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SURFACE CHARACTERIZATION OF INDUCTIVELY COUPLED RADIO FREQUENCY PLASMA TREATED GLASSY CARBONS BY X-RAY PHOTOELECTRON SPECTROSCOPY AND SCANNING ELECTRON MICROSCOPY

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Charles William Miller

* * * * *

The Ohio State University

1986

Reading Committee: Approved By
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Dr. Larry B. Anderson Department of Chemistry
DEDICATION

To my father Carl W. Miller who always taught me to be curious about nature.

To my children Carl Clinton and Julie Ann.

To my wife Suzy.
ACKNOWLEDGEMENTS

The author sincerely appreciates the support and guidance of Professor Theodore Kuwana during these studies. All members of the research group at The Ohio State University, including Dr. Paul Forshey for his help in learning the computer system used in obtaining, storing, and processing the XPS data, and Dr. Dale Karweik for help in maintaining the XPS instrument electronics.

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<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
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<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>BE</td>
<td>Binding Energy</td>
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<tr>
<td>CMA</td>
<td>Cylindrical Mirror Analyzer</td>
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<tr>
<td>CME(s)</td>
<td>Chemically Modified Electrode(s)</td>
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<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>ESR</td>
<td>Electron Spin Resonance</td>
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<td>eV</td>
<td>Electron volt</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray Absorption Fine Structure</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum peak Height</td>
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<td>GC</td>
<td>Glassy Carbon</td>
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<td>GPSA</td>
<td>General Purpose Side Arm</td>
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<tr>
<td>HOPG</td>
<td>Highly Ordered Pyrolytic Graphite</td>
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<td>IHS</td>
<td>Introduction Handling System</td>
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<td>Instrument Response Function</td>
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<td>ISA</td>
<td>Isolation Side Arm</td>
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<td>KE</td>
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<td>LC</td>
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<td>LEED</td>
<td>Low Energy Electron Diffraction</td>
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<td>PG</td>
<td>Pyrolytic Graphite</td>
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RFP  Radio Frequency Plasma
RS  Raman Spectroscopy
S/N  Signal to Noise ratio
SEM  Secondary Electron Microscopy
SERS  Surface Enhanced Raman Spectroscopy
Sig  Sigradur Glassy Carbon
SIMS  Secondary Ionization Mass Spectrometry
TDMS  Thermal Desorption Mass Spectrometry
TFAA  Trifluoroacetic Anhydride
UHV  Ultra High Vacuum
XPS  X-Ray Photoelectron Spectroscopy
CHAPTER 1

INTRODUCTION

In electrochemistry, the electrode surface plays an important role in the electron transfer process. Altering the electrode surface conditions may have a distinct effect on its redox reversibility, catalytic ability, or stability. Electrode modification by chemical means is presently an active area of research with the objective of producing chemically modified electrodes (CMEs) with predictable, reproducible and useful electrochemical properties. The modification, in effect, introduces electroactive species onto the surface or introduces precursors for subsequent selective attachment of electroactive species or mediators. The mediators then act as electron "bridges" between the electrode and the solution substrate. For example, the lowering of the overpotential for the oxidation of NADH and ascorbic acid [1,2] can be accomplished by generation of "oxidized" surfaces by periodically potentiostating the electrode at relatively high positive overpotentials or by treating with radio frequency plasma in the presence of oxygen. It is thought that surface quinone/hydroquinone groups act as the mediator [3]. The electrode surface modification approach has enormous potential for replacement or conservation of precious metals such as Pt and for the design of electrodes with a high degree of selectivity or catalytic effect in their reactions.

Graphitic or glassy carbon materials are particularly attractive for CMEs since these materials exhibit a variety of surface functional groups which may be utilized for chemical modification. Surface groups such as hydroxyl, ketone or quinone, and carboxyl groups have been exploited for modification purposes [1,17]. In addition carbon is relatively cheap and it should remain plentiful for many years. In order to fully realize the potential of carbon based CMEs and to rationally design new
Modification procedures, an understanding of the carbon surface at the molecular and atomic level is required.

Today very powerful methods are available for the analysis of surfaces. These methods may be generally classified as vacuum techniques such as X-Ray Photoelectron Spectroscopy (XPS or ESCA), Auger Electron Spectroscopy (AES), Low Energy Electron Diffraction (LEED), Secondary Ion Mass Spectrometry (SIMS), Thermal Desorption Mass Spectrometry (TDMS), Scanning Electron Microscopy (SEM). Non-vacuum techniques such as Ellipsometry, Reflectance Spectroscopy, Raman (RS) and Surface Enhanced Raman Spectroscopy (SERS), and Extended X-Ray Absorption Fine Structure (EXAFS) also can assist in surface elucidation studies. The vacuum spectroscopies have the advantage of being very sensitive to the "upper" layers of a material and the disadvantage of requiring the sample to be vacuum compatible. Sensitivity to only the surface is especially important for the characterization of modified surfaces since the results of modification may only extend from less than a monolayer to a few layers of material, thereby, presenting an inherently poor signal to noise (S/N) ratio. An additional problem of signal (detection of the modified surface) to the background (unaltered subsurface) exists for modified carbon electrodes. Significant changes in the surface modified layer may result in only slight changes in the observed spectrum. When the the modification results in the introduction on atomic species not found in the substrate, this new species can be used a "marker" atom to follow the progress of the modification.

In this work SEM and XPS were utilized for the physical and chemical characterization of glassy carbon surfaces which had been chemically modified by radio frequency plasma (RFP) gas treatments. The RFP method was first employed in our laboratory for the surface modification of pyrolytic graphite (PG) [2]. XPS revealed that the oxygen/carbon (O/C) ratio of the surface increased by a factor of ca. 2.5 over an untreated surface. Etching of the surface was also observed with SEM. Electrochemical characterization by cyclic voltammetry and differential pulse polarography combined with results from chemical derivatization studies indicated
the presence of primarily quinone/hydroquinone and carboxyl groups on the modified surface. The RFP method was also extended to modification of glassy carbon (GC) and highly ordered pyrolytic graphite (HOPG) [16].

"Glassy" or vitreous carbon, produced from the solid state pyrolysis of polymeric carbons, was first described by Yamada and Sato [18]. Pyrolysis of polymeric carbons is not a recent development. In 1880, Thomas Edison heated bamboo fibers and pitch in an iron mold to form conductive filaments for use in electric lights [19]. Various polymer starting materials such as poly(vinylidene chloride), poly(acrylonitrile), poly(furfuryl alcohol), poly(divinylbenzene), as well as many formaldehyde and polyimide resins have been used. The final composition, degree of carbonization and graphitization depends on the starting material, the heating conditions, and the maximum temperature employed [20]. Up to 500°C the chemical composition consists mainly of carbon and heteroatoms. Between 500°C and 1000°C, C-H bonds are broken and above 1000°C, C-N and C-O bonds are broken leading to loss of H₂O, CO, CO₂, H₂, and N₂.

ESR studies [18] have been used to follow the changes occurring during the pyrolysis. As the most reactive bonds are broken, free radical sites are generated. With increased heating, the concentration of free radicals builds up, rearrangement takes place to form more stable intermediates, and ultimately the radicals combine to form condensed aromatic ribbon molecules oriented in a randomly tangled three dimensional state. Figure 1 [21] shows a schematic model for glassy carbon. The layers are thought to be covalently bound to each other at the edges of the layers. The stack height and width are on the order of 40 Å and 100 Å respectively. The random orientation of the ribbons results in the formation of micropores with a diameter of ca. 50-100 Å. The bond types in GC are predominately sp² and sp³, which occur at edges and defects [20,22]. The final product is a very pure form of carbon in a glass-like state. Its appearance is that of black glass. Like glass, GC is fragile and impervious to gases and liquids and has good thermal and electrical conductivity properties. It is resistant to chemical attack. The covalent bonding at the edges of the ribbons
account for the chemical inertness of GC since no "loose ends" or edge planes are readily available for attack. For more detail about the formation and properties of GC, see references [18,20-24].

The excellent electrical and physical properties of GC have made this material a potential replacement for other types of carbon as well as metal and metal oxide electrodes. Miller and Zittel [25] first pointed out the advantage of a wider, usable potential range than electrodes such as Hg and Pt.

Utilization of GC as an electrode material requires some sort of pretreatment to form a reproducible surface prior to use [6,12,15, 26-28]. Various methods of surface treatments have been reported. Condensed phase oxidations with dichromate or permanganate [11,29] and reductions with LiAlH₄ or B₂H₆ [11] have received limited attention. Thermal oxidations [9,27] by heating in air have been reported. Mazur [28] has reported the production of reactive "oxide free" surfaces by heating graphitic samples in a vacuum. Surface quinone/hydroquinone like groups have been reported on the surface of PG by our lab [16]. These groups can be generated by heating in the presence of oxygen or air, wet chemical treatment with an oxidizing agent, or by oxygen RFP [2,11,12,16]. Carboxylic acid groups have been utilized to form amide linkages to the surface [1-6,11], and surface hydroxyl groups can be activated by coupling with cyanuric chloride [8,17,29].

Carbon surfaces exhibit a variety of carbon-oxygen groups suitable for derivatization. The plasma surface modification approach offers a new, potentially simple, rapid, and contaminant free method for introducing carbon-oxygen surface groups. The ability to selectively introduce a single type of carbon-oxygen functional group in lieu of others would allow greater surface coverage by further chemical derivatization. The possibility also exists for introducing synthetically useful non-oxygen groups. This would allow derivatization of surfaces utilizing different reaction chemistry. For example, a halogen on a carbon surface may be suitable for the formation of carbon-carbon surface attachment via Grignard or organolithium reagents. Preliminary experiments in our laboratory have indicated synthetically
useful amine groups could be introduced by NH$_3$ RFP, but HBr RFP failed to produce a brominated surface [16]. The XPS analysis of the aminated surface indicated that, although NH$_3$ was used as the RFP gas, a significant amount of oxygen remained on the surface.

The XPS studies of the RFP modifications were compromised by the experimental requirement of sample removal from the plasma reactor prior to introduction into the XPS analysis chamber. In a similar experiment, Anson [30] exposed argon RFP treated samples to amine vapor and then analyzed the surfaces by XPS. Little or no decrease in the surface oxygen content was found. The inability of the non-oxygen gases to "remove" oxygen from the surface was attributed to the formation of reactive sites on the surface, which take up oxygen or water upon exposure to air, although air leaks or impurities in the gases were not ruled out [16,30,31]. This same inability to remove oxygen on surfaces has been observed previously in RFP treatments of polymers [32,33].

Radio frequency plasmas have been widely used in chemical processing. The species generated by the inductive coupling of radio frequency to a gas are ions, radicals, vibrationally excited molecules and free electrons [34]. The composition of a plasma and its interactions with solid surfaces are very complex and depend on the type of gas and the nature of the surface [35-37]. Extensive studies on RFP to modify the surfaces of polymers or to form polymers by plasma initiated gas phase polymerization have been reported [38,39]. Although complex, the general features of RF plasmas excited at low power (less than 100 watts) are those of a "cold" plasma. That is, the energy distribution of radical, ion, and neutral species corresponds to ambient temperatures, while the electron temperature is considerably higher. The electron energies are in the range of 0–10 eV. The concentrations of ions, electrons and metastable species are approximately equal. The free electrons gain energy from the imposed electric field and lose energy through collisions with neutral molecules forming new radicals, ions or atoms which can combine to form new gas phase species or collide with any surface present in the plasma [34,37,38].
When reactive plasma species contact a solid surface to form volatile products, the surface is etched away exposing the material below. An analogous situation exists for deposition of reactive species when the surface reaction does not lead to the formation of volatile species. The relative importance of the etching and deposition processes has been discussed by Yasuda (Chapter 2 of reference 39). Plasma modification is confined to the surface layers because the mean free path of ions or metastable species is on the order of a monolayer [35]. The resulting surface may remain very reactive after termination of the plasma treatment.

Reilly et. al. [32] have examined polymers (polyethylene and polystyrene) subjected to argon and nitrogen plasmas by XPS. Although these polymers did not contain oxygen, they found that oxygen was incorporated on the surface after plasma treatment. The source of oxygen was unclear since these polymers were exposed to the atmosphere prior to entry into the XPS spectrometer. Clark and Dilks [33] have studied the modification of polymers treated in a plasma reactor attached directly to the insertion port of an electron spectrometer. Such an arrangement allowed direct insertion of the sample into the analysis chamber following plasma treatment. Despite this experimental improvement, oxygen was still incorporated. The source of oxygen was attributed to oxygen adsorbed on the plasma chamber walls. The oxygen having entered the chamber during sample insertion. Oxygen could also be evolved from within the polymer. Air leaks between the "O" ring seal and the probe rod during plasma treatment and sample insertion may also account for oxygen contamination.

The reactive species generated in a plasma are determined by the composition of the gases present and can be easily changed by small amounts of contaminants [35]. Post-plasma reactions, upon sample exposure to the atmosphere, where "reactive sites" are able to combine with oxygen or water vapor, are also possible and make an assessment of the plasma effects on surfaces difficult.

Differentiation of the basic plasma effects on a sample surface may be better evaluated if the uncertainties of post-plasma reactions or surface degradation during sample handling are eliminated. Thus, a sample introduction/handling system [40]
was designed to transport samples under high vacuum between a plasma reactor chamber and the analysis chamber of an electron spectrometer. Samples may be plasma treated, transported for analysis, returned for post-plasma gas exposures, and reanalyzed for resulting changes while maintaining sample surface integrity via this system. Plasma chamber pretreatment or "conditioning" to remove adsorbed gases or contaminants from the chamber walls prior to sample introduction (under vacuum) can be easily accomplished. The ability to control the sample environment provided by the system combined with the analytical capabilities of XPS provided a method for the systematic study of plasma modification.

XPS is a well established surface analytical technique which depends on the energy analysis of electrons which emerge from the surface of materials. When x-rays of appropriate energy irradiate a sample, electrons are ejected by the photoemission process. The development of a high resolution electron spectrometer by Siegbahn and co-workers [41] provided a means for accurately measuring the the energy of the emitted electrons. When the detected electrons emerge with their initial energy (i. e. no inelastic energy loss processes have occurred), the measured electron energies are characteristic of the atomic core energy levels of the atom from which the photoelectrons originate. Their discovery that these energy levels shift as the chemical state of the atom changed [42], led to the rapid development of Electron Spectroscopy for Chemical Analysis (ESCA or XPS) [43].

Turner and co-workers [44] carried out a parallel development of ultraviolet radiation induced photoemission for the study of valence electrons. They used very narrow He I (21.22 eV) and He II (40.8 eV) resonance lines as a photon source in a high resolution spectrometer to study the vibrational fine structure of molecules. Ultraviolet photoelectron spectroscopy (UPS) has developed to be a valuable technique for the study of the valence electrons and the nature of molecular orbitals.
Auger electrons are also observed in XPS spectra. The Auger process, described by Pierre Auger in 1923 [45], involves three electrons. A core level electron is ejected by the incident x-ray photon creating a core level vacancy. This core vacancy is then filled by an electron dropping from a higher shell with a simultaneous ejection of a second electron (the Auger electron), resulting in a doubly charged ion. The measured Auger electron energy is characteristic of the differences of the atomic core and valence energy levels and is characteristic of the atom from which the Auger electron originates. Auger electrons may also be generated by electron impact rather than x-rays. The advantages of using electron impact to obtain Auger electron spectra are the higher signal levels and the improved spatial information attainable from finely focused electron beams.

XPS, UPS, and AES comprise a family of induced electron emission techniques which are often combined in a single analysis chamber to provide complementary information on surfaces. They are generally considered "non-destructive". The high intensity of the electron beam in AES may, however, cause extensive beam damage and serious sample charging problems for delicate and insulator samples [46,47]. XPS and AES will be described in more detail in Chapter 2.

With the availability of commercial instruments since the early 1970's, a rapid growth has occurred in the application of surface analysis techniques to practical problems in many areas of chemistry, physics, biology, geology, and materials science. Over 2500 references are listed in the six annual (1978-1983) review issues of Analytical Chemistry. Of the total, approximately 50% of the reported investigations involve the application of XPS alone or in combination with other techniques such as AES, SIMS, etc. The wide acceptance of XPS as a research tool is a result of its unique ability to provide information about elemental identity and atomic oxidation states from the upper most surface layers of a material. In addition, its freedom from excessive charge buildup on high resistivity materials has established XPS as an important technique for studying organic and polymeric materials. The impact of such a valuable technique is also evidenced by the awarding of the 1981 Nobel
prize in physics to Kai Siegbahn for his development of the high resolution electron spectrometer.

In this work, XPS and SEM were used to characterize the surface of GC before and after plasma treatment. The plasma treatments were carried out to determine: (1) the effects of plasma on the GC surface, (2) to determine to what extent plasma treatment can selectively introduce oxygen and non-oxygen functional groups to the GC surface, and (3) to determine the reactivity of plasma treated surfaces to air and water vapor.

The remainder of this work consists of five chapters. Chapter Two briefly describes XPS and SEM to provide an overview of the techniques as they have been applied in this work. Chapter Three describes a custom built sample introduction and handling system which is attached to the XPS analysis chamber. This system with its appended plasma chamber provides the capability to plasma treat and transfer a sample for XPS analysis while maintaining sample surface integrity. It also provides a means for exposing freshly plasma treated samples to water vapor and air in a controlled manner to simulate the uncontrolled laboratory environment. Because of the unresolved nature of XPS spectra, extensive use of data processing were employed to detect and highlight changes to the GC surface resulting from plasma treatments. These data analysis techniques are described in Chapter Four. The last two chapters describe changes observed following plasma treatment of GC samples. Chapter Five presents the experiments and results from plasma treatments using several oxygen containing source gases. Chapter Six presents the results from plasma treatments using nitrogen and chlorine containing source gases. It is expected that the information presented will help in the understanding of the plasma modification of carbon surfaces.
A highly simplified three-dimensional structural model of glassy carbon. The structure is composed of layers of condensed aromatic ribbon molecules randomly arranged. Micropores present in the network are between 50–100 Å. Strong confluences occur where ribbons merge into each other; weak confluences occur where ribbons overlap. Values for $L_A$ and $L_C$ are on the order of 100 Å and 40 Å respectively. (Taken from reference 21.)
CHAPTER 2
METHODOLOGY OF SURFACE CHARACTERIZATION

Introduction

The physical and chemical characterization of GC before and after plasma treatment can be accomplished by the use of scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) analysis. Today the use of SEM to examine surface features is well established and widely practiced. Modern SEM instruments provide high magnification, large depth of field images which are easily interpreted in terms of surface roughness, pits, cracks, phase separations, and other topographical features. XPS provides a chemical analysis of the uppermost surface layers of a sample. Currently, XPS is the only surface analytical technique which can readily provide elemental and chemical state information about a sample without significantly degrading it. The "clean atmosphere" of the vacuum chamber and the non-destructive analysis of XPS provide the experimental prerequisites necessary to maintain sample integrity during analysis.

This chapter briefly reviews some of the experimental aspects of the SEM and XPS techniques to provide an overview of how the information obtained can be applied to the characterization of glassy carbon surfaces.

Scanning Electron Microscopy (SEM)

An electron beam impinging on a sample results in various signals being generated [1]. Secondary electrons, Backscattered electrons, Auger electrons, characteristic and continuum x-rays, cathodoluminescence, and adsorbed current signals can be detected. In SEM, an intense, highly focused electron beam is raster-scanned across the sample surface, and the detected signal is used to form an image of the sample on an oscilloscope by a time sequencing technique. The various signals can be collected separately to provide different types of information. Surface features
(topography) may be obtained from secondary and backscattered electrons or absorbed current signals, while characteristic x-rays and Auger electrons provide elemental and spatial distribution information. Several excellent books are available which describe in detail the various aspects of signal generation, detection, display, and interpretation [1-4].

The depth and lateral resolution obtained depends on the type of signal detected. Figure 2 illustrates the sample volumes from which the various signals originate. Secondary electrons are produced when the primary electrons of the focused electron beam undergo inelastic scattering prior to escaping the surface. These electrons have energies of less than 50 eV and originate from depths of up to 500 Å [4]. Backscattered electrons, electrons elastically or inelastically scattered with little energy loss, have high kinetic energy and escape from a depth on the order of a few microns. Characteristic x-rays and secondary x-ray fluorescence signals are detectable from a much larger sample volume than electron signals.

Very high resolutions may be obtained by SEM instruments. Images of single isolated heavy atoms are now possible [5]. Images formed from secondary electrons provide very good surface topographic detail with a lateral resolution approaching the size of the primary electron beam. A beam size of 100-200 Å can be obtained with conventional heated tungsten filaments. Heated lanthanum hexaboride sources can improve the resolution limits to 20-50 Å [3,6]. This resolution limit is mainly the result of sample-beam interactions and surface contamination. The sample will also limit the resolution when (a) the inelastic scattering of the impinging electrons is severe, resulting in secondary electrons escaping from a surface area larger than the electron beam, or (b) the sample contains no detectable detail below a certain level even though the electron beam size and scattering volume are much smaller.

In this work, the structural features of glassy carbon and plasma treated glassy carbon were obtained using a Cambridge Stereoscan S4-10 electron microscope (Department of Geology and Mineralogy, The Ohio State University). A schematic diagram of the instrument is shown in Figure 3. The electron beam from a tungsten
hairpin filament was operated at 10 kV accelerating potential with an emission current of 150-200 microamps. The electron beam was reduced by the three condenser lens system to approximately 200 Å. The magnification ranges available were from 20x to 100,000x as defined by the ratio of the dimensions of the oscilloscope display (10 cm x 10 cm) to the raster size on the sample. The sample chamber pressure was about 10^-6 torr during signal acquisition. For the samples observed in this investigation, only the secondary electron images were used for picture formation, because the samples were composed of carbon with a surface modified layer of carbon bound to oxygen and nitrogen. This kind of sample does not provide many of the signals (x-rays, cathodoluminescence, etc.) that are possible to detect.

**X-Ray Photoelectron Spectroscopy (XPS)**

Unlike SEM, XPS is currently a large surface area analysis technique which provides very poor spatial resolution. Turner et. al. [7] have, however, recently demonstrated that photoelectron images of microscopic surface structure can be obtained using energy-analyzed electrons.

When a sample surface is irradiated with monochromatic soft x-rays such as Mg Kα₁,₂ (1253.6 eV) or Al Kα₁,₂ (1486.6 eV), photoelectrons are emitted from all atomic core levels having electron binding energies less than the energy of the exciting radiation. In this process, illustrated in Figure 4, energy must be conserved, and the process can be approximated as:

\[
KE = h\nu - BE
\]

where \(KE\) is the kinetic energy of the emitted electron, \(h\nu\) is the x-ray photon energy and \(BE\) is the binding energy of the core or valence electron. Minor corrections to equation 1 such as the work function of the spectrometer, recoil energy at the site of ejection, and various definitions of \(BE\) are omitted for simplicity. These are discussed in most XPS books and reviews [8-14].

Since the binding energies of atomic core levels are characteristic of a particular element, a photoelectron spectrum will produce an elemental analysis of a sample surface. Lines from atoms adjacent to one another in the periodic table are well
separated (e.g. Carbon 1s (C_{1s}) electrons have binding energies of 284 eV; Nitrogen 1s (N_{1s}) electrons have binding energies of 400 eV) and are easily identified. A few lines do overlap, for example O_{1s}/Sb_{3d}, C_{1s}/Ru_{3d}, Al_{2s,2p}/Cu_{3s,3p} but generally, the observation of a second core line will identify the element(s) present. Lists of atomic binding energies have been tabulated and are readily available. (See references 9, 10, 13.)

XPS is essentially a non-destructive technique [10, 11]. The low x-ray flux irradiating a sample is such that no sample decomposition occurs during the time required to record a spectrum except for exceptionally delicate samples [12, 13]. For example, the reduction of Pt(IV) to Pt(II) compounds by x-ray exposure has been reported [15]. Ioffe et al. [16] have proposed a method for correcting XPS spectra of compounds undergoing x-ray induced decomposition based on their studies of copper and cobalt complexes. In the absence of decomposition, surfaces examined by XPS may be considered to be unaltered from their original state. They may then be subjected to other studies or treatments in situ or ex situ without accounting for sample degradation due to a prior analysis.

XPS provides additional information about the sample. The exact BE of an atomic core level depends on the chemical environment of the atom. Information about the oxidation state of an atom can be obtained by observing the "chemical shift" in the measured BE. The observed chemical shift is determined by the magnitude of the electronic charge on the atom from which the photoelectron originates. A change in charge is reflected in core energy level shifts as valence electron density is drawn away from or concentrated on an atom [9, 12]. Chemical shifts for atoms such as carbon, nitrogen and sulfur in, for example, organic systems are on the order of 7-8 eV. (See appendix 3 of reference 9 for listings of the binding energies for compounds of many of the elements in the periodic table.) Unfortunately, the photoelectron lines observed are quite broad due to the line width of the exciting radiation and broadening by the analyzer. Typical line widths observed in XPS have full widths at half-maximum peak height (FWHM) of 1-2 eV for spectra obtained
using magnesium anodes. A sample containing several chemically shifted species will, therefore, appear as a set of unresolved bands. Methods of analyzing these line shapes will be discussed in Chapter 4.

Apparent binding energy shifts can be caused by sample charging. Normally the positive charge left behind by the ejected electron is neutralized by electrical conduction from the spectrometer ground and by capture of slow electrons generated by x-rays striking the chamber walls, sample holder and the x-ray gun window. When the sample volume irradiated by x-rays is electrically isolated from ground, i.e. no neutralization by conduction, the sample charges positively since it can not capture enough slow electrons to remain neutral. Ejected electrons have their energies "retarded" by the positively charged surface, and the detected signal is displaced to a higher binding energy by the magnitude of the surface charge. The observed charge shifts are generally on the same order of magnitude as the observed chemical shifts leading to interpretation errors if not detected and appropriately corrected. Various correction methods for charge shifts include use of internal standards [17,18], external standards [8,19–21], charge neutralization by an electron flood gun [22], thin film preparations [23,24] and the use of UV radiation to produce sufficient low energy electrons to neutralize the surface charge [25]. The internal and external standard approach has been discussed [17–19]. The disadvantage of the electron flood gun is the possible over-correction of the charge shift [12]. Thin film preparations have limited applicability. When the charge buildup on the surface is uniform (as is usually the case for x-ray flooded samples), all the lines in the spectrum are shifted equally, and binding energy differences, ΔBE, may be used to determine the oxidation state of elements [26].

Other spectral features can provide information about the sample. Shake-up and shake-off satellite lines are found on the high BE (low KE) side of a core level peak. They occur when the photoelectron transition simultaneously causes a valence electron transition, leaving the ion in an excited state. The energy separation of the satellite from the main line equals the KE lost by the photoelectron during the
process [9,11,13,27]. Satellites for transition metals and paramagnetic ions can be a reliable guide to oxidation and spin states. Shake-up satellites for carbon atoms in pi-bonded systems (e.g. polystyrene) are observed at 5-8 eV higher BE and are diagnostic of aromatic character [28]. Shake-off satellites result from the ejection of a valence electron as the electron cloud reorganizes after a core electron has been ionized [9,11].

Valence level lines observed in XPS have limited applications since they require a valence band description and molecular orbital theory for interpretation. In addition valence electrons have a low photoelectron yield for Mg and Al x-rays. Signal averaging is usually required to obtain spectra with a satisfactory signal to noise (S/N) ratio. Polymer identification can be accomplished by observing characteristic changes in the valence band region [29,30].

In addition to the photoelectrons ejected in the photoelectric emission process, other signals are generated. The core vacancy created by the departing photoelectron can be filled by an electron from an outer shell. This relaxation process, illustrated in Figure 4, is accompanied by either a radiative (x-ray emission) or non-radiative (Auger electron ejection) process. The x-ray emission process is negligible for the electron energies observed in electron spectroscopy [9].

The energy of an Auger electron can be estimated for the example of a K-L\textsubscript{I}L\textsubscript{II} process [9]:

\[ E_A = E_K - E_{\text{L I}} - E_{\text{L II}} \]

where \( E_A \) is the KE of the Auger electron resulting from the filling of the K shell vacancy, and \( E_K \) and \( E_{\text{L I}} \) are the binding energies of the K and L\textsubscript{I} levels for a neutral atom. \( E_{\text{L II}} \) is the BE of an electron in the L\textsubscript{II} shell of the ion with a vacancy in the L shell. Chemical shifts for Auger lines (involving three atomic levels) can be greater than the chemical shifts of photoelectrons lines. Wagner and Biloen [31] have attributed this effect to the higher polarization of the doubly charged final state. Since the magnitude of chemical shifts of Auger and photoelectron lines differ, Wagner [32] has suggested the KE separation between the strongest photoelectron line and
the most intense Auger line (the Auger parameter, $\alpha$) be used as a measure of chemical state identification [32,33]. Accurate values of $\alpha$ can be measured and these values are independent of charge shifts and energy referencing complications [32]. A plot of the Auger KE versus the photoelectron BE for a species in different types of compounds yields a two dimensional chemical state diagram [32,33] which may be used to derive useful information. Auger lines with the final vacancy in the valence band also show characteristic line shapes and separations for different classes of compounds [32].

Surface Sensitivity and Sampling Depth

For solids, XPS is extremely surface sensitive. Only the electrons ejected from the uppermost surface layers will maintain their characteristic energy. Electrons emerging from atoms at greater depths lose their discrete energy by inelastic scattering, and contribute to the broad background plateaus characteristic of XPS spectra. The XPS sampling depth is determined by the electron mean free path which is a function of the sample matrix and the KE of the electron. In the energy range of 100-1500 eV, the mean free path can be approximated as [34,35]:

$$\lambda = k \left[ \text{KE} \right]^{0.5}$$

where $k$ is a constant. $\lambda$ is defined as the distance over which the fraction $1/e$ of the photoelectrons travel without being inelastically scattered. Penn [34] has calculated theoretical values of $\lambda$ in the KE range of 200-2400 eV for elemental solids, except rare earth and actinides. Shea and Dench [36] have compiled published electron mean free path data for electrons with kinetic energies of 0-10,000 eV. They derived an empirical equation for calculating values of $\lambda$ for various materials. In general, $\lambda$ values are in the range of 5-15 Å for metals, 15-25 Å for inorganic compounds, and 10-50 Å for organic compounds. The intensity of photoelectrons originating from various depths in the sample is given by [37]:

$$I_d = I_t \left( 1 - e^{-d/\lambda} \right)$$

where $I_d$ is the photoelectron peak intensity emerging from the sample from a depth $d$ normal to the surface, and $I_t$ is the total measured peak intensity. If $3 \lambda$ is arbitrarily
chosen as the effective sampling depth, then 95% of the detected photoelectron signal will originate from a depth of $3\lambda$ or less. Other factors influencing the depth sampled are: detectors at non–perpendicular angles to the surface, orbital asymmetry factors as a function of x–ray incident angle, surface roughness, analyzer transmission functions and the area sampled [38,39].

Quantitation

XPS has been applied to a wide variety of surface quantitation studies. Wagner [26] has done a detailed study of the factors affecting XPS quantitation. He has concluded that quantitation to within ±10% is possible when using photoelectron signals with similar energies. Quantitation of transition elements is, however, more complicated due to multielectron shake–up and shake–off processes which decrease the intensity of the main photoelectron line.

Absolute quantitation depends on many parameters. The photoelectron intensity for a given atomic line from a clean sample is given by:

$$I = F \Omega N A T y f(\lambda, x, \phi)$$

where $F$ is the x–ray flux, $\sigma$ is the photoelectron cross section for a given atomic subshell and x–ray energy, $N$ is the number of atoms per cubic centimeter, $A$ is the area sampled by the analyzer, $y$ is the fraction of photoelectrons emitted which do not lose energy to shake–up and shake–off processes, $\lambda$ is the electron mean free path dependence, $x$ is the depth at which the signal originates and $\phi$ is the angular intensity asymmetry of photoemission and depends on the instrumental geometry [38]. The intensity asymmetry is a result of the angular dependence of the photoelectron cross section which has the form [40]:

$$\frac{d\sigma}{d\phi} = \frac{\sigma_t}{4\pi} \left[ 1 - \beta \left( \frac{3}{2} \cos^2 \alpha - 1 \right) \right]$$

where $\frac{d\sigma}{d\phi}$ is the differential cross section observed by an analyzer with a solid acceptance angle $d\phi$. $\beta$ is an orbital asymmetry parameter depending on element and subshell [41]. $\alpha$ is the angle between an unpolarized photon beam and the photoejected electron. When $\alpha$ equals $54^\circ 44'$, $\frac{d\sigma}{d\phi} = \sigma_t$ and the relative intensities
of the photoelectrons are equal to the relative intensities integrated over all angles.

The relative intensities of photoelectron lines measured will, therefore, depend on the spectrometer geometry. If all the parameters in equation 5 are known, then an absolute value of \( N \) can be determined. The x-ray flux can be maintained constant by using power regulating circuitry [42]. \( \sigma \) values have been theoretically calculated for Mg K\( \alpha \) and Al K\( \alpha \) x-rays by Scoefield [43]. The electron mean free path, area analyzed, analyzer transmission and the angular asymmetry factors are more difficult to determine and depend on the type of analyzer and its geometry [44]. Sample placement in front of the analyzer effects the signal intensity. For example, the intensity of a photoelectron line varies by a factor of two for a sample displacement of about 0.5 mm along the axis of a cylindrical mirror analyzer [45], which has a shallow depth of focus. Absolute quantitation is, therefore, difficult to carry out since many of the factors involved vary from sample to sample and are subject to many errors.

A more reasonable approach is to determine relative concentrations. When relative intensities of photoelectron lines are used, many of the instrumental (\( F, A, T \)) and angular (\( f(\phi) \)) factors in equation 5 cancel or become negligible. The relative atomic ratio for a two component system reduces to:

\[
\frac{I_a}{I_b} = \frac{N_a \lambda_a \sigma_a}{N_b \lambda_b \sigma_b}
\]

We can approximate \( \lambda_a = \lambda_b \) when line intensities with similar kinetic energies (\( \Delta E < 300 \) eV) are used for the atomic ratio calculations [46]. Thus the calculation of relative concentrations reduces to:

\[
\frac{N_a}{N_b} = \frac{I_a \sigma_b}{I_b \sigma_a}
\]

The atomic ratios are easily calculated once the photoelectron intensity of all the species present are obtained and corrected by their photoelectron cross section.
An alternative method involving the use of standards for relative atomic concentrations has been reported by Lin et al. [47]. This method involves the use of standard reference compounds with a known stoichiometry and with a matrix similar to the sample's. A knowledge of the photoelectron cross section is not required. Unfortunately, for many samples, no suitable reference standards are available for comparison.

**Depth Profiling**

The existence of a depth profile (any change in the composition below the surface of a material within the XPS sampling depth) complicates the straightforward quantitation approach of equation 7, since the relative concentration ratios will reflect the "average" composition of the sample. For the situation where a thin overlayer exists (surface contamination, oxide layer formation, etc.), a marked deviation in the intensity ratio of two widely spaced photoelectron lines relative to the ratio obtained from homogeneous "standards" will provide depth profile information. An overlayer will attenuate the low KE signal more than the high KE signal since the sampling depth (3λ) is dependent on the electron energy (equation 2). Equation 7 may be modified to account for loss of signal intensity due to the presence of an overlayer such that [12]:

\[
\frac{I_a}{I_b} = \frac{N_a \sigma_a e^{-d_0/\lambda_a}}{N_b \sigma_b e^{-d_0/\lambda_b}}
\]

where \(d_0\) is the thickness of the overlayer and \(\lambda_a\) and \(\lambda_b\) are the electron mean free paths in the overlayer for electrons with kinetic energies corresponding to the two photoelectron lines. Combining equation 7 and 9 yields an expression relating the intensity ratio changes to the intensity ratio obtained from a homogeneous "clean" surface in terms of overlayer thickness and electron mean free paths:

\[
\frac{[I_a/I_b]_o}{[I_a/I_b]_h} = \frac{e^{-d_0/\lambda_a}}{e^{-d_0/\lambda_b}}
\]

where \([I_a/I_b]_o\) and \([I_a/I_b]_h\) are the intensity ratios measured for the overlayered
and clean surfaces, respectively. A knowledge of the mean free path values will allow a calculation of the overlayer thickness. Conversely, if the overlayer thickness is known by some independent means, the difference in the electron mean free paths can be calculated.

Intensity variations as a function of electron emission angle with respect to the surface (the electron "take off" angle) provides enhanced surface sensitivity. The change in a photoelectron peak intensity with respect to the electron take off angle is derived from equation 4:

$$I_d = I_t(1 - e^{-d/\lambda \sin \theta})$$

where $\theta$ is the electron take off angle measured with respect to the sample surface. The enhancement in surface sensitivity (decrease in effective sampling depth) as the electron take off angle decreases is illustrated in Figure 5. The effective sampling depth is $3\lambda$, $1.5\lambda$ and $0.52\lambda$ for analyzer entrance placement at electron take off angles of $90^\circ$, $30^\circ$, and $10^\circ$, respectively. Fadley [44] has extensively studied the variation of signal intensity vs. take off angle. Deviations from the intensity variations predicted by equation 11 occur when: a. the sample is not accurately aligned with the analyzer axis, b. the sample dimensions are not large relative to the area sampled by the analyzer, c. sample roughness is large relative to $\lambda$ (powdered samples cannot be studied) and d. the sample is a single crystal which yields diffraction intensity enhancement along specific crystal directions. Relative peak intensity changes may be used to cancel some of these complications. Intensity changes as a function of electron kinetic energy or as a function of electron take off angle may only be used to detect depth profiles to a depth determined by the least energetic photoelectron observed. These methods are, therefore, limited to depths of approximately 100 Å.

Ion sputtering (etching) can also be used to develop depth profiles [34,39,49]. Unlike the other methods, sputtering is a destructive process. This method has been the most popular for profiling since profiles may be obtained to several thousand Angstroms. In ion sputtering, various gases, (Ar, Xe, Ne, N$_2$, O$_2$), can be ionized and accelerated to bombard and remove the sample surface. After sputtering, XPS
or other suitable techniques can be used to determine the new surface composition. The ion sputtering process is a very complex phenomena. Both qualitative and quantitative interpretations can be complicated by artifacts such as differential sputtering, ion bombardment induced reductions, subsurface lattice damage by ion implantation or knock-in effects, and non-uniform etching due to surface contamination or roughness. Non-uniformity of the ion beam energy distribution and misalignment of the ion beam impact and analyzer sampling areas are instrumental factors which can contribute to errors in derived depth profiles. Calibration of sputtering rates may also be required as experimental conditions and sample type change. Distortions from the actual depth composition will occur if these complications are not adequately considered.

In this work, the XPS data were obtained using a Physical Electronics Industries, Inc. (PHI) model 548 electron spectrometer equipped with a Mg x-ray source, argon ion sputtering gun, electron gun and a double-pass cylindrical mirror analyzer. A schematic diagram of the spectrometer is shown in Figure 6. All samples were introduced to the spectrometer via the sample introduction/handling system described in Chapter 3. The pressure in the analysis chamber was maintained between $4 \times 10^{-9}$ and $2 \times 10^{-10}$torr during sample introduction and analysis. Signal averaged high resolution spectra were obtained at 25 eV pass energy with a Nova 3S minicomputer (Data General Corp.) equipped with 32K word of MOS memory (Mostek Inc., model MK-8003), two diablo disk drives (1.2 M work) and X-Y plotting facilities. The minicomputer controlled the voltage scan, data acquisition and processing. A block diagram of the electron spectrometer and minicomputer is shown in Figure 7.

Problems in Surface Analysis

XPS is a powerful instrumental technique which provides valuable information about the chemical composition of the sample. There are, however, several problems encountered in the application of XPS. The surface sensitivity of XPS also makes it very susceptible to signal attenuation or loss due to surface contamination. Unintentional changes as a result of careless sample handling or sample degradation
prior to analysis will confuse or make interpretation of data ambiguous. Care must be taken to insure the analysis is meaningful. Improved methods of sample treatment and handling will be beneficial to the successful application of XPS.

The overlapping bands observed in an XPS spectrum require the data to be interpreted by line shape analysis techniques such as curve deconvolution, differentiation, spectral subtractions and comparison to standard reference samples.

Standard reference compounds directly comparable to the sample(s) under investigation may be unavailable. Methods for developing and comparing standards to unknown systems are needed.

Sample decomposition during analysis will alter the line shapes obtained during signal averaging. Artifacts due to cleaning of the sample by ion sputtering may be observed and must be taken into account.

Instrumental stability, calibration, and linearity of the energy scale has been shown to be a problem [49]. A general round robin survey of 38 instruments from eight different manufacturers organized by the committee E-42 on Surface Analysis of the ASTM revealed significant problems. Measured photoelectron line positions varied by more than 2 eV, and intensity ratio values differed by more than a factor of ten for data obtained from pure metal foils. The variations of data from different instruments complicates comparison of data reported in the literature, however, this problem is not serious when data are obtained from a well calibrated instrument.
Figure 2. Signals Generated in an SEM.

The sampling depth and lateral resolution obtained for signals generated by an electron beam in an SEM. A: Auger electrons (ca. 50Å), B: Secondary electrons (ca. 500Å), C: Backscattered electrons (ca. 1 micron), D: Characteristic x-rays, E: Secondary fluorescence by continuum and characteristic x-rays, G: Absorbed current (ca. the size of the electron beam).

Figure 3. Schematic Diagram of the Cambridge Stereoscan S4-10.
Figure 4. The Photoelectron and Auger Electron Generation Process.

Schematic of the photoelectron (a.) and the Auger electron (b.) generation process. X-rays can eject a core electron. An ejection of a K electron is illustrated in a. The kinetic energy of the ejected photoelectron is related the energy of the core level from which it originated, and this energy is characteristic of the atomic species. The Auger electron is generated by the relaxation of an atom with a core vacancy. The relaxation process involves the filling of the core hole vacancy by an outer shell electron resulting in a doubly charged ion. A second electron (the Auger electron) is ejected in the process. A KLL process is illustrated in b. Chemical shifts for both the photo- and Auger electrons are observed in electron spectroscopy. The chemical shifts observed provide valuable information about the chemical environment of the atom from which these electrons originate.
Figure 5. XPS Sampling Depth.

The effective sampling depth as a function of electron takeoff angle. Effective sampling depth is defined as $3\lambda$, where $\lambda$ is the inelastic mean free path of an electron in the sample. $3\lambda$, $1.5\lambda$ and $0.52\lambda$ are the sampling depths for takeoff angles of 90°, 30° and 10° respectively. D is the detector entrance aperture. In all three examples the electron travels a distance of $3\lambda$ or less before emerging from the surface.

Figure 6. Schematic Diagram of the PHI Model 548 Electron Spectrometer.

Figure 7. Block Diagram of the PHI Model 548 Electron Spectrometer.
CHAPTER 3

SAMPLE HANDLING AND PLASMA GENERATION

Introduction

Previous experiments [1-2] in our laboratory have indicated the possibility that samples treated with a radio frequency plasma (RFP) undergo post-plasma chemical reactions upon exposure to an uncontrolled laboratory atmosphere during transfer from the plasma reactor to the XPS analysis chamber. To systematically study the effects of the RFP treatment on surfaces, a method of sample treatment and transfer in a controlled atmosphere or a vacuum from a plasma reactor to the XPS analysis chamber without fear of sample compromise is needed.

There have been many designs of sample handling and transfer systems reported [3-13] in addition to the commercial ones offered by various vendors. No commercially available system offers the flexibility required to transport a sample in a vacuum to an RFP reactor for treatment and then return the sample for analysis while maintaining sample surface integrity. This chapter describes a sample introduction/handling system (IHS) which provides a means of sample treatment, transfer and analysis without removal from the confines of an extended vacuum system.

Instrumentation

The IHS is divided into two sections [14]. The first section, the sample isolation sidearm (ISA), is attached directly to the Physical Electronics Industries (PHI) Model 548 Electron Spectrometer and is used to isolate the sample during its introduction into the spectrometer analysis chamber. The second section, a general purpose sidearm (GPSA), has provisions for introduction of samples and options for treating and analyzing samples. Samples in both sections are transported with magnetically coupled drive rods and can be transferred between drive rods or between a drive
rod and the carrousel sample stage in the XPS analyzer chamber. Unless otherwise noted in the following description, all parts of the system were constructed from Type 304 stainless steel.

Sample Introduction Handling System (IHS)

Figure 8a. shows an overhead schematic view of the combined system. The ISA, (1) is attached by a vacuum flange to the spectrometer bell jar (A). The GPSA, (2) with chemical modification provisions is attached at right angles to the ISA. Ultra high vacuum, UHV, gate valves (D) (Torr Vacuum, Model SVB-1.52VM) are used to provide isolation at the point of attachment to the spectrometer bell jar, between the ISA and GPSA, and at other points in the system. The two sidearms are pumped, independently of the spectrometer bell jar, by a differential ion/titanium sublimation pump combination (Perkin-Elmer, Model 210-1500) (b). The housings for the ISA and GPSA drive tubes are fabricated from 1.5" O.D. seamless tubing welded to a conflat flange, (CFF). The internal bore of the housing has been honed to reduce surface imperfections following the welding operations. Each of the drive housings is attached to one flange of a six-way cross through an intermediary flexible coupling (G). A transfer alignment mechanism (H) allows lateral and vertical positioning of the drive rods. Six-way crosses (C) are used at each junction point for the drive rods and are equipped with an observation viewport at each sample transfer location.

The side view of the GPSA in Figure 8b shows the location of the two appendage ports which support the plasma chamber (K) and the chemical treatment or electrochemical cell chamber (L). These chambers are isolated with UHV gate valves when not in use. The remaining CFF of the plasma appendage port six-way cross is used to introduce samples into the GPSA. Samples introduced through the vacuum lock (J), Figure 8a, can be rough pumped by a double liquid nitrogen trapped mechanical pump (not shown) via the gas outlet of the plasma chamber (Figure 8b). This pumping arrangement is also used to evacuate the plasma chamber during sample treatment. Samples can be transported and positioned on the appendage rod mounted in an 11" travel welded bellows (E) (Standard Bellows Co., Winsor Locks, CN). Rotary positioning
of the sample with a rotary feedthrough (Perkin-Elmer, Model 281-6070) attached
to the top of the appendage rod is also available at each port.

**Magnetic Drive Mechanism**

The magnetic drive mechanism is a modification of the design reported by Winograd
et. al. (4). The external magnetic drive ring, (I), contains twelve permanent Alnico
horseshoe magnets grouped symmetrically in four sets of three. The external magnetic
drive ring couples through the drive rod housing to the soft iron core mounted just
forward of the support cylinder as shown in Figure 9. The dimensions of the soft
iron core are not critical, provided enough clearance is maintained between the core
and the inner housing wall to prevent contact during operation.

A support cylinder containing two sets of bearings provides the rear support for
the drive rod. The bearings on each of the support arms contact the housing wall
and thereby center the drive rod and allow it to traverse with low friction. Additional
bearings are mounted internally at each end of the support cylinder and allow it
to rotate. Both bearing sets are radial full complement bearings (SR3C and SR4C,
respectively: Miniature Precision Bearings, Keane, NH). The front support for the
drive rod is a combination radial bearing and ball bushing (Thompson Industries
Inc., Manhasset, NY: Model CMB-500). This bearing combination which permits both
linear and rotational motion of the drive rod is shown in Figure 10. The mounting
for these bearings is lightly press fit into the flange end of the drive rod housing
and is machined with openings large enough to ensure efficient evacuation of the
drive rod housing.

**Sample Carriers, Pins and Transfers**

A sample carrier has been designed to allow the sample carrier to be transported
on a pin, Figure 10a and 10b or within an enclosing dock, Figure 10c and 10d, and
to allow carrier transfers (at right angles) alternating between pins and docks. The
sample carrier is formed from sheet stock to produce the structure shown in Figure
11 (bottom view). In the center of the carrier's 14 mm square top a fixed screw
(4-40) thread) is provided to attach an aluminum disk, which serves as the most
commonly used sample mounting fixture. The tabs visible on the under-side of the carrier base are provided with guide holes; a forward one is large enough to accept the major radius of the carrier pin. The rear one has a hole which will accept only the pin tip as shown in Figure 10b. A copper-beryllium, "H" spring is mounted and oriented below the carrier base so that the flat side of the "D" shaped carrier pin (Figure 10a) can be inserted past the protruding edge of the spring crossbar. A 180° rotation of the pin releases the pin which then can be withdrawn to complete the transfer. The use of the spring based positive locking mechanism alternately with the pin and the dock eliminates the need for and the aggravation from close fitting tolerances on the remaining pin/sample carrier/dock dimensions. This feature is especially welcome when alignment for a sample transfer is being accomplished.

The dock attached to the sample carrousel of the spectrometer is a modification of the dock used in the GPS. The carrousel currently in use has nine docks attached; The three remaining faces being reserved for standard reference materials and a Faraday cup. Figure 12 shows three docks attached to a carrousel. These docks are physically attached to aluminum blocks fastened to the bottom plate of the carrousel with a hinge pin to allow the dock to pivot as illustrated in the figure. A small steel spring fits into a notch in the side of the dock and provides an over-centering force to hold the dock up against the face for analysis. Samples are brought into the analysis chamber at a tangential angle and the dock is pivoted away from the carrousel face for a remote transfer. This remote, tangential transfer is required by the geometry of the sample carrier and the close spacing of the adjacent faces. Without the remote transfer, only the six alternate faces could be used to mount samples or reference materials. The remote transfer also protects an adjacent sample from accidental contact, contamination or damage by a sample carrier or drive rod as a new sample is introduced. The docks are pivoted into the analysis or transfer positions with a lever attached to a rotary feedthrough.
The vacuum characteristics of the IHS are summarized in Table 1. One of the added benefits of the ISA-GPSA combination is the ability to maintain the vacuum integrity of the analysis chamber at UHV levels even though samples introduced through the GPSA may initially be contaminated with volatile species and/or have undesirable outgassing characteristics. Using the appendage port drive rod pins and the GPSA drive rod dock for temporary storage, three samples can be introduced in a single pump down cycle. The system utilizes the spectrometer carrousel as a sample buffer to store samples and standards in the UHV environment of the analyzer chamber.

More important, in terms of the original design objective, the system can maintain sample integrity during transfer between the reaction chambers and the analyzer bell jar. The ability to pump down to a ISA-GPSA pressure of less than 5x10⁻⁷ torr within 4 min. following plasma treatments limits the exposure of the surface to only the reaction gases intentionally admitted into the GPSA system because all subsequent sample handling is done at or near the system base pressure.

Plasma Generator and Plasma Cell

The radio frequency generation is accomplished by applying the 27 Mhz frequency output of a citizens band radio (Hi Gain Model 2681) to the input of a linear amplifier capable of variable amplification of the generator from 4 to 35 watts. A block diagram of the plasma generator is given in Figure 13. The variable power amplifier was designed and built by the Chemistry Department Electronics Shop. A schematic of the RF amplifier circuit is given in Figure 14. The plasma chamber (Figure 15, L) is constructed from 38 mm diameter pyrex glass connected via a glass to metal seal. The gas inlet system, is constructed to be vacuum compatible with the introduction system. Stainless steel (1/8" O.D.) tubing (N) was used to connect the gas source (gas cylinder or volatile liquids in a glass container fabricated by the department glass shop) (A) to the plasma chamber. All connections are via standard Swagelok fittings (E). Bellows sealed shut-off (B) and Needle (N) valves are used to control the gas flow to the plasma chamber. A high vacuum pyrex stopcock valve isolates the gas inlet system from the plasma chamber. The gas pressure in the plasma
chamber is monitored by a thermocouple gauge (Teledyne Hastings-Raydist Model DV-6M) (F). The gas inlet, outlet, and thermocouple gauge are connected via 18/9 ball and socket glass joints (G). The gas inlet and thermocouple gauge are isolated from the plasma chamber by coarse glass frits (H) to confine the plasma to the chamber. The plasma is generated by the application of the RF power to a one turn primary coil (J). The plasma is generated by the inductive coupling of the secondary coil (K) (5 turns, 2" overall length, of 1/8" I.D. copper tubing) and resistance capacitance (RC) matching network. Samples may be entered into the plasma chamber by the appendage rod housed in the 11" travel bellows (Figure 8b, E). Samples can be positioned within the plasma coil or up to three inches above it (down-stream). Figure 16 shows the placement of the glassy carbon sample within the plasma chamber. The ISH described provides the necessary capability required for plasma treatment and analysis while maintaining sample integrity. Controlled post-plasma exposures to air, water vapor or other selected gases can easily be carried out in the GPSA. The system allows samples to be introduced and/or treated in the GPSA without interfering with the normal operation of the spectrometer. The system is readily expandable, and sample carriers which can accommodate samples of a variety of sized or shapes make the system versatile and adaptable for other needs.

The system described above has been used to study the RF plasma treatment of glassy carbon surfaces for the purposes of surface modification. Post-plasma exposure of the treated samples to air and water vapor was also carried out to assess the reactivity of the freshly treated surface. The results of plasma treatments with some oxygen containing gases are some non-oxygen gases are described in Chapter 5 and Chapter 6 respectively.
Figure 8. Schematic Diagram of the Introduction/Handling System.

Figure 8a. Overhead schematic view (not to scale) of the isolation side arm (ISA), (1) and general purpose side are, (GPSA), (2) as attached to the analyzer bell jar of the PHI spectrometer. Figure 8b. The right side view (not to scale) of the GPSA with the appendage port assemblies.

Legend: A - PHI analyzer bell jar; B - differential ion/titanium sublimation pump combination; C - standard six way cross; D - ultra high vacuum gate valve; E - welded 11" travel bellows; F - magnetic drive rod housing; I - external magnet drive ring; J - sample introduction lock; k - plasma appendage chamber; L - chemical treatment/electrochemical chamber; M - system expansion port. (Taken from reference 14.)
Figure 9. Drive rod soft iron magnetic core and rear support cylinder with support arms and bearings.
Figure 10a. Isolation side arm with mounted sample carrier pin also showing the front support bearing and mounting press fit into the flange end of the drive rod housing.

Figure 10b. The isolation side arm with a sample carrier locked onto the sample carrier pin.
Figure 10c. The general purpose side arm with a sample dock and the front support bearing assembly.

Figure 10d. The general purpose side arm with a sample carrier enclosed in the sample dock.
Figure 11. The Sample Carrier.
The bottom view of the sample carrier showing the formed Cu-Be "H" spring with locking tabs and the sample carrier pin guides.

Figure 12. The sample Carrousel. The PHI standard carrousell with three docks attached, two in the analysis position and the middle one in the remote transfer position. The rear dock is aligned to show the alignment and positioning stop of the dock structure. The mating holes in the floor of the dock structure are visible, with a machining jig hole in the center, in the forward most dock.
Table 1

SAMPLE INTRODUCTION/HANDLING SYSTEM PERFORMANCE

1. ISA - GPSA Base Pressure
   $3 \times 10^{-9}$ torr.

2. Analyzer Bell Jar Pressure (typical):
   a. During Normal Operation
      $5 \times 10^{-10}$ torr.
   b. During Sample Transfer
      $5 \times 10^{-9}$ torr.

3. ISA - GPSA Evacuation times (typical):
   a. Sample Introduction from Atmospheric Pressure.
      To 10 mtorr. ca. 4 min.
      To $5 \times 10^{-7}$ torr. ca. 6 min.
   b. Following Plasma Treatment at 100 mtorr.
      To 10 mtorr. ca. 2 min.
      To $5 \times 10^{-7}$ torr. ca. 4 min.

4. Nominal Sample Transfer Timing
   a. ISA - GPSA Transfer ca. 10-20 sec.
   b. ISA - Carrousel Transfer ca. 30-60 sec.

Sample transfer timing depends on operator proficiency since all transfers require visual alignment of the sample carrier with either the pin or the dock prior to accomplishing a successful transfer. (taken from reference 14.)
Figure 13. Block Diagram of the Radio Frequency Plasma Generator.

Legend: O – oscillator (27 MHz); BA – buffer amplifier; PA – variable power amplifier; PS – power supply; M – RF power/standing wave ratio meter; N – resistance/capacitance (RC) matching network; D – plasma discharge.
Figure 14. Schematic for the Variable Power Amplifier of the Plasma Generator.

List of Parts:

- C1, C5 70-350 pf (ARCO#424)
- C3 0.1 μf
- C7 2000 μf
- L1 0.08 μh
- L3 0.2 μh
- Q1 MFR 449A (Motorola)
- T1 Transformer (Power Stat T108)
- 50 ohm input from preamplifier
- SW Power switch

- C2, C6 250-1000 pf (ARCO #469)
- C4 0.001 μf
- R1 10 ohm, 1/4 W
- L2 0.56 μh
- L4 0.08 μh
- F1 Fuse 2 amp MDL
- T2 Transformer (Stancor P6378)
- 50 ohm output to plasma cell
Figure 15. Schematic diagram of the plasma reaction chamber.

Legend: A. gas source; B. bellows sealed shutoff valve; C. variable capacitor; D. bellows sealed needle valve; E. Swagelok connectors; F. thermocouple gauge; G. 18/9 ball and socket joint; H. coarse glass frit; I. pyrex Hi Vac valve; J. primary coil; K. secondary coil; L. plasma chamber; M. glass to metal transition; N. stainless steel tubing; O. gas outlet to liquid nitrogen traps and mechanical pump; R. resistor.
Figure 16. The Plasma Chamber.

The plasma chamber attached to the general purpose side arm with a glassy carbon sample mounted on a sample carrier and suspended approximately 1.5" above the plasma coil. Also visible is the plasma gas outlet.
CHAPTER 4

DATA HANDLING AND ANALYSIS TECHNIQUES

Introduction

The XPS analysis of RFP treated glassy carbon samples described in this work required the development of an analysis protocol to obtain maximum information about the chemical composition of the sample surface. To study the changes brought about by the plasma, several experimental problems must be overcome to provide a meaningful analysis. The relatively low photoelectron cross section of carbon, oxygen, and nitrogen results in an inherently low signal to noise (S/N) ratio. The low signal levels obtained from the GC require long signal averaging times to improve the S/N ratio of the high resolution spectra. The signal averaged spectra are used as the starting point for all further processing.

Another problem is extraction of the "desired" signal, originating from the modified surface from the "background" signal, arising from the unaltered subsurface layers. A third complicating factor is because the changes to the GC surface brought about by plasma treatments result in spectra with overlapping photoelectron lines forming an envelope of signals which must be interpreted in terms of the overall line shape. A fourth complication is the lack of "model" GC surfaces. The GC samples always exhibit an oxidized surface before and after polishing. Analysis of the changes following a plasma exposure (described in Chapter 5 and Chapter 6) must include not only a consideration of the new surface functional groups, it must consider also the surface functional groups removed by the treatment. A final complicating factor involves a lack of graphitic reference compounds with high concentrations of single functional group types from which to obtain accurate chemical shift and peak FWHM
values. Any analysis of the recorded data must not only take into account the above difficulties, but it must also induce minimal distortion to the data.

The XPS spectra obtained in this study were recorded in both the analog and digital mode. An initial 1000 eV wide survey scan of the sample was always obtained in the analog mode to identify the surface species present and to detect any unexpected chemical species or contamination. High resolution, typically 10 to 20 eV, narrow scans at 25 eV pass energy from the signal regions of interest were collected and stored under computer control of the XPS spectrometer. The digitized spectra are the starting point for further analysis. The data analysis techniques employed include data smoothing, inelastic background removal, difference spectra generation, curve fitting and comparison to homopolymer "standards". Resolution enhancement was attempted by deconvoluting the instrumental and x-ray line broadening contributions and the observed line shape, however, due to instrument stability, this technique is judged to be unreliable.

Data Smoothing

In general it is better to use unsmoothed data, since any smoothing procedure introduces distortions to the spectrum. Smoothing is required, however, when a prohibitively long time is needed to record a spectrum with a high S/N or when it is necessary smooth spectra as a prerequisite to further analysis.

In this work, the data smoothing procedure employs the n-point sliding least squares algorithm introduced by Savitzky and Golay [1]. This algorithm is equivalent to a non-linear least squares fit of the data to a polynomial equation, and it is easily implemented on a laboratory minicomputer. The procedure multiplies an odd number of experimental data points by a set of coefficients, summing and normalizing the result. The resulting value becomes the new (smoothed) value for the mid-point of the data set. Next, a new set of data points is chosen by indexing one experimental data point and repeating the procedure until all the data points are smoothed. The
set of coefficients employed determines the amount of smoothing realized. The algorithm leaves several end points in the experimental data set unsmoothed. The number of unsmoothed points remaining after the procedure is carried out is equal to one half the smoothing interval minus 1. For example, employing a seven point smoothing interval would leave the first and last three data points unsmoothed, \(((7-1)/2 = 3)\).

A complete description of the smoothing procedure is beyond the scope of this chapter. The reader is referred to references 1–4, 7, and 8 for excellent discussions on the properties of the smoothing algorithm and references 5 and 6 for its application to XPS data.

The degree to which noisy data is smoothed depends on both the smoothing interval and the set of coefficients used. Smoothing increases with the number of points used, however, more distortion is introduced with a large smoothing interval [4]. Second and third order polynomial fits improve the smoothing relative to 4th and 5th order fits, but they also introduce more distortion. Choosing a small smoothing interval with high order polynomial fit coefficients may not result in sufficient smoothing of the data. Repeated smoothing may be carried out if an adequate procedure can be applied to the unsmoothed end points during the repeat calculations. Setting the end points equal to the average of the unsmoothed points provides a method for using the end points in repeat smoothing. This is only possible when a relatively high S/N level spectrum is being smoothed and the spectral window is selected such that the end points are part of an effectively flat background.

Proctor and Sherwood [6] have suggested a procedure for predicting the value of the unsmoothed points and incorporated this procedure into their repeat smoothing algorithm. This method results in some "edge" effects, however, where the edges of the spectral range includes photoelectron signal, prediction of the end points may be preferable.
The choice of the smoothing range and coefficients will determine the amount of noise reduction and also the signal distortion induced by the smoothing procedure [3,4]. A smoothing range too wide will result in peak broadening. Proctor and Sherwood [6] have suggested an "effective smoothing interval" equal to 0.7 times the number of data points equal to the FWHM value of the narrowest peak expected combined with 2nd/3rd order polynomial coefficients. Empirically, this width and coefficient set is found to cause peak broadening. While the distortion induced may be acceptable for detecting low intensity signals in a noisy background, it complicates line shape analysis. For example, a 15 point, 2nd/3rd order smoothing routine on the Au doublet widens the 4f7/2 peak from an unsmoothed value of 1.2 eV to 1.5 eV after 200 passes. This interval corresponds to \(0.497 \times \left( \frac{\text{# points}}{\text{FWHM}} \right)\) value of the peak. No measurable distortion is observed using the 4th/5th order smoothing coefficients after 200 passes. Thus for the most exacting work, the higher order polynomial coefficients with narrow smoothing ranges and multiple smoothing passes are required for minimum distortion of the spectrum.

**Background Subtraction And Peak Area Integration**

Determination of peak areas by computer integration requires the removal of the background due to inelastically scattered electron upon which the photoelectron peak is superimposed. The background is assumed to be proportional to the integrated photoelectron intensity to higher kinetic energy. Determination of the background end points may be very subjective. Bishop [9] has shown that a systematic error for Fe2p peaks may be as great as 40% using "best estimates" of the background end points. Shirley [10] has popularized the integrated or "S" shaped background removal procedure used for background removal in this work. Although this method is not without criticism [11], the procedure has been adopted by several workers [12-14] as well as several commercial instrument suppliers as part of their data analysis packages. An alternative integrated background procedure has been suggested [5]. This procedure, similar to the Shirley method, requires several
iterations of the algorithm to reach a final background estimate. Whichever integrated background removal techniques is used, it is a prerequisite that the extreme ends of the spectral data region are a flat background with no photoelectron signal. After removal of the background, the remaining peak area can be summed and corrected for elemental sensitivities to determine relative elemental concentrations (Chapter 2).

**Difference Spectra**

Generation of difference spectra by subtracting two XPS spectra to highlight small changes in lineshape is a well known procedure \([15,16]\). The method used in this study requires the two spectra to be subtracted from each other to have the same number of data points per eV and to have the same starting and ending energies.

Prior to generating the difference spectrum, the spectra must be smoothed, background removed, normalized and scaled. Data smoothing is required to eliminate the increased noise level generated when obtaining the difference from noisy spectra. Increased noise levels in difference spectra will tend to mask small differences between the two spectra making interpretation more difficult. The spectra used to generate the various difference spectra presented in Chapter 5 and Chapter 6 were first smoothed an equal number of times using the same smoothing interval and coefficients. Treated in this way, the slight line shape distortions generated by smoothing will tend to cancel out since both spectra were treated similarly.

Following smoothing, the "S" shape background removal procedure is applied to each spectrum in preparation for normalizing, scaling and peak alignment. Normalization and peak alignment have been shown to be important experimental factors \([5]\) which must be considered prior to generating the difference spectrum. Peak height normalization and scaling requires the lowest count data point in each spectrum to touch the base line and the maximum count data point of each spectrum be set equal to some value chosen for convenient data display. Normalization such that each peak has equal integrated areas (peak area normalization) is also possible.
However, the peak height normalization procedure and resulting difference spectra appear to be easier to interpret.

Peak alignment is very important. Two spectra do not necessarily align with equivalent kinetic energies. Misalignments may be generated by slight drifts in the instrument calibration and sample charging effects. This is especially true when comparing the C$_{1s}$ lines from conductive glassy carbon samples to C$_{1s}$ lines obtained from homopolymers samples discussed below.

Slight misalignment of the spectra will lead to significant features being generated in the difference spectrum. Figure 17 is a high resolution C$_{1s}$ XPS spectrum (A) obtained from polished glassy carbon. The spectrum has been smoothed, background removed and peak height normalized. The difference spectra (B) correspond to displacement of the carbon spectrum by (a) 0.1 eV, (b) 0.06 eV, and (c) 0.02 eV prior to subtraction from the properly aligned spectrum. The difference spectra shown in Figure 17 emphasize that care must be taken when generating and interpreting difference spectra. A Fortran source code listing of the peak alignment procedure is provided in Appendix 1.

An artifact of height normalized and properly aligned peaks is that a negative difference at slightly higher kinetic energy is normal and can be used to judge the peak alignment [5]. For example, the reader is referred to Figure 28 (Chapter 5) which presents difference spectra of several modified glassy carbon surfaces.

**Curve Fitting**

Curve synthesis, sometimes called deconvolution, is carried out by summing a series of individual curves in order to produce a final function that closely matches the experimental spectrum. Curve fitting procedures carried out on the laboratory minicomputer involves smoothing, background removal, and scaling of the experimental data as discussed above. The experimental spectrum is then presented on an oscilloscope display. The synthetic curve is generated by choosing a set of parameters for each peak in the synthesis. The parameters required are the peak
position, FWHM value, peak intensity and peak shape. The XPS peak shape is assumed to be Lorentzian convoluted [17] with an instrumental response function (IRF) which is also a convolution of a finite Lorentzian x-ray line and a Gaussian lineshape due to the CMA analyzer. Fitting curves to C1s lines obtained from pyrolytic graphite and freshly cleaved highly ordered pyrolytic graphite indicate that a 25% Lorentzian and 75% Gaussian peak shape provides good fitting results under the instrumental resolution (25 eV pass energy) used.

After each peak position, FWHM value, and shape is defined, the minicomputer displays both the experimental and sum curve on the oscilloscope. Additional peaks are added or subtracted as desired. Each peak parameter may be individually adjusted by the operator until an acceptable fit is obtained. The "goodness" of fit, the Chi square difference between the experimental and synthetic curve, is also calculated for consideration.

The curve fitting procedure used is highly operator intensive and good chemical sense must be employed when using this procedure. Reasonable peak positions and FWHM values for various surface functionalities expected to be present on the surface must be used for meaningful results. Extraneous peaks added to "improve" the fit (decrease the Chi square value) should be avoided. A Fortran source code listing for the curve fitting procedure is provided in Appendix 1.

Homopolymers As Model Compounds

The lack of a "model" GC surface with high concentrations of known functional group type(s) presents an experimental difficulty when analyzing these surfaces. The relatively unoxidized pyrolytic graphites appear to have low levels of multiple oxygen functional groups. Homopolymeric materials are available with a wide variety of specific functional groups. XPS studies by various workers [18–21] have determined the chemical shifts experienced by a carbon atom resulting from formation of various functional groups. The chemical shift value observed by replacing a hydrogen or carbon atom to form: hydroxyl or ether (C-O) functions is 1.4 – 1.6 eV, ketone (C=O)
functions is 2.9 - 3.1 eV and carboxylic acid and ester functions is 3.9 - 4.1 eV. Aromatic ketone functions have been reported at a slightly lower chemical shift value of 2.5 eV [22].

XPS data obtained from homopolymer in this study is used as a guide for the analysis of the plasma effects on GC. The insulating properties of polymeric materials results in surface charging and charge shifting of the peak positions. Under the conditions of uniform surface charging, as is generally the case for non-monochromatic x-ray anode sources [18], the recorded high resolution spectra retain their proper line shapes. Charge correction by assigning the bulk C-C signal a value of 285.0 eV [18,19] is easily done and the remaining lines in the spectrum can be assigned values based on the energy offset from the bulk C-C value. In this way, binding energies, chemical shift values and FWHM values can be obtained from the same XPS instrument under the same operating conditions (x-ray power, instrumental resolution) as the plasma treated glassy carbons.

The homopolymers analyzed included polyvinyl alcohol, polyethylene oxide, polyvinyl ketone, polymethyl methacrylate and polyacrylic acid. The low resolution XPS survey scans detected only carbon and oxygen on the cast polymer films. The XPS results for the high resolution narrow scans for the C\textsubscript{1s} and O\textsubscript{1s} are shown in Figure 18 and 19, respectively. The spectra have been charge corrected by assigning the bulk C-C bond to 285.0 eV BE. Table 2 provides the observed C\textsubscript{1s} and O\textsubscript{1s} binding energy and FWHM values and the observed and theoretical O/C ratios. Curve fitting using a 75% Gaussian / 25% Lorentzian peak shape gives good fits to the carbon lines. The relative peak shifts obtained for the various functions in the polymers are also listed. The data from the homopolymers provides a basis for confidence when applying the curve fitting procedure to the treated GC samples as discussed in Chapter 5.
Resolution Enhancement

Improvement in the resolution realized from the spectral deconvolution of instrumental broadening effects from the experimental data to provide the "true" spectrum has been applied to XPS by several workers [17,23-30]. The instrumental broadening contribution to the true line shape consist of a combination of broadening effects due to the analyzer and the finite lineshape of the exciting x-rays. Successful removal of these instrumental line broadening effects would lead to improved resolution of the line shapes and improved assignments of peak positions, curve fitting results and difference spectra.

There are two distinct approaches to deconvolution. These are the Fourier transform methods and the van Cittert successive approximation technique. Excellent discussions of the deconvolution techniques are available [17,24]. The van Cittert technique was investigated as a possible approach to improving the resolution of the experimental data obtained from our instrument. Two different implementation of the van Cittert procedure were employed.

The first implementation utilized the procedures of Carley and Joyner [32]. Their procedure involves a two stage iteration to separately remove the x-ray line broadening followed by removal of the analyzer line broadening. Computationally, the procedure involves: (i) calculating the x-ray line shape [25], (ii) convoluting [31] and normalizing the smoothed and background removed experimental data with the x-ray line shape, (iii) calculating the chi-squared difference between the experimental and convoluted data and testing for convergence, and (iv) estimating a new trial deconvolute followed by smoothing. The procedure iterates through steps (ii), (iii), and (iv) until the chi squared difference converges to a minimum value. Once the x-ray line shape is removed, a calculation of the analyzer line shape is used in place of the x-ray line as in (i) and the procedure is repeated to convergence.

While the deconvolution procedure results in some resolution improvement for very high S/N level data such as the gold 4f peaks, large oscillations appear in both the signal and backgrounds of the glassy carbon spectra. The oscillations
increase in intensity during successive iterations.

The oscillations generated by this procedure result from the method used to estimate the trial deconvolute and use of smoothing during each iteration. Estimation of a trial deconvolute line is by taking the ratio of the experimental and the convoluted line as in equation 12:

$$D_j = D_{j-1} \left( \frac{\text{fexptl.}}{C_{j-1}} \right)$$

Where \(D_j\) is the new estimate of the lineshape, \(D_{j-1}\) is the current estimate of the line shape, \(C_{j-1}\) is the convolute of the x-ray or analyzer line shape with \(j\)th-1 estimate. When the \(C_{j-1}\) values are zero or negative, the new \(D_j\) value is set equal to zero. Smoothing of the new deconvolute line results in distortion in terms of line broadening [4]. As the successive deconvolute lines get more narrow, the line broadening due to smoothing becomes more severe. Additional smoothing causes severe distortions at the base line as the smoothing interval encounters rapid line shape changes brought about by setting data values to zero as required by the procedure.

A second procedure for deconvolution of the combined x-ray line shape and analyzer broadening was studied. This procedure utilizes an improved convolution algorithm [33] which decreases the computation time and a different deconvolute estimation procedure [17].

In this procedure data smoothing is accomplished with the 4th/5th order polynomial coefficients. A smoothing interval corresponding to approximately one half the FWHM value of the Au 4f7/2 peak. Using this smoothing procedure, no measurable peak broadening is observable after several hundred smoothing passes. No additional smoothing is used during the deconvolution. After smoothing, the inelastic background is removed as described above.

Following smoothing and background removal, an instrument response function (IRF) is calculated by convolution of the x-ray line shape [25,31] and the analyzer line broadening function. The IRF is used in a single stage deconvolution. The
Lorentzian x-ray line shape is calculated using the values for peak intensities, FWHM values, and peak separations given in reference 29. The analyzer line broadening, estimated as a Gaussian function, is calculated based on the CMA analyzer aperture and pass energy selected [34]. Under the instrumental conditions used the analyzer broadening function has a FWHM value of 0.4 eV (25 pass energy times 1.6% analyzer energy resolution/100).

The deconvolution uses a three step procedure. The first step (i) involves convolution of the IRF with the experimental data. The second step in the procedure (ii) involves peak height normalization of the convoluted spectrum and obtaining the chi square difference between it and the experimental data. In the third step (iii), a new trial deconvolute is estimated by [11]:

\begin{equation}
fi = f_{i-1} + f_o - f_{i-1} \otimes G
\end{equation}

where \(f_i\) is the ith estimate of the deconvolute, \(f_{i-1}\) is the estimate of the deconvolute from the previous iteration, \(f_o\) is the experimental data, and \(G\) is the IRF. The term \(f_{i-1} \otimes G\) is the convolution of the IRF with the experimental or i-1 deconvolute line. A Fortran source code listing of the deconvolution procedure used in this second method is provided in Appendix 1.

This second procedure also results in oscillations in the deconvoluted spectrum, however, the oscillations are less severe than observed in the first procedure. Figure 20 shows the C\(_{1s}\) line obtained from an oxygen RFP treated glassy carbon sample after applying the two deconvolution procedures investigated. The extraneous "peaks" and "inflections" which are obviously not real in a chemical sense make interpretation of the deconvoluted carbon spectrum more difficult.

The origin of the extraneous features in the spectrum can be traced to the x-ray generator. Although the x-ray generator has constant power circuity to adjust for drift in the electronics [34], there is a slowly varying change in the x-ray flux reaching the sample. This x-ray flux variation has been observed by other workers [35,36].
The x-ray flux variation generates a slowly varying ripple in both the background and photoelectron signal. Since the smoothing procedure used acts as a low pass filter [4], smoothing can never remove this low frequency "noise" component from the spectrum. Deconvolution by either procedure studied results in an emphasis of both the major peaks as well as the low frequency x-ray flux variation making this procedure unsuitable as an aid to interpretation of data.

Elimination of the x-ray flux variation via improvement in the x-ray generation system should allow useful application of the Van Cittert deconvolution procedure as an aid to data analysis.
TABLE 2
XPS DATA OBTAINED FROM "MODEL" HOMOPOLYMERS.

Peak positions\(^\dagger\), full width at half maximum (FWHM) values\(^\dagger\), measured and theoretical O/C ratios obtained from the homopolymers shown in Figure 18 and Figure 19.

<table>
<thead>
<tr>
<th>Signal</th>
<th>C(_{1})s</th>
<th>O(_{1})s</th>
<th>O/C ratio measured</th>
<th>O/C ratio theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl alcohol</td>
<td>287.2</td>
<td>534.8</td>
<td>0.349</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>[2.70]</td>
<td>[1.8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>2.88.6</td>
<td>534.4</td>
<td>0.542</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>[1.5]</td>
<td>[1.6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl ketone</td>
<td>287.4</td>
<td>534.4</td>
<td>0.214</td>
<td>0.333</td>
</tr>
<tr>
<td></td>
<td>[1.6]</td>
<td>[1.6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>287.6</td>
<td>535.6</td>
<td>0.347</td>
<td>0.400</td>
</tr>
<tr>
<td></td>
<td>[2.3]</td>
<td>[3.2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacrylic acid</td>
<td>299.2</td>
<td>535.7</td>
<td>0.489</td>
<td>0.666</td>
</tr>
<tr>
<td></td>
<td>[2.1]</td>
<td>[3.0]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^\dagger\) Peak positions measured at the center of the peak. The peak positions and FWHM values (in square brackets [ ] ) are given in eV. Peak positions are not corrected for charge shifting.
Figure 17. Effects of Peak Misalignment on Difference Spectra

(A) High resolution XPS carbon (C1s) spectrum obtained from polished glassy carbon.

(B) The difference spectrum obtained by subtracting (A) from itself after misalignment of the second spectrum by: (a) 0.1 eV, (b) 0.06 eV, and (c) 0.02 eV. The difference spectrum illustrates the importance of proper alignment of the spectra prior to performing the subtraction.
Figure 18. Carbon (C1s) XPS Spectra Obtained From "Model" Homopolymers.

High resolution carbon (C1s) XPS spectra obtained from homopolymer materials. Each polymer contains high concentrations of functional group types expected to be present on plasma treated glassy carbon. The spectra are from: (a) polyvinyl alcohol, (b) polyethylene oxide, (c) polyvinyl ketone, (d) polymethyl methacrylate, and polyacrylic acid. The spectra have been charge corrected to the bulk C–C binding energy of 285.0 eV. The lines drawn at +1.5, +2.5, and +4.0 eV higher BE are provided to guide the eye.
Figure 19. Oxygen (O\(_{1s}\)) XPS Spectra Obtained From "Model" Homopolymers.

High resolution oxygen (O\(_{1s}\)) XPS spectrum obtained from homopolymer materials. The spectra correspond to the polymer spectra shown in Figure 18. The spectra are from: (a) polyvinyl alcohol, (b) polyethylene oxide, (c) polyvinyl ketone, (d) polymethyl methacrylate, and polyacrylic acid. The spectra have been charge corrected relative to the bulk C–C binding energy of 285.0 eV.
Figure 20. Resolution Enhanced Carbon Spectra.

The high resolution carbon (C_1s) XPS spectra from oxygen RFP treated GC (a) after signal averaging, smoothing, and removing the inelastically scattered electron background, (b) after applying the first deconvolution procedure [24], and (c) after applying the second deconvolution procedure [33]. Both procedures result in some improvement in spectral resolution. The origin of some of the "peaks" and "inflections" (oscillations) in the spectral deconvoluted lines are due to instrumental instability. (See text.)
CHAPTER 5

OXYGEN PLASMA TREATMENT OF GLASSY CARBON

INTRODUCTION

This chapter describes the observed changes to the surface of GC resulting from plasma treatments using various oxygen containing gases. The treatments were accomplished using the radio frequency plasma (RFP) generator and the sample introduction / handling system described in Chapter 3. It is found that plasma treatment results in both physical and chemical changes to the GC surface. Analysis prior to and after sample exposures to water vapor and air was carried out to assess the reactivity of the modified surface and to simulate the uncontrolled conditions which occur when a sample is removed from an off-line plasma generator. The surface reactivity of plasma treated and sputter cleaned carbon surfaces when exposed to water vapor and air is also discussed. Reduction of surface functional groups using a commercially available reducing agent (Vitride) and subsequent XPS analysis of the reduced surfaces are discussed. An estimation of the surface functional groups generated by the plasma treatment is also presented.

EXPERIMENTAL

Sample Preparation

Glassy carbon samples were obtained from three different manufacturer’s. Three grades of Tokai glassy carbon were obtained from the Tokai Electrode Manufacturing Co., Tokyo, Japan. These three grades will be referred to as GC-10, GC-20 and GC-30 which correspond to the designated heat proof limits of 1300 °C, 2000 °C and 3000 °C, respectively. Two grades of Sigradur glassy carbon, obtained from Sigr Elektrographit GMBH, West Germany, are referred to as Sig K and Sig G with heat proof limits of 1000 °C and 2500 °C, respectively. The third glassy carbon, Atomergic, referred to
as V-19 with a heat proof limit of 1900°C, was produced by the Societe Le Carbon, Lorrain Fr. and was obtained from Gallard-Schilesinger Chemical Mfg. Co., Carle Place, NY. Table 21 gives some of the physical data taken from the literature supplied with these materials.

The carbon samples were obtained in sheet form and cut to the desired size with a silicon carbide saw. After cutting, the samples were washed with distilled water in an ultrasonic cleaner (Sonicor Model SC 50 TH, Sonicor Instrument Corp., Copiague, NY), air dried and stored in sample vials prior to further use. The GC samples were polished to a mirror like finish with the following procedure. First they were abraded with fine emery paper (wet/dry type) followed by polishing with successively finer grades of alumina (1.0, 0.03 and 0.05 micron size) (Buehler Ltd., Evanston, IL) on a glass optical flat (Polishing Kit, Harrick Scientific Corp., Ossining, NY). The polishing alumina was diluted with freshly distilled water. The samples and glass plate were thoroughly washed prior to polishing with a finer grade alumina. After polishing was completed, as judged by visual observation of a smooth and nearly scratch free surface, the sample blanks were given a final wash for ca. 10 minutes in the ultrasonic cleaner using distilled water, acetone, trichloroethane, methanol and distilled water. During the final washings, the samples were handled exclusively with degreased stainless steel forceps or tweezers to minimize the possibility of surface contamination. The samples were then air dried prior to mounting on the sample holders (described in Chapter 3). All sample holders were similarly washed and handled with forceps and tweezers. A limited number of samples were also treated and examined in the "as received" condition. These samples received only the final washing procedure prior to mounting on the sample holders.

Various methods of sample attachment to the aluminum holders were used. Samples were mounted on double sided tape, with graphite paste, silver conductive epoxy and cyanoacrylate adhesive. When the double sided tape was used, electrical contact between the sample and holder was achieved by painting a fine line of graphite paste across the tape to contact the metal of the sample holder. A small spot of
graphite paste was also used to ensure electrical contact between the sample and sample holder when using cyanoacrylate adhesive. The graphite/cyanoacrylate mounting method was found to be the most convenient and reliable method for sample attachment. This method was used exclusively during the latter stages of this investigation.

Each sample for SEM analysis had a portion of the surface masked with a sacrificial pressure sensitive tape during plasma exposure. Following plasma treatment, the sample was removed and mask stripped off the surface. After washing (as described above) to remove traces of residual adhesive from the surface, the samples were examined by SEM.

**Plasma Treatment**

All plasma treatments were accomplished at a standard power setting of ca. 35 watts. Tuning of the plasma generator to provide maximum RF power transfer to the plasma gas was achieved by the LC impedance matching network and monitored with the Standing Wave Ratio/RF Power Meter. The samples were positioned from 1/2" to 2" above the plasma generation coil. During all plasma exposures the samples were observed to be completely enveloped in the plasma glow. Samples for SEM analysis were exposed to a three minute plasma treatment, while the samples for XPS analysis were exposed to the plasma for periods ranging from 1 to 3 minutes.

Oxygen plasmas were generated using source gases of either USP grade (Liquid Carbonic) or dry oxygen (Linde, 99.6%) at 100–150 mtorr pressure. The water vapor plasmas using fresh doubly distilled and degassed water as the source gas were carried out at 100–150 mtorr pressure. Carbon monoxide (Linde, 99.0%) and carbon dioxide (Linde Bone Dry Grade, 99.8%) plasmas were carried out at 50–100 mtorr and 90–150 mtorr pressures, respectively.

Each sample for XPS analysis was withdrawn into the side arm and evacuated to less than 10 mtorr by the LN trapped mechanical pumping system prior to isolation and continued pump down by the ion pump of the sample introduction system. All samples were transferred to the analysis chamber under UHV conditions.
XPS Data Acquisition

Low resolution XPS survey spectra were taken by manually scanning the instrument at 100 eV pass energy over a 1000 eV range in the analog mode of instrument operation. High resolution spectra were recorded under computer control at 25 eV pass energy. The instrumental resolution at this pass energy is 1.2 eV FWHM using the Au 4f7/2 peak. The instrument energy scale was calibrated using the Au 4f7/2 peak at 83.8 eV binding energy. Multiple signal averaged scans were recorded to obtain high S/N spectra. Usually 6 to 10 second scans lasting 200 seconds each were recorded prior to data storage. Ten or 20 eV energy range windows were used for the C1s and O1s regions.

Ion Sputtering

Ion sputtering of the GC surfaces was accomplished by backfilling the analyzer chamber to an argon pressure of 5 x 10^-5 torr. The argon ion gun was operated at 20 milliamps and 2 KV accelerating potential. The Ar+ beam was defocused to insure a sputtered area larger than the XPS sampling area. Sputtering durations of from a few seconds to several minutes were used.

Wet Chemical Treatments

For comparison to plasma surface oxidation, samples of GC-30 and GC-20 were subjected to 30 minute exposures to a 0.2 M KMnO4 in 2 M H2SO4 solution at room temperature. After exposure, the samples were washed and mounted for XPS analysis as previously described.

Surface reductions were carried out using Vitride (Hexcell Corp., Zeeland, MI), a 70% solution of NaAlH2(OCH2CH2O CH3)2 in toluene. Plasma treated samples were removed from the plasma chamber and placed in screw top sample vials. The samples were then covered with Vitride solution. The vials were capped using a aluminum foil as a liner to seal out atmospheric moisture. Reduction periods ranged from 40 hours to 8 days at room temperature (approx. 20 °C) to 80 °C for 2 hours. After reduction, the samples were removed from the vials, washed in dry toluene, quenched and ultrasonically washed in distilled water. The samples were air dried, remounted, and
placed in the sample introduction system and pumped to UHV pressures as rapidly as possible. Total air exposure after removal from the Vitride was approximately 30 minutes. After each reduction, the reducing solution was checked for active hydrogen by the addition of distilled water and observing the evolution of hydrogen gas.

RESULTS AND DISCUSSION

The physical changes to all the glassy carbon surfaces resulting from oxygen plasma exposure was observed by SEM. SEM indicates that each carbon surface experienced significant etching during three minute plasma exposure. The three grades of Tokai GC (GC-10, GC-20, and GC-30) exhibited the widest physical diversity in the polished and plasma etched surface [1]. Figure 21 shows the SEM micrographs for the protected and exposed surfaces of polished GC-10, GC-20, and GC-30 samples. All three of the protected sample surfaces are smooth with some striations remaining after the polishing. There is an increase in the number and size of surface pits observed which parallels the increasing heat proof limits of the three Tokai carbon samples. This observation is consistent with the observations of other workers [2].

The GC-30, Figure 21c, sample (right side) has a random scattering of pits with a maximum diameter of ca. 5 microns. The GC-20, Figure 21b, sample (top half) also exhibits a random scattering of pits of ca. 2 microns maximum diameter. The GC-10, Figure 21a, sample (top half) is, in contrast, free of observable pits. All three surfaces have a distinct etch line at the terminus of the protective mask. As with the protected surface, the GC-10 plasma exposed surface is very smooth and pit free. The GC-20 and GC-30 treated surfaces show a significant increase in the number of observable pits with the largest pits occurring in the GC-30 sample. Figure 21d shows at higher magnification the details of pits from the etched GC-30 surface. The damage to the region of the pit is very evident.
The oxygen RFP effects on the Sigri Sig K, Sig G and Atomergic V-19 samples are shown in Figure 22a, b, and c respectively. These surfaces closely resemble those of the Tokai GC-10 sample. Each shows an etch line although in the pit free surfaces the etch line is more difficult to recognize. The pits present in the V-19 surface are clustered and not randomly distributed as in the Tokai samples.

Samples of the three unpolished Tokai carbons treated with a three minute plasma and examined by SEM exhibit very rough jagged surfaces (shown in Figure 23). Although they are less obvious due to the surface roughness, the micrograph indicates there is a random scattering of pits present which parallels the polished sample observations. The pits observed in the unpolished samples and the damage detected on the polished GC-30 surface (Figure 21d) indicate the pits are not simply exposed by erosion of the surface, but rather they appear to have been exploded outward perhaps from the thermal expansion of trapped gas bubbles. The physical data for the carbons are also consistent with these observations.

Table 3 is a compilation of the physical data on the carbons obtained from the manufacturer's literature. Comparative values for graphite are also listed. There is a direct correlation between the number and size of observed pits and the reported densities, porosity, hardness and gas permeabilities. The decreases in density and hardness and the increases in the gas permeability and apparent porosity for the Tokai carbons is diagnostic of the random distribution of the voids in the bulk material. High temperature oxidation of GC-30 carbons have been carried out by Reinoso and Walker [3]. Burn off rates were found to be consistent with a material which has an internal closed cell void like structure. This void structure accounts for the changes in the physical properties of these carbons as the heat proof limit goes up. Note that even though there were fewer pits observed for the Sig K, Sig G, and V-19 samples, the Sig K has a lower gas permeability then the higher temperature Sig G and V-19 carbons. Microscopic voids are known to form in the matrix of the carbon during manufacturing [4], and their relative size and distribution varies with the process used. There are no significant differences in the electrical conductivities
of the carbons listed.

Water vapor RFP treatments were carried out on the Tokai GC samples. Evans et. al. [5] were the first to show that water RFP treatments increased the oxygen content of metal oxide and graphitic surfaces. The effect of water vapor RFP on GC-10, GC-20, and GC-30 surfaces is shown in Figure 24. Again the upper portion of the micrographs shows the protected surface. The surface features parallel those found with the oxygen plasma treated samples. No pits are evident in the GC-10 sample while the GC-20 and GC-30 samples show an increase in size and number of pits. The absence of the extreme damage to the surface pits observed for oxygen RFP and a less distinct etch line between the exposed and protected surface suggests that water vapor plasma is a milder etchant gas than oxygen.

The remaining oxygen containing gases investigated were carbon monoxide (CO) and carbon dioxide (CO$_2$). Their etching effect on the GC-30 surfaces indicated they are less effective or milder etchant gases than oxygen and the treated surfaces appear very similar to water vapor treated surfaces.

The ability of all the oxygen source gases used in this study to physically etch the surface is evident. It does not appear from the micrographs that the etching is a function of the type or grade of carbon used. The appearance of an etch line at the relatively low (500x) magnifications employed, indicates a significant amounts of material is removed by the plasma with the subsequent exposure of the subsurface carbon layers. The "step" height between the etched and protected surface for the oxygen plasma treated GC-30 sample (Figure 21c) is estimated to be approximately 0.3 micron, the etch rate is therefore, on the order of 500 to 1000 Å/minute. Previously, Evans and Kuwana [6] have estimated an etch rate of ca. 100 Å/minute for oxygen plasma on pyrolytic graphite. This lower rate of etching reflects the differences in the plasma generation system and reaction chamber used in the studies. Etching rates on organic materials has been shown to be a function of applied power, gas flow rate, gas pressure, chamber geometry and sample placement in the reactor [7]. The current RF generator applies ca. 35 watts of power, while the previous reactor
delivered less than 15 watts and had a different physical geometry. The rapid rate of material removal by oxygen plasma suggests surface oxidation comes to equilibrium within a few seconds. For example, the O/C ratio of a oxygen plasma treatment of a polymer coating on PG disks reached 0.337 in only 15 seconds. The plasma generated oxygen "saturation" of PG surfaces occurs within two minutes for treatments in the off-line plasma reactor used previously [6].

The mechanism of the etching taking place during RFP could be by the physical interaction of sputtering [8] by energetic ions impinging on the surface in a process analogous to the rare gas ion sputtering used for surface cleaning and depth profiling or by chemical interactions [9] with active atomic radicals, molecular ions and molecules in metastable or excited molecular electronic states. Chemical interactions which can occur are chemisorption, adsorption and chemical reaction. Since the plasma is a "cold" or non-equilibrium plasma and the atomic and molecular species present are at near ambient temperatures, collision of these species with the surface will favor the chemical interactions. The atoms and ions are not thought to have sufficient energy to sputter the surface [10]. An oxygen RFP is expected to remove significant material by chemical action as the reactive oxygen species generated in the plasma react with the surface carbon to form volatile oxides which desorb and are pumped away. The other gases were observed to be weaker etchants relative to oxygen. The reduced etch rate may be because the gaseous species present in the plasma are already in the form of "volatile" oxides or they form reactive gaseous species which quickly recombine before they can react with the carbon surface.

The physical observation of the surfaces resulting from polishing and plasma treatment indicates, the GC-10 and Sig K carbons can be polished to the smoothest pit free surfaces. The oxygen RFP treatments cause considerably more surface etching and damage than the other gases used. From a structural point of view, the lower temperature grade carbons (GC-10, Sig K) combined with the milder etching gases such as water or carbon monoxide appear to offer the most favorable surface topography for surface modification.
Chemical Effects of Oxygen Plasmas

XPS examination of the oxygen plasma treated glassy carbons indicates there is a significant incorporation of oxygen into all the carbon surfaces. All samples were treated in the plasma chamber and immediately evacuated to near UHV pressures. The resulting surfaces examined are, therefore, representative of a plasma treated surface without exposure to the uncontrolled conditions which occurred previously in the off line plasma treatment chamber used in our laboratory [6,11] and by other workers [12-15]. Low resolution XPS survey scans obtained from "as polished", water vapor and oxygen plasma treated glassy carbon are shown in Figure 25. There is always a significant oxygen signal observed on a polished GC surface. The spectra indicate the sample surfaces contain only oxygen and carbon. The increase in the oxygen to carbon signal intensities observed for the water and oxygen RFP treated samples relative to the polished sample is easy to discern. Figure 26 shows the XPS survey scans of carbon dioxide and carbon monoxide plasma treated surfaces. A permanganate oxidized surface is shown for comparison. The O1s peak intensity of the CO2 plasma treated surface (spectrum a) indicates that CO2 does not incorporate an additional amount of oxygen into the GC surface. The CO2 plasma treatment was investigated as a possible reagent gas for "selectively introducing" carboxylic acid like groups on the carbon surface.

The carbon monoxide treated surface (spectrum b) has a significant increase in oxygen signal detected. The magnitude of surface oxygen incorporation is approximately the same as that observed for oxygen plasma treated samples (Figure 25c).

Figure 26c illustrates the results of permanganate oxidation of glassy carbon. The very intense oxygen signal indicates a highly oxidized surface. The spectrum also exhibits two other signals (Mn2p and Mn Auger lines) indicating the presence of a manganese contamination. The manganese is probably present as insoluble MnO2 since there is no evidence of a potassium signal which will be present if the manganese contamination is due to unreacted reagent. The problem of surface contamination
following chemical oxidation has been a complicating factor in previous investigations [6]. Contamination due to wet chemical treatments is a serious one and can easily affect the interpretation of results even when such contaminants are present in apparently small amounts. Based on the peak height of the manganese signal and the elemental sensitivity for manganese, approximately 7-10% of the observed oxygen signal is due to oxygen in MnO$_2$. The other "extra" signal present in the spectrum is from nitrogen (N$_{1s}$ line at 400 eV). The origin of this contaminant is not known.

The survey scans of the plasma treated samples provide valuable information about the nature of the surface, such as increases in surface species and the presence of new or unexpected contaminants. Survey scans alone provide little information about the oxidation state of the species present. High resolution spectra of the carbon and oxygen signals are helpful.

**Surface Chemistry**

The chemical nature of all the various GC samples appear to be equivalent. Examination of polished and plasma treated samples by XPS give effectively the same results without regard to manufacturer or heat treatment. Because no differences in the carbon samples was observed by XPS, the majority of work presented was accomplished using the smoother GC-10 and GC-20 samples. These samples are somewhat easier to polish to a mirror like surface.

The high resolution carbon C$_{1s}$ spectra from two minute RFP treatments with the oxygen source gases are shown in Figure 27. Table 4 lists data compiled from GC surfaces for the various treatments investigated. The vertical lines in the figure correspond to the binding energy chemical shifts associated with single bonded (+1.5 eV), double bonded (+2.5 eV) and carboxyl (+4.0 eV) carbon functional groups found for homopolymers (Chapter 4). The following data represents the combined results of multiple experiments. The high resolution, signal averaged spectra of polished GC yields a surface O/C ratio of 0.158 ± 0.026. The ratio was obtained by computer integration of the oxygen and carbon signals after digital smoothing and inelastic background removal (Chapter 4). The ratio is slightly higher then the O/C ratio
previously reported \((O/C = 0.14 \pm 0.2)\) \([16]\). This difference (ca. 7\%) is partially the result of employing the integrated background removal algorithm instead of the linear background approximation used for manual integration as well as the improved precision of the computer integration. As can be seen in the figure, spectrum a, the C\(_{1s}\) line (from a representative polished GC surface) has a high BE tail indicating there is a distribution of carbon–oxygen functional groups present. The corresponding O\(_{1s}\) peak for the polished sample is very broad and centered at 532.3 eV with a full width at half maximum peak height (FWHM) of 2.6 eV. The broadness of this peak also indicates a variety of oxide species are present. Spectra b, c, d, e, and f illustrate the effects of the RFP using the various oxygen containing gases. Figure 28 shows the corresponding difference spectra for the polished surface (Figure 27a) subtracted from the spectra of the other lines in Figure 27.

The effect of a water vapor plasma is illustrated in Figure 27b. This treatment increases the surface O/C ratio to 0.245 \(\pm 0.038\). An O/C ratio enhancement of about 1.5 relative to the polished surface. The carbon line shape is similar to that observed for the polished surface. The difference spectrum, however, emphasize the changes generated. The water vapor RFP increases the signal intensity corresponding to carbon–oxygen functional groups relative to the polished surface but has not preferentially increased a single functional group such as surface hydroxyl at the expense of surface ketone and carboxyl groups. It is known that the OH radical is present in considerable quantity in water vapor plasmas and that H\(_2\)O and O\(_2\) as well as H\(_2\)O\(_2\) are formed in the plasma \([17]\). The lack of preferential introduction of the expected hydroxyl surface groups may be due to the formation of other reactive oxygen species such as the oxygen radical or possibly abstraction of a hydrogen atom from an existing surface OH group by another hydroxyl radical to reform water leaving a reactive surface oxygen which can rearrange to give ketone/quinone or carboxyl like groups. Formation of ketone groups via keto–enol tautomerism may also be possible if hydrogen can migrate onto the neighboring carbon atoms.
Spectra c and d are from GC treated with an oxygen RFP. Spectrum c is from a USP oxygen plasma treated sample. Spectrum d is from a dry (99.6%) oxygen treated sample. Both spectra show a pronounced shoulder at +2.5 eV higher BE than the main carbon line. The less well defined valley in the spectrum of USP oxygen treated sample is indicative of a slightly higher concentration of hydroxyl groups. USP oxygen contains traces of water. The signal intensity at +2.5 eV higher BE is also observed more graphically in the difference spectrum, Figure 28, and emphasizes the increased surface oxidation by the plasma. The dry oxygen has preferentially introduced ketone or quinone functional groups at the expense of hydroxyl and carboxyl groups. The primary reactive species in an RF oxygen plasma have been determined to be the $O_2 1\Delta_g$ molecule and the $3P$ oxygen radical [7,18] which are known to react with organic substances. There is also more signal intensity in the hydroxyl (+1.5 eV) and carboxyl (+4.0 eV) regions. The O/C ratio for oxygen plasma treatments is 0.338 ± 0.018 which is an oxygen enhancement of ca. 2.1 compared to the polished surface. Previous oxygen RFP of GC gave an O/C ratio of 0.221. This increase in the oxidation of the sample surface is due to differences of the samples used, the RF power applied when generating the plasma, and sample handling after plasma termination.

Carbon monoxide plasma treatment results in a carbon spectrum which is strikingly similar to the observed dry oxygen spectrum. Again the very pronounced shoulder is present in the +2.5 eV region. The difference spectrum is also very similar. The O/C ratio is 0.303 ± 0.039 for an oxygen enhancement of ca. 1.9. The similarity between these two spectra suggest the the primary reactive species responsible for surface oxidation are the same for both plasmas. An oxygen plasma would rapidly build up a steady state atmosphere of CO and CO$_2$ in the plasma as the surface is etched. Studies of atomic oxygen reaction with graphite indicate that CO is the primary product of the surface reaction [19] and the formation of CO$_2$ requires reaction between atomic oxygen and a surface bound CO species. After reaction CO$_2$ species can then desorb to become constituents of the plasma gas.
The C\textsubscript{1s} spectrum for the CO\textsubscript{2} RFP treated surface is shown in Figures 27f and 28f. There is very little increase in the O/C ratio (0.164 vs 0.158) observed for this treatment gas. The C\textsubscript{1s} peak FWHM is decreased by about 0.1 eV relative to the carbon line of the polished sample. This narrowing of the line is emphasized by the two negative excursions on both sides of the main carbon line position in the difference spectrum and suggests the CO\textsubscript{2} plasma removes some of the single bonded C-O species which overlaps with and broadens the bulk carbon signal.

As can be seen from Figures 27 and 28, plasma treatment rapidly changes the carbon surface chemistry. The resultant surface carbon-oxygen functional groups introduced on the surface by a plasma is sensitive to the plasma gas used in the treatment. Dry oxygen and carbon monoxide are observed to be the most effective plasma gases for incorporation of ketone or quinone functional groups. Plasma modification of the surface chemistry is easily carried out in a very rapid, contaminant free fashion.

Reactivity of Plasma Treated Surfaces

The surface oxidation by the O\textsubscript{2} RFP is greater than that observed previously [6,11]. Additionally, the prominent feature at +2.5 eV higher BE had not been observed. The lack of this feature in the spectra of plasma oxidized samples treated in an off line plasma reactor is the result of changes in the surface chemistry during exposure to the laboratory atmosphere. Figure 29 shows the high resolution C\textsubscript{1s} spectra of oxygen and carbon monoxide treated surfaces before and after exposure to water vapor. Figure 30 shows the corresponding O\textsubscript{1s} spectra. Table 5 gives the corresponding C\textsubscript{1s} and O\textsubscript{1s} line positions, peak FWHM values and the O/C ratios.

The C\textsubscript{1s} line (spectrum a) is from the USP oxygen plasma treated sample. The O/C ratio is 0.358 indicating a highly oxidized surface. After exposure to water vapor in the side arm of the sample introduction system for 90 minutes at ca. 23 torr pressure, the C\textsubscript{1s} line has reduced intensity in the +2.5 eV region. The observed O/C ratio is 0.242 indicating a loss of ketone/quinone groups from the surface as a result of the water vapor exposure. The corresponding O\textsubscript{1s} spectra shown in Figure
30a and 30b also exhibit changes resulting from the exposure. The O$_2$ plasma treated sample has an O$_{1s}$ BE of 532.4 with a FWHM of 2.8 eV. After exposure to water vapor the oxygen line shifts to a lower BE of 532.2 eV and exhibits an increased FWHM to 3.4 eV. Spectra c and d of Figure 29 shows the C$_{1s}$ line for the "dry" oxygen plasma before and after water vapor exposure. The O/C ratio of 0.324 and the FWHM is 1.5 eV. After water vapor exposure, the C$_{1s}$ line shows a decrease of intensity in the +2.5 eV region. The FWHM of the line is broadened by 0.1 eV and the O/C ratio is decreased to 0.242. The same changes are observed in the O$_{1s}$ line. The center of the O$_{1s}$ line is shifted from 532.4 to 532.2 eV and the FWHM has increased from 2.7 to 3.1 eV. The final two spectra, e and f, of the figure are of a GC sample treated with a carbon monoxide plasma. Upon water vapor exposure, the O/C ratio decreases from 0.303 to 0.243 and O$_{1s}$ line position shifts from 532.3 eV to 532.1 eV. The C$_{1s}$ FWHM is unchanged for these two spectra, but the O$_{1s}$ FWHM has broadened by 0.1eV. The C$_{1s}$ line shape again shows a decrease in the +2.5 eV BE range.

The changes in the spectra described above are more graphically observed in the difference spectra. Figure 31 shows the C$_{1s}$ line difference spectra for the six spectra of Figure 30. The first difference (b-a) indicates a relatively large decrease in the 2.4 - 2.7 eV region and a lesser decrease in the 4.0 - 4.2 eV higher binding energy regions. There is a corresponding increase in the 1.0 - 1.5 eV BE region. The second difference (d-c) also indicates the effect. There is, however, a relatively smaller decrease in the 4.0 eV BE region and a relatively smaller increase in the 1.5 eV BE region compared to the previous difference. The third difference (f-e) is similar to the dry O$_2$ RFP treated sample, but there is little or no increase in the 1.0 - 1.5 eV higher BE region, which is consistent with the previous observations of a higher hydroxyl group content of the surface for oxygen plasma which contain traces of water vapor. A water vapor RFP sample exposed to air in the side arm did not show changes as did the O$_2$ and CO treated samples. No significant change in the surface was detected in the difference spectra obtained from the sample before
and after air exposure. The measured O/C ratio of 0.237 decreased to 0.232. The O/C ratios for the water vapor exposed oxygen and carbon monoxide plasma treated samples correspond closely to the ratio observed for water vapor RFP treatments. The C1s lines are very similar to each other. Difference spectra indicate that after water vapor exposure, the dry oxygen and CO plasma treated surfaces have only a slightly higher ketone/quinone like features in the spectra relative to the water vapor plasma treated sample.

In order to insure the observed changes were not actually a result of sample decomposition due to x-ray exposure, a sample was given an oxygen RFP treatment and the C1s line was recorded and then recorded again after 2.5 hours of x-ray exposure. The observed line shapes are very similar. Their difference spectrum is displayed as the fourth spectrum (e) in Figure 31. Although there is a slight difference, the changes which occurred required an x-ray exposure of ca. 2.5 times greater then the time required to record the initial spectra. To further check for x-ray decomposition, the XPS spectrum of a CO plasma treated sample was recorded within 16 minutes and after 10 hours of x-ray exposure. The measured O/C ratios before and after x-ray exposure are 0.219 to 0.201 respectively. The O/C ratio decrease is only 8.6% and this decrease is within the generally accepted ±10% accuracy of XPS. The lack of any significant carbon line shape change or decrease in the oxygen content of the surface upon prolonged x-ray exposure confirms the changes observed after sample exposure to water vapor are the result of a surface chemical reaction and cannot be attributed to x-ray induced sample decomposition.

The changes observed also indicate a plasma treated surface is extremely sensitive to post plasma exposure conditions, and the surface remains active even after an extended time in a vacuum system. Exposure to H2O vapor in the side arm leads to a 32% and 25% loss of oxygen from the surface for the USP and dry oxygen surfaces and a 20% loss for the carbon monoxide sample. Strongly adsorbed water can be ruled out as a surface species. Any significant water adsorption would lead to an increase in the oxygen signal and would increase the O/C ratio. Water vapor uptake
by activated carbons, outgassed at 1200 °C, at various temperatures from 200 - 1200 °C with the subsequent elimination of CO and CO₂ has been reported [20]. The decrease in signal intensity of the carbon line in the +2.5 eV and +4.0 eV regions suggests a surface reaction with water results in a loss of carboxyl and ketone/quinone groups. The resulting surface is "reduced" after water exposure.

The oxygen introduced by the polishing procedure of the plasma treatment is confined to the surface. Argon ion sputtering rapidly removes this oxygen leaving only carbon and implanted argon detectable by XPS. It is of interest to compare the sputter cleaned surface reactivity to air and water vapor. Sputter cleaning results in the breaking of chemical bonds as does reactive gas plasma exposure and polishing. Reactive or "dangling" bonds analogous to those reported by Mazur [21] should be generated and these reactive sites should be available for bond formation upon exposure to air or water vapor. Figure 32 shows the XPS survey scans for: (a) a one minute sputter cleaned GC surface, (b) the cleaned surface after 20 minutes water vapor exposure, (c) the cleaned surface after 20 minutes of air exposure, and (d) the initial as polished surface. The measured O/C ratios for the water vapor and air exposed surfaces are 0.024 and 0.054 respectively. These ratios are much less than the polished surface value of 0.158. The C₁s FWHM obtained from sputter cleaned GC (see Table 4) is 0.2 eV wider then the polished GC value, and the observed broadening indicates a sputter disrupted surface. The carbon line is further broadened (approx. 0.1 eV) by exposure to air. No broadening is observed for the water vapor exposed surface.

The oxygen lines observed after air and water vapor exposure have FWHM values of 2.9 and 2.2 eV respectively. Both peaks are centered at 532.1 eV. The water vapor exposed sample with the narrow O₁s line is assigned to adsorbed water because there does not appear to be any change is the C₁s line width to indicate bond formation to carbon. The air exposed surface has a much broader line and the observed broadening of the C₁s line suggests at least one type of oxygen functional group is introduced to the sputter cleaned surface. The width of the O₁s line, however, suggests multiple
oxygen species are present.

**Estimation of the Surface Functional Groups**

The changes to the surface chemistry resulting from plasma treatment are clearly recognizable in a qualitative sense by observing the changes in the carbon and oxygen signal intensities and line shapes. A semi-quantitative estimation of the relative amounts of the various types of surface functional groups can be obtained by the curve fitting procedures described in Chapter 4.

Figures 33, 34 and 35 illustrate the results of the curve fitting procedure on the polished, oxygen and carbon monoxide plasma treated samples and on the oxygen and carbon monoxide samples after exposure to water vapor. Table 6 summarizes the curve fitting results in tabular form. In the figures, components 2 thru 4 correspond to the various oxidized forms of carbon expected on the GC surface. Component 1 corresponds to the bulk or unoxidized carbon. Component 2 at +1.4 eV corresponds to C-O single bonded species such as hydroxyl or phenolic groups. Components 3 and 4 correspond to ketone/quinone and carboxyl groups respectively. Component 5 included in two of the fits is added to improve the fit at even higher binding energy. This component is probably due to the high binding energy tail typical of GC samples, however, higher oxidized species such as carbonate like groups cannot be ruled out.

Figure 33a and 33b show the curve fitting results comparing the polished and the water plasma treated surfaces. The line shapes are similar as noted above. The relative amounts of the individual components have changed. There is an increase in the +2.5 eV component region. This is reflected in the C-O/C=O ratio change from 3.4 to 1.6 (Table 6). The ratio of hydroxyl to carboxyl like components shows a similar change. The ratio of the sum of all the oxidized components to the bulk carbon peak (Cox/C-C) illustrates the increased oxidation of the water plasma treated surface.
Figure 34a and 34b have the curve fitting results for the oxygen and water exposed oxygen plasma treated samples. It is obvious from the figure and Table 6 that the major surface species are ketone or quinone groups. The C-O/C=C ratio is 0.71 compared to 1.6 for the water plasma surface. The C-O/C=C=0 ratio is only slightly changed. The Cox/C=C ratio is more than doubled relative the water plasma.

After exposure to water vapor, the surface components show a drastic change. The carbon line shape is now very similar to the water plasma sample. The C-O/C=0 and C-0/C=0/C=0 ratios are nearly the same (1.3 vs 1.6 and 1.8 vs 2.6, respectively) and the Cox/C=C ratios of 0.33 and 0.32 are effectively identical. These results parallel the changes in the O/C ratios (Table 6) of the oxygen plasma and water vapor exposed oxygen plasma surfaces.

The carbon monoxide and water vapor exposed carbon monoxide plasma treated samples show the same changes as the oxygen treated samples. The ketone/quinone like surface species predominate. The C-O/C=0 ratio of 0.61 compares well with the 0.71 value for the oxygen plasma. After water vapor exposure the major surface component is once again the C-O species. The Cox/C=C ratio of 0.36 and 0.27 before and after water vapor exposure do not show the changes (0.71 vs 0.33) observed for the oxygen samples discussed above.

The results shown in Figures 33 and 34 and the tabulated data in Table 6 indicate that both the oxygen and carbon monoxide plasma treatments after exposure to water vapor have nearly the same surface chemical species as a surface generated with the water plasma.

**Surface Reductions with Vitride**

In the experimental apparatus described above, it was not possible to introduce predominately a single surface species such as ketone/quinone or hydroxyl like groups. As an alternative to introducing specific surface species via plasma oxidation, surface oxidation by plasma (or other means) followed by reduction was investigated to determine the feasibility of this approach.
Surface reduction using Vitride was carried out on both plasma and KMnO₄ oxidized samples. All reductions were carried out off line of the sample introduction system. There was no attempt to determine optimum reaction conditions during the experiments.

Figure 36 shows the carbon 1s lines from GC after oxidation with KMnO₄ solution and oxygen, carbon monoxide and water RFP treatments followed by reduction with Vitride. The difference spectra after subtraction of the polished carbon line (Figure 27a) are shown in Figure 37. The very highly oxidized KMnO₄ surface (O/C = 0.387, Table 4) as reflected in the carbon line provides a comparison for the carbon lines obtained from the reduced surfaces shown in spectra 36b and 36c. Since the spectra shown in these two figures are from samples reduced off line, the possibility and/or extent of surface oxidation after removal of the samples from the Vitride (during sample washing and mounting for XPS analysis) is an experimental uncertainty which must be considered in any interpretation of the data.

Spectra (b) and (c) of Figures 36 and 37 illustrate the effect of the reaction conditions on the very highly oxidized GC surface. After reduction in Vitride for one hour at 50°C, the carbon surface shows a marked decrease in carbon-oxygen species compared to the unreduced surface (spectrum a). The difference spectra indicate the sample treated for two hours at 80°C is more reduced than the sample reduced for one hour at 50°C. The spectra also show that the predominant surface species after reduction is surface hydroxyl groups. The extent of surface reduction is reflected in both the spectra and in the O/C ratio values of 0.288 and 0.238 (Table 7) for the one hour and two hour reductions, respectively.

Spectrum (d) in the Figures is from an oxygen plasma sample reduced for one hour at 50°C. The carbon 1s line has a prominent shoulder at +2.5 eV and an absent of a valley at +1.5 eV as is observed for oxygen plasma treated samples (Figure 27d). The difference spectrum also indicates a high level of ketone/quinone functions present which appear to be of approximately equal intensity.
Spektrum (e) is from a carbon monoxide plasma treated sample reduced for 6 days at room temperature (approximately 20°C). The carbon line indicates this sample is more highly reduced than the other samples. The difference spectrum (note scale change) reflects the reduced nature of the surface. The O/C ratio for this sample is 0.191 which is only slightly higher than the polished sample value of 0.158.

The last spectrum in the figures is from a water plasma treated GC which was reduced for 4 days at room temperature. The carbon line shape and the large feature at +1.5 eV BE in the corresponding difference spectrum indicate the surface is extensively reduced and it has predominately hydroxyl groups present. The O/C ratio of 0.161 is nearly equal to the polished sample value, but as the spectrum indicates, most of the surface oxide groups are present as hydroxyl groups while the polished sample has multiple surface oxide groups.

The results of surface reduction presented in Figure 36 and Figure 37 indicate the reaction conditions affect the results. The more vigorous reducing conditions used for KMnO4 samples (one hour, 50°C vs two hours, 80°C) clearly indicate the improved surface reduction brought about by the higher temperature and longer reaction times. The oxygen plasma sample may be compared to the KMnO4 sample. The same reducing conditions did not produce identical results. This may be due to the initial degree of surface oxidation and possibly the functional groups initially present on the surface.

Surface oxidation while washing, drying and mounting the samples for XPS analysis may result in some introduction of additional oxygen functions. Any significant oxidation would tend to make the carbon line shapes similar. Since the C1s line shapes show significant differences as reflected in the figures, surface re-oxidation following Vitride reduction is not a significant problem.

Estimation of Surface Functional Groups After Vitride Reduction

Figures 38 thru 40 illustrate the results of the curve fitting procedure on the reduced samples shown in Figure 16. Table 7 summarizes the results of the curve fitting in tabular form.
Figure 38 shows the results for the KMnO₄ samples reduced by Vitride. The relative amounts of hydroxyl, ketone/quinone and carboxyl groups are approximately the same for both surfaces shown even though the two samples have differing degrees of oxidation. This is also reflected in the curve fitting data in Table 7. Both surfaces have approximately the same C-0/C=0 (2.9 vs 2.9) and O/C (0.288 vs 0.238) ratios indicate the surface treated for two hours at 80°C is more reduced than the surface treated at the more mild reducing conditions.

The curve fitting results for the reduced surfaces which had been plasma treated with O₂ (spectrum a) and CO (spectrum b) gases are shown in Figure 39. The oxygen treated sample was reduced for one hour at 50°C. The hydroxyl vs ketone/quinone like features in the spectrum are more nearly equal than observed for the reduced KMnO₄ treated samples (Figure 38). The C-0/C=0 and C-0/O-C=0 ratios of 1.3 and 3.7 confirm the surface has relatively fewer hydroxyl like groups than the reduced KMnO₄ treated sample. The Cox/C-C and O/C ratios of 0.52 and 0.23 also indicate the more highly reduced nature of this sample.

Figure 39b shows the results of a CO treated sample after reduction for 6 days at room temperature. Both the spectrum and the data of Table 7 indicate this surface is the most reduced of the samples investigated. The C-0/C=0 and C-0/O-C=0 ratios of 3.1 and 8.8 indicate that the surface hydroxyl groups are the predominant carbon-oxygen surface species. The surface is, however, more reduced (relative to the reduced surfaces discussed above) as is indicated by the observed Cox/C-C and O/C ratios of 0.31 and 0.161.

The curve fitting results for water plasma treated surface (shown in Figure 36f) reduced for four days at room temperature is shown in Figure 40b. A curve fitted spectrum obtained from a cast film of polyvinyl alcohol (Chapter 4) is also shown for comparison. The major surface species is the hydroxyl group. The high C-0/C=0 and C-0/O-C=0 ratios of 4.2 and 8.4 indicate that other more highly oxidized functional groups are still present. The close match of the polyvinyl alcohol spectrum confirms the primary surface functional group is the hydroxyl like species.
The differing degrees of surface reduction of GC subjected to RFP or KMnO₄ solution, followed by reduction by Vitride is evident from Figures 36 thru 39 and the data in Table 7. Although no attempt was made to optimize the reducing conditions, the different degrees of surface oxidation observed indicates the ability to tailor the degree of surface oxidation by combing oxidative treatment followed by Vitride reduction. This ability to tailor the surface chemistry of GC was accomplished despite exposure of the chemically reduced sample surface to the atmosphere while washing, drying and mounting the samples for XPS analysis.

CONCLUSIONS

The results of the experiments involving oxygen source gas RFP treatments in the sample introduction system show that the resulting surface chemistry of the GC is dependent on the source gas.

SEM examination of protected (masked) and plasma etched portions of the GC illustrates the etching of the sample by the plasma. The Tokai GC samples exhibited a wide diversity of surface pits and pores after plasma etching. Oxygen is the most effective etchant of the oxygen source gases. C-0, CO₂, and H₂ gases being more mild in their ability to remove the surface to expose the subsurface carbon. The observations on the number and size of surface pits exposed by the etching parallels the heat treatments given the various GC samples and the physical data for density and porosity.

The highest level of surface ketone/quinone functional groups result from the dry O₂ source gas. These samples also exhibit the highest surface oxygen content. The USP O₂ treated sample is shown to have higher XPS signal levels corresponding to surface hydroxyl groups. The increased level of hydroxyl groups is attributed to the trace water levels in the gas. The water vapor RFP results in the highest surface coverage of hydroxyl groups but this source gas does not preferentially introduce significantly higher concentrations of hydroxyl groups at the expense of ketone/quinone and carboxyl groups.
The similarity of the dry O$_2$ and CO plasma results is probably due to similar plasma atmospheres as a steady state gaseous composition forms composed of the source gas and volatilized carbon - oxygen species.

The surface reactivity of the O$_2$ and CO treated samples upon exposure to water vapor is confirmed. These surface reactivity results could not be obtained without the ability to maintain sample integrity in the introduction system attached to the spectrometer. The loss of oxygen from the GC following H$_2$O(v) exposure and the similarity of the spectra to the H$_2$O plasma treated carbons, indicates these surfaces are nearly equivalent.

Surface reductions with Vitride are easily carried out off-line. The C$_{1s}$ line shapes observed following reduction for the various treatments and reduction times explored indicate surface oxidation following the reduction is not severe. The degree of surface reduction appears to be dependent on both the initial degree of surface oxidation as well as the reduction conditions employed.
Table 3

PHYSICAL PROPERTIES OF GLASSY CARBON

Physical properties compiled from the various manufacturer's literature.

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<tr>
<th>GRADE</th>
<th>GC-10a</th>
<th>GC-20a</th>
<th>GC-30a</th>
<th>SIG Ka</th>
<th>SIGGb</th>
<th>V-19c</th>
<th>GRAPHITE</th>
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<td>Heat Proof Limit (°C)</td>
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<td>3000</td>
<td>1000</td>
<td>1900</td>
<td>3000</td>
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<td>Apparent Density (g/cm²)</td>
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<td>1.5-1.8d</td>
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<td>-----</td>
<td>-----</td>
<td>120-125</td>
<td>30-60</td>
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<td>Gas Permeability (cm²/sec)</td>
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<td>10-10-10-12</td>
<td>10-7-10-9</td>
<td>10-11</td>
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<td>ca. 0.1</td>
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a. Tokai glassy carbon  b. Sigri glassy carbon  c. Atomergic glassy carbon (extrapolated from manufacturers' data for samples with heat proof limits of 1000°C and 2500°C)  d. Maximum theoretical density of graphite = 2.25 g/cm³
Table 4

XPS DATA FOR GLASSY CARBON

Line positions, peak full width at half maximum (FWHM) values, oxygen/Carbon (O/C) ratios and oxygen/carbon ratio increase relative to the polished sample resulting from the various RFP treatments. All values are given in electron volts (eV). The full widths at half maximum peak height for the photoelectron lines are listed in brackets. The calculated standard deviation (1σ) is listed in parenthesis.

<table>
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<tr>
<th>Signal</th>
<th>C₁s [FWHM]</th>
<th>O₁s [FWHM]</th>
<th>O/C ratio*</th>
<th>O/C increase</th>
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<td>None</td>
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<td>532.3 [2.6]a</td>
<td>0.158b</td>
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<td>(0.2)(0.2)</td>
<td>(0.026)</td>
<td>(---)</td>
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<td>(0.2)(0.2)</td>
<td>(0.038)</td>
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<td>O₂ Plasma 2. H₂O(v)</td>
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<td>(0.039)</td>
<td></td>
</tr>
<tr>
<td>CO₂ Plasma 1. CO Plasma 2. H₂O(v)</td>
<td>284.2 [1.4]</td>
<td>532.1 [2.9]</td>
<td>0.243</td>
<td>1.54</td>
</tr>
<tr>
<td>KMnO₄</td>
<td>284.3 [3.87]</td>
<td>532.1 [3.1]</td>
<td>0.387</td>
<td>2.45</td>
</tr>
<tr>
<td>Argon Sputter</td>
<td>284.3 [1.8]d</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Argon sputter + O₂ exposure</td>
<td>284.3 [1.9]</td>
<td>532.1 [2.9]</td>
<td>0.054</td>
<td></td>
</tr>
<tr>
<td>Argon sputter + H₂O(v) exposure</td>
<td>284.3 [1.8]</td>
<td>532.1 [2.2]</td>
<td>0.024</td>
<td></td>
</tr>
</tbody>
</table>

* Corrected for atomic sensitivities (see ref. 22).

σ values based on: a. 14 samples, b. 12 samples, c. 7 samples, d. 8 samples, e. 3 samples, f. 2 samples
Table 5
XPS DATA FOR RFP TREATED GLASSY CARBON EXPOSED TO WATER VAPOR

Line positions*, full width at half maximum (FWHM) values*, O/C ratios and O/C ratio % differences resulting from RFP treatment followed by exposure to water vapor.

<table>
<thead>
<tr>
<th>Signal</th>
<th>C1s</th>
<th>FWHM</th>
<th>O1s</th>
<th>FWHM</th>
<th>O/C Ratio</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 plasma</td>
<td>284.3</td>
<td>1.6</td>
<td>532.4</td>
<td>2.8</td>
<td>0.358</td>
<td>32</td>
</tr>
<tr>
<td>O2 plasma + H2O(v)</td>
<td>284.2</td>
<td>1.8</td>
<td>532.2</td>
<td>3.4</td>
<td>0.242</td>
<td></td>
</tr>
<tr>
<td>Dry O2 plasma</td>
<td>284.2</td>
<td>1.5</td>
<td>532.4</td>
<td>2.7</td>
<td>0.324</td>
<td></td>
</tr>
<tr>
<td>Dry O2 plasma + H2O(v)</td>
<td>284.2</td>
<td>1.6</td>
<td>532.2</td>
<td>3.1</td>
<td>0.242</td>
<td></td>
</tr>
<tr>
<td>CO plasma</td>
<td>284.2</td>
<td>1.4</td>
<td>532.3</td>
<td>2.8</td>
<td>0.303</td>
<td>20</td>
</tr>
<tr>
<td>CO plasma + H2O(v)</td>
<td>284.2</td>
<td>1.4</td>
<td>532.1</td>
<td>2.9</td>
<td>0.243</td>
<td></td>
</tr>
</tbody>
</table>

* All line positions and FWHM values are in eV.
TABLE 6

ESTIMATION OF SURFACE FUNCTIONAL GROUPS ON RFP TREATED GLASSY CARBON.

Binding energy, estimation of the relative amounts of carbon – oxygen species on the glassy carbon surface, and ratios of the various components resulting from two minute plasma treatments and plasma treatment followed by exposure to water vapor. Data from spectra in Figures 33, 34 and 35.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
<th>OTHER</th>
<th>Cox./C-C</th>
<th>C-O/C=O</th>
<th>C-O/O-C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>POLISHED</td>
<td>284.1</td>
<td>285.5</td>
<td>286.7</td>
<td>288.1</td>
<td>----</td>
<td>0.25</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>79.8%</td>
<td>13.4%</td>
<td>3.9%</td>
<td>2.9%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>284.2</td>
<td>285.6</td>
<td>286.8</td>
<td>288.2</td>
<td>289.2</td>
<td>0.32</td>
<td>1.6</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>75.7%</td>
<td>10.9%</td>
<td>6.6%</td>
<td>4.2%</td>
<td>2.7%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂(99.6%)</td>
<td>284.1</td>
<td>285.5</td>
<td>286.7</td>
<td>288.1</td>
<td>----</td>
<td>0.71</td>
<td>0.71</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>65.2%</td>
<td>12.0%</td>
<td>16.9%</td>
<td>5.8%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂(99.6%)</td>
<td>284.2</td>
<td>285.6</td>
<td>286.8</td>
<td>288.2</td>
<td>----</td>
<td>0.33</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>+H₂O(v)</td>
<td>75.4%</td>
<td>11.4%</td>
<td>8.5%</td>
<td>4.6%</td>
<td></td>
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<tr>
<td>CO</td>
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<td>285.6</td>
<td>286.7</td>
<td>288.1</td>
<td>289.2</td>
<td>0.36</td>
<td>0.61</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>73.6%</td>
<td>7.3%</td>
<td>12.0%</td>
<td>4.5%</td>
<td>2.6%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO+H₂O(v)</td>
<td>284.1</td>
<td>285.5</td>
<td>286.6</td>
<td>288.1</td>
<td>----</td>
<td>0.27</td>
<td>1.2</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>78.5%</td>
<td>9.8%</td>
<td>7.8%</td>
<td>3.8%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fit parameters: FWHM = 1.4 eV; 75% Gaussian peak shape.

Binding energy shift positions for carbon – oxygen species corresponding to hydroxyl/phenol, ketone/quinone, and carboxyl functional groups used for the curve fitting are +1.4, 2.6, and 4.0 eV respectively. The component at +5.0 eV used in some fits may be due to asymmetric tailing of the component peaks.

The reduced Chi square difference (Chi square difference/simulation area) for all fits is less than 0.00007.

Cox/C-C is the ratio derived from the sum of the oxidized species relative to the unoxidized bulk carbon signal.
Table 7

Estimation of surface functional groups on RFP treated glassy carbon following reduction with Vitride.

Binding energy, estimation of the relative amounts of carbon-oxygen species, and ratios of the various components on the glassy carbon surface resulting from oxidative treatments followed by Vitride reduction. Data from Figures 38, 39, and 40.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>C-C</th>
<th>C-O</th>
<th>C=O</th>
<th>O-C=O</th>
<th>OTHER</th>
<th>COx./C-C ratio</th>
<th>C-O/C=O ratio</th>
<th>C-O/O-C=O ratio</th>
<th>O/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>% COMPONENT</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KMnO₄</td>
<td>284.4</td>
<td>285.7</td>
<td>286.9</td>
<td>288.4</td>
<td>289.4</td>
<td>0.71</td>
<td>2.9</td>
<td>5.2</td>
<td>0.288</td>
</tr>
<tr>
<td>Vitride 1hr., 50°C</td>
<td>58.5</td>
<td>25.0</td>
<td>8.7</td>
<td>4.0</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KMnO₄</td>
<td>284.4</td>
<td>285.8</td>
<td>286.9</td>
<td>288.4</td>
<td>----</td>
<td>0.46</td>
<td>2.9</td>
<td>5.5</td>
<td>0.238</td>
</tr>
<tr>
<td>Vitride 2hr., 80°C</td>
<td>68.5</td>
<td>20.8</td>
<td>7.0</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂ plasma</td>
<td>284.2</td>
<td>285.6</td>
<td>286.8</td>
<td>287.3</td>
<td>289.6</td>
<td>0.52</td>
<td>1.3</td>
<td>3.7</td>
<td>0.229</td>
</tr>
<tr>
<td>Vitride 1hr., 50°C</td>
<td>65.9</td>
<td>15.4</td>
<td>12.0</td>
<td>4.0</td>
<td>2.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO plasma</td>
<td>284.6</td>
<td>286.0</td>
<td>287.1</td>
<td>288.6</td>
<td>----</td>
<td>0.31</td>
<td>3.1</td>
<td>8.8</td>
<td>0.191</td>
</tr>
<tr>
<td>Vitride (room temp. 6 days)</td>
<td>76.1</td>
<td>16.7</td>
<td>5.4</td>
<td>1.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O plasma</td>
<td>285.2</td>
<td>286.6</td>
<td>287.8</td>
<td>289.2</td>
<td>290.6</td>
<td>0.91</td>
<td>4.2</td>
<td>8.4</td>
<td>0.161</td>
</tr>
<tr>
<td>Vitride (room temp., 4 days)</td>
<td>52.4</td>
<td>33.5</td>
<td>8.0</td>
<td>4.0</td>
<td>3.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 21. Scanning Electron Micrographs of Oxygen RFP Treated Tokai Glassy Carbons.

Scanning electron micrograph (500x magnification, bar equals 20μm) of polished Tokai glassy carbon GC-10 (a), GC-20 (b), and GC-30 (c) samples which have been treated with a three minute oxygen RFP. One side of each sample was masked to protect the surface during plasma treatment (shown in the upper portions of (a) and (b) and the right portion of (c)). A higher magnification (5000x magnification, bar equals 2 μm) of a typical pit in the GC-30 surface is shown in (d). Plasma conditions: O₂ pressure = 150 ±50 mtorr; RF power 35 W.
Figure 22. Scanning Electron Micrographs of Oxygen RFP Treated Sigri and Atomergic Glassy Carbons.

Scanning electron micrographs (500x magnification, bar equals 20 μm) of polished Sigri Sig K (a), Sig G (b), and Atomergic V-19 (c) samples which were exposed to a three minute oxygen RFP. The right side of each sample was masked to protect the surface during plasma treatment (shown in the upper portions of (a) and (c)). Plasma condition were the same as Figure 21.
Figure 23. Scanning Electron Micrographs of Unpolished Tokai Glassy Carbons treated with Oxygen RFP.

Scanning electron micrographs (500x magnification, bar equals 20 μm) of unpolished Tokai glassy carbon GC-10 (a), GC-20 (b), and GC-30 (c) samples which were exposed to oxygen RFP under the conditions of Figure 21.
Figure 24. Scanning Electron Micrographs of Water Vapor RFP treated Tokai Glassy Carbons.

Scanning electron micrographs (500x magnification, bar equals 20 μm) of polished Tokai glassy carbon GC-10 (a), GC-20 (b), and GC-30 (c) samples which were exposed to water vapor RFP under the conditions of Figure 21. The upper portions of the micrographs show the protected portion of the surface.
Figure 25. XPS Spectra From Oxygen RFP Treated Tokai Glassy Carbon

Low resolution survey XPS spectra from: (a) polished Tokai GC-10; (b) GC-10, 2 minute water vapor RFP; and (c) GC-10, 2 minute oxygen RFP. Plasma conditions as in Figure 21.
Figure 26. XPS Spectra From Carbon Dioxide and Carbon Monoxide RFP Treated and KMnO₄ Oxidized Glassy Carbon.

Low resolution survey XPS spectra from: (a) polished glassy carbon treated with carbon dioxide RFP, (b) polished glassy carbon treated with carbon monoxide RFP under the conditions of Figure 21. (c) A polished glassy carbon sample oxidized with KMnO₄ solution. The spectrum indicates that surface contaminants (Mn and N) remain on the surface after the washing procedure.
Figure 27. High Resolution Carbon (C₁₅) XPS Spectra From Glassy Carbons Treated with Oxygen Source Gas Plasma.

High Resolution Carbon (C₁₅) XPS Spectra From Glassy Carbons Treated With Oxygen Source Gas Plasma. High resolution carbon (C₁₅) spectra following smoothing and base line subtraction for various plasma treatments. The treatments include: (a) polishing only, (b) H₂O (doubly distilled, degassed) RFP, (c) O₂ (Liquid carbonic grade, USP) RFP, (d) O₂ (Linde, 99.6%) RFP, (e) CO (Linde, 99.0%) RFP, and (f) CO₂ (Linde, 99.8%) RFP. All spectra are scaled to the same arbitrary intensity for comparison. The vertical lines drawn in correspond to the binding energies associated with C-O (+1.5 eV), C=O (2.5 eV) and O-C=O (+4.0 eV) type functions found for homopolymer functionalities. (Chapter 4)
Figure 28. Carbon (C\textsubscript{1s}) Difference Spectra For Oxygen Source Gas RFP Treated Glassy Carbons.

High resolution difference spectra of the C\textsubscript{1s} lines shown in Figure 27 after subtracting the polished sample spectrum. The difference spectra emphasize the increased oxidation which occurs as a result of the plasma treatment. The differences resulting from the subtraction of the polished spectrum from: (a) itself (note scale), (b) H\textsubscript{2} RFP, (c) O\textsubscript{2} (USP grade) RFP, (d) O\textsubscript{2} (99.6%) RFP, (e) CO (99.0%) RFP, and (f) CO\textsubscript{2} (99.8%) RFP.
Figure 29. High Resolution Carbon (C₁s) XPS Spectra From Glassy Carbons Treated with Oxygen Source Gas Plasma Followed by Exposure to Water Vapor.

High resolution Carbon (C₁s) spectra illustrating the surface chemical changes to the RFP treated glassy carbon surface resulting from approximately 90 minute exposure to water vapor. The treatments were: (a) O₂ (USP) RFP, (b) as in (a) followed by H₂O(v), (c) O₂ (99.6%) RFP, (d) as in (c) followed by H₂O(v), (e) CO (99.0%) RFP, (f) as in (e) followed by H₂O(v). Table 5 lists the line positions, FWHM values, measured O/C ratios and the % differences for the treated surfaces before and after water vapor exposure. All spectra have been smoothed, background removed and scaled to equal intensity for comparison.
Figure 30. High Resolution Oxygen (O\textsubscript{1s}) XPS Spectra From Glassy Carbons Treated with Oxygen Source Gas Plasma Followed by Exposure to Water Vapor.

High resolution Oxygen (O\textsubscript{1s} spectra illustrating the surface chemical changes to the RFP treated glassy carbon surfaces. Each oxygen spectrum corresponds to the same treatment as in Figure 29. See also Table 5 for the measured line position and FWHM values.
Carbon (C\textsubscript{1s}) difference spectra emphasizing the surface changes resulting from RFP treatment followed by water vapor exposure. Each difference spectrum was generated by subtracting the spectra of Figure 29. Difference spectrum (g) is from a O\textsubscript{2} RFP sample recorded within 35 minutes of x-ray turn on and after 2.5 hours of x-ray exposure. The difference spectrum indicates there is no significant x-ray induced decomposition and that the changes observed in the difference spectra are the result of the water vapor exposure. The time required to obtain the C\textsubscript{1s} signals shown in Figure 29 was approximately 30 minutes.
Figure 32. XPS Spectra Obtained From Argon Ion Sputter Cleaned Glassy Carbons Exposed to Water Vapor and Air.

Low resolution survey XPS spectra obtained from Argon ion sputter cleaned glassy carbon surface (a), the cleaned surface followed by water vapor exposure (b) and the cleaned surface followed by exposure to air (c). The polished surface spectrum (d) is added for comparison.
Figure 33. Estimation of the Surface Functional Groups on Polished and Water Vapor Plasma Treated Glassy Carbon.

(a) A spectrum corresponding to Figure 27a (polished glassy carbon) deconvoluted into component 1 (79.8%) BE = 284.1 eV, component 2 (13.4%) BE = 285.5 eV, component 3 (3.9%) BE = 286.7 eV, and component 4 (2.9%) BE = 288.1 eV. (b) A spectrum corresponding to Figure 27b (H2O RFP) deconvoluted into component 1 (75.7%) BE = 284.2 eV, component 2 (10.9%) BE = 285.6 eV, component 3 (6.6%) BE = 286.8 eV, component 4 (4.2%) BE = 288.2 eV, and component 5 (2.7%) 289.2 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvoluted components is shown with the small circles. Table 6 summarized the deconvolution data for spectra corresponding to spectra in Figure 27a and Figure 29 and presented in Figures 33, 34 and 35. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
Figure 34. Estimation of the Surface Functional Groups on Oxygen Plasma Treated Glassy Carbon Before and After Exposure to Water Vapor.

(a) A spectrum corresponding to Figure 29c (O₂, 99.6% RFP) deconvoluted into component 1 (65.2%) BE = 284.1 eV, component 2 (12.0%) BE = 285.5 eV, component 3 (16.9%) BE = 286.7 eV, and component 4 (5.8%) BE = 288.1 eV. (b) A spectrum corresponding to Figure 29d (as in (a) + H₂O(v)) deconvoluted into component 1 (75.4%) BE = 284.2 eV, component 2 (11.4%) BE = 285.6 eV, component 3 (8.5%) BE = 286.8 eV, and component 4 (4.6%) BE = 288.2 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvolution components is shown with the small circles. Table 6 summarized the deconvolution data for spectra corresponding to spectra in Figure 27a and Figure 29 and presented in Figures 33, 34 and 35. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
Figure 35. Estimation of the Surface Functional Groups on Carbon Monoxide Plasma Treated Glassy Carbon Before and After Exposure to Water Vapor.

(a) A spectrum corresponding to Figure 29e (CO, 99.0% RFP) deconvoluted into component 1 (73.6%) BE = 284.2 eV, component 2 (7.3%) BE = 285.6 eV, component 3 (12.0%) BE = 286.7 eV, component 4 (4.5%) BE = 288.1 eV, and component 5 (2.6%) BE = 289.2 eV. (b) A spectrum corresponding to Figure 29f (as in (a) + H₂O (v)) deconvoluted into component 1 (78.5%) BE = 284.1 eV, component 2 (9.8%) BE = 285.5 eV, component 3 (7.8%) BE = 286.6 eV, and component 4 (3.8%) BE = 288.1 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvolution components is shown with the small circles. Table 6 summarized the deconvolution data for spectra corresponding to spectra in Figure 27a and Figure 29 and presented in Figures 33, 34 and 35. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
Figure 36. High Resolution Carbon (C₁s) XPS Spectra of Oxidized Glassy Carbons Reduced with Vitride.

High resolution C₁s spectra following smoothing and baseline subtraction for glassy carbon oxidized with KMnO₄ and various plasma treatments. The treatments include: (a) KMnO₄ oxidation, (b) as in (a) + Vitride reduction, 50°C, 1 hour, (c) as in (a) + Vitride reduction, 80°C, 2 hours, (d) O₂ (99.6%) RFP + Vitride reduction 50°C, 1 hour, (e) CO (99.0% RFP + Vitride reduction, room temperature, 6 days, (f) H₂ RFP + Vitride reduction, room temperature, 4 days.

The measured peak maximum and FWHM values are: (a) 285.2 eV, 2.65 eV FWHM, (b) 285.4 eV, 2.2 eV FWHM, (c) 284.2 eV, 2.2 eV FWHM, (d) 285.3 eV, 1.8 eV FWHM, (e) 285.4 eV, 1.5 eV FWHM, (f) 285.3, 3.1 eV FWHM.
Figure 37. Carbon (C$_{1s}$) Difference Spectra From Vitride Reduced Glassy Carbons.

Difference spectra obtained by subtracting the C$_{1s}$ spectrum for polished glassy carbon from the various spectra in Figure 36. The difference spectra emphasize the surface chemical changes brought about by the oxidative treatments followed by reduction with the commercially available Vitride reducing agent. The treatments are as in Figure 36.
Figure 38. Estimation of Surface Functional Groups on Glassy carbon Oxidized by KMnO₄ Followed by Vitride Reduction.

(a) A spectrum corresponding to Figure 36b deconvoluted into component 1 (58.5%) BE = 284.4 eV, component 2 (25.0%) BE = 285.7 eV, component 3 (8.7%) BE = 286.9 eV, component 4 (4.0%) BE = 288.4 eV, and component 5 (1.4%) BE = 289.4 eV. (b) A spectrum corresponding to Figure 36c deconvoluted into component 1 (68.5%) BE = 284.4 eV, component 2 (20.8%) BE = 285.8 eV, component 3 (7.0%) BE = 286.9 eV, and component 4 (3.8%) BE = 288.4 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvolution components is shown with the small circles. Table 7 summarized the deconvolution data for spectra corresponding to spectra in Figure 36 and presented in Figures 38, 39 and 40. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
Figure 39. Estimation of Surface Functional Groups on Glassy Carbons Oxidized by Oxygen and Carbon Monoxide Plasma Followed by Reduction of Vitride.

(a) A spectrum corresponding to Figure 36d deconvoluted into component 1 (65.9%) BE = 284.2 eV, component 2 (15.4%) BE = 285.6 eV, component 3 (12.0%) BE = 286.8 eV, component 4 (4.0%) BE = 287.3 eV, and component 5 (2.4%) BE = 289.6 eV. (b) a spectrum corresponding to Figure 36e deconvoluted into component 1 (76.1%) BE = 284.6 eV, component 2 (16.7%) BE = 286.0 eV, component 3 (5.4%) BE = 287.1 eV, and component 4 (1.9%) BE = 288.6 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvolution components is shown with the small circles. Table 7 summarized the deconvolution data for spectra corresponding to spectra in Figure 36 and presented in Figures 38, 39 and 40. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
Figure 40. Estimation of Surface Functional Groups on Water Vapor Plasma Treated Glassy Carbon Reduced with Vitride.

(a) A spectrum of the C_{1s} line from polyvinyl alcohol (Chapter 4) deconvoluted into component 1 (67.1%) BE = 285.0 eV (corrected for charge shifting) and component 2 (32.9%) at BE = 286.4 eV. (b) A spectrum corresponding to Figure 36f deconvoluted into component 1 (52.4%) BE = 285.2 eV, component 2 (33.5%) BE = 286.6 eV, component 3 (8.0%) BE = 287.8 eV, component 4 (4.0%) BE = 289.2 eV, and component 5 (3.4%) BE = 290.6 eV. The smoothed background removed spectrum is in solid line. The sum of the deconvolution components is shown with the small circles. Table 7 summarized the deconvolution data for spectra corresponding to spectra in Figure 36 and presented in Figures 38, 39 and 40. All components have fit parameters of 1.4 eV FWHM and 75% Gaussian, 25% Lorentzian character.
CHAPTER 6

NITROGEN AND CHLORINE PLASMA TREATMENT ON GLASSY CARBON

Introduction

The introduction of increased numbers of surface carbon – oxygen species by RFP proves to be easily carried out in a rapid contaminant free manner. Extension of the RFP method using source gases which do not contain oxygen provides a potentially useful route for incorporating synthetically useful non-oxygen surface functional groups onto GC. The RFP approach to surface modification may also provide unique synthetic routes for the formation of surface functional groups which are not possible by conventional means.

Previous experiments in our laboratory using ammonia (NH₃) RFP indicate nitrogen containing functional groups (amines, imines and amides) are easily introduced to pyrolytic and highly ordered pyrolytic graphite [1]. Bromination of the graphitic surfaces with hydrogen bromide (HBr) proved to be ineffective since XPS only detected trace levels of bromine. Introduction of high concentrations of synthetically useful nitrogen functional group is attractive for the utilization of amine chemistry for further surface modification. The introduction of a halogen to the carbon surface may be the requisite precursor for utilizing organometallic intermediates such as Grignard or organolithium compounds for the attachment of a surface modifying reagent via covalent carbon – carbon bond formation. Linking a surface modifier via a covalent carbon – carbon bond should provide a very stable surface linkage.

This chapter summarizes the results of exploratory plasma experiments for modification of the GC surface using a series of nitrogen and chlorine containing gases. The nitrogen series included Nitrogen (N₂), Ammonia (NH₃), Hydrazine (N₂H₄), and Ethylene Diamine (en = (CH₂NH₂)₂). A second series containing chlorine (Cl₂)
and Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) was used as possible surface chlorinating reagents.

Surface derivatization with trifluoroacetic anhydride (TFAA) was performed on the nitrogen modified surfaces to access the chemical nature of the nitrogen introduced to the GC via the RFP treatments.

**EXPERIMENTAL**

**Sample Preparation**

Samples were prepared for treatment by the polishing, washing, and mounting procedures described previously in Chapter 5. Gases used in the generation of the RFP were the following grades: Nitrogen (Matheson Prepurified grade), ammonia (Linde Anhydrous grade), chlorine (Linde, 99.5%). The liquids used as source gases, hydrazine, ethylenediamine, and dichloromethane (J. T. Baker Chemical Co, Reagent Grade). The liquids were degassed by placing a few ml of the liquid in the liquid cell (Chapter 3). Attaching the cell to the plasma system gas inlet, freezing the liquid with liquid nitrogen, and allowing the liquids to melt while pumping on the vessel for several minutes prior to generation of the plasma.

All plasma treatments were accomplished at a standard power setting of ca. 35 watts. Tuning of the plasma generator to provide maximum RF power transfer to the plasma gas was achieved by the LC impedance matching network and monitored with the Standing Wave Ratio/RF Power Meter. During the plasma treatments the sample was observed to be completely enveloped in the plasma glow. Plasma exposure times ranged from 1 to 5 minutes. After plasma termination the samples were withdrawn into the introduction system and pumped down as described in Chapter 5. Data acquisition using the analog and computer controlled collection of survey and high resolution narrow scans was previously described in Chapter 2.

**Surface Derivatization**

Samples treated with the nitrogen RFP series gases were removed from the introduction side arm, demounted, placed in sample vials and covered with a solution of 0.05 M triethyl amine in benzene. Approximately 0.5 ml of TFAA (Aldrich, Gold Label, 98+) was quickly added to the solution, the vials were capped, agitated
and warmed slightly, and allowed to stand for approximately one hour. The reaction was quenched by placing the samples in a 1:1 methanol–water solution (v/v), followed by washing, drying, and mounting as described previously. The samples were reintroduced to the sample side arm for transfer the the ESCA spectrometer as rapidly as possible.

RESULTS AND DISCUSSION

Nitrogen Source Gas Plasma Treatment

The results of the RFP with the nitrogen containing series of gases indicates the ease with which this method can rapidly change the surface chemistry of GC. The XPS survey scans of GC after the various nitrogen plasma treatments are presented in Figure 41.

The top spectrum (a) is from the N\textsubscript{2} RFP sample. Only carbon, nitrogen, and oxygen are detected on the surface. The incorporation of nitrogen into the GC is obvious. The presence of a significant O\textsubscript{1s} signal following RFP treatment indicates that the N\textsubscript{2} RFP is ineffective in removing oxygen from the surface while at the same time incorporating nitrogen onto the GC surface. The second spectrum (b) is from the NH\textsubscript{3} RFP treatment. This spectrum is similar to (a) except the N\textsubscript{1s} signal is increased and the O\textsubscript{1s} signal is less intense following treatment. The results of the N\textsubscript{2}H\textsubscript{4} treatment shown in the third spectrum (c) is qualitatively similar to that of the NH\textsubscript{3} treatment. The last spectrum (d) is from the en treatment. This spectrum has the lowest oxygen signal intensity for all the treatments in the series.

The presence of the oxygen signal in the spectra indicates that under the plasma conditions used, the RFP method of surface modification does not completely remove surface oxygen. N\textsubscript{2} is the least effective while en is the most effective in reducing the surface oxygen. Periodically turning off the plasma generator, while still pumping, during the treatment further reduces the surface oxygen indicating that at least some of the observed surface oxygen results from recombining of volatilized oxygen with the GC before it can be pumped away. The resident time of the volatilized oxygen species in the plasma reactor is longer than its reaction time. These results are
unattainable without the use of the reaction chamber attached to the introduction system.

The oxygen signal observed for the nitrogen source gas plasmas have all decreased from the polished value (0.158 ±0.026, Table 4). The previous work on graphitic samples [1] showed an increase in surface oxygen following RFP. This increase was attributed to exposure of the reactive surface to air and water vapor upon transfer of the sample to the XPS chamber. As can be seen in Table 8, all the samples show increases in the measured O/C ratios after air exposure in the introduction chamber. Unlike the previous investigations, the final oxygen content is significantly less than the polished surface value. The differences observed in this investigation can be attributed to the plasma chamber design and the improved sample handling.

The effect of aging on the freshly plasma treated surface prior to air exposure is not known. Following the RFP treatment, each sample was transferred for XPS data acquisition. The time delay and surface exposure to both x-rays and the electron flux generated by the x-ray gun nozzle and aluminum window may alter the surface reactivity to oxygen and water vapor when exposed to air. The direct comparison of the treatments described here to the samples prepared in an off line plasma reactor may not be valid since the samples were exposed to oxygen and water vapor within several minutes of treatment.

The relative concentrations of nitrogen to carbon (N/C ratios) for the sample surfaces show slight decreases after air exposure (Table 41). The exception is the en treated sample which shows no decrease. The decrease in the nitrogen content of the samples may be due to reaction of the nitrogen species with oxygen or water vapor to form volatile species which desorb from the surface.

Following the en treatments, a brown discoloration was observed on the plasma chamber walls. The presence of this material indicates that under the conditions employed, the en RFP forms a plasma polymerization product on the glass surface of the chamber. The formation of a polymer in the plasma suggests the nitrogen incorporation observed on the GC is in actuality a "thin" deposit of an en polymer
product over the GC rather than a direct change in the GC surface. The apparent reduction of surface oxygen resulting from the en RFP may, therefore, be due more to attenuation of the O$_{1s}$ signal by the overlying polymer. The en polymer formed in the plasma proved to be very well adhered to the chamber walls. Oxygen plasma failed to completely remove the polymer from the walls. After each en plasma, the plasma chamber had to be physically scrubbed to remove the polymer to prevent contamination of the surfaces of GC in subsequent plasma treatments. The degree to which oxygen is incorporated into the polymer product or the extent to which nitrogen is actually incorporated into the GC surface is not known.

The nitrogen plasmas will contain a host of free radical species (ex. N*, H*, NH*, NH$_2$*, RN* + others) [2,3]. Additional excited states of molecular species can also be expected to be resident in the plasma[4,5]. Radicals and excited state molecules should be very reactive and readily react with the GC. Additionally, as the source molecule becomes more complex (nitrogen through en) the make up of the plasma atmosphere can be expected to become more complex. The complexity of the en molecule allows the production of "monomeric" like species which enter gas phase polymerization reactions to form even more complex species. The deposition of the polymer product is obviously taking place at a faster rate than any ablation mechanism [16].

The nature of the nitrogen species observed attached to the GC following RFP may be inferred from the observed nitrogen line positions and changes to the carbon line shapes. Figures 42 and 43 show the high resolution C$_{1s}$ and N$_{1s}$ spectra corresponding to the spectra in Figure 41. Table 8 lists the peak positions, peak FWHM values and measured atomic ratios for the spectra in Figures 41 and 42. Data for the oxygen lines from the spectra (not shown) are provided in the table. The changes to the RFP treated surface after exposure to air are also listed. Figure 44 presents the difference spectra after subtracting the carbon line corresponding the the polished surface (Chapter 5, Figure 27a) from each of the carbon lines obtained from the nitrogen source gas plasma modified surfaces.
The \( N_{1s} \) lines are observed at 399.2 – 399.4 eV BE for the first three gases while the en treated surface nitrogen species are observed at a somewhat higher BE of 400.2 eV (Table 8). The higher BE observed for the en RFP nitrogen may be a consequence of surface charging of the en polymer product produced rather than a difference in the nitrogen species formed. It may be an indication of a nitrogen contained in a polymer as opposed to a nitrogen species attached to GC. Binding energies in the 399–400 eV BE range are typical of amine, imine and amide type groups \([6-10]\) and is consistent with the previous observations \([1]\).

The effect of exposing the plasma treated samples to air is also shown in the table. In each case, a slight increase in surface oxygen is reflected in the increase in the measured O/C ratios. The oxygen increase observed is approximately the same as the increase detected after a sputter cleaned surfaces is exposed to water vapor or air. The increase in oxygen upon exposure to air is in contrast to the oxygen loss observed upon exposure of oxygen source gas plasma treated GC to water vapor (Chapter 5).

The measured N/C ratios decrease slightly after air exposure. The exception is the en sample which showed no change. The surface oxygen increase and slight nitrogen decrease indicate, like the oxygen/carbon monoxide RFP samples, that the nitrogen source treated surfaces remain reactive for extended periods of time in the vacuum chamber. The highest O/C ratio, \( N_{2}\)plasma + air, is still significantly less than the polished value 0.158.

The nitrogen species formed on the surface cannot be nitro or nitroso groups since these species show \( N_{1s}\) binding energies in the 402 – 406 eV range \([6-10,14]\). Thus it can be concluded that the surface nitrogen species generated are not oxidized by combining with surface or volatilized oxygen species to form –N–O type bonds on the surface.
The carbon C1s lines show a broadening near the main carbon peak. No extensive higher binding energy species (beyond +2.5 eV above the C-C bond energy) are evident as is observed for the O2 and CO RFP. The difference spectra emphasize the principle changes to the carbon line shape relative to the polished sample. Each surface shows increased intensity in the +2.5 eV region of with the largest increase being exhibited by the en difference. The nitrogen difference spectrum shows no intensity difference in the +1.5 - +1.0 eV higher BE region relative to the polished sample, while the ammonia, hydrazine and en difference spectra show very significant increases indicating more -N-H species are formed. The line broadening observed in the C1s spectra and difference spectra parallel the effectiveness of the RFP treatments in reducing the observed surface oxygen (measured O/C ratios, Table 8). The degree with which the en C1s line shape and difference spectra reflect charge broadening of the polymer film due to irradiation with x-rays during analysis or the variety of surface nitrogen functional groups formed on GC cannot be determined from the spectra and data.

The difference spectra indicate that the presence of hydrogen as a constituent in the source gas leads to increased carbon – nitrogen groups then the N2 RFP.

Surface Derivatization

The degree to which the surface species contain basic nitrogen groups with at least one N-H bond may be evaluated by surface derivatization with trifluoroacetic anhydride (TFAA) to form a surface amide group. TFAA has been shown in analytical applications to react only with nitrogen functional groups such as amines with at least one ionizable hydrogen and a very limited number of oxygen-containing functional groups [11]. Reilly and Everhart [12] have used TFAA to confirm amine functional groups which had been introduced on polyethylene by nitrogen RFP treatment. TFAA extends the sensitivity of XPS by adding three fluorine atoms for each derivitized amine group. The XPS sensitivity to fluorine is 2.63 times greater then nitrogen [10]. Thus a net signal gain of 7.89 (3 x 2.63) toward amines will be realized when using TFAA derivitized surfaces by monitoring the fluorine introduced.
to the GC following the nitrogen source gas plasma treatments.

XPS survey scans showing the results of TFAA reaction with the nitrogen source gas RFP treated glassy carbons are shown in Figure 45. Fluorine is detected on all the GC surfaces following the derivatization reaction. A polished GC sample treated with TFAA as a control shows a trace fluorine (F1s) signal at the limit of quantitation (ca. 3 times root-mean-square base line noise). Since no significant fluorine is detected on the polished surface following the derivatization, the F1s detected on the treated GC must be the result of reaction with the basic nitrogen groups. The spectra all indicate a intense F1s signal indicating significant concentration of amine groups are present on these carbon surfaces.

Comparison of of the measured O/C and N/C ratios in Table 8 and Table 9 indicates increased oxygen and decreased nitrogen following derivatization. Each TFAA molecule adds both carbon and oxygen to the surface as it reacts with surface amine groups. Not all the increases in oxygen and carbon can be unequivocally assigned to the TFAA. The derivatization, carried out off-line, exposes the sample to air, solvent and water during reaction and washing. Possibility surface oxidation cannot be ruled out, and this possibility complicates interpretation of the experimental results.

The presence of the en polymer on the surface following derivatization as indicated by the high N1s and F1s signals is evidence that the polymer formed on the GC surface is very tightly bound as is observed for the polymer deposited on the plasma chamber walls. If it were not strongly attached, decreased levels on nitrogen and fluorine would be expected as the action of the solvents and ultrasonic cleaning procedure remove some of the material.

The peak positions, FWHM values, and calculated elemental ratios (corrected for atomic sensitivities [10]) are summarized in Table 9. The F1s signal observed at 688 - 689 eV binding energy indicates the fluorine is present as an organo-fluorine. Inorganic fluorides appear at lower binding energies, ca. 685 eV,[6,8,10]. Thus the presence of the surface fluorine cannot be the result of decomposition
of the reagent. The F/N ratios listed indicate the N\textsubscript{2} and en RFP are the the least and most effective treatments for introducing amine functional groups to the GC. The NH\textsubscript{3} and N\textsubscript{2}H\textsubscript{4} reagent gases show an intermediate ability to introduce the amines. The degree to which the amines are introduced to the surface parallels the signal levels observed in difference spectra in Figure 44.

The F/N ratios listed in Table 9 indicate that not all the nitrogen species generated in the RFP contain primary or secondary amines. The theoretical F/N ratio is 0.333 if all nitrogen groups have at least one N–H present. The remaining nitrogen functional groups are probably aromatic amines (pyridine or pyrrole-like) or possibly tertiary amines.

All the reagent gases except N\textsubscript{2} contain hydrogen and the reactive species which combines with the surface is expected to contain some intact N–H bond. Nitrogen does not contain measurable hydrogen, thus any N–H surface species formed during this plasma treatment must be from the sample or residual hydrogen in the vacuum system. Never the less, it is evident from the F/N ratios that a significant concentration of amine groups is generated by the plasma.

The development of an online reaction vessel to provide a protective or inert atmosphere during the derivatization and washing procedures should be capable of differentiating between the formation of amine groups directly by the RFP and the possible formation of the amines during offline derivatization.

The high resolution C\textsubscript{1s} and N\textsubscript{1s} lines derived from the samples shown in Figure 45 are shown in Figures 46 and 47 respectively. These line positions and FWHM values are presented in Table 9. The carbon lines all show some increased signal intensity at higher BE. The conversion of amine to amide by the TFAA will add signal intensity at higher BE of about +2.4 eV [13] from the amide carbon which is added to the surface by the reaction with TFAA. The most extensive increases observed for these lines also parallels the degree to which fluorine is incorporated into the sample following derivatization.
Chlorine Source Gas Plasma Treatment

Formation of a surface carbon – bromine bond in an attempt to form a halogenated surfaces was unsuccessful during previous investigations [1]. The exploratory plasma treatment of GC by chlorine source gas plasmas in this investigation have proved at least partially successful. Figure 48 shows the low resolution XPS spectra obtained from treating polished GC with chlorine (Cl$_2$) and Dichloromethane (CH$_2$Cl$_2$) RFP treatments. The peak positions, FWHM values and atomic ratios (corrected for sensitivity) are summarized in Table 10.

The Cl$_2$ treated sample spectrum (a) has prominent chlorine peaks which correspond to the Cl$_{2p}$ and Cl$_{2s}$ signals. Also obvious from the spectrum is that a significant amount of oxygen remains on the surface following the treatment. The measured O/C ratio of 0.14 is only slightly less than the polished value of 0.158 listed in Table 4. Apparently, under the experimental conditions used, the Cl$_2$ RFP treatment is capable of chlorinating the GC without any significant removal of oxygen.

Etching of the surface by the chlorine source gases was not investigated by masking and SEM observation of the surface. The high oxygen content on the sample surface as observed by the O/C ratio, however, suggests the chlorine RFP does not significantly etch the surface. Any extensive surface etching would significantly decrease the oxygen content as the volatilized oxygen is pumped away during the plasma generation as was observed for the nitrogen plasmas.

The presence of the Cl$_{2p}$ at 200.0 eV BE is an indication that the chlorine is attached to carbon since chloride ions appear at somewhat lower BE around 199.0 eV. The chlorine cannot be oxidized because species such as ClO$_3$ or ClO$_4$ since these species have binding energies of 206 - 208 eV [6,8,10].

The difference spectrum derived from subtracting the high resolution C$_{1s}$ XPS spectrum from the polished C$_{1s}$ spectrum (Figure 27a) is shown in Figure 49. The +1.5 eV BE region above the bulk C-C signal region indicates the changes in the carbon line shape resulting from the Cl$_2$ RFP. The line shape change at +1.3 - +1.5 eV is consistent with the observed shifts of +1.2 - +1.4 eV found for C-Cl bonds.
in chlorinated polymers [13,14].

The spectrum from the CH$_2$Cl$_2$ plasma, Figure 48b, is quite different from the Cl$_2$ treated GC. The most intense signal in the spectrum is from chlorine. The Cl/C ratio value of 0.65 is more than 3.6 times the ratio observed on the Cl$_2$ treated sample. The surface still has a significant oxygen signal (O/C = 0.10) of about the same intensity of the N$_2$ RFP treated sample. The CG surface appeared a uniformly dark metallic blue after termination of the plasma. The color and appearance of this carbon is similar to GC samples which had been coated with a thin paralene polymer film. The apparent color of the surface is ascribed to the well known thin film diffraction of light reflecting back off the mirror polish of the GC. The very high Cl/C ratio and the color development are indications that the CH$_2$Cl$_2$ RFP forms a plasma polymerization product which deposits uniformly on the surface of the GC.

The polymer formed on the GC is observed to be hydrophobic since it does not wet. When washed with water, the water beads up. This is in contrast to the wetting action of water observed for GC. Unlike the en polymer, the chlorinated polymer is not very tightly bound to the surface because it is washed off by methyl alcohol.

The high resolution XPS carbon (C$_{1s}$) and chlorine (Cl$_{2p}$) spectra are shown in Figure 50 and Figure 51, respectively. The C$_{1s}$ lines are significantly different. The chlorine treated surface with a C$_{1s}$ line at 284.3 eV and a FWHM value of 1.5 eV is typical of an oxidized GC. The CH$_2$Cl$_2$ treated carbon (C$_{1s}$) is shifted to 285.8 eV BE and has a FWHM of 2.8 eV. The Cl$_{2p}$ lines are very similar. The FWHM value for both signals is 2.8 eV, however the Cl line from the CH$_2$Cl$_2$ treatment is shifted +0.6 eV. The shifted line positions and broad C$_{1s}$ line with a high BE tail suggests a multitude of carbon – chlorine species are present and supports the formation of an overlying polymer.

The very broad nearly flat peak combined with the very high chlorine content of the surface is similar to the spectrum reported for polyvinyl chloride [13]. The high FWHM value and the high BE tailing observed for the CH$_2$Cl$_2$ treated GC is not the result of charge broadening by the polymer because the Cl$_{2p}$ peak does not show
peak broadening as it must if the polymer is experiencing asymmetric charging. Since charging is not significant, the formation of the broad C_{1s} line is an indication of formation of multiple C-Cl species. With two Cl atoms/molecule of CH_2Cl_2, it is probable that carbon – chlorine species with up to three C-Cl bonds are formed. The chemical shifts expected from carbon atoms with two or three C-Cl bonds would lead to broadening of the C_{1s} line, but not the Cl_{1s} line.

The ease with which Cl_2 RFP introduces chlorine onto the GC in contrast to HBr RFP [1] may be due to the presence of hydrogen in the reagent gas. Formation of C-Br bonds on the surface might readily be broken by a hydrogen radical to reform the volatile HBr. Formation of HCl cannot occur to any significant extent in the Cl_2 RFP since the only source of H radicals will be the GC itself or residual hydrogen in the vacuum system. In the absence of hydrogen only multiple C-Cl bonded species such as CCl_4 or higher carbon chain chlorinated species can form volatile species which can desorb form the surface. The rate of production of these species is less likely and would require a longer formation time to form the multiple C-Cl bonds. Thus the chlorine remaining on the surface following plasma termination should remain firmly attached as no more chlorine is added to the surface. It seem reasonable that Br_2 and I_2 source gases would also halogenate the surface since these gases will be expected to form free radicals and other reactive species in the RFP while avoiding the presence of hydrogen radicals which can form "volatile" species on the surface.

**CONCLUSIONS**

The nitrogen source gas RFP treatment introduces high levels of amine and imine like groups to the GC surface. Derivatization with TFAA indicates the amine content decreases with the source gas used in the order ethylene diamine > NH_3 > N_2H_4 > N_2. The formation of the ethylene diamine polymer product which is firmly attached to the GC exhibits the lowest oxygen content, however, this may be due to attenuation of the surface oxygen rather than removal of it.
The oxygen detected on the surface of samples treated with the other nitrogen source gases may be due to the inability of these gases to form volatile C-O species which desorb from the surface, although recombination of volatilized C-O species with the surface may be occurring before they can be pumped away.

Extension of the RFP treatment to chlorine source gases proves the utility of plasma modification of GC. This ability to modify the surface chemistry by RFP should be readily applied to other forms of graphitic materials. The chlorine content of the surface resulting from treatment with Cl₂ plasma is very high indicating extensive surface chlorination. The C₁s line shape observed suggests primarily single C-Cl bond formation on GC in contrast to the multiple C-Cl bonds formed in the polymer produced by the CH₂Cl₂ source gas.

Extension of the plasma technique to halogenate graphitic samples with Br₂ and I₂ plasma treatment seems plausible. Halogenation of a carbon surface may provide the requisite surface functional group necessary to form C-C surface linkages by reaction with organolithium or Grignard reagents.

The development of an online reaction vessel to eliminate the uncertainty introduced during offline reductions or derivatization would be beneficial in evaluating the possible oxidation of the sample surface following the treatments.
Figure 41. Carbon (C\textsubscript{1s}) XPS Survey Spectra of Nitrogen Source Gas Plasma Treated Glassy Carbon

The XPS survey spectra from glassy carbon after RFP treatment with the nitrogen reagent gas series. The treatments are: a. Nitrogen (N\textsubscript{2}), b. Ammonia (NH\textsubscript{3}), Hydrazine (N\textsubscript{2}H\textsubscript{4}), and d. Ethylene Diamine (en = (CH\textsubscript{2}NH\textsubscript{2})\textsubscript{2}). O\textsubscript{A} and N\textsubscript{A} indicate the oxygen and nitrogen Auger lines respectively.
Table 8

XPS DATA FOR NITROGEN SOURCE GAS PLASMA TREATED GLASSY CARBON

Peak positions\(^+\), full width at half maximum (FWHM) values\(^+\), and measured atomic ratios for glassy carbon samples treated with nitrogen (N\(_2\)), ammonia (NH\(_3\)), hydrazine (N\(_2\)H\(_4\)) and ethylene diamine (en = (CH\(_2\)NH\(_2\))\(_2\)) RFP.

<table>
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<tr>
<th>Signal</th>
<th>C(_{1s})</th>
<th>N(_{1s})</th>
<th>O(_{1s})</th>
<th>O/C ratio</th>
<th>N/C ratio</th>
</tr>
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<td>Treatment:</td>
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<td></td>
</tr>
<tr>
<td>N(_2) plasma</td>
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<td>399.4</td>
<td>531.8</td>
<td>0.095</td>
<td>0.17</td>
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<td>[1.4]</td>
<td>[3.0]</td>
<td>[2.2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(_2) plasma + Air</td>
<td>284.2</td>
<td>399.4</td>
<td>531.8</td>
<td>0.10</td>
<td>0.14</td>
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<td>[1.5]</td>
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<td>[2.9]</td>
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<td>532.5</td>
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<td>[1.8]</td>
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<td>[2.6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH(_3) plasma + Air</td>
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<td>399.4</td>
<td>532.5</td>
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<td>0.10</td>
</tr>
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<td>[2.5]</td>
<td>[2.4]</td>
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<td>399.4</td>
<td>532.4</td>
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<td>[2.5]</td>
<td>[3.2]</td>
<td></td>
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<td>532.4</td>
<td>0.067</td>
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<td>[2.5]</td>
<td>[3.0]</td>
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<tr>
<td>en plasma(^*)</td>
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<td>400.2</td>
<td>trace</td>
<td>----</td>
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</tr>
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<td>[2.25]</td>
<td>[2.5]</td>
<td>[---]</td>
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<tr>
<td>en plasma + Air</td>
<td>285.2</td>
<td>400.2</td>
<td>532.6</td>
<td>0.059</td>
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<td>[2.0]</td>
<td>[2.6]</td>
<td>[2.8]</td>
<td></td>
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</tr>
</tbody>
</table>

\(^+\) Peak position and FWHM values (in square brackets [ ] ) are given in eV.

\(^*\) Peak is charge shifted due to the formation of a plasma polymerization product on the glassy carbon.

All peak areas corrected for atomic sensitivities [10] prior to calculation of atomic ratios.
Figure 42. High Resolution Carbon (C$_{1s}$) XPS Spectra For Nitrogen Source Gas Plasma Treated Glassy Carbon.

High resolution Carbon (C$_{1s}$) XPS spectra obtained from the same RFP treated samples corresponding to Figure 41. The nitrogen reagent gas series RFP treatments are: (a) Nitrogen (N$_2$), (b) Ammonia (NH$_3$), (c) Hydrazine (N$_2$H$_4$), and (d) Ethylene Diamine (en = (CH$_2$NH$_2$)$_2$).

Spectrum (d) with peak maximum at 285.1 eV has been corrected to 284.6 eV for comparison to the other spectra. See Table 8 for binding energies, full width at half maximum (FWHM) values and measured elemental ratios.
Figure 43. High Resolution Nitrogen (N$_1^s$) XPS Spectra From Nitrogen Source Gas Plasma Treated Glassy Carbons.

High resolution Nitrogen (N$_1^s$) XPS spectra obtained from the same RFP treated samples corresponding to Figures 41 and 42. The nitrogen reagent gas series RFP treatments are: (a) Nitrogen (N$_2$), (b) Ammonia (NH$_3$), (c) Hydrazine (N$_2$H$_4$), and (d) Ethylene Diamine (en = (CH$_2$NH$_2$)$_2$).

See Table 8 for binding energies, full width at half maximum (FWHM) values and measured elemental ratios.
Figure 44. Carbon (C$\text{1s}$) Difference Spectra From Nitrogen Source Gas Plasma Treated Glassy Carbons.

Difference spectra obtained by subtracting the C$\text{1s}$ spectrum for polished glassy carbon (Figure 27a) from the various spectra in Figure 42. The difference spectra illustrate the smaller binding energy chemical shifts observed for C-N type bonds for the amine type functions. The vertical lines drawn in correspond to the binding energy shifts associated with C-O (+1.5 eV) and C=O (+2.5 eV) relative to the bulk C-C lines found for homopolymers (Chapter 4). All difference spectra are displayed times 1 (x1).
Figure 45. XPS Survey Spectra From Nitrogen Source Gas Plasma Treated Glassy Carbons Derivitized With Trifluoroacetic Anhydride.

Low resolution XPS survey spectra for glassy carbon treated with the nitrogen source gas series (as shown in Figure 41) RFP followed by surface derivatization with trifluoroacetic anhydride (TFAA). The treatments are: a. Nitrogen (N₂), b. Ammonia (NH₃), Hydrazine (N₂H₄), and d. Ethylene Diamine (en = (CH₂NH₂)₂). Oₐ, Nₐ, and Fₐ indicate the oxygen, nitrogen and fluorine Auger lines respectively.
Table 9

XPS DATA FOR TRIFLUOROACETIC ANHYDRIDE DERIVITIZED NITROGEN SOURCE GAS PLASMA TREATED GLASSY CARBON.

Peak positions\textsuperscript{+}, full width at half maximum (FWHM) values\textsuperscript{+}, and atomic ratios for glassy carbon treated with nitrogen (N\textsubscript{2}), ammonia (NH\textsubscript{3}), hydrazine (N\textsubscript{2}H\textsubscript{4}) and ethylene diamine (en = (CH\textsubscript{2}NH\textsubscript{2})\textsubscript{2}) RFP followed by reaction with trifluoroacetic anhydride (TFAA).

<table>
<thead>
<tr>
<th>Signal</th>
<th>C\textsubscript{1S}</th>
<th>N\textsubscript{1S}</th>
<th>O\textsubscript{1S}</th>
<th>F\textsubscript{1S}</th>
<th>O/C ratio</th>
<th>N/C ratio</th>
<th>F/C ratio</th>
<th>N/F ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N\textsubscript{2} plasma + TFAA</td>
<td>284.4 [1.6]</td>
<td>399.6 [2.7]</td>
<td>532.4 [3.2]</td>
<td>688.2 [2.0]</td>
<td>0.143</td>
<td>0.089</td>
<td>0.064</td>
<td>1.63</td>
</tr>
<tr>
<td>NH\textsubscript{3} plasma + TFAA</td>
<td>284.4 [1.6]</td>
<td>399.8 [2.9]</td>
<td>532.4 [2.6]</td>
<td>688.5 [2.6]</td>
<td>0.071</td>
<td>0.10</td>
<td>0.097</td>
<td>1.053</td>
</tr>
<tr>
<td>N\textsubscript{2}H\textsubscript{4} plasma + TFAA</td>
<td>284.4 [2.0]</td>
<td>399.2 [2.6]</td>
<td>532.6 [2.9]</td>
<td>688.1 [2.0]</td>
<td>0.10</td>
<td>0.12</td>
<td>0.082</td>
<td>1.49</td>
</tr>
<tr>
<td>en plasma + TFAA</td>
<td>285.6 [1.8]</td>
<td>401.1 [2.7]</td>
<td>533.6 [2.6]</td>
<td>689.8 [2.1]</td>
<td>0.094</td>
<td>0.12</td>
<td>0.16</td>
<td>0.736</td>
</tr>
</tbody>
</table>

\textsuperscript{+} Peak position and FWHM values, (in square brackets), are given in eV.

\textsuperscript{*} Theoretical N/F ratio is 0.333 if each nitrogen introduced to the glassy carbon surface has one N-H bond capable of reacting with TFAA.

All peak areas corrected for atomic sensitivities \[10\] prior to calculation of atomic ratios.
Figure 46. High resolution Carbon (C$_{1s}$) XPS spectra obtained from the same trifluoroacetic anhydride (TFAA) derivitized samples as in Figure 45.

The treatments are: (a) N$_2$ RFP + TFAA, (b) NH$_3$ RFP + TFAA, (c) N$_2$H$_4$ + TFAA, and (d) en RFP + TFAA. Table 9 lists the peak positions and FWHM values for the spectra.
Figure 47. High Resolution ($N_{1s}$) XPS Spectra From Nitrogen Source Gas Plasma Treated Glassy Carbons Derivitized With Trifluoroacetic Anhydride.

High resolution Nitrogen ($N_{1s}$) XPS spectra obtained from the same trifluoroacetic anhydride (TFAA) derivitized samples as in Figure 45. The treatments are: (a) $N_2$ RFP + TFAA, (b) $NH_3$ RFP + TFAA, (c) $N_2H_4$ + TFAA, and (d) en RFP + TFAA. Table 9 lists the peak positions and FWHM values for the spectra.
Figure 48. XPS Survey Spectra From Chlorine Source Gas Plasma Treated Glassy Carbon.
Low resolution XPS spectra obtained from plasma treatment with the chlorine series of gases. The treatments are: (a) Chlorine Cl$_2$ RFP, and (b) Dichloromethane (CH$_2$Cl$_2$) RFP. The peak positions, FWHM values and measured atomic ratios are presented in Table 10.
Table 10

XPS DATA FOR CHLORINE SOURCE GAS PLASMA TREATED GLASSY CARBON.

Peak positions*, full width at half maximum (FWHM) values*, and measured atomic ratios for glassy carbon treated with chlorine (Cl\(_2\)) and dichloromethane (CH\(_2\)Cl\(_2\)) RFP.

<table>
<thead>
<tr>
<th>Signal</th>
<th>C(_1s)</th>
<th>O(_1s)</th>
<th>Cl(_2p)</th>
<th>O/C ratio</th>
<th>Cl/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl(_2) Plasma</td>
<td>284.3 [1.5]</td>
<td>532.4 [3.4]</td>
<td>200.0 [2.8]</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>CH(_2)Cl(_2) plasma</td>
<td>285.8 [2.8]</td>
<td>533.2 [3.3]</td>
<td>200.6 [2.8]</td>
<td>0.10</td>
<td>0.65</td>
</tr>
</tbody>
</table>

* Peak positions and FWHM values, (in square brackets [ ]), are given in eV.

All peak areas corrected for atomic sensitivities [10] prior to calculation of atomic ratios.
Figure 49. Difference spectrum (b) obtained by subtracting the C$_{1s}$ spectrum for polished glassy carbon (Figure 27a) from the C$_{1s}$ spectrum (a) from Cl$_2$RFP treated glassy carbon shown in Figure 48a.

The vertical lines drawn in correspond to the binding energy shifts associated with C=O (+1.5 eV) and C=O (+2.5 eV) relative to the bulk C-C lines found for homopolymers (Chapter 4).
Figure 50. High Resolution Carbon (C\textsubscript{1\alpha}) XPS Spectra From Chlorine Source Gas Plasma Treated Glassy Carbons.

High resolution Carbon (C\textsubscript{1\alpha}) XPS spectra obtained from the same chlorine source gas RFP treated samples as shown in Figure 48. The treatments are: (a) Chlorine Cl\textsubscript{2} RFP, and (b) Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) RFP. Table 10 lists the peak positions, FWHM values and measured atomic ratios obtained from the spectra.
Figure 51. High Resolution Chlorine (Cl$_2$) XPS Spectra From Chlorine Source Gas Plasma Treated Glassy Carbons.

High resolution chlorine (Cl$_2$) XPS spectra obtained from the same chlorine source gas RFP treated samples as shown in Figure 48. The treatments are: (a) Cl$_2$ RFP and (b) CH$_2$Cl$_2$ RFP. Spectrum (b) is shifted to higher BE due to charge shifting of the polymer formed on the glassy carbon by the plasma. Table 10 lists the peak positions and FWHM values for the spectra.
APPENDIX

COMPUTER PROGRAMS FOR XPS DATA PROCESSING

1. "XDECON" for Curve Synthesis.

2. "Ualign" subroutine for aligning two XPS spectra prior to obtaining the difference spectrum.

3. "Miller" Deconvolution program for removing the Instrumental Response Function from high resolution XPS spectra.
EXPLANATION OF PROGRAM PARAMETERS

XDECON – Program to calculate simulated spectrum

Arrays And Parameters

NL(I)  Integer array for display of experimental data on oscilloscope
EDAT(I)  Floating point array with experimental data
NH(I)  Integer array for display of simulated spectrum
IDATA(I,J)  Individual components of simulated spectrum
H(I)  Height of ith component
W(I)  FWHM of ith component in data points
A(I)  Peak position in data points
L(I)  Peak shape desired of ith component
G(I)  % Gaussian peak shape
SEVO  Starting eV value (high BE)
FEVO  Final eV value (low BE)
PTEV  Data points per eV
XYDIFF  Calculates individual components
XDREMOVE  Removes background
XDSMOOTH  Smooths experimental data
XDAREA  Calculates area of sum spectrum and individual components
FWHM  Full Width at Half Maximum peak height in eV
PKPOS  Peak position in eV
RMAX,RMIN  Maximum and minimum values of stored data
ASCAL  Scale factor for oscilloscope display of data

All other arrays, subroutine calls, tasks, and parameter values are specific to the computer system and interface or are self explanatory.
C HANTASK 12,2
MASTER XDECON(512 PTS)
EXTERNAL XDScope, SC0PE2
COMMON/COM1/ H(7), W(7), A(7), L(7), G(7)
COMMON/COM2/ NDAT(512), NSDRT(512)
COMMON/COM3/ NH(512), NI(512)
COMMON/COM4/ NCOMP, EDAT(512)
COMMON/COMS/ NAR(256), NAME(5)
COMMON/COM6/ IDat(7,512), ASCAL
N0=512
CALL HAZEL
CALL FTASK(XDScope, #1001, 7)
1000 CALL XDEOP2
100 DO 52 I=1, N0
52 NL(I)=0
DO 50 I=1,7
50 CONTINUE
51 IDat(I,J)=0,0
DO 54 I=1,7
54 H(I)=0,0
L(I)=0,0
G(I)=0,0
W(I)=0,0
R(I)=0,0
ICOMP=0
NCOMP=0
RMIN=22000
RMAX=0
DO 74 I=1, N0
74 IF NDAT(I), LT, RMIN) RMIN=NDAT(I)
IF NDAT(I), GT, RMAX) RMAX=NDAT(I)
RMAX=RMAX-RMIN
ASCAL=3900/RMAX
DO 72 I=1, N0
72 NL(I)=(NDAT(I)-RMIN)*ASCAL+0.5
K=0
310 WRITE(3,200)
200 FORMAT(1X, "NUMBER OF SMOOTHING PASSES DESIRED", 2)<
READ(4) IPAS
IF IPAS EQ 0 GO TO 301
CALL XDSMOOTH(IPAS)
K=K+IPAS
WRITE(3,202) K
202 FORMAT(1X, "TOTAL NUMBER OF SMOOTHING PASS=", I4)
WRITE(3,203)
203 FORMAT(1X, "DO YOU WANT ADDITIONAL SMOOTHING 1=YES", 2)<
READ(4) NEAS
IF NEAS EQ 1 GO TO 310
IPAS=K
301 WRITE(2) "DO YOU WANT BACKGROUND REMOVAL? 1=YES"
READ(4) IBAS
IF IBAS EQ 1 GO TO 9
DO 70 I=1, N0
J=(N0+1)-I
70 NSDRT(J)=NL(I)
CALL XDREMOVE
DO 71 I=1, N0
139

XDECON 6/1/82 7:51:23

139

71  
9  CONTINUE
WRITE(2) "DO YOU WANT TO PLOT DATA(=1) OR CONTINUE(=2)"
READ(4) JBAS
IF(JBAS.EQ.1) GO TO 77
SEVO=NAR(21)/10.
FEVO=NAR(22)/10.
PTEV=10**((SEVO-FEVO))

44  IF(ICONP.EQ.0) GO TO 77
ICONP=ICONP+1
NCOMP=ICONP
46  WRITE(3)
WRITE(2,22) NCOMP
22  FORMAT(1X,"OLD VALUES FOR PEAK #",I4)
FM=FM-NCOMP/PTEV
PK=SEVO-R(NCOMP)/PTEV
IHEIGHT=IHEIGHT/NCOMP
WRITE(3,24) FM,PK,IHEIGHT
24  FORMAT(1X,",","FM= ",F5.2," AT ",F6.2," EV HEIGHT= ",I4)
WRITE(3)
WRITE(2,59) NCOMP
59  FORMAT(1X,"FOR PEAK ",I4)
I=NCOMP
30  WRITE(3,60)
60  FORMAT(1X,"GAUSSIAN(1), LORENTZIAN(2) OR G&L(3) ",Z)
READ(4) L(I)
IF(L(I).GT.2) GO TO 30
IF(L(I).GT.1) GO TO 62
31  WRITE(3,63)
63  FORMAT(1X," X OF GAUSSIAN = ",Z)
READ(4) G(I)
IF(G(I).GT.100) GO TO 31
G(I)=G(I)+0.01
62  WRITE(3,61)
61  FORMAT(1X,"INPUT FHMM AND PEAK POSITION IN EV ",Z)
READ(4) FHMM,PKPOS
IF(PKPOS.LT.SEVO .AND. PKPOS.GT.FEVO) GO TO 22
WRITE(3)"PEAK POSITION ERROR POSITION IS OUT OF THIS SPECTRAL RANGE"
GO TO 62
22  W(I)=FHMM*PTEV
R(I)=(SEVO-PKPOS)*PTEV
J=SEVO-FKPOS*PTEV
NEXP=NL(J)
WRITE(3,64) NEXP
64  FORMAT(1X,"INPUT HEIGHT. SUGGESTED HEIGHT =",1X,15.2X,Z)
READ(4) H(I)
DO 90 I=1,N0
CALL XVDIF(I,IDATA(NCOMP,I),NCOMP)
90  WRITE(3,20)
20  FORMAT(1X," ADD (=1) OR SUBTRACT A PEAK (=2) OR OTHER (=3) ",Z)
READ(4) IBAS
IF(IBAS.EQ.1) GO TO 46
IF(IBAS.GT.2) GO TO 95
21  WRITE(3,21)
21  FORMAT(1X," SUBTRACT WHICH PEAK (1 THRU 7) ",Z)
READ(4) NCOMP
IF(NCOMP.GT.8) GO TO 22
IF(NCOMP.EQ.0) GO TO 99
DO 45 I=1,N0
45 NH(I)=NH(I)-IDATA(NCOMP,I)
GO TO 46
97 WRITE(2) "NO MORE COMPONENTS ALLOWABLE"
GO TO 99
95 WRITE(I,68)
68 FORMAT(1X:"TYPE 1 TO REHASH SAME DATA, 2 TO PLOT, 3 FOR NEW DATA",Z)
READ(4) IBAS
IF(IBAS.EQ.1) GO TO 100
IF(IBAS.EQ.2) GO TO 1000
IF(IBAS.GT.2) GO TO 95
77 CALL XDPOLE(I,COMP,IPAS)
CALL XDAREA (ICOMP)
WRITE(I,67)
67 FORMAT(1X:"TYPE 1 FOR NEW DATA",Z)
READ(4) IBAS
IF(IBAS.EQ.1) GO TO 1000
GO TO 69
1001 WRITE(10) "NOT ENOUGH TCB'S"
69 STOP
END
EXPLANATION OF PROGRAM PARAMETERS

UALIGH – Subroutine used to align two experimental spectra after smoothing, background removal, and scaling of each spectrum

Arrays And Parameters

NK1(I) Spectrum desired
NK2(I) Spectrum to be subtracted
NH1(I) Spectrum of NK1(I) displayed on oscilloscope
NH2(I) Spectrum of NK2(I) displayed on oscilloscope
NSDAT(I) Array used to shift spectrum and zero out data array points which do not match after shifting

NH1MAX,NH2MAX Position of maximum array values for NH1(I) and NH2(I)
INDIFF Difference between NH1MAX and NH2MAX

All other values are self explanatory
SUBROUTINE URLIGN
COMMON/COM2/NSDAT(512)
COMMON/COM3/NH1(512),NH2(512)
COMMON/COM6/NI1(512),NI2(512)
501 DO 500 I=1,512
500 NH1(I)=NH1(I)
NH2(I)=NH2(I)
NPTS=0
NH1MAX=NH1(1)
IND1=1
DO 21 I=2,512
IF(NH1MAX-NH1(I)) 20,21,21
20 NH1MAX=NH1(I)
IND1=1
21 CONTINUE
NH2MAX=NH2(1)
IND2=1
DO 24 I=2,512
IF(NH2MAX-NH2(I)) 23,24,24
23 NH2MAX=NH2(I)
IND2=1
24 CONTINUE
WRITE(*,10) IND1,IND2
10 FORMAT(1X,"SPECTRA #1 MAX AT: ",I4," SPECTRA #2 MAX AT: ",I4)
INDIFF=IND2-IND1
WRITE(*,50) INDIFF
50 FORMAT(1X,"INDIFF=",I5)
WRITE(*:"MOVE SPECTRA HOW MANY POINTS? ")
READ(*) NPTS
IF(NPTS.EQ.0) GO TO 22
IF(IND2-IND1) 20,20,22
20 NPTS=NPTS
INDIFF=512-INDIFF
DO 60 J=1,NDIFF
I=INDIFF+J
60 NSDAT(I)=NH1(J)
DO 61 I=1,INDIFF
NSDAT(I)=0
61 NH2(I)=0
DO 62 I=1,512
62 NH1(I)=NSDAT(I)
GO TO 502
50 NDIFF=NPTS
NDIFF=512-NDIFF
DO 70 J=1,NDIFF
I=INDIFF+J
70 NSDAT(I)=NH2(J)
DO 71 I=1,INDIFF
NH1(I)=0
71 NSDAT(I)=0
DO 72 I=1,512
72 NH2(I)=NSDAT(I)
502 WRITE(2) "REALIGN PEAKS(=1), CONTINUE(=2)"
READ(4) IBEAS
IF(IBEAS.EQ.1) GO TO 501
42 WRITE(10,600) NPTS
600 FORMAT(1X,"SPECTRA SHIFTED ",I4," POINTS")
RETURN
END
EXPLANATION OF PROGRAM PARAMETERS

MILLER - Program to deconvolute instrument response function from the XPS spectrum

Arrays And Parameters

EDAT(I) Experimental data array
YS(I) Temporary array used by smoothing subroutine
G(I) Instrument response function (IRF) array
NL(I) Array for plotting and display on oscilloscope
F(I) Trial deconvolute data array for convolution with the IRF array
FAG(I) Convolute of trial deconvolute array with the IRF array
DDIFF(W) Chi squared difference between experimental and convoluted spectra for the Wth iteration
W Iteration number
FAGMAX,FAGMIN Maximum and minimum of convolution spectrum
MLINE Subroutine to call instrument response function
IX9SMOOTH Subroutine using a 9 point 4th/5th order smoothing filter
MREMOVE Subroutine for background removal
MPLLOT Subroutine for plotting display data
MDIFF Subroutine to calculate the chi squared difference between the experimental and convolute spectra

DO LOOP 90 The convolution routine for method two (Chapter 4)
DO LOOP 414 Estimate of new trial deconvolute line

All other arrays, subroutine calls, tasks, and parameter values are specific to the computer system and interface or are self explanatory.
C
MASTER MILLER
COMMON/COM1/NAME1(5),NL(256),NDAT(1024),EDAT(300)
COMMON/COM2/NAME2(5),G(200),F(200),FAG(300)
COMMON/COM3/Y(300),YS(300)
COMMON/COM4/NAR(256)
DIMENSION DDIFF(20)
INTEGER W,H
CALL HAZEL
1000 CALL MOPEN
 CALL MLINE
 WRITE(2,105)
105 FORMAT(1X:"DO YOU WANT SMOOTHING PRIOR TO DECONVOLUTION (1=YES) ",I1,Z)
 READ(4) INST
 IF(INST.NE.1) GO TO 206
 WRITE(3,106)
106 FORMAT(1X:"INPUT NUMBER OF SMOOTHING PASSES DESIRED ",I1,Z)
 READ(4) N
206 WRITE(2,104)
104 FORMAT(1X:"REMOVE BACKGROUND BEFORE DECONVOLUTION (1=YES)",I1,Z)
 READ(4) INST
 IF(INST.NE.1) GO TO 27
 DO 20 I=1,256
 J=I+22
20 VS(I)=EDAT(J)
 NK=0
 CALL IXSSMOOTH(N,NK)
 DO 21 I=1,256
 J=I+22
21 EDAT(J)=VS(I)
27 IF(INST.NE.1) GO TO 24
 CALL MREMOVE
24 EMIN=22000.
 EMAX=1.
 INDE=1.
 GMAX=G(24)
 GMIN=22000.
 INDG=1.
 DO 1 I=23,278
 IF(EDAT(I).GE.EMAX) INDE=I
 IF(EDAT(I).GE.EMAX) EMAX=EDAT(I)
 IF(EDAT(I).LT.EMIN) EMIN=EDAT(I)
 IF(G(I).GE.GMAX) INDG=I
 IF(G(I).GE.GMAX) GMAX=G(I)
1 IF(G(I).LT.GMIN) GMIN=G(I)
 EMAX=EMAX-EMIN
 GMAX=GMAX-GMIN
 DO 2 I=23,278
 EDAT(I)=(EDAT(I)-EMIN)/EMAX
2 G(I)=(G(I)-GMIN)/GMAX
 DO 3 I=1,22
 EDAT(I)=EDAT(24)
 J=277+I
 EDAT(J)=EDAT(277)
 G(I)=G(23)
3 K=277+I
 G(I)=G(277)
 K=INDG
 WRITE(10,100) K,INDE
100 FORMAT(1X:"IRF LINE MAX. AT",I4," DATA MAX. AT",I4)
DO 19 I = 1, 256
   J = I + 22
   NL(I) = EDAT(J) * 2100.
   CALL MPLLOT
DO 10 I = 1, 256
   J = I + 22
10   NL(I) = G(J) * 2100.
   CALL MPLLOT
DO 14 I = 1, 300
14   F(I) = EDAT(I)
C ---------------------------------------------------------------------
DO 90 W = 1, 20
   WRITE(10, 202) W
202 FORMAT(1X, "ITERATION NO. ", I3, Z)
   DO 400 I = 1, 300
      L = K - I
      RC = 0.
      DO 401 J = 1, 200
         H = L + J
         IF (N . GT. 200) GO TO 2000
         IF (N . LT. 1) GO TO 2801
         RC = RC + G(N) * F(J)
      GO TO 2002
2000   RC = RC + F(J) * G(200)
      GO TO 2002
2001   RC = RC + G(J) * F(J)
      GO TO 2002
2002   CONTINUE
401   CONTINUE
      FAG(I) = RC
400   CONTINUE
   FAGMIN = 32000.
   FAGMAX = 0.
   INDFAG = 22
   DO 6 I = 22, 278
      IF (FAG(I) . GE. FAGMAX) INDFAG = I
      IF (FAG(I) . GE. FAGMAX) FAGMAX = FAG(I)
      IF (FAG(I) . LT. FAGMIN) FAGMIN = FAG(I)
      FAGMAX = FAGMAX - FAGMIN
   DO 7 I = 1, 300
      FAG(I) = (FAG(I) - FAGMIN) / FAGMAX
      CALL MDIFF(DIFF1)
      DIFF1 = DIFF1 + 1000.
   WRITE(10, 201) DIFF1
201   FORMAT(1X, "DIFF = ", F10.4)
   DDIFF(W) = DDIFF1
   GO TO 87
C CHECK FOR MINIMUM IN DIFF BY COMPARING WITH PREVIOUS VALUE
89   CONTINUE
87   CONTINUE
   IF (W . EQ. 20) GO TO 26
   CALL IXSWITCH(NSW)
   IF (NSW . EQ. 2) GO TO 26
   GO TO 25
25   DO 11 I = 1, 256
      J = I + 22
   11   NL(I) = EDAT(J) * 2100.
CALL MPlot
DO 12 I=1,256
   J=1+22
   NL(I)=FAg(J)+2100.
   CALL MPlot
   DO 12 I=1,256
   J=1+22
   NL(I)=F(J)+2100.
   CALL MPlot
   CALL IXSWITCH(NSW)
25   AS=1.
   IF(NSW.EQ.1) AS=-1
   IF(NSW.EQ.0) GO TO 80
   DO 414 I=1,256
   F(I)=AS+EDAT(I)+F(I)-AS*FAg(I)
   FMAX=F(I)
   INF=1
   FMIN=32000.
   DO 8 I=1,250
     IF(F(I).GE.FMAX) INF=I
     IF(F(I).GE.FMAX) FMAX=F(I)
     IF(F(I).LT.FMIN) FMIN=F(I)
   C   WRITE(10,103) FMAX,FMIN,INF
   103  FORMAT(1X,"FMAX=",F10.4," FMIN=",F10.4," FMAX AT",I4)
   FMAX=FMAX-FMIN
   DO 9 I=1,250
8      F(I)=(F(I)-FMIN)/FMAX
   C   CONTINUE
88   WRITE(3)"NEW DATA=1".GO HOME=2.STORE DECONVOLUTED SPECTRA=1"
   READ(4) IBAS
   IF(IBAS.EQ.1) GOTO 1000
   IF(IBAS.EQ.2) GO TO 999
   DO 994 I=1,256
     J=1+22
994  NL(I)=F(J)+3000.
   WRITE(2,996)
996  FORMAT(1X,"INPUT FILENAME FOR DECONVOLUTED SPECTRA ",A)
   READ(4,995) NAME2
995  FORMAT(5S2)
   CALL CFILW(NAME2,3,2,IER)
   IF(IER.NE.1) WRITE(10) "CREATE FILE ERROR...IER=",IER
   WRITE(10,102) NAME2
102  FORMAT(1X,"DECONVOLUTED SPECTRA FILENAME= ",5S2)
   CALL OPEN(1,NAME2,3,IER)
   IF(IER.NE.1) WRITE(10) "CALL OPEN ERROR...IER=",IER
   CALL WRBLK(1,0,NAR,1,IER)
   IF(IER.NF.1) WRITE(10) "WRITE INFORMATION BLOCK ERROR...IER=",IER
   CALL WRBLK(1,1,NL,1,IER)
   IF(IER.NE.1) WRITE(10) "WRITE BLOCK ERROR...IER=",IER
   CALL CLOSE(1,IER)
   IF(IER.NE.1) WRITE(10) "CALL CLOSE ERROR...IER=",IER
   GO TO 997
997  STOP
END
BIBLIOGRAPHY

CHAPTER 1


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45. M. P. Auger, Compt. Rend., 177, 169 (1923); Ibid, 180, 65 (1925); Ibid, 182, 773, 1215 (1926).


CHAPTER 2


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CHAPTER 4


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CHAPTER 5


CHAPTER 6