

In-situ functionalization of tetrahedral amorphous carbon by filtered cathodic arc deposition

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Abstract

Modification of surface chemistry of carbon based nanomaterials is often necessary in order to meet application specific demands. Literature provides a variety of different post-fabrication treatments, such as acid, oxidizing plasma and heat treatments. These methods offer modification of some surface properties, but their specific effects to materials surface chemistry is only vaguely reported. Thus, in order to meet the application specific demands via carbon nanomaterials surface functionalization, it is necessary to understand the effects of treatments used in detail. Here we report an in-situ method to functionalize tetrahedral amorphous carbon (ta-C) thin films by introducing high purity oxygen into the vacuum chamber during the film fabrication at the end of the deposition process, effectively changing the surface chemistry. Additionally, we report and compare the effects of post-treatment with nitric acid and oxygen plasma to untreated and in-situ functionalized tetrahedral amorphous carbon thin films. Using x-ray absorption spectroscopy (XAS), we show that introducing oxygen during deposition decreases the sp^2 content of the surface, accompanied by an increase in carboxyl-like functionalities. Subsequent oxygen plasma further decrease the sp^2 and ketone/aldehyde content and increase the amount of carboxyl groups. The same trends are observed with reference ta-C under oxygen plasma treatment. For both materials, a concentrated nitric acid treatment has only a subtle effect, which follows the same trend as the oxygen plasma treatment. Using this knowledge, we can selectively produce materials with higher functional group surface loading than has been reported earlier, paving the way for application specific material fabrication.

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Introduction and experimental

Modifying a material's surface chemistry to better meet the application requirements is done in a variety of applications such as sensing¹, energy storage and harvesting^{2,3}, surface wettability^{4,5}, covalent attachment of enzymes and antibodies⁶, cell viability⁵ etc. We have previously studied the effects of surface chemistry on sensing where electrochemical reactions are tightly connected with the surface functionalization of the materials⁷⁻¹². These studies also evidenced that even a short concentrated nitric acid treatment has a marked effect on the sensing performance of carbon nanomaterials¹³. Thus, understanding the effects of different post-fabrication processes on materials surface chemistry and their associated effect on the observed properties are of very high importance. Here, we show the effects of some post-fabrication treatments and in-situ oxygen doping by introducing high-purity oxygen at the end of the filtered cathodic vacuum arc (FCVA) deposition process, resulting in a surface functionalization process of the tetrahedral amorphous carbon (ta-C) thin films.

Detailed description of the film fabrication process is published elsewhere¹⁴. Briefly, ta-C films were deposited on boron-doped <100> Si wafers (n-type) with <0.005 Ω cm resistivity (Sievert Wafer, Germany). Direct current magnetron sputtering was used to deposit a 20 nm Ti adhesion layer on the Si wafer after which a 7 nm ta-C top layer (550 pulses) was deposited with FCVA. Two series of ta-C films were made. The first series are reference films (labeled ta-C) that were made without oxygen in the fabrication chamber, and the second series (labeled ta-C + O₂) were deposited so that during the last 2 nm (150 pulses) 99.9999% pure O₂ gas was bled into the chamber with a flow of 35 sccm (O₂ flow decreased the vacuum to ~E-4 Torr which could result in a film-thickness slightly less than the nominal 2 nm that 150 pulses would have resulted in in E-7 Torr range). During the depositions the films were rotated to ensure homogeneous deposition over the film area (rotational velocity 17 rpm).

Prior to X-ray absorption measurements a sample from each batch was treated with 50 W RF plasma with 20 sccm O₂ flow for 1 minute (Gatan Solarus Model 950) at 15 mTorr vacuum and another sample from both batches was treated with 10 ml of concentrated nitric acid (70%, purified by redistillation, Sigma Aldrich) for 5 minutes by submersion, after which they were rinsed by submerging in 200 ml of deionized water (> 18 M Ω) three times, with fresh deionized water for

each subsequent submersion. After rinsing the sample was tilted perpendicular to working surface and its side touched to a kimwipe to drain excess water from the surface. The sample was left under the fume-hood to dry until the surface was visually observed to be dry (about 5 minutes).

Data from the ta-C and ta-C + O films and their nitric acid and oxygen plasma treated samples were acquired at a 55° incidence angle (the “magic angle” at which the absorption intensity does not depend on the molecule orientation¹⁵) of X-ray incidence using the bending magnet beamline 8-2 at the Stanford Synchrotron Radiation Lightsource (SSRL). Beamline 8-2 is equipped with a spherical grating monochromator, operated using $40 \times 40 \mu\text{m}$ slits corresponding to a resolution of around 0.2 eV. The spot size at the interaction point was around $1 \times 1 \text{ mm}^2$ and a flux of 1×10^{10} photons/sec at which beam damage is not noticeable even for extended exposure. The X-ray energy for the Carbon 1s, Titanium 2p and Oxygen 1s edges were scanned from 260 eV to 350 eV, 450 eV to 490 eV and 520 eV to 580 eV, respectively. The data were collected in total electron yield (TEY) and Auger electron yield (AEY) modes using the drain current amplified by a Keithley picoammeter and a Cylindrical Mirror Analyzer (CMA) operated with a Pass Energy of 200 eV and set to record the main Auger line for the various edges, respectively. The incoming flux was recorded using a nickel grid with Au sputtered film.

Results, discussion and conclusions

The results of the two different films and their nitric acid and oxygen plasma treated counterparts are shown in Figure 1a and b (TEY) and Figure 2a and b (AEY). The TEY spectra show that the reference ta-C surface contains several oxygen functionalities of which the keto-type groups appear to be most abundant. This is consistent with recent computational studies showing that when small amounts of oxygen are incorporated close to amorphous carbon (a-C) surfaces the keto groups are the most abundant surface species^{16,17}. It was also shown in the same study that, if the temperature of the system is increased, CO starts to form due to bond breaking reaction of carbon and oxygen leading to a loss of material from the surface region¹⁶. The present results clearly show that when the oxygen surface loading is significantly increased by introducing oxygen to the deposition chamber during film fabrication, it results into a marked increase in the carboxyl functional groups and decrease in the keto-type groups present on the surface in comparison to the reference sample. The increase in the carboxylic groups is nearly comparable to the post-fabrication oxygen plasma treatment in the case of the reference ta-C. In fact, the surface containing the largest amount of oxygen functional groups is realized by further treating the ta-C + O₂ sample with oxygen plasma. Additionally, the already clearly amorphous (wide sp² π* peak and broad spectral shape in general) carbon matrix loses some of the sp² π* contribution. It is likely that this decrease is connected to the forced-increase of oxygen in the system leading to an increase in the bonding between the carbon and oxygen. The above observations are more dominant in the surface according to the AEY shown in Figure 2a and b. At the very top surface (that AEY probes), the intensity increase of the carboxyl group compared to the intensity of the sp² π* peak is even more pronounced as is the intensity decrease in the sp² π* peak.

Some of the observed surface oxygen loading can be attributed to a marginally exposed fraction of the Ti adhesion layer (as shown in Figure 4). However, both the C1s (TEY and AEY) and the O1s spectra results strongly support the conclusion that the total carbon-oxygen bonding is increased during deposition as well as the oxygen plasma treatment. This subsequently results into decrease in the keto-type of functional groups and marked increase in carboxylic groups. The latter increase is especially evident from the O1s spectra (as shown in Figure 3)¹⁸.

The decrease in sp^2 bonded carbon and the associated increase in carbon-oxygen functionalities, is expected to arise from the surface modification due to the oxygen during the deposition, which (i) introduces highly energetic oxygen bombardment of the surface and (ii) provides oxygen to react with the newly formed reactive dangling-bonds at the surface. We have seen that the oxygen plasma both induces defects that interrupt the sp^2 network and also promotes formation of carbon oxygen functionalities. The sputtering nature of the oxygen plasma is expected to also introduce localized defects which in turn exposes less stable carbon sites at the edges of the local sp^2 defect that are prone to reaction with oxygen. We hypothesize that the introduction of the high-purity oxygen gas into the deposition chamber induces collisions between these reactive carbon sites resulting in forced carbon-oxygen bonding at the sample surface. It is also likely that due to the high kinetic energy involved in this process some of the surface carbon atoms could be sputtered away as CO or CO₂¹⁶, although the distinction between that process with that of regular detachment processes upon bond formation is outside the scope of this study. This, together with the disordering induced by the energetic incoming oxygen species, would result in the observed decrease in the sp^2 bonded carbon, which is predominantly located at the surface region¹⁹. The surface sensitive nature of the process is further supported by the AYE data coming mainly from the surface region where the above described changes are more pronounced than in the TEY data which have a deeper probing depth. It is also interesting to note that according to a very recent computational study¹⁷, carboxylic groups exhibit the smallest adsorption energy among various oxygen based functionalities on different local reactive sites on a-C surfaces. Thus, it appears that in order to functionalize a-C surfaces preferentially with carboxyl groups a combination of reactive oxygen and high kinetic energy might be necessary. Thus, the realization of this *in-situ* surface functionalization methodology is significant, as it provides us with additional degrees of freedom over more traditional post-fabrication treatments such as acid-, ozone and/or plasma treatments. To further explore the possibilities of this *in-situ* functionalization scheme, follow-up studies with other gases such as Ar, N, H, CO₂ and H₂O should be carried out. Computational studies augmented by machine learning will also be combined with the experimental investigations to obtain a more in-depth understanding of the phenomena taking place in the systems under investigation. With the results presented here, it is expected that by selecting and tuning the gas type and flow rate it is possible to alter the resulting materials surface functionalization to meet specific demands of applications.

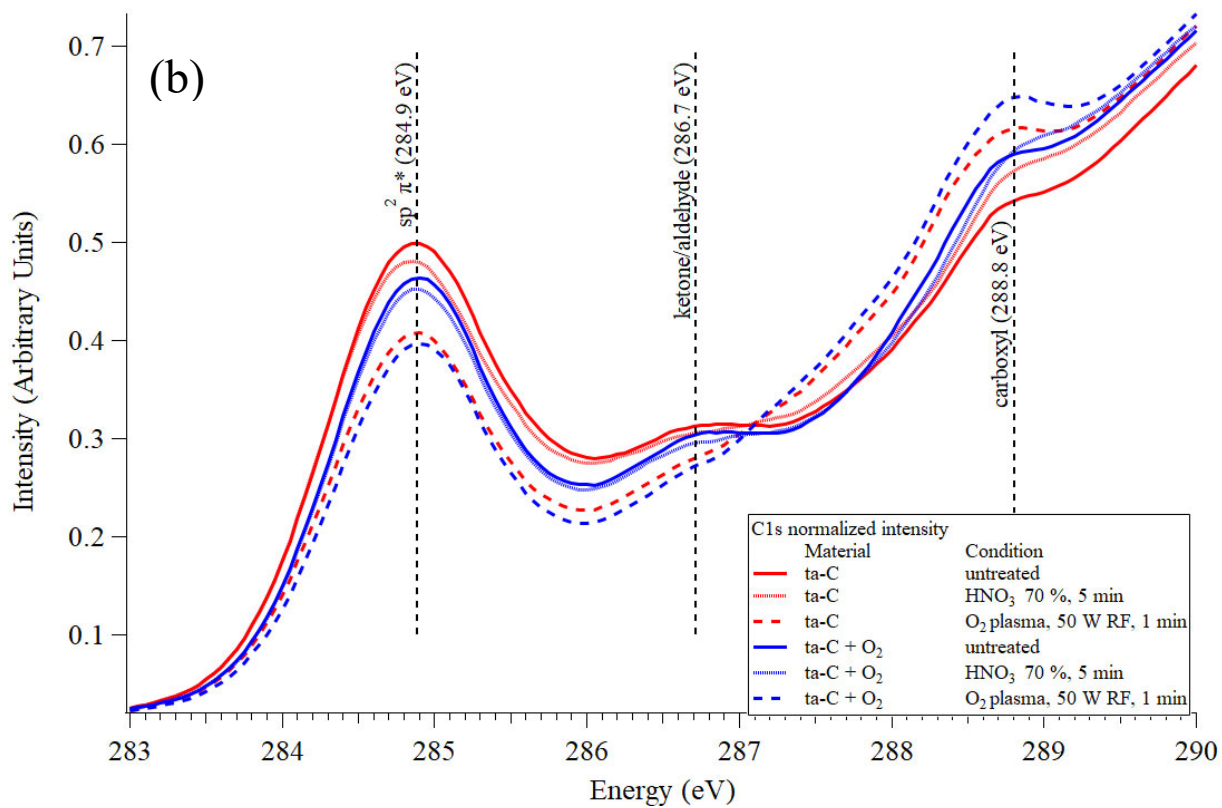
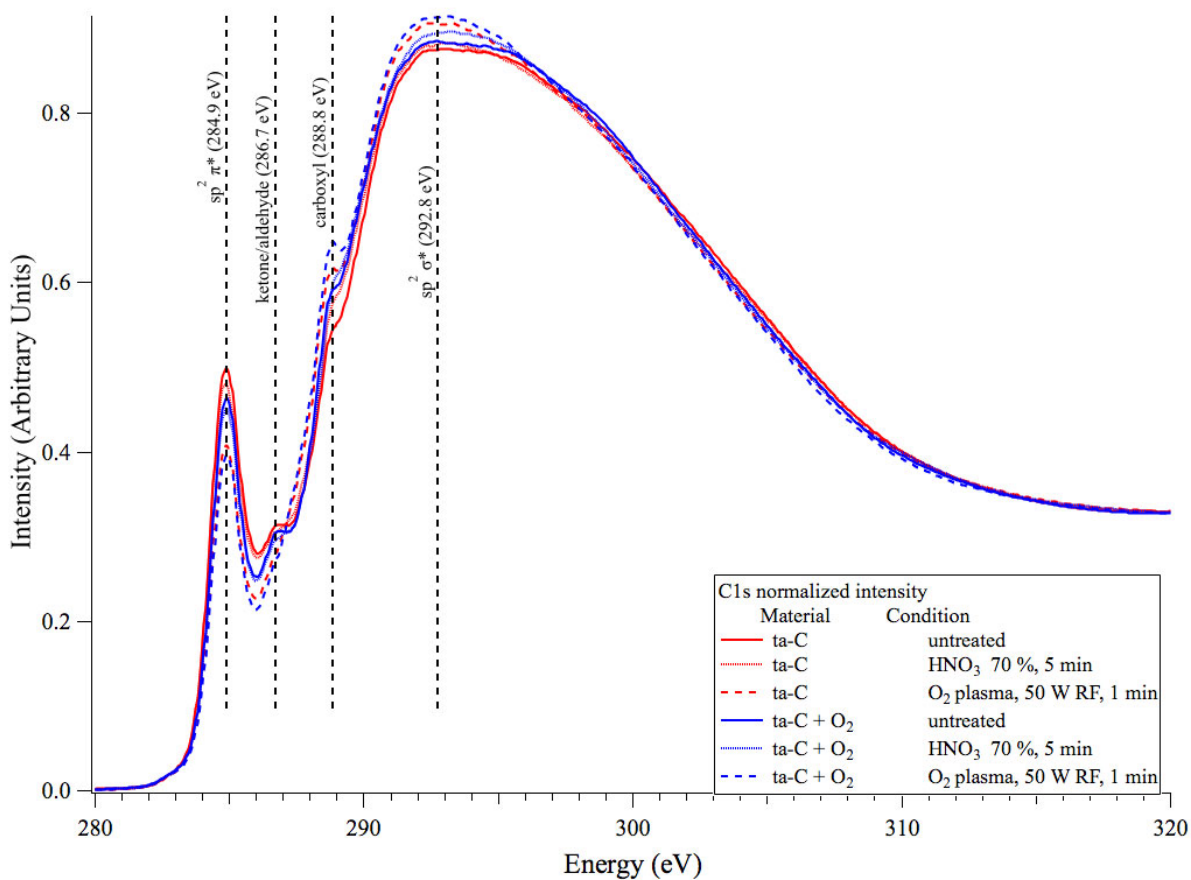


Figure 1: (a) C1s TEY spectra of ta-C and ta-C + O₂ thin films with their respective HNO₃ and O₂ plasma treated counterparts. By introducing oxygen to the deposition chamber it is possible to increase the carboxyl functionalities (at 288.8 eV) while decreasing the sp² π intensity (at 284.9 eV). The effect is even stronger when the reactive oxygen plasma treatment was used. Nitric acid treatments effects, however, seem very subtle. (b) Magnification of the C1s spectra in (a) to improve visibility of the spectral shape between the sp² π* and the carboxyl functionalities.*

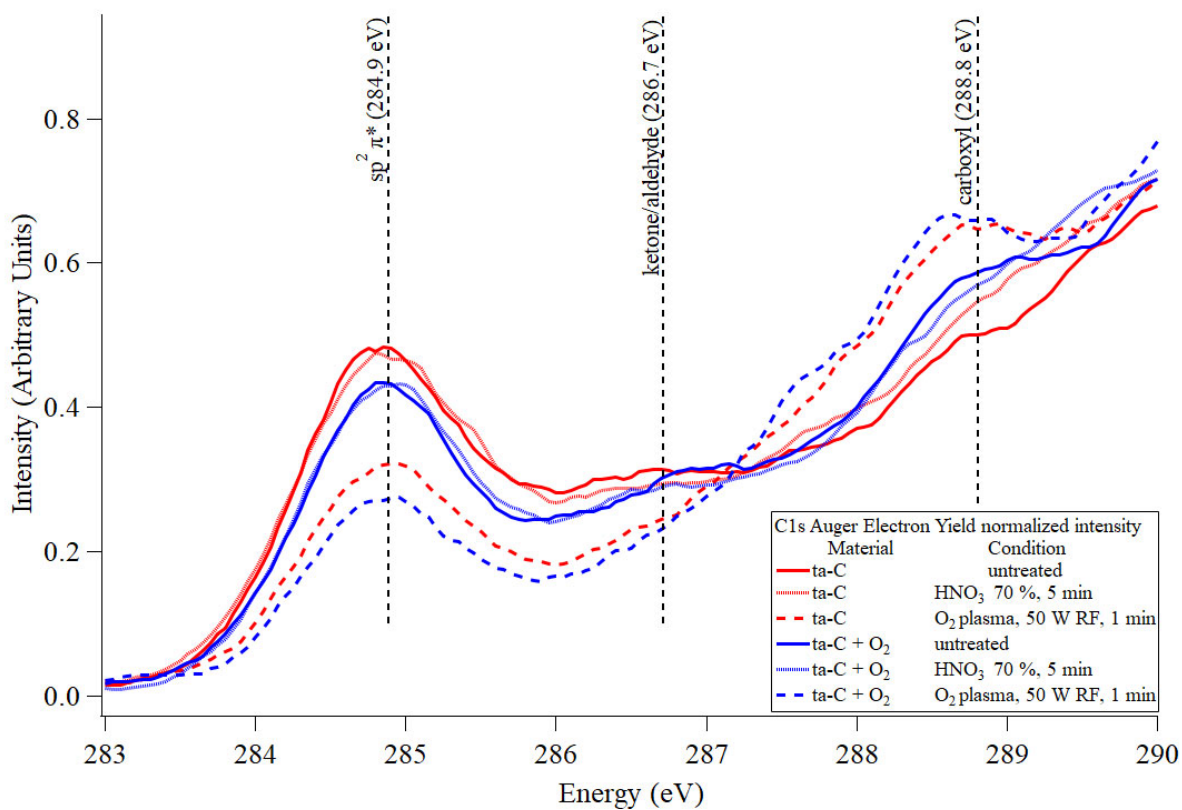
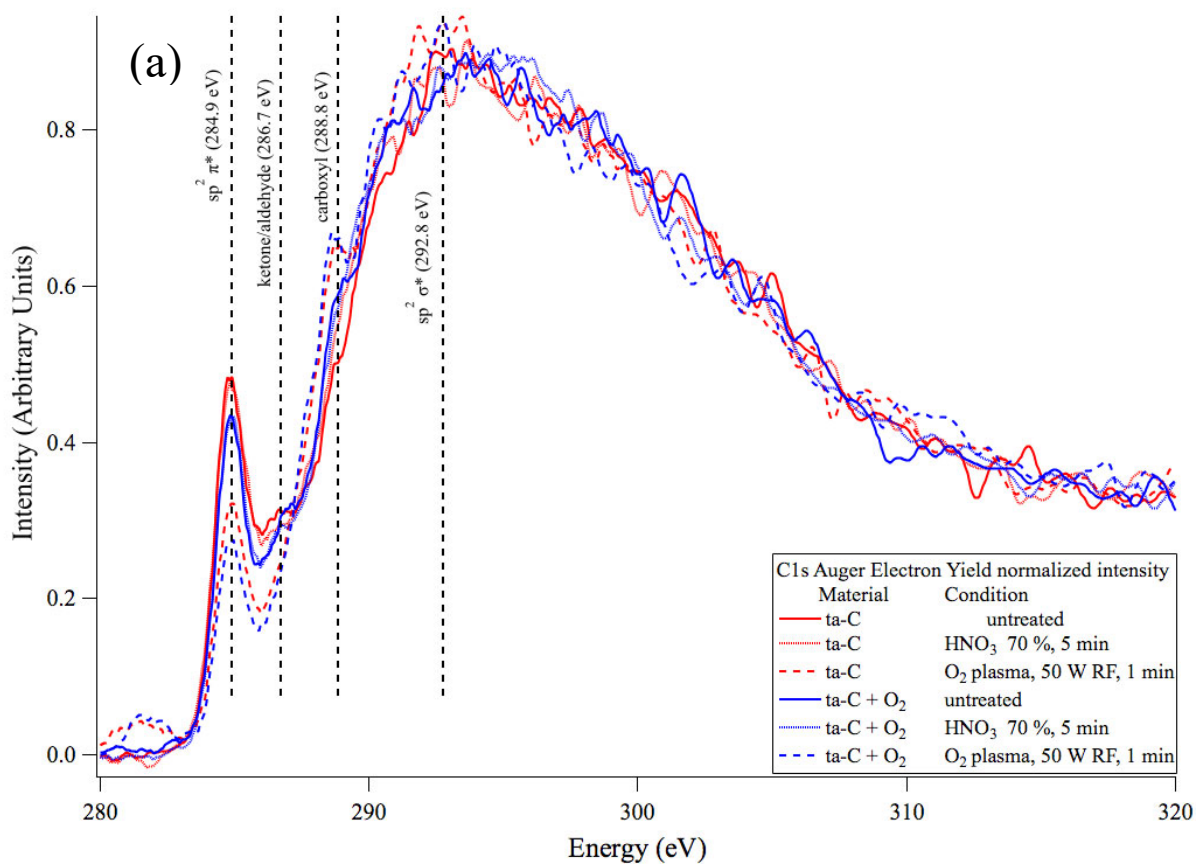


Figure 2: (a) C1s AEX spectra of ta-C and ta-C + O₂ thin films with their respective HNO₃ and O₂ plasma treated counterparts. The observed changes in the increase of oxygen in the surface layer are more pronounced than in the TEY spectra shown in Fig. 1 (a) and (b). (b) Magnification of the C1s AEX spectra in (a) to improve visibility of the spectral shape between the sp² π* and the carboxyl functionalities.

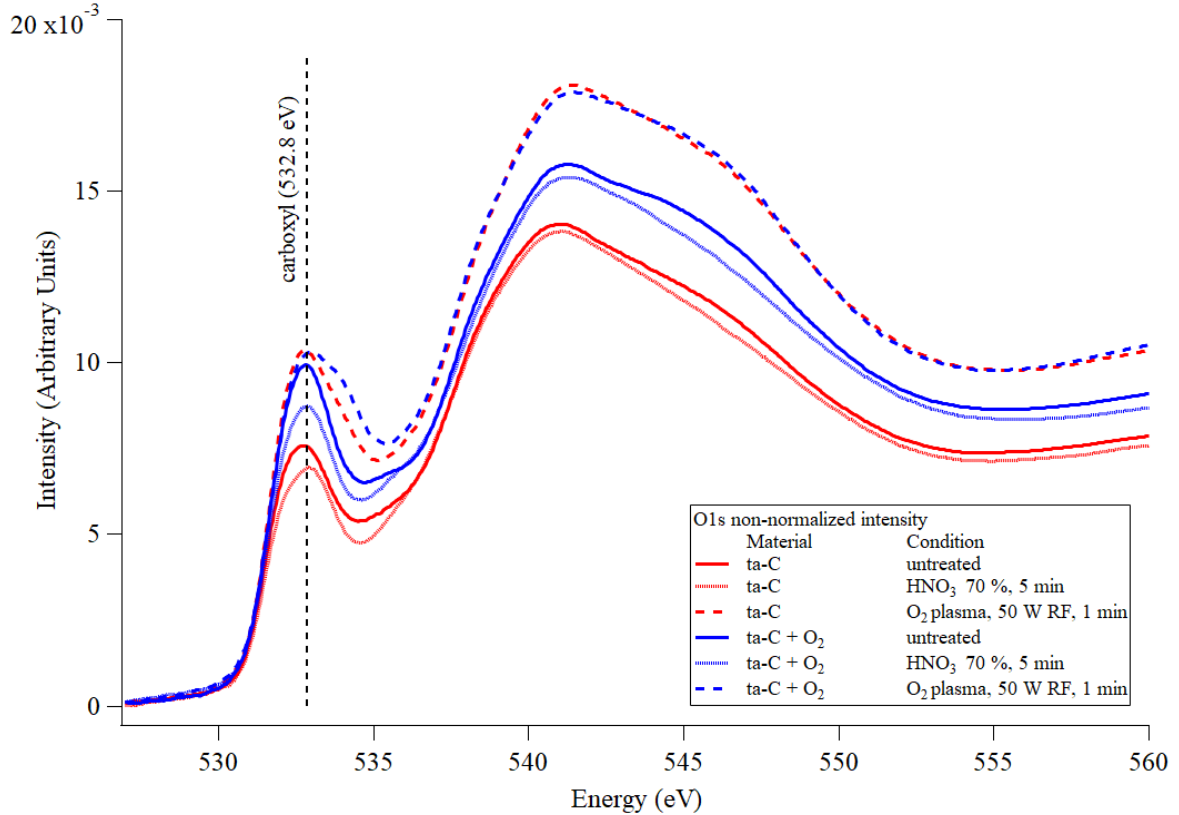


Figure 3: O1s spectra of ta-C and ta-C + O₂ thin films with their respective HNO₃ and O₂ plasma treated counterparts. The O1s spectra is consistent with the observed increase in carboxyl seen in C1s TEY and AEX spectra. We also notice that the peak is slightly broader after plasma treatment, indicating an increased presence of other carbonyl species with high electronegative coordination.

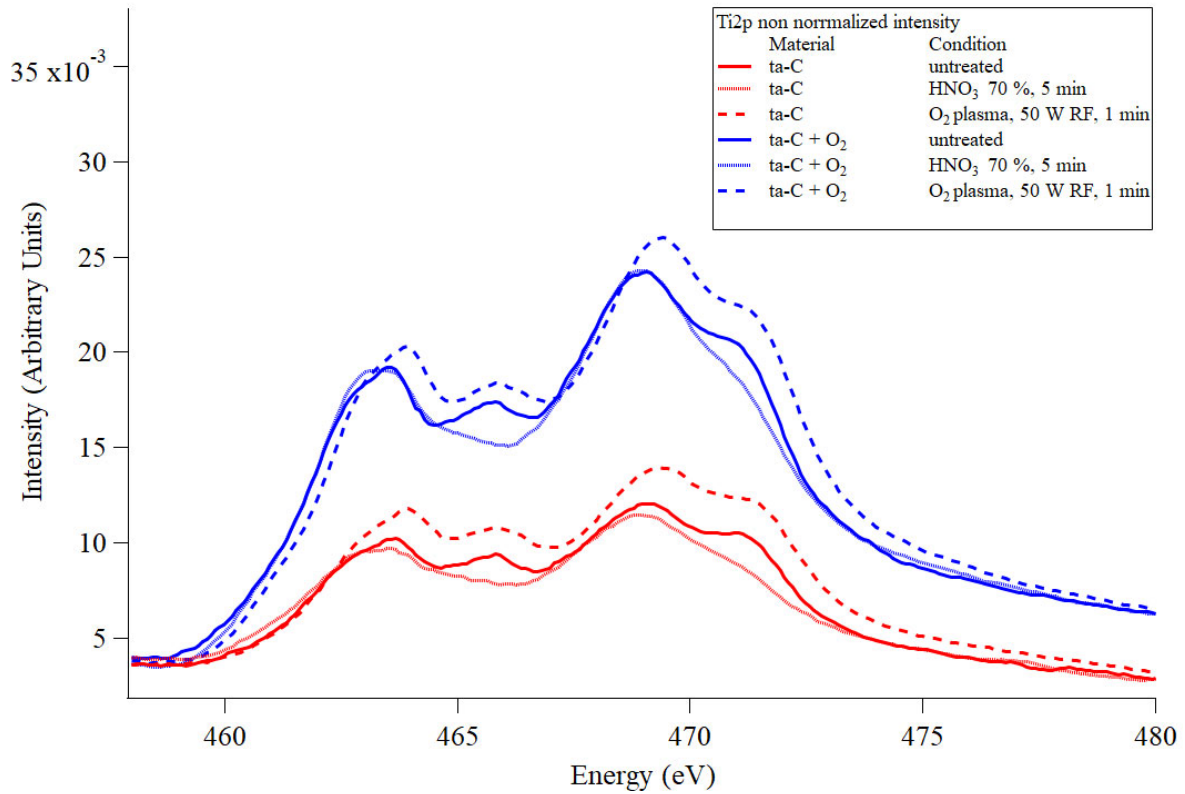


Figure 4: Ti2p spectra of ta-C and ta-C + O₂ thin films with their respective HNO₃ and O₂ plasma treated counterparts. We note that there is a noticeable increase of the total intensity of the Ti by the introduction of oxygen during the deposition process, indicating that the underlying Ti (TiO_x) is slightly more exposed.

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