Investigation of Interface Bonding Mechanisms between Glassy Carbon Microelectrodes and Polyimide Substrate through Fourier Transform Infrared Spectroscopy

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With increasing innovations in lithographically patterned glassy carbon (GC) microstructures supported on a flexible polyimide substrate, interest in understanding the nature and strength of the interface between these two materials has come to the forefront. However, although polyimide and glassy carbon have been both extensively studied independently, interface bonds between them in a composite structure have not been investigated. The work presented here investigates the interaction between GC and polyimide at their interface by comparing the infrared spectra of the composite microstructures (GC bonded to polyimide) to the spectra of both materials alone. A significant difference in the hydroxyl and anhydride peaks between the polyimide, carbon, and composite was found, indicating the presence of not only hydrogen bonding, but also covalent bonding in the composite microstructure.

Over the past several years, significant progress has been made in the development of novel and mechanically robust microelectrode arrays in response to increased research and clinical interest in brain signal recording and stimulation using stable and biocompatible materials.1-6 Although metal microelectrodes dominate the market for neural probes,2 these microelectrodes typically fail as a result of harsh in vivo biological conditions and stimulation protocols that break weak chemical bonds within the electrode and cause corrosion and, in some cases, complete failure.4 Thus, the successful translation of neural probe technology from lab conditions to clinical applications for the study and treatment of neuropathologies relies on the development of devices capable of withstanding these harsh electrical and in vivo conditions for 3-5 years without electrode corrosion or separation from the substrate. To address this, we had recently introduced neural probes with pyrolytic (glassy) carbon electrodes which have good resistance to corrosion, mechanical and electrical stability, high charge injection and storage capacity along with wide electrochemical window.4,5 Leveraging these unique advantages, progress in making glassy carbon (GC) a compelling platform for neural implants that require simultaneous recording and electrical stimulation over an extended period (3-5 years) continues.

In the meantime, however, while fullerene carbon structures such as carbon nanotubes and graphene continue to be of interest in broad areas of applications including neuroprosthetics, the fact that their dominant material properties are in the direction of growth of the sp2 hybridized plane poses a limitation for applications requiring electrical and mechanical properties to carbon, the fullerene structure orientations must be randomly dispersed. This is often done using isolated carbon nanotubes and dispersing them randomly in a matrix. However, the process of adding these nanotubes into a matrix requires formation of new bonds that disrupt the sp2 orbitals that act as a conducting band for the carbon, thereby increasing impedance.10-13 On the other hand, GC synthesized through pyrolysis of a polymer precursor, forms 3-dimensionally interlaced ribbons of sp2 hybridized carbon atoms connected through a combination of electrostatic interactions and sp2 bonds.14-18 Through Transmission Electron Microscopy (TEM) and Raman Spectroscopy, GC structures patterned using microfabrication techniques (photolithography) have been shown to have both amorphous and crystalline properties that change with increasing temperature in the same fashion as polymer-derived graphite.14,15,19

However, while lithographically patterned GC is gaining traction with increasingly diverse areas of applications, its typical fabrication on rigid substrates such as silicon and quartz had limited its further growth and expansion in areas requiring mechanical flexibility. To address this challenge, therefore, a new technique of transferring lithographically patterned GC microstructures to a flexible polyimide substrate was recently introduced by our group.7,9 Polyimides are a class of solvent-resistant, thermally stable, and structurally durable polymers synthesized though the reaction of dihydridediamines and diamines in the presence of a dipolar aprotic solvent to produce poly(amic acid) intermediates. These intermediates are then imidized through the application of heat to produce the final polymer product.20 This final product has both polar imides and amine components that facilitate strong inter- and intra-chain charge transfer complexes and electron polarization. These modes of polymer-polymer interaction are what provide the material with its robust and rigid properties.22,23 The rigidity can be altered by incorporating flexible linkage groups into the backbone, which disrupt the charge transfer complexes and allow for a more flexible polymer. Furthermore, when combined with a photo initiator, polyimides can be used as a photosensitive resist in photolithography.21 Given their good resistance to chemicals, structural robustness, thermal stability, and low dielectric constant, polyimides make an excellent insulator for electrical devices.

While GC and polyimide materials have been extensively studied independent from one another, their interaction at the interface remains relatively unknown. Currently, there are few reports in the literature on polyimide interaction with different types of carbon nanotubes to generate a composite material.10,12,23 These works suggest that sp2...
hybridized carbon bonds well with polyimide, forming robust composites, but do not address the mechanism behind the interaction of the two materials. Without addressing this mechanism, therefore, the stability and in vivo performance of the composite structure consisting of GC and polyimide cannot be optimized for long-term implantation applications.

In this study, therefore, the interfacial bonding between these two materials, shown in Figure 1, is critically and rigorously investigated. Figure 1 shows a neural probe with lithographically patterned GC microelectrodes supported on a polyimide substrate where the interface bond between GC and polyimide is expected to enable a long-term implantation. For a detailed investigation of this interface, test structures that are a good representation of such probe but with larger diameter microelectrodes and that meet standards for sample preparation for chemical testing were fabricated. The test structures are 5 circular microelectrodes 2.5 mm in diameter and 3 mm center to center spacing, arranged in a circular manner in 1 cm × 1 cm die. To determine what type of bonds are present at the interface, diamond FTIR-ATR (Fourier Transform Infrared Spectroscopy - Attenuation Total Reflectance) was performed on the GC/polyimide test structures, and the spectra of the interface structure was compared both to GC on silicon and to bare polyimide. Because covalent bonds are not expected to form spontaneously, it is likely that bond formation will occur during the fabrication process when the energy input is high enough, either after oxygen plasma etching of GC or after curing of polyimide. Thus, to isolate unique bond formation, the changes in the FTIR spectra were analyzed as a function of oxygen plasma etching and polyimide curing temperature.

Materials and Methods

Microfabrication of test microstructures.—Samples consisting of simple 2.5 mm diameter microelectrodes were microfabricated using a pattern transfer method described in detail in a previous publication. In brief, for each sample, a 50% dilution of SU-8 10 (MicroChem) in acetone was spun at 4000 rpm onto a silicon wafer with 0.5 μm of silicon dioxide layer and patterned as shown in Figure 2. These samples were then pyrolyzed at 1000 °C to generate GC structures thin enough (< 2 μm) to enable probing of the interface between the GC and silicon through FTIR-ATR spectroscopy. Each sample was then plasma etched for 30 or 120 seconds, at a pressure of 500, 600, or 750 mTorr. Some of the control samples were not plasma etched at all. After plasma etching, HD4100 photosensitive polyimide (Hitachi Chemical, DuPont, MicroSystems) was applied immediately to the surface of the sample and spin coated on at 3000 rpm. Pre-baking was done for 1 min at 90 °C followed by an additional 1 min at 120 °C. Ultra-violet light exposure at 350 mJ/cm² was used to crosslink the polyimide, and then each sample was post-baked at 80 °C for 1 minute. After post-baking, each sample was cured at 1 of 4 temperatures: 150 °C, 200 °C, 300 °C, or 375 °C. The samples were then lifted-off the silicon/silicon dioxide substrate using buffered hydrofluoric acid. A total of 29 samples were prepared, using all possible combinations of plasma etching time, plasma etching pressure, and curing temperature.

FTIR spectroscopy.—FTIR-ATR spectroscopy was done using a Nicolet iS50 FT-IR Spectrometer equipped with a Smart iTR diamond ATR cell (Thermo Scientific, Court Vernon Hills, IL). For each sample, a spectrum of the GC electrodes on silicon was taken before the GC electrodes were plasma etched and transferred to the polyimide. To achieve this, three of the five GC electrodes (the three that were most intact per sample) were washed with methanol, dried, and placed on the diamond cell. 128 spectral scans were recorded, which was sufficient to achieve good resolution within a reasonable timeframe. The scans for each electrode were then compiled and all 102 discreet GC spectra averaged, resulting in a single original GC spectrum. Once the GC electrodes were transferred to the polyimide, the same three electrodes originally scanned for each sample were again washed with methanol, dried, and placed on the diamond for the optimal 128 scans. The 3 spectra per sample were averaged to produce the interface spectrum for that parameter. Polyimide spectra were taken at the edge and at the center of each assembled sample, and again 128 spectral scans were performed and compiled. The spectra of each sample cured at the same temperature were then averaged.

Scanning electron microscopy.—Scanning Electron Microscopy (SEM) images were taken using an FEI Quanta 450 FEG Scanning Electron Microscope (ThermoFisher Scientific, Waltham, MA). Samples that were plasma etched at 600 mTorr for 120 seconds and cured at 375 °C were first coated with 6 nm of platinum to increase conductivity and minimize charging of the surface during imaging. They were then loaded onto a stage tilted at 45° and imaged at 20 kV using secondary electron detection. Images were taken at magnification levels ranging from 100x to 75,000x to provide a thorough visual representation of the microstructures of the interface between the GC electrodes and the polyimide base.

Methods of data analysis.—Once FTIR spectra were obtained, Matlab script was used for analysis of the vibrational peaks in the raw data. The scatter plots generated display error bars corresponding to twice the standard deviation (2σ) in order to reflect a 95% confidence.
1. The local maxima, or zero slope locations (defined by 3 consecutive metrics, width, minima, and midpoint), were defined as follows: midpoint of the peaks of interest were chosen as metrics to characterize the bonds present for each parameter. For this study, the three metrics, width, minima, and midpoint, were defined as follows:

1. The local maxima, or zero slope locations (defined by 3 consecutive points of the same value), within the region of interest were taken to be the outer limits of the peak ((x\textsubscript{min}, y\textsubscript{min}) and (x\textsubscript{max}, y\textsubscript{max}) in Figure 3). The distance between these points was defined as the width. For asymmetric peaks or broad peaks where x\textsubscript{min} and y\textsubscript{min} were difficult to determine, the midpoint was calculated as the average between x\textsubscript{1} and x\textsubscript{2}.

In order to pick up small changes in the peaks, data was collected from the baseline corrected FTIR signal, an example of which is shown in Figure 3.

Distinguishing small changes in bond conformation can be challenging in FTIR.\textsuperscript{26} Therefore, a robust and statistically relevant approach is required to analyze the data and confirm the presence of bonds and statistically significant changes in peak (and, therefore, bond) with 95% confidence. For this analysis, the width, minima, and midpoint of the peaks of interest were chosen as metrics to characterize the bonds present for each parameter. For this study, the three metrics, width, minima, and midpoint, were defined as follows:

1. The local maxima, or zero slope locations (defined by 3 consecutive points of the same value), within the region of interest were taken to be the outer limits of the peak ((x\textsubscript{min}, y\textsubscript{min}) and (x\textsubscript{max}, y\textsubscript{max}) in Figure 3). The distance between these points was defined as the width. This metric is commonly used in FTIR analysis to detect a change in the chemical bonding either at full-width or full-width-half-the-maximum.\textsuperscript{26} In this study, the full-width was used in place of the full-width-half-the-maximum to ensure the capture of very slight changes in width due to overlapping of peaks that may not show up at half-the-maximum.\textsuperscript{25} The width allows for insight into the range of vibrational modes for a given bond type; the wider the peak, the more types of vibrational modes, and thus the less consistent the conformation.\textsuperscript{25,26}

2. Minima were defined as the wavenumber at which the peaks of interest reached their minimum transmittance (shown in Figure 3 as (x\textsubscript{min})). While the y-values are often used to determine concentration, variability in the fabrication process and thus the amount of sample present renders y\textsubscript{min} an unreliable metric. However, x\textsubscript{min}, sometimes referred to as the frequency band, is not dependent on the amount of sample, and is, therefore, used to determine the most likely bond (the dominate vibrational mode) and its degree of stability.\textsuperscript{25,26} Downshift in minima (i.e. a slight shift in the location on the x axis from where it is expected) indicates a dominant lower frequency vibration of the bond, implying better stability and thus stronger bonding.\textsuperscript{25,26}

3. Midpoint is defined as the average of x\textsubscript{1} and x\textsubscript{2}. While this metric is not commonly used in FTIR, we submit that it is especially useful when width and minima alone are not enough to describe the peak. For symmetric peaks, midpoint and minima will have the same wavenumber. For asymmetric peaks, however, the wavenumber of the midpoint differs from that of the minima, implying a significant change in bond organization has occurred, but not enough to shift the local minima all together.

Each of the above three metrics describes distinct characteristics of the material being imaged. Thus, if a statistically significant difference between GC, polyimide, and the interface is observed in any one of the metrics, it is reasonable to conclude that a unique bond has formed at the interface.

**Results and Discussion**

In this section, both the complete FTIR spectrum and the microstructures visualized with SEM are reviewed. In the FTIR spectra (shown in Figure 4), the boxed areas indicate the areas of interest: hydroxyl peaks, carbonyl peaks, and ether/anhydride peaks. Hydroxyl peaks and carbonyl peaks were analyzed to determine the presence of hydroxyls, carboxyls, or carboxylic acids. The presence of hydroxyls or carboxylic acid dimers would imply participation in hydrogen bonding at the interface. Additionally, carbonyl and ether/anhydride peaks were used to determine the presence of anhydride bonds at the interface. Table 1 summarizes the peaks of interest and the corresponding spectrums investigated. Figure 5 through 8 show the average interface spectrum, polyimide spectrum, GC spectrum, and the interface spectrum of the control (no plasma etching) cured at 375 °C. Arrows on plotted spectra indicate measured minima in sharp peaks; in broad peaks, arrows indicate zero slope points used to calculate width and midpoint.

In Figure 5, the first panel showing the polyimide spectra demonstrates that the polyimide contains an amine (peak at 3300 cm\textsuperscript{−1} that decreases in amplitude with increased curing temperature and the C–N peak at 1610 cm\textsuperscript{−1} (2018)), aromatic carbonyl (1777 cm\textsuperscript{−1} and 1710 cm\textsuperscript{−1}), and others (1070 cm\textsuperscript{−1} and 1240 cm\textsuperscript{−1})\textsuperscript{25,26} The presence of an aromatic backbone is suggested by the characteristic tetra-substituted benzene peaks at 1970 cm\textsuperscript{−1}, 1650 cm\textsuperscript{−1} (overtones), and 800 cm\textsuperscript{−1}.\textsuperscript{25} These peaks are consistent with those found in pyromellitic dianhydride (PMDA)-oxydianiline (ODA), a common form of photosensitive polyimide.\textsuperscript{27} Thus, throughout the rest of this study, we assume the PMDA-ODA configuration of polyimide.

Figure 5 also outlines the functional groups that are likely to participate in bonding: hydroxyl, carbonyl, and ether groups. The presence of strong carbonyl peaks in the plasma etched interface that are not present in the control interface samples suggests that plasma etching increases the number of carboxyls on the surface. In Figure 6, three broad hydroxyl peaks are shown. While these peaks are broader than the traditional hydroxyl peaks, the breadth can be explained by the high level of conjugation in the glassy carbon structure. From Figure 6, it can be seen that hydroxyl peaks are only more prominent in the plasma etched interface spectrum, indicating that hydroxyl groups are likely generated by plasma etching. In Figure 7, a peak consistent with that of ethers part of a non-cyclic anhydride is shown. Because this peak was not detectable in the GC samples nor in the non-plasma etched interface samples (but was clearly present in both the plasma etched interface samples and the polyimide), we argue that anhydrides are likely generated as a result of both plasma etching and polyimide curing. Figure 8 shows a peak that could be indicative of a cyclic anhydride or of ethers that are not part of an anhydride. The peak can be seen in the interface controls but is more prominent in the plasma etched interface. This suggests that the application of the polyimide or the fabrication process itself aided in the development of cyclic anhydrides. While many peaks shown in the polyimide are also seen in the interface, there are small differences between the two that distinguish one from the other. However, without statistical analysis, the significance of the differences seen in Figure 5 through 8 are difficult to determine. Thus, the averages and standard deviations of each peak’s characterizing metrics were calculated, as described in Scanning electron microscopy section, and plotted in scatter plots.

**Effects of oxygen plasma etching.—**Oxygen plasma etching is known to induce acyl groups onto graphitic surfaces through radical
Figure 4. Full Spectrum: Average of all glassy carbon on silicon spectra before plasma etching and pattern transfer (GC), Average of all polyimide spectra taken (cured at 375 °C) (Polyimide 375 °C), Average of all interface spectra with polyimide cured at 375 and plasma etched (Interface 375 °C) and Average of all non-plasma etched interface spectra cured at 375 (Control Interface 375 °C).

chemistry. Among these are carboxylic acids, hydroxyls, esters, or even epoxides, which can interact with functional groups intrinsic to many polyimide monomers. It is hypothesized that one possible mechanism for polyimide bonding to GC is through the interaction between carboxylic acids on the polyimide and on GC, which can form covalent anhydride linkages. Thus, plasma etching GC and then transferring it onto polyimide is likely to form these strong covalent bonds. The proposed mechanism for polyimide-GC bonding can be seen in Figure 9. Figure 9a shows a graphitic island (black -C) with a carboxylic acid functional group. If a polyimide precursor (green-C) were to come into close contact with the carboxylic acid (red-C), hydrogen bonding through carboxylic acid dimers could form at the interface as shown in Figure 9b. With enough energy input, the interaction between the carboxylic acids would allow the formation of anhydride bonds at the surface (red in Figures 9c and 9d).

Plasma etching and hydroxyl peak.—Significant changes due to plasma etching were seen in hydroxyl-carboxylic acid peak as well as hydroxyl-carboxylic acid dimer peak. The hydroxyl-carboxylic acid dimer can be seen in Figure 10. In IR spectra, these dimers are seen as a downshifted hydroxyl peak somewhere between 3300 cm⁻¹.

Table I. Summary of types of peaks of interest, bonding group, and algorithm for determination of their presence. Ambient energy corresponds to pre- and post-baking treatments and UV exposure during lithography.

| Peaks of Interest | Spectrum | Bonding Group | Enabling Condition | Metric Used |
|------------------|----------|---------------|-------------------|-------------|
| Hydroxyl         | 1. GC    | Carboxylic    | Ambient energy    | Width       |
|                  | 2. Polyimide | Acids       |                   |             |
|                  | 3. Interface Control |              |                   |             |
|                  | 4. Interface |            |                   |             |
|                  | 1. GC    | Carboxylic    | Ambient energy    | Not Significant Difference between samples |
|                  | 2. Polyimide | Acids       |                   |             |
|                  | 3. Interface |            |                   |             |
|                  | 4. Interface Control | Anhydride | | |
| Ether            | 1. GC    | Cyclic       | Ambient energy    | Minima, Width |
|                  | 2. Polyimide | Anhydride |                   |             |
|                  | 3. Interface |            |                   |             |
|                  | 4. Interface Control |            |                   |             |
| Ether            | 1. GC    | Non-Cyclic   | Annealing >200°C & O₂ plasma etching | Midpoint, Width |
|                  | 2. Polyimide | Anhydride |                   |             |
|                  | 3. Interface |            |                   |             |
and 2400 cm$^{-1}$, as well as a carbonyl peak between 1780 cm$^{-1}$ and 1720 cm$^{-1}$. Because various types of carbonyl peaks exist around 1700 cm$^{-1}$, the presence of the carbonyl peak alone cannot definitively prove the presence of carboxylic acid dimers. Thus, to confirm the presence of carboxylic acid dimers at the polyimide/GC interface, as well as any influence of oxygen plasma etching, the downshifted hydroxyl peak was used as the primary indicator.

Figure 10 shows that the hydroxyl-carboxylic acid peak exists on the bare GC before pattern transfer onto polyimide but has a much larger width when compared to any interface sample, implying that these carboxylic acids are distinct from those at the interface. This type of clear distinction, however, is not present when comparing the non-plasma etched and plasma etched interfaces. Interface samples etched at 750 mTorr and 120 secs have a larger width, up to 300 wavenumbers larger than the rest. This large increase in width is likely due to the unsteady plasma; at higher pressures, particularly those above 700 mTorr for the equipment and power used, the plasma generation is less stable. The variability in the plasma would then translate into variability in conformation of groups generated at the surface by the plasma. Since the width of the peak represents the degree of variability in the conformations of the functional groups, an increase in width with an increase in plasma variability is expected. Overall, there is no discernible trend with pressure or time, suggesting that plasma etching has a relatively uniform effect regardless of parameter within the range tested, and that this effect is not significantly different from samples with no plasma etching at all.
However, since a previous work has demonstrated that oxygen plasma etching of GC does induce carboxylic acids, it would be expected that the non-plasma etched interface sample would display the same hydroxyl-carboxylic acid peak as the bare GC. The substantially smaller peak width in non-plasma etched interfaces could be explained by the interface fabrication process itself using up carboxylic acids, thus decreasing the width. If this were the case, however, then some statistical difference between the plasma etched and non-plasma etched interface samples would still be expected. The nearly negligible statistical difference implies that either (a) the effects of plasma etching on the surface are less significant than other changes due to the fabrication process, or (b) the functional groups induced by plasma etching are immediately used up in another reaction when combined with polyimide. For example, the carboxylic acids generated during plasma etching could interact with the carboxylic acids native to the polyimide to create an anhydride.

**Plasma etching and anhydride peaks.**—The non-cyclic anhydride ether peak (formed from 1 carboxylic acid rather than the 2 used in the cyclic form) is not present at all in the GC before plasma etching nor in the non-plasma treated interface samples. Since anhydrides cannot be created by plasma etching process alone, their unexpected presence after plasma etching suggests that the functional groups (namely carboxylic acids) created on the GC allowed for the formation of anhydride bonds when polyimide was added. This chain of reactions further supports the hypothesis that plasma etching generates carboxylic acids that are then immediately used.

The high variability within the plasma etching samples effectively removes any trend with pressure or time. However, while some of the peak widths of the interface samples lie within the $2\sigma$ range (Figure 11) of the polyimide, the difference of at least 20 wavenumbers between the interface minima (Figure 11b) and the polyimide minima confirms that the non-cyclic anhydrides present at the interface are distinct from functional groups generated by plasma etching.

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**Figure 7.** Non-Cyclic Anhydride Peaks: Anhydride existence at the interface is likely a result of plasma etching, since this peak is not seen in either the glassy carbon or the non-plasma etched interface.

**Figure 8.** Cyclic Anhydride Peak: The change between the plasma etched and non-plasma etched interface suggests that cyclic anhydrides were formed from functional groups generated by plasma etching.
Effects of curing temperature.—Once the glassy carbon (GC) is plasma etched, as discussed in Effects of oxygen plasma etching section and shown in detail in our previous work, the GC microstructure has many acyl functional groups, including carboxylic acids, carbonyls, ethers, and hydroxyls at the termination of the graphitic sheet. At these functional groups, the carbon is able to interact with polyimide. When polyimide is added to the plasma etched GC at room temperature, hydrogen bonding between available polyimide and GC dicarboxylate occurs, creating favorable conditions for dianhydride formation. Anhydride formation from carboxylic acids also becomes more likely with higher input energy, and thus with increasing temperature. The results presented in Effects of oxygen plasma etching section demonstrate that samples etched at 500 mTorr had more consistent results; thus, the figures in the following section only show the interface samples etched at 500 mTorr or not etched at all.

Figure 9. (a) Glassy carbon with carboxylic acid functional group (b) Hydrogen bonding between polyimide carboxylic acids and glassy carbon carboxylic acids (c) dianhydride model between glassy carbon and polyimide (d) zoom of (c).

Figure 10. Hydroxyl-Carboxylic Acid Peak: The width of the OH peak is not detectable in the bare glassy carbon spectra and significantly different in the polyimide. Thus, even without plasma etching, unique carboxylic dimers are forming between the glassy carbon and the polyimide.

Figure 11. Non-cyclic anhydrides: Bare GC and the non-plasma etched interface control spectra had no peaks associated with non-cyclic anhydride region. The interface, however, clearly has these peaks, which differ from the polyimide peaks in width (a) and minima (b), indicating that plasma etching allowed for the generation of cyclic anhydrides. Higher variability in the midpoint in plasma etched samples is due to the randomness of the plasma etching process. '0 Torr' on the plot indicates no plasma etching.
Figure 12. Carboxylic Acid Measurements: Width prove carboxylic acids at the interface are distinct from polyimide and glassy carbon.

**Temperature and hydroxyl peak.**—In Figure 12, the hydroxyl peak around 2500 cm$^{-1}$ is shown. There is a clear difference between the polyimide, glassy carbon, and interface samples, in both width and midpoint, across all curing temperatures. While GC, polyimide and interface samples all do display a carboxylic acid dimer peak, the significant difference in width ($\sim$200 cm$^{-1}$) between the polyimide and interface and between the bare GC and interface samples ($>100$ cm$^{-1}$, $\sim$400 cm$^{-1}$ for most data points) and width suggests that the carboxylic acids at the interface are not the same as those native to the polyimide. Additionally, the overlap of the non-plasma etched and plasma etched samples implies that the presence of the dimers is not a function of plasma etching, but rather that of the interaction of the polyimide and GC at the interface. Since a decrease in width implies increased uniform bond conformations, the decrease in width at the interface implies that the bond between the GC and the polyimide includes carboxylic acid dimers with a very specific conformation.

Temperature and carbonyl peak.—Figure 13a shows that the minima of all plasma etched interface samples at all temperatures considered match the minima displayed by the polyimide alone, whereas the minima of the non-plasma etched interface samples aligns with that of the bare GC alone. In contrast, Figure 13b shows that the width of both the plasma etched and non-plasma etched samples aligns with that of the bare GC. The alignment of the non-plasma etched samples to the bare GC in both minima and width makes it challenging to distinguish clearly between bonds present at the interface and bonds native to the GC. However, the contrast of the plasma-etched samples (alignment with polyimide in minima and GC in width) is sufficient to indicate that a unique bond exists at the plasma etched interface that is not displayed in either the bare GC or the polyimide.

It is known that for polyimide, a minimum at 1777 cm$^{-1}$ can be the result of a carbonyl that is indicative of a dihydride bond. The match of the plasma etched interface samples’ minima to that value thus suggests the presence of an anhydride at the interface as well. Additionally, the increasing width of the carbonyl peak with increasing temperature in the plasma etched samples is a trend that suggests formation of anhydrides is more significant at higher curing temperatures, provided the sample has been plasma etched.

**Temperature and anhydride peaks.**—Unlike carbonyls, which are present in bare glassy carbon (GC), polyimide, and at the interface, anhydride peaks are only detectable in the polyimide and at the interface. Additionally, there is a clear statistical difference between those anhydrides native to the polyimide and those at the interface. Since a decrease in width implies increased uniform bond conformations, the decrease in width at the interface implies that the bond between the GC and the polyimide includes carboxylic acid dimers with a very specific conformation.

Figure 13. Carbonyl Peak Measurements: Measurements at 1777 are indicative of an asymmetric carbonyl peak which can be part of an anhydride bond. Differences are not conclusive without the presence of an anhydride peak.

Figure 14. Cyclic anhydride: The minima shows that the interface does change significantly at temperatures above 200°C, high enough to imply anhydride formation. The width shows that there is no carbon-native anhydrides, and again at higher temperatures the trend supports the distinction between the polyimide anhydride and the plasma etched interface anhydride. It is therefore likely that a combination of higher curing temperature and plasma etching is required for unique anhydride generation at the interface.
that the interface has a different anhydride vibration in the 1275 cm\(^{-1}\) region. Moreover, the fact that the interface samples are more discreet from the polyimide with increasing temperature is itself significant. The downshift in minima of the plasma etched samples indicates that some reaction occurs to form more stable bonds. The observed downshift begins at 200°C temperature at which anhydrides form from carboxylic acids,\(^3\) which implicates new anhydride formation at the interface as the cause of the downshift at higher temperatures.

Unlike the cyclic anhydrides, the minima of the non-cyclic anhydrides (Figure 15) show a clear difference from the polyimide samples. However, though there is no clear trend in the plasma etched interface samples, there is a statistically significant change in variability between different plasma etch parameters as the curing temperature increases. In the non-cyclic anhydride region, the plasma etched samples reach minimum variability in width at 200°C. This suggests that the bonds become more organized and take on the same or similar conformations that vibrate at the same frequency. Because the temperature at which the variability converges is close to the temperature at which anhydride formation between two carboxylic acids, we can conclude that at least some the bonds generated at the interface are anhydrides.

**Scanning electron microscopy images.**—Scanning Electron Microscopy (SEM) was used to visually support the findings that plasma etching and higher curing temperatures create strong bonding between GC electrodes and polyimide substrate. Figure 16a shows the topography of a GC electrode and polyimide at 100 times magnification; the bright line across the images indicates a clearly formed interface between the two materials. In Figure 16b, the interface is shown again at 17,000 times magnification. In this image, the GC and polyimide microstructures can be seen more clearly. The GC, farther from the interface, has both smooth and porous areas; the smooth areas are likely the areas where the oxygen plasma did not interact with the surface. In the GC porous areas, the oxygen plasma was able to break through the smooth surface and expose the more porous interior portions of the electrode. The polyimide structure, visible at the bottom of the image, appears rough but not porous. However, closer to the interface, the topographic differences between the two materials blends together, suggesting local material dispersal across the GC/polyimide boundary.

Figures 16c and 16d show a further magnified view of this stretch of interface at 50,000 times magnification and 75,000 times magnification respectively. The dashed interface lines in 16c and 16d delineate where the glassy carbon meets the polyimide. Here, the high
magnification shows the sheets of glassy carbon interlacing with the chains of polyimide. The linking between the chains and sheets supports the findings that the two materials form new and unique intermolecular bonds at the interface.

Conclusions

Glassy carbon (GC) and polyimide are materials with very significant potential in the electrical and electrochemical sensor industry, especially when used together to form a composite structure. However, without a firm knowledge and understanding of how the two materials interact on a molecular level, the interface will always be assumed to be the weakness of any polyimide/GC composite device. The findings of this study will have an impact on our understanding of the mechanical robustness of these composite structures.

In summary,

1. Detailed statistical analysis of individual IR vibrations depicted in the IR spectra at the interface of 128 samples was carried out to determine if peaks observed in the IR of the interface were statistically significantly different from those in the polyimide and/or the GC IR. A significant difference (95% confidence) was seen in peaks associated with hydroxyls on carboxylic acids and ethers in cyclic and non-cyclic anhydrides.

2. It was found that both the plasma etching of the GC and the fabrication process of the polyimide/GC devices itself generated hydroxyl-carboxylic acid peaks, implying the presence of carboxylic acid dimers.

3. Additionally, hydroxyl-carboxylic acid peaks found at the interface were distinct from peaks found in the GC and the polyimide alone across all curing temperatures.

4. Cyclic anhydrides are also formed naturally at the GC/polyimide interface, as consequence of polyimide deposited on GC microstructures. However, the downshift in the peak that indicates cyclic anhydride formation only occurred at temperatures higher than 200 °C.

5. Non-cyclic anhydrides can be formed at the interface when energy input is high.

6. Energy input is reliably high enough to form these non-cyclic anhydrides when the polyimide is cured about 200 °C, when the GC is plasma etched prior to polyimide application, or both.

7. The decrease in sample variability with increasing curing temperature also implicates more reliable formation of non-cyclic anhydrides.

8. SEM of interface confirms the formation of a well-bonded interface.

We submit that, taken together, these findings confirm that the lithography processes used to fabricate GC/polyimide composite devices allows for strong covalent bonding between these two materials that can be further maximized through optimal curing and plasma etching conditions.

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