions. A very noticeable transport phenomenon in undoped polycrystalline diamond is electric field-activated conductivity according to Poole's Law as first noted in polycrystalline diamond films by Huang and Reinhard [14]. Other sources have since observed and verified the same field dependent conductivity [15,16,17].

Defects in the crystal lattice, impurities, and grain boundaries can give rise to localized Coulombic potentials that behave as carrier traps. Associated with the Coulombic potentials is an ionization energy required to free trapped carriers. When a bias is applied, a reduction in ionization energy with rising electric field results in a very noticeable decrease in trapped carriers and subsequent increase in carrier concentration [14]. At low fields, the I-V relationship is primarily ohmic because the electric field is not large enough to appreciably lower the barrier, so there is no change in carrier concentration and conductivity remains constant. However, as the electric field increases, conductivity increases due to an increase in carrier concentration resulting

from a reduction in the ionization energy of Coulombic potentials. When the Coulombic potentials are non-overlapping, the field-activated conductivity follows the Poole-Frenkel effect which goes as:

$$\sigma = \sigma_0 e^{\frac{(q^3 E/\varepsilon)^{1/2}}{kT}}$$
[2.03]

where σ_0 is the conductivity resulting from thermionic emission, E is electric field, ε is the dielectric constant of the film, k is Boltzmann's constant, and T is temperature [18]. When the Coulombic potentials are overlapping, the field-activated conductivity follows Poole's Law and goes as:

$$\sigma = \sigma_0 e^{\alpha E}$$
 [2.04]

where α is a function of temperature and spacing between Coulombic potential centers [18]. Therefore, the total conductivity of the sample including the ohmic conductivity, σ_{00} , becomes:

$$\sigma = \sigma_{00} + \sigma_0 e^{\alpha E}$$
 [2.05]

The total field-activated conductivity according to Poole's Law has been experimentally observed in polycrystalline diamond films at electric fields on the order of 10^5 V/cm and higher [14,15,17]. At sufficiently high enough fields, the field-activated conductivity was reported to dominate the electrical conductivity of the polycrystalline diamond films. Since field-activated conductivity was observed in the diamond films in this study, Poole's law will be examined in more detail in Chapter 5.

2.5 Schottky barrier diodes

The primary focus of this research was developing diamond-based Schottky barrier diodes; therefore, a brief background on Schottky barrier diodes is presented for the reader. As with any topic in solid-state electronics, the details behind the inner working of realized solid-state devices is long and detailed and the topic of Schottky barrier diodes is no different. This section only presents fundamental relations and properties of Schottky barrier diodes and the curious reader is advised to reference any of a number of solid-state text books available for a more advanced analysis of Schottky barrier diodes. In particular, much of the information contained in this section has been referenced from Casey's introductory text [19].

As a quick reminder to the reader, semiconductors have distinct energy levels where electrons reside due to the periodicity of atoms in the crystal lattice. For current flow, only the electrons inhabiting the outer two energy bands are involved. We designate the outer most energy band the "conduction" band and the carriers are electrons. The energy band directly below is called the valence band and the carriers are "holes", or electron vacancies. At zero Kelvin, the conduction band is free of electrons and the valence band is completely full resulting in no current flow, characteristic of a semiconductor. As temperature increases, electrons gain enough energy to cross the "bandgap" on into the conduction band, leaving behind a vacancy in the valence band, or hole as defined above. Both carrier types are free to move about their respective bands, and under the influence of an electric field, provide the means to conduct current through the material.

One such device that takes advantage of the unique properties of a semiconductor is a Schottky barrier diode. The construction of a Schottky barrier diode is essentially a metal to semiconductor junction. If conditions are right, a "built-in potential" will form around the interface of the two materials, allowing current flow of primarily one carrier type in, ideally, only one direction. Formation of a Schottky barrier is essential in these devices and is dependent on the work function of the materials. A work function is the amount of energy required to raise an electron from the Fermi energy to zero energy vacuum level where there are no longer any forces acting on the electron leaving it energy free. Thus, in both metals and semiconductors, the work function is the potential difference between zero energy vacuum level and the Fermi level. In metals, the Fermi level is fixed and known for each metal. However, in semiconductors, the Fermi level is dependent on the doping concentration and, for nondegenerate semiconductors, falls in between the conduction band and valence band.

To produce a built-in potential, the work functions of the two materials must be considerably different to form a significant barrier at the metal-semiconductor junction. The built-in potential is the difference between the metal work function, Φ_m , and the semiconductor work function, Φ_s , defined as:

$$V_{bi} = \Phi_m - \Phi_s \tag{2.06}$$

where Φ_s is given as the following for an n-type semiconductor:

$$\Phi_s = X + [E_c - E_f]/q$$
 [2.07]

and p-type semiconductor:

$$\Phi_s = X + [E_g - (E_f - E_v)]/q$$
[2.08]

In this expression, E_c is the bottom of the conduction band, E_v is the top of the valence band, E_f is the Fermi energy, E_g is the bandgap, and X is the electron affinity. The electron affinity, X, is defined as the difference in potential energy between vacuum level and the bottom of the conduction band, E_c .

The built-in potential "blocks" carriers of a particular type from crossing from the semiconductor and into the metal. Carriers coming from the other direction, crossing from the metal into the semiconductor, are blocked by a potential called the "barrier height", φ_B , and is defined as:

$$q\varphi_B = q(\Phi_m - X)$$
 [2.09]

for an n-type semiconductor and:

$$q\varphi_B = qX + E_g - q\Phi_m \qquad [2.10]$$

for a p-type semiconductor. The built-in potential and barrier height are essential to these devices and govern the forward and reverse I-V characteristics that define their functionality.

The best way to visualize the built-in potential and barrier height along with corresponding energy levels is through the energy-band diagram. Shown in Figure 2.1 are the before and after joining representative energy-band diagrams for both a metal to n-type semiconductor and metal to p-type semiconductor. Figure 2.1(a) shows the two materials in equilibrium. Upon initial contact, the electrons in the n-type semiconductor's conduction band will transfer to the metal where the energy is lower until the Fermi energy levels align and the subsequent built-in potential develops and blocks any more electrons from transferring. The resulting energy diagram can be seen in Figure 2.1(b). The same process follows for the p-type semiconductor in



Figure 2.1 Energy band diagram for (a) n-type equilibrium (b) n-type Schottky barrier formation (c) p-type equilibrium (d) p-type Schottky barrier formation

Figure 2.1 (c), except holes transfer to the metal upon initial contact and continues to do so until the Fermi energy levels align and subsequent built-in potential develops and prevents anymore holes from transferring as shown in Figure 2.1 (d).

Upon application of an electric field across the device, with an applied voltage V, the energy bands of the semiconductor will increase or decrease depending on orientation of the field. If the electric field is applied in a manner to counter-act the built-in potential (forward bias), the built-in potential will decrease as $q(V_{bi} - V)$ and majority carriers will move from semiconductor to metal inducing a current flow through the device. An electric field applied in the direction of the built-in potential (reverse bias) will only increase the built-in potential as $q(V_{bi} + V)$ and only a small current flows under this condition. The following expression deemed the "Schottky" diode equation relates the applied voltage to the current flow induced within the device and is given as:

$$I = I_s \left[\exp\left(\frac{qV_a}{nkT}\right) - 1 \right]$$
 [2.11]

where V_a is applied voltage, positive for forward bias and negative for reverse bias, *n* is ideality factor, *k* is Boltzmann's constant and *T* is temperature. The saturation current, I_s , is the relatively small current arising from majority carriers in the metal possessing enough energy to overcome the barrier height, φ_B , and cross into the semiconductor. The saturation current is given as:

$$I_s = AA^*T^2 \exp\left(\frac{-q\varphi_B}{kT}\right)$$
[2.12]

where A is cross-sectional area and A^* is the effective Richardson's constant.

Therefore, using the I-V relationship defined above along with the

aforementioned relations and others not covered in this brief overview, several properties can be extracted from experimental data to help characterize a fabricated device. These properties include but are not limited to: saturation current, the ideality factor, the barrier height, the built-in potential, activation energy, depletion capacitance, bulk resistance and the cross sectional area of the device. The inclusion of these properties into a generalized Schottky diode model allows one to accurately predict the behavior of the fabricated device. For complete device characterization, both an AC model and DC model are commonly developed; however, the focus of this research was DC analysis and subsequent DC modeling of the diamond-based Schottky barrier diodes.

2.6 Previous studies of Schottky barrier diodes

Due to the difficulty in doping diamond n-type [20], most research on diamondbased electronic devices has focused on unipolar structures such as Schottky barrier diodes and field effect transistors (FET). Preliminary studies of diamond as semiconductor devices began as early as 1955 with Brophy [21] where the Hall Effect, electrical conductivity and point contact rectification was examined on natural diamond. Reports of Schottky barrier diode fabrication and extensive study of the capacitancevoltage characteristics of Schottky barrier diodes formed on laboratory grown, borondoped single crystalline diamond was reported as early as 1973 by Grover [22]. With the later development and interest in polycrystalline films deposited through the chemical vapor deposition (CVD) process, interest in diamond electronics increased. Schottky

barrier diodes fabricated from these films were first reported in 1988 by Gildenblat et al [23]. A subsequent review of the progress in device fabrication from polycrystalline diamond films in that era was published by Gildenblat a few years later [10].

As mentioned in section 2.5 above, Schottky barrier diodes rely primarily on the transport of one carrier type which can be influenced by doping. Diamond based Schottky barrier diodes have been p-type where diamond plays the role of a p-type semiconductor. This p-type behavior comes either from intentional boron doping of diamond or from a highly conductive p-type surface layer resulting from defect acceptor-like states present at or near the surface of the diamond. The details of this latter phenomenon are currently not well understood [24,25]. Devices specifically utilizing this unique surface conductivity have been realized to develop Schottky barrier diodes and FETs with one such example of a FET coming from Glueche et al in 1997 [5]. It should be noted that alteration of this p-type surface layer by exposing the surface to hydrogen and oxygen through hydrogenation, cleaning, and oxidation modifies the behavior of metal to semiconductor interfaces [26] and is therefore an important variable in diamond Schottky barrier diode fabrication.

Development of diamond based Schottky barrier diodes has continued to the present as represented by a recent report by Butler et al on the development of a Schottky barrier diode fabricated on boron-doped, single crystalline diamond with a breakdown voltage over 6 kV [4]. Thus, diamond-based Schottky barrier diodes currently represent one of the leading contenders for an electronic device that takes advantage of diamond potential for high temperature and high power devices. Indeed, as noted by an article recently published in Science Magazine titled "A dawn for carbon electronics?" there is

currently high interest in diamond based electronics [27].

2.7 Flexible Diamond

A novel approach to the research presented in this thesis was the development of flexible diamond-based electronics. Research into fabrication of diamond membranes and sheets and application to curved surfaces was reported by Reinhard et al [6]. The diamond sheets developed in this research were drapable, capable of being wrapped around cylinders as demonstrated in the paper. Several thin diamond films of varying grain sizes were produced with thicknesses on the order of 1-3 µm and as large as several cm². The films were then floated on an aqueous solution were they could be applied to stainless steel frames as freestanding films. Due to the films flexibility and limp behavior when wet, the authors were able to successfully wrap the diamond films around a stainless steel tube. Although no electrical devices were produced from these flexible diamond films, the research demonstrates the potential for eventual electronic device fabrication.

Chapter 3

Experimental Methods

3.1 Introduction

This chapter reports on the methodology employed for Schottky barrier diode fabrication, sample preparation, current-voltage and diamond thickness measurements completed for this thesis. Nanocrystalline and ultrananocrystalline diamond film growth, contact metallization, silicon back-etching, electrical sample configurations, I-V measurement using an HP4145B semiconductor parameter analyzer, I-V measurement using a Tektronix 577 curve tracer, and diamond-film thickness measurement using transmission spectroscopy are all discussed in the following sections.

3.2 Diamond Films

The Schottky barrier diodes fabricated for this work were primarily developed from nanodiamond grown on silicon wafers by Booth [28]. The nanodiamond film was grown inside a Microwave Cavity Plasma Reactor (MCPR) designed by Asmussen et al. and built at Michigan State University [29]. Microwave Plasma-Enhanced Chemical Vapor Deposition (MPECVD) was the growth process from which the diamond films were created. MPECVD is the technique of mixing a number of reactive gases in a

microwave-induced plasma environment where the byproduct is, ultimately, deposited on the surface of the substrate. Details of the MPECVD process used specifically for diamond growth are explained by Asmussen et al [29].

A Booth nanodiamond sample, denoted as FB23, was used principally for this work. This particular diamond sample was reported to have been grown under the following conditions: a substrate temperature of 660°C, deposition pressure of 33 Torr, H_2 gas flow of 200 sccm, CO_2 gas flow of 8 sccm, CH_4 gas flow of 3 sccm, 700 W of absorbed microwave power, and a deposition time of 7 hours. The nanodiamond film was grown on a 3" diameter (100) p-type silicon wafer with a resistivity of 1-10 ohm-cm and a thickness of approximately 250 μ m. For more details of the nanodiamond growth process for the FB23 sample, the reader is referred to the work completed by Booth [28].

Additionally, preliminary studies were performed on ultrananocrystalline (UNCD) diamond films. The UNCD films were grown by Angela Moon in Professor Grotjohn's research group using the same MCPR reactor and MPECVD diamond growth process mentioned earlier but with a different chemistry [30]. The UNCD sample used for this work, denoted as A9, was reported to have been grown under the following conditions: a substrate temperature less than 650°C, deposition pressure of 120 Torr, H₂ gas flow of 1 sccm, Ar gas flow of 100 sccm, CH₄ gas flow of 1 sccm, and 1.1 KW of absorbed microwave power.

3.3 Metallization

Metallization studies in this work included indium, gold, titanium/gold, graphite based "paint", zirconium, and pressure contacts against tungsten, platinum, and stainless steel. Metallization was performed on both diamond film on silicon and freestanding diamond. Metallization issues with contact reliability, consistency, and I-V behavior led, ultimately, to zirconium as the chosen Schottky metal contact. Specific issues encountered included inconsistent I-V behavior with pressure contacts and poor surface adhesion with melted indium pellets. Aluminum has previously been reported as a good Schottky metal contact for diamond. However Al was not investigated in this study after the initial success with zirconium. Non-Schottky (ohmic) contacts on diamond were formed primarily with gold. In one case, a titanium/gold film was sputtered on a freestanding diamond film; however the film broke and curled after the process, presumably due to stresses in the film after the addition of the sputtered layers.

The use of gold for ohmic contacts requires further comment. A perfect ohmic contact is one that has zero contact resistance. A practical ohmic contact is one for which the contact resistance is small relative to the bulk or series resistance of the device to which contact is being made. For the diamond films used in this study, gold was a practical ohmic contact so long as the diamond thickness was on the order of a micrometer. For such structures, with gold as one contact and silicon as the other, the I-V curves were symmetric, i.e. the rectifying ratios were essentially unity. However, for very thin diamond, i.e. on the order of $0.25 \,\mu$ m, the rectification ratio could be as high as 200. Thus, gold acted as an ohmic contact only if the diamond was sufficiently thick to

have a substantial bulk series resistance.

As mentioned above, zirconium was the chosen metal for contact metallization in fabricating the Schottky barrier diodes. The zirconium metallization was performed by Mr. Michael Becker of the Fraunhofer Center for Laser Coatings and Applications. Due to the difficulty in producing zirconium metal in vapor form, a simple sputtering physical vapor deposition (PVD) process could not be used. A PVD Arc process provided the necessary means for zirconium deposition. A shadow mask with over 400 circular, 500 μ m diameter holes was fastened to the diamond surface and the metal was deposited through the mask. The zirconium was deposited under the following conditions: a pressure of 1.13 x 10⁻² Torr, two cathodes each with a current of 90 A, a sample bias of -50 V, and a deposition time of 3.3 min. The metallization process resulted in distinct zirconium contacts, each with a diameter of 450 μ m (± 25 μ m) and a height of approximately 50 nm.

3.4 Back-Etch

Since the principal motivation of this research was to explore issues related to "flexible" diamond-electronics, various degrees of silicon back-etching were desired throughout this research. The nanodiamond/silicon sample was submerged in an acid solution and the acid was allowed to breakdown the silicon wafer leaving the diamond film and a portion of the silicon wafer if desired. The principal acid solution used was mixed from quantities of the following chemicals: five parts HNO₃, 4 parts H₂O, and 2
parts HF. The silicon side of the sample was scratched with sand paper to expedite the silicon etching process and then placed, silicon side up, into a Teflon holder and then both were placed in the acid solution. The acid solution, containing the diamond/silicon sample, was then placed on a hotplate to raise the solution temperature to about 50-60°C. The sample remained in the solution for approximately 30 minutes. After visual confirmation that silicon had been etched away, the sample was placed into de-ionized water (1 μ S/cm), providing a clean acid wash and a non-destructive environment for maneuvering the fragile diamond film onto a substrate if all silicon was removed.

Two degrees of silicon back-etching were performed on the diamond/silicon samples. The first degree of silicon back-etching was limited to etching only half of the silicon substrate, leaving the other half for the same diode fabrication mentioned above. The reasoning for this particular etch was to research the affect of the acid etch treatment on the chemical structure of the diamond surface. Chapter 2 discussed the importance of the chemical structure of the diamond surface in regard to band-bending and Schottky barrier formation with a metal. If the chemical structure of the surface was altered, then diodes fabricated out of that particular sample would, most likely, not behave the same as diodes fabricated from an as-grown diamond/silicon sample. The actual result from this etch was no apparent change in diode behavior compared to un-etched samples. It was concluded the acid etch treatment did not have a significant affect on the chemical structure of the diamond surface.

The second degree of silicon etching was complete removal of the silicon substrate. Two types of nanodiamond/silicon samples were etched. One sample contained no zirconium contacts (the zirconium was deposited after the silicon was

removed) and was etched using the HNO_3 solution mentioned above. The other sample had zirconium contacts already deposited on the diamond surface prior to silicon removal and required the use of a KOH etch to prevent damage to the zirconium contacts. The KOH silicon etch consisted of a 44/56 weight percentage KOH/H₂O solution and was performed at a temperature of 55-60°C. The reasoning behind etching a sample that already contained zirconium contacts was to provide protection to the chemical structure of the diamond surface covered by the metal contact. If the acid etch treatment did alter the surface, the hypothesis was that the diamond surface under the contacts would not be altered and any Schottky barrier present would be protected.

However, both of these samples presented experimental difficulties. For the sample of which zirconium was deposited on the diamond after complete silicon removal, the zirconium contacts appeared faint, bubbly, and had poorly defined edges. For the sample of which zirconium was deposited prior to silicon removal, a majority of the zirconium contacts came off during the silicon etch. A few contacts did survive but when the film was placed on a flat copper coated circuit board for microprobing the probes cracked the film and prevented measurement of those remaining contacts. Thus both the metallization procedures for thin freestanding ($\leq 1 \mu m$) film and the subsequent testing of such structures requires further development and investigation.

3.5 Electrical sample configurations

For measurements of Schottky barrier diodes on nanodiamond films still attached

to the silicon substrate, the following procedure was used. After contact metallization, the silicon surface of the nanodiamond/silicon sample was attached to an aluminum plate using a graphitic-carbon and water paste commonly referred to as "carbon paint". The carbon paint solidified and created a low resistive connection, relative to the highly resistive diamond, between the silicon and aluminum plate. This provided a back contact to the Schottky barrier diodes which was approximately ohmic over the current-voltage range investigated. A drawing of the final structure is shown in Figure 3.1.



Figure 3.1 Nanodiamond/silicon Schottky barrier diode structure

Electrical samples were also formed from freestanding films. Using the back-etch procedure mentioned in the previous section; silicon was removed from samples of both nanocrystalline-diamond/silicon and ultrananocrystalline-diamond/silicon samples. While still in the de-ionized water bath, the diamond film was maneuvered onto a steel washer. An insulating washer, comprised of a neoprene washer and plastic washer, was then attached to the exposed surface of the diamond film using epoxy. The holes in each of the washers were aligned with each other to form a diamond film window in the center of this structure. Gold was then deposited on both sides of the washer-diamond-washer

sample. The gold overlapped onto the steel washer surface providing one electrical contact, Electrode 2. The gold covering the surface of the insulating washer was removed to ensure no conductive path between gold layers on both sides of the diamond film. A metallic pin was inserted into the top of the insulating washer. A gold wire was then attached to the gold deposited on the insulating washer side of the diamond film with silver paste and connected to the pin. This provided another electrical contact, Electrode 1, insulated from the other contact via the insulating washer. A drawing of the final structure for this second device configuration is shown in Figure 3.2.

A 3rd sample configuration involved wrapping a flexible 1.6 μm thick nanocrystalline diamond film around a 6.35 mm diameter stainless steel tube, with the metal tube providing one electrode (Electrode 2) and graphite paint providing the other (Electrode 1). A picture of this device is shown in Figure 3.3. As shown in the figure, the carbon paint contact is connected to Electrode 2 via a gold wire.



Figure 3.2 Freestanding diamond film sandwiched by two washers



Figure 3.3 Flexible nanodiamond wrapped around stainless steel tube

3.6 I-V measurement setup - HP4145B semiconductor parameter analyzer

The majority of the Schottky barrier diode current-voltage (I-V) data collected for this work was performed by an HP4145B semiconductor parameter analyzer. The HP4145B is specifically designed to measure the DC characteristics for a variety of semiconductor devices. The device has the capability to perform arithmetic calculations, display measurement results on a built in CRT, perform graphical analysis, and provide various measurement options due to a number of voltage controls and connections. The HP4145 is limited to a maximum power output of 2 Watts with an absolute maximum voltage of 100 V. These limitations were reached several times throughout this study, eventually, resulting in the need of another I-V measurement apparatus, which is discussed in the following section.

Software developed to communicate with the HP4145B via a connected computer provided the means for automated measurement and data storage to aid in this work [Appendix]. A wafer probing station was used to provide the necessary contact connections while providing shielding from electromagnetic interference. Two of four available Stimulus/Measurement Units (SMU) on the HP4145B were connected to the probe station providing the necessary source and ground electrical contacts to the sample. Using the computer, the HP4145B was sent the necessary instructions for measurement setup including: measurement type, SMU connection information, starting sweep voltage, ending sweep voltage, and voltage increment. The HP4145B then proceeded to perform I-V measurements on the sample and when finished, the data was transmitted to the computer and stored as a text file.

The HP4145B measurement apparatus for the zirconium/nanodiamond/silicon sample, including electrical connections to the sample, is shown in Figure 3.4 and an example I-V plot is shown in Figure 3.5 for a diamond film approximately 0.25 µm thick. Due to the p-type behavior of the Schottky barrier diodes, a negative-bias voltage dropped across the diode from the zirconium contact to the aluminum plate put the device into forward bias. To represent the diode in forward bias using a more traditional positive-voltage scale, SMU1 and SMU2 were respectively chosen to be the "negative" and "positive" connections to the HP4145B.



Probe Shielding Box





Figure 3.5 Example zirconium/nanodiamond/silicon I-V plot

For the diamond films mounted on steel washers (Figure 3.2), a similar HP4145 measurement apparatus to that of Figure 3.4 was used for this sample. The zirconium/nanodiamond/silicon sample was replaced with the washer sample and SMU1 and SMU2 were connected to Electrode 2 and Electrode 1, respectively. In this case, the samples are basically resistors. The configuration allows one to test for piezoresistive effects, however with applied differential pressures up to about 15-20 psi no discernable effects were observed in both the ultrananocrystalline and nanocrystalline diamond. Piezoresistivity is generally associated with boron-doped diamond, and films in this study were undoped.

A representative plot of I-V data collected from the diamond/washer sample is shown in Figure 3.6 for a diamond film approximately 1 µm thick. As shown in this figure, the negative I-V data plotted in the negative quadrant very closely mirrors the data in the positive quadrant. This relationship shows that both the top and bottom gold/nanodiamond contact have the same I-V characteristics. As will be described, the nonlinear I-V behavior in Figure 3.6 can be attributed to a physical phenomenon present in the nanodiamond film rather than contact effect.

As noted in chapter 2, high electric fields can induce field-activated conductivity in the diamond-film. Poole-Frenkel lowering of Coulombic trapping potentials was discussed as one such phenomenon that has been observed in diamond. For a fixed film thickness, the conductance of a material associated with Poole's Law has an exponential relationship with voltage. As shown in Figure 3.7, I-V data plotted in Figure 3.6 is replotted to show the conductance versus voltage characteristics of the freestanding gold/nanodiamond/gold sample. The data, plotted on a logarithmic scale, shows a linear



Figure 3.6 Representative I-V plot for freestanding nanodiamond structure



Figure 3.7 Conductance versus voltage plot for freestanding nanodiamond

trend from about 55 to 100 volts. This is consistent with a conductance exponentially related to voltage, characteristic of Poole's Law. As noted in equation [2.05], Poole's Law results in field-activated conductivity repeated here for convenience as:

$$\sigma = \sigma_{00} + \sigma_0 e^{\alpha E}$$
[3.01]

or for conductance and voltage:

$$G = G_{00} + G_0 e^{aV}$$
 [3.02]

The exponential region of the field-activated conductance of Figure 3.7 indicates $\alpha = 1.0 \times 10^{-5} \text{ cm/V}$ and $\sigma_0 = 1.79 \times 10^{-13} (\Omega \text{ cm})^{-1}$, in good agreement with previous reports of Poole's Law in polycrystalline diamond films [14]. Prior to field activation, the conductance G_{00} is approximately 1.5 x 10⁻⁸ S. Given the contact radius of 2 mm and film thickness of approximately 1 μ m, this corresponds to a conductivity σ_{00} of approximately 1.0 x 10⁻¹¹ ($\Omega \text{ cm}$)⁻¹. Thus it appears that the gold provides ohmic contacts to a film that exhibits field-activated conductivity according to Poole's Law.

I-V measurements were also performed on a freestanding ultrananocrystalline diamond sample using the same sample configuration shown in Figure 3.2 and HP4145B measurement setup shown in Figure 3.4. A representative plot of I-V data collected from the ultrananodiamond/washer sample is shown in Figure 3.8 for a diamond film approximately 1.57 μ m thick. Although the data shows a non-linear relationship similar to that of Figure 3.6, there appears to be no discernable evidence of Poole's Law when plotted on a logarithmic scale.

The flexible nanodiamond film wrapped around the stainless steel tube (Figure 3.3) also used a HP4145B measurement apparatus similar to that of Figure 3.4. The



Figure 3.8 Representative I-V plot for freestanding ultrananodiamond

zirconium/nanodiamond/silicon sample was replaced with the stainless steel sample and SMU1 and SMU2 were connected to Electrode 2 and Electrode 1, respectively. A representative I-V plot created using data taken with HP4145B is shown in Figure 3.9. Although the plot is nonlinear, Poole-Frenkel lowering of Coulombic trapping potentials attributed to the I-V behavior of the gold/nanodiamond/gold sample and evident in Figure 3.7, is not apparent in the data collected from this sample. Also, the data lacks the same degree of symmetry across the y-axis, which can be attributed to the difference in contact materials. Electrode 1 is made of carbon paint and Electrode 2 is a stainless steel pressure contact. Finally, it is noted that the current in Figure 3.9 is much less that in Figure 3.6. These observations combine to indicate a lack of good ohmic contacts. Therefore, a large amount of voltage is lost to the high resistance of this contact and electric fields present in the diamond are too small to induce Poole's Law. One may speculate that the stainless steel pressure contact is the likely cause of this.



Figure 3.9 Representative I-V plot for nanodiamond wrapped tube structure

3.7 I-V measurement setup – Tektronix 577 curve tracer

Due to the current limitations of the HP4145B discussed in the proceeding section, a Tektronix 577 curve tracer with Tektronix 177 test fixture was used to source voltages and currents beyond those capable of the HP4145B. The Tektronix curve tracer and test fixture is specifically designed to measure the DC characteristics of semiconductor devices. The Tektronix 577 curve tracer has no digital interface or storage and is limited to only manual control. The measurement data must be visually read off of the built-in CRT monitor; therefore, accuracy is not as high compared with digital models. The device does not posses any graphical analysis tools and is unable to perform arithmetic calculations unlike the HP4145B. However, despite the lack of functionality, the advantage of the Tektronix for this study comes from its power output capability which can reach a maximum of 100 Watts with an absolute maximum voltage of 1600 V.

After using the HP4145B to the extent of its power handling capabilities, the Tektronix 577 curve tracer with Tektronix 177 test fixture was connected to the probe station and, subsequently, connected to the sample contacts. Data was then collected in 10-20 volt steps beyond the 100 volt maximum imposed by the HP4145B. To test the limits of the device, the voltage across the diodes were increased and data was collected until breakdown, a phenomena discussed in the subsequent chapters. Due to the lack of an auto-range feature, the display was constantly adjusted to display a meaningful reading that could be easily read of the CRT and recorded. The measurement apparatus is similar to Figure 3.4 except the HP4145 is replaced with the Tektronix curve tracer and a computer system is not present in the measurement setup.

3.8 Transmission spectroscopy

Several times throughout the course of this study, thickness measurement of a diamond-film was desired and transmission spectroscopy was the chosen tool. The transmission spectroscopy setup included: a Bausch & Lomb monochromator, Bausch & Lomb light source, lenses, Newport 818-IR optical power sensor and Newport 835

optical power meter. The Bausch & Lomb light source fed the monochromator with its Tungsten filament quartz bulb. Inserting an appropriate filter between the light source and monochromator eliminated higher order wavelengths and allowed a monochromatic beam of light to pass through the diamond-film sample. Transmitted light power was detected and measured using the optical power sensor and optical power meter, respectively. A lens was inserted before the sample at a distance from the sample where the light beam spot was sufficiently small for an accurate thickness measurement. A second lens was inserted after the sample at a specific distance from the sensor to recollect refracted light and tighten the light beam down to a sufficiently small dot on the optical power sensor. The wavelength of the transmitted light was varied from 700 nm to 1050 nm and the transmitted power was recorded at every 10 nm step. The sample was then removed and the same experiment was completed again providing transmission power versus wavelength for air. The transmission spectroscopy measurement setup is shown in Figure 3.10.

After the data was collected, the wavelength was converted to wavenumber and the optical transmission of the diamond sample, relative to air, was plotted versus wavenumber. An example relative transmission versus wavenumber plot is shown in Figure 3.11. The diamond-film thickness can be determined from the transmission and reflection theory of dielectrics. For details, the reader is referred to the Macleod text book for an in depth explanation of transmission and reflection through multiple mediums with multiple refraction indexes [31]. However, for this study, the resulting formula for dielectric thickness of an air-dielectric-air arrangement simplifies to:

$$t = \frac{1}{2n\Delta WN}$$
[3.03]



Figure 3.10 Transmission spectroscopy measurement apparatus



Figure 3.11 Example plot of relative transmission vs. wavelength

where *n* is the index of refraction for the material (2.38 was used for diamond) and *WN* is the wavenumber. The change in wavenumber, ΔWN , is determined by plotting the relative transmission versus wavenumber and choosing two consecutive "peaks" in the transmission plot. The difference in wavenumber between these two peaks is the ΔWN present in equation [3.03]. With the 700 nm to 1350 nm wavelength range used in this work, the plots created were limited to only two peaks and, therefore, one choice in choosing consecutive peaks.

Chapter 4

Experimental Results of Zirconium/Nanodiamond Diodes on Silicon

4.1 Introduction

This chapter reports on the observed and measured characteristics of the fabricated diamond-based Schottky barrier diodes on silicon. Key parameters of a diode include rectification ratio and breakdown voltage, both of which are presented here. In the process of performing higher power forward bias measurements on some of the diodes, an unexpected change was induced that resulted in a permanent and repeatable behavioral change. The characteristics of both "initial-state" and the changed diodes are reported in this chapter. While this chapter primarily presents the experimental data, most of the subsequent diode modeling and analysis is discussed in the following chapter.

4.2 I-V characteristics of initial-state diodes vs. thickness at 300K

All diodes described in this chapter were formed on a diamond film coated silicon wafer created by Booth and denoted as FB-23 [28]. The diamond-based Schottky barrier diodes exhibited consistent and predictable I-V behavior across the entire silicon wafer. Diodes with lower diamond film thickness exhibited higher rectification ratios than the diodes with thicker diamond films. Transmission spectroscopy was used to verify an increase in diamond film thickness moving away from the outer edge of the film towards the center of the wafer where its thickest region was located. Thus, for a given wafer, higher rectification ratio diodes were located near the wafer's edge. Natural color fringes on the diamond surface were used as a visual reference for thickness variation across the wafer. Fringes were identified by numbering them sequentially from the wafers edge. A relative change in diamond film thickness of about 0.13 μ m between any two consecutive color fringes was measured using transmission spectroscopy.

After completion of the current-voltage measurements reported in the later sections of this chapter, the silicon was etched away and diamond-film thickness was measured optically for Fringe 5 as described in section 3.8. The remaining fringe thicknesses were approximated by subtracting multiples of 0.13 um from the Fringe 5 thickness. The thickness values for the five fringes referred to in this chapter are shown in Table 4.1.

Fringe	Fringe Thickness (µm)
1	0.249
2	0.379
3	0.509
4	0.639
5	0.769

Table 4.1 Diamond thickness values for the five fringes

As described in chapter 3, using an HP4145B semiconductor parameter analyzer,

current measurements were taken between 0 and 100 volts for both forward and reverse bias at a temperature of 300 K. The I-V plot of a typical Schottky barrier diode found along Fringe 1 is shown in Figure 4.1. The plateau at the peak of the curve in the forward bias region represents the limit of the HP4145B output current restricted to 20 mA.



Figure 4.1 I-V plot of typical Schottky barrier diode located on Fringe 1

The rectification ratio is defined as the ratio of forward bias current to reverse bias current at a given and identical absolute value of forward and reverse bias voltage, or:

Rectification Ratio =
$$\left| \frac{I_F(V_F)}{I_R(V_R)} \right|$$
 [4.01]

where $|V_F| = |V_R|$. A large rectification ratio is always desired for diode applications.

For this study, Fringe 1 diodes were found to have the highest rectification ratios

on the wafer. Fringe 1 represents the diodes located in the thinnest region of the diamond coated silicon wafer. Specifically, the highest rectification ratio was for device (10, 1) where the forward bias current at 80 volts was 19.7 mA and the reverse bias current at -80 volts was 1.78 μ A, leading to a rectification ratio of 1.107 x 10⁴. Other Fringe 1 diodes measured had rectification ratios within 0.1-0.3 x 10⁴ of the largest.

Further diodes were chosen randomly across the entire nanodiamond/silicon wafer on each color fringe and I-V characteristics were measured. For consistency in thickness variation, only diodes located in or near a purple color fringe were studied. Figure 4.2 and Figure 4.3 shows the forward bias and reverse bias I-V data, respectively, on a logarithmic scale for typical diodes located on all 5 fringes of the wafer sample. The plateau at the top of both "Fringe 1" and "Fringe 2" plot lines are the result from the HP4145B's current limiter safety circuit capped at 20 mA. The resolution of the HP4145 and probe station appears to be around 100 pA in this series of measurements.

A composite I-V plot of Figure 4.2 and 4.3 is shown in Figure 4.4. The reverse bias current varies slightly with respect to fringe while the forward bias current varies more severely with respect to fringe. For example, the current at 78 volts for the fringe area diodes under forward bias varies by more than 3 orders of magnitude, from about 18 mA to about 7 uA. In contrast, the current at 78 volts for the fringe area diodes under reverse bias varies by less than one order of magnitude, from about 2 μ A to about 0.5 μ A. This observation would indicate a consistent metal to semiconductor Schottky barrier formation for all diodes regardless of thickness, which is discussed in detail in the following chapter.







Figure 4.3 I-V plot of fringe area diodes in reverse bias



Figure 4.4 I-V plot of fringe area diodes in both forward and reverse bias

Rectification ratios calculated for the initial-state diodes with respect to fringe location are shown in Figure 4.5. Examination of the data shows that the rectification ratio reaches a maximum of about 200 for the thickest diodes (Fringe 5) and 11,000 for the thinnest diodes (Fringe 1). In contrast, when gold is used instead of zirconium, the rectification ratios are on the order of unity and 200 for the thickest and thinnest, respectively. This shows that the diode behavior is dependent on the work function of the metal. In fact, as noted in Chapter 3, if the diamond is sufficiently thick, gold acts as an ohmic contact for these films. Evidence for surface conductivity along the top surface of the diamond film was also investigated. When the SMU1 and SMU2 probes are connected to two zirconium top surface contacts, the resulting I-V characteristics are that of back-to-back diodes. This indicates the lack of any appreciable surface conductivity. In summary, one may conclude, that the observed diode action is at the metal-diamond interface and that the lower the work function, the better the rectification ratio.

Furthermore, both reverse bias and forward bias IV characteristics were also measured with the curve tracer allowing the rectification ratios to be determined beyond the 20 mA limitation of the HP4145. The rectification ratios of these devices continued to increase with bias until they reached a maximum rectification of about 1.0-2.0 x 10⁴, near that of the calculated Fringe 1 maximum. At the point of maximum rectification, the current abruptly increased resulting from a breakdown in the diode's physical structure. This phenomenon is further discussed in a later section.





Figure 4.5 Rectification ratios calculated for initial-state diodes vs. fringe

4.3 I-V characteristics of initial-state diodes vs. thickness and temperature

The I-V characteristics of diamond film Schottky barrier diodes were investigated for varying diamond film thickness and varying temperature. The same fringes discussed in the previous section were used in this experiment for consistency in thickness variation. Using a Signatone S-1060 QuieTemp System hot chuck and Fluke 80T-150U Temperature Probe, I-V data was collected at 5 more temperatures from diodes on all 5 fringes. The temperature was varied from 300 K to 425 K with I-V data collected every 25 K. At every 25 K step, I-V data was collected from -100 to 100 volts for diodes on every fringe. The forward bias and reverse bias I-V plots for a typical Fringe 1 diode versus temperature are shown in Figure 4.6 and Figure 4.7, respectively.



Figure 4.6 I-V plot of a Fringe 1 diode under forward bias versus temperature



Figure 4.7 I-V plot of a Fringe 1 diode under reverse bias versus temperature

It should be noted that even though the I-V data collected in the previous section has a resolution of about 100 pA, the data collected for this particular experiment has a resolution of about 1 nA. The measurement apparatus was used for each experiment but data was collected on different days. The particular reason behind the variation was not determined and any attempt to eliminate this difference in resolution failed. Therefore, the I-V curves present in the figures of this section become increasingly noisy as the current approaches 1 nA. However, despite the low-current noise, the general trends in the data are readily apparent to the reader.

As shown in Figure 4.7, only the data collected between 10 and 70 volts is displayed in the figure. The reason for displaying data in this particular range deals with

the current limitations of the HP4145B. The Fringe 1 diode reaches this maximum allowed current at 73 volts operating at a temperature of 425 K. The rest of the I-V curves run into this maximum current at slightly larger voltages. As a result, the data was deemed not relevant and was omitted from the figure. To maintain consistency in the following forward bias figures for the remaining fringe diodes, data from the same voltage range is used in all figures.

The forward bias and reverse bias I-V plots for a typical Fringe 2 diode versus temperature are shown in Figure 4.8 and Figure 4.9, respectively.

The forward bias and reverse bias I-V plots for a typical Fringe 3 diode versus temperature are shown in Figure 4.10 and Figure 4.11, respectfully. As shown in Figure 4.10, the 300 K and 325 K I-V curves show a different trend in data at low voltages compared to the other temperatures in the figure, or in previous figures. The reason for this behavior is due to corrupted data collected during the original experimental undertaking. The I-V data displayed for the 300 K and 325 K temperatures is data recollected after the sample wafer was exposed to the complete range of temperatures used for the experiment. The corrupted data was not discovered until after the device had been subjected to tests at all five temperatures. Therefore, the 300 K and 325 K I-V curves show an increase in current at low voltages as a result of a physical change in the diodes themselves brought upon by the temperatures they were exposed to. Note that this change is limited to the impact on current at lower voltages. The trend in data above 30 volts is consistent with the data shown in previous figures and figures to come. It's reasonable to assume the original data at 300 K and 325 K collected below 30 volts would have followed the same trend.



Figure 4.8 I-V plot of a Fringe 2 diode under forward bias versus temperature



Figure 4.9 I-V plot of a Fringe 2 diode under reverse bias versus temperature



Figure 4.10 I-V plot of a Fringe 3 diode under forward bias versus temperature



Figure 4.11 I-V plot of a Fringe 3 diode under reverse bias versus temperature

Figure 4.11 also has one curve (300 K) with a similar difference in data trends as Figure 4.10; however, the explanation for this behavior is not the same. As shown, the 300 K I-V curve does not follow the same data trend at voltages below 30 volts as the other I-V curves in the figure, although, all data was collected at the same point in time. The change in the 300 K I-V curve appears to be more dramatic, not gradually changing like the I-V curves from the previous figure. The explanation for the discrepancy is not as apparent but most likely can be attributed to a momentary glitch in the HP4145B machine during the measurement process. Further instances of these random but rare "glitches" were experienced and the data gathered within this small voltage range is not representative of the diode's true behavior.

The forward bias and reverse bias I-V plots for a typical Fringe 4 diode versus temperature are shown in Figure 4.12 and Figure 4.13, respectfully. The same difference in low-voltage data curve trends at 300 K and 325 K of Figure 4.10 is present in Figure 4.12. As with the Fringe 3 diode, the original data collected for the 300 K and 325 K temperatures was corrupted for this diode. Again, the data displayed in the figure for the 300 K and 325 K I-V curves is data re-collected after the diodes were exposed to all temperatures used in this experiment. The result is an increase in current at voltages less than about 30 volts. As shown in Figure 4.13, the same discrepancy in Figure 4.11 also appears in this figure concerning the 300 K I-V curve. Again, the explanation determined for the "jump" in current around 30 volts is a random glitch in the HP4145B during the measuring process.

The forward bias and reverse bias I-V plots for a typical Fringe 5 diode versus temperature are shown in Figure 4.14 and Figure 4.15, respectfully.



Figure 4.12 I-V plot of a Fringe 4 diode under forward bias versus temperature



Figure 4.13 I-V plot of a Fringe 4 diode under reverse bias versus temperature



Figure 4.14 I-V plot of a Fringe 5 diode under forward bias versus temperature



Figure 4.15 I-V plot of a Fringe 5 diode under reverse bias versus temperature

I-V plots of both Fringe 1 and Fringe 5 diodes comparing the two temperature extremes are shown in Figures 4.16 and 4.17, respectively. The change in temperature has a larger impact on the diode while in reverse bias than forward bias. Using 70 volts as an example, the reverse bias current in both figures increase by over two orders of magnitude from 300 K to 425 K while the forward bias current for diode 1 and diode 5 increase by one order of magnitude or less.



Figure 4.16 I-V plot of Fringe 1 diode for both temperature extremes

After the reverse bias curves break away from their respective forward bias curves, these current-temperature relationships hold fairly steady up to the maximum voltage used in this experiment. Using Figure 4.16 as an example, at approximately 40 volts, the reverse bias curves have split off from the forward bias curves and they maintain two orders of magnitude current difference up to 100 volts. This observation



can be made with both forward bias and reverse bias I-V curves in both figures.

Fringe 4.17 I-V plot of Fringe 5 diode for both temperature extremes

4.4 Reverse breakdown voltage vs. thickness for initial-state diodes

Using a Tektronix 577 Curve Tracer with a Tektronix 177 test fixture, the reverse bias breakdown voltage was measured for diodes with varying thickness. Unlike the case of the HP4145B where the data was logged automatically by a computer, this data was taken manually by setting the voltage to a particular value and reading the current from the Curve Tracer screen. Reverse bias I-V curves for diodes from all 5 fringes are shown in Figure 4.18. The last data point shown for each I-V curve is the last recorded before the current began to increase almost vertically. Shown in Figure 4.18 for 4 out of the 5 I- V curves, as the diodes approach their respective breakdown voltage, the current begins to increase exponentially. The breakdown voltages along with calculated electric fields are recorded in Table 4.2.



Figure 4.18 Reverse bias breakdown curves for diodes of varying thickness

Fringe	Reverse Breakdown Voltage (V)	Electric Field (10 ⁶ V/cm)
1	225	9.04
2	255	6.73
3	270	5.31
4	280	4.38
5	300	3.90

Table 4.2 Observed breakdown voltages and electric fields for the fringe diodes

4.5 Initiation of a change in initial-state diode characteristics

On select diodes, a Tektronix 577 Curve Tracer with a Tektronix 177 Test Fixture was used to push the diodes in forward bias beyond the 20 mA current limit imposed by the HP4145B. On all devices subjected to this treatment, when the power reached a critical value, an abrupt change in I-V characteristics was observed. The change exhibited itself as a dramatic drop in forward voltage for a given forward bias current. The initial impression of the high power induced change was that of a thermal breakdown short circuit in forward bias. However, upon closer examination, it was observed that the devices were still highly rectifying, but with a much lower forward voltage drop.

Identification of the physical basis of the change was beyond the scope of this thesis. One may speculate that the high power levels caused a temperature increase which in turn caused a change in carbon atom configuration, from a highly resistive diamond state to a highly conductive carbon configuration. In any case, the nomenclature of "phase-change" diodes is used in this thesis.

Initial-state diodes from Fringe 1, Fringe 2, Fringe 3 and Fringe 5 were tested and subsequently modified. Fringe 1 diodes reached 32-60 mA at 80-90 volts before they reached thermal breakdown. Fringe 2 drew the highest power of 5.58 Watts with a maximum current of 45 mA at 124 volts. Fringe 3 and Fringe 5 diodes reached currents of 33 mA at 120 volts and 20-30 mA at 130-140 volts, respectively. The absorbed power ranged from about 4 to 5.58 Watts, corresponding to power densities of over 2 kW / cm².

4.6 I-V characteristics of phase-change diodes vs. thickness at 300K

The resulting "phase-change" led to improved I-V characteristics. The "phasechange" diodes delivered much larger currents at smaller voltages while often increasing their rectification ratio. A maximum rectification ratio of 1.69×10^5 was measured at ± 10 V. Due to the large increase in current, I-V data was collected from only -10 to 10 volts to avoid reaching another thermal breakdown and destroying the diode. The curve tracer was used to induce this permanent change in several devices to verify repeatability. The I-V plot of an example phase-change diode is shown in Figure 4.19.

The forward bias and reverse bias I-V plots for the phase-change diodes versus fringe are shown in Figures 4.20 and 4.21, respectively. In the previous section, the dominating variable for I-V behavior of the initial-state diodes was shown to be the thickness of the diamond film. Sampling diodes from different fringes resulted in a consistent change in I-V characteristics; however, this is not the case for the phasechange diodes as evident by the I-V data presented in the figures. Data from multiple diodes from the same fringe are displayed in each figure to demonstrate this fact. Figure 4.20 includes three Fringe 5 diodes with differing forward bias I-V curves where the same fringe has diodes with both the largest forward bias current and the smallest. In this same figure, a Fringe 1 diode has an almost overlapping I-V curve with the highest Fringe 5 curve, which is not consistent with the initial-state diode's I-V behavior.

The reverse bias data in Figure 4.21 demonstrates the same lack of dependence on film thickness. The three Fringe 5 diodes occupy the top three I-V curves while Fringe 3 has the lowest with the Fringe 1 diode curves residing in between. Again, this does not


Figure 4.19 I-V plot of a phase-change Schottky barrier diode



Figure 4.20 I-V plot of phase-change diodes under forward bias versus fringe





Figure 4.21 I-V plot of phase-change diodes under reverse bias versus fringe

conform to the behavior of a device where film thickness is the dominating variable. From previous data, we would expect to see a more consistent change in I-V behavior from fringe to fringe. Therefore, thickness may still be a variable in I-V behavior for these phase-change devices, but the difference in device-to-device behavior is the dominating variable.

Rectification ratios calculated as a function of voltage for phase-change diodes from Fringe 1, 2, 3 and 5 are shown in Figure 4.22. Multiple phase-change diodes from Fringe 1 and Fringe 5 were studied but only data from diodes with the highest rectification ratios were plotted in this Figure. Rectification ratios as a function of voltage for all Fringe 1 and Fringe 5 diodes are plotted in Figure 4.23. Figure 4.23



Figure 4.22 Rectification ratios calculated for phase-change diodes vs. fringe



Figure 4.23 Rectification ratios calculated for phase-change diodes vs. fringe

provides another example of the lack in consistency between I-V characteristics from device to device, where both devices are located on the same fringe.

4.7 I-V characteristics of phase-change diodes vs. thickness and temperature

To identify the temperature dependence, the phase-change diodes were exposed to the same temperatures as the initial-state diodes. At every 25 K step in temperature, I-V data was collected from the diodes from -10.0 to 10.0 V along with a detailed measurement from 0.1 to 0.7 V. Only diodes from Fringe 1, Fringe 2 and Fringe 5 were used in this study. Forward bias and reverse bias I-V plots of a Fringe 1 diode versus temperature are shown in Figures 4.24 and 4.25, respectively.



Figure 4.24 I-V plot of Fringe 1 phase-change diode in forward bias vs. temp

From 1 to 10 V, where bulk series effects dominate forward bias current, Figure 4.24 shows a slight monotonic increase of forward bias current with increasing temperature. The temperature variation is substantially less than for initial-state diodes. However, the variation in current with respect to temperature in Figure 4.25 is pronounced. As was the case for initial-state diodes, there is over two orders of magnitude increase in reverse bias current from 300 K to 425 K. As will be discussed in chapter 5, the reverse bias I-V characteristics are dominated by the metal-semiconductor barrier for initial-state diodes, but this is not the case for phase-change diodes.

1.00E-04



Figure 4.25 I-V plot of Fringe 1 phase-change diode in reverse bias vs. temp

More forward bias temperature dependence is seen in Figure 4.26, for an I-V plot of a Fringe 1 phase-change diode, over a voltage range of 0.1 to 0.7 volts. In this voltage region, diode barrier affects dominate the current, particularly up to about 0.4 volts. Initially, a considerable distance separates all curves from each other; however, as the voltage increases beyond 0.4 volts, the curves begin to pinch together as bulk series effects come into play. Referring to Figure 4.24, the curves remain pinched together for the extent of the measured voltage range.

I-V plots for a Fringe 2 diode in forward and reverse bias with varying temperature are shown in Figure 4.27 and Figure 4.28, respectively. Figure 4.29 shows a detailed I-V plot for the diode under forward bias from 0.1 to 0.7 volts. The same trends in forward data appear for the Fringe 2 diode as the Fringe 1 diode, although, there is slightly more temperature dependence from 1 to 10 volts.



Figure 4.26 I-V plot of Fringe 1 phase-change diode in forward bias vs. temp





Figure 4.27 Plot of Fringe 2 phase-change diode in forward bias vs. temp

1.00E-03



Figure 4.28 I-V plot of Fringe 2 phase-change diode in reverse bias vs. temp



Figure 4.29 I-V plot of Fringe 2 phase-change diode in forward bias vs. temp

Forward bias and reverse bias I-V plots for the final phase-change diode tested, Fringe 5, are shown in Figures 4.30 and 4.31, respectively. Figure 4.32 shows a detailed plot of the diode under forward bias from 0.1 to 0.7 volts. Again, the data trends of the Fringe 5 diode resemble that of both Fringe 1 and Fringe 2; however, Fringe 1 and Fringe 2 are much closer in current values. Both Fringe 1 and Fringe 2 current values fall within the range of 10⁻⁴ to 10⁻² amps while Fringe 5 falls within 10⁻⁵ to just over 10⁻⁴ amps.

There is a slight discrepancy with Figure 4.32. The 300 K I-V curve does not follow the same pattern as the other I-V curves from this figure and other diode figures. The exact reason for this odd behavior has not been determined.





Figure 4.30 I-V plot of Fringe 5 phase-change diode in forward bias vs. temp



Figure 4.31 I-V plot of Fringe 5 phase-change diode in reverse bias vs. temp



Figure 4.32 I-V plot of Fringe 5 phase-change diode in forward bias vs. temp

It should also be mentioned that the reverse breakdown voltage of these phasechange diodes was tested but not to the same degree as the initial-state diodes. Of the few diodes tested, the reverse breakdown voltage fell around 120 volts, roughly half the breakdown voltage of the equivalent initial-state diodes.

Chapter 5

Analysis and Discussion

5.1 Introduction

This chapter presents an analysis and discussion of the results shown in chapter 4. A general DC model proposed for the nanocrystalline diamond based Schottky barrier diodes and discussion of field-activated conductivity according to Poole's Law observed in these devices is presented in the first two sections. Electric field dependency in forward biased structures along with temperature dependence in both forward and reverse bias is considered in the next three sections. Finally, a DC model for the phase-change diodes through characterization of these devices is investigated in the last section of this chapter.

5.2 General model

As shown in chapter 4, the nanocrystalline diamond films are highly resistive at low to moderate electric fields. Application of a sufficiently high voltage across the diamond film results in a field-activated conductivity modeled by Poole's Law where the relationship follows from equation [2.04]. Thus, the current-voltage characteristics of a two terminal structure with one rectifying contact can be modeled by a voltage variable resistor in series with a diode as shown in Figure 5.1.



Figure 5.1 General model for two-terminal rectifying structure

Consider, as a conceptual example, where the current-voltage characteristics of the resistive film and rectifying junction are as shown in Figure 5.2 with the dashed line representing the I-V characteristics of the junction and the solid line representing the I-V characteristics of the diamond film with field-activated conductivity. Since the two model elements are in series, the voltage will be divided between the two. Given the I-V characteristics shown in Figure 5.2, for forward bias voltage, the current will be limited by the high resistance of the diamond film. For reverse bias current, at low voltages the current will be limited by the diamond film but at high voltages the current will be limited by the rectifying junction. The resulting film limited forward-bias current (solid line) and junction limited reverse-bias current (dashed line) for the two-terminal rectifying structure is shown in Figure 5.3. In fact, this conceptual illustration is qualitatively comparable with the experimental data, as shown in Figure 5.4. It is this general approach that is used in analyzing the rectifying structures described in chapter 4, where the structures may be analyzed as a voltage variable resistance in series with a Schottky rectifying junction.



Figure 5.2 IV plot of rectifying junction (dashed) and field-activation (solid)



Figure 5.3 I-V plot of two-terminal rectifying structure with series resistance



Figure 5.4 I-V plot of diamond based Schottky barrier diode

5.3 Poole's Law

Field-activated conductivity in our polycrystalline diamond film follows Poole's Law as described in Chapter 2 and experimentally observed in Chapters 3 and 4. This section considers the physical origin of this phenomenon in order to further investigate the implications of these findings. Under moderate electric fields, current density follows thermionic emission and is proportional to $\exp(-q\varphi_i/kT)$ where φ_i is the potential barrier of the trapped carrier. Application of a high electric field results in a reduction of the potential barrier by an amount:

$$\Delta \varphi = qEs/kT$$
 [5.01]

where E is electric field and s is the distance between Coulombic centers [32]. If the distance traveled by the carrier after emission is proportional to s, meaning the carrier is immediately recaptured at the next available Coulombic potential, then the current density is proportional to [32]:

$$J \propto s \exp\left(\frac{-q\varphi_i}{kT}\right) \left[\exp\left(\frac{qEs}{2kT}\right) - \exp\left(\frac{-qEs}{kT}\right) \right]$$
[5.02]

or at large E:

$$J \propto s \exp\left(\frac{-q\varphi_i}{kT}\right) \exp\left(\frac{qEs}{2kT}\right)$$
[5.03]

However, if the distance that the carrier travels after emission is proportional to E, then the current density is proportional to [32]:

$$J \propto E \exp\left(\frac{-q\varphi_i}{kT}\right) \exp\left(\frac{qEs}{2kT}\right)$$
 [5.04]

or in terms of conductivity:

$$\sigma = \sigma_0 \exp\left(\frac{qEs}{2kT}\right) = \sigma_0 \exp(\alpha E)$$
[5.05]

where σ_0 is proportional to:

$$\sigma_0 \propto \exp\left(\frac{-q\varphi_i}{kT}\right)$$
 [5.06]

and:

$$\alpha = qs/2kT$$
 [5.07]

Equation [5.05] is defined as Poole's Law. Therefore, the total conductivity of the sample including the ohmic conductivity, σ_{00} , becomes:

$$\sigma = \sigma_{00} + \sigma_0 \exp(\alpha E)$$
 [5.08]

Equation [5.08] is the most convenient form of Poole's Law and was used in the analysis of the field-activated conductivity present in the nanocrystalline diamond layer of the Schottky barrier diodes.

5.4 Field-activated conductivity in forward-biased rectifying structures

Current-voltage data collected from the diamond-based Schottky barrier diodes under forward bias, presented in section 4.2, is used to investigate the field-activated conductivity according to Poole's Law in these structures. Calculating conductivity and electric field and plotting the data on a semi-log scale displays an exponential relationship at high fields indicative of Poole's Law. Due to the magnitude of the electric fields approached in this study, it is believed that electrons reaching saturation velocity introduced non-linearity into the data curves around 1.5 MV/cm. Therefore, Poole's Law was investigated in the linear portions of the data curves before the data became nonlinear at higher electric fields. Data from thicker films retained this linear portion of the data curve for more of the voltage range as opposed to thinner films whose linear portions are much smaller. Electrons in the thinner films would reach saturation velocity at lower voltages due to the higher electric fields for a given voltage. A plot of conductivity versus electric field for all five fringe thicknesses is shown in Figure 5.5 and the Poole's Law variables calculated from the data curves are shown in Table 5.1. The ohmic conductivity, σ_{00} , was found to be approximately 1-10 x 10⁻¹³ (Ω cm)⁻¹ where

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accuracy was reduced by the current limitation of the measuring apparatus.

Figure 5.5 Conductivity vs. electric field plot versus fringe thickness

Fringe	Thickness (µm)	a (10 ⁻⁵ cm/V)	$\sigma_0 [10^{-14} (\Omega \text{ cm})^{-1}]$	$\sigma_{00} [10^{-12} (\Omega \text{ cm})^{-1}]$
1	.249	0.781	0.737	~ 1-10
2	.379	0.969	1.468	~ 1-10
3	.509	1.200	0.993	~ 1-10
4	.639	1.321	0.933	~ 1-10
5	.769	1.331	1.598	~ 1-10

Table 5.1 Calculated Poole's Law variables for the five fringe thicknesses

Ideally, the Poole's Law expression characterizing the field-activated conductivity for each of the five film thicknesses would be equal, having no dependence on thickness. In other words, the equation variables α , σ_0 , and σ_{00} would be the same for each film thickness which is what would be expected for a homogeneous diamond film. Although the variables are within a factor of two in this study, there is a systematic increase in α with increasing film thickness. The relationship between diamond thickness and slope, α , can be seen in the table and is more apparent in Figure 5.6.



Figure 5.6 Plot of a versus diamond thickness

As shown in Figure 5.6, the Poole slope, α , increases and eventually plateaus as diamond thickness increases. This would suggest the structure of the film is not completely homogeneous with depth, but varies in the initial stages of growth,

influencing the field-activated conductivity. As thickness increases, this difference in diamond structure becomes less noticeable and α eventually stabilizes. However, despite this effect, all five values calculated for a specific variable in the Poole's Law expression, and shown in Table 5.1, are in relatively close proximity of each other for each of the three variables. Moreover, the Poole slopes are within the ranges previously reported for thin diamond films [14].

5.5 Temperature dependence of forward-biased rectifying structures

I-V data collected from the Schottky diodes while exposed to six different temperatures ranging from 300 K to 425 K, presented in section 4.3, was used to further investigate the temperature dependence of the field-activated conductivity in the context of Poole's Law. Plots of conductivity versus electric field for Fringe 1 through Fringe 5, each with six separate temperature plot lines, were created. Two example conductivity versus electric field plots are shown in Figure 5.7 and Figure 5.8 for Fringe 1 and Fringe 5, respectively. For each temperature plot line the Poole's Law variables, α and σ_0 , were calculated. Again, due to non-linearity at higher electric fields, the data range used to calculate α and σ_0 was limited to the smaller linear region in the middle of the plot lines. All computed values of α and σ_0 for each fringe and temperature are shown in Table 5.2 and Table 5.3, respectively.



Figure 5.7 Conductivity vs. electric field plot for Fringe 1 diode



Figure 5.8 Conductivity vs. electric field plot for Fringe 5 diode

α (10 ⁻⁵ cm/V)	Fringe 1	Fringe 2	Fringe 3	Fringe 4	Fringe 5
200 K	0.711	0.002	0.065	1.042	1 1 4 1
300 K	0.711	0.902	0.965	1.043	1.141
325 K	0.694	0.943	0.940	1.013	1.207
350 K	0.698	0.942	1.031	1.090	1.183
375 K	0.667	0.897	0.926	1.063	1.146
400 K	0.661	0.833	0.838	0.990	1.055
425 K	0.609	0.782	0.808	0.843	0.964

Table 5.2 The Poole slope, α , calculated for each fringe and temperature

$\sigma_0 (\Omega \text{ cm})^{-1}$	Fringe 1	Fringe 2	Fringe 3	Fringe 4	Fringe 5
300 K	2.36x10 ⁻¹⁴	2.97x10 ⁻¹⁴	5.71x10 ⁻¹⁴	6.22x10 ⁻¹⁴	5.86x10 ⁻¹⁴
325 K	5.36x10 ⁻¹⁴	3.70x10-14	1.20x10 ⁻¹³	1.40x10 ⁻¹³	6.59x10 ⁻¹⁴
350 K	9.58x10 ⁻¹⁴	7.34x10 ⁻¹⁴	1.12x10 ⁻¹³	1.51x10 ⁻¹³	1.56x10 ⁻¹³
375 K	2.55x10 ⁻¹³	2.15x10 ⁻¹³	4.97x10 ⁻¹³	3.76x10 ⁻¹³	4.18x10 ⁻¹³
400 K	2.73x10 ⁻¹³	5.93x10 ⁻¹³	1.37x10 ⁻¹²	9.86x10 ⁻¹³	1.12x10 ⁻¹²
425 K	1.49x10 ⁻¹²	1.83x10 ⁻¹²	3.80x10 ⁻¹²	4.60x10 ⁻¹³	3.95x10 ⁻¹²

Table 5.3 The Poole conductivity, σ_0 , calculated for each fringe and temperature

The separation, s, between Coulombic centers can be determined using Equation [5.07] which provides the relation between α and s. Due to the inverse temperature dependence of s, plotting α versus inverse temperature for all five diamond thicknesses and determining the slope of the linear line provided the average separation distance, s, for a particular fringe thickness. The values of α used in the plot are shown in Table 5.2.

An example plot of α versus inverse temperature is shown in Figure 5.9 for Fringe 1. The method of least squares regression was used to fit an appropriate linear trend line to the data. The slope from this line for Fringe 1 along with the slopes calculated for Fringes 2-5 are presented in Table 5.4.



Figure 5.9 Plot of α versus inverse temperature for Fringe 1

The potential barrier, φ_i , is proportional to σ_0 as described in equation [5.06]. The potential barrier was determined by plotting the natural $\log \sigma_0$ versus inverse temperature. An example plot of natural $\log \sigma_0$ versus inverse temperature is shown in Figure 5.10 for Fringe 1. The values of σ_0 used in the plot are shown in Table 5.3. The method of least squares regression was used to fit an appropriate linear trend line to the data. The slope of this line provided the potential barrier, φ_i , for a given thickness. The slope from this line for Fringe 1 along with the slopes calculated for Fringes 2-5 are presented in Table 5.4. Ideally, for a film that is homogeneous with thickness, the potential barrier should not be dependent on thickness. Although the values are different, they are all reasonably close in value ranging from 0.330 to 0.375 V, within range of previously reported [17].



Figure 5.10 Natural log of σ_0 versus inverse temperature for Fringe 1

Fringe	s (nm)	φ _i (V)	
1	1.55	0.330	
2	2.24	0.368	
3	2.76	0.366	
4	2.42	0.346	
5	3.28	0.375	

Table 5.4 Separation, s, and barrier height, φ_i , calculated for each fringe thickness

Looking at Table 5.4, a trend of increasing *s* with increasing fringe thickness is apparent. Diamond growth by a CVD process is Columnar, with larger grains surviving at the expense of smaller grains as the thickness increases. Thus, the diamond grains, or crystallites, increase in size as diamond is grown. The separation size, *s*, was found to be smallest in the thinner films which is appropriate because at this thickness the crystallites have not had a chance to grow very large. Therefore, the Coulombic potentials arising from defects associated with grain boundaries are at a relatively high concentration giving a small value of *s*. Taking *s* to be equal to $N^{-1/3}$, where *N* is the concentration of Coulombic potentials, for Fringe 1 *N* equals 2.69 x 10²⁰ cm⁻³, or approximately one center per 658 carbon atoms since the atomic density of diamond at 300 K is 1.77 x 10²³ atoms/cm³. The opposite can be said for the thicker films where the crystallites are larger leading to a larger separation in grain boundaries and a larger value of *s*. For Fringe 5, the density is 2.83 x 10¹⁹ cm⁻³, or one Coulombic center per 6,254 atoms. The *N* and *s* values are within proximity of other reported values for polycrystalline diamond [15,16].

As can be seen in Figure 5.9 and 5.10, the data does not fit the regression line perfectly; therefore, error is present in the slope values. The error in the slope of the least squares regression line was computed for both s and φ_i . An 80% confidence interval was found for both variables of Fringe 1 such that separation, s, has a range of 1.55 ± 0.37 nm and potential barrier, φ_i , has a range of 0.330 ± 0.042 V. The error range of s does not span values calculated in Table 5.4 giving more evidence to a legitimate relationship between s and thickness. The error range of φ_i does overlap all calculated φ_i values which may challenge the appearance of a dependency of φ_i . Note, however, that the extracted barrier height does monotonically increase with film thickness. This suggests a large effective barrier height on thicker films with a smaller Coulombic defect density. This may result from an effective lowering of barrier height due to increased overlap of potentials with higher N values.

5.6 Temperature dependence of reverse-biased rectifying structures

As stated in section 5.2, the general model of the rectifying device can be divided into two sub-devices in series. Under forward bias and high electric field, the current is limited by the diamond film exhibiting field-activated conductivity. Under reverse bias and high electric field, the current is limited by the Schottky junction formed between the zirconium contact and nanodiamond film. In this case, we are able to characterize the Schottky junction by extracting the potential barrier height, φ_B , from the reverse I-V data collected from the devices shown in Chapter 4.

Using the Schottky diode equation stated as Equation [2.11] in Chapter 2, the temperature dependence of the barrier height can be investigated. Under a large reverse bias voltage, the exponential term dependent on applied voltage reduces to zero leaving the saturation current, I_s , as the dominating contributor to the current through the device. The saturation current is defined in Equation [2.12] and has a strong exponential dependence on the barrier height, φ_B , and temperature. I-V data collected at -100 V (the Image Force Effect was ignored in this analysis) was used to produce a plot of natural log I_s versus inverse temperature resulting in a linear relationship. The method of least squares regression was used to fit an appropriate linear trend line from which the barrier

height could be extracted. An example plot of natural log I_s versus inverse temperature for Fringe 1 is shown in Figure 5.11. The extracted barrier height, φ_B , from this slope and the barrier heights for the rest of the fringes are shown in Table 5.5. The values are within range of previously reported for thin submicrocrystalline diamond [33].



Figure 5.11 Natural log of I_s versus inverse temperature for Fringe 1

Fringe	<i>\varphi_B</i> (V)
1	0.427
2	0.455
3	0.473
4	0.482
5	0.470

Table 5.5 Table of φ_B calculated for each diamond fringe thickness

As shown in Table 5.5, there is an apparent relationship between barrier height and fringe thickness. As thickness increases, φ_B increases until it reaches a maximum around 0.47-0.48 V. A plot of φ_B versus fringe thickness is shown in Figure 5.12. This increasing barrier height trend is believed to be attributed to the polycrystalline diamond structure within the film. As mentioned previously, as the diamond film grows in thickness, the individual crystallites grow in height and width changing trap location and density. It's reasonable to assume that a Schottky junction formed on the surface of the film at different thicknesses and subsequently different distances between grain boundaries will result in the formation of different effective potential barriers. Since the barrier height appears to level off at larger thicknesses, the barrier formation within the diamond eventually stabilizes as the film grows.



Figure 5.12 Barrier height, φ_B , versus fringe thickness

In the general Schottky diode case, the thermionic emission theory is sufficient for explaining the current transport process from metal to semiconductor. The equation for current flow in a Schottky diode according to thermionic emission, previously stated in [2.11] and [2.12] and repeated here as one equation for convenience, is:

$$I = AA^{*}T^{2} \exp\left(\frac{-q\varphi_{B}}{kT}\right) \left[\exp\left(\frac{qV_{a}}{nkT}\right) - 1\right]$$
[5.09]

and Richardson's constant, A^* , is equal to:

$$A^* = 4\pi q m^* k^2 / h^3$$
 [5.10]

The thermionic emission theory is for high-mobility, single-crystalline semiconductors. When a semiconductor does not fall into this category, other theories on current transport in a Schottky junction exist such as the diffusion theory for low-mobility semiconductors and the thermionic-diffusion theory which is a synthesis of the previous two [34]. Just as in the thermionic emission case, the current flow according to these two theories has a strong dependence on applied voltage, V_a , and the barrier height, φ_B . The current equation for an n-type sample according to the diffusion theory is defined as:

$$I_n = A \frac{q^2 D_n N_C}{kT} \left[\frac{q(V_{bi} - V_a) 2N_D}{\varepsilon_s} \right]^{1/2} \exp\left(\frac{-q\varphi_B}{kT}\right) \left[\exp\left(\frac{qV_a}{nkT}\right) - 1 \right]$$
 [5.11]

where A is cross sectional area, D_n is diffusitivity, N_C is the conduction band effective density of states, V_{bi} is built-in potential, N_D is donor density, and ε_s is permittivity. The current equation for an n-type sample according to the thermionic emission-diffusion theory is defined as:

$$I_n = A \frac{qN_C \upsilon_R}{1 + \upsilon_R / \upsilon_D} \exp\left(\frac{-q\varphi_B}{kT}\right) \left[\exp\left(\frac{qV_a}{nkT}\right) - 1\right]$$
[5.12]

where v_R is the thermal velocity and v_D is the diffusion velocity through the sample.

Based on the thermionic theory and potential barrier, φ_B , solved for the five fringes, the Richardson constant should be easily extracted from the data. However, the Richardson constant calculated for the devices fabricated in this study was several orders of magnitude below a realistic value. Therefore, the thermionic theory is not sufficient in explaining the transport process within the nanodiamond film. This is a reasonable conclusion considering the thermionic emission theory is used to describe the transport process in high-mobility, single crystalline films which is not the case for the nanocrystalline diamond films used in this study. However, investigating further into the other transport processes discussed previously requires a more detailed investigation and is beyond the scope of this study. Despite the shortcomings of the thermionic emission theory for these films, the alternative theories also have a principal temperature dependence for the saturation current proportional to $\exp(-q\varphi_B/kT)$. Thus, the extracted values of φ_B are valid in any case.

5.7 Modeling of phase-change rectifying structures

As previously mentioned in Chapter 4, the phase-change diodes are believed to be the result of a thermal breakdown in the diamond layer from high voltage/current combinations subjected to the original initial-state diodes. It is speculated that high power levels caused a temperature increase which in turn caused a change in carbon atom configuration, from a highly resistive diamond state to a conductive carbon configuration. A filament of conducting carbon between the top zirconium contact and the silicon substrate, where the zirconium/carbon-filament forms a Schottky barrier with the silicon, is thought to exist within the diamond layer directly below the zirconium contact. However, the filament is believed to occupy only a fraction of the area where the majority of the carbon between the zirconium and silicon substrate still remains in the highly resistive diamond state. A proposed DC model for the phase-change diode structure is shown in Figure 5.13. There may be additional transitional materials between the conductive carbon filament and the original diamond.



Figure 5.13 DC model of the phase-change diode

Using the I-V data collected from the Fringe 1 phase-change diode, presented in Chapter 4, several characteristics can be extracted to help explain the reverse-bias and forward-bias behavior. The forward-bias I-V behavior resembles a typical Schottky diode; however, the reverse bias I-V characteristics show an unexpected linear relationship. This linear relationship would suggest that the reverse bias current is not primarily originating from the reverse biased Schottky barrier junction but is traveling through a leakage path in the surrounding diamond or other transitional material. Due to the low voltage, any field-activated conductivity is negligible. Therefore, the leakage path behaves as an ohmic resistance. A current-voltage plot of the reverse bias data collected from the Fringe 1 phase-change diode at 300 K is shown in Figure 5.14. The leakage current for the phase-change diode as shown in this figure is higher than the leakage current for the original diode in Figure 4.7. This implies that either the surrounding diamond was also affected by the thermal breakdown or that there is some other transitional material between the conducting filament and the diamond.



Figure 5.14 Reverse bias I-V plot of Fringe 1 phase change diode at 300 K

The resistance of the leakage path has temperature dependence. Resistances for the Fringe 1 phase change diode at each temperature are shown in Table 5.6. Activation energy for the leakage path can be found by plotting natural log of the resistance versus inverse temperature. The plot is shown in Figure 5.15 where the slope of the line, acquired through the method of least squares, gives activation energy equal to 0.480 eV.

Temperature (K)	Leakage Path Resistance (M Ω)
300	138.0
325	59.2
350	21.0
375	5.25
400	1.49
425	0.765

 Table 5.6 Fringe 1 phase-change diode resistances under reverse bias

The Fringe 1 saturation current, I_s , can be extracted from the forward I-V plot in Figure 4.26 for the first three temperatures, 300-350 K, by extrapolating the linear region to zero volts. This was not possible for the other temperatures due to lack of a sufficient linear region in the plot line. The saturation currents are shown in Table 5.7. The ideality factor, n, can also be determined through the slope of these same three linear regions using the following equation derived from the Schottky current equation:

$$n = \frac{q}{kT} \frac{V_1 - V_2}{\ln(I_1 / I_2)}$$
[5.13]

where (V_1, I_1) and (V_2, I_2) are two points on the linear portion of the plot line. The n

values are also shown in Table 5.7.



Figure 5.15 Natural log resistance vs. inverse temp for Fringe 1 phase-change diode

Temperature (K)	I _s (nA)	n
300	2.0	1.88
325	4.0	1.69
350	15.0	1.67

Table 5.7 I_s and *n* values for Fringe 1 phase-change diode

The temperature dependence of the saturation currents presented in Table 5.7 can be used to estimate the barrier height of the Schottky junction. Plotting the natural log of I_s versus inverse temperature and using the method of least squares regression to fit a linear line provides the slope from which the barrier height can be extracted. However, since there are only three data points, the computed barrier height should be taken only as an estimation. The natural log of I_s versus inverse temperature plot for Fringe 1 is shown in Figure 5.16. The barrier height extracted from the slope of this line was found to be 0.306 V.



Figure 5.16 Natural log I_s vs. inverse temp for Fringe 1 phase-change diode

At higher voltages, a small parasitic resistance, R_s , in series with the diode limits the current through the diode. To take these effects into account, the Schottky diode equation must be modified to include the voltage drop due to this resistance which is defined as:

$$I = I_s \left[\exp\left(\frac{q(V - IR_s)}{nkT}\right) - 1 \right]$$
[5.14]

Solving the equation in terms of R_s yields the following:

$$R_{s} = \frac{1}{I} \left[V - \frac{nkT}{q} \left(\ln \frac{I}{I_{s}} \right) \right]$$
[5.15]

The resistance, R_s , was calculated for voltages from 5-10 V and was fairly constant throughout this range. The resistance calculated for the temperatures 300-350 K are shown in Table 5.8. The change in R_s may be considered to be within experimental error. However, the monotonic decrease of R_s with increasing temperature (see Table 5.8) is noted to be characteristic of semiconducting material, such as graphite or moderately doped silicon, rather than metallic.

Temperature (K)	$R_{s}(\mathbf{k}\Omega)$
300	2.35
325	2.25
350	2.05

Table 5.8 R_s values versus temperature for Fringe 1 phase-change diode

The research of phase-change diodes in this study is rather preliminary, only seven such diodes were subjected to experiment and the phase change was induced with varying amounts of power from device to device. Other phase-change diodes were not measured as extensively as the diode corresponding to Figures 5.14, 5.15, 5.16 and Tables 5.6, 5.7, and 5.8. However, some characteristics of the diodes were investigated as a partial analysis and used as a comparison to the Fringe 1 phase-change diode values reported earlier.

Not all diodes showed the same linear behavior (from an ohmic resistance) under reverse bias, so the model proposed in Figure 5.13 may only be valid for some of the phase-change diodes, which includes diodes from Fringe 1, Fringe 2, and Fringe 3 but excluding all three Fringe 5 diodes reported in this study. Figure 5.17 shows the linear relationship in the reverse bias I-V data for Fringe 1 and Fringe 3 diodes at 300 K. Both Fringe 1 and Fringe 3 diodes have resistance values at a temperature of 300 K in close proximity to the 300 K resistance value in Table 5.6. The Fringe 2 diode with temperature dependence data up to 350 K has resistance values around half of those in Table 5.6; however an activation energy was unable to be extracted because the device had inconsistent reverse-bias behavior at certain temperatures resulting in a non-linear log (I_s) versus inverse temperature plot. A linear I-V plot of Fringe 2 phase-change diode versus temperature is shown in Figure 5.18.

Both saturation current, I_s , and *n* values were extracted from the Fringe 2 forward bias data and were in proximity to those obtained for Fringe 1. A barrier height of 0.274 V was calculated using these values; however, this value is based on only two temperature data points. Although this value should also be taken only as an estimation due to lack of data points, interestingly enough, it is in proximity to the 0.306 V barrier height calculated earlier for Fringe 1. Using these same I_s and *n* values to determine the diode series resistance, R_s , provided resistance values in close proximity to those in Table 5.8.


Figure 5.17 I-V reverse bias plot of phase-change diodes showing linearity at 300 K



Figure 5.18 I-V reverse bias plot of Fringe 2 diode vs. temperature showing linearity

Chapter 6

Conclusion and Recommendations for Future Research

6.1 Introduction

This chapter presents a brief overview of the accomplishments made from this research with discussion on possible improvement through future research.

6.2 Two-terminal nanodiamond based structures

This thesis has investigated the electrical properties of two-terminal structures with nanocrystalline diamond films of thickness ranging from approximately a quartermicrometer to one micrometer. Several electrode types were investigated including indium, gold, zirconium, titanium, graphite paint, and pressure contacts to metals. Also, several sample configurations were considered. Freestanding 1 µm thick nanodiamond films with gold contacts on each side provided symmetric current-voltage relations. These behaved as voltage-variable resistors through the field-activated conductivity according to Poole's law exhibited in the nanodiamond films. Also, flexible diamond film wrapped around a stainless steel tube with carbon paint acting as one electrode and the tube acting as another was studied. Ultimately, a silicon-nanodiamond-zirconium configuration was fabricated from which over a hundred Schottky barrier diodes were fabricated with varying diamond film thickness. The Schottky junction formed between the zirconium contact and diamond film where the silicon behaves as the ohmic contact. Much of the data presented in the thesis was collected from these Schottky devices.

6.3 Nanocrystalline diamond based Schottky barrier diode results

Undoped nanocrystalline diamond based Schottky barrier diodes exhibiting rectification ratios up to 1.1×10^4 at ± 80 V were fabricated and studied in this research. Investigation into the DC current-voltage characteristics of these devices versus temperature and diamond film thickness was presented. Devices were fabricated with diamond film thickness from about 250 - 770 nm and tested at temperatures from 300 -425 K. A voltage variable resistor in series with a Schottky barrier diode was developed as a DC model where the forward bias current was limited by the field-activated conductivity in the diamond film and the reverse bias current was limited by the Schottky junction. Following this proposed model, device characterization was completed and presented in Chapter 5. Field-activated conductivity according to Poole's Law was observed in the diamond film at all temperatures and thicknesses from which a separation distance, *s*, and barrier height of a trapped carrier, φ_i , was extracted from the data. Barrier height, saturation current, and reverse breakdown voltage for the Schottky junction were extracted from the reverse-bias data.

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6.4 Phase-change material Schottky barrier diodes

Under very high forward bias voltages, the nanocrystalline diamond based Schottky diodes, or initial-state diodes, mentioned in the previous section would experience a sharp increase in current resulting in a permanent change in current-voltage characteristics. These current-voltage characteristics were investigated under the same testing conditions mentioned above where rectification ratios as high as 1.69×10^5 at $\pm 10 \text{ V}$ were observed. This "phase-change" is speculated to be a physical change in the diamond film where a conductive carbon filament, formed directly below the zirconium contact, is believed to form a Schottky barrier junction with the silicon substrate. A DC model was proposed for these devices where the forward bias current is limited by the Schottky junction and the reverse bias current is limited by the surrounding diamond or other transitional material, behaving as an ohmic resistance. Device characterization then followed in Chapter 5 where an estimation of barrier height, forward bias and reverse bias resistance, reverse bias activation energy, saturation current, and ideality factor was found.

6.5 Recommendations for future research

The goal of this research was investigation into the fabrication of flexible diamond based electronics. As mentioned above, a freestanding diamond film structure with top and bottom electrodes along with a stainless steel tube with diamond wrapped around were investigated. Obviously, much more research needs to be conducted into this area. Voltage-variable resistors were created from these structures, but more advanced electronic devices such as Schottky barrier diodes need to be researched and developed. Structural problems due to post-metallization diamond film cracking, unintentional contact removal upon back-etching, and loss of rectification prevented the development of a flexible Schottky barrier diode when silicon was removed from diodes created in this thesis. One possibility would be to take the same zirconiumnanodiamond-silicon sample configuration and etch away most of the silicon leaving a very thin layer capable of being flexed to the same degree as the diamond film, hopefully retaining the diode's rectification. However, as for the mechanical problems, more investigation needs to be done to identify a possible solution.

Also, recommended future work into the nanocrystalline diamond based Schottky barrier diodes would include research into thinner diamond films and boron doped diamond. It is of interest to determine the ultimate thinness of a grown diamond film that would be possible for creating a Schottky barrier diode especially when this research showed an improvement in rectification ratio as thickness decreased. Also, doped diamond would be the next logical step in these devices potentially showing an improvement in rectification ratio since the field-activated conductivity would no longer be a limitation to the amount of current through these devices. Future research into other metals for Schottky contacts, other types of polycrystalline diamond film, and AC analysis would also be of interest, too.

Finally, only a few of the phase-change diodes were created and studied throughout this research providing limited data. Although data was limited and

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subsequent analysis was not performed extensively on these phase-change diodes, some device characterization was possible leaving the reader with at least a general impression of these unexpected devices. Further investigation into the phase-change state including the physics behind the formation, material analysis of the presumed carbon-filament/diamond structure, and detailed device characterization is necessary beginning with a more controlled setup to instigate the phase-change. Though this was beyond the scope of this thesis, it would most surely be of interest in future research.

APPENDIX

HP4145B I-V Measurement Software

15 ' Set up program for MS-DOS HP-IB I/O Library 20 ' For use independent of the PC instrument bus system 25 ' 30 DEF SEG 35 DATA &H32CD, &H00CB 40 DIM GETDS%(2) 45 READ GETDS%(0): READ GETDS%(1) 50 ADDR% = VARPTR(GETDS%(0)) 55 CALL ADDR% 60 CLEAR, &HFC00 65 I = &HFC00 70 ' 75 ' PCIB.DIR\$ represents the directory where the library files 80 ' are located 85 ' PCIB is an environment variable which should be set from MS-DOS 90 ' i.e. A:> SET PCIB=A:\LIB 95 ' If there is insufficient environment space a direct assignment 100 ' 105 ' can be made here, i.e 110 ' PCIB.DIR\$ = "A:\LIB" 115 '. Using the environment variable is the preferred method 120 ' 125 PCIB.DIR\$ = ENVIRON\$("PCIB") 130 I = PCIB.DIR\$ + "\IBHPIB.LIB" 135 BLOAD I\$, &HFC00 140 CALL I(I%) 145 PCIB.SEG = I%150 ' 155 ' Define entry points for setup routines 160 ' 165 DEF SEG = PCIB.SEG 170 IOABORT = 3175 IOCLEAR = 6180 IOCONTROL = 9185 IODMA = 12190 IOENTER = 15195 IOENTERA = 18200 IOENTERAB = 21

```
205 IOENTERB = 24
210 IOENTERS = 27
215 IOEOI = 30
220 IOEOL = 33
222 IOFASTOUT = 36
225 IOGETTERM = 39
230 IOLLOCKOUT = 42
235 IOLOCAL = 45
240 IOMATCH = 48
245 IOOUTPUT = 51
250 IOOUTPUTA = 54
255 IOOUTPUTAB = 57
260 IOOUTPUTB = 60
265 IOOUTPUTS = 63
270 IOPEN = 66
275 IOPPOLL = 69
280 IOPPOLLC = 72
285 IOPPOLLU = 75
290 IOREMOTE = 78
295 IORESET = 81
300 \text{ IOSEND} = 84
305 \text{ IOSPOLL} = 87
310 IOSTATUS = 90
315 IOTIMEOUT = 93
320 IOTRIGGER = 96
325 DEF.ERR = 99
330 '
335 'Establish error variables and ON ERROR branching
340 '
345 PCIB.ERR$ = STRING$(64, 32): PCIB.ERR = 0
350 PCIB.NAME$ = STRING$(16, 32): PCIB.GLBERR = 0
355 CALL DEF.ERR(PCIB.ERR, PCIB.ERR$, PCIB.NAME$, PCIB.GLBERR)
360 PCIB.BASERR = 255
365 ON ERROR GOTO 395
370 '
375 GOTO 460
380 '
385 ' Error handling routine
390 '
395 IF ERR = PCIB.BASERR THEN GOTO 410
400 PRINT "BASIC error #"; ERR; " occurred in line "; ERL
405 STOP
410 TMPERR = PCIB.ERR
415 IF TMPERR = 0 THEN TMPERR = PCIB.GLBERR
420 PRINT "HPIB error #"; TMPERR; " detected at line "; ERL
425 PRINT "Error: "; PCIB.ERR$
```

```
430 STOP
```

435 '

```
440 ' COMMON declarations are needed if your program is going to chain
```

```
445 ' to other programs. When chaining, be sure to call DEF.ERR as
```

```
450 ' well upon entering the chained-to program
```

455 '

```
460 COMMON PCIB.DIR$, PCIB.SEG
```

```
465 COMMON DEF.ERR, PCIB.BASERR, PCIB.ERR, PCIB.ERR$, PCIB.NAME$, PCIB.GLBERR
```

```
470 COMMON IOABORT, IOCLEAR, IOCONTROL, IOENTER, IOENTERA,
IOENTERS, IOEOI, IOEOL, IOGETTERM, IOLLOCKOUT, IOLOCAL, IOMATCH,
IOOUTPUT, IOOUTPUTA, IOOUTPUTS
```

```
475 COMMON IOPPOLL, IOPPOLLC, IOPPOLLU, IOREMOTE, IORESET,
IOSEND, IOSPOLL, IOSTATUS, IOTIMEOUT, IOTRIGGER, IODMA, IOPEN,
IOENTERB, IOENTERAB, IOOUTPUTB, IOOUTPUTAB, IOFASTOUT
```

480 '

485 FALSE = 0

```
490 \text{ TRUE} = \text{NOT FALSE}
```

```
495 \text{ NOERR} = 0
```

```
500 EUNKNOWN = 100001!
```

```
505 ESEL = 100002!
```

```
510 ERANGE = 100003!
```

```
515 ETIME = 100004!
```

```
520 ECTRL = 100005!
```

```
525 EPASS = 100006!
```

```
530 ENUM = 100007!
```

```
535 EADDR = 100008!
```

```
540 COMMON FALSE, TRUE, NOERR, EUNKNOWN, ESEL, ERANGE, ETIME, ECTRL, EPASS, ENUM, EADDR
```

545 '

```
550 'End Program Set-up
```

```
555 'User program can begin anywhere past this point
```

```
1010 ' Connect to HP4145B, Begin Remote control
```

```
1030 OPTION BASE 1
```

```
1040 INFO$ = SPACE$(13)
```

```
1050 \text{ DINFO} = 20
```

```
1060 CODES$ = SPACE$(50)
```

1070 ISC = 7: PARA = 17

```
1080 \text{ HP4145B} = \text{ISC} * 100 + \text{PARA}
```

```
1090 CALL IORESET(ISC)
```

```
1110 TIMEOUT = 5
```

```
1120 CALL IOTIMEOUT(ISC, TIMEOUT)
```

```
1130 IF PCIB.ERR \bigcirc NOERR THEN ERROR PCIB.BASERR
```

1140 CALL IOCLEAR(ISC)

1150 IF PCIB.ERR <> NOERR THEN ERROR PCIB.BASERR 1160 CALL IOREMOTE(ISC)

4010 CLS : LOCATE 5, 15

4020 PRINT "This program will perform a 2 terminal measurement!"

4030 CLS : LOCATE 6, 15

4040 PRINT "Perform the following connections before beginning measurements:"

4050 PRINT ""

4060 LOCATE 8, 20

4070 PRINT "- Connect the + end to SMU1 "

4080 LOCATE 9, 20

4090 PRINT "- Connect the - end to SMU2"

4120 LOCATE 15, 15

4130 PRINT "Once finished choose one of the options below"

4140 LOCATE 16, 20

4150 PRINT " B - To Begin taking measurements"

4180 LOCATE 17, 20

4190 PRINT " Q - To QUIT program "

4200 INPUT " ENTER LETTER OF YOUR CHOICE: "; B\$

4210 IF B\$ = "B" OR B\$ = "b" THEN CLS : GOTO 4300

4230 IF B\$ = "Q" OR B\$ = "q" THEN GOTO 9000

4240 GOTO 4200

4310 INPUT "Give filename where data will be stored "; FPUT\$

4320 FPUT\$ = FPUT\$ + ".DAT"

4330 INPUT "Start (V): "; SVD

4340 INPUT "End (V): "; EVD

4350 INPUT "Voltage step (V): "; VDSTEP

4390 NDAT = (ABS(EVD - SVD) / VDSTEP) + 1

4400 GOSUB 8000 'Initialize data file

4410 CLS

4420 PRINT ""

4430 PRINT ""

4450 PRINT " Setting Up HP4145B - Measurements will begin shortly "

4470 PRINT ""

4480 '****** Setting up 4145B ******

4490 CODES\$ = "IT1 CA1 DR0 BC": GOSUB 8500

4500 CODES\$ = "DE CH1,'VN','IN',3,3": GOSUB 8500

4510 CODES\$ = "CH2,'VP','IP',1,1": GOSUB 8500

4520 CODES\$ = "CH3;CH4;": GOSUB 8500

4540 CODES\$ = "VS1;VS2;VM1;VM2": GOSUB 8500

```
4550 CODES$ = "SS VR1," + STR$(SVD) + "," + STR$(EVD) + "," +
STR$(VDSTEP) + ",.1": GOSUB 8500
4570 CODES$ = "SM DM1 XN 'VP',1," + STR$(SVD) + "," + STR$(EVD): GOSUB
8500
4580 CODES$ = "YA 'IP',1,0,.1": GOSUB 8500
4590 CODES$ = "MD ME1": GOSUB 8500
4600 INPUT "Press F once HP4145B has finished taking measurements"; F$
4610 IF F$ = "F" OR F$ = "f" THEN CLS : GOTO 4630
4620 GOTO 4600
4630 PRINT ""
4650 PRINT " Transferring and Saving Data to Computer "
4670 PRINT ""
4680 CODES$ = "DO 'IP'": GOSUB 8500
4700
    FOR N = 1 TO NDAT
4710
     GOSUB 8700 'GET DATA
4720
      OPEN FPUT$ FOR APPEND AS #1
    VDrain = SVD + (VDSTEP * N) - VDSTEP
4730
4740
     PRINT VDrain; INFO$
4760
      PRINT #1, VDrain, MID$(INFO$, 2, 12)
4770
      CLOSE (1)
4780
     NEXT N
4800 GOTO 8800
8010 OPEN FPUT$ FOR APPEND AS #1
8030 '** PRINT #1,"% SAMPLE: "; SAMPLE$
8040 PRINT #1, "IV measurement using HP4145B and probe station"
8130 CLOSE (1)
8140 RETURN
8310 OPEN FPUT$ FOR APPEND AS #1
8320 CLOSE (1)
8330 RETURN
8510 LENGTH = LEN(CODES)
8520 CALL IOOUTPUTS(HP4145B, CODES$, LENGTH)
8530 IF PCIB.ERR <> NOERR THEN ERROR PCIB.BASERR
8540 RETURN
8700 '*********************** Listen to HP4145B *********************************
8710 CALL IOENTERS(HP4145B, INFO$, DINFO, ACINFO)
8720 IF PCIB.ERR \Leftrightarrow NOERR THEN ERROR PCIB.BASERR
8730 RETURN
```

8810 GOSUB 8300

8820 PRINT ""

8840 PRINT " Data Transfer Complete "

8860 PRINT ""

8870 INPUT "Press W once you have finished viewing data from HP4145B"; H\$

8880 GOTO 1000

9000 END

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