Chemical Modification of CVD Diamond Electrodes

Robert Matthew Johnson
Old Dominion University

Follow this and additional works at: https://digitalcommons.odu.edu/chemistry_etds

Part of the Physical Chemistry Commons

Recommended Citation
https://digitalcommons.odu.edu/chemistry_etds/127

This Thesis is brought to you for free and open access by the Chemistry & Biochemistry at ODU Digital Commons. It has been accepted for inclusion in Chemistry & Biochemistry Theses & Dissertations by an authorized administrator of ODU Digital Commons. For more information, please contact digitalcommons@odu.edu.
CHEMICAL MODIFICATION OF CVD DIAMOND

ELECTRODES

by

Robert Matthew Johnson
B.S. May 1996, Virginia Polytechnic Institute and State University

A Thesis Submitted to the Faculty of Old Dominion University in Partial Fulfillment of the Requirement for the Degree of

MASTER OF SCIENCE

CHEMISTRY

OLD DOMINION UNIVERSITY
December 1998

Approved by:

John B. Cooper (Director)

Sacharia Albin (Member)

Kenneth Brown (Member)
ABSTRACT
CHEMICAL MODIFICATION OF CVD DIAMOND ELECTRODES.

Robert Matthew Johnson
Old Dominion University, 1998
Director: Dr. John B. Cooper

The micro-array behavior of boron doped CVD diamond thin film electrodes has been studied in acetonitrile containing two redox couples. The analytical technique employed in these studies was cyclic voltammetry. One system is 0.4 mM ferrocene containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAH). This reversible redox system is not only well-known, but also involves only one electron transfer with no breakage/formation of chemical bonds, thus making it a simple system for analysis. The second test is 0.8 mM cobaltocenium hexafluorophosphate, with 0.4 mM ferrocene as an internal standard. Unlike ferrocene, which is neutral initially, cobaltocenium is positively charged, and is reduced at negative potentials. These two systems were used for their simplicity, reversibility, and because of their different charges.

Oxygenated surface sites enhance the determination of Cobaltocenium, a positively charged species, in solution at negative potentials. This enhancement is greater when the oxygenated species are negatively charged. The oxygenated surface sites can result from exposure to atmosphere, exposure to an oxygen plasma, or from organic reactions involving powerful oxidizing agents such as bromine or perchloric acid.
Oxygenated functional groups have been manipulated by changes in pH to enhance the determination of cobaltoceneium. Also, alcohol functional groups have been protected from oxidation using a common organic technique, the formation of silyl ethers. The protective group may then be removed with acid and oxidation of alcohol sites resumes.

The surface chemistry of diamond is not well known, and can open the door for a variety of promising applications such as flat-top displays and chemical sensors. The surface chemistry of diamond also offers the possibility of protecting a material already viewed as one of the most robust, from further reactivity.

For the first time, the electrochemistry of diamond thin film electrodes has been studied with respect to functional groups on the material’s surface, and the first room temperature reactions for diamond have been performed.
Trust in the LORD with all your heart and lean not on your own understanding; in all your ways acknowledge him, and he will make your paths straight (Proverbs 3: 5-6). This thesis is dedicated to the Lord God Almighty without whose guidance and help I would not have succeeded in what has been a challenging journey.
ACKNOWLEDGEMENTS

I would like to thank Dr. John B. Cooper for his guidance, help, and enthusiasm for this project. I would also like to thank him for having faith in me to do the work without excessive supervision. A big thanks must also go out to Dr. Albin and his research group for supplying the diamond electrodes. Special thanks to my committee members: Dr. Kenneth Brown and Dr. Sacharia Albin. Dr. Brown willingly joined the committee fairly late in the research after the departure of Dr. Frank Scully. Dr. Scully was instrumental in the development of much of the organic theory proposed in this thesis and I thank him for all his help with the project.

I would also like to express my appreciation to Jo Ingram, Michele Purrington, Cristin Keary, and Robin Branch, each in Dr. Brown’s research group for adopting me as a member of their group and putting up with me during the rather stressful time of writing this thesis. And thanks to all my friends who kept me motivated to reach the end of what often times has been a rough road to travel.

An enormous debt of gratitude must go to my parents and sister for their inspiration, their love, and their support. The greatest debt of gratitude goes to Jesus Christ, Lord and Savior who carried me when the burden became too great for me to bare alone.
# TABLE OF CONTENTS

LIST OF FIGURES ................................................................................... vii

Chapter

I. INTRODUCTION .......................................................................... 1

   Diamond: the Structure ............................................................. 1
   Diamond: the Material .............................................................. 4
   Diamond: the Semiconductor ................................................... 6
   Diamond: Hydrogen Terminated and Surface Reconstruction ................. 7
   Diamond: Early Attempts at Modification ........................................ 17
   Diamond: the Organic-like Molecule ............................................... 23

II. ELECTROCHEMISTRY: PRINCIPLES AND CONCEPTS .................. 31

   A Solid-State Perspective ................................................................. 31
   Micro-electrodes vs. “Macro”-electrodes ......................................... 39
   Cyclic Voltammetry .................................................................. 43

III. EXPERIMENTAL DETAILS .......................................................... 44

   Instrumental Design .................................................................... 44
   Reagents and Glassware Preparation ................................................. 44
   Fabrication of Electrodes .............................................................. 45
   Electrochemical Cell ................................................................... 46

IV. DIAMOND’S FUNCTIONAL GROUPS: MANIPULATION AND EVALUATION ................................................ 49

   Presence of Oxygen Sites .............................................................. 49
   Bromine .................................................................................. 50
   Silylation ................................................................................. 52
   Bromination Leading to Oxygen Sites .............................................. 58
   Glassy Carbon and Tungsten ........................................................ 59
   Self-Assembled Monolayers and Micro-Electrode Arrays ...................... 65
   Microelectrode Array Model ......................................................... 66

V. RESULTS AND DISCUSSION .......................................................... 71

VI. CONCLUSIONS ............................................................................. 92
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Scanning electron micrograph of a single microwave plasma CVD grown diamond crystal on a tungsten plate</td>
<td>2</td>
</tr>
<tr>
<td>2. (100) plane in a unit cell</td>
<td>3</td>
</tr>
<tr>
<td>3. (111) plane in a unit cell</td>
<td>3</td>
</tr>
<tr>
<td>4. Unreconstructed (100) surface: dihydrogen terminated</td>
<td>12</td>
</tr>
<tr>
<td>5. 2x1 π-bonded dimer row reconstructed (100) surface</td>
<td>13</td>
</tr>
<tr>
<td>6. Atomic structure of the monohydrogenated dimer (top), ideal dihydrogenated surface, and 2x1 π-bonded reconstructed (100) surface</td>
<td>14</td>
</tr>
<tr>
<td>7. (001) 2x1: 2H structure where two dangling bonds per carbon are terminated by hydrogen</td>
<td>15</td>
</tr>
<tr>
<td>8. Dimer reconstruction on the (100) plane</td>
<td>16</td>
</tr>
<tr>
<td>10. Representation of the oxidation and reduction processes of species A in solution at an electrode surface</td>
<td>36</td>
</tr>
<tr>
<td>11. Diagram of the basic double layer region of an electrode in solution</td>
<td>37</td>
</tr>
<tr>
<td>12. P-doped semiconductor in contact with solution based redox species whose effective Fermi Level lies within the band gap of the electrode</td>
<td>38</td>
</tr>
<tr>
<td>13. Scanning electron micrograph of a continuous diamond thin film electrode</td>
<td>41</td>
</tr>
<tr>
<td>14. Scanning electron micrograph of single micro-crystallite diamonds grown on a tungsten tip</td>
<td>42</td>
</tr>
<tr>
<td>15. Schematic of the proposed chemistry taking place on the diamond (100) surface</td>
<td>53</td>
</tr>
<tr>
<td>16. Conversion of bromine sites to alcohol sites</td>
<td>54</td>
</tr>
<tr>
<td>17. Formation of alkyl hypobromites on diamond surface</td>
<td>55</td>
</tr>
</tbody>
</table>
18. Proposed mechanism for addition of bromine to the diamond (100) surface ............ 56

19. Second proposed mechanism for addition of bromine to the diamond (100) surface ........................................................................................................................................ 57

20. Raman spectra of a CVD grown diamond ............................................................................................................. 60

21. Glassy Carbon electrode before and after bromine exposure ................................................................. 61

22. Glassy Carbon electrode after exposure to bromine: first and second scans ........................................ 62

23. Glassy Carbon electrode after exposure to bromine and subsequent exposure to lithium aluminum hydride ................................................................................................................................. 63

24. Tungsten electrode in 0.4 mM ferrocene and 0.8 mM cobaltocenium in TBAH/Acetonitrile ......................................................... 64

25. Microelectrode array model 1 .......................................................................................................................... 68

26. Microelectrode array model 2 .......................................................................................................................... 69

27. Microelectrode array model 3 .......................................................................................................................... 70

28. CVD diamond electrode in TBAH/Acetonitrile .............................................................................................. 72

29. Diamond electrode before and after oxygen plasma: cobaltocenium region only ........................................... 78

30. CV of diamond electrode exhibiting semi-enhanced cobaltocenium reduction .................................................. 79

31. Microelectrode behavior of CVD diamond thin film electrode ....................................................................... 80

32. Cyclic Voltammogram of CVD diamond electrode before and after oxygen plasma .................................................. 81

33. Diamond electrode after oxygen plasma and then silylation ........................................................................ 82

34. Diamond electrode exposed to oxygen plasma, protected and subsequently exposed to bromine .................. 83

35. Cyclic Voltammograms for CVD diamond electrode exposed to bromine ................................................... 84
36. Effect of functional groups on cobaltocenium detection ......................... 85

37. Diamond electrode in 0.4 mM cobaltocenium at moderate scan
    rates of 25, 50, 100, 150 mV/sec .................................................... 86

38. Cyclic voltammograms of diamond electrode in 0.4 mM
cobaltocenium at scan rates of 200, 300, 400, and 500 mV/sec ............... 87

39. Cyclic voltammograms of diamond electrode in cobaltocenium
    at slow scan rates of 5, 10, 20, 25 mV/sec ..................................... 88

40. Reaction of acid and base with oxygen surface groups which lead
    to enhanced cobaltocenium currents at negative potentials ............... 89

41. Cyclic voltammogram for the oxidation of ferrocene in acetonitrile
    at a CVD diamond electrode before and after exposure to bromine
    followed by thorough rinsing of the electrode with the solvent .......... 90

42. Cyclic voltammograms for the oxidation of ferrocene in acetonitrile
    at a CVD diamond electrode demonstrating that protection of
    surface oxygen sites with a covalently bound silane prevents
    significant reaction with bromine ................................................ 91

43. Background CV’s in acetonitrile/TBAH for a CVD diamond
    electrode before pretreatment, after silylation of surface and
    subsequent exposure to bromine, and before silylation but after
    exposure to bromine. .................................................................. 91
CHAPTER I

INTRODUCTION

For centuries diamond has been coveted by mankind for its beauty, its rarity, and its hardness. With the development of chemical vapor deposition (CVD), diamond has begun a renaissance of sorts as it has found uses as coatings for cutting and grinding tools, as polishing agents, and as electrode surfaces. Diamond's wide array of properties makes it an excellent material for a variety of functions.

Diamond: the Structure

First and foremost, diamond is a hard crystalline material composed of sp³ hybridized carbons. Diamond varies from the other allotropic forms of carbon because of its sp³-tetrahedral structure, which leads to its hardness. The lattice can be considered to be a face-centered cubic unit cell with one half of the tetrahedral holes occupied by carbon atoms. CVD grown diamond deposited on tungsten exhibits a high degree of faceting with clearly recognizable {111} and {100} planes (see Figs. 1-3).

Covalent bonding provides strong attractive forces between carbon atoms in the diamond structure. The four valence electrons in carbon are shared with adjacent atoms to form a three dimensional lattice.

Text modeled after Analytical Chemistry.
Figure 1. Scanning electron micrograph of a single microwave plasma CVD grown diamond crystal on a tungsten plate. Distinct (111) plane on top and (100) plane are exposed.
Figure 2. (100) plane in a unit cell. Each face is a (100) plane.

Figure 3. (111) plane in a unit cell.
The strength of these bonds gives rise not only to diamond's hardness, but also to the extremely high temperature to which it can be heated before being disrupted by thermal energy. The structure of diamond is dependent not upon available space or closest packing, but rather upon the number of bonds carbon is able to form. This makes it quite different from its metal counterparts, whose structures are determined by their size rather than bond angles and bond lengths.

**Diamond: the Material**

The properties of diamond are a direct result of its structure. These properties have led to a variety of uses for thin film, as well as bulk diamond. Diamond is the hardest known natural material. While this makes it ideal for cutting, grinding, and drilling, its rarity and cost have previously made it uneconomical for many applications. In the past decade or so, microwave assisted chemical vapor deposition has enabled diamond to be industrially grown at high levels of purity, but this diamond is limited to thin films. Despite this limitation, diamond has found a myriad of uses in technical applications and technology including high power electronic devices, protective anti-corrosion coatings, and cutting tools.²

One intriguing application of diamond thin-film technology is the development of this material into flat panel displays.³ CVD diamond has been shown to be a promising material for field emitters with low turn-on electrical fields and high current densities.³ Additionally, there has been a focus on the fluorination of diamond in order to reduce the high coefficients of friction.
associated with diamond surfaces when there is adsorbed water or oxygen present.⁴ Some researchers have even focused on the effect surface termination has on electrical conductivity.⁵ All the current literature points in one direction: the effect of diamond’s structure on its properties, and a desire to control or enhance diamonds properties through various means.

Diamond has been shown to be a promising material for electronic applications including electron emitters for such devices as magnetrons, electron multipliers, displays, and sensors. This is a result of diamond having a very small or negative electron affinity. In other words, the material is willing to readily give up injected electrons.⁶ Much interest has focused on the surface treatment of diamond films because the terminal group greatly affects the electron emission properties of the material. While a hydrogen-terminated surface is ideal, an oxygen-terminated surface introduces states that significantly decrease the diamond’s electron emission abilities. Efforts to increase this property of diamond have been conducted including treating the surface with cesium to form an O-Cs surface. Altering the dopant in the growth process has also been a possible technique for enhancing the electron field emission for the diamond.⁷

Fairly early on in the development of diamond as a semiconductor, the presence of oxygen containing groups on the diamond surface was thought to be the cause of certain hysteresis.⁸ This hysteresis was found when studying the dark current-potential characteristics of diamond electrodes.
Diamond has proven to be a promising material for various electronic devices including light emitting diodes, photovoltaic cells, and electroluminescence devices. Diamond's unique optical properties have led to much research toward the production of optoelectronic devices. Insulating diamond possesses luminescence centers in the UV, visible, and near-IR regions, which can lead to a variety of light emitting structures including transmitters.

Diamond was first developed as a microelectrode after diamond microparticles were successfully grown on etched tungsten wires using microwave-assisted CVD processes. The growth of microcrystallite diamond on tungsten has also been shown as an effective STM tip. Diamond particles were shown to have a cubo-octahedral shape with clearly defined {111} and {100} surfaces.

Diamond: the Semiconductor

Natural and CVD-grown diamonds are both insulators with high resistivities (typically >10^8 ohm-cm), but when doped with boron, diamond becomes a semi-conductor. Undoped diamond has a wide band gap of approximately 5.4 eV. Doping diamond with boron forms a p-type semiconductor. The boron acts as an electron sink, or hole, in the material due to its empty p orbital.

It has been shown previously that the electrical resistivity of CVD diamond can be decreased several orders of magnitude by incorporating hydrogen in the growth process. This resistivity is further decreased by in-situ doping of
the material with an impurity such as boron. This enables the production of diamond thin films suitably conductive for electrochemical measurements.

Microwave-assisted CVD diamond is grown from a methane-hydrogen gas mixture, with a methane to hydrogen ratio of about 1:200. In the growth process, methane and molecular hydrogen are broken by microwaves into hydrocarbon radicals and atomic hydrogen. The exact mechanism of diamond growth is not completely known, but involves the reconstruction of the various surfaces and a continuous replacement of hydrogen with carbons. The growth process is terminated by slowly decreasing the methane flow and termination of diamond growth is performed in a pure hydrogen plasma in order to decrease the formation of sp² carbon.

Diamond as a semiconductor has been shown to be an effective material for electrode production. Diamond thin films and microcrystallites grown on metal substrates have been developed into both macro and microelectrodes. Diamond electrodes have previously been shown to have extraordinary chemical stability, low double layer capacitance, and stable electrode response. By decreasing the size of the diamond electrode, kinetic studies become less difficult. All of this makes diamond a promising material as a semiconductor material.

**Diamond: Hydrogen Terminated and Surface Reconstruction**

The surface science of diamond is a result of attempts to understand the growth process of CVD diamond. Diamond grown with a high concentration of
hydrogen in comparison to the methane concentration leads to higher quality diamond films. Consequently much research has focused on the mechanism for diamond growth in an attempt to obtain higher quality diamond. Much focus has been on the reconstruction of diamond \{111\} and \{100\} surfaces.\(^{13}\)

Isolated dangling bonds on the surface of diamond at the termination of growth are believed to be the active sites for diamond growth. These dangling bonds may connect with each other on some surfaces, particularly the \{100\} surface. Reconstruction of this surface has been shown to lead to the formation of \(\pi\)-chains and dimer bonds in order to reduce surface free energies. These \(sp^2\) hybridized chains may be viewed as templates for the growth of graphite. This graphitic growth is controlled by the use of hydrogen plasma in the growth process.\(^{14}\)

Hydrogen is believed to have dual role in diamond growth. First, hydrogen atoms are believed to preferentially etch away graphitic components and terminate surface carbon atoms to maintain the \(sp^3\) hybridization of diamond. Secondly, gas phase hydrogen atoms are able to abstract top layer hydrogen atoms, thus opening available sites for continued diamond growth.\(^{15,16}\)

Diamond surfaces have been found to undergo rearrangement due to the hydrogen termination as a function of increasing temperature in an ultra high vacuum. Dangling bonds on the (111) surface have been found to form \(\pi\)-bonded dimers. The dangling bonds on the (111) surface may also be singly terminated by hydrogen. Also, methyl groups may cap the (111) surface’s dangling bonds. \(Small \text{ amounts of chemisorbed hydrogen atoms have been shown to induce a}\)
phase transition on the (111) surface from 2x1 to 1x1 structure. The 2x1 structure is one in which the dangling bonds have formed π dimers, while the 1x1 structure is the monohydride terminated surface. This transition is rapid and has been observed by LEED and AES at high temperatures in an ultra-high vacuum.  

The (111) surface is ideally considered to have either one or three dangling bonds, leading to monohydride or methyl terminal groups.  

Reconstruction of the 2x1 (100) surface has been determined to be that of π-bonded dimers at temperatures exceeding 1000°C. Figures 4-6 depict the arrangement of carbon atoms on the reconstructed and non-reconstructed (100) surfaces. Termination of the surface with single hydrogens is considered the most stable (100) surface during diamond growth. While termination of both dangling bonds by hydrogen is possible, theoretically there would be a strong repulsion between hydrogen atoms on adjacent carbons (see figure 7). This would be due to the small interatomic distances in the diamond lattice (1.54 Å).  

While many researchers agree that the C(100) 1x1:2H surface is unfavorable due to repulsion, LEED patterns suggest the surface is common on hydrogen terminated (100) planes. It is possible the dihydride structure, while energetically unfavorable, may indeed exist to some degree such as at terrace steps on the surface.  

From a solid state perspective, the hydrogen free 2x1 reconstructed diamond surface reveals strongly dispersed occupied surface states for both the (100) and (111) surfaces. This surface state dispersion agrees with the π-bonded dimer model. It is also in agreement with a formation of π-bonded dimer
chains on the (111) surface. STM images have shown the diamond (100) surface to consist of terraces with alternating 2x1 and 1x2 mono-hydrogen terminated dimers.\textsuperscript{21} These dimer chains have the potential for reactivity, and therefore an introduction of new surface states in the diamond band model. These new surface states are the key to unlocking the electrochemistry of boron doped diamond thin films. Figure 8 depicts the monohydrogen terminated dimer surface, as well as adjacent dihydrogen carbons.

The surface termination by hydrogen has been shown to supply a p-type semiconductive layer on the undoped diamond surface.\textsuperscript{17,19,22} This conduction is limited to the surface of the diamond, and does not incorporate the bulk material, hence the need for boron doping. The conduction mechanism is not well understood, but is found to be related to the hydrogen termination, perhaps by surface band bending. CVD diamond surfaces covered with hydrogen atoms remove the surface states in the band gap\textsuperscript{23}, while oxygen introduces new states that greatly affect diamond's electrochemical properties. Surface termination can also play a crucial role preventing surface reconstruction at high temperatures. For example, CVD diamond surface treatment by CrO\textsubscript{3} prevents graphitization due to the chemisorbtion of oxygen and chromium atoms, thus forming a complex and stable states.\textsuperscript{23} Once bound to the surface, oxygen thermally desorbs as CO, rather than O\textsubscript{2}, indicating the strength of the corresponding bond.\textsuperscript{23,24} Hydrogen, which has an electronegativity similar to that of carbon desorbs as molecular hydrogen.
Depending on the mobility of hydrogen atoms on the surface of diamond, it is possible for surface rearrangements on the (100) surface to lead to active sites on the (111) surface. Surface rearrangement involves the making and breaking of many carbon-carbon bonds, and is therefore subject to a variety of possible final structures.

Along the same lines as surface reconstruction, surface migration of bridging CH$_2$ and CCH$_2$ groups and radical vacancies may migrate on the diamond {100} surface. Hydrogen atoms are able to migrate from one surface to another, thus opening surface active sites and closing others. This migration is a key to promoting or suppressing various surface reactions. Migration of hydrogen on the {111} surface is thought to be unimportant due to large potential energy barriers (76-113 kcal/mol).

Understanding the migration of species on the diamond surface is important for various reasons. First, it is a step toward understanding the mechanism for the growth of diamond. Secondly, it is important because it provides a reasoning for the reactivity of diamond both in the growth process and afterwards as surface reconstructions take place.
Diamond (100) unreconstructed dihydrogen terminated. Only top layer of carbons shown for clarity. Looking down on the surface, top carbons are shaded and other carbon atoms are below the surface but still visible.

Figure 4. Unreconstructed (100) surface: dihydrogen terminated.
Figure 5. $2\times1$ $\pi$-bonded dimer row reconstructed (100) surface. Surface atoms are filled.
Figure 6. Atomic structure of the monohydrogenated dimer (top), ideal dihydrogenated surface, and 2x1 π-bonded reconstructed (100) surface.
Dihydrogen terminated (100) surface.

Figure 7. (001)-2x1:2H Structure where two dangling bonds per carbon atom are terminated by hydrogen.
Figure 8. Dimer reconstruction on the (100) plane. A π-dimer would be a double bond between the 2 carbons and no hydrogen termination.
**Diamond: Early Attempts at Modification**

Diamond is a material of great technological interest because of its chemical stability and high-carrier mobility compared to other semiconductors. The presence of various functional groups on solid surfaces can affect the surface conductivity of the solid. Interest in surface modification of diamond developed from its new roles in electrical and electrochemical applications. Because of the wide-ranging applications of diamond materials, many attempts at modification have focused on increasing the properties of diamond that make it such an important material. All of the previous chemical modification has been a result of either excitation of atoms through atomic beams or plasmas, or through high temperature reactions. No low temperature reactions have been previously reported.

It has been shown that at high temperatures, a small quantity of chemisorbed hydrogen atoms can induce phase transformations on the C (111) plane from (2x1) π-bonded surface to mono-hydrogenated (1x1). Once formed, the sp³ hybridized structure of diamond remains stable to high temperatures.¹⁵ Fluorine was believed to react with the π-bonded chains. P₂ orbitals can protrude from the carbon atoms on the diamond surface forming the next layer providing an ideal site for reactivity. Consequently fluorine was found to adsorb to diamond, most likely at these sites.²⁶

Halogenation of diamond (100) and (111) surfaces by atomic beams provides insight into the reactivity of the two surfaces.²⁷ Adsorption of halogens
on the (111) surface is proportional to the concentration of open sites on the surface, while on the (100) surface, the adsorption is dependent upon the steric hindrance on that surface. This hindrance prevents ordered adsorption on the (100) surface. Chlorine was found to weakly chemisorb on the (100) surface and desorbs rapidly with increasing temperature. Only small concentrations of chlorine remain bound to the surface at high temperatures, most likely a result of binding at defect sites in the diamond lattice. Adsorption of fluorine and chlorine were predicted using molecular modeling calculations to be more stable at much higher temperatures than had been measured, which may be due to electronic repulsion effects as the halogenation reaches monolayer coverage.\(^{28}\)

Because diamond film coatings can significantly improve the surface properties of many materials for a variety of applications, efforts have been made to enhance lubricity and enhance stability of the diamond films by surface modification. The strong bonding of fluorine to the diamond has shown promise as one method of modifying diamond. Many methods have dealt with extreme measures of fluorinating the diamond, including the use of plasmas and corrosive gases.\(^{29}\) A less extreme method of fluorination was found to be the x-ray irradiation of perfluoroalkyl iodide layers on the surface.\(^{30}\) The perfluoroalkyl radicals chemically bond to the surface and then thermally decompose to produce surface bound C-F bonds that are stable at high temperatures.\(^{30}\)

As stated previously, diamond is simply sp\(^3\)-hybridized carbons tetrahedrally bound to one another. Diamond can be viewed in some respects simply as an organic macromolecule with the potential for reactive surface
functional groups. CVD grown diamond is initially hydrogen terminated, but depending on the environmental conditions and the history of the diamond film, oxygenated surface sites may form. Diamond thin film electrodes which have “sat around” for several months without exposure to chemicals appear to form surface oxygen sites. Diamond thin films exposed to an oxygen atmosphere or to an oxygen plasma can form a variety of oxygenated functional groups such as carbonyls, alcohols, and ether linkages. These functional groups on the diamond surface hold the potential for a variety of interesting organic reactions, and can explain much of the hysteresis documented by several researchers.\textsuperscript{31-38} Acid has been shown to affect the response of diamond thin film electrodes, enhancing the current for hexacyanoferrate (III)/(II) in KCl at positive potentials\textsuperscript{39}, thus providing more evidence for the effect of surface functional groups on detection of charged species in solution.

Research on the chlorination of diamond powders has been shown to lead to the formation of OH, NH, and CF groups on the diamond surface.\textsuperscript{40} Surface chlorination was determined using x-ray photoelectron spectroscopy, diffuse reflectance IR Fourier-transform spectroscopy, and temperature-programmed desorptic spectroscopy. While chlorination of the diamond surface occurs, it is not possible to cover the surface to a high degree due to the steric factors from the size of the chlorine atoms.

Hydrogen atoms chemisorbed on the diamond surface were substituted with chlorine, and were indicated by an increase in the mass of the diamond with respect to timed exposure to chlorine. At higher temperatures the chlorination
was found to increase until reaching a maximum at 250°C and then decreasing slightly at higher temperatures. As chlorine species are adsorbed on the surface, other chlorine atoms are desorbing. At higher temperatures, it was shown that C-H stretching vibration decreased as hydrogen was replaced by chlorine.

After exposing the chlorinated diamond to air for a period of 60 minutes, peaks indicative of O-H bending and stretching vibrations increased in intensity, and C-O and C-O-C peaks appeared in the region 900-1500 cm⁻¹, indicative of the formation of oxygenated sites on the diamond. At higher temperatures in the presence of water vapor, a greater concentration of oxygenated species on the surface was found.

Going a step beyond the formation of oxygenated species on the diamond surface, Ando and co-workers studied the animation of the chlorinated diamond surface. By reacting the chlorinated surface with ammonia, they were able to observe peaks corresponding to N-H bending and stretching vibrations, thus suggesting the formation of NH species on the surface. It is important to note that the reaction of ammonia did not occur on the surface of unchlorinated diamond, thus indicating the usefulness of halogenation as a precursor for reactivity.⁴⁰

This provides key evidence for the formation of oxygenated sites on diamond as a result of halogenation. The apparent chemistry would be akin to that of an Sn1 mechanism in which the chlorine acts as a leaving group, thus opening a reactive site on the diamond molecule, and is subsequently replaced by oxygenated species at room temperature. The end result is chlorine acting as a
reactive intermediate in what is a potentially rewarding chemistry of diamond surfaces.

Using x-ray photoelectron spectroscopy (XPS), the chemical structures of oxy-functional groups of diamond were studied. Analysis of the spectra permitted the establishment of the presence of hydroxyl, carbonyl, and carboxyl-like groups on the surface of natural diamond and graphite.

Ultrafine diamond powder, used in composite electrochemical coatings, was modified using thionyl chloride. Alcohol sites and acid sites were converted to chlorinated sites, while carbonyl and ether linkages are unreactive toward thionyl chloride. The acid chloride groups were converted to amides using hexamethylenediamine.

In order for diamond to be used successfully as a cold cathode material, it is necessary for the material to exhibit a low threshold voltage for electron emission. Research has focused on treating the surface of diamond in various ways to enhance its properties for uses in vacuum microelectronics such as Field-emission Displays. The key to diamond’s successful use as a material for these devices is a negative electron affinity.

A hydrogen-terminated diamond is said to have “negative” electron affinity. In other words injected electrons readily escape from the surface, which is important for photo- and cold-cathode emitters. Negative electron affinity is measured by ultraviolet photoemission electron spectroscopy (UPS). This method involves photoexcitement of hot electrons to the conduction band. The electrons cool in the process of energy relaxation and collect in the conduction
band minimum. For negative electron affinity surfaces, the injected electrons are emitted into a vacuum without any energy barrier.

Negative electron affinity can be described by two possible methods: true or effective negative electron affinity. If the depletion band bends at the surface of the semiconductor, it is possible to have the minimum of the conduction band above the vacuum energy level. It is possible for oxygen functional groups to introduce low-lying surface states within the band gap. While from the perspective of electron emission this is an undesirable effect, it may have desirable effects on things such as the electrochemistry of diamond thin films.

However, the presence of some "defects" such as non-diamond carbon (i.e. sp\(^3\) hybridized carbon) and oxygen functional groups, as well as dopant levels\(^{45}\), can alter this negative electron affinity drastically, thus reducing diamond's effectiveness as a material for vacuum microelectronics. Oxygen termination was found to raise electron affinity by 3.7eV above that of the clean surface.\(^{46}\) Treatment of the diamond with laser annealing, hydrogen passivation, and argon/oxygen plasma etching was found to degrade the electron emission performance.\(^{47}\) It has been shown that cesium can reverse the effects of oxygen by shifting the 2.45 eV positive electron affinity to 0.85 eV negative electron affinity by forming Cs-O-C bonds with the diamond surface.\(^{48}\) Oxygen on the surface is believed to form a surface dipole, increasing the emission barrier height, thus making the surface more electron affinitive and is approximately the same whether the oxygen is singly or doubly bonded to the surface.\(^{49}\) Thus far,
the most effective surface of diamond as a negative electron affinity material is that which is hydrogen terminated.

Previous attempts at modifying the diamond’s surface to enhance its physical properties open the door for a variety of new experiments. If functionality of the surface can be controlled and/or manipulated in a controlled manner, the properties of the material may indeed become enhanced. It would also be possible to protect diamond surfaces from further reactivity.

**Diamond: the Organic-like Molecule**

For many years, the chemistry of diamond was thought to be closely related to that of the adamantane molecule. Adamantane is quite inert and is composed of entirely perfect chair six-membered rings, giving it substantial stability and thermodynamic favorability. For example, bromination of the “capped” site occurs only at extremely high temperatures.

The Czech chemist Stanislav Landa first discovered adamantane in the 1930’s in trace quantities in petroleum. Kuchar and others in the 1960’s focused on ways to modify the adamantane molecule.\(^{50-52}\) Reactions included the conversion of functional groups on the molecule.\(^{54}\) Trichloroethoxycarbonyl was found to be quite suitable for the protection of the amine group on adamantamine.\(^{56}\) Also, by capping individual adamantane molecules, larger, macromolecules may be formed. For example, by capping adamantane once, diamantane is formed. A second cap forms triamantane, and a third forms one of several tetramantane isomers. By continuously capping adamantane molecules
polyadamantane is formed, and ultimately diamond. While this is a novel approach to the synthesis of diamond, it is hardly a convenient method (Figure 9).

Bromination has been shown to occur at selected sites on diamantane at varying conditions. For example it is possible to add a single bromine to the diamantane molecule at 25°C and a second one at higher temperatures. The chemistry of adamantane is a rich area that has been explored to a great degree, but it appears in many ways that CVD diamond is a unique beast in itself with its own reactivity.

The focus on diamond’s structure and applications has led to the desire to study not only diamond’s bulk properties, but also those of the surface. Studies have shown that diamond surfaces are normally terminated by hydrogen when fresh from the CVD chamber. This stabilizes the surface (1x1) symmetry by bonding with any “dangling” bonds on the diamond surface. Hydrogen may desorb from the surface at temperatures exceeding 1273 K, and a surface reconstruction may occur to achieve a (2x1) π-bonded symmetry.
Figure 9. Synthesis of Diamond from Adamantane: the template for diamond chemistry.
It is believed that dangling bonds on a CVD diamond’s surface at the completion of diamond growth may connect with each other in some areas of the surface forming $\pi$-chain or dimer bonds in order to stabilize the surface and reduce energy. These $\pi$-chains can be viewed as the basis for graphite growth because of their $sp^2$ hybridization. Three possible scenarios describe what may occur at the conclusion of diamond growth. First, some or all dangling bonds may be terminated by hydrogen. Second, dangling bonds may interact, forming carbon-carbon bonds. Finally, dangling bonds may interact and form $\pi$ type bonding. These may lead to possible reactive sites on diamond surface, opening doors to a variety of organic reactions on the surface of the diamond.$^{59,60}$

Work with diamond powders has shown perchloric acid to oxidize diamond and form oxygenated functional groups including ethers, esters, alcohols, ketones and carboxylic acids. The concentration of these functional groups on the diamond surfaces was determined by titration with bases of varying strength.$^{61}$ This provides evidence for functional groups on a diamond surface.

These varying surface structures lead to a variety of possible organic reactions that may be performed on the diamond’s surface. For example, any remaining $\pi$-bonded sites would be readily subjectable to bromination, possibly through the formation of a bromonium ion. While alkene reactivity with bromine is usually limited to anti addition, the diamond surface prevents this. It is possible for the syn addition to occur through a competing mechanism, perhaps through the formation of a carbocation. Bromination on one of the carbons may induce the formation of a carbocation adjacent to it, which, in order to reduce
surface free energy, may abstract a proton and forming a double bond. The brominated surface in turn may react with base, or readily with water in an Sn1 type reaction leaving an alcohol site. These π bridges may also react slowly with moisture or oxygen in order to minimize surface free energy. Each of these oxygenated sites would be subjectable to a variety of interesting organic reactions. Additionally, it is proposed bromine may form hypobromite moieties on the diamond surface by covalently bonding to oxygen atoms. While from a strict organic sense this may seem counter-intuitive, the reaction is occurring in a dry aprotic solvent. These hypobromite sites would be very reactive to moisture and would convert readily to alcohols in a humid atmosphere.

While various sites on the diamond molecule may indeed undergo organic-like reactions, it is important to note that diamond as a whole, despite being carbon, is subject to its own chemistry quite unlike that of an alkane. It is easy to oversimplify the diamond molecule as an organic molecule, when in fact it exhibits a myriad of properties unlike that of simple organic structures.

The development and selective control of organic functional groups has the potential for a wide variety of promising applications. Electrocatalysis has the potential to make a significant economic impact. For example, the oxidation of ethylene to form ethylene oxide, the hydrodimerization of formaldehyde to form ethylene glycol (a 20 billion pounds per year market), and the electrochemical dimerization of acrylonitrile62-64 are each industrially important. Hydrogenation of 2-cyclohexen-1-one to cyclohexanone has been found to occur electrocatalytically, and there is presumably a myriad of other selective organic
reactions that can occur through electrolysis but may be dependent upon the type of electrode used. Electrocatalytic effects may also be used to generate highly selective and highly sensitive chemical sensors. Diamond thin film electrodes have been found to efficiently reduce nitrate to ammonia electrochemically.

Electrocatalytic effects arise from the interaction, such as physisorption/chemisorption, of the reactants with the electrode surface. Consequently there is no direct effect of the work function of the electrode. Any effect of the work function on the rates of reaction is due to the indirect relations between the work function and the potential of zero charge and the adsorption of reactants. In this respect, it is well regarded that the nature of the electrode surface effectively controls the rate of the electrocatalytic reaction. In general, there are two methods in which electrocatalysis can be initiated. One involves the electrosorption of reactants to a metal electrode surface, which subsequently exerts an electrocatalytic effect. The second involves the use of a surface modified electrode to enhance interaction between the reactants and the surface to ultimately bring about an electrocatalytic effect. In the former method, the electrocatalytic effect is highly dependent on the crystal face which is exposed to the solution, due to preferential binding which occurs as a result of atomic spacing. In the latter method, the most abundant examples involve oxidation of metal electrodes to yield surfaces with preferential binding sites. An excellent example is the Kolbe synthesis of hydrocarbons at a platinum electrode surface. For the Kolbe synthesis, for efficient electrocatalytic conversion, the surface must first be converted to a high order phase oxide. A more recent approach to
the latter method is the use of derivatized electrode surfaces using molecules/molecular ions to mediate and enhance electron transfer mechanisms at the surface. For example, porphyrin modified electrodes have been used for the electrocatalytic reduction of alkyl halides\textsuperscript{73-75}; Nonaka and coworkers have generated chiral electrode surfaces using asymmetrical organic molecules which selectively yield an optical isomer\textsuperscript{76}; and Kyriacou and Jannakondakis have bound organo siloxane species to the surface of tin oxide\textsuperscript{77}. In addition, a rapidly growing field has involved the use of self-assembled monolayers of electron transfer mediators on electrode surfaces, with binding of thiol modified species to gold surfaces representing the largest percentage of such derivatizations\textsuperscript{78}. Although the use of derivatized electrodes is a promising area of research, the reactivity of the surface that allows facile derivatization often results in modified surfaces that are not robust. In particular, these types of electrodes appear to have the greatest lifetimes when they are used to mediate electron transfer reactions involving simple solution based redox ions. When adsorption becomes an intimate part of the reaction (i.e., electrocatalysis) the lifetimes often degrade significantly (for example, the electrocatalytic reduction of oxygen at porphyrin modified electrodes)\textsuperscript{79}. In this respect, modified diamond electrode surfaces provide a unique advantage. While the dangling bonds at the surface provide a reactive template, underlying the surface is a strongly bound bulk whose three dimensional covalent bonding causes it to be non-reactive, and to prevent surface reconstruction. In essence, the diamond surface presents an ideal electrode surface for derivatization. It is possible to use the vast and well-characterized
body of knowledge of organic functional group reactivity to specifically tailor the surface of diamond for a particular application. The electrode’s stability is based on the anchoring of covalent bonds attaching the modified species to the surface (as opposed to being dependent on the stability of the underlying surface or the stability of ionic/adsorption interactions holding the modifier to the surface). Diamond electrodes, like their graphitic counterparts, suppress the hydrogen evolution reaction allowing their use in cathodic reactions in aqueous solution. In contrast to the graphite electrodes, diamond thin films are crystalline/microcrystalline in nature providing a highly ordered surface on which to carry out derivatizations.

By modifying diamond electrodes, their use in electrocatalysis have the potential for a wide array of applications including: 1) specialty chemical synthesis, 2) chemical detection, 3) bioanalysis, and 4) environmental analysis.
CHAPTER II

ELECTROCHEMISTRY: PRINCIPLES AND CONCEPTS

A Solid-State Perspective

Electrochemistry is a potent tool for chemical characterization, and consequently is an ideal technique for evaluating surface functional groups on diamond. Faradaic processes occurring at electrodes involve the transfer of electrons across a solution-electrode interface. At the cathode, molecules or ions gain electrons to produce reduced molecules or ions. From a solid state perspective, as an electrode is driven to more negative potentials, the Fermi level is raised until it is able to transfer electrons to the Lowest Unoccupied Molecular Orbital (LUMO) of the analyte. The Fermi level can be considered to be the Highest Occupied Molecular Orbital of the electrode. This HOMO-LUMO interaction is of primary concern. As electrons flow from the electrode to the solution, a reduction current is formed. If a positive potential is applied to the electrode, the Fermi level can be dropped to such a degree that electrons can flow from the HOMO of the analyte to the electrode surface. This process is called oxidation and results in oxidized species in solution (figure 10).

There exists a concentration of charge on both sides of the electrode-solution interface. The electrode surface can have an excess of charges, either positive or negative, depending on an excess or deficiency of electrons. To compensate for this excess, different layers will form in the solution. The layer in contact with the electrode surface is called the inner Helmholtz plane and
consists predominantly of solvent molecules. It is possible, if the ions are not strongly solvated, for some ions to enter the inner Helmholtz plane. The next layer, or outer Helmholtz plane, is where most cations and some anion are encountered. The final layer is the bulk solution and consists of a diffuse mixture of charges. The sum of the three layers must be equal and opposite in charge to the electrode surface.

The double layer capacitance is the combination of the compact (the Helmholtz layers) and diffuse layers in series (see figure 11). The diffuse layer is concentration dependent, while the compact layer is independent of concentration. The thickness of the diffuse layer affects not only capacitance, but also the “drop of potential across the diffuse layer”. To prevent complications due to these effects, a supporting electrolyte is used that is typically at least 0.1 M in concentration. This supporting electrolyte is inert, aids in the transport of electricity in the solution, but is neither oxidized nor reduced.

Diamond in its natural state is an insulator with a band gap of 5.45 eV. During the growth process of CVD diamonds, it is possible to p-dope the electrode through the introduction of impurities such as boron. The resulting diamond is conducting and is regarded as a p-type semiconductor. For an extrinsic semiconductor like boron doped diamond, the majority carriers are holes in the valence band. The boron acts as an electron sink with its half-empty $p_z$ orbital, accepting one electron. Because of this doping, the energy difference between the acceptor level, $E_a$, is much less than the full energy gap for the
undoped diamond. There remain electron holes in the valence band that are available as positive carriers for p-type semiconduction.

Electrode charge is concentrated on the electrode surface for metal electrodes in contact with solution. For semiconductor electrodes with few surface states, the charge is spread out inside the electrode in a region referred to as the space-charge region of the semiconductor. Secondly, there is a significant energy gap (band gap) between the highest energy (valence) filled orbitals of the bulk electrode (the valence band) and the highest energy unoccupied orbitals of the bulk electrode (the conduction band). The band gap is analogous to the HOMO-LUMO gap in molecules and is in contrast to the continuum of states found in metal electrodes.

Due to the presence of the space-charge region in the semiconductor, "bending" will occur in the valence and conduction bands as they approach the surface. This band bending, as well as the band gap of the semiconductor, has a significant effect on the observed electrochemical response for diamond electrodes. For a solution based redox species, there will be an energy distribution of both acceptor orbital levels (LUMOs) and donor levels (HOMOs) due to solvation, surface orientation, etc. There exists an effective Fermi level for the redox species lying midway between the HOMO-LUMO states (see figure 12).

When a p-doped extrinsic semiconductor, such as boron-doped diamond, is placed into a solution containing a redox species, there are two scenarios to consider. One involves a redox species where the solution-side Fermi level lies
above the Fermi level of the electrode, and another where the solution-side Fermi level lies below that of the electrode. In the first scenario, the electrode reaches equilibrium by accepting electrons from the solution based redox species (i.e., anodic current flows). At equilibrium the Fermi levels are equal and net current ceases to flow. Both the valence and conduction bands bend down at the surface due to a depletion of carriers (in this case holes) near the surface (i.e., formation of space-charge region). If a positive bias is now applied to the electrode, the Fermi level of the electrode is lowered and anodic current flows. Note that application of the positive bias (if sufficiently large) results in a reversal of the band bending so that hole accumulation occurs at the surface, hence facilitating the electron transfer process. In the case of applying a negative bias, with a metal electrode, one would expect a cathodic current to flow; however due to band bending for the semiconductor, there are no surface electrons of appropriate energy (i.e., at the redox Fermi level). Thus for cathodic current to occur, the electrons must tunnel the space-charge region. For an electrode having a large depletion depth, this is not likely, due to the large distance involved. However, if the semiconductor electrode is heavily p-doped (approaching the metallic limit) or if a large overpotential is applied, the tunneling distance may decrease sufficiently to allow cathodic current to flow. The other scenario involves a redox species having an effective Fermi level lying below that of the semiconductor. In this case, application of either a positive or negative bias to the equilibrated electrode will result in current flow. Thus for a p-doped extrinsic semiconductor such as diamond, one expects to obtain a cathodic
electrochemical response (involving the valence band) for redox species as long as the effective Fermi level of the species does not lie within the band gap of the semiconductor or higher. This assumes that the band edges are pinned at the surface regardless of the applied potential. However, introduction of surface localized states could enhance electron transfer by providing mediating pathways for electron transfer from the electrode to the redox species, or hinder electron transfer to the electrode via interaction with holes at the surface.82
Figure 10. Representation of the oxidation and reduction processes of species A in solution at an electrode surface.
Figure 11. Diagram of the basic double layer region of an electrode in solution. The inner and outer Helmholtz planes are labeled.
Figure 12. P-doped semiconductor in contact with solution based redox species whose effective Fermi Level lies within the band gap of the electrode.
Micro-electrodes vs. "Macro"-electrodes

CVD diamond single microcrystallite electrodes (Figure 14) and continuous thin film electrodes (Figure 13) have been developed previously. The term microcrystallite electrode refers to a single crystal grown on a tungsten wire and sealed in glass. A continuous thin film electrode is one in which a continuous diamond film is grown on the tungsten wire and may or may not be sealed in glass. Both are technically microelectrodes because their dimensions are on the micrometer scale. Macro electrodes are those that are greater than 1mm in diameter. It is important to understand the difference between the types because oxygen sites appear to function as a microelectrode array, and these electrodes appear to have characteristics of both. The macro-electrode relies primarily on planar diffusion, as the analyte species approaches from one general direction. The microelectrode on the other hand is dominated by radial diffusion as the analyte species approaches and departs the electrode surface from all directions. Large electrodes exhibit a very thick depletion layer near the electrode surface resulting in a decrease of analyte concentration with respect to time. A microelectrode has a very thin depletion layer, and the analyte concentration remains very high for long periods of time. Continuous thin-film electrodes appear to be a hybrid of the two.

The presence of oxygen sites on diamond has several effects on diamonds properties. Previously (Chapter 1) the effect of oxygen was discussed with respect to its reversal of negative electron affinity. From a different perspective, the introduction of oxygen species introduces new surface states that are in the
band gap.\textsuperscript{83} These states are below the conduction band, and while this destroys negative electron affinity, it aids in the conduction of electrons, and may therefore enhance electrochemical response of some charged species in solution.
Figure 13. Scanning electron micrograph of a continuous diamond thin film electrode.\textsuperscript{11}
Figure 14. Scanning electron micrographs of single micro-crystallite diamonds grown on a tungsten tip.¹
Cyclic Voltammetry

The technique employed throughout this research was cyclic voltammetry because of the vast amount of information obtainable regarding not only the redox species of interest, but also surface phenomena. Cyclic voltammetry, much like linear-sweep voltammetry, involves the increase of potentials from an initial value to a second value, but unlike linear-sweep, the potential is reversed back to the initial value. In other words, the voltage scan is reversed well after the current reaches a maximum (peak) for the reduction of the species. Scanning continues in the negative direction beyond the peak and subsequently reversed and scanned in the positive direction. This gives the user far more information about the electrochemical process, including the properties and characteristics such as chemisorption, physisorption, and side reactions. Reactions that are considered reversible and involve only one electron transfer have a peak to peak separation of approximately 59 mV (the distance between the oxidation peak and the reduction peak of the species is 59 mV).

For microelectrodes where radial diffusion dominates, steady state voltammograms can be obtained. A steady state voltammogram is sigmoidal in shape with a current plateau, and the current separation between two consecutive current plateaus is called the limiting current. This also applies to microelectrode arrays in which conductive sites adsorbed to the electrode’s surface act as a set of ultra-microelectrodes and whose responses are dependent upon radial diffusion.
CHAPTER III

EXPERIMENTAL DETAILS

Instrumental Design

All cyclic voltammograms were acquired using a Cypress Systems 1090 potentiostat coupled to a 486 IBM compatible computer. The system is attached to a bubbling tower and nitrogen tank. All measurements were performed in a grounded Faraday Cage using a covered 2mL glass electrochemical cell. A platinum counter electrode and Ag/AgCl reference electrode were employed.

Solutions were purged with ultra-pure nitrogen gas in order to eliminate possible interference by oxygen. The nitrogen gas was saturated with pure, dry solvent using a bubbling system. The nitrogen gas was kept over the cell throughout each experiment to prevent interference by oxygen.

Reagents and Glassware Preparation

HPLC grade acetonitrile from Aldrich was continuously distilled off of CaH₂ under a nitrogen atmosphere using a continuous recycling still. Tetrabutylammonium hexafluorophosphate was purchased from Aldrich and recrystallized a minimum of twice in hot absolute dehydrated (200 Proof) ethanol and dried under vacuum prior to use. Ferrocene and cobaltocenium hexafluorophosphate were purchased from Aldrich and used as received. Lithium aluminum hydride was purchased from Aldrich and used in a nitrogen glovebox
and was replaced every few weeks in order to prevent the formation of aluminum oxide on the diamond surface. Bromine was used as purchased and stored in darkness to prevent formation of free radicals. Chloro-trimethylsilane was stored at approximately 20°C in a freezer.

Glassware was cleaned using ethanol followed by rinsing with deionized water, then soaked in hot nitric acid, and subsequently rinsed thoroughly with deionized water and dried in a 200°C oven. All sample cells were rinsed thoroughly with freshly distilled acetonitrile prior to use. All reactions were performed in ½ dram vials.

Reduction of diamond surfaces using lithium aluminum hydride (LAH) was performed in a nitrogen-filled glove box. Electrode tips were immersed in LAH, immediately rinsed with diethyl ether, and subsequently rinsed thoroughly with deionized water and then soaked in fresh acetonitrile.

Fabrication of Electrodes

The fabrication of electrodes begins with electrochemical etching of the tungsten wire. In order to form a sharp tip, the wire is etched electrochemically by applying 30 VAC thus forming a tungsten tip. Another 10 VAC was applied for 10 seconds to polish the shape of the tip. The resulting tip was then washed with copious amounts of DI water and dried in a nitrogen stream.

Diamond films were grown as previously reported\textsuperscript{1,11} using a microwave plasma CVD system (ASTEX) fitted with automatic pressure, temperature, and gas controllers. Typical growth conditions were: gas mixture of 0.1 to 5% CH\textsubscript{4} in
H₂, pressure of 10 to 60 Torr, susceptor temperature of 500 to 950°C, and microwave power of 700 to 1500 W. Diamond films were grown on tungsten wire-tips that were electrolytically etched and polished prior to use. Selective nucleation was carried out prior to film growth by a cantilever method of pressing the tip against a surface coated with diamond paste containing 0.1-mm diamond particles. The diamond microcrystals were doped in-situ using either a solid or liquid source of boron. The solid source being a pellet of boron placed on the susceptor, while boric acid dissolved in acetone is the liquid source.

The electrodes studied were continuous thin films grown on the tungsten substrate. The electrodes were sealed in glass capillaries using epoxy.

**Electrochemical Cell**

A three-electrode system was employed in order to minimize errors. In this case current flows between the working electrode and the counter electrode as the potential of the working electrode (in this case the diamond electrode) is measured with respect to the Ag/AgCl reference electrode. This reduces iR drop and avoids internal polarization of the reference electrode.

Electrochemically, the three electrode system can be demonstrated by the following example. Ferrocene, which undergoes a single electron oxidation to form ferrocenium, loses one electron to the working electrode.

\[
\text{FeCp}_2 \rightarrow \text{FeCp}_2^+ + e^-
\]
The electron is forced to pass through the circuit and back into the solution at the counter electrode in order to prevent the formation of large potential differences. As oxidation is occurring at the working electrode, reduction is occurring at the counter electrode. The degree of reduction at the counter electrode is equivalent to the degree of oxidation at the working electrode.

The supporting electrolyte used in all experiments was tetrabutylammonium hexafluorophosphate (TBAH). The supporting electrolyte in aprotic solvents is customarily a tetraalkylammonium salt. TBAH is more difficult to reduce than tetraethylammonium salts, thus allowing for maximum cathodic range. Other electrolytes such as those with halide counterions do not provide a good anodic range because they are more easily oxidized. TBAH permits both a maximum anodic and cathodic range in which to study the diamond's surface.

The reference electrode should exhibit a variety of important properties including reversibility, Nernstian behavior, stable potential with respect to time, little or no hysteresis, and the solid phase should not be substantially soluble in the electrolyte. The silver-silver chloride electrode is one of the most reproducible and reliable reference electrodes.

The working electrode employed was the diamond thin film electrode. This electrode differs from the previously reported microelectrodes in that in many cases they have a competition between planar and radial diffusion. While a typical macroelectrode such as a glassy carbon electrode relies on planar diffusion as the predominant form of mass transport to and away from the
electrode surface, and the microelectrode is dominated by radial diffusion, the thin film electrodes studied in these experiments were a hybrid of both. Because of the high degree of facets on a diamond film, there is increased ability for radial diffusion despite the electrode surface being greater than a single microcrystallite. Consequently, it is possible to obtain a steady-state concentration of analyte at the electrode surface even when it is polarized. As previously discussed\textsuperscript{84-86} this can allow the electrode to be used in solutions with extremely low concentrations of electrolyte or in solutions with nonpolar solvents.

Because the measurement of small DC currents without noise interference is necessary with microelectrodes, a Faraday cage is employed. This acts as a shield against electronic noise.

The solvent used in each experiment is acetonitrile because of its resistance to both oxidation and reduction. The combination of TBAH and acetonitrile provides a very large potential window in which to study redox reactions. In addition, HPLC grade acetonitrile is quite pure, and continuously distilling the solvent removes any remaining impurities.

Ferrocene was used as an internal standard throughout these experiments because it exhibits a highly reversible one-electron oxidation but is resistant to reduction. The positive charge on ferrocene is delocalized over the 10 equivalent CH’s on the cyclopentadienyl rings. Ferrocene’s redox couple does not affect the redox of cobaltocenium, which makes it an excellent internal standard. Additionally, ferrocene is well studied and well understood.
CHAPTER IV
DIAMOND'S FUNCTIONAL GROUPS: MANIPULATION AND EVALUATION

Presence of Oxygen Sites

During typical ME-CVD diamond growth, methane and hydrogen gases are used during the growth procedure. The diamond growth is halted by first stopping the flow of methane in order to prevent deposition of non-diamond carbon on the surface. Therefore, the final step of the growth process is exposure of the generated diamond to a hydrogen plasma resulting in a hydrogen terminated surface. It is well known that subsequent exposure of the CVD diamond thin-films to the atmosphere results in surface bound oxygen which dramatically effects the electron emission and surface conductivity properties of the diamond. Considering the highly reactive nature of molecular oxygen, it is reasonable to suspect that these changes are due to the reaction of atmospheric oxygen with the hydrogen terminated surface via autoxidation of the surface, i.e., the slow conversion of a surface C-H bond to an alkyl hydroperoxide (COOH) by atmospheric O₂, a diradical (R-H + O₂ → R-O-O-H). This process is autocatalytic because the hydroperoxide residues that form catalyze further oxidation. The hydroperoxides formed generally react further to form alcohols (C-OH), carbonyls (C=O), and other oxygenated products. Consequently, electrodes may exhibit different responses due to the number and type of oxygen sites on the diamond surface. If those sites can be manipulated or controlled,
then it would be possible to carry out a variety of reactions on the diamond surface.

**Bromine**

Diamond thin-film electrodes *briefly* exposed to liquid bromine (a potent oxidizing agent) in a darkened bottle can result in dramatic alteration of the electrode characteristics (Figures 40-42). These electrodes exhibit a strongly enhanced anodic current at positive potentials. This response is stable and reproducible as a function of both time and potential cycling in acetonitrile/TBAH. If this electrode is then treated with LiAlH₄, the original response is regenerated.

Bromine appears to have several possible roles in its interaction with the diamond surface. First, it appears the bromine oxidizes secondary alcohol sites to carbonyls⁹¹ (Figure 15). Second, it appears bromine may potentially brominate sites on the diamond, which then leads to the formation of more oxygen sites via hydrolysis (Figures 16 and 17). This may appear counter-intuitive to many organic chemists, but with a boron-doped CVD diamond the focus must be on the surface of a large molecule acting in concert, rather than individual carbon atoms. Therefore, what may not seem probable on a pure alkane, may indeed be possible on a diamond thin film. For example, diamantane, a diamond precursor, has been shown to brominate at select sites at room temperature depending upon the conditions.⁵⁵ Third, diamond appears to form alkyl hypobromites upon exposure
to bromine (Figure 17). Each of these functional groups will be discussed in the Results section.

Bromine, in a similar method as the chlorine discussed previously, may act as an intermediate to surface modification. Bromine is traditionally a good leaving group in an Sn1 type reaction, opening up a reactive carbocation site, stabilized through induction. Also, brominated sites react readily with water, leaving alcohol sites. Depending on the surface, these sites may be secondary or tertiary alcohols.

Bromine, as discussed earlier, may react with the diamond surface through a bromonium ion type mechanism in which any double bonds on the surface attack the bromine molecule. The bromonium ion would then rearrange to give a tertiary carbocation stabilized through induction, which would then react with bromine to add bromine in a syn fashion. While bromination of alkenes is normally anti-addition, there are instances where syn additions occur. Here, steric factors would force the addition to be syn (figure 18).

Bromine may also react with the highly strained carbon-carbon single bond of the monohydrogenated surface in order to reduce surface free energy, forcing a surface rearrangement that leads to further bromine sites on the surface. Here a bromonium ion would form followed by a carbocation formation, which would then react with an adjacent carbon causing a proton to be lost (figure 19). Whatever the mechanism, bromine appears to add to the diamond surface and greatly affects the electrochemical response of diamond electrodes.
Silylation

Organic chemists often use “protective” groups to prevent certain functional groups from reacting in a mechanism, or to retain some form of chirality. Using this same principle, chloro-trimethylsilane was used to “protect” oxygen sites from further oxidation by bromine and from the formation of alkyl hypobromites. Alcohol sites were converted to silyl ethers. It is doubtful all alcohol sites would be converted to silyl ethers because of the steric strain, especially on the (111) surface, but this is dependent upon oxygen coverage. When exposed to the silylizing agent and subsequently exposed to bromine, the large anodic current is no longer seen, thus lending credence to formation of alkyl hypobromites. Furthermore, the protective group may be removed in the presence of a mild acid. It is possible, if the electrode is not neutralized in sodium bicarbonate or some other mild base, to leave acid sites or possibly protonated alcohol sites on the diamond surface. In any case, once the protecting group is removed and the electrode is re-exposed to bromine, the large anodic current appears, further indicating the formation of alkyl hypobromites.
Figure 15. Schematic of the proposed chemistry taking place on the diamond (100) surface. Bromine oxidizes secondary alcohols to carbonyls, which because of their dipole may give an enhanced cobaltocenium current. This reaction is believed NOT to be responsible for the electrocatalytic behavior shown after exposure to bromine.
Figure 16. Conversion of bromine sites to alcohol sites. A small amount of water will rapidly convert brominated sites to hydroxyls via hydrolysis. This may occur simply in a humid atmosphere.
Figure 17. Formation of alkyl hypobromites on diamond surface. Part of the proposed chemistry taking place on the diamond surface which is responsible for the electrocatalytic oxidation of solvent. Protecting alcohol sites by forming silyl ethers prevents reaction of the site with bromine.
Double bond on strained ring reacts with bromine to lower ring strain. Tertiary carbocation formation stabilized through induction. Bromine added syn to double bond because of steric factors.

Figure 18. Proposed mechanism for the addition of bromine to the diamond (100) surface.
Figure 19. Second proposed mechanism for the addition of bromine to the diamond (100) surface. Here bromine adds to the (100) surface, forcing a surface rearrangement. This reaction then could continue along the diamond surface leading to more bromine sites.
**Bromination Leading to Oxygen Sites**

If indeed bromination occurs on the diamond surface, what evidence lends credence to the formation of further oxygen sites? From an organic chemist’s perspective, bromine is a rather good leaving group for an Sn1 type reaction mechanism. It is quite possible for the bromine to follow this type of mechanism, leaving as HBr in either a humid atmosphere, or in the presence of water, and then be replaced by an OH⁻. A freshly grown diamond thin film electrode was exposed to chloro-trimethylsilane and subsequently exposed to bromine. This electrode exhibited a strong anodic current, caused by a reaction of bromine with the oxygen sites. All previous attempts to protect oxygen sites from these reactions have been successful, including diamond film exposed to oxygen plasma. Therefore, a possible mechanism is one in which the diamond surface is brominated, perhaps only at certain sites, and subsequently is oxygenated in a humid atmosphere, or by trace amounts of water in the bromine. Another possibility could be the location of oxygen sites on the diamond film. It is conceivable that only a portion of those sites can be protected by the silylizing agent due to steric concerns depending on the oxygen coverage. The trimethylsilane can be viewed as a rather bulky functional group akin to the t-butyl group. This may indeed prevent other silyl groups from protecting oxygen sites on the film, however, one would suspect it would also prevent bromine from approaching the unprotected site. In any case, there is no doubt there are oxygen sites on diamond films, and these sites lend some exciting properties to the electrode.
Glassy Carbon and Tungsten

Naturally it is important to distinguish the electrode responses observed with the diamond electrode from those of the metal substrate and from possible impurities in the diamond thin film. While Raman spectroscopy clearly indicates the purity of the diamond films being used, exposure of the glassy carbon electrode to bromine further supports both notions. First, it is quite apparent that the diamond films have extremely low levels of sp² hybridized carbons, which would be an impurity in the film. From the Raman spectrum (Figure 20), it is apparent there is some weak scattering intensity near the 1550 cm⁻¹ region indicative of some graphitic or amorphous carbon (sp²) impurities most likely on the diamond’s surface. Most likely, this is the result of π-dimers as discussed earlier.

Second, voltammograms obtained from the exposure of glassy carbon to bromine indicate a small adsorption and small increase of anodic current, which may be indicative of bromination of the glassy carbon electrode (Fig. 21). Using LAH, the glassy carbon electrode’s anodic current after bromine can be reduced (Fig. 23). Also, the adsorption peak appears to decrease with consecutive scans (Fig. 22). This is further indication that in this case the bromine is adsorbing to the surface. If it were simply Br₂, it would not be possible for it to be oxidized as a species in solution. The adsorption peak increases with increased exposure to bromine. While the maximum exposure time for these experiments was only 30 seconds, it would appear that a glassy carbon electrode can indeed be brominated, but the response seen is quite different from that of the diamond thin film.
Figure 20. Raman spectra of a CVD grown diamond.
Figure 21. Glassy Carbon electrode before and after bromine exposure.
Figure 22. Glassy carbon electrode after exposure to bromine: first and second scans.
Figure 23. Glassy Carbon electrode after exposure to bromine and subsequent exposure to lithium aluminum hydride.
Figure 24. Tungsten electrode in 0.4 mM ferrocene and 0.8 mM cobaltocenium in TBAH/Acetonitrile.
As for the metal substrate, the tungsten electrode exhibited no change after exposure to bromine. Also, it is important to note the response given by tungsten with its strong cathodic response at negative potentials (Fig. 24). This is not seen for the diamond thin film electrodes.

**Self-Assembled Monolayers and Micro-Electrode Arrays:**

Typically, the term self-assembled monolayers (SAM) deals with the strong adsorption of thiols, disulfides, sulfides and other species to metals, particularly gold. These monolayers are single molecular layers bound in some fashion to the metal’s surface. These monolayers can have a variety of effects on an electrode’s electrochemistry. SAM’s may be nonelectroactive, meaning they block electrochemical response, or they may be electroactive, enhancing an electrochemical response. The monolayers may form on a particular face, or all faces. It is greatly dependent upon the material’s structure and reactivity.

Monolayers may have ionic or neutral terminal groups. These groups may greatly alter the electrochemical response of the electrode. For example, if a monolayer is terminated with a carboxylic acid group, the response seen in neutral solution may vary quite significantly from those in acidic or basic mediums.

Diamond, with its oxygenated functional groups, may be viewed as having a self-assembled monolayer. This monolayer can greatly affect the electrochemical measurement of charged species in solution, while having little
or no measurable effect on uncharged species. Depending on the locations, types, and concentrations of surface sites, the electrochemistry of a charged species may be enhanced or suppressed. These specific sites can be viewed almost as a microelectrode array, specific for charged species. This SAM/micro-electrode array concept is demonstrated in the Results section.

**Microelectrode Array Model:**

A diamond surface with less than one monolayer oxygen coverage may be considered a microelectrode array. The current measurements for cobaltocenium, a positively charged redox species reduced at negative potentials, has been found to be dependent upon the presence and type of oxygen on the diamond electrode’s surface. In the microelectrode array model, the rate of electron transfer is greatly dependent upon the spacing and number of oxygen sites on the electrode surface.

An electrode with oxygen sites whose separation distance is quite large would give a less defined cobaltocenium response (Fig. 26), while one whose oxygen separation is small would give a more defined cobaltocenium response (Fig. 27). When separation between oxygen sites is large, the microarray can be viewed as a set of microelectrodes on the surface. These “microelectrodes” replace the “peak” shape of the voltammogram with a plateau shape indicative of a steady-state voltammogram, but if the concentration is extremely small the response is merely a rise in current (Fig. 25). For the most part, the electrodes studied have demonstrated behavior that fall between the steady-state microelectrode behavior and non-detection of cobaltocenium. As discussed
previously, the oxygen coverage is dependent upon the predominant type of surface for the electrode. An electrode that is predominantly (111) will have few if any oxygen sites, while a (100) may have a large number of oxygen sites.

A wide range of behavior has been seen in the cyclic voltammograms of the redox species cobaltocenium. For example, a slow rise in current with no visible peaks or plateaus has been noted. The rise in current is due to electron transfer at the oxygen sites on the electrode. The lack of peak or plateau is indicative of a very small concentration of oxygen sites on the surface. Also a distinct limiting current has been found for some electrodes, indicative of either a high number of dispersed oxygen sites, or perhaps a very high localized concentration of oxygen sites. By increasing the concentration of oxygen sites throughout the entire diamond surface, the limiting current for cobaltocenium would be enhanced.
Figure 25. Microelectrode array model 1. A) Schematic of a microelectrode array in which oxygen sites are few and have large distances between them. B) the proposed electrochemical response for this type of electrode in cobaltocene.92
Figure 26. Microelectrode array model 2. A) schematic of a microelectrode array in which there are a moderate number of oxygen sites in fairly close proximity. B) the proposed electrode response for this type of electrode in cobaltocenium.92
Figure 27. Microelectrode array model 3. A) schematic of a microelectrode array in which there is high oxygen coverage. B) the proposed electrode response for this type of electrode in cobaltocene.92
CHAPTER V
RESULTS AND DISCUSSION

The electrochemistry of fresh CVD grown diamond in Tetrabutylammonium hexafluorophosphate initially exhibits a previously unrecorded response, which may be indicative of the desorption of atomic hydrogen consistent with the surface rearrangement theory (Fig. 28). This signal was shown by 4 different electrodes, all grown in the same batch. Previous electrodes have been allowed to “sit around” for anywhere from several weeks to several months before being studied, therefore desorption of atomic hydrogen had probably already occurred.

Despite CVD diamond thin films being hydrogen terminated at the completion of growth, oxygen functional groups develop as a function of exposure to a humid atmosphere over a period of time. As discussed earlier, these species are a result of an auto-oxidation reaction with molecular oxygen, forming a variety of functional groups. Electrodes have shown varying responses toward cobaltocenium, a positively charged redox species, in acetonitrile/TBAH. In order to determine the effect of oxygen on the determination of cobaltocenium, an electrode was exposed to an oxygen plasma for 2 minutes.

Oxygen plasma, a low temperature plasma, produces oxygen radicals that may then react with a material’s surface. An electrode exposed to an oxygen plasma for 2 minutes demonstrated several interesting phenomenon.
Diamond electrode in TBAH/Acetonitrile: first and second scans

Figure 28. CVD diamond electrode in TBAH/Acetonitrile. Response shown in first scan believed to be result of desorption of atomic hydrogen.
First the electrode was studied in a solution of acetonitrile/TBAH with ferrocene as an internal standard (0.4mM), and cobaltocenium hexafluorophosphate (0.8mM) as the species of interest. Exposure to the oxygen plasma resulted in an enhancement of the cobaltocenium current, while only minor change was observable for the ferrocene. The overall voltammogram shows an increase in electrode capacitance corresponding to the increased oxygen coverage. It is quite conceivable for the oxygen plasma to have introduced oxygen functional groups on surfaces that had not previously had oxygen functional groups (i.e. the (111) surface). It is apparent that the presence of oxygen sites enhances the detection of positively charged cobaltocenium at negative potentials. The functional groups introduced as a result of the oxygen plasma are various and include alcohol, carbonyl, and ether sites. The cyclic voltammograms in Figure 29 show the enhanced cobaltocenium after the oxygen plasma. Here cobaltocenium reduction has reached a limiting current, while before the oxygen plasma the response is simply a drawn out rise in current. Figures 30 and 31 show the varying cobaltocenium responses for diamond electrodes.

Electrodes exposed to bromine, a powerful oxidizing agent, have exhibited electrocatalytic responses in acetonitrile/TBAH. The response is an electrocatalytic oxidation of the solvent. First inclination would be that the bromine has oxidized secondary alcohol sites to carbonyls and this is in turn responsible for the electrocatalytic response. However, the electrode exposed to the oxygen plasma did not demonstrate this response, which it would have had the response been due to carbonyl sites (Fig. 29).
It is proposed that bromine bound to the surface is responsible for the electrocatalytic response. Bromine may be bound as atomic bromine or as alkyl hypobromite functional groups (R-O-Br). Several electrodes have been silylated using chloro-trimethylsilane with varying results. Silylation converts alcohol sites to silyl ethers, which are then unoxidizable by bromine and unreactive. This method of “protection” is used often in organic chemistry to prevent side reactions. Figure 33 shows some minor hysteresis as a result of converting the alcohol sites to silyl ethers. It is important to note that while alcohol sites would be converted to the silyl ethers, other oxygen sites such as carbonyls would not. The electrode exposed to the oxygen plasma was protected and subsequently exposed to liquid bromine. The electrode demonstrated only minor hysteresis compared to the unprotected surface. This may be attributable to a small degree of bromination of surface sites. Figures 24 and 25 demonstrate the effectiveness of using silyl ethers to prevent reactivity. The silyl ethers were removed using 0.5M hydrochloric acid, and subsequently re-exposed to bromine. A strong anodic current was once again measured, indicative of electrocatalytic oxidation of the solvent. Minor hysteresis was noted after the acid rinse, attributable to the formation of acid sites or the protonation of some alcohol sites. The electrocatalytic response could not be attributed to the formation of carbonyls on the surface or the same response would have been seen after the oxygen plasma. It is therefore proposed that bromine forms alkyl hypobromites on the diamond surface. Protection of the alcohol sites by silylation prevents the formation of these hypobromites, but once the silyl ethers are converted back to alcohols they
are readily available to react. It is important to note that while Figure 35 shows a strong anodic current, it is not as strong as has been shown for other electrodes. It is strongly believed that bromination of the diamond surface occurs at various sites thus giving the strong anodic current. An early attempt at protecting the diamond’s surface is shown in figures 40-42. Figure 40 shows the extremely large anodic current usually associated with diamond reacting with bromine. The slight hysteresis shown in figure 41 after protection and exposure can be attributed to bromine bound to the diamond surface. The greater the number of bromine atoms or hypobromites formed on the surface, the greater the electrocatalytic response. Figure 42 shows the background cyclic voltammograms for the diamond electrode showing the electrocatalytic response as well as before exposure to bromine and after protection and exposure. Bromine undeniably plays an important role in the surface chemistry of diamond.

Again this may seem counter-intuitive from an organic chemistry standpoint, but diamond is quite different from its alkane counterparts. For example exposing an alkane to an oxygen atmosphere will not result in the transformation of the alkane to an alcohol, but a diamond exposed to an oxygen atmosphere will form oxygenated sites over a period of time. And while diamond will react with perchloric acid to form oxygen sites, an alkane will not. There are distinct differences between the chemistry of diamond surfaces despite the similarity in structure.

Electrodes exposed to bromine have shown an enhancement of the detection of cobaltocenium in solution. This is attributable to the self-assembled
monolayer and microelectrode array theory. Secondary alcohol sites oxidized to carbonyls are more polar than the original alcohols. A carbonyl can be viewed as having a partial positive charge on the carbon, while the more electronegative oxygen has a partial negative charge. The partial negative charge attracts the cobaltocenium's electron transfer, thus enhancing the measured current. Also, this would explain several instances of adsorption of cobaltocenium on the electrode surface. Cobaltocenium, being a positively charged species, would much more strongly adsorb to a negatively charged functional group than to a neutral functional group. Also, the bromine may have introduced additional oxygen sites that would enhance the detection of cobaltocenium.

Ferrocene, the internal standard throughout these experiments, is a neutral molecule and demonstrated no significant change in reduction current before or after oxygen plasma, but a decrease in oxidation current partially attributable to concentration discrepancies and possibly certain oxygen sites. It is important to note that the ferrocene response may be shifted by as much as 100 mV after oxidation, and the redox couple may also be drawn out. This may be attributable to iR drop or a change in the rate of electron transfer.

If cobaltocenium response is indeed tied to the oxygenated functional groups, and charged species are enhanced by oppositely charged sites on the electrode surface, then altering the functional groups in such a way as to make them all charged or all neutral should affect the electrochemical response. An electrode rinsed with KOH gave a definite enhanced response, which as would be expected. A strong base such as KOH would rip hydrogens off of acidic
functional groups as well as deprotonate some if not all alcohol groups. This is most likely a function of timed exposure to the strong base. Exposure to a strong acid, such as HCl, should not only reprotonate negatively charged functional groups, but may also protonate some alcohol groups giving \( \text{OH}_2^+ \) on the diamond surface. It is important to note that oxy-acids such as perchloric or nitric have the ability to introduce more oxygen species to the surface, thus affecting the results. This experiment was repeated four times by alternating between hydrochloric acid and potassium hydroxide, each exposure resulting in the same responses: enhanced cobaltocenium after base, and suppressed cobaltocenium after acid (Figs. 36 & 40). This strongly supports the microelectrode array of functional groups effecting the measured responses for charged species in solution.

Scan-rate dependence measurements were made for different electrodes exhibiting a relatively enhanced cobaltocenium response. Responses for cobaltocenium have been found to range greatly, again dependent upon the electrode's history. Moderately slow scan rates were ideal (20 mV-100 mV), while fast and extremely slow scan rates gave less defined cobaltocenium responses. This may be due in part to the number of oxygen sites, the type of oxygen site, and their location on the surface. Figures 37, 38, and 39 show the varying responses with respect to scan rate. At fast scan rates a second peak appears, perhaps due to adsorption of the species on the electrode surface.
Figure 29. Diamond electrode before and after oxygen plasma: cobaltoceneum region only.
Figure 30. CV of diamond electrode exhibiting semi-enhanced cobaltocenium reduction.
Figure 31. Microelectrode behavior of CVD diamond thin film electrode. Cobaltocenium reduction very drawn out. Oxidation of ferrocene very strong with limiting current.
Figure 32. Cyclic Voltammogram of CVD diamond electrode before and after oxygen plasma.
Effect of Chloro-trimethylsilane on Diamond Surface

Figure 33. CVD Diamond electrode after oxygen plasma and then silylation.
Effect of Bromine on a Protected CVD Diamond Electrode

Figure 34. Diamond electrode exposed to oxygen plasma, protected and subsequently exposed to bromine.
Figure 35. Cyclic voltammograms for CVD diamond electrode exposed to bromine.
Diamond Electrode: Effect of Functional Groups on Cobaltocenium Detection

Figure 36. Cyclic voltammogram of CVD diamond in ferrocene/cobaltocenium-TBAH/Acetonitrile solution. After rinsing with base, enhanced cobaltocenium is measured with a distinct limiting current, while after acid rinse the response is changed. This is reproducible with each rinse.
Diamond electrode in cobaltocenium: Scan Rate Dependence—moderate scan rates

Figure 37. Diamond electrode in 0.4mM cobaltocenium at moderate scan rates of 25, 50, 100, 150 mV/sec.
Figure 38. Cyclic voltammograms of diamond electrode in 0.4 mM cobaltocenium at scan rates of 200, 300, 400 and 500 mV/sec.
Figure 39. Cyclic voltammograms of diamond electrode in cobaltocenium at slow scan rates of 5, 10, 20, 25 mV/sec.
Figure 40. Reaction of acid and base with oxygen surface groups which lead to enhanced cobaltocene currents at negative potentials.
Figure 41: Cyclic voltammogram for the oxidation of ferrocene in acetonitrile at a CVD diamond electrode before and after exposure to bromine followed by thorough rinsing of the electrode with the solvent.
Figure 42: Cyclic voltammograms for the oxidation of ferrocene in acetonitrile at a CVD diamond electrode demonstrating that protection of surface oxygen sites with a covalently bound silane prevents significant reaction with bromine.

Figure 43: Background CV's in acetonitrile/TBAH for a CVD diamond electrode before pretreatment, after silylation of surface and subsequent exposure to bromine, and before silylation but after exposure to bromine.
CHAPTER VI
CONCLUSIONS

The electrochemistry of boron-doped CVD diamond thin film electrodes appears to be at least partially dependent upon the functional groups bonded to the diamond’s surface. Oxygen functional groups develop on the diamond surface through a variety of possible mechanisms:

1) auto-oxidation by reacting with oxygen/H$_2$O over a period of time
2) reaction with bromine which serves as an intermediate for the formation of oxygen containing functional groups
3) reaction with perchloric acid and other oxy-acids
4) exposure to an oxygen plasma

These functional groups introduce the possibility of a variety of exciting reactions on the diamond’s surface, which may lead to the development of better electronic sensors, selective electrodes, and flat-top displays.

Oxygen sites on the diamond appear to react with bromine by forming hypobromites as well as converting secondary alcohols to carbonyls. This is the first low temperature reaction introduced thus far for diamond materials. The reaction has been shown to be prevented by converting surface alcohol sites to silyl ethers, which then may be removed with mild acid.

Oxygen sites have been shown to enhance cobaltocenium response at negative potentials. This is most likely a function of oxygen introducing states in the band gap that aid in the flow of electrons from the surface to the charged
species in solution. This is further enhanced when the surface functional group is negatively charged, either completely as in the formation of an alkoxide, or partially as in the formation of a carbonyl.

While it appears that the redox current of positively charged species may be enhanced at negative potentials by the presence of oxygen sites, neutral species like ferrocene appear to be unaffected. The surface sites appear to form a self-assembled monolayer type microelectrode array on the surface of the diamond with respect to the charged species. Using base, the oxygen sites can be converted to alkoxides and consequently enhance the detection of cobaltocenium. Acid reverts the alkoxides to alcohol sites, thus diminishing the cobaltocenium response.

For the first time, room temperature chemistry to diamond thin film electrodes has been performed and controlled to some degree. By controlling the chemistry of diamond surfaces it will be possible to enhance the material’s properties for a variety of applications, both electronic and electrochemical. The surface chemistry of diamond appears to be a rich area of chemistry that remains to be exploited.
REFERENCES


27. Freedman, A. J. Appl. Phys. 1994, 75, 6, 3112


VITA

Robert M. Johnson

EDUCATION:

Aug. 96 – Aug. 98
Old Dominion University Norfolk, VA
Master of Science (Chemistry)
Thesis: Chemical Modification of CVD Diamond Electrodes
GPA: 3.6/4.0

Aug. 92 – Aug. 98
Virginia Tech Blacksburg, VA
Bachelor of Science (Chemistry/double major in History)
GPA: 2.5/4.0

PROFESSIONAL EXPERIENCE

Aug. 96 – Aug. 98
Old Dominion University Norfolk, VA
Graduate Teaching Assistant

• General Chemistry Labs
• Organic Chemistry Lab

Graduate Research Assistant
Materials Chemistry


PROFESSIONAL MEMBERSHIPS: ACS Member

EXTRACURRICULAR ACTIVITIES: Omicron Delta Kappa, Residence Hall Federation President, National Residence Hall Honorary, NACURH 95, SGA House of Representatives, Chemistry Club, Order of the Gavel, Commission on Student Affairs