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# HIGH FREQUENCY ELECTRICAL PROPERTIES OF POLYCRYSTALLINE DIAMOND

By

Mohannad M. Bataineh

## **A DISSERTATION**

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

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### ABSTRACT

# HIGH FREQUENCY ELECTRICAL PROPERTIES OF POLYCRYSTALLINE DIAMOND

By

### Mohannad M. Bataineh

Diamond is a material of great interest for various high frequency electronic applications stemming from its constellation of material properties, including large energy gap, high breakdown field, and high free carrier saturation velocity, among others. However, there are several outstanding questions regarding the frequency dependent electrical properties of diamond. For example, it is not clear whether observed frequency dependencies are mainly due to inter-grain or intra-grain effects. Also it is not clear whether grain boundary effects on frequency dependent conductivity is mainly due to hopping or to potential barrier capacitive effects. This dissertation addresses these basic questions by analyzing results over a broad frequency range so as to separate the roles of these phenomena.

The impedance spectroscopy method is used to study electrical conduction in diamond over a frequency range from dc to 1GHz. Both thick, free-standing films (200 to 400  $\mu$ m thickness) and thin films on silicon (3 to 6  $\mu$ m thickness) are investigated. Experimental results fit well to an electrical model which includes both a hopping conduction path and a path representing cross-grain-boundary conduction. For finer-grain, thin film samples, the data indicates that hopping plays the larger role. However, this was not the case for the larger-grain, thick film samples for which the cross-grain-boundary path dominated the frequency dependent admittance between 1 MHz and 100 MHz.

Correlations are investigated between the dc and ac electrical properties of diamond, and the input and output growth parameters. The study of the relationship to deposition parameters implies that the hydrogen flow rate is the single most dominant parameter in determining the dc as-grown electrical resistivity. As for the ac properties, the effects of annealing and temperature on electrical conductivity and on the ac circuit model parameters suggest that the incorporation of hydrogen in the diamond films takes place at the grain boundaries, and not within the crystallites themselves.

In conclusion, the study shows that the frequency dependent electrical properties of polycrystalline diamond, beyond those expected as a result of the samples geometric capacitance, are principally associated with grain boundaries. Both hopping and cross-grain boundary conduction paths play important roles in the total conduction process of the diamond films.

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To my wonderful parents and my sweet wife.

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# **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Motivation**

There is a considerable interest in the electrical properties of diamond stemming from its constellation of material properties. These include a large energy gap, a large breakdown field, and a high thermal conductivity which provides a potential for high-temperature, high-power electronic device operation. Diamond's hardness and chemical inertness offer the possibility of device operation in hostile environments. Diamond is also considered a material of potential interest for certain high frequency electronic applications because of its high carrier saturation velocity. However, the ac properties of diamond have received less attention in the literature than the dc properties. It is the frequency dependent electrical properties that are the subject of this dissertation.

There are several questions regarding frequency dependent electrical properties of polycrystalline diamond and diamond devices which need to be

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answered if diamond is to be effectively used in electronic devices. For example, it is not currently clear whether the observed frequency dependencies are primarily due to inter-grain or intra-grain effects [1][2][68]. This research study attempts to answer these questions by developing a physical model which includes multiple paths of conduction through the grains and the grain boundaries. The individual contribution of conduction paths to the total ac electrical conductivity of a wide variety of chemical vapor deposited (CVD) diamond samples is investigated over a frequency range from dc to 1 GHz.

For many electronic applications, it is important to understand the dc and ac electrical properties of diamond films over a wide range of frequencies and temperatures, and correlate them to the input and output parameters of the growth process. Other researchers have studied and characterized diamond films in terms of input parameters of growth processes [70][71][72]. However, many questions remain unanswered. For example, does crystalline orientation play any role in determining the electrical resistivities of diamond films, and if so, how? Does higher Raman quality films imply better diamond insulators at high frequencies? What are the major relationships between the growth input parameters and the film's electrical properties? These and other questions need to be answered from both an electrical and a physical point of view. This research study aspires to answer and explain such inquiries.

#### **1.2 Objectives**

The main objective of this study is to add to the current understanding of electronic conduction mechanisms in both free-standing, thick polycrystalline diamond samples and in thin diamond films on silicon. To accomplish this objective, both the dc and the ac electrical impedance is measured and analyzed over a frequency range from dc to 1 GHz, with temperatures varying from 300 to 550 °K. The measurements are designed to generate experimental data in a form that can be fitted into an electrical circuit model. It is important that this model corresponds to a physical understanding. The impedance spectroscopy (IS) technique is found to be a useful tool for obtaining a model which explains the relative role of contributors to the frequency dependent conductivity in diamond.

The second objective of this study is to add to the experimental understanding of the relationship between the electrical properties of diamond and the growth input and output parameters. The films are analyzed in the as-grown and annealed states. As part of this task, the as-grown dc resistivity of the films is correlated to four growth output parameters, namely average grain size, Full-Width-at-Half-Maximum (FWHM), diamond to graphite signal ratio, and growth parameter,  $\alpha$ . In addition, the ac properties are analyzed in terms of the developed model.

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#### **1.3 Preview of Thesis**

Chapter 2 reviews previous studies of dc and ac conductivities in polycrystalline materials, and more specifically in diamond, and examines the electrical and physical models proposed by other researchers.

Chapter 3 describes the experimental setup and equipment used in this study. Also included in this chapter is a description of the sample preparation process.

Chapter 4 provides detailed background on the impedance spectroscopy (IS) technique used to analyze experimental results, and describes the modeling method used to fit the data into an electrical circuit model.

Chapter 5 presents the IS results of both free-standing, thick diamond samples and thin diamond films on silicon. Also included in chapter 5 is an analysis of how the results obtained are explained by the model developed in chapter 4.

Chapter 6 explains the relationship between the as-grown electrical properties of CVD thin diamond films and the growth input and output parameters. Also investigated in this chapter are the annealing and temperature effects on electrical conductivity and ac circuit model parameters for the as-grown and annealed diamond films.

Chapter 7 concludes this study with an analysis of the presented results and a discussion of the open research issues and identifies ideas for future work.

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## **CHAPTER 2**

### BACKGROUND

#### **2.1 Introduction and General Facts**

Carbo, latin for carbon, is one of the most diverse elements on earth. It has several material forms with different physical structures known as allotropes. One of them is the form of diamond. Table 2.1 gives a historical perspective of carbon and its allotropes and several important dates in the development of carbon technology.

In nature, diamond is often found in combination with other carbon allotropes. To identify it as a separate material from all other forms of carbon, different techniques can be used. One of them is the x-ray diffraction technique which reveals the crystalline structure of bulk diamond or graphite. However, when the material is composed of a mixture of diamond, graphite, and amorphous constituents, the diffraction technique has to be interpreted cautiously because the electron diffraction patterns of polycrystalline diamond are very similar to those of

First "lead" pencils	1600's
Discovery of carbon composition of diamond	1797
First carbon electrode for electric arc	1800
Graphite is recognized as a carbon polymorph	1855
First carbon filament	1879
Chemical vapor deposition (CVD) of carbon patented	1880
Production of first molded graphite (Acheson process)	1896
Carbon dating with <sup>14</sup> C isotope	1946
Industrial production of pyrolytic graphite	1950's
Industrial production of carbon fibers from rayon	1950's
High Temperature /High Pressure synthesis of diamond by GE	1955
Development of production of vitreous carbon	1960's
Development of PAN-based carbon fibers	1960's
Development of pitch-based carbon fibers	late 1960's
Discovery of low pressure diamond synthesis	1970's
Production of synthetic diamond suitable for gem trade	1985
Development of diamond-like carbon (DLC)	1980's
Discovery of the fullerene molecules	late 1980's
Industrial production of CVD diamond	1992

 Table 2.1: Chronology of Carbon Technology [33]

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basal-plane oriented polycrystalline graphite. An alternative way to identify diamond is by using a laser-optical technique called Raman spectroscopy. This technique can determine the bonding states of the carbon atoms by displaying their vibrational properties [33][34]. The sp<sup>2</sup> bonding yields graphite, and the sp<sup>3</sup> bonding yields diamond. Other forms of carbon, such as fullerenes, may contain mixtures of sp<sup>2</sup> and sp<sup>3</sup> bondings. Figure 2.1 shows the distinction in Raman spectra between diamond and graphite samples. The single crystal diamond shows a sharp Raman peak at 1332 cm<sup>-1</sup> (wave numbers) while the graphite shows a broader peak at 1570 cm<sup>-1</sup>.

The diamond structure is cubic and may be considered as two face-centered interpenetrating cubic lattices, one with origin at (0,0,0) and the other at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , with parallel axes. In Figure 2.2, two different representations of the diamond structure are displayed [35][36]. The carbon atom bond in diamond has a very high bond energy of 711 KJ/mol, and a small bond length of 0.154 nm [33][35].

Thus, the diversity of carbon materials has led to diverse and significant applications. This study is concerned with a particularly interesting form of carbon, namely diamond.



FIGURE 2.1: Raman Spectrum of diamond and polycrystalline graphite[42] Polycrystalline Graphite film was grown on Cobalt substrate. Recording parameters: spectral resolution=1.6 cm<sup>-1</sup> and laser wavelenght=514.5 nm.



FIGURE 2.2: Schematic diagram of the diamond cubic structure.

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#### **2.2 Electrical Properties of Single Crystal Diamond**

Single crystal diamond is considered one of the best known materials because of its fame as a gem and because of its unparalleled hardness. However it is also has a combination of electronic properties which in principle may offer performance advantages for electronic application. Some of these electrical and related properties are listed in Table 2.2. Single crystal diamond has a 5.5 eV bandgap and is considered one of the best solid electrical insulators. The strong electron bonding in diamond makes it unlikely for an electron to jump out of the valence band even at elevated temperatures. Consequently, as listed in Table 2.2, the resistivity of pure diamond can exceed 10<sup>18</sup> ohm-cm. However, the presence of impurities and the inclusion of graphite can considerably change the resistivity of diamond, and can be reflected on the material's electronic properties.

The question that comes to mind here is what so special about those properties listed in Table 2.2? And what specifically makes diamond an attractive material for a variety of electronic applications? Let us tackle some of those properties individually. The wide bandgap is mainly responsible for the high breakdown fields in diamond [83] which when combined with the high carrier mobilities at both room and elevated temperatures makes diamond an excellent material for high temperature electronic devices which require high current driving capabilities and speed [61][69][82]. The high saturated electron velocity ( $2.7 \times 10^7$ )

Energy gap	5.5 eV
Resistivity, ohm-cm	Type IIa 10 <sup>18</sup>
Dielectric constant @ 300 K	5.7±0.05
Dielectric strength, V/cm	10 <sup>7</sup>
Saturated electron velocity, 10 <sup>7</sup> cm/s	2.7
Carrier mobility, cm <sup>2</sup> /V.s Electron Hole	2200 1600
Thermal conductivity @ 293 K, W/m.K	Туре Ia 600 - 1000 Туре Па 2000 - 2100

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**Table 2.2: Electrical and Related Properties of Diamond** 

cm/s) and the dielectric strength  $(10^7 \text{ V/cm})$  are other advantages of diamond. As defined in [65] by Johnson, Equation 2.1 results in Johnson's figure of merit (JFM) for diamond to be much higher than that of silicon. The ratio of  $(JFM)_{diamond}$  to  $(JFM)_{silicon}$  equals to 8206 [62][63][64].

$$JFM = \frac{E_c v_s}{2\pi}$$
(2.1)

 $E_c$  is the breakdown field, which is for diamond equals to 10<sup>7</sup>, and  $v_s$  is the charge carriers saturation velocity, which is for diamond equals to 2.7x10<sup>7</sup>.

Another important figure of merit which researchers use to estimate a material's potential for digital integrated circuits is Keyes figure of merit [66] (KFM.) As defined by Keyes, Equation 2.2 gives the meaning of that figure.

$$KFM = \lambda \left(\frac{cv_s}{4\pi\varepsilon_r}\right)^{\frac{1}{2}}$$
(2.2)

where  $\lambda$  is the thermal conductivity, c is the velocity of light in vacuum, and  $\varepsilon_{r}$  is the dielectric constant of the material. With Keyes' measures, the ratio of (KFM)<sub>diamond</sub> to (KFM)<sub>silicon</sub> came out to be equal to 32.2 [61]. Indeed, diamond, as compared to other semiconducting materials, has excellent material electrical properties to be considered unique. For example, the Keyes figure of merits for gallium arsenide (= 0.456) and silicon carbide (= 5.8) are much lower than that of diamond. Also comparing the numbers for Johnson's figure of merit for those two materials with diamond shows that  $JFM_{diamond}$  is over a thousand times higher than that of GaAs, and over ten times higher than that of SiC.

On the other hand, doped diamond also possesses excellent semiconducting properties, and has good potential as a semiconductor material [37]. It has the widest indirect bandgap of any other semiconductor material, which makes it a perfect semiconducting material to be used at high temperatures when long carrier important [61][69][73][74][75][76][81]. Compared to other lifetime is semiconductors, such as silicon and GaAs, diamond has a low dielectric constant (5.7) which reduces capacitive effects. And unlike silicon or gallium arsenide, diamond has an upper limit semiconductor temperature of 500°C or higher. Those excellent properties of diamond have motivated many researchers to try to form synthetic diamond under economical conditions on non-diamond substrates with areas large enough for electronic applications. To date, this has resulted primarily in polycrystalline diamond rather than single-crystal diamond. The properties of polycrystalline semiconductors can differ considerably from those of single-crystal materials. In the following section, first issues related to polycrystalline semiconductors in general are described, then in particular polycrystalline diamond.

### **General Considerations**

Most of the transport mechanisms for electrical conduction in polycrystalline, semiconducting films in general, that have been proposed by researchers in past years, have focused on the effect of the inherent intercrystalline boundaries, or grain boundaries [3]. Although researchers have described generalized techniques to explain the electrical conduction behavior due to grain boundaries, the techniques must be viewed as models which correctly explain the electrical behavior of the films under an explicit set of conditions of experimental and material circumstances.

The most cited theoretical analysis of transport mechanisms in polycrystalline thin films is that of Petritz [8] who based his model on the assumption of energy barriers between crystallites. In this case, the conductivity of polycrystalline semiconductors is dominated by the thermionic emission of carriers over the barriers between grains [3][8]. The current-voltage relationship for the barrier in his model was expressed, analogous to simple diode theory, as

$$\mathbf{j} = \mathbf{M} \cdot \mathbf{n} \cdot \exp(-\mathbf{q} \mathbf{\phi}_{\mathbf{b}} / \mathbf{k} \mathbf{T}) \left[ \exp(\mathbf{q} \mathbf{V}_{\mathbf{b}} / \mathbf{k} \mathbf{T}) - 1 \right]$$
(2.3)

where j is the current density, n is the mean majority carrier density in the grains,  $\phi_b$ 

is the potential height of the barriers,  $V_b$  is the voltage drop across the barriers, and M is a factor that is barrier dependent but independent of  $\phi_b$  and is given by  $M=\mu_b n_c kT$ , where  $n_c$  is the number of grains per unit length along the film. If the film has many barriers (i.e small grain sizes), the voltage drop across any one is small compared to kT/q, and the equation 2.1 may be written as

$$\mathbf{j} = \mathbf{M} \cdot \mathbf{n} \cdot \exp(-\mathbf{q} \mathbf{\phi}_{\mathbf{b}} / \mathbf{k} \mathbf{T}) \cdot (\mathbf{q} \mathbf{V}_{\mathbf{b}} / \mathbf{k} \mathbf{T})$$
(2.4)

Thus, the conductivity can be expressed as

$$\sigma = j/\epsilon = q\mu_b n \exp(-q\phi_b/kT)$$
(2.5)

where  $\varepsilon$  is the electric field. Figure 2.3 shows the energy band structure of an n-type polycrystalline semiconductor thin film with grain size  $l_1$ , grain boundary width  $l_2$ , and grain boundary barrier potential  $q\phi_b$ . Petritz explicitly derived an equation for the mobility in the film,  $\mu_g$ , as

$$\mu_{g} = \mu_{b} \exp(-q\phi_{b}/kT)$$
(2.6)

where  $\mu_b$  is the bulk or single-crystal mobility value, and  $q\phi_b$  is defined to be equal to kT ln(n<sub>1</sub>/n<sub>2</sub>), where n<sub>1</sub> and n<sub>2</sub> are the carrier densities in the grain and grain boundary regions, respectively.



FIGURE 2.3: Energy band structure of n-type polycrystalline thin film.

A simpler model was proposed earlier by Volger [9] to explain the electrical conductivity mechanism in polycrystalline semiconductor films. He based his model on that the polycrystalline films consist of two separately homogenous regions, the grains and the grain boundaries, in which no space charge regions exist, and where the grain boundaries region has a higher electrical resistivity than that of the grains region. Defining  $l_1$  and  $l_2$  as the grain and the grain boundary widths, he derived an expression for the effective mobility as follow

$$\mu_{g} = \mu_{b} \left\{ \left[ 1 + (l_{2}/l_{1}) \exp(q\phi_{b}/kT) \right]^{-1} + (l_{2}/l_{1}) \right\}$$
(2.7)

where  $\mu_g$  is the film mobility, and  $\phi_b$  is the barrier potential due to the concentrations in the grain and grain boundary.

Several other models have been proposed to interpret the electrical conductivities in polycrystalline semiconductor films, and among them are more complicated approaches based on electrical component modeling of the polycrystalline films. Kuznicki [10] has proposed an equivalent electrical model to represent the grains and the grain boundaries in the films as shown in Figure 2.4. The model was used to numerically verify the static electrical characteristics of CdSe films. The simulated results of this model fitted well with his experimental data.

In summary, a variety of conduction models for polycrystalline


FIGURE 2.4: Kuznicki's electrical model of polycrystalline CdSe thin film.

semiconductors have been proposed in the literature, however a key feature of all is the role of the grain boundaries. Additional insight is obtained by considering the frequency and temperature dependent of conductivity.

# 2.4 Frequency- and Temperature-Dependent Electrical Conduction in Polycrystalline Semiconductors: General Considerations

The temperature and frequency dependent electrical conductivities of polycrystalline materials have been studied by several researchers [1][3][11][12]. The frequency dependent electrical conductivity in hopping systems,  $\sigma(\Omega)$ , was first observed and reported by Pollak and Geballe in 1961[18][19]. Pollak has observed in his study of the non-steady-state (i.e. ac) band and hopping conductions that the two conduction mechanisms have basically different ac behaviors. Band conduction current is carried by electrons (or holes) in Bloch states, and so, it is necessary only to disturb the equilibrium distribution of the electrons to achieve a finite current. However, in the hopping conduction process, the states are localized and there is no current associated with any electronic state. In this case, the conduction current is a result of transition of electrons from state to state, i.e. the hopping of electrons produces the current. In his study, Pollak derived formulas for the real parts of the band and hopping conductions, and they are given in the following equations

$$\Re \sigma_{\text{band}}(\omega) \propto \frac{1}{1+\omega^2 \tau^2}$$
 (2.8)

$$\Re \sigma_{\rm hop}(\omega) \alpha \frac{\omega^2 \tau}{(1+\omega^2 \tau^2)}$$
 (2.9)

where  $\tau$  is the Boltzman transport equation's relaxation time and is usually in the order of pico-seconds for band conduction, and  $\omega$  is the angular frequency of the applied field. The first equation clearly shows that for frequencies less than  $10^{11}$  Hz,  $\omega^2 \tau^2$  will be much less than unity, and the conductivity due to band conduction will not show any considerable dependence on frequency. However, in the higher ranges of frequencies (>  $10^{11}$  Hz), the first equation predicts that the real part of conductivity will be a decreasing function of frequency.

Jonscher [20] also experimentally studied the frequency dependence of conductivity in hopping systems, mainly non-metallic solids, in which the flow of current occurs by hopping of localized carriers, whether electrons or ions. He pointed out that the same dependence is found in semiconducting amorphous systems and in a broad group of insulators. He observed in his study that at sufficiently low frequencies and down to dc there is a constant level,  $\sigma_0$ , of conductivity, and there follows a region where conductivity is an increasing function of frequency. He expressed this dependence, supporting Pollak and Geballe's observation, by the empirical relation

$$\sigma \alpha \omega^n$$
 (2.10)

where n takes values in the range 0.5 < n < 1.0, depending upon temperature. Jonscher added, however, that the principal drawback of the various theories lies in the difficulty of obtaining an adequate physical insight into the suggested conduction mechanisms, especially in view of the extremely wide range of systems involved [21]. Even though Jonscher's results do not agree completely with Pollak's, similar observations were reported by other researchers [1][2][3][4][11][22][23][24][25] for different types of polycrystalline materials. However, the appearance of  $\omega^2$ -dependent conductivity was also reported by Jonscher and by other researchers [20][26][27]. Jonscher related the  $\omega^2$ dependency to a possible spurious effect of even very small resistance and inductance associated with the leads external to the films. Street, et al. [26] clarified the  $\omega^2$ -dependence of As<sub>2</sub>Se<sub>3</sub> amorphous films with the aid of the circuit model shown in Figure 2.5. The parameters C<sub>L</sub> and R<sub>L</sub> are the lead capacitance and resistance, and C<sub>s</sub> and R<sub>s</sub> are the capacitance and resistance of the sample, respectively. The equivalent capacitance and resistance of the circuit are given by



FIGURE 2.5: Street's model of the bulk material and the leads.

the following equations:

$$R_{P} = R_{L} + \frac{R_{S}}{1 + \omega^{2} \tau_{R}^{2}}$$
(2.11)

$$C_{P} = C_{L} + \frac{\left(\frac{R_{S}}{(R_{L} + R_{C})}\right)^{2}C_{S}}{1 + \omega^{2}\tau_{C}^{2}}$$
(2.12)

where

$$\tau_R^2 = \left( C_S^2 R_S^2 R_L \right) / (R_S + R_L)$$
(2.13)

$$\tau_C^2 = \left(C_S^2 R_S^2 R_L^2\right) / \left(R_L + R_S\right)^2$$
(2.14)

Under the assumption that  $R_S \gg R_L$ , they divided the frequency-dependent electrical conductivity into three different regions. For the low-frequency region where  $\omega \ll 1/\tau_R$ , one finds  $R_P \approx R_S$  and  $C_P \approx C_L + C_S$ . For the mid-frequency

region where 
$$1/\tau_R < \omega < 1/\tau_C$$
 one finds  $R_P \approx 1/\omega^2 C_S^2 R_L$  and  $C_P \approx C_L + C_S$ .

Note that in this case the measured  $R_P$  shows an  $\omega$  dependence which is an artifact due to the presence of  $R_L$ . And finally, in the high-frequency region where  $\omega >>$   $\frac{1}{\tau_C}$ ,  $R_P \approx R_L$  and  $C_P \approx C_L + (C_S/\omega^2 \tau_C^2)$ . Consequently, the frequency

dependence of the measured  $R_P$  may not reflect the actual behavior of the sample resistance,  $R_S$ , at sufficiently high frequencies.

In a similar study of the electrical conductivity in amorphous materials by Elliot [28], an equation for the ac electrical conductivity was derived. He proposed a model, correlated barrier hopping (CBH), to interpret the dependence on both frequency and temperature of the ac electrical conductivity. In his model, he assumed that an electron in a charged defect state hops over a potential barrier of height  $\overline{W}$  given by

$$\overline{W} = W_m - \frac{4ne^2}{\epsilon R}$$
(2.15)

where  $W_m$  is the maximum energy required to take an electron from a hopping site to the conduction band,  $\varepsilon$  is an effective dielectric constant which may be taken to be the same as the bulk dielectric constant, e is the electronic charge, n is the number of electrons that hop, and R is the distance between the hopping sites. He eventually derived the final expression for the  $\sigma_{AC}(\omega)$  to be equal to:

$$\sigma_{AC}(\omega) = \left[\frac{\pi^2 N^2 \varepsilon}{24} \left(\frac{8e^2}{\varepsilon W_m}\right) \frac{\omega^s}{\tau \beta}\right]$$
(2.16)

where  $\beta = 6kT/W_m$ ,  $s=1-\beta$ , N = concentration of localized states and  $\tau$  is of the order of an atomic vibrational period,  $10^{-13}s$ . This model, in disagreement with Pollak's theoretical model, shows that the exponent, s, cannot be greater than unity. However, both models did not take into account the effect of lead resistances and inductances. Moreover, Elliot's model shows that the exponent of  $\omega$  directly depends on the temperature and the maximum energy height.

On the other hand, other researchers [8][9][29][47][48] directly related the frequency-dependent electrical conductivity of polycrystalline semiconductor materials to the electrical properties of grain boundaries rather than hopping. Werner [29], in his study of the electronic properties of grain boundaries, suggested that the application of a small ac voltage leads to a time periodic change of the potential barrier between grains which leads to a periodical variation in the hole concentration at the interface between grains. This change drives a periodic capture and emission of holes by the interface states. The difference between the capture and emission rates produces a displacement current given by:

$$J = Y \delta \phi \tag{2.17}$$

where Y is the characteristic admittance of the traps, and  $\delta \phi$  is the applied ac voltage.

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Concerning the temperature dependent electrical conductivity, Elliot and other researchers [12][30][31][32] showed that both the dc and the ac electrical conductivities are functions of temperature. However, Elliot did not explicitly show in his model how the temperature affects each individual conductivity path within the polycrystalline materials he studied. It has been subsequently shown by other researchers [1][11][44][45][46] that the dc electrical conductivity can be expressed as a sum of three components:

$$\sigma = \sigma_1 \exp(-E_1 / kT) + \sigma_2 \exp(-E_2 / kT) + \sigma_3 \exp(-E_3 / kT)$$
(2.18)

where  $E_1$ ,  $E_2$ , and  $E_3$  are the activation energies for the high, medium, and low temperature ranges, respectively. Researchers have also studied the ac temperature dependent electrical conductivity in different materials systems, and found out that temperature plays a major role in hopping conductions as well as in conductions within the grain boundaries [21][32]. It has been shown by many researchers that the exponent n in the empirical relation of equation 2.10 is a function of temperature, approaching unity at low temperatures and decreasing to 0.5 or less at higher temperatures. In a recent study by Hari, et al.[32], the complex impedance of n-BaTiO<sub>3</sub> ceramics have been studied. They explicitly studied and analyzed the contributions of grains and grain boundaries to the total resistance of the samples, and they have concluded that the observed Positive Temperature Coefficient of Resistance (PTCR) in dc resistivity is mainly due to the increase in grain boundary resistivity. They have clearly showed that the grain boundary resistivity jumps are relatively high compared to the change observed in the grain resistivities versus temperatures, confirming the major contribution to the PTCR effect is from the grain boundaries, not the grain interiors.

In summary, it seems that the frequency-dependent electrical conductivity, particularly in amorphous semiconductors and non-metallic polycrystalline solids, can be related either to hopping, which can occur either as a bulk phenomena or via states between grains, or to a grain boundaries' electronic potential properties. Hopping between localized states within a crystallite, for example, is considered to be a pure bulk phenomena where the SCL currents and currents due to the capture and emission of holes by the interface states are related to changes in the grain boundaries potential barriers. Finally, the ac electrical conductivity measurements versus temperature, of different semiconductor materials, were very helpful in differentiating between variable-range hopping conduction through the films' surface conducting layers and through paths along the grain boundaries, and

conduction due to the thermal excitation energy of electrons.

#### **2.5 Electronic Properties of Polycrystalline Diamond**

#### 2.5.1 DC Properties of Polycrystalline Diamond

Concerning polycrystalline diamond, several researchers have studied the static and dynamic electrical conduction mechanisms in both thin and thick diamond films grown by different techniques and under different conditions [1][3][4][11][12][13][14][77][78][80]. Ohmic and non-ohmic current flow behavior has been reported and in some cases diamond films, with different electrode materials and sample geometries, show both ohmic and non-ohmic portions of the current-voltage characteristics [15][79]. Iwasaki et al. [15] concluded, in their study of the formation of ohmic contacts on semiconductor CVD diamond, that the current-voltage characteristics of Al/ and Mg/p-type diamond contacts change from ohmic to non-ohmic as the resistivity of the semiconductor diamond films increases, while the Au/p-type diamond contact shows good ohmic behavior. Also, a contact resistance,  $R_c$ , of less than  $10^3 \Omega cm^2$ was found to be necessary for obtaining ohmic contacts on semiconductor CVD diamonds regardless of the metal. However, it should also be noted that other researchers [17] have successfully fabricated Schottky diodes using gold contacts on thin diamond films obtained by plasma assisted CVD process.

Muto et al. [7] have studied the electrical conduction along conducting layers between grains in CVD polycrystalline diamond films and have concluded that the conductivity in the ohmic region in the as-grown films is mainly caused by variable range dc hopping along the disordered graphitic region between diamond grains. This type of hopping has often been observed in amorphous semiconductors with dense localized defects. They have also observed that the conductivity decreased drastically after the sample was annealed at 670 K. This decrease in the conductivity was related to the removal of the disordered graphitic region. However, in their study of the nonlinear portion of the current-voltage characteristic of thin diamond films (1-2  $\mu$ m), they suggested that the electrical conduction in this region is more likely due to the Poole-Frenkel emission as opposed to the Schottky emission. This conclusion is consistent with those of Huang and Reinhard [16] who investigated the voltage dependence of the photoconductivity and showed that the high-voltage increase in polycrystalline diamond thin films' conductance is due to an increase in dark carrier concentration rather than an increase in mobility. And this, theoretically, agrees with the Poole-Frenkel mechanism of electrical conduction. Thus, the currents, at sufficiently high voltages, may no longer be determined by only the bulk carrier densities that were present in the absence of the applied voltage.

At reasonably high voltages, excess carriers, injected from one of the electrodes, may also have a considerable contribution to the total current flowing in the bulk material. These currents, arise from a space charge of excess carriers, are called Space-Charge-Limited (SCL) currents [23][56][57][58][59][60]. Figure 2.6 shows a bulk insulator with two contacts where the low work function cathode is assumed to supply electrons in the conduction band. Those electrons will be drawn into the space between the cathode and the anode by the applied voltage.

The current-voltage relationship of this type of currents flow is given by the following equation

$$I = CV/T_r \tag{2.19}$$

where C is the geometric capacitance, V is the applied voltage, and  $T_r$  is the transit time of an electron from cathode to anode, and is a function of the applied voltage. This type of currents' contribution can also be responsible for the increase in the material's electrical conductivity at high dc voltages.

Even though the steady-state measurement techniques, i.e. dc methods, are very helpful in determining and understanding the different conduction mechanisms of polycrystalline materials including diamonds, such as Poole-Frenkel emission as opposed to space-charged-limited current, they do not easily





reveal the information whether the conduction in the materials happens in a band or by hopping of electrons from localized states. Therefore, the need for an extensive study of the frequency and temperature dependent electrical conductivity comes up.

#### **2.5.2 Frequency and Temperature-Dependent ac Properties of**

#### **Polycrystalline Diamond**

The frequency dependent electrical conductivity,  $\sigma(\omega)$ , of CVD diamond films has been the subject of investigations by Sugino and Muto et al. [2][3][7][22] and by Sokolina and Ermakova et al. [1][4][11]. Both groups experimentally find that the electrical conductivity of as-deposited CVD diamond depends on frequency at sufficiently high frequencies greater than 10<sup>4</sup> Hz. However, the annealed films showed a frequency dependence at lower frequency ranges, less than 10<sup>4</sup> Hz.

Sugino and Muto et al. studied and analyzed the frequency-dependent electrical conductivity of thin CVD diamond films  $(1-2 \mu m)$  and concluded that the conductivity in the as-deposited polycrystalline diamond films is caused by conduction through disordered graphitic regions between grains and at the surface of the films. This conclusion was reached from the correlation between the electrical characteristics of the films and Raman spectra. It was also reported by them that the ac electrical conductivity decreases drastically by several orders of magnitude on thermal annealing. However, hydrogenation after annealing did not change their results as much.

The frequency-dependent electrical conductivity of polycrystalline diamond films was expressed by the known empirical relation  $\sigma(\omega) \propto \omega^n$ , where the exponent, n, was believed to be a function of temperature approaching unity at low temperatures and decreasing to 0.5 or less at higher temperatures. However, a frequency-independent conductance was observed, on some of their samples, at high temperatures, which suggests that thermally activated band conduction is dominant in the higher temperature region. They suggested that the total ac conductivity consist of three types of conduction:

$$\sigma = \sigma_{o} + \sigma_{h} + \sigma_{t} \tag{2.20}$$

where  $\sigma_o$ ,  $\sigma_h$  and  $\sigma_t$  are the band, hopping and conduction related to thermal emission of carriers, respectively. The  $\sigma_t$  is a frequency dependent conductivity caused by the thermal emission of carriers from traps, and is obtained as a broad peak centered at a frequency  $f_0$  [2]. The reciprocal of that frequency,  $1/f_0$ , represents the time constant,  $\tau_0$ , for the thermal emission of carriers from relevant trap levels, and is given by Arrhenius relation:

$$\mathbf{r}_{o} = 1/f_{o} = \left(\frac{B}{T^{2}}\right) e^{\left(\frac{E_{t}}{kT}\right)}$$
(2.21)

where B is a constant determined by the effective mass and the capture cross section of traps.

Sokolina et. al and Ermakova et. al also studied the temperature and frequency dependence of the electrical conductivity of diamond films in vacuum at temperatures in the range T = 150 - 900 °K. The films were grown on a tungsten substrates, and the films' thicknesses varied from a few microns to tens of microns. After plotting the measured conductivity as a function of frequency,  $\log \sigma_{ac}$  vs. log f, they observed a power dependence of the ac electrical conductivity on frequency. In agreement with Sugino and Muto, they found that the power dependence of the electrical conductivity decreases, approaching 0.5 or less, on increase in temperature. Nevertheless, they hypothesize that polycrystalline diamond films consist of conducting grains and coherent scattering regions of different sizes and shapes. They considered that at the boundaries between the grains and the coherent scattering regions the structure of the crystal is distorted and impurities can accumulate. This, as a result, gives rise to localized electron states in the band gap. They proposed a model consisting of a bulk resistance, R<sub>b</sub>, of a micro grain in series with a parallel combination of a barrier capacitance, C<sub>w</sub>, and a barrier

resistance,  $R_w$ . Consequently, a polycrystalline film can be represented by a set of such chains.

In conclusion, the electrical conductivity of diamond films have shown a frequency dependence as well as a temperature dependence. It has been proposed by different researchers that the frequency dependence electrical conductivity could be either due to hopping conduction within the crystalline grains or within the grain boundaries or due to conduction across grain boundary potential barriers. However, it has not been clearly shown how each individual part contributes towards the total ac electrical conductivity of the films, and in what capacity. In this research work, we will propose a physical model which distinguishes between the two types of frequency dependent conductions within the diamond films.

# **CHAPTER 3**

## **EXPERIMENTAL METHODS**

## **3.1 Introduction**

This chapter describes the dc and ac equipment used to perform the necessary measurements for this investigation. The sample preparation techniques are described, and the details of the measurements' setups are also discussed.

### **3.2 Equipment**

HP4145B Semiconductor Parameter Analyzer: The Hewlett Packard model 4145B semiconductor parameter analyzer was used to measure and graphically display the dc current-voltage characteristic of the diamond samples. It is equipped with four programmable Source/Monitor units (SMU's). Each SMU can be set up to function as a voltage source/monitor, current source/monitor, or source common. A simplified circuit diagram of an SMU is illustrated in the Figure 3.1. Two SMU's, one as a variable voltage source and the other as a common current source, are used in setting up a two-probe circuit for the sake of measuring the dc current-voltage characteristic of the diamond films. The HP4145B monitors currents as low as 0.05 pA and up to 105 mA divided over nine different ranges. The resolutions of the measurements are different from range to range.

HP4192A LF Impedance Analyzer: The Hewlett Packard Model 4192A LF Impedance Analyzer is a fully automatic, high performance test instrument to measure a wide range of impedance parameters as well as gain, phase, and group delay. The internal frequency synthesizer provides a sinusoidal wave test signal that has an accuracy of 55 ppm and can be set to measuring frequency within the range from 5 Hz to 13 MHz with 1 mHz maximum resolution. The instrument has four UNKNOWN terminals:  $H_{cur}$ ,  $L_{cur}$ ,  $H_{pot}$ , and  $L_{pot}$ . The test signal is output from the OSC OUTPUT connector, H<sub>cur</sub> of the UNKNOWN terminals as shown in the Figure 3.2, and its level can vary from 5 mV<sub>rms</sub> to 1.1 V<sub>rms</sub>. The purpose of the current terminals is to cause a measurement signal to flow through the sample, where the potential terminals are to detect the voltage drop across the sample. The four terminal method, as shown in the configuration of Figure 3.2, provides the shielding required for high-impedance, high-frequency measurements. Since the same current flows through both the center conductors and the outer shield



#### FIGURE 3.1: HP4145B Source/Monitor Unit Circuit Diagram



# FIGURE 3.2: HP4192A Test Signal Terminals

conductors (in opposite directions), no external magnetic fields are generated around the conductors. In this research, the HP4192A is used to measure the conductance, G, and the susceptance, B, of different diamond samples over the range of frequency from 5 Hz up to 13 MHz. The measurement's range of G/B for this instrument is 1nS to 12.999S. Consequently, samples with resistances greater than  $10^9 \Omega$  will not be accurately and stably measured with this instrument.

Signatone S-1160 High-Frequency Probing System: The S-1160 is a general purpose analytical probe station designed for probing various geometries from 10 mils to 1 micron. It is equipped with a Signatone QuieTemp DC Hot Chuck System model S-1060. The system is capable of conducting measurements in a temperature range from room temperature to 300°C. This specific system is controlled by an ATHENA temperature/process controller model XT-25, and a NESLAB recirculating chiller model CFT-33. Multipurpose, high speed, passive, model 10 GGB picoprobes are used with this probing station to conduct high-frequency measurements. The range of operation for those specific picoprobes is dc to 3.5GHz. The whole system is shielded with a Signatone Light-Tight box model PSDB-1160 to protect the measurements from any noise signals (photoconductive) that may disturb the accuracy of the output measurements.

HP16191A Side Electrode SMD Test Fixture: The Hewlett Packard model 16191A high frequency test fixture is used in conjunction with the HP4291A impedance analyzer, described below, to accommodate and measure the conductance, resistance, susceptance, and reactance of the diamond films over the frequency range from 1 MHz to 1 GHz. The unwanted electrical properties of the fixture, such as the phase rotation due to the physical length of the electrodes and other unwanted stray parasitics between electrodes, can be fully compensated for by automated calibration techniques.

HP4291A RF Impedance/Material Analyzer: The Hewlett Packard model 4291A RF impedance analyzer is an integrated package designed to provide testing at higher frequencies than the previously described HP4192A unit. It uses the RF I-V method, as apposed to the conventional reflection coefficient method, to measure impedance as a one-port, lumped element from a ratio of voltage and current. Figure 3.3 shows the circuit design for both measurement techniques. The RF I-V method ensures higher measurement accuracy through a wide frequency and impedance range.

The RF impedance analyzer operates at frequencies from 1 MHz and up to 1.8 GHz with a frequency resolution of 1 mHz. The ac voltage oscillation level varies between 0.2 mV<sub>rms</sub> to 1 V<sub>rms</sub> with an ac voltage resolution between 0.002  $mV_{rms}$  to 2 mV<sub>rms</sub>. The RF analyzer has been extensively used in this research work with two different measurement configurations. One uses the S-1160 probing station with the model 10 picoprobes, and the other uses the HP16191A high

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**Reflection Coefficient Method**  $\Gamma = V_r / V_i$ 



I-V Method



frequency test fixture. With either configuration, the system is calibrated (short/ open/load) at the probes' tips very close to the device under test to eliminate the unwanted stray parasitics. The results are displayed on the HP4291A monitor and stored on disks for later analyses.

#### **3.3 Sample Preparation**

Thin and thick diamond films, synthesized under different growth conditions, are used in the impedance spectroscopy study. The thin diamond films are provided by Dr. Jes Asmussen and Dr. Saeid Khatami at Michigan State University. The thick, free-standing films were provided to us by a commercial supplier. The sandwiched configuration, shown in Figure 3.4, is used for both thin and thick diamond films. Large area contacts, in the range of 0.1 cm<sup>2</sup> to 0.7 cm<sup>2</sup>, are used to reduce the sample resistance to within the range of measurement apparatus.

For the thin diamond films (3 to 6  $\mu$ m), grown on silicon substrates, the samples are sandwiched between two conducting layers. One is attached to the back of the films, on the silicon side of the sample, and the other is in the form of dot contact at the top surface of the films. Contact materials are selected to provide ohmic I-V behavior over the voltage range of interest. In the impedance spectroscopy study of thin films, two types of methods are used to form ohmic



b. High resistive thin diamond film on silicon



c. Free-standing, thick diamond film

FIGURE 3.4: Schematic diagram of diamond samples configurations

contacts to CVD diamond. On samples with low resistivity, less than approximately  $1 \ge 10^6 \Omega$ -cm, silver paint produced linear current-voltage characteristics. On the higher resistivity samples, however, non-linear characteristics resulted with silver paint, and sputtered gold contacts are used to generate linear I-V characteristics.

The thick, free-standing diamond samples were synthesized by the arc-jet method. The samples are 1 cm x 1 cm with thickness ranging from approximately 200 to 400  $\mu$ m and of gray to dark-gray visual appearance. Large area silver paint contacts on opposing sides of some samples were adequate to produce linear current-voltage (I-V) characteristics. On other samples, gold was needed.

In the sandwiched type samples, measurements may include a considerable inter-grain conduction as apposed to intra-grain conduction. Figure 3.5 shows a schematic diagram of two possible paths for the conduction current flow through a diamond film in the vertical direction.

Samples did not receive any special cleaning to remove conducting surface layers. However, the applied conducting contacts covered a large fraction of the surface area, in any case. Some of the samples were annealed as part of the process to study the effect of annealing on the dc and ac electrical properties of the films as well as on the films' ac electrical circuit model parameters. The annealing process was taken place in a class-100 clean room using a furnace with a nitrogen gas ambient.

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FIGURE 3.5: Schematic diagram of conduction paths in a diamond film

#### **3.3.1 Measurement Setup**

In order to determine the complex impedance as a function of frequency, this study used instruments which apply a single frequency signal to the sample and measure the ratio of the voltage and current, in terms of both phase and amplitude, to determine the real and imaginary parts of the impedance. Three instruments and two sample connection methods were used to cover the frequency range from dc to 1 GHz. For the dc I-V measurements, a Hewlett-Packard model 4145B semiconductor parameter analyzer was used. Hewlett-Packard model 4192A and model 4291A impedance analyzers were used to measure the real and imaginary parts of the small signal impedance from 5 Hz to 1 MHz and 1 MHz to 1 GHz, respectively. The small signal rms amplitude was less than or equal to 1 V, well within the linear range of the I-V characteristics. From dc to 1 MHz, the sample electrodes were contacted by coaxial probes on a micro-probing station. From 1 MHz to 1 GHz, a test fixture, model HP16191A, designed specifically for high frequency probing with the HP4291A was used.

Both impedance analyzers have frequency-dependent upper limits on the measured impedance which affect sample selection, particularly for thicker samples. The upper impedance limit on the low frequency impedance analyzer is 1 M $\Omega$  Considering for example a 500  $\mu$ m thick sample with contact areas on the order of 0.5 cm<sup>2</sup>, the system places an upper limit on resistivity of 10<sup>7</sup>  $\Omega$ -cm.

Consequently, higher resistivity thick samples were not within the scope of this study. At 1 GHz, the upper impedance limit drops to  $1K\Omega$ . However this limit places less restrictions on sample selection, since the sample capacitance is sufficient to keep the impedance less than the high frequency limit.

# **CHAPTER 4**

## **MODELING TECHNIQUE**

### **4.1 Introduction**

This chapter begins with a description of the general basics of the impedance spectroscopy technique which is used in the physical modeling of thin and thick diamond films. Later, some circuit model examples will demonstrate how this technique can be ambiguous if the results are not carefully interpreted in a way which agrees with the physical properties of the material. Section 4.3 introduces the basic four path ac circuit model which is used for data fitting. Finally, in section 4.4, a sample Matlab program shows how the modeling optimization process is achieved by calculating the minimum error between experimental and modeled results.

#### **4.2 Impedance Spectroscopy Technique**

Impedance spectroscopy (IS) is considered a powerful technique to measure and analyze many properties of electronic materials. It can be used to investigate the ac electrical properties of liquids as well as solid materials: ionic, semiconducting, mixed electronic-ionic, and insulators [49]. One of the very first papers to deal with IS was that of Buerle in 1969. He applied the technique to accurately determine the conductivity of solid electrolytes [50]. More recently, researchers [51][52][53][55][84][85] have used the technique to study and analyze the ac electrical conductivity of polycrystalline and single crystal electronic materials, and to derive equivalent circuit models to describe the different ac conduction mechanisms in materials.

The IS technique can be used in either the time domain or the frequency domain [49]. Appropriate Fourier transforms can also be applied to go from one form to the other. In the time domain measurement, a step function of voltage may be applied to the system under test, and the time-varying current measured. The ratio of voltage to current can then be used to define what is called time-varying impedance. However, this would not be the same impedance defined in the IS technique. A Fourier transform is needed to convert the results from the time to the frequency domain to be used in the IS analyses.

The most common approach nowadays in the IS analyses is to measure

impedance directly in the frequency domain. This can be accomplished by applying a small ac voltage signal of fixed frequency and measuring the real and imaginary parts of the impedance directly as the frequency is stepped from one value to the next. The availability of sophisticated commercial instruments which automatically measure the impedance as a function of frequency makes this approach the method of choice for researchers to accomplish their goals. Macdonald and Johnson [49] have proposed a flow chart to present the general characterization process using IS. The details are shown in Figure 4.1. After impedance results for a given material have been obtained experimentally, data fitted to an existing mathematical model based on a valid physical theory, or an empirical equivalent circuit can be developed which predicts results similar to the experimental ones.

One disadvantage of this technique is associated with potential ambiguity in choosing the appropriate equivalent circuit which believed to be the most consistent with the expected behavior of the material under test. This difficulty comes from the possibility that more than one electrical equivalent circuit may result in a particular impedance response. Take for example the two circuits shown in Figure 4.2 [54]. They both produce the same impedance response for all frequencies when the values of their elements are properly chosen and related. However they would represent different physical phenomena and structures. For example, the circuit in Figure 4.2 (a) could represent an ac model for a sample with a Schottky barrier

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FIGURE 4.1: Flow chart for IS characterization process. [49]



**(b**)

**(a)** 



FIGURE 4.2: Two equivalent circuits which can have the same impedance response at all frequencies if parameters were chosen properly.
contact at one end. In this case, C1 and R1would represent the barrier and C2 and R2 would represent the bulk material. Figure 4.2 (b) would represent the model of a sample with a dc bulk current path represented by R1 and a bulk capacitance C1. In addition, a cross-grain polycrystalline path would be represented by R2 and C2. However, this ambiguity could be resolved by other measurements, in this case dc measurements. For the cases illustrated in Figure 4.2, if a Schottky barrier did exist, as suggested by part (a), then non-linear, rectifying characteristics would result as opposed to the linear characteristics expected for a dc conduction path.

In this research study, the IS technique was used in the frequency domain where both the real and the imaginary parts of the complex impedance were measured as a function of frequency. Data are presented as a plot of the imaginary part of the impedance vs. the real part of the impedance. Consider the simplest possible case where the diamond is considered to have a frequency independent conductivity and permittivity. In that case, the sample impedance is represented as the parallel combination of a resistor and a capacitor. The resistor value is  $R = d/\sigma A$ where A is the cross sectional area of the sample, d is the sample thickness, and  $\sigma$  is the electrical conductivity. The capacitance value is  $C = \varepsilon A/d$  where  $\varepsilon$  is the permittivity. R may be obtained experimentally from the measured dc resistance and C may be calculated from geometric considerations, using a relative dielectric constant of 5.5 for diamond. The combined impedance is

$$Z = \frac{R}{1 + \omega^2 R^2 C^2} - i \frac{\omega R C}{1 + \omega^2 R^2 C^2}$$
(4.1)

where  $\omega = 2\pi f$  is the frequency in radians per second and i is the imaginary unit. An impedance spectroscopy plot of the imaginary part of the impedance on the vertical axis and the real part of the impedance is shown in Figure 4.3 for the hypothetical case of R = 100  $\Omega$  and C = 10 pF.

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#### **4.3 Basic Four Path Model**

The impedance spectroscopy results of thin and thick diamond films were more complex to analyze and model than the simple case of a parallel combination of a resistor and a capacitor. Previous reports in the literature have identified either hopping or, alternatively, grain-barrier effects as contributors to frequency dependent electronic conduction in diamond. Another question to be answered is whether the electrical properties of grain boundaries are likely to be similar to or significantly different from those of the grains themselves. The answer may depend on whether the properties are intrinsic or extrinsic to the material under test. With such questions, the impedance spectroscopy instrumentation comes to offer the possibility of a comprehensive characterization of the films and in particular, the characterization of the ac electrical conduction. Consider first hopping. It has been very well established for many years that the frequency dependent electrical



FIGURE 4.3: Impedance Spectroscopy Results of a Parallel R-C Circuit

conductivity in many electronically and ionically conducting materials shows a frequency independent dc component at low frequencies and a frequency dependent ac component at high frequencies [38][39][40][41]. As discussed in chapter 2, the conductivity dependence on frequency is of the form

$$\sigma(\omega) = B\omega^n \tag{4.2}$$

where B is a constant depending on the particulars of the sample and the value of n is generally between 0.5 and unity, as also described in chapter 2. Frequency dependent conduction in diamond which is indicative of hopping with n = 0.8 has been previously reported by Sugino et al. [2][22], while Sokolina et al. [1][4][11] have proposed that conduction can be modeled by a path consisting of a series of grains, each consisting of a bulk resistance in series with a grain-boundary potential barrier. The latter group proposed a model consisting of a resistor, representing a micro-grain's bulk resistance, in series with a parallel combination of a barrier capacitance and a barrier resistance.

There are always difficulties associated with choosing a circuit model to represent the complex impedance data as explained earlier and shown in Figure 4.2. Once an equivalent circuit model has been chosen, it is always necessary to make a link between the circuit model elements and the region of the sample responsible for each.

In our study of the frequency dependent electrical conduction in both thin and thick diamond films, the impedance response can not be represented with a simple RC circuit model. Consequently, it is necessary to add to the impedance model in order to represent frequency dependent phenomena in the diamond. Since the literature suggests evidence for both hopping and grain-boundary potential barrier effects, it was decided to incorporate both effects in an IS equivalent circuit model. As a result, to the basic model of a parallel combination of a capacitor and a resistor, a frequency dependent conductance equal to  $B\omega^n$  was added. In addition, a path consisting of a grain resistance  $R_g$  in series with a grain capacitance  $C_g$  was added in parallel with the other paths in order to compensate for conduction across the grain boundaries. It is necessary to note here that if multiple grains are in series in a conduction path, the individual resistance and capacitance associated with each grain can be combined into an equivalent circuit consisting of  $R_g$  and  $C_g$  as shown in Figure 4.4. A sample model which contains both hopping and grain-barrier containing paths is shown in Figure 4.5.

## 4.4 Model Fitting

The model of Figure 4.5 contains six parameters (R, C, B, n,  $R_g$ , and  $C_g$ ) which may be fit to the experimental IS data. The first two parameters are obtained



FIGURE 4.4: Schematic Diagram Of An Equivalent Grain Boundaries Path consisting of an equivalent resistor, R<sub>g</sub>, in series with an equivalent capacitor, R<sub>g</sub>.



# FIGURE 4.5: Impedance Spectroscopy Sample Circuit Model

consisting of four paths: dc resistance, geometric capacitance, hopping, and grain boundaries.

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independently. The parameter R is obtained from the frequency independent measured dc resistance, and the parameter C is obtained from the frequency dependent geometric capacitance calculated based on the thickness of the sample and the area of the metal contact. In order to obtain best fit values for the remaining five, the parameters were systematically stepped through a range of values. Figure 4.6 shows a sample program used in calculating best fit for the model parameter values. The exponent n, for example, was stepped through a range of values from 0.5 to 1 with an increment of 0.1. This range of values for n is reasonable and experimentally reported by researchers studying the ac conductivities of polycrystalline materials at room temperature. However, at higher temperatures, the exponent n can reach values lower than 0.5. The rest of the parameters were also stepped through a wide range of relevant values to produce a large number of combinations for the model parameters. In the case of the sample Matlab program shown in Figure 4.5, we considered over 3.5 million different combinations in order to come up with the best parameter values to produce the minimum percentage error. For each set of parameter values, a net difference between experimental and modeled IS results was calculated by determining the normalized cumulative percent error, E. This difference between experimental and modeled IS results can be defined in several ways. Equation 4.3 defines the error, E, as follow:

```
%contains measured resistance and reactance
load datafile.m:
f=datafile(:,1);
                  % first column contains frequency values
r=datafile(:,2);
                  %second column contains resistance data
                  %third column contains reactance data
x=datafile(:,3);
ze=sqrt(r^2+x^2); %total experimental impedance
                  %angular frequency
w=2*pi*f;
Rb=1e3:
                  %measured dc resistance
                  %calculated geometric capacitance
Cb=1e-12:
for a1=0.5:0.1:1.5; %to precisely find the grain capacitance value
for a2=0.5:0.1:1.5;%to precisely find the hopping coefficient value
                  %starting value for the grain capacitance
Cg=a1*1e-12;
B=a2*1e-12:
                  %starting value for hopping admittance coefficient
for n=0.5:0.1:1:
                  %exponent n steps through 6 values
for Rg=0:10:1000; %Rg steps through 1000 values
while Cg <= 1e-6; %the highest allowed value for grain capacitance
while B <= 1e-6; %the highest allowed value for hopping coefficient
v1=1/Rb;
v2=i*w*Cb:
y3=B*w^n;
y4=(i*w*Cg)/(1+i*w*Rg*Cg);
ym=y1+y2+y3+y4;%total modeled admittance
zm=1./vm:
                  %total modeled impedance
for l=1:1:m:
                  %m is the total number of points measured
error(l)=abs((zm(l)-ze(l))/zm(l));
end:
total_error=0;
for l=1:1:m:
total_error=total_error+error(I);
end:
percent_error=100*(total_error/m); %must be minimized
                  %B-while statement
end:
                  %Cq-while statement
end:
end:
                  %Rg-for loop
end:
                  %n-for loop
end:
                  %a2-for loop
                  %a1-for loop
end:
```

FIGURE 4.6: Sample Program To Produce Model Parameters With Minimum Percent Error

$$E = \frac{100}{N} \sum_{\omega} \left| \frac{Z_m - Z_e}{Z_m} \right|$$
(4.3)

where the summation is over the frequency range from dc to 1 GHz, with N representing the several hundred points between these limits. At each value of  $\omega_n$ ,  $Z_e$  is the magnitude of the experimental impedance, including both real and imaginary parts, and  $Z_m$  is the magnitude of the modeled impedance. This equation is used later in chapter 5 to calculate and minimize the error and choose the parameters for the IS circuit model. There are other ways to define the cumulative percent error. For example, one can calculate and minimize the difference between the real parts of experimental and modeled IS data. The same can also be applied to the imaginary parts of the complex impedances. However, our results showed that the set of parameters used is not sensitive to the method of calculating the error. More detailed examples will be discussed in chapter 5 when we describe the error calculation of specific sample results.

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# **CHAPTER 5**

# APPLICATION OF THE FOUR-PATH MODEL TO THIN- AND THICK-FILM DIAMOND AT ROOM TEMPERATURE

# **5.1 Introduction**

This chapter describes the application of the four-path circuit model to interpret the impedance spectroscopy results. It describes how the model fits to experimental results for a specific population sample of two thick-films and two thin-films. Although the model parameter numerical values are found to vary appreciably from one sample to another, the same basic model is successful in matching experimental results for all four samples, even though they differ considerably in their physical structure and growth conditions.

#### **5.2 Thin-Film Diamond**

# 5.2.1 Film Growth And Structural Properties

Thin films on silicon are used in this study to investigate the high frequency electrical properties of CVD diamond. In this section, two representative samples are considered in the analysis and modeling of the frequency dependent conductivity study of thin diamond films on silicon, namely SK-13 and SK-179. These films were grown by Dr. S. Khatami at Michigan State University. The films were prepared on <100> oriented, p-type silicon substrates with resistivities ranging from 1-10  $\Omega$ -cm by microwave plasma assisted CVD. Table 5.1 shows the deposition conditions for these undoped polycrystalline thin diamond films. Prior to conducting any electrical measurements, it was necessary to determine whether the films are in fact diamond, and to characterize the films qualities. Two different techniques were used to accomplish this task. The Raman spectroscopy technique was used to ascertain  $sp^3$  carbon bonding in the films. A 514.5 nm light source, argon ion laser [42] was used to determine Raman scattering from 1200 to 1600 wavenumbers and to determine the presence of diamond and any non-diamond carbon contents in the films. This helps in predicting any conduction that may be caused by the presence of graphitic regions in the polycrystalline material. The

Table 5.1: Deposition	<b>Conditions</b> for	or Thin	Diamond	Films

Sample	SK-13	SK-179
Flow Rate, sccm	400	400
%CH <sub>4</sub> /H <sub>2</sub>	1.75	1.5
T <sub>s</sub> , <sup>o</sup> C	1000	850
Deposition Time, hours	8	8
Pressure, Torr	70	41
Thickness, µm	5.97	3.68

films structural properties were investigated by the Scanning Electron Microscopy (SEM) technique. Microscopic pictures of the growth surface of the films were taken to define the film morphology including the dimensions of grains and the crystal orientation. The Raman spectra of the film samples, as shown in Figure 5.1, show the characteristic diamond peak at 1332 cm<sup>-1</sup> for both samples. However, the Raman spectrum for sample SK-13 shows a wide peak around 1580 cm<sup>-1</sup> which indicates the presence of graphite content in the sample. This resulted in a lower dc resistance compared to the other thin film sample as will be discussed a later section. Figures 5.2 show the surface morphologies of the two films grown at different temperatures, as indicated in Table 5.1. Both the SEM pictures and the Raman results were provided by S. Khatami.

# 5.2.2 Instrumentation Setup and Results for Thin-Film Diamond Samples

The samples were prepared for the electrical conductivity measurements by adding circular shape silver paint contacts on the top surface of the films, the diamond side, as well as on the bottom side, the silicon wafer side, as shown in the sample configuration of Figure 4.3(a). The HP4145B Semiconductor Parameter Analyzer was then used to conduct dc I-V measurements. Figure 5.4 shows a



FIGURE 5.1: Raman Spectra of Two Thin Diamond Films (a) SK-13, (b) SK-179

Measured with an argon laser at 514 nm.



FIGURE 5.2: Scanning Electron Microscopy Picture of The Thin Diamond Films (a) SK-13, (b) SK-179 [43]





FIGURE 5.3: Schematic diagram of the dc measurement setup using two Source/Monitor units, SMU1 and SMU2

schematic diagram of the dc measurement setup. Two Source/Monitor Units (SMUs) were used to accomplish this purpose. SMU1 was used as a variable voltage source, and SMU2 was used as a common current return path. The dc current-voltage relationship of both samples were found to be linear within the voltage range of interest. To conduct the ac measurements on the samples, two different impedance analyzers were used with two different sample contact setups. HP4192A and HP4291A impedance analyzers, described in chapter 3, were used to measure the real and the imaginary parts of the complex impedance of diamond films in the frequency domain to cover the frequency range from 5 to 1 MHz and from 1 MHz to 1 GHz, respectively. Figure 5.5 shows the low frequency measurement setup for the frequency range from 5 Hz to 1 MHz using the HP4192A instrument. The frequency was increased systematically from the 5 Hz low frequency limit of the instrument up to 1 MHz, while the values of the resistance and the reactance of the film under test were measured and stored in a floppy disk. Note that the probes used in this type of measurement were special high frequency coaxial probes. For the higher frequency range, the films were placed in the HP16191A high-frequency test fixture, which is connected to the HP4291A analyzer as shown in the schematic diagram of Figure 5.6. This instrument is able to cover the range of frequency from 1 MHz to 1 GHz. Both instruments operate so as to measure and plot both the resistance and the reactance



#### HP4192A LF Impedance Analyzer

FIGURE 5.4: Schematic diagram of the ac measurement setup

for the frequency range from 5 Hz to 1 MHz



FIGURE 5.5: Schematic diagram of the ac measurement setup for the frequency range from 1 MHz to 1 GHz

(modeled in parallel) versus frequency. The amplitude of the applied ac voltage signal was fixed for both analyzers at  $1 V_{rms}$ .

The current-voltage relationship of thin diamond samples are shown in Figure 5.6. The applied voltage was gradually changed from -2 to +2 volts with an increment of 0.02 volt. The dc measurements were taken at room temperature, and show essentially ohmic behavior for both films. The value of the resistance of the films was calculated from the slope of a first-order best-fit polynomial. The ac measurements of the real and the imaginary parts of the complex impedance of the samples were stored in floppy disk and imported into a mathematical software, Matlab, then plotted and compared to the four path electrical model over the complete frequency range from dc to 1 GHz.

Consider the thin film sample SK-13 which has a resistance, R, of 2.4 K $\Omega$  as obtained from the dc current-voltage characteristics shown in Figure 5.7(a) and a capacitance, C, calculated from the area and thickness to be 73 pF. Figure 5.8 shows that the experimental IS results differ considerably from those predicted by a simple R-C parallel combination. Consequently, it was necessary to add to the impedance model in order to represent frequency dependent phenomena in diamond.

This research study assumes that the total ac conduction in diamond consists of three types, namely band, hopping, and conduction through the grain



FIGURE 5.6: The Current-Voltage Characteristics of Thin-Film Samples. (a) SK-13, (b) SK-179



FIGURE 5.7: Comparison Between Measured [o] and Model [+] IS Results Based on The Measured dc Resistance and The Geometric Capacitance for SK-13.

boundaries. The experimental results were compared with a circuit model which includes, in addition to the basic RC circuit, two parallel paths of conduction. One represents hopping and the other represents conduction through grain boundaries, as described in more details earlier in chapter 4. Our investigations, however, illustrated the necessity to add to the chapter 4 model a series contact resistance,  $R_c$ . This may be expected since all metal-semiconductor contacts have a finite, non-zero, contact resistance. Later in this chapter, the importance of this contact resistance component in the circuit model will be discussed in more details.

Although the two thin-film diamond samples have different Raman qualities and different surface morphologies, our suggested model was adequate in best fitting the experimental IS results of both samples by minimizing the cumulative percent error, as described in chapter 4, and assigning relevant values to circuit model components. Table 5.2 shows the chosen model parameter values for each of those samples. Figure 5.8 and 5.9 show a comparison of model results with measured results for the thin film samples, SK-13 and SK-179, respectively.

Earlier in chapter 4 the issue of error calculation methods was discussed, and it was stated that the set of model parameters is not sensitive to the method of calculating the error. Take for example the thin diamond sample SK-13. We ran three simulation programs were run to obtain the best fit model parameters using three different methods to minimize the cumulative percent error. The first is by

Parameter	SK-13	SK-179
R (Ω)	$2.4 \times 10^3$	3.02x10 <sup>4</sup>
C (pF)	73	103
$R_{g}(\Omega)$	9	65
C <sub>g</sub> (pF)	100	24
B (Ω <sup>-1</sup> )	1.1 x 10 <sup>-9</sup>	2.2x10 <sup>-9</sup>
n	0.9	0.8
R <sub>c</sub> (Ω)	0.7	1.9

**Table 5.2: Best-Fit Model Parameters For Thin Diamond Films** 



Figure 5.8: Comparison of Model [0] and Measured [+] IS Results

For Thin-Film Sample, SK-13.



Figure 5.9: Comparison of Model [0] and Measured [+] IS Results

For a Thin-Film Sample, SK-179.

minimizing the difference between the real parts of the complex impedance, E\_real, the second is by minimizing the difference between the imaginary parts only, E\_imag, and the third is calculating the error as described in equation 4.3. Table 5.3 shows the resultant model components from each of the above methods.

## **5.3 Results of Thick-Film Diamond Samples**

The thick diamond films used in this study, synthesized by the arc-jet method, were provided by a commercial supplier and were free-standing, thick films ranging between 200 to 400  $\mu$ m in thickness. Since we do not have any information about the growth conditions of the films, the films were categorized by colors ranging from white to dark grey. However, due to some instrument limitations, as described in chapter 3, we were not able to obtain any impedance measurements on the white type of films.

In this section, the results of two representative samples, TDF-12 and TDF-18, will be presented to show the dc and the high frequency ac behaviors of this type of sample. Both samples were categorized as dark grey. The sample TDF-12 is 198  $\mu$ m in thickness, and ohmic contact is obtained by evaporating a layer of gold on the back side of the sample, which was the nucleation (smoother) side, and by adding a circular-shape silver paint contact on the top side, the growth side. However, for sample TDF-18, it was necessary to sputter gold on the top surface of

Table 5.3: Model Parameters	s For Sample	e SK-13 Using	g Different
-----------------------------	--------------	---------------	-------------

	E_real	E_imag	Е
B (Ω <sup>-1</sup> )	1x10 <sup>-9</sup>	1x10 <sup>-9</sup>	1.1x10 <sup>-9</sup>
n	0.9	0.9	0.9
$R_{g}(\Omega)$	8	10	9
C <sub>g</sub> (F)	1.2x10 <sup>-10</sup>	1x10 <sup>-10</sup>	1x10 <sup>-10</sup>
$R_{c}(\Omega)$	0.6	2	0.7
%Error	0.54	3.1	1.1

,

# **Error Calculation Methods**

the sample to achieve that. The dc and ac measurement setups were similar to those of thin-film diamonds. Figure 5.10 shows a linear current-voltage relationship for both samples. As shown in Figure 5.11, the Raman spectra on both samples shows a diamond peak at 1332 cm<sup>-1</sup> and shows no signs of any graphite layers associated with the films. Figure 5.12 shows the surface morphologies of the free-standing thick diamond films. Although the Raman qualities and the surface morphologies of both films look very similar, the resistivity of the films were considerably different. Table 5.4 lists the best-fit model parameter values which gives the minimum cumulative percent error as calculated from equation 4.3. Figures 5.13 and 5.14 show the comparison between the measured and the calculated results of the impedance spectroscopy.

## **5.4 Results Analyses**

It is of interest to consider the relative role of the various model components in fitting modeled IS results with experimental results. Considering the sample SK-13, when only the dc resistance, R, and the geometric capacitance, C, are included in the model, as is the case for Figure 5.7, the E value is 62%. By adding only a hopping path the best fit E value is 9.7% as obtained with hopping prefactor B = 1.4x 10<sup>-9</sup>  $\Omega^{-1}$  and frequency power n = 0.9. By adding only a grain-barrier conduction



Figure 5.10: Current-Voltage Relationship of Two Thick Diamond Films

(a) TDF-12, (b) TDF-18



Figure 5.11: Raman Spectra of Two Thick Diamond Films

(a) TDF-12, (b) TDF-18



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Figure 5.12: Scanning Electron Microscopy of Thick Diamond Films

(a) TDF-12, (b) TDF-18

Parameter	TDF-12	TDF-18
R (Ω)	149	822
C (pF)	8.8	3.3
$R_{g}(\Omega)$	35	320
C <sub>g</sub> (pF)	900	11
B (Ω <sup>-1</sup> )	1.1 x 10 <sup>-6</sup>	3.8 x 10 <sup>-12</sup>
n	0.5	0.9
$R_{c}(\Omega)$	0.4	2.0

**Table 5.4: Best-Fit Model Parameters For Thick Diamond Films** 



Figure 5.13: Comparison of Modeled [0] and Measured [+] IS Results

For Thick Diamond Sample, TDF-12



Figure 5.14: Comparison of Model [0] and Measured [+] IS Results

For Thick Diamond Sample, TDF-18
path the best fit E value is 12.3% as obtained with  $R_g = 2 \Omega$  and  $C_g = 180$  pF. By adding both the hopping and grain-barrier conduction paths, the best fit E value is 7.1% as obtained with model values of n = 0.9,  $B = 1.1 \times 10^{-9} \Omega^{-1}$ ,  $R_g = 9 \Omega$ , and  $C_g$ = 100 pF. Finally, using the entire model adding a best fit  $R_c$  value of 0.7  $\Omega$ , the E value is reduced to 1.1%.

Now, consider one specific component of the circuit model, the contact resistance,  $R_c$ . Note that although  $R_c$  is quite small it plays an important role at high frequencies, above approximately 500 MHz, as shown in Figure 5.15. The importance of  $R_c$  comes from the fact that at high frequencies the real part of the equivalent impedance of the circuit model will be dominated by the value of the contact resistance, as shown in the series of Equations 5.1 through 5.5. If we substitute the values of the model circuit components for the diamond sample SK-13, as given in Table 5.4, at the high frequency limit of 1 GHz, we conclude that the real part of the total equivalent impedance converges to the value of the contact resistance,  $R_c$ . At 1 GHz, the total equivalent value of the real part of the impedance equals to 0.8  $\Omega$ , which is dominated by the  $R_c$  value of 0.7  $\Omega$ 

$$Real(Z_T) = \frac{T_1 + T_2}{T_3 + T_4} + R_c$$
(5.1)

where,



Figure 5.15: The Effect of Model Parameter,  $R_c$ , on IS Results

(a) Without Adding  $R_c$  to The Model, (b) With  $R_c$ 

$$T_1 = B\omega^n R^2 - \omega^2 R^2 C R_g C_g$$
(5.2)

$$T_2 = \omega^2 R R_g C_g (R_g C_g + R C + R C_g + R_g C_g B \omega^n)$$
(5.3)

$$T_3 = \left(B\,\omega^n R - \omega^2 R C R_g C_g\right)^2 \tag{5.4}$$

$$T_4 = \omega^2 (R_g C_g + RC + RC_g + R_g C_g RB \omega^n)^2$$
(5.5)

Similar results were obtained for the other samples. Table 5.5 shows the best E values obtained by considering five different models: (1) the basic R-C model, (2) R-C with the addition of hopping only, (3) R-C with the addition of a grain-barrier path only, (4) R-C with the addition of both a hopping path and a grain-boundary path, and (5) with the full model.

#### **5.5 Relative Role Of The Model Components**

A strong frequency dependence of electronic conduction in polycrystalline diamond was observed for both sample types. Such a result can be indicative of hopping via localized sates or of current transport across potential barriers associated with grain boundaries. When dc conduction involves paths through potential barriers at grain boundaries, non-linear characteristics result. However,

Model	TDF-12	TDF-18	SK-13	SK-179
R and C only	70.6%	32.0%	61.5%	15.5%
With only hopping added	16.6%	11.1%	9.7%	8.6%
With only grain- barriers (G.B) added	18.4%	3.6%	12.3%	4.8%
With hop- ping and G.B. added.	6.6%	2.8%	7.1%	4.6%
With full model	6.3%	2.8%	1.1%	2.7%

.

Table 5.5: Normalized Cumulative Percent Error, E.

the samples in this study were limited to those with essentially linear dc I-V characteristics. Consequently, electrode to electrode paths exist which do not involve transport across significant potential barriers. Such paths can have a substantial number of defect states as evidenced for example by Poole-Frenkel emission at high electric fields [16] and it may be expected that such states would contribute to frequency dependent conduction [3][4]. However this does not preclude the role of carrier flow across interfaces at higher frequencies where the potential barriers are shorted by capacitive currents. The results indicate that both transport across grain barriers and hopping contribute to the impedance spectroscopy results for these samples. The inclusion of both types of frequency dependent conduction paths in the IS model give better agreement with experiment than either one alone.

It is instructive to consider the relative roles of the various contributors. On the thin film samples, the admittance due to the hopping path was an order of magnitude or more higher than the admittance due to the grain-boundary path over the entire frequency range. This was not the case, however, for the thick-film samples. Figure 5.16 shows the relative contribution of the parallel conduction paths for thick-film sample TDF-12. From approximately 1 MHz to 100 MHz, the frequency dependent admittance due to the grain-boundary path was larger than that due to hopping. Above 100 MHz, the hopping path dominated the frequency dependent admittance.

It has been suggested [3][4], that the localized states that contribute to hopping are associated with grain-boundaries. This would be consistent with the dominant role of hopping in the thin-film samples since for the finer grain, thin-film samples, grain-boundaries make up a larger fraction of the total sample volume. If the hopping states are principally associated with the grain boundaries, then it may be stated that the frequency dependent current-voltage characteristics for polycrystalline diamond, beyond those expected as a result of the sample's geometric capacitance, are principally associated with grain-boundaries, either due to hopping conduction within the boundaries or due to capacitive effects associated with grain-boundary potential barriers.

Thus far, all measurements were conducted at room temperature (T=300 <sup>o</sup>K.) One may question whether the proposed circuit model, used successfully to fit the experimental IS results of both thin and thick diamond film samples at room temperature, is valid at higher temperatures. It is also of interest to further investigate the relationship between the structural properties of the films and the model results. Chapter 6 addresses these relationships and tries to find answers to other temperature related questions by studying the correlation of model results with sample morphology and Raman quality, and by testing the validity of the circuit model at higher temperatures.



Figure 5.16: Individual Model Contributions to The Admittance

For Thick Diamond Sample, TDF-12

#### **5.6 Sensitivity of Model to Changes in Parameter Values**

This section investigates the effect of changing a parameter value on the simulated results of the model. This is done by fixing one parameter value, obtained as an output result for a similar sample, and running the simulation model to determine the other values. Tables 5.6 and 5.7 show the results obtained after fixing the values of n, Rg, and Cg, for two samples, namely SK-13 and TDF-18. The values at which the parameters are fixed at for sample SK-13 are obtained from the output results of the thin film sample SK-179, as listed in Table 5.2. Similarly, the fixed values used for testing TDF-18 are acquired from the results of the other thick film sample, TDF-12. The first row in both tables shows the original values obtained by the model for each sample, as described earlier. The next three rows display the model's output values, including the percentage error, when each of the three parameters is fixed separately. Note that the values of R and C for each sample are fixed for all runs.

From Table 5.6, it is observed that forcing even a slight change in n, from 0.9 to 0.8, causes the error value for the thin film sample to more than double. This is consistent with our previous observation of the dominant role of hopping in thin film samples. It also suggests that the variations in n values among the thin film samples are significant. In Table 5.7 however, a large force change in n, from 0.9 to 0.5, does not cause much change in the error value. This is consistent with our

Fixed Parameter	B (Ω <sup>-1</sup> )	n	$\mathbf{R}_{\mathbf{g}}$ ( $\Omega$ )	C <sub>g</sub> (pF)	$\mathbf{R}_{\mathbf{c}}\left(\Omega\right)$	%Error
none (original run)	1.1x10 <sup>-9</sup>	0.9	9	100	0.7	1.1
n	4x10 <sup>-9</sup>	0.8	2	160	1.2	2.7
R <sub>g</sub>	1.2x10 <sup>-9</sup>	0.9	65	70	0.1	6.4
C <sub>g</sub>	1x10 <sup>-8</sup>	0.8	30	24	0.4	13.7

 Table 5.6: Sensitivity Results for Thin Film SK-13

 Table 5.7: Sensitivity Results for Thick Film TDF-18

Fixed Parameter	<b>Β</b> (Ω <sup>-1</sup> )	n	R <sub>g</sub>	Cg	R <sub>c</sub>	%Error
none (original run)	38x10 <sup>-13</sup>	0.9	320	11	2	2.8
n	15x10 <sup>-9</sup>	0.5	338	10	0.1	3.1
R <sub>g</sub>	17x10 <sup>-9</sup>	0.6	35	0.9	30	8.3
C <sub>g</sub>	1.3x10 <sup>-9</sup>	0.7	888	900	0.1	17.4

previous observation that hopping is not dominant in thick film samples. These results suggest that the model variation of n in the thick film samples may not be significant. Interestingly, force variation in  $R_g$  and  $C_g$  produce significantly larger error in both thin film and thick film samples.

## **CHAPTER 6**

# EFFECTS OF GROWTH CONDITIONS AND FILM ATTRIBUTES ON AC ELECTRICAL CONDUCTION IN CVD DIAMOND FILMS

#### **6.1 Introduction**

In this chapter, our effort is focused on correlating the dc and ac electrical properties, especially conductivity, of a wide selection of polycrystalline diamond films to four other key film properties, namely (1) the Raman diamond to graphite signal ratio ( $I_d/I_g$ ), (2) the Full-Width-at-Half-Maximum of the diamond Raman signal, (3) the crystalline morphology as quantified by the growth parameter,  $\alpha$ , and (4) the average grain size. The electrical properties are also correlated to two deposition parameters, namely substrate temperature and gas flow rate. The effect of test-temperature on as-grown and annealed films' electrical behavior is also carefully considered.

#### **6.2 Sample Description And Experimental Procedure**

Three sets of thin CVD films, grown on silicon wafers, are considered for this study. Each set includes three films grown at the same hydrogen flow rate and three different substrate temperatures of 850, 900, and 1000 °C. The samples are chosen to have the same percent methane concentration, %CH<sub>4</sub>/H<sub>2</sub>, of 1.5%. Figures 6.1 through 6.5, and Figures 6.6 through 6.9 display the SEM and Raman spectra for all samples, respectively. The samples, the Raman data, and all the SEM pictures were provided by Dr. S. Khatami, a former Ph.D. student of Dr. J. Asmussen, at Michigan State University. Table 6.1 shows the deposition parameters and some other key properties of the samples. Included in Table 6.1 are the average grain size, determined by the method of linear intercepts, the full width at half maximum (FWHM) of the diamond Raman peak, and the diamond to graphite peak ratio,  $I_d/I_g$ . The latter is calculated from the peak at 1332 (diamond) divided by the peak at 1580 (graphite.) Figure 6.6(a) shows the method of obtaining this value. Even though this method of calculation does not yield the actual ratio of  $sp^3$  to  $sp^2$  bonds, it gives a simple and consistent measure of the graphite content in the samples. The growth parameter  $\alpha$  is defined as  $\sqrt{3}\frac{V_{100}}{V_{111}}$ , where  $V_{100}$  and  $V_{111}$ are the growth rates in the <100> and <111> directions, respectively [89][90][91].

The  $\alpha$  values ranges between 1 for a cube and 3 for an octahedron.



(b)



FIGURE 6.1: Top Surface SEM Pictures of (a) SK-182 (b) SK-183 [43] [See Table 6.1 for growth conditions and film attributes]





FIGURE 6.2: Top Surface SEM Pictures of (a) SK-12 (b) SK-179 [43] [See Table 6.1 for growth conditions and film attributes]









FIGURE 6.3: Top Surface SEM Pictures of (a) SK-62 (b) SK-72 [43] [See Table 6.1 for growth conditions and film attributes]





FIGURE 6.4: Top Surface SEM Pictures of (a) SK-209, and (b) SK-177 [See Table 6.1 for growth conditions and film attributes]



FIGURE 6.5: Top Surface SEM Pictures of Sample TKB [See Table 6.1 for growth conditions and film attributes]



FIGURE 6.6: Raman Spectra of (a) SK-12 (b) SK-179



FIGURE 6.7: Raman Spectra of (a) SK-62 (b) SK-72

x 10⁴ Raman spectrum of SK209r sample 1.4 1.3 1.2 Counts per second 1.1 1 0.9 0.8 0.7∟ 1200 0 1400 1450 1 Shift Wavenumber 1/cm 1300 1350 1500 1550 1600 1650 1250 **(a)** 1.6 × 10<sup>4</sup> Raman spectrum for SK177 sample 1.5 1.4 Counts per second 1.2 1.1 1200 1350 1400 1450 Shift Wavenumber 1/cm 1300 1500 1550 1250 1600 **(b)** 

FIGURE 6.8: Raman Spectra of (a) SK-209 (b) SK-177



FIGURE 6.9: Raman Spectra of (a) SK-183 (b) TKB

Sample	%CH4/H2	Flow Rate, sccm	T₅, ⁰C	α	FWHM	I <sub>d</sub> /I <sub>g</sub>	Grain Size, μm
SK-62	1.5	60	850	1	9.09	1.3	1.14
SK-72	1.5	60	900	3	9.67	1.3	1.1
SK-182	1.5	60	1000	mixed			2.4
SK-177	1.5	200	850	1	7.05	1.3	1.5
SK-183	1.5	200	900	3	10.5	1.3	1.23
SK-209	1.5	200	1000	3	7.05	1.5	1.98
SK-179	1.5	400	850	3	12.04	1.2	0.65
ТКВ	1.5	400	900	3	12.9	1.4	0.42
SK-12	1.5	400	1000	3	11.2	1.9	1.1

 Table 6.1: CVD Thin Diamond Films' Key Properties

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All films were prepared for measurement in a similar way as described earlier in chapter 5. Two types of metals are used to form the top surface contacts, sputtered gold and silver paint. The back side of the sample, the silicon wafer side, is placed on a gold-plated metal piece. Both dc and ac measurements are conducted in the direction perpendicular to the surface of the film. Table 6.2 lists the metal contact type and behavior as related to the dc resistivities of the films.

The ac complex impedance was measured from dc to 100 MHz over a broad temperature range. The ac measurement setup is slightly different from the one described in chapter 5 due to equipment limitations, namely that the HP 16191A high frequency test fixture was not designed to operate at temperatures higher than room temperature. As a result, the high frequency coaxial probes were used to conduct the ac measurements.

# 6.3 Relationship of As-Grown Electrical Properties to Film Attributes and Deposition Parameters

This section discusses the correlations investigated in this study, which are depicted in Figure 6.10. The information about the samples' deposition parameters and other key properties are listed in Tables 6.1 and 6.2. There are two objectives in this investigation. The first discusses the correlation between the films' dc electrical resistivity,  $\sigma_{dc}$ , and the deposition parameters, namely the substrate temperature,

Sample	Metal Type	Contact behavior	Thickness, µm	Resistivity, Ω–cm
SK-12	Gold	ohmic	5.28	8.1x10 <sup>7</sup>
SK-209	Gold	ohmic	4.68	1.8x10 <sup>8</sup>
SK-177	Gold	ohmic	3.77	1.3x10 <sup>6</sup>
SK-62	Gold	ohmic	3.15	1.8x10 <sup>9</sup>
SK-72	Gold	ohmic	3.82	2.5x10 <sup>9</sup>
SK-179	Gold	ohmic	3.68	6.4x10 <sup>6</sup>
SK-182	Silver	ohmic	4.202	7x10 <sup>8</sup>
SK-183	Silver	ohmic	4.42	1.5x10 <sup>8</sup>
ТКВ	Silver	ohmic	4.196	1.8x10 <sup>6</sup>

Table 6.2: Samples' Contact Properties and as-grown dc Resistivities



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Figure 6.10: Schematic Diagram Showing The Investigated Correlations

 $T_s$ , and the hydrogen flow rate, and the selected film attributes. The second part of the investigation of as-grown films at room temperature deals with the correlation between the ac electrical conductivity,  $\sigma_{ac}$ , specifically hopping,  $\sigma_{hop}$ , and grainboundary,  $\sigma_{GB}$ , conductivities, and the films' deposition parameters and growth output properties.

Regarding  $\sigma_{dc}$ , Figure 6.11 displays a map with the substrate temperature and the hydrogen flow rate as inputs, and the measured resistivity and the morphology measure,  $\alpha$ , of all samples as outputs. Figures 6.12 through 6.14 display the as-grown dc resistivity versus the individual CVD film properties listed in Table 6.1. Looking at these Figures, it appears that the clearest relationship that can be concluded is that the as-grown dc resistivity of diamond films decreases as the hydrogen flow rate increases. The decrease in resistivity at higher flow rates may be attributed to the incorporation of more hydrogen atoms in the film during the CVD growth process [61][69][87][92][93]. Landstrass et al. [92][93] believe that the presence of atomic hydrogen in diamond films results in the passivation of electrically active interband defect states which leads to lower film's resistivity. As for the relationship between the as-grown dc resistivity and other properties, there may be suggestion of an increase in resistivity with increasing grain size and decreasing FWHM. However, the single most dominant parameter appears to be flow rate.



## Substrate Temperature,<sup>o</sup> C

equivalent to (100) morphology, i.e.  $\alpha = 1$ equivalent to (111) morphology, i.e.  $\alpha = 3$ Resistivity, shown numerically, is measured in  $\Omega$ -cm



parameter, shown by symbol, and growth input parameters



Figure 6.12: Relationship between films' as-grown dc resistivity and (a) Flow rate, in sccm, and (b) Substrate temperature,  $T_s$ , in <sup>o</sup>K.



Figure 6.13: Relationship between films' as-grown dc resistivity and (a) Growth parameter,  $\alpha$ , and (b) Full Width at Half Maximum, FWHM.



Figure 6.14: Relationship between films' as-grown dc resistivity and (a)  $I_d/I_g$  ratio, and (b)

Grain size, µm

To study  $\sigma_{ac}$ , six Matlab simulation programs, similar to the one showed in Figure 4.6, were run to obtain the best fit parameter values, with minimum percent error. Table 6.3 shows a list of the IS simulation results at room temperature. Sample SK-182 is omitted because its Raman data is not available and it has a mixed morphology ( $\alpha$ =1 and  $\alpha$ =3) which makes it harder to fully compare its results with any of the other samples.

First, consider the hopping conduction path. Two correlations were observed in the investigation of thin films with similar morphology,  $\alpha$ . The first relates the ac hopping conductivity,  $\sigma_{hop} = B\omega^n$ , to the  $I_d/I_g$  ratios, and the second relates it to the grain size of the films. Plotting  $\sigma_{hop}$  versus the other parameters showed no conspicuous correlations. Figure 6.15 shows how hopping, at high frequencies, increases as  $I_d/I_g$  decreases. The data points were calculated at 100 MHz frequency for each of thin film sample using the  $B\omega^n$  relation and the numbers listed in Table 6.3. Moreover, Figure 6.16 indicates that the  $\sigma_{hop}$  is also inversely proportional to the film's grain size. However, the crystal size and the  $I_d/I_g$  ratio of the films are not clearly related. The first observation may suggest that hopping is mainly caused by conduction along the graphitic region between diamond grains and the surface of the films. This coincides with the conclusions of Sugino et al. [3][22]. The second observation indicates that the smaller the film's grain size, the higher the role of hopping admittance. This is again consistent with the fact that the finer grain films,

Sample	<b>R</b> (Ω)	C (pF)	<b>Β</b> (Ω <sup>-1</sup> )	n	<b>R</b> <sub>g</sub> (Ω)	C <sub>g</sub> (F)
ТКВ	9.5x10 <sup>3</sup>	92	1x10 <sup>-8</sup>	0.7	87	40x10 <sup>-12</sup>
SK-179	3.02x10 <sup>4</sup>	103	2.2x10 <sup>-9</sup>	0.8	65	24x10 <sup>-12</sup>
SK-12	3.38x10 <sup>5</sup>	116	6x10 <sup>-8</sup>	0.5	4800	13x10 <sup>-10</sup>
SK-72	3x10 <sup>7</sup>	41	5x10 <sup>-9</sup>	0.7	389	17x10 <sup>-12</sup>
SK-62	1.85x10 <sup>7</sup>	47.3	9x10 <sup>-9</sup>	0.7	171	9x10 <sup>-11</sup>
SK-183	1.61x10 <sup>6</sup>	45.7	55x10 <sup>-11</sup>	0.8	540	31x10 <sup>-12</sup>
SK-177	1.6x10 <sup>4</sup>	39.6	1x10 <sup>-12</sup>	0.5	39330	1x10 <sup>-9</sup>
SK-209	4.23x10 <sup>5</sup>	138.2	1.7x10 <sup>-9</sup>	0.7	10145	26x10 <sup>-11</sup>

 Table 6.3: IS Model Parameters for as-grown Films at Room Temperature





Figure 6.16: The Relationship Between ac Hopping Conduction And Grain Size

grain boundaries make up a larger fraction of the total sample volume. This was previously noted in chapter 5, comparing large grain free-standing films with MWPCVD films. It is informative to note that for one of the film samples, SK-177 with morphology growth parameter  $\alpha = 1$ , it was observed that the film exhibited a low hopping conduction relative to other {111} films at all frequencies. This could be related to the alignment of the grains at the grain boundary. The other  $\alpha = 1$  film in this study does not have low hopping, however it has a smaller grain size.

Now, consider the other ac conduction path, namely the cross-grain boundary path, and its correlation with film properties and deposition parameters. Figure 6.17 displays the relationship between the conductivity of the cross-grainboundary path and the film's grain size. It can be stated that the higher the film's grain size, the lower the admittance of the cross-grain boundary path. A comparison of the data indicates that at 100 MHz this is mainly due the fact that larger grain size have larger  $R_g$  values. With regard to correlations with other film's attributes, such as the  $I_d/I_g$  and the growth parameter  $\alpha$ , and the deposition parameters, such as  $T_s$  and the flow rate, again no confirmative conclusions were derived.



Figure 6.17: The Relationship Between Grain Boundary Conduction and Grain Size
## 6.4 Annealing and Temperature Effects on Electrical Conductivity and ac Circuit Model Parameters

It is important to study the electrical conductivity of semiconducting materials at various temperatures in order to add to the understanding, and to better characterize the electrical behavior of different conduction mechanisms. This section discusses the annealing and temperature effects on the electrical conductivity and the ac circuit model parameters for four selected samples. Two of those samples, namely SK-62 and SK-72, are grown at the same flow rate of 60 sccm but at substrate temperatures of 850 °C and 900 °C, respectively. The other two samples, namely SK-209 and SK-12, are grown at the same substrate temperature of 1000 °C but at flow rates of 200 sccm and 400 sccm, respectively. When the samples, in the as-grown state, were tested at elevated temperatures, they showed time-varying behavior. Figure 6.18 shows the resistivity behavior in the case of sample SK-72. In fact, this behavior was caused by annealing carried by the measurement temperature. Sugino et al. showed that temperatures as low as 300 °C were sufficient to anneal their films and to cause a sharp increase in resistivity. As a result, our samples were annealed in a hydrogen furnace at 400 °C for one hour in order to stabilize the film's behavior at elevated temperatures. After annealing the samples showed a sharp increase in dc resistivity. The literature suggests that the



Figure 6.18: dc I-V Behavior of SK-72 in the as-grown state versus temperature, showing

annealing effect at higher measurement temperatures.

increase in dc resistivity after annealing could be due to the removal of hydrogen atoms from the films. Figure 6.19 shows the dc I-V characteristics before and after annealing, and Table 6.4 lists the calculated resistivity for all four samples. It is worth noting that two of the samples, namely SK-12 and SK-209, have lost the linear behavior of their contacts after annealing. This, in turn, may have a substantial effect on the ac measurements, especially at high frequencies, if a significant voltage drop develops across the contact [86][88]. It is the higher flow rate films that become non-ohmic. After annealing, all the films showed stable behavior at elevated temperatures, and the measured dc resistance showed a decrease as temperature increases.

To study the effect of annealing on the ac circuit model, consider the two thin film samples, SK-62 and SK-72, which have {100} and {111} morphologies, respectively, and which maintained ohmic characteristics after annealing. Figure 6.20, first, shows the after annealing temperature dependent behavior of the dc resistance for both thin film samples, SK-62 and SK-72. The activation energies illustrated in the lines shown in the plots of Figure 6.20 are calculated and found to be approximately equal to 0.5 eV for the {100} film and 0.7 eV for the {111} film. There is not a big difference between the activation energies of the two samples considering the uncertainty of the experimental measurements. A plot of the log of conductivity versus  $T^{1/4}$  to check for the characteristic temperature dependence of



Figure 6.19: I-V characteristics (a) Before Annealing, and (b) After Annealing

Sample	Resistivity Before Annealing, Ω-cm	Resistivity After Annealing, Ω-cm		
SK-12	8.1x10 <sup>7</sup>	9.8x10 <sup>9</sup>		
SK-209	1.8x10 <sup>8</sup>	1.8x10 <sup>10</sup>		
SK-62	1.8x10 <sup>9</sup>	2.1x10 <sup>12</sup>		
SK-72	2.5x10 <sup>9</sup>	1.2x10 <sup>12</sup>		

Table 6.4: Resistivity of Selected Films Before and After Annealing



Figure 6.20: dc Resistance as a function of temperature for (a) sample SK-62, and (b) sample

hopping would require more data points and less experimental uncertainty. In comparison with other researchers' results, Sugino et al. [68] have observed three trap levels with activation energies of 0.62, 1.38, and 0.95 eV for their annealed samples, while only one trap with activation energy of 0.95 was observed after a hydrogenation treatment of the samples. Sugino's observation, again, supports the theory of Landstrass et al. [93] in which they stated that the incorporation of atomic hydrogen in CVD films results in the passivation of electrically active traps leading to the enhancement of the films' conductivity. Figure 6.21 demonstrates how the conductance for both CVD thin films changes after annealing, and at different temperatures from 300 to 550 °K. Similar results have been reported in the literature, and there has been disagreement among researchers on the main cause of this behavior [2][4][78]. Sugino et al. [3][77] have observed that the frequency dependent conductance of annealed films are less frequency dependent at higher temperatures. They concluded that thermally activated band conduction dominates in the conduction process in the low frequency region. On the other hand, Fiegl et al. [78] have disagreed and reported that conductivity in polycrystalline diamond films can be completely understood in terms of hopping conductivity within grain boundaries. As for the results shown in Figure 6.21, the following ac observations can be deduced. First, and in support of the dc measurements, there was considerable decrease in conductivity at low frequency between the as-grown and



Figure 6.21: ac Conductance for samples in the as-grown, annealed, and annealed and tested at higher temperatures, (a) SK-62, and (b) SK-72

-.-. As-grown and tested at 300 °K

- C O Annealed and tested at 425 °K
- $\triangle$  Annealed and tested at 300 °K
- \* Annealed and tested at 350 °K
- ♦ Annealed and tested at 550 °K

annealed samples. Second, at higher frequencies, the samples seem to be only weakly dependent on temperature. This may indicate, as reported by Ermakova et al. [1][4], that polycrystalline diamond films are thermally stable at high frequencies, that is, at high frequencies the conductivity of the films does not vary as much with changing temperature. The third observation is related to fitting the data to the four path ac circuit model, described earlier in chapter 4. Again, the IS experimental results are compared with the four path ac circuit model, and the model best-fit parameter values are obtained. The individual contribution of each path in the model is looked at separately. Table 6.5 lists the parameter values for two CVD thin film samples, SK-62 and SK-72, in the as-grown, annealed, and annealed and tested at 550  $^{\circ}$ K states.

According to the listed data in Table 6.5, the exponent n tends to have higher values for the annealed films than for the as-grown ones. This may support similar observations reported by other researchers [2][3][7][22][68][77]. However, and in disagreement with the work of Muto et al. [2], it is also observed that the exponent n is a temperature dependent variable decreasing with increasing temperature. Although Table 6.5 shows a value of 0.1 for the exponent n in the case of sample SK-62 when tested at 550  $^{\circ}$ K, it is believed that this is a result of the parameter best-fit method used in simulation, and does not have any physical significance. Figure 6.21 (a) shows that the conductance is almost independent of frequency in

	SK-62			SK-72		
Parameter	As-grown	Annealed	Annealed and tested at 550 °K	As-grown	Annealed	Annealed and tested at 550 °K
R (Ω)	1.85x10 <sup>7</sup>	2.2x10 <sup>10</sup>	5.5x10 <sup>5</sup>	3x10 <sup>7</sup>	1.4x10 <sup>10</sup>	2x10 <sup>6</sup>
B (Ω <sup>-1</sup> )	9x10 <sup>-9</sup>	9x10 <sup>-13</sup>	1x10 <sup>-5</sup>	5x10 <sup>-9</sup>	1.3x10 <sup>-12</sup>	1.4x10 <sup>-10</sup>
n	0.7	0.9	0.1	0.7	1	0.8
$R_{g}(\Omega)$	171	66	609	389	28	473
C <sub>g</sub> (F)	9x10 <sup>-11</sup>	1x10 <sup>-11</sup>	9x10 <sup>-12</sup>	1.7x10 <sup>-11</sup>	6x10 <sup>-12</sup>	7x10 <sup>-12</sup>
% Error	13.1	16.5	12.8	14.4	7.9	11.4

 Table 6.5: Best-fit Parameter Values For Two Thin Film CVD Samples

the low frequency region, and is very close in value to the dc measured conductance. Table 6.5 also reveals that the values of  $R_g$  after annealing, for both type of samples, are decreased. This may suggest that the incorporation of hydrogen in the films affects the grain boundaries not the crystallites themselves, that is, the diamond crystals in polycrystalline diamond films may not contain any hydrogen even in the as-grown state. In this study, these results are demonstrated in two samples, namely SK-62 and SK-72.

To study and analyze the individual contribution of hopping and cross-grainboundary paths to the total conduction in thin diamond films, consider Figures 6.22 and 6.23. Part (a) of each figure shows the ratio of the hopping path's admittance to the total admittance, and part (b) shows the ratio of the cross-grain-boundary path's admittance to the total admittance for the as-grown samples SK-62 and SK-72, respectively, and according to the data listed in Table 6.5. The Figures clearly show that hopping conduction is dominating in the low frequency region while crossgrain-boundary conduction is not as significant. As we move to higher frequencies, higher than  $10^5$  Hz, conduction across the grain boundaries' potential barriers becomes more active, and contribute over 20% of the total admittance for sample SK-72, and close to 60% for the case of sample SK-62, in certain frequency regions. The hopping admittance to the total admittance ratio shows a sharp decrease for frequencies higher than  $10^5$  Hz, however, still plays a considerable



Figure 6.22: Individual path contribution to the total admittace for the as-grown sample SK-62



Figure 6.23: Individual path contribution to the total admittace for the as-grown sample SK-72

role in the total conduction of the as-grown film. These conclusions are demonstrated with both samples with disregard to the films' morphologies.

Now, consider the case where the samples are tested at elevated temperatures higher than room temperature. This case is established in this study by testing the two annealed samples, SK-62 and SK-72, at 550 °K temperature. Figure 6.24 shows a comparison between experimental and modeled ac conductance, based on the numbers shown in Table 6.5, for both thin film samples. To understand the contribution of each path, the absolute value of the total simulated admittance, the absolute value of the ac hopping admittance, and the absolute value of the cross-grain-boundary admittance are plotted as functions of frequency for both samples. Figures 6.25 and 6.26 display the results for SK-62 and SK-72 samples, respectively. Part (a) of each Figure displays the results in the frequency range from 100Hz to 1 MHz, and part (b) displays the results in the frequency range from 10 MHz to 100 MHz. The Figures indicate that hopping admittance plays a bigger role at lower frequencies than cross-grain boundary admittance. However, and in contrast to the results shown for the same samples in the as-grown state, the contribution of cross-grain boundary conduction to the total conduction at high frequencies is higher than the contribution of hopping conduction. These results justify the claim for the need to add both hopping and cross-grain-boundary paths to the ac circuit model in order to explain the high



Figure 6.24: Comparison between experimental and modeled ac conductance for annealed samples, (a) SK-62, and (b) SK-72 at measurement temperature of 550 °K



Figure 6.25: Comparison of ac conductance for sample SK-62 with both hopping and grain boundary paths of the ac circuit model in two frequency regions: (a) 100 Hz to 1 MHz, and (b) 10 MHz to 100 MHz.

>Total admittance, o Hopping admittance, and + Grain Boundary admittance



Figure 6.26: Comparison of ac conductance for sample SK-72 with both hopping and grain boundary paths of the ac circuit model in two frequency regions: (a) 100 Hz to 1 MHz, and (b) 10 MHz to 100 MHz.

▷ Total admittance, o Hopping admittance, and + Grain Boundary admittance

frequency electrical conduction phenomena in polycrystalline diamond films.

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## **CHAPTER 7**

## **DISCUSSION AND FUTURE WORK**

This chapter summarizes the results of the research work which is described in earlier chapters, and discusses related research issues which need to be further investigated.

The ac electrical conductivity of polycrystalline thin and thick, free-standing diamond samples is investigated in the frequency range from dc to 1 GHz. The impedance spectroscopy results are well modeled over this frequency range by the developed four path ac circuit model described in chapter 4. The model contains two frequency dependent conduction paths, one representing hopping and the other representing transport across grain boundaries, in addition to the basic electrical model of the sample. The contact resistance, although small enough to produce a negligible voltage drop at dc, plays a non-trivial role at high frequencies, on the order of several hundred MHz. The results indicate that both transport across grain barriers and hopping contribute to the impedance spectroscopy results for both types of samples. The inclusion of both conduction paths in the IS model is

essential and is in better agreement with experiment than either one alone. After studying the relative role of various contributors, this study concluded that the frequency dependent current-voltage characteristics for polycrystalline diamond, beyond those expected as a result of the sample's geometric capacitance, are principally associated with grain boundaries, either owing to hopping conduction within the boundaries or to capacitive effects associated with grain boundary potential barriers.

The correlation between the dc electrical properties of CVD diamond films and the growth input and output parameters are also investigated in this study. Results clearly show that the as-grown dc resistivity of CVD films is related to the hydrogen flow rate used during the growth process. It is hypothesized that this is mainly caused by the incorporation of hydrogen atoms within the film's grains. This results in the passivation of electrically active defect states in diamond which leads to a decrease in resistivity. There may also be a suggestion of an increase in resistivity with increasing grain size and decreasing FWHM.

Investigating the as-grown film's ac electrical properties using the developed ac circuit model reveals the individual role of conduction paths within the film, and helps relate these properties to key film attributes. For example, it is observed that the ac hopping admittance is inversely proportional to both the diamond to graphite signal ratio,  $I_d/I_g$ , and to the average grain size. The second observation indicates

that hopping is mainly associated with grain boundaries, as noted in chapter 5. It is also observed that the ac cross-grain-boundary admittance is inversely proportional to the film's average grain size.

The temperature and annealing effects on dc electrical resistivity and ac circuit model parameters were also investigated. The dc resistivity of the films show sharp increase after annealing. This is believed to be related to the expulsion of hydrogen atoms from the films. When the IS results of the annealed samples are fitted to the four path circuit model, the numbers reveal a slight decrease in the grain boundary resistance,  $R_g$ , and a large decrease in hopping conductivity. This may suggest that the incorporation of hydrogen in the films takes place at the grain boundaries, and not within the crystallites themselves. This again emphasizes the important role that grain boundaries play in the total conduction mechanism in polycrystalline diamond films.

In conclusion, it is demonstrated that the frequency dependent electrical properties of polycrystalline diamond, beyond those expected as a result of the samples geometric capacitance, are principally associated with grain boundaries. Both hopping and cross-grain-boundary conduction paths play important roles in the total conduction process of both thin and thick, free-standing polycrystalline diamond films.

To achieve more comprehensive understanding of this subject, future

research is required in the following areas. (1) Study the importance of the depositing system's purity, particularly the role of nitrogen, in producing diamond films with pre-determined characteristics. (2) Study the correlation between the films' electrical properties and plasma diagnostics. (3) Given the apparent important role of grain boundaries in determining the electrical properties of polycrystalline diamond, it would be useful to use other techniques such as TEM to provide additional information that may add to the understanding of their role. (4) Study the effect of hydrogenation on both dc and ac electrical properties of the films. (5) Apply the findings of the current research study on a wider variety of diamond samples grown by different techniques and at different conditions. (6) Use more advanced temperature measurement equipment to achieve more accurate results.

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