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ELECTRICAL CONDUCTIVITY OF HETEROEPITAXIAL DIAMOND

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MAHDOKHT BEHRAVAN

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ELECTRICAL CONDUCTIVITY OF HETEROEPITAXIAL DIAMOND

Bу

Mahdokht Behravan

A DISSERTATION

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

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Abstract

ELECTRICAL CONDUCTIVITY OF HETEROEPITAXIAL DIAMOND

By

Mahdokht Behravan

The purpose of this research is to understand the electrical conduction mechanisms of heteroepitaxial diamond by performing direct current (DC) electrical Of particular interest is the temperature dependence of the DC measurements. conductivity. The project takes advantage of recent advances at Michigan State University in the growth of diamond by chemical vapor deposition on lattice-matched substrates, i.e., by heteroepitaxy. This investigation represents the first detailed study of an electrical transport property of heteroepitaxial diamond. The characterization of the electrical properties of a wide bandgap, high resistivity material such as diamond requires low current, high temperature measurements. A number of new techniques were developed to perform reliable electronic measurements at elevated temperatures. The magnitude of the DC conductivity of heteroepitaxial diamond was found to be remarkably similar to that of high-purity, Type IIa natural diamond. Heteroepitaxial diamond exhibits thermally activated conductivity, with a single activation energy of 1.40±0.03 eV from 250 °C to 550 °C. This result is similar to previous measurements by other workers on Type IIa natural diamond, suggesting the presence of electronic states at comparable concentrations in materials of completely different origin.

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Chapter 1 Introduction

Single crystal diamond is a wide band-gap semiconductor, $E_g = 5.5 \text{ eV}$, that has shown outstanding electrical properties, such as very high carrier mobilities and a large dielectric breakdown field, coupled with unsurpassed room temperature thermal conductivity and mechanical hardness. These unique properties make diamond an excellent material for electronic devices such as transistors, high-voltage capacitors and radiation detectors.

It was found recently that homoepitaxial diamond (diamond grown on a diamond substrate) has larger mobilities for electrons and holes than Type IIa natural diamond (high purity natural diamond with only trace nitrogen impurities present) [1]. This has raised questions about the fundamental electronic properties of diamond. Some electrical properties of diamond and other semiconductors are compared in Table 1 [2]. It can be seen that diamond has the largest bandgap and dielectric breakdown field. The room temperature electron mobility of homoepitaxial diamond is exceeded only by GaAs.

The major problem with growing homoepitaxial diamond is the lack of large diamond substrates at reasonable cost. This limitation opens up an area of research for heteroepitaxial diamond (diamond grown on non-diamond substrates). The potential advantage of heteroepitaxial diamond over homoepitaxial diamond is substrate scale and cost, provided suitable high-quality, lattice-matched substrates can be found.
 Table 1 Comparison of mobility, electric field break down, and band gap of diamond.

Semiconductor	Mobility	Maximum	Band-
		Electric field	gap
	cm ² V ⁻¹ s ⁻¹	V cm ⁻¹ (E _m)	eV (E _g)
Natural Diamond IIa	2000- 2800(electron)	10 ⁷	5.5
	1800-2100 (hole)		
Homoepitaxial Diamond	4500 (electron)	10 ⁷	5.5
	3800 (hole)		
Silicon carbide (SiC)	700 (electron)	3.0 x 10 ⁶	3.26
Gallium nitride (GaN)	2000 (electron)	2.0 x 10 ⁶	3.0
Gallium arsenide (GaAs)	8500 (electron)	4.0 x 10 ⁵	1.42
Silicon (Si)	1500 (electron)	3.7 x 10 ⁵	1.12
	450 (hole)		
Ge	3900 (electron)	2.0 x 10 ⁵	0.66
	1900 (hole)		

PROPERTIES OF DIAMOND AND OTHER SEMICONDUCTORS

Only a few investigations of the transport properties of natural diamond have occurred, and no research to date has been done on the transport properties of heteroepitaxial diamond. The mobilities of heteroepitaxial diamond have yet to be reported. Heteroepitaxial diamond with areas of 10 mm² and thicknesses up to 50 μ m has been grown on Ir/SrTiO₃ substrates by the Golding group.

Using this newly available material, this dissertation will address the issues of performing electrical measurements on heteroepitaxial diamond, describing research methods that have led to the following results:

- 1. Current-voltage (I-V) characteristics of heteroepitaxial diamond at high temperatures.
- 2. Temperature dependence of the DC conductivity.
- 3. Activation energy of the DC conductivity.

Chapter 2 Properties of Group IV Semiconductors

2. 1 Structure

The group IV elements of the periodic table, C (in diamond form), Si, and Ge are important due to their semiconducting properties. Their lattice structure is fcc with basis (0, 0, 0), (1/4, 1/4, 1/4) [3]. There are eight atoms per cubic cell with each carbon bonded to four nearest neighbors that form a tetrahedron. The cubic cell is shown in Figure 1. The neighboring atoms form hybridized sp³ covalent bonds.



Figure 1 Cubic unit cell of diamond.

The interatomic distances, lattice parameters and bond energies of diamond, silicon and germanium are compared in Table 2 [4]. It can be seen that diamond has the shortest interatomic distance, lattice parameter, and the largest bonding energy.

 Table 2 Comparison of interatomic distance, lattice parameter, and bonding energy of diamond,
 Si, and Ge.

Material	Interatomic Distance	Lattice Parameter	Bond Energy
	(nm)	(nm)	(KJ/mol)
Diamond	0.153	0.357	347
Silicon	0.235	0.543	196
Sheon	0.235	0.343	190
Germanium	0.245	0.565	163

2. 2 Electronic Structure

The first Brillouin zone of the fcc structure is shown in Figure 2 [5].



Figure 2 fcc first Brillouin zone.

The energy gaps of diamond, Si, and Ge are 5.5 eV, 1.1 eV, and 0.66 eV, respectively. Their energy band structures are shown in Figure 3 [6, 7]. They all are indirect bandgap materials, and have four valence bands. Three p bands and one s band form sp^3 hybrids. Diamond has a larger band gap due to its shorter atomic distances and larger bonding energy (Table 2).



3 (a)







Figure 3 Energy band structure of: (a) diamond, (b) silicon and (c) germanium.

2. 3 Impurities and Defects

In general, even nominally pure materials have defects and unintentional dopants. These defects and dopants can act as donors, acceptors or trap centers with energy levels that lie between the conduction and valence bands, i.e., within the bandgap. Since these states may affect the transport properties, understanding the electrical properties of crystals requires a good understanding of their defects. Here, general forms of defects in semiconductors are reviewed. Four different types of defects are described: point defects, line defects, area defects, and volume defects. General forms of point defects are shown in Figure 4 [8]. A point defect may be: (a) incorporation of a different type of atom or impurity into a substitutional site, or (b) interstitial site, (c) a vacancy in the lattice caused by a missing atom, or (d) a lattice vacancy and an interstitial host atom (Frenkel defect). Vacancies are classified according to their charge states: V° (neutral vacancy), V^{-} (acceptor vacancy), V^{2-} (double-charged acceptor vacancy), V^{+} (donor vacancy), and so on.

The various types of point defects, i.e., vacancy (V), self-interstitial (I), and foreign interstitial and substitutional atom, that may form in diamond are shown in Figure 5 [9].



Figure 4 (a) Substitutional impurity (b) interstitial impurity, (c) vacancy, and (d) Frenkel defect.



Figure 5 Various types of point defects in diamond [9].

Line defects, i.e. dislocations, may occur in a crystal as edge or screw types. These defects are shown in Figure 6 [8]. The edge dislocation is visualized as the insertion of an extra plane of atoms AB into a section of the lattice (a). This insertion causes compression of the atoms in that section and extension of the atoms in the nearby section. The screw dislocation is the sliding of one half-plane of the crystal over a lower plane (b). Impurities may be trapped at line defects and may alter the electrical conductivity of the crystal.



Figure 6 (a) Edge and (b) screw dislocation.

Dislocations, both edge and screw type, can also occur in diamond. The screw type is most prominent and is shown in Figure 7 [9]. The screw dislocation structure (13-12-11-10-9-8-7) can be distinguished from the normal hexagon form (1-6-5-4-3-2-1). Dislocation densities of 10^8 cm⁻² have been found in Type IIa natural diamond [9].



Figure 7 Screw dislocation in diamond [9].

Area defects can occur either on the surface or inside a crystal. Typical forms of area defects are twins and stacking faults. Formation of an oriented plane of a lattice with respect to the un-deformed plane is twinning. Twinning can form between the grain boundaries and on the surface of a single crystal. A stacking fault can be either intrinsic or extrinsic (Figure 8) [8]; a missing layer section is intrinsic (a), and an inserted layer is extrinsic (b).



Figure 8 (a) Intrinsic and (b) extrinsic stacking fault (generic).

Twins and stacking faults in diamond originate at dislocations and impurity atoms and they often appear together. The coexistence of monolayer twins and <111> stacking faults in the diamond structure is shown in Figure 9 [9].



(a)



Figure 9 Intrinsic (a) and extrinsic (b) stacking fault in diamond [9].

Dislocations and vacancies may coexist. Point defects can interact with other types of defects. A vacancy may combine with another defect and form a larger vacancy. Dislocations can trap point defects and impurities. These dislocations can be sources of dangling bonds, and form charged regions. They can scatter phonons and electrons, affecting mobilities, and trap carriers and recombine with them, influencing the lifetime of carriers.

2. 4 Conduction Mechanisms

2.4.1 Effective Mass

The electron mass in a solid may appear to deviate from the free electron mass. This deviation is caused by the interaction between accelerated electrons in an electric field and the crystal lattice. Scattering between electrons and ions can slow down the electrons resulting in a larger effective mass. The velocity of an electron moving in an energy band can be written as [5]:

$$v_g = \frac{d\omega}{dk} = \frac{1}{\hbar} \frac{dE}{dk}$$
 1

where, v_g is the group velocity of a wave packet from which the acceleration can be found:

$$a = \frac{dv_g}{dt} = \frac{1}{\hbar} \frac{d^2 E}{dk^2} \frac{dk}{dt}.$$

Taking the first derivative of $p=\hbar k$ with respect to time will give dk/dt:

$$\frac{dp}{dt} = \hbar \frac{dk}{dt}$$
3

Acceleration of the electron is found by combining Equations 2 and 3:

$$a = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \frac{dp}{dt} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} F$$
4

where, F can be considered the classical force causing the electron to accelerate:

$$a = \frac{F}{m}$$
 5

Equating Equations 4 and 5 gives an expression for the effective mass:

$$m^* = \hbar^2 \left(\frac{d^2 E}{dk^2}\right)^{-1} \tag{6}$$

This shows that the effective mass is proportional to the inverse of the second derivative of the energy with respect to the wave number, i.e., the curvature of a band. The effective mass is small for large curvatures and large for small curvatures.

A simple band structure (a), the first derivative (b), and inverse of the second derivative of E- k_x (c) within the first Brillouin zone for an electron are shown in Figure 10. The effective mass is small and positive near Γ , the center of the Brillouin zone, and increases with k_x . The effective mass can be negative or diverge to infinity for k_x far from the energy band minimum. Generally, the effective mass depends on direction and has a tensor form.



Figure 10 (a) Free electron band structure (b) First derivative (c) Effective mass.

The concept of the effective mass is useful in understanding the shape of energy versus k bands. The light and heavy hole masses (relative to the electronic mass m) for diamond, silicon and germanium are compared in Table 3 [10]. Light and heavy hole masses of diamond are larger than for silicon and germanium.

Table 3 Light and heavy hole masses.

Material	Light	Heavy
	hole mass	hole mass
Diamond	0.7	2.12
Silicon	0.16	0.52
Germanium	0.043	0.34

The conduction band has a minimum between Γ and X. As the energy surface in proximity to the minimum is not perfectly spherical, effective mass is different along two directions, defining a longitudinal mass m_l^* and transverse mass m_t^* [5].

2.4.2 Carrier Density

The number of carriers depends on the band gap, E_g , and temperature. For an intrinsic semiconductor at T>0 K the number of carriers in the conduction band and valence band are equal. Therefore, the Fermi energy lies midway in the band gap assuming $m_e^*=m_b^*$ (Figure 11) [5].



Figure 11 Schematic band diagram and Fermi-Dirac function F(E) for T>0.

The density of electrons, or holes, in the conduction band, or valence band, of an intrinsic semiconductor increases exponentially with temperature. Figure 12 shows density of electrons in the conduction and holes in the valence band for an intrinsic semiconductor [5].



Figure 12 Density of electron and holes vs. energy.

The carrier concentration N_i , in cm⁻³, for either electrons or holes is a function of the effective mass and temperature, and is given by the following equation [5]:

$$N_{i} = 4.84 \times 10^{15} \left(\frac{m^{*}}{m_{o}}\right)^{3/2} T^{3/2} \exp\left[-\left(\frac{E_{g}}{2k_{B}T}\right)\right]$$
 7

The exponential term dominates the temperature dependence of N_i.

If a semiconductor is doped (extrinsic semiconductor), the Fermi level is not in the middle of the band gap, and depending on the impurity type and level it shifts toward either the conduction or valence band. The impurity atoms contribute to the carrier concentration. For an n-type semiconductor, the relationship between the density of donors N_D , ionized donors N^+_D , donor energy relative to the conduction band minimum E_D is given by [6]:

$$N_D^+ = N_D \left[1 - \frac{1}{1 + \frac{1}{g} \exp\left(\frac{E_D - E_F}{k_B T}\right)} \right]$$
 8

For p-type material with acceptor density N_A , ionized acceptors N_A , and acceptor energy relative to the valence band E_A one has:

$$N_{A}^{-} = \left[\frac{N_{A}}{1 + g \exp\left(\frac{E_{A} - E_{F}}{k_{B}T}\right)}\right]$$
9

where g is the ground state degeneracy of the impurity level.

At 0 K, impurities cannot contribute to the electrical conduction. For T finite but small, the impurities ionize and provide extra charge carriers. At higher temperature, all the impurities are ionized and do not provide additional charges. At still higher temperature, the intrinsic carriers add to the number of carriers. This behavior for electron density for a specific doped semiconductor can be seen in Figure 13 [5].


Figure 13 Conduction electron density vs. temperature at low doping.

2.4.3 Mobility

Mobility is the drift velocity, v, of the carriers in unit electric field, E,

$$\mu = v/E \qquad 10$$

and is related to the carrier relaxation time, τ , by:

$$\mu = \tau e/m \tag{11}$$

The mobility of the electron, μ_e , differs from the mobility of the hole, μ_h . In cases of interest here, mobilities of electrons and holes generally decrease with increasing temperature due to phonon scattering. This behavior is shown in Figure 14 [5].



Figure 14 Temperature variation of the electron and hole mobilities.

In a doped semiconductor, the mobility may also depend on the dopant concentration. Experimentally, the mobility of a lightly doped semiconductor varies with temperature as $T^{3/2}$ at low temperature, due to scattering of the carriers by impurities. At high temperatures the mobility of the lightly doped semiconductor will vary with temperature as $T^{-3/2}$, due to scattering of the carriers by phonons. [3].

2. 5 DC Conductivity

2.5.1 Intrinsic Behavior

In an intrinsic semiconductor, the conduction mechanism is controlled by the properties of the pure crystal, and is given by [3]:

$$\sigma = N_e e \mu_e + N_h e \mu_h \tag{12}$$

where e and h stand for electron and hole, respectively, and:

 σ = conductivity

 N_i = density of charge carriers of type *i*

 μ_i = mobility of carrier type *i*

e = electron charge.

The temperature-dependent intrinsic conductivity can be obtained by combining Equations 7 and 12 [5]:

$$\sigma = 4.84 \times 10^{15} \left(\frac{m^*}{m_o}\right)^{3/2} T^{3/2} e(\mu_e + \mu_h) \exp\left[-\left(\frac{E_g}{2k_B T}\right)\right]$$
 13

The mobility and the number of charge carriers depend on temperature. The dominant temperature factor in Equation 13 is the density of charge carriers, as the exponential term varies faster than $T^{3/2}$. Therefore, the conductivity variation with temperature mainly follows the change in the carrier concentration. Thus the temperature dependence of the intrinsic conductivity varies as:

$$\sigma = \sigma_{\circ} \exp\left(-E_g/2k_BT\right)$$
 14

and is governed by the bandgap energy.

2.5.2 Extrinsic Behavior

A semiconductor may have sources of carriers other than the intrinsic carriers, such as dopant impurities and defects. The impurities and defects can produce states in the band gap and affect the electrical conductivity. The conductivity generally increases with temperature provided there is a dominant single carrier type. Figure 15 shows a typical variation of conductivity with temperature [3]. At very low temperatures (D), the conductivity arises from electrons hopping between states within the band gap. Hopping is triggered by the exchange of energy of an electron with a phonon, and requires the presence of both occupied and empty states. In this range of temperature, hopping conduction is very small because the electrons can only hop from one site to the next, limited by the weak overlap of their wave functions. At higher temperatures, the electron concentration increases rapidly (C). Electrons at the dopant level absorb enough energy to reach the conduction band, dramatically increasing conductivity. This effect saturates with temperature when nearly all of the electrons at the dopant level become ionized. At this point, the carrier concentrations become largely independent of temperature, and the mobility determines the conductivity (B). At temperatures above this region, the conduction corresponds to the intrinsic behavior of the material (A).



Figure 15 Typical conductivity behavior of a semiconductor with T^{-1} .

The magnitude and variation of the extrinsic conductivity with the temperature depends on the dopant concentration. Figure 16 is an example of the variation of the conductivity for high and low dopant concentrations. For low dopant concentration, 10^{12} cm⁻³, the conductivity decreases with temperature for T<300 K (decreased mobility), and increases with temperature for T>300 K (increased number of carrier). For high dopant concentration, 10^{16} cm⁻³, the conductivity is mostly controlled by the higher carrier concentration.



Figure 16 Conductivity of high and low doped semiconductor with temperature.

An empirical expression for the conductivity of a highly doped semiconductor can be expressed as [11]:

$$\sigma = \sigma_1 \exp(-E_1/k_B T) + \sigma_2 \exp(-E_2/k_B T) + \sigma_3 \exp(-E_3/k_B T) \quad 15$$

where $E_1 > E_2 > E_3$, and E_1 , E_2 , E_3 are activation energies arising from different conduction mechanisms. The first term is related to the activation from the impurity level to the valence or conduction band. The second term corresponds to conduction in an impurity band. This mechanism occurs when the impurity concentration is high enough that conduction occurs through a narrow band of singly filled neutral donor states within the band gap. The third term corresponds to nearest neighbor hopping.

2.5.3 Variable Range Hopping Conduction

According to the Davis-Mott model [12], another form of hopping conduction may occur in semiconductors. At lower temperatures, carriers may hop to larger distances to find unoccupied localized states with energies equivalent to or lower than nearest neighbors. Localized states in the band gap considered in this model may correspond to localized impurity or vacancy states in semiconductors. At very low temperatures, conduction can occur by thermally assisted tunneling between states at the Fermi level. This is called variable range hopping (VRH) conduction, and for a 3-dimensional system is given by [12]:

$$\sigma = \sigma_{\circ}(T) \exp\left(-AT^{-1/4}\right)$$
 16

where;

$$\sigma_{\circ}(T) = \frac{e^2}{2(8\pi)^{1/2}} \nu_{ph} \left[\frac{N(E_F)}{ck_B T} \right]^{1/2}$$
 17

$$A = 2.1 \left[\alpha^3 / k_B N(E_F) \right]^{1/4}$$
 18

where;

 $N(E_F)$ = Density of states at the Fermi energy e = Electron charge v_{ph} = Phonon frequency $k_B = \text{Boltzmann constant}$

T = Temperature

 α = Inverse range of the wave function

2. 6 AC Conductivity

AC conductivity provides more information about the conduction mechanism in a material. The frequency dependent conductivity is different for charge transfer in extended states than for hopping in the localized states. Conductivity due to charge excitation into the extended states is generally frequency independent below a few GHz. Hopping conduction between localized states, on the other hand, requires electrons to interact with phonons, and is expected to vary with frequency as [12]:

$$\sigma(\omega) = C\omega^{0.8}$$

where C is a constant.

Hopping near the Fermi energy can be distinguished from hopping between the band tails of localized states by studying the temperature behavior of the conductivity. Band tail conduction depends exponentially on the temperature because the charge carrier density increases exponentially with temperature, $\exp(-1/T)$. For this mechanism, AC conduction is similar to DC conduction in terms of temperature dependence. For hopping at the Fermi energy level, the AC conductivity varies linearly with temperature, as the number of carriers remains relatively constant. This can be compared with the aforementioned variation of the DC conductivity with temperature, $\exp(-T^{-1/4})$.

2. 7 Diamond Transport

2.7.1 Surface Properties

The lattice is discontinuous at a surface and is thus not periodic in the perpendicular direction to the plane of the surface. The surface discontinuity may produce dangling bonds with localized energy states (Figure 17) [8]. Such a surface has a large surface energy and is very reactive. Some materials, including silicon, germanium and diamond, reconstruct their surface by re-bonding, as a way to lower their surface energy. The surface termination of diamond is very important as it affects both the surface electrical and contact properties.



Figure 17 Dangling bonds on the interrupted surface of a crystal.

Surface sensitive techniques like photoelectron spectroscopy (PES), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), high resolution electron energy loss spectroscopy (HREELS) have been used for studying the surface of materials including diamond.

Initially, it was thought that diamond reconstructs its surface to graphite, as graphite is the stable phase of carbon. However it was found that the clean surface of diamond is different from graphite and is more closely related to reconstructions that occur in germanium and silicon [13].

Different diamond planes at the surface undergo different reconstructions. Figure 18 shows a clean diamond (100) surface before and after surface reconstruction. The neighboring carbon atoms form carbon dimers (C=C) to reconstruct to 2×1 symmetry [13].



(a) Truncated-Bulk C(100) 1x1 (b) C(100) 2x1

Figure 18 (a) Truncated bulk and (b) dimerized (100) surface [13].

The surface of diamond can be terminated by foreign atoms as well. Two important diamond surface impurities are hydrogen (Figure 19) and oxygen (Figure 20), as they may appear in various stages of the diamond growth process. However, very little oxygen has been found on as-grown CVD diamond using XPS even when a CO/H₂ gas mixture was used [14]. A single hydrogen bonded to carbon, C(100) 2×1 :H, was found by the HREELS technique [15]. Hydrogen termination of the (100) diamond surface can be by found in two forms: (a) two hydrogen atoms bonded to one carbon, $C(100) 1 \times 1:2H$ or (b) a disordered form, where two hydrogens bond to a carbon and one hydrogen bonds to one carbon atom, a combination of $C(100) 1 \times 1:2H$ and $C(100) 2 \times 1:H$ (Figure 19). The latter is found on (100) surfaces of germanium and silicon as well [13].



Figure 19 Top and side views of two models for hydrogen terminated (100) surface, (a) 1×1:2H, (b) 1×1:H and :2H [13].

Oxygen can form CO with the diamond surface in two ordered structures of C(100) 1×1:O, bridging between two carbon atoms and bonding to only one carbon atom (Figure 20) [13].



Diamond (100) 1×1:O Bridging structure

Diamond (100) 1×1:O Double-bonded structure

Figure 20 Two models for oxygen terminated (100) surface, bridging and double bonded structures [13].

Hydrogen and oxygen can be removed from the diamond surface by annealing. Annealing at 1300 K is reported to be sufficient for a C(100) surface to free oxygen and hydrogen and to obtain a clean C(100) 2×1 surface [13]. Hydrogen desorption is reported to commence at 1000 K [16]. Oxygen on the diamond surface is stable up to 1173 K [14]. It is interesting to note that the surface of clean diamond can be exposed to a hydrogen or oxygen plasma, and recover the hydrogen [17] or oxygen terminated diamond surfaces (Figure 21) [18-20]. This can be used to change the surface properties of diamond. It can be seen that the surface of as-grown diamond has a low resistance which is increased by three orders of magnitude after oxygen plasma treatment. The low resistance state is partially recovered after hydrogen plasma treatment. A band bending model explains the surface conduction in the next section.



Figure 21 I-V relation of the as-grown, hydrogen and oxygen plasma treated undoped homoepitaxial diamond surfaces. Note reversible behavior with alternate plasma exposures [18].

2.7.2 Surface Conduction

The electrical conductivity of the diamond surface depends on its termination and adsorbants. The presence of the adsorbates causes band bending near the surface. The band bending direction, upward or downward, depends on the surface termination.

Surfaces terminated with hydrogen and oxygen have shown conductive and nonconductive behavior, respectively. This shows that hydrogen and oxygen on the diamond surface introduces surface states. A band bending model for the diamond surface shows that the hydrogen termination has low resistivity due to upward band bending caused by hole accumulation (Figure 22) [18]. According to this model, a high density of acceptor type surface states below the bulk Fermi level produces the hole accumulation on the diamond surface with the Fermi level at $E_v+0.9$ eV. This model relates the high resistivity of oxygen terminated surfaces to downward bending produced by hole depletion. The depletion layer is produced by donor type surface states around $E_v+1.7$ eV.



Figure 22 Energy diagram of the hydrogenated/oxygenated diamond surface [18].

Ristein et al. [16] have shown how the diamond surface conductance varies with surface treatment. It can be seen from Figure 23 that the as-grown surfaces and surfaces exposed to hydrogen plasma have a surface conductance greater than 1×10^{-6} S. But annealed surfaces in vacuum, acid treated surfaces, and air heated surfaces at 500 K have surface conductance of less than 1×10^{-11} S. It was also shown that hydrogen surfaces are less stable in air than in a vacuum.



Figure 23 Surface conductance of different diamond samples [16].

The hydrogen terminated diamond surface shows p-type surface conductivity. A proposed model [16], suggests that an aqueous phase on the top of the diamond extracts an electron from the valence band of the diamond, and forms $\frac{1}{2}$ H₂ by reacting with H₃O⁺ and leaving HCO₃⁻ on the surface. This would leave holes accumulating in the diamond near the surface--and negative charges of HCO₃⁻ on the diamond surface--resulting in band bending near the surface and thus a finite surface conductivity (Figure 24). Hydrogen-terminated diamond is surface conductive in air because it is invariably exposed to water vapor, but is not conductive after the surface water layer is removed by vacuum evaporation.







The origin of the surface states may also be related to surface structural defects, which are not necessarily due to the type of surface termination. The surface of diamond may go through more surface constructions than silicon because diamond can change to sp^1 , sp^2 , and sp^3 while silicon generally forms only sp^3 bonds.

The surface conductivity can be removed or changed by various surface treatments; chemical cleaning of the surface with acids such as HF, HNO₃, HCl, H₂SO₄,

CrO₃, HClO₄ [14, 21-41], electrochemical cleaning [42], oxygen annealing [20], heating in ultra-high vacuum at 950 °C [43], heating in air 700 °C [44], oxygen plasma cleaning [14, 24, 36], N₂-Ar plasma [37], and He-O₂ plasma [34].

2.7.3 Metallization

The metal-semiconductor contact may be rectifying or Ohmic. To find the bulk electronic properties of a material, Ohmic contacts are advantageous. A good Ohmic contact should have good adhesion, low contact resistance, and high thermal stability. Poor Ohmic contacts can be a substantial source of noise, with errors introduced if a significant voltage drop occurs across the contact. Fabrication of Ohmic contacts to diamond can be problematic, since a potential barrier usually forms at the metal-diamond interface. This is presumed to be due to the differing work function of the two materials or the high density of states at the interface caused by diamond covalent bonds.

A high density of surface states can produce a surface barrier on the surface even before metallization. The surface states are affected by the surface termination, either hydrogen or oxygen. These surface states may trap charge carriers. For example, in an ntype semiconductor, the surface states can extract some electrons from the donors in the bulk of the semiconductor, and become negatively charged resulting in ionization of donor atoms. The region near this negatively charged area will be positive to maintain the charge neutrality. Therefore, the ionized donor atoms produce a charge density and potential barrier. This potential barrier makes the contact rectifying [45].

If there are a lot of surface states, $\sim 10^{12}$ cm⁻², the Fermi level cannot change substantially and is said to be *pinned*. As the density of dangling bonds may be two orders of magnitude larger than this value [18], dangling bonds can also pin the Fermi

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level. When the Fermi level is pinned, the barrier height does not depend on the metal and its work function [46, 47].

Much research has been performed on metal-diamond interfaces. Different kinds of metals have been deposited on diamond to investigate the effect of surface treatments and the role of the metal work function on the type of contact and I-V behavior. Mori has studied characteristics for eleven kinds of metals (Table 4). It was found that if the surface is oxygen-free, the I–V behavior depends on the metal work function and its electronegativity. If oxygen is on the surface, this dependence vanishes [14].

Table 4 Dependence of the type of the contact metal on the work function and electro-negativity and surface treatment. Treatment A is CrO₃ in H₂SO₄, and treatment C is O₂ plasma. Φ_M and X_M are metal work function and electro-negativity [14].

Metal	Ф _М (eV)	X _M (eV)	As-grown	After treatment A	After treatment C
Pt	5.65	2.2	Ohmic	Schottky	Schottky
Ni	5.15	1.8	Schottky	Schottky	Schottky
Au	5.10	2.4	Ohmic	Schottky	Schottky
Cu	4.65	1.9	Ohmic	Schottky	Schottky
Sn	4.42	1.8	Schottky	Schottky	Schottky
Zn	4.33	1.6	Schottky	Schottky	Schottky
Ti	4.33	1.5	Schottky	Schottky	Schottky
Al	4.28	1.5	Schottky	Schottky	Schottky
Ag	4.26	1.9	Ohmic	Schottky	Schottky
Ta	4.25	1.5	Schottky	Schottky	Schottky
In	4.12	1.7	Schottky	Schottky	Schottky

This is in agreement with Baumann, who found that the metal-diamond interfaces, where diamond is hydrogen-terminated with negative electron affinity, lower the Schottky barrier heights (SBH) [42]. The SBH is highest for positive electron affinity, oxygen terminated, and is the lowest for a clean surface [42, 48]. This is shown for various metals in Figure 25.



Figure 25 Schottky barrier height for various metals on clean and oxygen-terminated surfaces; UPS: UV photoemission spectroscopy. [48]

A variety of methods have been used to fabricate Ohmic contacts on diamond, including damaging the diamond surface by mechanical roughening, sputtering, and exposure to uv laser radiation. A contact made by these methods is Ohmic for metals such as W probes, Ag paint, and evaporated Al [49, 50] but is mechanically fragile and electrically noisy. Also, laser damage may produce graphite on the surface, leading to poor metal adhesion.

Doping during growth or doping the region under the contact to make a p-type layer is another technique used to make Ohmic contacts to diamond. Boron is commonly used to dope the region under the contact to reduce the width of Schottky barrier. The advantage of this method is that it is easy to control the concentration and depth of the dopant.

Using the chemical reaction between diamond and carbide-forming metals by annealing also produces Ohmic contacts. This method gives a contact with good adhesion with small contact resistivity. A low specific contact resistivity of 10⁻⁵ Ohm-cm² for single crystal diamond with a carrier concentration of 10¹⁶ cm⁻³ was achieved [49]. A plot of the reduction of specific contact resistance versus annealing temperature for Mo and Ti is shown in Figure 26 [26]. The samples were polycrystalline diamond, boron-doped at 10¹⁸-10²⁰ cm⁻³. The specific contact resistance of the Ti contact decreases near 300 C, and remains close to the same value at higher temperatures. The specific contact resistance of the sample with larger dopant levels changes less with temperature compared to samples with lower dopant levels.



Figure 26 Dependence of specific contact resistivity of Ti and Mo versus annealing temperature [26].

Different kinds of metals have been used for making Ohmic contacts using chemical reactions. Titanium has been used on polycrystalline, doped polycrystalline, and boron-doped homoepitaxial diamond [14, 21, 24-26, 30-33, 35-37, 43, 51-54]. Ta was used on B-doped polycrystalline diamond to obtain an Ohmic contact [27]. Nb was used to make an Ohmic contact on natural diamond [55].

Titanium is most often used as a carbide-forming metal. TiC forms at temperatures above 430 °C, and changes the contact from Schottky to Ohmic [21, 30-33,

35-39, 51, 52, 54, 56]. Figure 27 shows the effect of annealing on the I-V behavior of boron doped polycrystalline diamond, becoming nearly Ohmic after a 430 °C anneal.



Figure 27 I-V behavior with temperature for titanium on boron doped polycrystalline diamond [56].

The chemical reaction between the metal and diamond can be explained using the Gibbs free energy (ΔG) of carbide formation. ΔG is negative at 430 °C, which forces the reaction to form titanium carbide. The carbide can form in solid reactions by annealing because the free energy of the carbonizing reaction is minimized for IVa metals (Ti, Zr, Hf) and Va metals (V, Nb, Ta) [21].

It appears that carbide acts as a defect layer which lowers the barrier height or enhances tunneling, or both. It is possible that annealing may increase the local disorder by introducing point defects. The model to explain the Ohmic contact resulting from carbide formation is shown in Figure 28. There is a barrier at the metal and diamond interface before annealing (a). The carbide formation produces point defects at the surface of the diamond. These defects can either decrease the width of the depletion layer, and therefore enhance the probability of tunneling for the carriers (b), or reduce the effective barrier height (c).



Figure 28 Band diagram of Ti contact on diamond; (a) as deposited, (b) narrowed depletion layer by defects, (c) decreased barrier height by defects [49].

The role of the annealing temperature to make Ti contacts Ohmic has been investigated: 400 °C by Shiomi and Nakanishi and Chen and Craciun [21, 26, 32, 33, 43], 430 °C by Tachibana [38, 39, 56], 450 °C by Conte [35, 52], 500 °C by Nebel and

Alexander [36, 51], 700 °C by Chen [32, 33], 800 °C Waytena and Hoff and Landstrass [30, 53, 57]. However, Tareji did not find the Ti-diamond contact Ohmic for P-doped n-type diamond annealed at 600 °C, and TiC formation did not make the contact Ohmic [29]. Yokoba obtained non-Ohmic behavior for Ti on p-type polycrystalline diamond annealed at 600 °C [25]. Gonon found identical I-V behavior for both Au and Ti on polycrystalline diamond, with some of the contact area doped with boron, but did not relate the Ohmic behavior to carbide formation under the metal [37]. He suggested a conductive layer between diamond and the metal makes the contact Ohmic.

These results are in contradiction to another group that found Ohmic contacts for Ti. An interesting finding for the annealed contact is that when carbide-forming metals are removed from the surface, small carbide islands are identified at the surface. These islands may cause an inhomogeneous current density [48, 58].

Most of the research on Ohmic contacting has been performed on doped diamond or polycrystalline materials. Vandersande and Zoltan have used sputtered Nb [55], Pt, and Ir foil (pressure contact) [59] to make Ohmic contacts to natural diamond at high temperatures. None of the research cited has fully explained different contact behaviors. If there is a high density of states at the surface, then the contact may not be Ohmic, and other forms of voltage-dependent conduction may be observed. Therefore, it is reasonable to think that annealing changes the interface density of states by forming TiC. Since no study to date has been conducted on Ohmic contacts to heteroepitaxial diamond, one of the intermediate goals of this research is the fabrication of Ohmic contacts to this material.

2.7.4 Bulk Conduction of Diamond

Research has been carried out previously on the electrical properties and conduction mechanisms of doped and undoped CVD diamond and Type Ib natural diamond (with nitrogen concentrations of 50-150 ppm) [60] and Type IIb (with boron concentration of 5×10^{16} cm⁻³) [31]. Only a little research has been performed on the electrical conductivity of Type IIa natural diamond and CVD-grown homoepitaxial diamond. This may be due to difficulties in performing DC electrical measurements on material with very small conductivity.

Type IIa natural diamond has a very low conductivity, believed to be lower than $10^{-16} (\Omega \text{-cm})^{-1}$ at room temperature. Two common dopants found in natural diamond are boron and nitrogen. Boron acts as an acceptor, with a level 0.37 eV above the valence band. Nitrogen is a donor, with a level 1.7 eV below the conduction band. As 1.7 eV is fairly deep, even a high concentration of nitrogen does not cause significant conductivity at room temperature [61]. A conductivity of 10^{-6} to $10^{-12} (\Omega \text{-cm})^{-1}$ has been found at room temperature for polycrystalline CVD diamond, 4 to 8 orders of magnitudes larger

than the conductivity of the best natural diamond. The larger conductivity of polycrystalline diamond is related to the dangling bonds at grain boundaries.

Variation of the conductivity of Type IIa natural diamond and two other CVD polycrystalline diamond films grown by Applied Sciences and by Crystallume was reported by Vandersande (Figure 29) [55]. It can be seen from Figure 29 that the conductivity of the polycrystalline diamond films is larger than that of natural diamond by a few orders of magnitudes below 500 °C, and less than natural diamond at temperatures >800 °C. An activation energy of 1.4 eV was found for Type IIa natural diamond between 300 and 1200 °C, and activation energies of 0.9 eV and 1.8 eV were found for CVD diamond films between 200 and 800 °C and between 600 and 1200 °C, respectively.



Figure 29 Electrical conductivity of natural diamond IIa and two CVD diamond vs. 1/T [55].

An activation energy of 0.9, 1.8, or 1.4 eV cannot be due to intrinsic conduction. Vandersande and Zoltan suggested that the lower activation energies could be due to donor levels from interstitial carbon or acceptor levels caused by isolated vacancies. Activation energies in Type IIa natural diamond and polycrystalline diamond were also found to be between 1.5-1.6 eV in another report by Vandersande and Zoltan [59]. The conductivity of five diamond samples vs. 1/T is shown in Figure 30, with four polycrystalline CVD and one IIa sample [59]. Two samples are from Crystallume (one 6 μ m thick on silicon and one free standing 300 μ m thick), one sample from Norton (free standing 1.1 mm thick), one sample from Raytheon (free standing 660 μ m), and one Type IIa natural diamond (1mm).



Figure 30 Electrical conductivity versus 1/T for two Crystallume, Norton diamond, Raytheon, and Type IIa natural diamond [59].

As it can be seen from Figure 30, the conductivities of the Raytheon and one of the Crystallume samples are smaller than that of natural diamond, in the range of 300 °C to 1000 °C. Vandersande and Zoltan suggested that CVD samples are less defective and more pure than Type IIa natural diamond, and the conductivity in all of those samples was governed by the same type of conduction mechanism with the activation energies in the range of 1.5-1.6 eV. This activation energy was related to the isolated substitutional nitrogen with the activation energy of 1.7 eV [59, 62].

The activation energies of 1.4 eV and 1.5-1.6 eV can indicate that point defects are the source of the thermally activated conductivity in those diamonds. But, the discrepancy between the measured activation energy of 1.5-1.6 eV and the expected value of 1.7 eV for nitrogen impurity is not explained.

The activation energy of 1.5-1.6 eV might be a result of a combination of different conduction mechanisms. One could be due to vacancies with activation energy \sim 1.3 eV and one due to nitrogen centers with activation energy 1.7 eV. Measurements at higher temperature should result in an activation energy of 1.7 eV and possibly dominate the 1.3 eV energy if the conductivity is caused only by the nitrogen.

Activation energies of 1.3 and 1.0 eV were observed for homoepitaxial diamond grown on B-doped homoepitaxial and HPHT Type IIb substrates, respectively (Figure 31) [36, 60]. The origin of those activation energies was not certain. The activation energies of 1 and 1.1 eV are related to the polycrystalline diamond [31, 36] as grain boundaries are believed to give activation energies in this range. It should be pointed out that the activation energy for both natural diamonds, Types IIa and Ib (with nitrogen $\sim 5 \times 10^{18}$ cm⁻³) are found to be 1.7 eV. This indicates that although the substitutional

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nitrogen impurity density is small in diamond IIa, it may influence the conductivity, and look similar to Ib.

It is reasonable to believe that the smaller conductivities of the Raytheon and the Crystallume samples may be due to lower nitrogen levels. But, as those samples are polycrystalline, it is unlikely that they are less defective than single crystalline diamond. Grain boundaries scatter carriers and lower the mobility, another possible reason for the lower conductivities of the polycrystalline diamond samples.



Figure 31 Electrical resisitivity of diamond type IIa, Ib HPHT, and two undoped homoepitaxial diamond grown on type IIb and boron doped substrates [60].

Another source of carriers in CVD diamond could be hydrogen. Hydrogen is incorporated during growth at structural defects such as dislocations at high concentrations, and is distributed homogenously in CVD diamond. Hydrogen-related defects in the bulk are more stable against thermal treatments compared with surface hydrogen, which desorbs at 900-1000 $^{\circ}$ C [63]. The activation energy for CVD diamond with hydrogen incorporation is stated to be 1.8 eV below the conduction band [64, 65].

Diamond surface properties change with heat treatment leading to experimental difficulties. As an example, heating and cooling curves are shown for Norton diamond sample in Figure 32 [59]. This plot shows the effect of cleaning on conductivity and the change in conductivity for heating and for cooling, which do not overlap. This is related to the leakage through the surface of the sample according to Vandersande and Zoltan. It is thought that the surface of the sample is reconstructed- to either non-diamond or graphitic carbon when heating above 900 °C. However, after cleaning the sample, the same heating conductivity curve was obtained again. This could also be due to changes in the metallic contacts.



Figure 32 Log conductivity vs. I/T for Type IIa natural diamond and Norton diamond (before and after cleaning for both heating and cooling) [59].

Chapter 3 Heteroepitaxial Diamond Growth

3. 1 The Epitaxial Process

Heteroepitaxial diamond is presently grown on Ir/ SrTiO₃ or (Ir/sapphire) in the laboratories of the Golding group. This requires a series of steps from substrate preparation to CVD diamond growth. The lattice parameter for iridium is only 7.5% greater than that of diamond, making the iridium (001) surface suitable for epitaxial growth of diamond. The process steps are shown schematically in Figure 33 [66]. First, (001) Ir is grown on (001) SrTiO₃. Then, diamond is grown on Ir. Finally, the substrate can be removed to make a free standing diamond wafer.



Figure 33 Growth of heteroepitaxial diamond [66].

The Ir substrate is grown epitaxially as a thin film on $(5\times5\times0.5 \text{ mm}^3)$ SrTiO₃ with orientation $(001)_{Ir}||(001)_{SrTiO_3}$ and $[110]_{Ir}||$ $[110]_{SrTiO_3}$ prior to diamond deposition. This means that the interface of iridium and SrTiO₃ is in the (001) plane and that all cubic axes are aligned in that plane. The SrTiO₃ structure is shown in Figure 34. The lattice mismatch between this surface and iridium is small (1.7%).



Figure 34 Surface and structure of SrTiO₃ [67].

The iridium deposition process begins with etching of the SrTiO₃ in buffered HF. Iridium is grown by electron beam evaporation at a substrate temperature of 900-950 °C in an initial vacuum <10° Torr. The SrTiO₃ is heated for 20-120 minutes at 900 °C before iridium is deposited at a rate of 2.4 nm/min. The thickness of the iridium film is typically 150 nm.

Diamond is grown by chemical vapor deposition (CVD). Prior to the CVD growth, a biasing process induces nucleation of diamond on the Ir surface. Biasing leads to an enhanced nucleation density of diamond near 10^{12} cm⁻² [67]. This high nucleation density provides the sites for deposition of carbon radicals during the growth step.

3. 2 CVD Diamond Growth

To initiate the process, CH₄ (99.999%) and H₂ (99.9995%) gases are introduced into the reaction chamber following a vacuum state <10⁻⁷ Torr. When the gas pressure reaches the desired level, microwave power at 2.45 GHz is applied to the chamber to create a plasma that forms just above the Ir/SrTiO₃ substrate. The microwave power dissociates and ionizes the gas into positive ions and electrons. For the biasing process, a voltage between -150 and -200 V is applied to the stage containing the substrate. Positive ions in the plasma are accelerated toward the substrate surface. After approximately 60 minutes, the bias is turned off, nucleation occurs, and diamond growth proceeds by deposition of the plasma species. The substrate temperature is between 600-700 °C during biasing and growth.

During biasing, a high-density carbon layer forms on the iridium, which provides the precursor for diamond nuclei. The layer is believed to be an amorphous or nanocrystalline sp³ carbon. Nuclei appear on the surface as small carbon clusters, and lead to arrays of diamond nanocrystallites that cover the iridium surface. Scanning electron microscope (SEM) images show sp³ carbon with high contrast at 20 minutes and at 60-80 minutes biasing (Figure 35 and Figure 36). The dark areas are Ir. When biasing is interrupted before complete surface coverage, the crystallites form a pattern that is oriented predominantly along Ir [110] directions. The lengths of the blocks are 100-200 nm. As can be seen in Figure 36, the dark area is significantly covered after 60 minutes biasing; from 75% coverage after 20 minutes to 89 % coverage after 60 minutes.


Figure 35 SEM image after 20 minutes biasing (20-Jul-02) [68].



Figure 36 SEM image after 60 minutes biasing (18-Jul-02) [68].

After biasing the parameters are set for the Growth I step as shown in Table 5. Parameters given in Table 5 for the Growth II stage are applied when thicker films are desired. The parameters given in Table 5 were applied to grow the sample (04-May-04) used for the electrical measurements in this research.

	Bias Conditions	Growth I	Growth II
Bias current	30-40 mA		
CH ₄ /H ₂ ratio	2%	1%	0.8%
Pressure	18 Torr	18 Torr	28 Torr
MW power	1070 W	1100 W	1100 W
Time	60 min	180 min	37.5 hr
Temperature	655-665 °C	600 °C	720 °C

Table 5 Parameters for biasing and growth of thick diamond used for electrical measurement.

Figure 37 is an SEM image of the diamond growth after (a) 20 and (b) 180 minutes. The dark area is reduced for longer periods of the growth, as the film becomes thicker when coalescence is complete. A thickness of $0.54 \pm 0.02 \ \mu m$ was found for 180 minutes of growth (23-Jun-01) [67].



Figure 37 SEM image after (a) 20 and (b) 180 minutes growth on (17-Jul-00) and (23-Jun-01)

[67].

3. 3 Characterization

The diamond sample and the substrate are characterized by different techniques such as optical microscopy, SEM, atomic force microscopy (AFM), Raman, and X-ray diffraction (XRD).

AFM of the epitaxially grown iridium (thickness ~300 nm) is used to study the morphology of the iridium (Figure 38). The dark circular areas represent voids in the iridium film. The AFM measurement confirms a mean iridium surface roughness of only a few nanometers.



Figure 38 AFM of epitaxially grown iridium [67].

XRD is used to identify crystallographic phases in the sample and the substrate, and to obtain information on the atomic arrangements at the interface. A {111}-\$\$ scan of a diamond sample grown for three hours confirms the epitaxial growth of iridium on SrTiO₃ and diamond on iridium (Figure 39); that is, (100)_{dia}<110>_{dia}||(100)_{lr}<110>_{tr} $\|(100)_{SrTiO_3} < 110 > _{SrTiO_3}$. The rotation angle of the sample (Φ) is with respect to <001> direction.



It can be seen that the four peaks of diamond, iridium, and SrTiO₃ appear at the same angles, which shows epitaxial alignment.

Figure 39 XRD of diamond grown on Ir/SrTiO₃ after 180 minutes [67].

Raman spectroscopy was also used on free standing (001) crystal 25 μ m thick to characterize the diamond (Figure 40). The expected peak for diamond is at 1332 cm⁻¹; a peak at 1331 cm⁻¹ with a linewidth of 8 cm⁻¹ is found. The shift of the diamond peak is due to the stress in the diamond, caused by the lattice mismatch between the iridium and diamond. The small set of peaks at about 1500 cm⁻¹ may be due to the presence of a small amount of graphite.



Figure 40 Raman spectrum of a free standing 25 µm (001) diamond [67].

AFM was used to reveal the surface topography of a diamond sample grown for 12 hours on $Ir/SrTiO_3$ (Figure 41). Some steps, with the average height of 20 nm, can be seen on the surface.



Figure 41 AFM of a 12 hour diamond growth [67].

Figure 42 shows optical microscope images of the 20 μ m thick sample used in our experiments. The sample area is 3×2.2 mm². The dark spots are areas with macroscopic defects. A piece of this sample was used for the present electrical measurements.

SEM images of this sample are shown in Figure 43 and 44. Figure 43 (a) and (b) are taken from the central region. The size of the inclusions ranges from 1 μ m to 10 μ m. One of the inclusions with a size of 2-10 μ m with different facets can be seen in (b). Figure 44 (a) and (b) are taken from the areas near the edge of the diamond film. These images show a different texture –macrosteps– with fewer defects.

Figure 45 shows SEM images of the cross section of the diamond sample. Figure 45 (a) is with a sample tilt of 5 deg around the y axis (taking z as the normal to the surface and x pointing down in the image plane). This allowed imaging of the surface and cross section simultaneously. The lower portion of (a) is the surface with macrosteps, and the upper portion is the cross section with the growth side on the top of the image.

The thickness of the diamond sample was found by SEM in Figure 45 (b) and (c) and optical microscopy in Figure 46 (a) and (b). The thickness varies from 18 μ m near the edge to 24 μ m at center. An average thickness of 20 \pm 1 μ m was found for the diamond piece used for the electrical measurement. Smaller thickness of the edge can be seen in (b) and larger thickness can be seen in (a), which is about 0.5 mm far from the edge.



Figure 42 (a) diamond sample at 5X, (b) dark spots at 20X, and (c) spiral type defect detected by optical microscope at 20X (diamond grown by Z. Dai on 04-May-04).



Figure 43 SEM images of (a) the center of the diamond surface, and (b) a magnified inclusion. (04-May-04)



Figure 44 (a) and (b) SEM images of the area near the edge of the sample at two magnifications (04-May-04).



Figure 45 SEM image of (a) the tilted sample showing the surface and cross section simultaneously, (b) and (c) cross section. The iridium side in (a) and (b) is on the top side of the images.



Figure 46 Optical microscope images of the cross section of the diamond with the iridium side up at 20X (a) 0.5 mm far from the edge, and (b) near the edge.

The optical microscope image of the free standing heteroepitaxial diamond grown with a 35 μ m thickness 3.5 mm diameter is shown in Figure 47 [68]. The image shows that the diamond film is transparent.



Figure 47 Free standing transparent heteroepitaxial diamond, Diameter: 3.5 mm, Thickness: 35 µm [68].

Chapter 4 Experimental Methods

The goal of the electrical measurements is the determination of the bulk DC electrical conductivity of CVD heteroepitaxial diamond. The sample is highly resistive, $\rho > 10^{-14} \Omega$ -cm at room temperature, with lateral dimensions of a few mm. To facilitate measurements, a geometry was chosen that takes advantage of the much smaller diamond thickness, approximately 20 μ m. With metal contacts on the lateral faces, the current flow is perpendicular to the faces, provided surface currents can be made negligible. The contact to diamond from the metallic electrodes should be highly Ohmic.

At room temperature, the conductance of the sample is too low for accurate measurement. Therefore, it was necessary to heat the sample well above room temperature where the conductance is sufficiently high. This requirement led to the design of a novel sample holder and sample mounts that enabled thermal control with sufficient stability for accurate electrical measurements. These points are discussed in the following sections.

4. 1 Contact Geometry

A "sandwich" geometry was developed for the electrical contacts, Figure 48. Since the sample was grown on a 250 nm Ir substrate, it seemed useful to leave Ir in place, serving as a lower electrode, provided the Ir-diamond contact proved Ohmic. For the top electrode, Au was deposited on top of a thin Ti adhesive layer. A similar deposition was carried out on the Ir layer, initially to facilitate wire-bonding. The top electrode was as large as possible to increase the contact area.



Figure 48 Schematic of the sample electrode geometry.

An estimate of the minimum measurable conductivity is readily made for this geometry. The conductivity of the diamond is given by $\sigma = (G)(t/A)$, where G is the transverse conductance, t is the sample thickness, and A is the area of the top electrode. With an electrode diameter of 0.5 mm and t = 0.02 mm, the geometrical factor is approximately 1 cm⁻¹. By Ohm's Law, G = I/V, at a bias voltage V = 1 volt, and with an accuracy of 10 fA for pA range, we require $\sigma > 10^{-14} (\Omega \text{-cm})^{-1}$ for a measurement to be meaningful.

4. 2 Electrode Fabrication

It is necessary to prepare metallic contacts to diamond that are Ohmic, with low specific contact resistance, and that exhibit strong adhesion, even at elevated temperatures. This requires that a number of processing steps be taken that involve sample cleaning, multi-step thermal evaporation of metals, thermal annealing, and a final oxygen plasma treatment, as described below.

4.2.1 Chemical Cleaning

CVD diamond growth leaves the surface of the crystal covered with graphitic surface residues and carbon particulates. The residues prevent good adhesion between the diamond surface and evaporated metal films and may contribute to electrical surface leakage. Chemical cleaning removes graphite, loose particles, and oxidizes the surface of the diamond. The procedure is:

- 1. Rinse diamond sample with acetone and methanol.
- 2. Clean and rinse with Alconox and DI water.
- 3. Let stand in $1H_2O_2$: $1H_2SO_4$ solution for 30 minutes (30% H_2O_2 with 95%-98% H_2SO_4) to remove non-diamond phases and organics.
- Let stand in 3HCl:1HNO₃ solution for 10 minutes (CMOS grade HCl with 68%-70% HNO₃) to remove specific ionic and some metal surface contaminants.
- 5. Let stand in 24.5%HF:75.5%H₂O solution for 10 minutes (48% HF) to remove some metallic particles which cannot be removed with other acids.
- 1NH₄OH:5H₂O₂ for 1h at 65 °C with NH₄OH 28%-30%, H₂O₂ 30% to remove organic material causing surface contamination.

The sample is rinsed with deionized water (DI) water thoroughly after each chemical treatment.

4.2.2 Electrode Deposition

To define the deposition area, a mask and sample holder were designed for loading the sample and depositing the electrodes. A shop drawing is shown in Figure 49, a photograph in Figure 50. A stainless steel mask, 0.25 in square and 0.005 in thick, with a 0.02 in diameter aperture, fit into a recess in the center of the mask holder. A phosphor bronze clip secured the sample against the mask from its back surface, Figure 51.



Figure 49 Drawing of the stainless steel holder, side view and top view.



Figure 50 Stainless steel holder with the mask on the right.



Figure 51 Optical microscope image of a loaded sample, with iridium side up, in the holder pocket held with the clip.

The mask was first placed in the recess of the holder, the sample positioned over the mask aperture, and the clip placed against the sample. The openings for 2-56 screws on the holder allow it to be mounted on the Edwards evaporator in the KMF cleanroom. This holder design allows for electrode deposition on irregular sample shapes and various sample sizes.

The Edwards Auto 306 thermal evaporator, a turbo pumped system with base pressure 10^{-7} Torr, was used for Ti and Au deposition. The Au was deposited immediately after the Ti deposition with care taken to maintain a good vacuum in the system. The top electrode on the diamond growth surface consisted of Ti (13 nm) and Au (250 nm). The Ir electrode was Ti (10 nm) and Au (300 nm). The diameter of the evaporated electrodes was measured by optical microscope to be $495\pm10 \mu$ m. Figure 52 shows an optical microscope image of diamond sample (04-May-04) and top electrode. The dark horizontal line above the electrode is a partial cleavage fracture that occurred when the sample was accidentally broken into a few pieces.



Figure 52 Optical microscope images of diamond sample (04-May-04) and top Ti/Au electrode. Electrode diameter is approximately 0.5 mm.

4.2.3 Thermal Annealing

Following metal deposition, the sample was annealed at 650 °C for 20 minutes with an initial pressure of 2×10^{-8} Torr. The system (APX Multigun Sputtering Facility) is turbopumped and features a programmable SiC heater. The sample was mounted in its evaporation mask holder as the temperature was ramped up and down over a period of a few hr. The sample was cooled to room temperature in vacuum before exposing it to air.

4.2.4 Oxygen Plasma Treatment

Although an acid treatment is generally effective in oxidizing the diamond surface and destroying its surface conductivity, it is possible that the annealing procedure could alter surface termination. Therefore, the sample was subsequently exposed to an oxygen plasma. Exposure of the sample to an oxygen plasma for 30 seconds removes the surface conduction. A 30 s oxygen rf plasma treatment in a March Instruments PX-250 reactive ion etcher in the KMF was carried out. Conditions were: O₂ gas flow at 40 sccm and at 135 W power.

4.3 High Temperature Measurement and Thermal Isolation

A system was designed to allow heating of the diamond to at least 550 °C. Since diamond reacts with air above 500 °C, measurements were performed in a vacuum chamber. In a good vacuum, heat transfer by gaseous conduction and convection is negligible. Thus, small resistive heaters attached to a small sample holder, allowed heating to the desired temperatures with only modest power.

Other design considerations were: small sample holder size to minimize thermal time constants and weak thermal coupling to the sample holder environment to minimize heat leaks. The assembly was mounted in a small metal box with coaxial feedthroughs for the conductance measurement that also provided isolation from external electrical interference.

4.3.1 Vacuum System

An existing bell jar system was used to perform the experiments. It was equipped with an liquid nitrogen trapped, oil-based diffusion pump capable of 2×10^{-7} Torr. Coaxial cables were brought into the bell jar via a QF flange with 3 BNC coaxial feedthroughs. The feedthroughs were supplied with hermetic seals between the center conductor and insulator. Vacuum seals between the connectors and flange were made with Stycast-1266 epoxy. A shop drawing of the modified QF flange and connectors is shown in Figure 53.

Inside the bell jar, two standard RG-58 coaxial cables, with outer jacket removed, ran between the flange and an aluminum minibox with dimensions $4.3 \times 3.2 \times 1.6$ inches. The bell jar, with box inside, is shown in Figure 54. To connect the thermocouple wires and heaters another QF flange with pin connectors on the bell jar system was used.

Blank Qf50 flange + 3 holes for BNC connectors



Figure 53 QF flange design; for feed-through BNC connectors.



Figure 54 Bell jar showing QC flange, coaxial cables, and aluminum minibox inside.

4.3.2 Sample Holder

A schematic drawing of the sample holder is shown in Figure 55. The diamond sample sits on a 10 mm ×10 mm ×0.5 mm single crystal sapphire substrate. The sapphire not only provides a platform for the sample but also serves as a contacting surface for electrical leads. The low electrical conductivity of sapphire below 600 C, $<10^{-15} (\Omega-cm)^{-1}$ [69], allows electrical isolation between Au contact pads at several places on the substrate. Its nominal resistivity at room temperature is quoted as $>10^{18} (\Omega-cm)$ [70]. Its

high thermal conductivity implies a homogeneous temperature distribution and short thermal time constants. Heaters were attached to the sapphire from below. The components were held together with stainless steel spring clips since it was found that conductive adhesives, such as silver paint, were unsuitable owing to their high vapor pressure at high temperatures (T>400 $^{\circ}$ C).



- A: Diamond (thickness=20 micron)
- B: Ti(10 nm)/Au(250 nm) Top Electrode
- C: Au Wire (0.002 ")
- D: Ti(100 nm)/Au(320 nm) pad on Sapphire
- E: Sapphire (thickness=0.5 mm)
- F: Heater (thickness=0.15 mm)

Figure 55 Side view of the sample holder assembly (not to scale).

Electrical connections to the diamond electrodes are shown in Figure 56. The diamond was placed on a 3 mm diameter gold pad, deposited in the center of the sapphire, which served as an electrical contact to the back electrode of the diamond. A total of three Ti(10 nm)/Au(320 nm) pads were deposited. To contact the top electrode, a

 $50 \ \mu m$ Au wire was held against the electrode with a small stainless steel spring clip. A sapphire chip between the sample and the clip prevented damage to the Au electrode.

Owing to the small size of the diamond crystal, it was not possible to mount a thermocouple directly on the sample. Instead, a spotwelded thermocouple junction of 5 mil (1 mil = 0.001 in = 25 μ m) Alumel and Chromel wires (thermocouple type-K) was clipped to the sapphire substrate, see Figure 57.



Figure 56 Detail of the electrical connections to the diamond sample.



Figure 57 Top view of the sample on the sapphire substrate.

Figure 57 also shows the thermocouple position on the substrate, the two leads to the diamond sample, and the three Pt miniheaters protruding from beneath the sapphire substrate. A 50 μ m Au wire, clipped to the central Au pad in contact with the Ir side of the diamond sample, ran directly to the center conductor of a BNC connector in the minibox. The Au contact from the top diamond electrode was run directly to the center conductor of the BNC connector on the opposite side of the minibox.



Figure 58 Photograph of assembled sample holder with all connections in place. The top of the minibox has been removed for clarity. The sample holder is suspended by Chromel wires that run from substrate clips to the minibox. Gold electrical leads run from the diamond to BNCs (one is visible on the right). Thermocouple and heater leads pass through small holes in the sidewalls of the box. A radiation shield is mounted above the floor of the box.

A stainless steel clip (Clip 1) was used to hold the heaters, stainless steel radiation shield, Cu-sheet, the sapphire substrate, and the sample together. The assembly was suspended with wires of Chromel, a low thermal conductivity metallic alloy, inside an Al-shielded box (Figure 58).

4.3.3 Thermal Isolation

The two major contributors to heat transfer from the sample holder assembly to its environment are by conduction through leads and by radiation. To minimize radiative losses, the size of the sapphire substrate was made as small as practicable. An estimate of heat transfer by radiation between the sample holder at 600 °C and the minibox at 25 °C was made using $\dot{Q} = \sigma \epsilon A \left(T^4 - T_0^4\right)$ [71], where σ , ϵ , A, T, and T₀ are Stefan's constant (5.67×10⁻⁸ W/m²K⁴), emissivity, area, and system temperature and room temperature, respectively. Surface areas of the high temperature components are: sapphire substrate (10×10×0.5 mm³), stainless steel clip (Clip 1, 4 mm×24 mm×0.004 in), and a sapphire disk (9mm×0.005 in) at the bottom of the assembly. Radiated powers of 1.8, 1.3, and 0.8 Watts at 600 °C, respectively, were calculated, totaling 3.9 W. Experimental data showed that 4.3 W was needed to reach 600 °C, in remarkably good agreement with the estimate considering that emissivities are probably known only to 20-30%. A plot of heater power vs. temperature is shown in Figure 59.



Figure 59 Heater power versus temperature.

To minimize conductive losses, the sample assembly was suspended by wires connected to the minibox. Conductive heat transfer resulted from: (1) two Chromel wires (10 mil dia, 5 in long) holding the setup, (2) two Au wires (2 mil dia, 2 in long) used for wiring the contacts, (3) two Cu wires (5 mil dia, 8 in long) spot welded to the heater leads, and (4) two 5 mil, 7 in long thermocouple wires (Chromel-Alumel). Estimates of heat transfer using $\dot{Q} = K(A/L)\Delta T$ [71] was made, where K, A, L, and ΔT are the thermal conductivity, area, length, and temperature difference. Using K_{Chromel}=19 W/m-K, K_{Au}=320 W/m-K, K_{Cu}=400 W/m-K, and K_{Alumel}=32 W/m-K, the thermal losses through Chromel, Au, Cu, and thermocouple wires were estimated at 0.01, 0.02, 0.04, and 0.003 W, respectively. Thus conductive losses through all wires were virtually negligible

relative to radiative losses throughout the temperature region explored. These losses were less than <1% of the applied power, 4.3 W, required to heat the setup to 600 °C.

4.3.4 Temperature Measurement

Temperature of the sample was measured with a K-type (Chromel-Alumel, diameter 5 mil) thermocouple in contact with the surface of the sapphire substrate. This thermocouple was mounted at one of the corners of the sapphire with a stainless steel clip (Clip-2). The temperature of the Al-box was measured with another K-type (Chromel-Alumel, diameter of 10 mil) thermocouple. This thermocouple was held at one of the corners on the top of the Al-box under a screw head. In one of the runs, the temperature of the Al-box was measured as 40 °C when the temperature of the sapphire was at 400 °C.

4.3.5 Heaters

Platinum micro-heaters (Heraeus, Pt-100) were used to heat the sample. A drawing of the heater is shown in Figure 60. These are thin-film Pt heating elements encapsulated in a ceramic alumina casing. Three heaters, wired in series, were attached to the underside of the sapphire substrate with clips. Here, it was possible to make connections between heaters by spot-welding their leads. A Cu-sheet (10mm×8 mm× 0.125 mm) was sandwiched between the heaters and the sapphire substrate to improve thermal contact. A stainless steel sheet (8mm×10 mm ×0.2 mm) placed on the other side of the heaters served as a radiation shield.



Figure 60 Platinum micro-heater (Heraeus, dimension in mm).

Heater resistance was nominally 7 Ω at room temperature, increasing to 21 Ω at 600 °C. The heaters are specified for use up to 500 °C and a maximum current of 2 A. Nevertheless, it was found that three heaters, wired in series, can heat the sapphire substrate to 600 °C. Series connection yields lower current for a given power, so that the Cu lead wires of the heaters do not exceed their burn-out rating. An initial experiment, using only a single heater, found that the heater burned out at 3.7 W.

4.3.6 Thermal Time Constant

The thermal relaxation time τ between an object of heat capacity C at a given temperature, connected to its environment at a different temperature by a thermal resistance R, is given by $\tau = RC$. The internal time constant τ of the sample assembly is determined by properties of sapphire and the interfacial thermal resistance between sapphire and diamond. The time constant between the sample assembly and its environment τ_e was found by introducing an abrupt change in the heater power and measuring the thermocouple voltage as a function of time. An exponential function was fit to thermocouple voltage vs. time data at different temperatures (Figure 61). The time

constant is strongly temperature-dependent. At 283 °C, $\tau = 81$ s; at 502 °C $\tau = 45$ s. Since the thermal resistance of the leads is essentially temperature independent, or increases slightly with temperature, it cannot be responsible for the relaxation time. On the other hand, radiative losses increase strongly with temperature, leading to a shortened thermal relaxation time.



Figure 61 Thermocouple voltage, corresponding to temperature, versus time between: (a) 496 and 508 °C, and (b) 265 and 300 °C.

4. 4 High Resistance Measurement Considerations and Electrical Isolation

4.4.1 Current Leakage

Low current measurements require that current paths other than those through the sample be eliminated or minimized. Current leakage may occur in various forms: (1) Current may leak at the instrument input due to internal instrument circuitry when voltage biased. This is called input bias current. Its value is very small, less than 3 fA for the electrometer (Keithley 6514) used for current measurement. (2) Current may leak through the electrometer's internal circuitry, through the insulator and devices inside the instrument, even when it is open. This can be partially nulled by zero check of the instrument.

Another source of error in current could be voltage burden, which is caused by a small voltage drop at the input terminals of the instrument. Voltage burden values are given in the manual of the electrometer for various current ranges. The voltage burden introduces an error of $(V_B/V_S)100\%$, where V_B and V_S are voltage burden and source voltage, respectively. The maximum voltage burden of <100 μ V is given for 200 pA range. The minimum voltage source for the measurements was 0.1 V. Using these voltages, the voltage burden error was estimated to be <0.1% of the measured current. This did not affect our measurements.

The current leakage problem in our measurement circuit was mainly eliminated by placing the electrometer at the low side of the measurement circuit. Therefore, only the current passing through the sample went to the electrometer, without the addition of any leakage current. This can be seen in the circuit diagram in Figure 65. Also, the top electrode was wired directly. This assured that the current went to the sample and that the measured current was not leakage current from other components.

Testing the circuit with 10 G Ω , 100 G Ω , and 1T Ω standard resistors showed that the leakage currents did not interfere with the measurements. The circuit was tested by performing I-V measurements on these standard resistors. The given tolerances of the standard resistors were 1%, 1%, and 5%, respectively. The measured resistance for the 10 G Ω resistor was found to be 9.97±0.01 G Ω . The measured resistance for the 100 G Ω resistor was found to be 99.7±0.1 G Ω . The measured resistance for the 1 T Ω resistor was found to be 1.14 ± 0.01 T Ω . The 9.97 and 99.7 G Ω measured values differ from the 10 and 100 G Ω values by <0.3%, within the specified 1% tolerance of these standard resistors. The error of the measured value of the 1 T Ω resistor is 14%. This is not due to the inaccuracy of the measurement, which is 1% of the reading for the electrometer pA range. This error was not due to Johnson noise, as the peak-to-peak Johnson noise for a 1 T Ω resistance is estimated at 10⁻¹⁷ A using $I_{th-Noise} = 5\sqrt{4k_BTB/R}$, where $I_{th-Noise}$, k_B , T, B, and R are peak to peak thermal noise current, Boltzmann's constant (1.38×10^{-23}) J/K), the absolute temperature (K), the band width (Hz), and the resistance (Ω), respectively [70]. The bandwidth was estimated using $B = \pi/4\tau_{cir} = \pi/(4 \times 260) = 0.003$ Hz, where τ_{cir} is the circuit time constant. This is much smaller than the electrometer reading error for pA range current, 1% of reading. Since this error is systematic, it is most likely that the error is due to a miscalibrated resistor.

4.4.2 Noise

Noise can be internal or external to the measurement system. The origin of the internal noise is in the measurement system such as thermal noise (Johnson noise), shot noise, and flicker noise. The external noise is mostly 60 Hz pickup, atmospheric noise, and cosmic ray noise. Reducing the noise level is very important in low current measurement. The major source of external noise is background noise (60 Hz radiation). This is reduced by placing the sample setup in an aluminum box, using coaxial cables and connectors in the circuit, and grounding the low end of the circuit.

The most common form of the internal noise in a resistor is thermal noise, which is temperature dependent. The thermal noise for the diamond sample was estimated from: $I_{th-Noise} = 5\sqrt{4k_BTB/R}$. The bandwidth, B, was estimated using $B = \pi/4\tau_{cir}$ [70] to be 0.1 Hz with estimated circuit time constant, τ_{cir} , of 10 seconds at 300 °C. The bandwidth at higher temperature was determined by the longer time constant of the integration time, $\tau_{int} = 6$ (power line cycle) × (1/60Hz) = 0.1 s. The bandwidth was estimated using $B = 0.314/\tau_{int}$ [70] to be 3 Hz at 550 °C. Using these bandwidths, the thermal noise for 300 and 550 °C was found to be approximately 1×10⁻¹⁵ A and 2×10⁻¹³ A, respectively. The thermal noise at 300 °C and 550 °C is not significant compared with the accuracy of the current at those temperatures, 10⁻¹⁴ A and 10⁻¹¹ A, respectively.

Shot noise arises from fluctuations in the number of carriers due to charge quantization. The shot noise was estimated from: $I_{sh-Noise} = \sqrt{2qIB}$ [72], where q and I are the charge of the electron, and current, respectively. The shot noise for 300 and 550 °C was found to be 2×10^{-16} A and 10^{-13} A, respectively. The shot noise at 300 °C is about

at the detection limit of the electrometer, 10^{-16} A, but is much smaller than the error in current reading, ~0.01%. The thermal noise at 550 °C is above the detection limit, but is not significant compared with the measured current, ~0.001 %.

4.4.3 Voltmeter Input Resistance

The input resistances of the voltmeter in parallel with the sample can introduce an error to the current reading of high resistance materials. The size of this error depends on the input resistance of the voltmeter and the sample. To reduce this error the input resistance of the meter must be much larger than that of the sample. For example, for an error less than 1% the input resistance must be 100 times larger than the impedance of the sample.

$$I_m = I_s \frac{R_{in}}{R_{in} + R_s}$$

where I_m , I_s , R_{in} , and R_s are the measured current, the applied current, the input resistance, and the resistance of the sample, respectively.

Many voltmeters or multimeters have input resistance of 10 G Ω . This value can cause significant errors for our sample with resistance > 100 T Ω at room temperature. This error is eliminated in our measurements by placing the voltmeter--with an input resistance of 10 G Ω for--in parallel with the electrometer and sample (Figure 65, circuit diagram). This eliminates the current error, and there will be no voltmeter error because the electrometer has approximately zero resistance.

4.4.4 Time Constant

Another important concern in high resistance measurements is the electrical circuit time constant, $\tau = RC$, where τ , R and, C are the time constant, total resistance,

and capacitance of the circuit, respectively. Reducing the error in the current reading to <1% requires waiting five time constants. The main source of the capacitance in the circuit is the capacitance of the coaxial cables. The capacitance of the sample was estimated to be $C = k\varepsilon_0 A/l \sim 1$ pF, where C, k, ε_0 , A = 0.5 mm, and l = 0.02 mm are the capacitance, diamond dielectric constant (6-7), space permittivity (9×10⁻¹² F/m), area of the electrode, and the sample thickness, respectively. This was insignificant compared with the capacitance of the coaxial cables, a few hundreds of pF. The capacitance in the coaxial cables (~30 pF/ft) couples with the large resistance of the sample (>10¹⁴ Ω) at room temperature, resulting in a very long time constant at room temperature. Therefore, minimizing the coaxial cable lengths of the circuit reduces the time constant.

The capacitance of the measurement circuit is reduced by grounding the center conductor at the low side of the circuit. The length of the cable without grounding was 14 ft, which was reduced to 5-6 ft resulting in a shorter time constant. Even so, a 5-6 ft cable length (150-180 pF) was estimated to give a very large time constant ~4 hours making a measurement difficult. This problem is alleviated at high temperatures as the sample resistance decreases. The time constant decreases significantly, for example, to less than one second at 300 °C.

4. 5 DC Measurement

4.5.1 **Probe Station Circuit**

To test the surface conduction before and after the oxygen plasma treatment, I-V measurements were performed on the sample in air at a probe-station, which was equipped with a Keithley 236 measurement system. Using this unit, the voltage was sourced and swept across the desired voltage range and the current was measured with

the same unit simultaneously. A schematic of the circuit is shown in Figure 62. The data was recorded by a computer.

For these measurements, the sample was cleaned in acetone and methanol. Then four electrodes (Ti/Au) were deposited on the sample. A silicon substrate with Au-pad was placed on the metal base inside the metal box (shield box) of the probe-station for both the purpose of electrical isolation and to contact the iridium, if needed. Then, the sample was placed on the Au-pad/silicon substrate. For the measurements, two probes were placed on either of two electrodes on the top surface or one on the top and the other on the Au-pad on the silicon (iridium contact) (Figure 63 and 64). These measurements were performed in air.



Figure 62 Schematic of the probe-station circuit.



Figure 63 Diamond sample on the Au-pad of the silicon substrate.



Figure 64 Sample setup at the probe-station.

4.5.2 Measurement Setup

The components in the high temperature circuit are: (1) a variable DC voltage source providing voltages between -12 and +12 Volts, which is made with 7 1.5 Volt Li batteries in series, a potentiometer, and a three-position switch, (2) a multimeter (HP-
3457A) with 10 μ V resolution and 0.002% accuracy of ≤ 3 V, (3) an electrometer (Keithley 6514) with 0.1 fA resolution and 1% accuracy, and (4) an aluminum box (4.3 $\times 3.2 \times 1.6$ in³) that contains and shields the sample setup. The circuit diagram can be seen in Figure 65. The electrometer is placed at the low side of the circuit in series with the sample and the battery allowing current measurement independently. This avoids current leakage from the cables into the electrometer. The multimeter is placed in parallel with the sample and electrometer; this configuration eliminates the multimeter as an alternate current path around the sample under test. The input resistance of the multimeter is in parallel, and is shown as R-input. The resistance and capacitance due to coaxial cables, R_{leakage} and C_{leakage} , are in parallel as well. The DC source is a voltage divider that has a potentiometer and battery, which allows setting the voltage. The DC source has a three positions switch by which the polarity can be reversed or set to zero. The variable DC source is shown with the arrow on the battery in the circuit diagram. A more detailed schematic of the measurement system is shown in Figure 66. All the cables are coaxial, with lengths shown in feet.



Figure 65 DC circuit diagram of the measurement system.



Figure 66 Schematic of the DC measurement system.

Another circuit diagram is shown in Figure 67 that includes all the electronics. The upper part shows the thermocouple circuit including the resistance of the thermocouple and the voltage created by the thermoelectric effect. The switch on the upper left side of the diagram belongs to the two-channel multimeter, which allows reading the voltage corresponding to the temperature and the bias voltage to the sample.



Figure 67 Circuit diagram: measurement circuit, microheater circuit, thermocouple circuit, diffusion pump circuit, and DC-Source (voltage divider).

The lower part is the microheater circuit in series with a DC power supply and a digital voltmeter for current reading, and in parallel with a digital voltmeter for voltage reading. The lower right side is the diffusion pump heater in series with its ac source. The details of the DC source (voltage divider) is shown on the mid-right hand side of the Figure 67.

The measurements were performed as follows: after reaching a base pressure of 10^{-6} Torr, the heater was gradually heated to 300 °C in 2 hours. When the temperature settled, data were taken. The data were acquired by pc running Labview code. The code records the time, the temperature, the voltage, and the current. The number of current readings can be entered as required. The code is shown in Appendix C.

The current readings were taken for each temperature after setting the voltage manually. The voltage was first set to zero, and increased to higher values for positive polarity, and was lowered back to zero. Similarly, negative voltage was applied, and the current readings were taken. After taking data at 300 °C, the temperature was increased to 350 °C, and I (V) measurements were similarly performed. This was continued up to 550 °C. Then, the temperature was lowered and data were taken while cooling the sample down for comparison with the heating data.

Chapter 5 Results

In this chapter, measurements of the temperature-dependent conductivity of heteroepitaxial diamond are presented. The current-voltage (I-V) characteristics show a linear (Ohmic) relationship for voltages |V| < 1 volt at temperatures above 250 °C. After extracting the conductance from these data, the bulk conductivity of diamond is calculated. At temperatures above 300 °C, the conductivity exhibits a thermally activated behavior with a single activation energy.

5. 1 DC results

In this section, it is demonstrated that the conductance of CVD diamond measured perpendicular to the surface using front and back contacts can be ascribed to current transport in the bulk diamond. Surface conductance is shown to be largely eliminated by sample processing. In certain temperature and bias regions, Ir and Ti/Au contacts are shown to be Ohmic.

5.1.1 Surface Conductance

I-V measurements at room temperature, in the probe station, taken between top and bottom contacts before and after oxygen plasma exposure for two top electrodes (RT and RB electrodes in Figure 63- probe station system) are shown in Figure 68 and 69. With bias in the range of ± 3 V, the current is in the range of μ A prior to oxygen treatment but is reduced to the noise level, 0.1 pA, following treatment. This is interpreted as elimination of surface conduction, a result of transforming the hydrogen-terminated diamond surface to an oxygen-terminated surface. However, no conclusions about the actual conductance of the sample at room temperature could be drawn, other than it is less than or of order 10^{-13} (Ω^{-1}). This indicates that bulk conduction could not be measured at room temperature with this system.



Figure 68 I-V before exposure to oxygen plasma for two top electrodes.



Figure 69 I-V after exposure to oxygen plasma for two top electrodes.

5.1.2 Estimate of Surface Conductance

To estimate the magnitude of any remaining surface leakage following the oxygen plasma treatment, additional measurements in vacuum were made using combinations of the two top electrodes and the back electrode. Test measurements were performed near 220 °C. First, the current was measured with ± 5 V bias between the two top electrodes (Figure 70) with the back contact floating. Then, the measurement was repeated with the back contact grounded (low side). In both cases, the left electrode was connected directly to the electrometer, see Figure 71.

Currents at 5 V (-5 V) were approximately 0.3 pA (-0.4 pA), with a floating back contact (Figure 72). With the back contact grounded, the current fell below the

electrometer noise level for pA range, approximately 0.01 pA. The small offset current in Figure 72 is a result of a thermoelectric effect.

It is now argued that the observed current is not from surface conductance but it represent transport through the bulk. The circular contacts are separated by a distance of 0.4 mm, measured from the closest electrode edges. The shortest distance between top and back contacts is 20 µm. Let us assume first that a substantial surface conductance exists. The shortest path connecting the two top electrodes is not solely on the surface, but to the closest edge of the sample, across the edge, through the low resistance back contact, and then via a similar path to the other top electrode. This surface path on the diamond has a total length of about 0.2 mm. If there were surface leakage by this path, by connecting the iridium contact to the low (ground) potential, the current registered would be about one third the value measured with a floating back contact, approximately 0.1 pA. Instead, it was found that the current remained at the noise level of the electrometer, even with ±12 V bias applied when the back contact was grounded. It was concluded that the surface leakage at this temperature is below the detectable level of the measurement circuit under these conditions. The conclusion is that the measured current was due to bulk conduction, and the bulk conductance is much larger in the perpendicular direction than the lateral direction



Figure 70 Heteroepitaxial diamond with two Ti/Au electrodes- with diameter of -0.38 mm- on the top surface and iridium on the back.



Figure 71 Circuit for measurement with two top electrodes; the bottom electrode can be switched between a floating and grounded state.



Figure 72 Total current I vs. time at ± 5 V bias with floating back contact (above) and with grounded back contact (below).

Evidence for surface contamination by silver paint

In a preliminary set of I-V measurements, using the back contact and one of the top electrodes, the effective conductance was observed to increase abruptly from 7×10^{-10} (Ω^{-1}) at 350 °C to 6×10^{-7} (Ω^{-1}) at 400 °C, three orders of magnitude increase for a temperature change of 50 °C. This is surprising inasmuch as the conductance increased from 3×10^{-11} (Ω^{-1}) at 300 °C to 70×10^{-11} (Ω^{-1}) at 350 °C, a factor of 25 for the same temperature difference, see Figure 73. Having increased the temperature to 400 °C, measurements at lower temperature did not yield significantly lower conductances. After cooling to room temperature and following chemical cleaning of the sample, the low conductance was restored, yielding currents at the noise level, about 10 fA. The near irreversible increase in the conductivity is thought to be due to surface contamination caused by silver paint. It is suggested that components in the Ag paint can evaporate, or the Ag may sublime, leading to a thin conductive layer on the diamond surface. As a result of this finding, it was decided that all high temperature contacts should be made without adhesives, using only highly temperature stable components.



Figure 73 I-V at 300 °C, 350 °C, and 400 °C.

5.1.3 I-V Characteristics

The next section describes successful experiments at temperatures above 250 °C that were used to obtain the diamond conductivity. Two sets of I-V measurements were performed. In Run-1 (25-Jan-05), the sample was heated from room temperature to 450 °C, and in Run-2 (30-Jan-05) a similar procedure was followed with a maximum temperature of 545 °C. The I-V characteristics showed that the bottom and top contacts were Ohmic between 250 and 550 °C for voltages between -0.5 and 0.5 volt. The I-V plots from Run-2 are shown in Figure 74-81 for heating cycle. The conductance at different temperatures was found from a linear fit of I vs. V using y = A + Bx (Origin program) with voltages between +5 V and -5 V, where *B*, the conductance G, and A, the

zero-offset, are the fit parameters. The results are shown in Table 6 for Run-2. Conductivity is found using electrode diameter of $d = 495\pm4 \mu m$ ($\Delta A/A=2\%$) and thickness of $t = 19\pm1 \mu m$ ($\Delta t/t = 5\%$). Conductivity is found using $\sigma = G(t/A)$, where G, t, and A are the slope of the I-V plot, the thickness of the sample, and the area of the electrode, respectively.

Temperature	B=Conductance	A=Zero-Offset	Conductivity	Duration
(°C)	(Ω ⁻¹)	(A)	(Ω.cm) ⁻¹	(min)
265±2	$1.5 \times 10^{-12} \pm 6 \times 10^{-13}$	2×10 ⁻¹⁴	1.5×10 ⁻¹²	35
301±2	$6.80 \times 10^{-12} \pm 3 \times 10^{-14}$	2×10 ⁻¹⁴	6.80×10 ⁻¹²	40
350±2	5.09×10 ⁻¹¹ ±2×10 ⁻¹³	2×10 ⁻¹⁴	5.09×10 ⁻¹¹	30
399±2	$3.14 \times 10^{-10} \pm 1 \times 10^{-12}$	4×10 ⁻¹⁴	3.14×10 ⁻¹⁰	40
428±2	8.58×10 ⁻¹⁰ ±1×10 ⁻¹²	1×10 ⁻¹³	8.58×10 ⁻¹⁰	20
452±2	1.946×10 ⁻⁹ ±2×10 ⁻¹²	3×10 ⁻¹³	1.95×10 ⁻⁹	30
495±3	7.724×10 ⁻⁹ ±6×10 ⁻¹²	1×10 ⁻¹²	7.72×10 ⁻⁹	20
545±2	3.197×10 ⁻⁸ ±2×10 ⁻¹¹	5×10 ⁻¹²	3.20×10 ⁻⁸	35

Table 6 Data from linear fits to I-V for Run-2.

The error bars in the I-V plots are found as the sum of the standard deviation in current over 10 readings and the instrument error. The measurement errors and the instrument errors are used to find the total error, ΔI , using $\Delta I = \sqrt{\sigma_I^2 + \sigma_M^2}$, where σ_M is the measurement noise standard deviation (noise from environment) and σ_I is the instrument noise standard deviation.

The instrument noise is calculated from table values given in the electrometer manual. These values are dependent on the measurement range. As an example, for 1 pA operating in the 20 pA range, the table values for percentage of current reading, count, and resolution are given as 1%, 30 counts, and 100 aA, respectively. This yields an instrumental noise standard deviation of 0.013 pA, as shown in the following equation:

$$\sigma_I = (\% rdg) \times I_{ave} + count \times resolution$$

$$\sigma_I = \%1 \times (10^{-12}) + 30 \times (100 \times 10^{-18}) = 0.013 \text{ pA}$$

The error bars are larger for larger current values in the same range of the electrometer. The total current error readings were calculated as < 1 % in all experiments.



Figure 74 I-V at 265 °C: Run-2



Figure 75 I-V at 301 °C; Run-2.



Figure 76 I-V at 350 °C; Run-2.



Figure 77 I-V at 399 °C; Run-2.



Figure 78 I-V at 428 °C; Run-2



Figure 79 I-V at 425 °C; Run-2.



Figure 80 I-V at 495 °C; Run-2.



Figure 81 I-V at 545 °C; Run-2.

Resistance versus temperature is plotted in Figure 82 for the heating cycle in Run-1, and for heating and cooling cycles in Run-2. The two heating Runs are in good agreement for T>350 °C over much of the temperature range although for T<300 °C a larger discrepancy is evident. It can be seen that there is a difference in the resistance between cooling and heating in Run-2. However, since the circuit time constants increase at lower temperatures it may be that data at 300 °C and 265 °C in Run-2 were taken before settling. It is also possible that the lower resistance during the cooling cycle may be due to changes in the diamond surface at high temperatures that increase surface conductance relative to the bulk conductance. The annealing that occurs at the highest temperatures might alter the interface by increased formation of TiC.



Figure 82 Resistance versus temperature for Run-1 (Heating1) and Run-2 (Heating2 and Cooling2).

The I-V characteristic does not show Ohmic behavior at 300 °C for voltages >1 V (Figure 83). However, it is anti-symmetric with respect to the current axis. This behavior is a field effect. No convincing explanation for this non-Ohmic behavior has been advanced for highly resistive diamond. The scale at which nonlinearity sets is close to that expected for potential barriers at interfaces, a few eV. As the diamond band gap is 5.5 eV, voltages above 5 V would also lead to strong nonlinearities.



Figure 83 I-V at 300 °C for voltages between -12 and 12 volts.

5.1.4 Temperature Dependent Conductivity of Heteroepitaxial Diamond

The natural logarithm of σ versus *1/T* is plotted for the two sets (Figures 84 and 85). If σ is thermally activated, then we expect it to follow the functional form,

$$\sigma = C \exp(-E/k_B T)$$

where E is the activation energy, k_B is the Boltzmann constant and T is temperature in K. Since $\ln \sigma = \ln C - E/k_BT$, we expect a straight line in a plot of $\ln \sigma$ vs. 1/T. An unweighted linear fit was used to find the slope, where $B = E/k_B$ and $A = \ln C$ are the fit parameters. For both Runs, the fits yield $E = 1.40 \pm 0.03$ eV. The details of the fits are shown in Table 7. Data in Run-2 at 265 °C are excluded from the fit as the data at that temperature were taken before current settling. The ranges of the fits are from 300 to 453 °C and 300 to 545 °C in Run-1 and Run-2, respectively. Conductivity of heteroepitaxial diamond changes from $5 \times 10^{-12} (\Omega \text{-cm})^{-1}$ at 300 °C to $2 \times 10^{-9} (\Omega \text{-cm})^{-1}$ at 453 °C, by three orders of magnitude, in the first run, and from 7×10^{-12} $(\Omega \text{-cm})^{-1}$ at 300 °C to $3 \times 10^{-8} (\Omega \text{-cm})^{-1}$ at 545 °C, by four orders of magnitude, in the second run.

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Run no.	T _{min} (°C)	$T_{max}(^{\circ}C)$	No. of Points	A=ln C	B= <i>E/K</i> (T)	<i>E</i> (eV)
1	301	453	4	2	16182±297	1.40±0.03
2	301	545	7	3	16269±328	1.40±0.03



Figure 84 Conductivity of heteroepitaxial diamond versus inverse temperature; Run-1.



Figure 85 Conductivity of heteroepitaxial diamond vs. 1/T; Run-2.

Chapter 6 Discussion of Results/Analysis6. 1 Comparisons with other measurements

The temperature-dependent conductivity of heteroepitaxial diamond is compared here with natural diamond: two Type IIa crystals (containing only trace amounts of nitrogen) and one Type Ib crystal (with 50-100 ppm nitrogen) diamond. Two different groups obtained results for the DC conductivity as shown in Figure 86. A single slope in the $\ln\sigma$ vs 1/T plot is observed for each sample, indicating an activated process with a single activation energy. Three of the samples, the heteroepitaxial crystal and two Type IIa crystals, show conductivities within one order of magnitude of each other at the same temperature. The conductivity of the Type Ib diamond crystal is larger by four orders of magnitude. Although detailed information on impurity content is not available, the difference is most likely due to its higher nitrogen concentration.

Although all four samples show activated behavior of the conductivity, the activation energies differ and the measurement temperature regions are somewhat different. For heteroepitaxial diamond, we found an activation energy of 1.4 ± 0.03 eV between 300 and 550 °C. Vandersande [55]found 1.4 eV for Type IIa diamond between 300 and 1200 °C. Borst [60]quoted an activation energy of 1.7 eV for Type IIa diamond between 180 to 350 °C and the same for Type Ib diamond between 100 to 280 °C.

To see if some of the differences had occurred in the data analyses, we performed a least squares fit to the data taken by the other groups in the temperature region shown in Figure 86. For Type IIa diamond, activation energies of 1.46 ± 0.02 eV and 1.67 ± 0.01 eV were found for the data of Vandersande and Borst, respectively, and 1.8 ± 0.04 eV for

Borst's Type Ib diamond. Possible origins of these activation energies are discussed in the next section.



Figure 86 Comparison of conductivity vs. 1/T between heteroepitaxial \bullet , natural type IIa Δ [55], type IIa \Box and type Ib diamond \blacksquare [60].

6. 2 Origin of activated behavior

In general, the temperature-dependent electrical conductivity of diamond might be the result of several different sources that introduce carriers into current-carrying states. As noted in Chapter 2, even a small concentration of defects or impurities can strongly influence electrical transport in semiconductors. In the case of diamond, there are relatively few impurities that can be incorporated into the lattice owing to the small C-C interatomic distance. These are generally light atoms, such as H, B, N, O, P, Si, etc. In addition, there are native defects that may exist alone, in clusters, or in combination with impurities. Examples are carbon interstitials and carbon vacancies. These may be located randomly or may be associated with structural defects, particularly dislocations.

Information about impurity and defect states is obtained from a number of sources: from measurements such as those described in this thesis, from optical spectroscopy (including cathodoluminescence, photoluminescence, and photothermal absorption) and from electron spin resonance (ESR), to mention some of the most useful. These methods are often complementary inasmuch as some centers may be invisible to certain probes. For example, electron spin resonance is only sensitive to defects that have unpaired electron spins. Furthermore, a defect may exist in more than one charge state. That state could be controlled by interactions with other defects.

Thermally activated conductivity by intrinsic carriers, with an activation energy of $E_g/2 = 2.7 \text{ eV}$, is not observed. The activation energies that are observed, in the range of 1.4 to 1.7 eV, must have other origins, presumably from localized impurity states and/or defects whose energy levels lie within the bandgap of diamond. As noted previously, an activation energy of 1.7 eV has been related to the substitutional nitrogen donor. This activation energy was found by Borst [60] for Type Ib diamond (50-100 ppm nitrogen) and it is reasonable to suppose that nitrogen could be contributing electrons to the conduction band, although there is no independent knowledge of the carrier density. It is somewhat surprising that the Borst result for Type IIa diamond also indicates an activation energy near 1.7 eV inasmuch as there should be < 1 ppm nitrogen in this crystal. Since there is about two orders of magnitude difference in nitrogen concentration between the two Borst crystals, the observed conductivity difference of four orders of

magnitude would appear to be inconsistent with a single type of dopant or defect. This is especially true if the carrier mobility increases significantly in the purer Type IIa crystal, owing to the lower probability of scattering by neutral or charged N impurity states.

The result for Type IIa by Vandersande[55], 1.4 eV, does not agree with the Borst result, 1.7 eV, on Type IIa diamond. Since detailed impurity analyses are not available for these crystals, it is entirely possible that different concentrations of trace impurities are responsible for the different activation energies. It should be noted that the Borst crystal has a conductivity at least an order of magnitude greater than the Vandersande crystal. Also, the temperature ranges of the two measurements do not overlap appreciably.

If we accept that the Vandersande crystal is appreciably purer than the other natural diamond crystals measured, its comparison with the heteroepitaxial crystal is the most appropriate. Our finding of an activation energy of 1.4 eV for heteroepitaxial diamond, in close agreement with the Vandersande result for Type IIa diamond, is therefore striking. Since the heteroepitaxial process used here does not intentionally introduce nitrogen into the growth process, the crystal is expected to exhibit nitrogen concentrations below 1 ppm, as does the clean Type IIa diamond. Note that the statistical error bars on the fits are sufficiently small to rule out overlap with the Borst results.

One impurity that is introduced into all CVD diamond is hydrogen. Measurements of the hydrogen concentration in a heteroepitaxial sample grown three years earlier by the same process in the same reactor exist. The concentration was estimated from the absorption strength of the infrared-active CH_2 vibrational doublet in the vicinity of 2900 cm⁻¹. The result of 360 ppm hydrogen is within a factor of 2-3 of the

typical residual hydrogen content of CVD diamond and thus appears reasonable. There may be more hydrogen present that is not detected since it may not contribute to vibrational modes in this spectral region. Natural diamond may also contain high concentrations of hydrogen.

The role of hydrogen in diamond is particularly intriguing as it is known to complex with donors and acceptors. In the case of B-doped diamond, hydrogen can effectively passivate the boron acceptor. More relevant to the present situation is the case of the hydrogen-vacancy center. Unlike Si:H [73], the hydrogen in diamond does not form in a bond-centered configuration, i.e., in a position midway between two carbons. Instead, it appears that a more favorable situation occurs when a carbon vacancy occurs. Here, the hydrogen bonds to a single carbon, leaving two bonded carbons and carbon dangling bond. The electron on the dangling bond renders the defect paramagnetic allowing ESR to determine the symmetry properties and geometry of the state. This has been facilitated by the observation of weak sidebands to the main $\Delta m = 0$ transition brought about by hyperfine coupling between the electron and the nuclear spin of the hydrogen. [74]

This defect, referred to as the H1 hydrogen-vacancy center, is remarkably stable: it does not show signs of annealing out at temperatures up to 1500°C. Although it was first investigated[74] in polycrystalline diamond leading to the suggestion that the center is associated with distorted bonds at grain boundaries, it has more recently been studied[75] in CVD heteroepitaxial diamond similar to the material studied in the present investigation. It was found from ESR that the hydrogen concentration is about 200 ppm, representing only hydrogen associated with the H1 center.

The formation of a paramagnetic state by introducing hydrogen into a semiconductor appears to be contrary to conventional practice, in which hydrogen is used to passivate dangling bond states in materials such as Si or SiO_2 . In diamond, it would appear that the environment in the vicinity of the carbon vacancy is somewhat distorted, yielding a single site most favorable to forming a C-H bond. Two of the remaining carbons bond to each other leaving a dangling bond state at the other carbon. Apparently, there is not enough space for a second hydrogen to passivate the dangling bond. Thus, the net effect of hydrogen is to create a paramagnetic center in diamond.

In the situation in which both hydrogen and nitrogen are present in diamond, it was found [74]that increased hydrogen concentrations causes a decrease of the neutral nitrogen donor. At H concentrations above 10 ppm, the nitrogen donor is reduced by over an order of magnitude, suggesting that hydrogen may directly passivate the nitrogen or that H1 may act as a compensating center for the nitrogen. Despite considerable effort using density functional theory to calculate defect energy levels, including H1 in diamond, the methods are not sufficiently accurate to warrant serious comparison with substantiated experimental data. At this point, there is no evidence, experimental or theoretical, that can be used to confirm the assignment of an H1 state approximately 1.4 eV from a band extremum.

Native defects, those that are independent of impurities, appear to be electrically active in diamond. For example, the single vacancy has an acceptor level that lies near midgap. Single and double interstitial defects appear in various configurations but all appear to be quite deep, making assignment to the 1.4 eV state improbable. It would be

helpful if information were available on the sign of the charge carriers as well as the concentrations of impurities known to produce shallow levels [60, 64].

In conclusion, the single activation energy of 1.4 eV found in heteroepitaxial and natural diamond argues for a single type of electrically-active defect that is responsible for the thermally activated conductivity in these materials.

6. 3 Outlook

There are a number of questions that remain to be answered if the origin of the thermally activated conductivity of heteroepitaxial diamond is to be understood. For example, what is the carrier type, the carrier mobility, and the origin of the defects or impurities that contribute the carriers?

Further experiments are suggested to answer these questions. The carrier type can be determined with Hall effect measurements. Using the van der Pauw method, the Hall mobility and carrier sign can be found in a quasi-2D geometry using four edge mounted electrodes. A perpendicular magnetic field will need to imposed. The impurity and its concentration can be determined by secondary ion mass spectroscopy (SIMS). With this technique, hydrogen, nitrogen, and oxygen concentrations with the detection limits of 5×10^{18} cm⁻³, 10^{17} cm⁻³, 10^{18} cm⁻³, respectively, can be detected in the diamond sample.

Finally, it is suggested that future measurements employ a guard ring that surrounds the top electrode in the sandwich geometry structure. This will insure that surface leakage currents can be shunted away from the current-measuring device and will not contribute to the conductivity.

Appendix A Metallization Repair and Removal

Since one often encounters poor adhesion of the electrode to the diamond surface, it may be necessary to remove part of the thin film. Since the diamond sample was not cleaned with ultrasound owing to the possibility of damage, it was initially cleaned with Alconox solution, acetone and methanol. Four Ti/Au electrodes were deposited on the sample. Then the sample was heated in air to 250 °C for surface leakage tests. The electrodes came off the surface due to poor adhesion after heating. Another set of the electrodes was deposited and annealed in vacuum, but failed by peeling off partially or fully, and by bubble formation. The optical microscope images of a broken electrode indicating poor adhesion, and a bubbled electrode are shown in Figure 87. The reasons for peeling and bubbling were thought to be either gas trapped or formed during annealing (for example, oxidation of titanium when heating in air) or the presence of loose particles on the surface not removed by the limited cleaning process.



Figure 87 Optical microscope images of (a) a broken Ti/Au electrode, and (b) The circular pad is a Au electrode- with diameter of 0.015 inches- on the diamond surface, a bubbled electrode.

The bad electrodes peeled off completely in a methanol spray. After the electrodes came off, the sample was cleaned only with aqua regia. It appeared that the electrodes were removed from the surface when viewed by optical microscope. However, SEM imaging revealed electrode material still on the surface (Figure 88). Four circular electrodes, each with three overlapped electrodes from three individual sets of electrode depositions were identified in Figure 88. The electrode residue is most likely Ti, TiO₂ or TiC. Titanium oxide was possibly formed as the sample was heated in air after electrode deposition in the first sets of measurements at the probe-station before annealing the electrodes in a vacuum.



Figure 88 SEM image of overlapped electrodes residue; electrode diameter: 0.015 inches.

To remove the electrode residue, wet chemical etching was used. Initially, the sample was placed in 1NH₄OH:5H₂O₂ for 70 minutes. This solution can attack both Ti and TiC. Figure 89 (a) shows SEM images after 70 min etching. Figure (a) shows the upper right electrode of Figure 88 is partially etched. The small particles spread around

the electrode following etching- seen in Figure 89 (b) and (c)- show definite crystal structures.

To remove Ti more aggressively, and possibly TiC formed deep in the electrodes, HF was used. The SEM image in Figure 90 shows the lower right electrode of Figure 88 is partially etched after 100 minutes exposure to HF. Figure 91 (a) and (b) compare the SEM images of the upper right electrode of Figure 88 after 100 minutes and 170 minutes HF etching, respectively. It can be seen from these images that most of the electrode is etched.



Figure 89 SEM images of (a) partially etched electrode after 70 minutes exposing to ammonium solution, and (b) and (c) particles that came off the electrode.



Figure 90 SEM image of partially etched electrode after 100 minutes HF etching.



Figure 91 SEM images of electrode after (a) 100 minutes, and (b) 170 minutes HF etching.

There was an important observation made while researching and establishing the chemical recipe for electrode removal. The SEM images of the sample showed bright electrodes pads remained on the surface even after hours (~5 hours) of HF etching. The bright area can be seen in the SEM images of Figure 92 (a) and (b). These bright areas indicate different surface texture than diamond, possibly TiC formed on the surface after annealing. These areas may be similar to the metal carbide islands that Werner observed on boron doped polycrystalline diamond surfaces after etching aluminum contacts from the silicon surface by phosphoric acid (Figure 93).



(a)



(b)

Figure 92 SEM images of electrode residue after ~5 hours of HF etching (a) and (b).



Figure 93 SEM image of metal carbide islands on boron doped polycrystalline diamond surfaces after etching aluminum contacts from the silicon [58].

After chemical cleaning, a very good adhesion between the electrode and the diamond surface was obtained. A primary test for adhesion- spraying alcohol to the electrode- did not cause electrode peeling. The optical microscope inspection of the electrode did not show any bubbling or electrode deformation after annealing (Figure 94b). Figure 94 shows: (a) a portion of the diamond sample after chemical cleaning and before one of the successful electrode depositions (20X), and (b) a portion of the Ti/Au electrode on the diamond surface after electrode deposition and annealing (50X).



Figure 94 Optical microscope images of cleaned diamond surface before electrode deposition at 20X (a), and after electrode deposition at 50X showing no electrode deformation (b).

The following procedure was established for removing the Ti/Au electrode:

- 1) 3HCI:1HNO3 for 10 minutes. This removes Au.
- 1H₂O₂:1 H₂SO₄ for 30 minutes. This can attack TiO₂ in addition to non-diamond phases and organics.
- 3) 24.5%HF:75.5%H20 for 3h. HF can attack both Ti and TiO2.
- 1NH₄OH:5H₂O₂ for 3h at 65 °C. This can attack TiC in addition to organic materials.

The sample is rinsed with DI water after each treatment. Each chemical solution is composed of the same concentration as given in the cleaning procedure. The first step is to etch the Au, and the follow steps are to etch Ti, and possible TiO₂ and TiC formed after annealing in air and vacuum. In addition to HF, other acids such as HCl, HNO₃, and H_2SO_4 can attack Ti. The treatment time can be varied depending on the thickness of the Ti and Au electrode.
Appendix B Setup Procedure

1- The big stainless steel clip (clip-1) was made. Chromel wire with diameter of 0.010" was passed through the two holes on each side of the clip.

2- Thermocouple junction was made by welding 0.005 inch alumel and chromel wires (thermocouple type-K).

3- A small stainless-steel clip (clip-2) with the thickness of 0.004 inch was made to hold the thermocouple near one of the corners in contact with the top side of the sapphire substrate, Au-pad side.

4- The three micro-Pt-heaters were welded in series. A Cu-wire (d=0.005 in, L=7 in) was welded to each free end of the three heaters.

5- The sapphire substrate was placed inside clip-1.

6- The three heaters were placed between the Cu-sheet and stainless steel sheet, radiation shield, like a sandwich, and this sandwich is inserted between the bottom of the sapphire substrate and clip-1, keeping the Cu-sheet in contact with the back of the sapphire substrate and the stainless steel sheet in contact with clip-1.

7- To make contact with the Ir, one Au-wire (0.002 in) was placed on the Au-pad of the sapphire substrate. Then, clip-4 was pushed, while lifted slightly with tweezers, from one side of the sapphire substrate- opposite to the heaters' leads side- and released on the top of the Au-wire. Then, the sample was placed on the Au-pad of the sapphire substrate. Another piece of Au-wire (0.002 in) was used to make contact with the top electrode. One end of the Au-wire and a small piece of sapphire are placed on the top electrode, respectively, and clip-3 is positioned on the top of small sapphire, with the

same technique as clip-4, to hold the small sapphire /Au-wire/electrode-sample. This was all done under the light microscope.

8- The lead of the Al-box was removed, and the setup was held with tweezers with one hand on the top of Al-box. While holding the setup, tweezers were used to pass the thermocouple wires through the two the hole on one side of the Al-box. Then, Culeads of the heaters are passed through the hole on the opposite side of the Al-box.

9- The free ends of chromel wires (four free ends) coming from clip-1 was wrapped a couple of turns around the screws that are holding the BNC panel.

10- Ag-paint was used to connect the free ends of the two Au-wires, coming from the two electrodes of the sample, terminating at the core of the two BNCs on the Al-box.

11- The Al-lead was placed back on the Al-box.

12- Each heater lead was passed through a piece of Refrasil (a flexible woven glass insulating jacket) (L=10 mm). The Refrasil prevented the leads from contacting the minibox. Each of the heaters' lead was welded to a pin connector.

13- Each of the thermocouples' lead was passed through a piece of refrasil (L=10 mm). The refrasil piece was pushed toward the Al-box, and placed in the hole on the Al-box. Thermocouple wires were connected to a connector; alumel to the negative pin and chromel to the positive pin.

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Appendix C LabView Code

























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