Photo-oxidation of polymer-like amorphous hydrogenated carbon under visible light illumination

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Abstract

Amorphous hydrogenated carbon (a-C:H), a polymer-like network typically synthesized by plasma chemical vapor deposition, has long been known to exhibit optical absorption of visible light ($\lambda > 400$ nm). Here, we report that this absorption is accompanied by rapid photo-oxidation (within minutes) that behaves in most respects like classic polymer photo-oxidation with the exception that it occurs under visible light illumination rather than ultraviolet illumination. Lower plasma power during deposition produces a-C:H that is less crosslinked, is less absorptive, has longer photoluminescence lifetimes, and has a slower photo-oxidative degradation than a-C:H deposited at higher plasma power. The optical gap of the material deposited here is ~ 2.5 eV, and we correspondingly observe photo-oxidation at photon energies of 2.7 and 3.1 eV. A reduced photo-oxidative response is observed at sub-gap energies, suggesting that defect states or absorption tails enable absorption at lower energies. The photo-oxidation depends on both the total accumulated dose as well as the intensity of the illumination,

suggesting either a transport limitation of O₂ in the a-C:H or a complex reaction pathway. Under typical laboratory lighting conditions, plasma CVD a-C:H continues to photo-oxidize for more than 20 weeks, demonstrating that any characterization of the long-term behavior of a-C:H under use conditions requires control of not only atmospheric conditions but also ambient lighting environment.

Keywords: Amorphous hydrogenated carbon; plasma polymer; photo-oxidation; visible light; aging

1. Introduction

Amorphous hydrogenated carbon (a-C:H) films have attracted attention for a number of decades.¹⁻⁵ The most common method of producing a-C:H is through the decomposition of a hydrocarbon in H₂ plasma (chemical vapor deposition, or CVD), resulting in the formation of a polymer-like network of hydrogen and carbon as a growing film. The ability to deposit hard, chemically inert, and adherent films from inexpensive hydrocarbon feedstocks has made them attractive candidates as protective, tribological, biocompatible, and insulating coatings. One of the disadvantages of plasma CVD a-C:H (and plasma CVD organic materials in general) is their propensity to age over time, leading to a change in physical and chemical properties.⁶⁻⁹ Understanding and controlling the aging behavior are critical to utilizing a-C:H materials in practical applications.

The thermomechanical stability, low film stress, and low average atomic number make plasma CVD a-C:H suitable ablaters for high energy density and inertial confinement fusion experiments at large laser facilities (e.g., the National Ignition Facility in Livermore, California

and the Omega Laser Facility in Rochester, New York). Ablators fabricated from a-C:H have been central to efforts in creating laboratory fusion for several decades.¹⁰⁻¹³ These ablaters have stringent requirements on the total amount of acceptable oxygen as well as spatial variations in oxygen content,^{14,15} motivating us to understand of the oxidation pathways of a-C:H.

One such pathway is the photo-oxidative pathway common to many polymers under ultraviolet (UV) illumination ($\lambda < 400$ nm). For most hydrocarbon plastics, this pathway is activated by UV-induced bond cleavage, followed by the creation of free radicals which then react with ambient O₂ to form carbonyl or hydroxyl bonds (e.g., aldehydes, ketones, carboxylic acids, alcohols).¹⁶⁻¹⁸ We recently reported that plasma CVD synthesized a-C:H photo-oxidizes when illuminated by lower energy light in the visible range ($\lambda=405$ nm).¹⁹ Despite decades of study on the optical and structural characteristics of a-C:H, little is known about their photochemistry.

In this study, we report on the unique spectral and intensity response of the photo-oxidation of a-C:H as well as the role of plasma power in generating photoactivity in plasma CVD a-C:H. Our results indicate that future studies on the aging behavior of plasma CVD a-C:H must control for ambient light exposure and that caution is warranted when interpreting previous literature on plasma polymer aging if the lighting environment is not reported. For the remainder of this paper, we refer to plasma CVD a-C:H as “glow discharge polymer” (GDP) for consistency with previous literature regarding ablaters and to emphasize the polymer-like nature of this material. However, it should be understood to refer to a-C:H as often found in the literature.

2. Materials and Methods

2.1. *Synthesis of plasma CVD a-C:H (GDP)*

GDP was synthesized in a custom-built inductively-couple plasma reactor.^{12,20} The chamber was maintained at 0.1 Torr while *trans*-2-butene (95%, Matheson Tri-Gas) and H₂ (ultra-high purity grade, Air Liquide) flowed into the chamber at flowrates of ~0.1 sccm and 10 sccm, respectively. The plasma frequency was 43.015 MHz and the power was 13.5 W, unless otherwise specified. Additional details on the reactor configuration can be found elsewhere.^{12,20} Following deposition, all samples were immediately annealed for 26 hours under flowing N₂ at 300 °C. Deposition substrates were either potassium bromide (KBr) or fused quartz.

2.2. *Spectral characterization*

Samples on KBr substrates were characterized by Fourier transform infrared spectroscopy (FTIR, Thermo-Fisher Nicolet iS10). Transmission spectra were gathered at a resolution of 0.482 cm⁻¹ and peak area integrations were performed with OMNIC software. Samples on quartz substrates were characterized by ultraviolet/visible light absorption (UV-Vis, Ocean Optics USB2000+XR1 spectrometer with DH-2000-BAL deuterium/halogen light source) with 1 ms integration time and averaging over 1000 scans. Optical absorption coefficients were determined by utilizing Beer's Law and correcting for the sample thickness. Film thickness on the quartz substrates was determined by spectral reflectometry (FilmMetrics F20). Photoluminescence (PL) measurements were performed with an excitation wavelength of $\lambda = 405$ nm on a home-built apparatus capable of capturing the emission spectrum and lifetime. It has been described in detail previously.^{21,22} PL decay was characterized by measuring emission in the $\lambda=500$ -550 nm range.

2.3. Real-time photo-oxidation

Real-time photo-oxidation data were gathered by collecting FTIR spectra while simultaneously illuminating a sample with a light emitting diode (LED, ThorLabs, M-series). The LEDs had a spectral bandwidth of 10 nm (FWHM) around their nominal wavelength with the exception of the green LED which had a spectral bandwidth of 20 nm (FWHM). LED intensity (I) was measured with a silicon photodiode power meter (ThorLabs, S120C). The sample was mounted in a flow cell with a ~1 mm spacer (Harrick Scientific, DLC-M25). One window in the cell was uncoated KBr while the other window was coated with the GDP sample to be analyzed. The sample was mounted such that the GDP faced the flow channel while dry air (Air Liquide, Ultra Zero grade) flowed through the cell.

3. Results and Discussion

We will briefly comment on the role of precursor materials and thermal annealing in synthesizing GDP. *Trans*-2-butene is the hydrocarbon precursor which flows into the plasma CVD reactor, where it decomposes in H₂ plasma to form reactive fragments. These fragments recombine at a substrate to form a growing deposit. The identity of the hydrocarbon precursor is immaterial; GDP formed from an aromatic precursor (divinylbenzene) is essentially indistinguishable from that formed by *trans*-2-butene as characterized by UV-Vis, PL, and FTIR (Figures S1-S3, Supplemental Information). This observation is consistent with literature reports that the properties of a-C:H are independent of the identity of the precursor hydrocarbon when the reaction occurs in H₂ plasma.^{5,23} The results presented in this study are therefore likely to

hold for a wide variety of precursor and deposition conditions for a-C:H, with differences in degree and not kind.

Thermal annealing of GDP is necessary prior to investigating its photo-oxidation behavior because the as-deposited material contains residual radicals which spontaneously oxidize in the presence of ambient O₂. This reaction is common to nearly all plasma-deposited hydrocarbon materials. The spontaneous oxidation is effectively quenched by thermally annealing GDP.^{24,25} All the GDP samples synthesized for this work were thermally annealed at 300 °C for 26 hours under flowing N₂ so that photo-oxidation would not be conflated with spontaneous oxidation.

Figure 1 shows the effect of 600 seconds of exposure to a blue LED ($\lambda = 405$ nm, $I \sim 500$ mW/cm²) under various atmospheres as characterized by FTIR. The reaction occurs only in the presence of O₂ and results in the formation of carbonyl (~ 1700 cm⁻¹) and hydroxyl (~ 3350 cm⁻¹) groups. Careful inspection of the spectra also reveals that the photo-oxidized GDP has a slightly stronger CH₃ stretching contribution (2955 cm⁻¹), indicating scission of the cross-linked carbon network and the formation of terminal methyl groups. These observations are consistent with classical polymer photo-oxidation, where a photon absorption event breaks a bond and creates a carbon-centered radical, which then reacts with O₂ in the atmosphere to eventually form aldehydes, ketones, carboxylic acids, and/or alcohols. While photo-oxidation of plasma polymers under UV irradiation have been previously reported,²⁶ the distinguishing feature of the photo-oxidative effect in a-C:H observed here and in our prior report¹⁹ is that it occurs with a relatively low energy $\lambda = 405$ nm photon.

Figure 1: FTIR spectra of GDP after 600 seconds of illumination ($\lambda = 405$ nm, $I \sim 500$ mW/cm²) in various atmospheres. Pre-exposure spectrum is shown for reference. The asterisks (*) mark the location of the hydroxyl (3350 cm⁻¹) and carbonyl (1700 cm⁻¹) peaks.

We previously reported that the photoactive defects leading to oxidation are distinct from residual free radicals (sourced from the plasma deposition) in GDP because thermal annealing tends to increase, rather than decrease, the photoactivity of GDP. The strength of the photoactivity, as measured by PL, is correlated with the rate of photo-oxidation. The PL behavior is consistent with a phenomenon known as quasi-continuum PL (QCPL), which arises from interaction among a high density of interacting absorbers.²² Because the PL is present in the as-deposited GDP (prior to thermal annealing), we hypothesized that plasma parameters may play a role in the formation of photoactive absorbers.

The nominal plasma power for the GDP deposited in this work was 13.5 W. We also synthesized GDP at higher (50 W) and lower (3.7 W) powers to examine the effect of plasma parameters. The FTIR spectra in the C-H stretching region in Figure 2 show that higher

deposition power is associated with peak broadening, suggesting a greater variability in local chemical environments caused by greater plasma-induced fragmentation of the precursor and/or plasma-surface interactions with the growing film. A key structural difference can be observed by examination of the peak at 2955 cm^{-1} , which is strongest in the sample deposited at the lowest power. This peak is assigned to the CH_3 stretch in GDP and occurs in non-network forming terminal methyl groups. The increased strength of this stretch indicates that the GDP deposited at 3.7 W has a lower degree of cross-linking.^{10,27}

Figure 2: FTIR spectra in the C-H stretching region of GDP deposited at different powers. The lowest power deposition has the strongest CH_3 contribution (2955 cm^{-1}), indicating a lower degree of crosslinking.

The time dependence of the PL decay is shown in Figure 3a. The short lifetime of the PL ($\sim 10\text{ ns}$) is a hallmark of QCPL and is caused by a high density of interacting absorbers. The photoluminescence does not decay as a simple exponential; the decay is best modeled as a log-normal distribution of lifetimes following a procedure we described earlier.²² The modeled

lifetime distributions are shown in Figure 3b and range from 10^{-2} ns to 10^2 ns. Higher deposition power is correlated with a faster decay times. The faster decay of the GDP deposited at higher plasma power can be attributed to a higher density of interacting absorbers, a conclusion also supported by the PL emission spectra (Figure S4, Supplementary Information). This is consistent with the FTIR spectra in Figure 2, where higher deposition power was associated with structural characteristics indicative of greater plasma-induced crosslinking in GDP. The PL emission spectra (Figure S4, Supplementary Information) are extremely broad, another hallmark of QCPL and an effect previously seen in a-C:H.²⁸

Figure 3: (a) PL decay for GDP deposited at different plasma powers showing multi-exponential decay. PL signal is normalized to the maximum signal which occurs near $t = 0$ ns. (b) Lifetime distribution of PL obtained by fitting the decay curves to an ensemble of lifetimes with continuous log-normal distribution.

The transmission UV-Vis measurements in Figure 4 show that GDP absorbs light well into the visible region, typical for a-C:H.²⁹ These absorption curves are corrected for the sample thickness as determined by spectral reflectometry. The increase in the density of absorbers with deposition power indicated by the PL data is consistent with the UV-Vis transmission

measurements; higher plasma power during deposition is associated with increased absorptivity of GDP.

Figure 4: Absorption coefficient as measured by UV-Vis for GDP deposited at different plasma powers.

Photo-oxidation of the GDP deposited at different plasma powers was tracked in real time by simultaneously illuminating GDP with an LED ($\lambda = 405$ nm, $I = 6.5$ mW/cm²) while collecting FTIR spectra. Because the broad hydroxyl stretch at 3200-3700 cm⁻¹ is relatively isolated from other peaks, we utilized the integrated area under this peak to semi-quantitatively analyze the extent of photo-oxidation. To account for thickness variations among samples, the area under the hydroxyl peak was normalized to the area under the peak corresponding to the hydrocarbon backbone of GDP (2750-3100 cm⁻¹). The photo-oxidation of the samples deposited at different powers is shown in Figure 5. The spectral characterization in Figures 3-4 indicates that higher plasma power increases the density of absorbers in GDP; the photo-oxidation data also show that higher plasma power was associated with a faster rate of photo-oxidation. In

particular, GDP deposited at 3.7 W has lower absorptivity and a lower density of absorbers than GDP deposited at higher powers, which is in turn correlated with the slower rate of photo-oxidation observed in Figure 5. The rate of photo-oxidation is similar for the GDP deposited at 50 W and at 13.5 W, suggesting that there may be a saturation effect at higher deposition powers.

Figure 5: Photo-oxidation ($\lambda = 405$ nm, $I = 6.5$ mW/cm²) as measured by OH peak area in FTIR spectra.

Perhaps the most striking feature of GDP photo-oxidation is that it occurs under visible illumination, in contrast with the UV illumination commonly associated with polymer photo-oxidation.¹⁶ This is a direct result of optical absorption since photo-oxidation begins via absorption of a photon. The optical absorption behavior of a-C:H has long been known to be unlike most hydrocarbon polymers: rather than a sharp band edge in the UV, there is a broad shoulder extending from the UV out through the visible region. It is not clear what the actual photoactive group or groups leading to absorption in a-C:H are, but both the broad absorption and QCPL behavior suggest an ensemble of interacting absorbers. For example, models that rely

on $\pi \rightarrow \pi^*$ transitions to explain absorption in behavior in a-C:H require a high density of clustered sp^2 bonded islands.^{3,4,30}

Despite the complexity of the physical processes leading to optical absorption in a-C:H, the optical gap has been experimentally observed to vary between 1-2 eV.^{3,4,30} This remarkably small value corresponds to light with wavelengths $\lambda = 690$ -1240 nm. Following the standard procedure of Tauc,³⁴ we estimate the optical gap of GDP to be ~ 2.5 eV (corresponding to $\lambda = 500$ nm).

Combined with the observation that GDP photo-oxidizes at $\lambda = 405$ nm, the small optical gap and absorption of visible light suggested that photo-oxidation can occur at wavelengths of even lower photon energy. We therefore investigated the spectral response of GDP photo-oxidation at wavelengths up to 625 nm using a series of LED sources. The photo-oxidation at various illumination wavelengths is shown in Figure 6a. For each experiment, the intensity was fixed at 13 mW/cm^2 . The GDP photo-oxidized under illumination until at least $\lambda = 530$ nm, well into the visible region. No trend can be discerned from the data from illumination at $\lambda = 625$; if photo-oxidation occurs at this wavelength, it is beyond the sensitivity of our measurement.

The slope for each curve in Figure 6a is linear in the region where the dose is less than 20 J/cm^2 (note the data do not appear linear in Figure 6a due to the semilog scale). Figure 6b shows this initial slope, which is a measure of photo-oxidation rate (in arbitrary units), as a function of photon energy. The sharp change in photo-oxidation rate between $\lambda = 530$ nm (2.7 eV) and $\lambda = 455$ nm (2.3 eV) is consistent with the estimated optical gap of 2.5 eV, shown as a dashed line in Figure 6b. Sub-gap photo-oxidation at $\lambda = 530$ nm is indicative of the fact that GDP contains defects such as dangling bonds that are common to plasma polymers. The disordered, amorphous

nature of a-C:H can also lead to Urbach absorption tails which extend into the gap, which can also contribute to sub-gap photo-oxidation.³¹⁻³³ While deposition conditions can affect the size of the optical gap, gaps of 1-2 eV in a-C:H as reported in the literature suggest that photo-oxidation under visible illumination will be common to other forms of a-C:H.

Figure 6: (a) Spectral response of photo-oxidation (for fixed illumination intensity of $I = 13 \text{ mW/cm}^2$), as measured by OH peak area in FTIR spectra. (b) Initial slope of photo-oxidation rate as a function of photon energy. The dashed line represents the estimated optical gap in GDP based on a Tauc analysis.

The photo-oxidation does not have a simple dose-dependent behavior. Figure 7 shows the photo-oxidation of GDP under $\lambda = 455 \text{ nm}$ illumination at three different intensities: 13 mW/cm^2 , 1.3 mW/cm^2 , and 0.13 mW/cm^2 . The intensities were reduced through the use of neutral density filters. Note that the horizontal scale is the accumulated energy dose, which is the product of intensity and illumination time. Because the intensities were separated by two decades, the experiments were performed at very different time scales (2 hours at 13 mW/cm^2 , 16 hours at 1.3 mW/cm^2 , and 40 hours at 0.13 mW/cm^2) so that the total doses would overlap. Long exposure at low intensity causes the fastest photo-oxidation as a function of dose. This may

be due to the transport limitations of O_2 through the GDP; low-intensity, long-time exposures may allow for sufficient transport time for O_2 through the $\sim 1.5 \mu\text{m}$ thick GDP film.³⁵ The reaction mechanism may also have a non-linear dependence on intensity.

Figure 7: Intensity dependence of photo-oxidation upon illumination at $\lambda=455 \text{ nm}$, as measured by OH peak area in FTIR spectra.

The photo-oxidation behavior of the GDP under visible light illumination suggested that even ambient lighting can play a role in the aging of a-C:H materials such as GDP. To test this hypothesis, we placed a GDP film in a dry air chamber and exposed it to $I \sim 0.15 \text{ mW/cm}^2$ illumination from a fluorescent lamp, conditions typical of a well-lit laboratory. The spectral output of a fluorescent lamp ranges predominantly from 400 nm to 630 nm, containing the spectral range determined to cause photo-oxidation in Figure 6. The FTIR spectra shown in Figure 8 were gathered periodically over the course of more than 20 weeks. Significant photo-oxidation was observed in this sample, while a control sample placed in the same environment but shielded from light showed little change (not shown).

As photo-oxidation proceeds, the peaks between 2750-3100 cm^{-1} decrease in intensity as CH bonds are replaced by carbonyl ($\sim 1700 \text{ cm}^{-1}$) and hydroxyl bonds ($\sim 3350 \text{ cm}^{-1}$). While the incorporation of oxygen results in the formation of these well-defined species, other byproducts are not as easy to identify. A wide variety of overlapping peaks evolve over the entire fingerprint region (500-1500 cm^{-1}), corresponding to the formation of different types of C-C bonds.³⁶ Specific peak assignments are not possible due to the broadness of this feature. Quantification of the photo-oxidation by simple integration of the OH peak was not feasible as the stretch broadened and was convoluted with the remaining CH peak. After this long photo-oxidation period it can be seen that the OH peak has substantial contribution between 3500-2400 cm^{-1} ; this unusually broad OH stretch is typical of hydrogen bonding between carboxylic acid groups.³⁷ As in Figure 1, an increase in the terminal CH_3 contribution ($\sim 2950 \text{ cm}^{-1}$) again indicates chain scission is part of the oxidation process.

Inspection of the spectra also shows that the GDP continued to photo-oxidize even after 20 weeks of exposure to ambient light. The rate of change slows at long times (many months). The lack of significant oxidation observed in the control sample placed in a dark, dry air environment shows that the oxidative aging of GDP can be almost entirely attributed to a photo-oxidative effect. Therefore, any future studies examining aging effects of a-C:H must consider the ambient lighting environment as an important variable.

Figure 8: FTIR spectra of GDP exposed to ambient light from a fluorescent lamp in a dry air environment over the course of 20 weeks.

4. Conclusion

Like other plastics, GDP reacts with O_2 in the atmosphere when exposed to light that excites electrons across the optical gap. UV light is required for this process in most polymers, but the unique optical absorption properties (due to a small optical gap, presence of electronic defects such as dangling bonds, and possible contribution of an Urbach tail) of a-C:H allow visible light to excite these transitions. We observed photo-oxidation at wavelengths as long as $\lambda = 530$ nm, with photo-oxidation being most pronounced at photon energies above the estimated optical gap of 2.5 eV. The lack of a simple dose-dependence suggests that the reaction mechanism is either complex or depends on the transport of O_2 through the material. Thus, GDP can undergo photo-oxidation even under ambient lighting conditions and indeed can be a major contributor to the long-term aging of so-called plasma polymers.

Since GDP is simply a-C:H synthesized by plasma decomposition of a hydrocarbon, we expect that these results will be applicable to a a-C:H synthesized by other means (e.g., sputtering) so long as the optical gap is in the visible light regime. In the case of plasma-synthesized a-C:H such as GDP, the deposition conditions affect the molecular structure of GDP, which in turn are linked with the PL and photo-oxidation behavior. The processing-structure-property relationships already explored for a-C:H materials therefore extend to photo-oxidative aging. These relationships may be complex, as our results show that increasing the plasma deposition power increases crosslinking, photoactivity, and photo-oxidation but that these trends may saturate at higher powers. Efforts to control photo-oxidative aging as a degradation mechanism in a-C:H may therefore involve tuning fabrication parameters and tradeoffs between other material properties. For example, the GDP deposited at 3.7 W photo-oxidized at a slower rate but also had greater terminal methyl content, indicating that it likely has lower thermal and mechanical stability.

Several studies have reported on the aging properties of plasma polymers, including a-C:H, but it does not appear that these previous reports appreciated the impact that ambient light can have on the oxidation of these materials.^{7,8,26,38-41} Our results show that ambient light management is an important factor and should be considered for future studies of a-C:H aging.

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