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# Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy

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## ABSTRACT

Several nanometer-thick graphene oxide films deposited on silicon nitride-on silicon substrates were exposed to nine different heat treatments (three in Argon, three in Argon and Hydrogen, and three in ultra-high vacuum), and also a film was held at 70 °C while being exposed to a vapor from hydrazine monohydrate. The films were characterized with atomic force microscopy to obtain local thickness and variation in thickness over extended regions. X-ray photoelectron spectroscopy was used to measure significant reduction of the oxygen content of the films; heating in ultra-high vacuum was particularly effective. The overtone region of the Raman spectrum was used, for the first time, to provide a “fingerprint” of changing oxygen content.

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## 1. Introduction

Thin films composed of graphene oxide or reduced graphene oxide platelets (such platelets are also referred to as “sheets”) have recently attracted attention due to their unique mechanical and optical properties [1–4]. As a result of the extensive oxidation of the precursor graphite (resulting in graphite oxide which is then dispersed as layers in an aqueous colloidal suspension), ‘graphene oxide paper’ [1] is considered not to be electrically conductive by electron or hole transport. However, it is possible to make reduced graphene oxide films that are electrically conductive [2–5]. By tuning the chemistry of the platelets either prior to or after formation of the thin film, the film’s electrical conductivity, optical properties, and chemical character (hydrophobicity, etc.) can also be tuned

[1–6]. Such chemical tuning could also have a significant impact on the thermal conductivity, which to the best of our knowledge has not yet been studied.

The objective of this study is to evaluate any chemical changes of very thin films composed of graphene oxide platelets due to heat and/or chemical treatment by using X-ray photoelectron spectroscopy (XPS) and Micro-Raman spectroscopy. This study complements previous work conducted on other chemically modified graphene (CMG)-based materials, including ordered multilayer stacks of graphene oxide (thus, graphite oxide crystals, about which there is an extensive literature), thick ‘paper-like’ films of graphene oxide platelets, [1] and “chemically reduced graphene oxide” (CReGO) that is created by exposing an aqueous suspension of graphene oxide sheets to hydrazine, [7] as well as by the methods

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discussed in the aforementioned work [2–6]. Our group has also previously performed an XPS study of the impact of hydrazine treatment of a thin film that after curing consisted of separated graphene oxide platelets embedded in silica, deposited on a silica substrate [3]. These approximately 30 nm-thick silica/CMG composite films, derived from a sol-gel process, contained about 4 to 8 separated CMG platelets in any region in the through-thickness part of the silica film for the highest loading of the CMG platelets that was tested.

XPS is a surface sensitive technique used to analyze surface chemical composition and bonding. A sample is irradiated with an X-ray beam while the number of electrons that escape and their kinetic energy are simultaneously measured [8]. Raman spectroscopy is used to characterize the vibrational modes of molecules. Micro-Raman spectroscopy allows the probing of a small volume by combining a confocal microscope with the spectroscopy system [9]. The ability to collect Raman data from a very small area ( $\sim 350$  nm in diameter) can in some situations reduce undesirable background signals and enhance chemical sensitivity. We have used micro-Raman spectroscopy in this study and refer to the spectra obtained as “Raman spectra”.

## 2. Experimental

Graphite oxide was prepared by the modified Hummers method [7,10] and was then dispersed in water by sonication for 2 h. (GO was synthesized from natural graphite (SP-1, Bay Carbon, MI) by the modified Hummers method. Conc.  $\text{H}_2\text{SO}_4$  (50 mL) was added into a 250 mL flask filled with graphite (2 g) at room temperature. The flask was then cooled to  $0^\circ\text{C}$  in an ice bath, followed by slow addition of  $\text{KMnO}_4$  (7 g); the flask was then allowed to warm to room temperature. The temperature was then raised to  $35^\circ\text{C}$  with a water bath, and the mixture was

then stirred with a Teflon-coated magnetic stirring bar (stirring rate: 800 rpm) for 2 h. The reaction mixture was then cooled with an ice bath, followed by addition of excess purified water (17.4 M $\Omega$ ) to the mixture.  $\text{H}_2\text{O}_2$  (30 wt% in water from Aldrich) was then added until gas evolution ceased. Filtration with glass frit filter with medium pore size afforded brown powder (GO) which was washed by purified water/conc. HCl mixed solvent (9/1 volume ratio) three times, followed by suction-drying for 12 h in the glass filter and then drying in the vacuum at room temperature for 12 h.) Thin films composed of graphene oxide platelets were prepared by depositing a droplet from an aqueous suspension of graphene oxide onto silicon nitride-on silicon substrates that had been oxygen plasma-cleaned prior to deposition. The samples were then air dried under ambient lab conditions. XPS and micro-Raman measurements were performed before and after each film treatment. The as-deposited ‘graphene oxide films’ were the primary samples. Secondary samples were the same films (a) exposed to one heat treatment, or (b) exposed to gas phase hydrazine. A tertiary sample involved taking the same sample as (a), and exposing it to an additional heat treatment, as outlined further below.

The flow diagram of processing steps and measurement with XPS and Raman spectroscopy is shown in Fig. 1. The heat treatments consisted of placing the samples in a tube furnace, with initial temperature at room temperature and final temperatures at  $200^\circ\text{C}$  (2 min to reach  $200^\circ\text{C}$ ; 5 min from  $200^\circ\text{C}$  to room temperature),  $500^\circ\text{C}$  (4 min to reach  $500^\circ\text{C}$ ; 30 min to reach  $200^\circ\text{C}$ , then another 5 min to reach room temperature as at  $200^\circ\text{C}$ , the oven top was opened by hand), or  $1000^\circ\text{C}$  (6 min to reach  $1000^\circ\text{C}$ ; 50 min to reach  $200^\circ\text{C}$ , then another 5 min to reach room temperature after opening the oven top by hand) in flowing Ar, or in flowing Ar and  $\text{H}_2$ . The ramp up time from room temperature is given in paren-

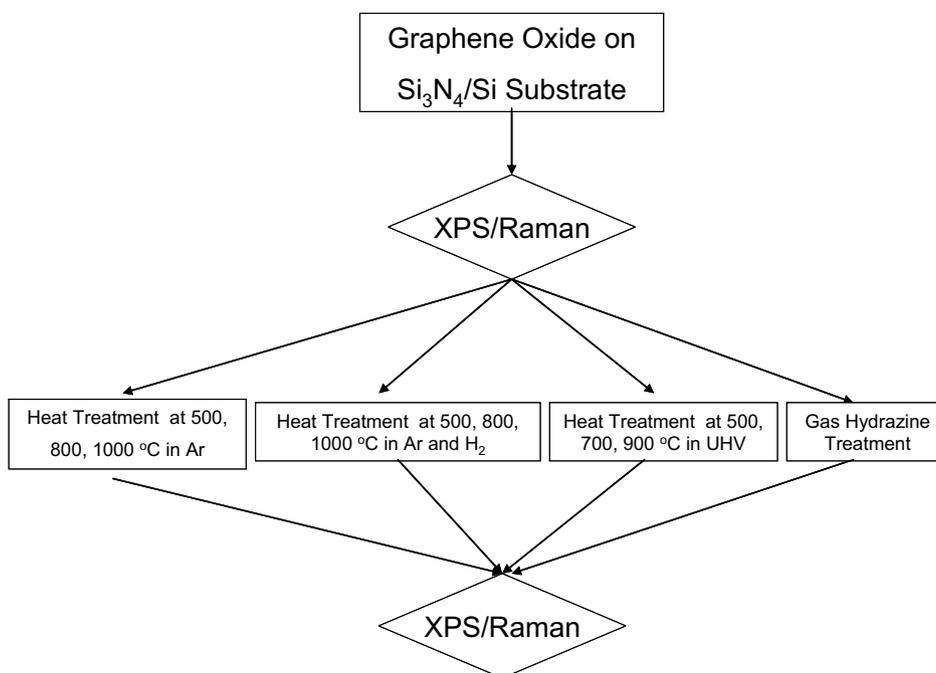


Fig. 1 – Flow chart of the experimental procedure.

theses first, and the second statement is the time to cool down to room temperature. Heat treatment #1 maintained the temperature at 200 °C for 30 minutes, heat treatment #2 at 500 °C for 30 minutes, and heat treatment #3 at 1000 °C for 30 min. A control sample (oxygen plasma-etched Si<sub>3</sub>N<sub>4</sub>-Si) had heat treatment #2. XPS spectra obtained before and after this heat treatment for this control sample showed no obvious change.

In addition to the heat treatments described above that were carried out at atmospheric pressure, three samples were heated under ultra-high vacuum (UHV) conditions. The base pressure of the UHV chamber was  $6 \times 10^{-11}$  Torr. Heat treatment #4 maintained the temperature at 500 °C for 15 minutes, heat treatment #5 at 700 °C for 15 min, and heat treatment #6 at 900 °C for 15 min. For heat treatments #4, #5 and #6, the duration of the ramp from room to the final temperature was 20 min, and it took about 45 min for the system to return to room temperature at the end of the heating cycle. Pressure rises in the low  $10^{-8}$  Torr range were observed during these heat treatments.

The chemical treatment was performed by exposing the films to gas evolving from hydrazine monohydrate (98%, Aldrich) at room temperature. A simple glassware vacuum system consisting of two connected flasks evacuated by a vacuum pump was used; one flask contained hydrazine monohydrate at room temperature, and the second held the film sample and was immersed in a 70 °C oil bath. A photo of this configuration is shown in Fig. 2. (In this photo the flask with sample is shown above the oil bath for clarity. The flask was inserted in the oil bath just prior to pumping the system down.) The system was pumped to 30 mTorr pressure with an Edwards RV3 Mechanical pump (this took 30–60 min; a liquid nitrogen trap is used in the Schlenk line that was employed). The vacuum line was then isolated, and the valve above the hydrazine monohydrate was opened to establish a steady state vapor pressure and that configuration was maintained for 24 h. The valve above the hydrazine monohydrate was then closed, and then the flask containing the sample was lifted out of the oil bath and allowed to cool to room temperature. The dead space was pumped down, and then opened to

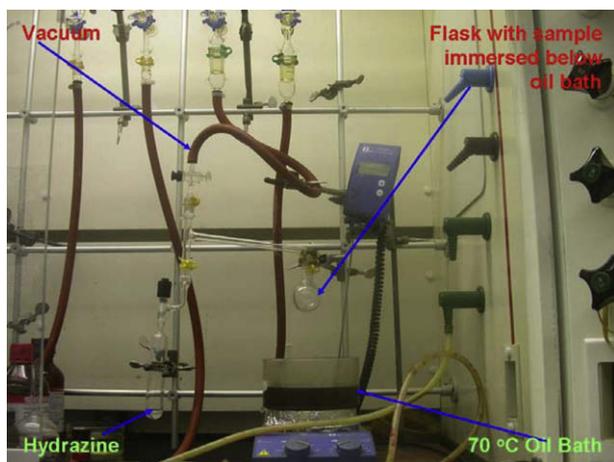


Fig. 2 – The system used for ‘gas phase hydrazine’ treatment.

atmosphere so that the sample could be removed and used for XPS and Raman measurements. The control sample (oxygen plasma etched Si<sub>3</sub>N<sub>4</sub>-Si) was also treated with the hydrazine monohydrate experimental configuration in an identical manner; no obvious difference was found for the XPS spectra obtained before and after this treatment for this sample.

XPS measurements were performed with an Omicron ESCA Probe (Omicron Nanotechnology, Taunusstein, Germany) using monochromatic AlK $\alpha$  radiation ( $h\nu = 1486.6$  eV); Kratos Vision v 2.2 software was used to perform curve fitting and to calculate the atomic concentrations. AFM images were generated by either a Park Scientific model CP “Research” (now, VEECO) with a contact force setting of 1 nanoNewton or a PSIA model XE-100S using non-contact mode at 300 kHz. Micro-Raman measurements were made with a WiTec Alpha300 system with 532 nm wavelength incident laser light and a 100 $\times$  objective. The incident laser power was carefully tuned to avoid sample damage or laser induced heating and measurements were thus performed at around 5 mW incident laser power.

### 3. Results and discussion

An AFM image of a typical several-nanometer thick film of graphene oxide platelets deposited on the silicon nitride-on-silicon substrate is shown in Fig. 3. This film is made up of overlapping graphene oxide platelets so that a given region might consist of one layer (about 1 nm thick) or overlapped layers, with the overlapped regions typically having two overlapped platelets.

#### 3.1. Heat treatment with flowing argon or with flowing argon and hydrogen

##### 3.1.1. X-ray photoelectron spectroscopy

The C1s and O1s XPS spectra are shown in Fig. 4a and b, respectively, of the graphene oxide film on Si<sub>3</sub>N<sub>4</sub>-on-Si after

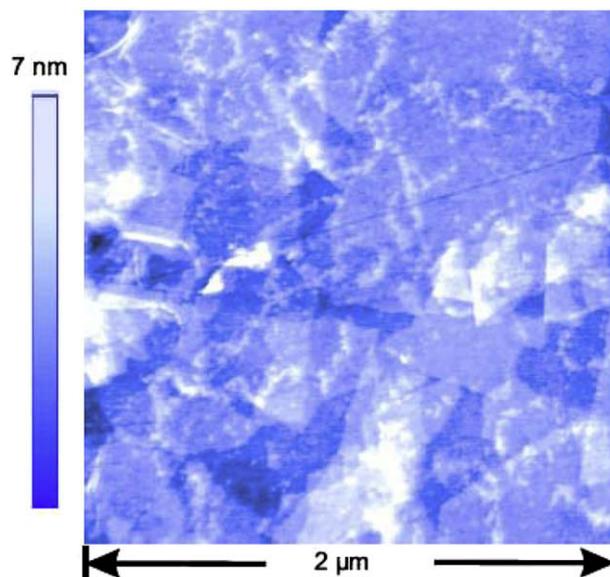
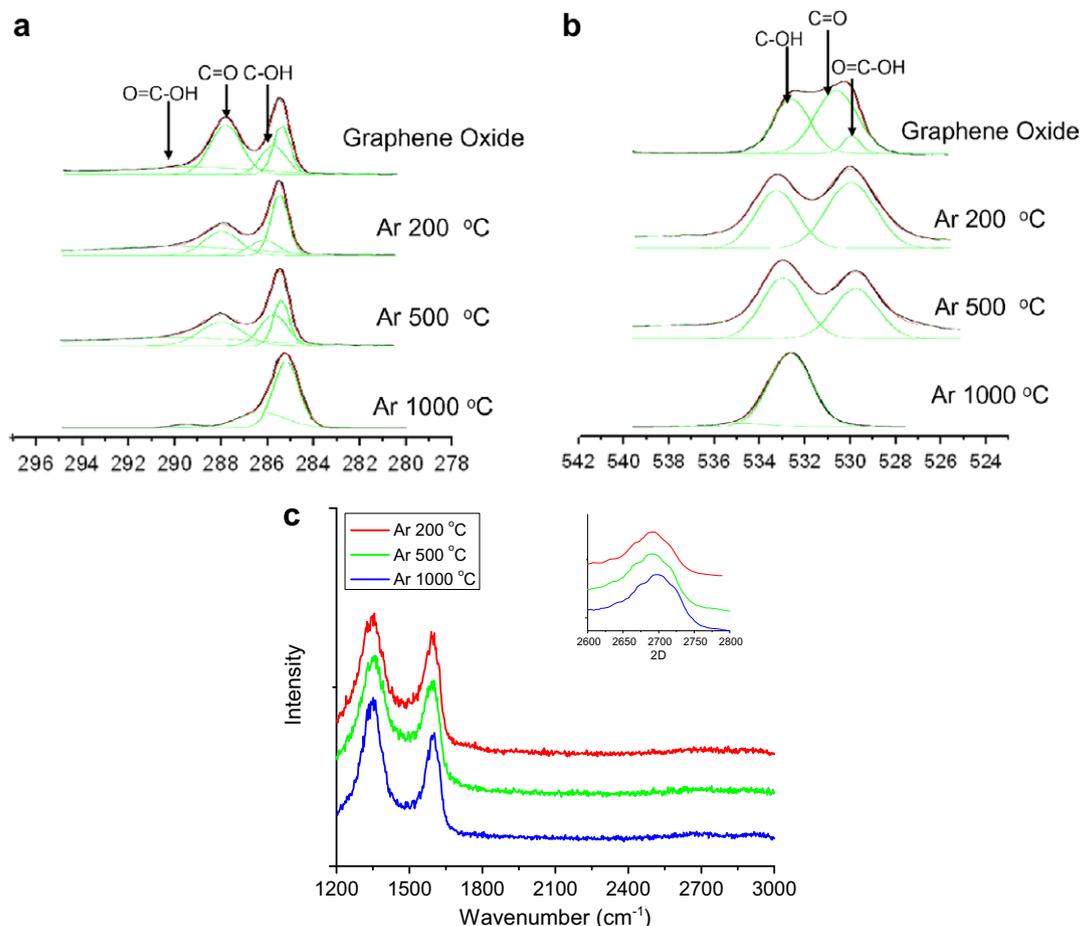


Fig. 3 – AFM image of graphene oxide film on silicon nitride-on silicon.

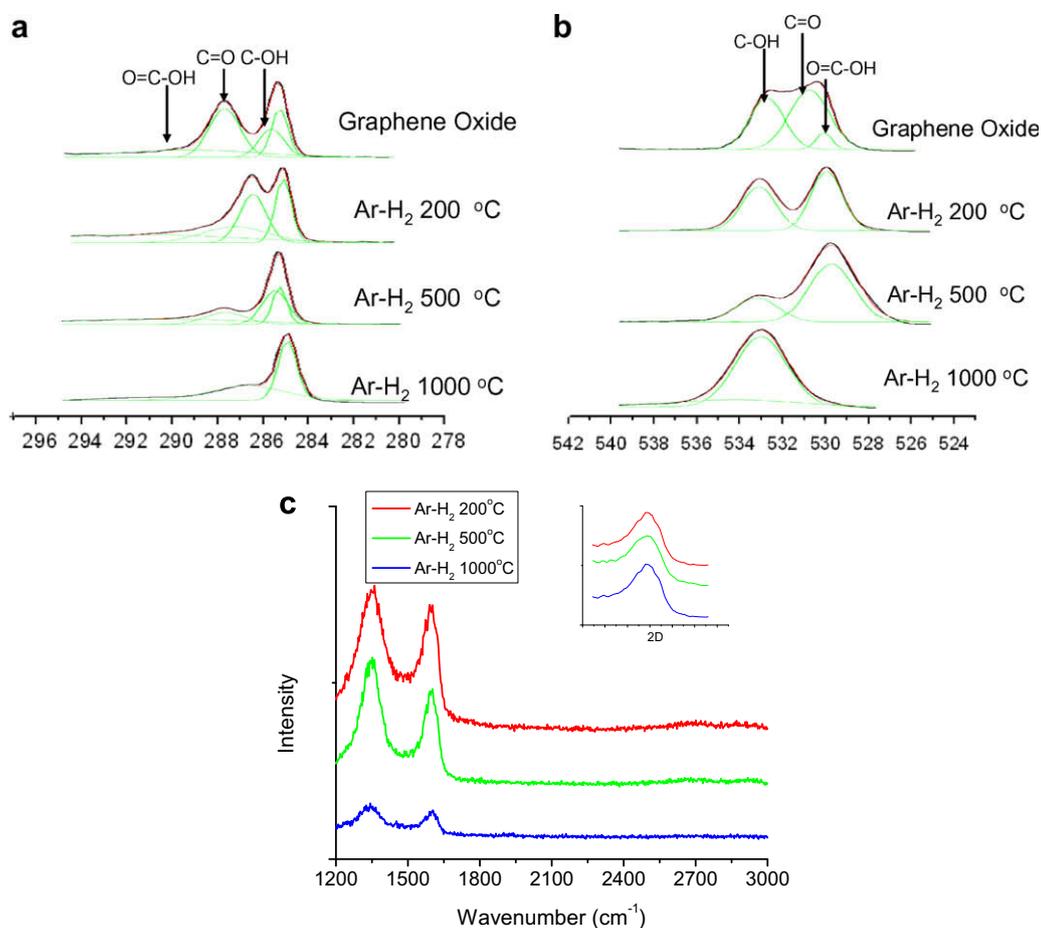


**Fig. 4 – XPS spectra for graphene oxide films on  $\text{Si}_3\text{N}_4$ -on Si substrate after 200, 500, and 1000 °C treatment in flowing Argon: (a) comparison of C1s peaks, (b). comparison of O1s peaks, and (c) Raman spectra of D and G band, with inset showing the 2-D band.**

heat treatments at 200 °C, 500 °C, and 1000 °C in Argon. The C1s and O1s XPS spectra are shown in Fig. 5a and b, respectively, of the graphene oxide films with identical heat treatments but in a mixture of Argon and Hydrogen. Curve fitting of the C1s and O1s spectra was performed using a Gaussian-Lorentzian peak shape after performing a Shirley background correction. The binding energy of the C–C and C–H bonding are assigned at 284.5–285 eV and chemical shifts of +1.5, +2.5 and +4.0 eV are typically assigned for the C–OH, C=O, and O=C–OH functional groups, respectively [11,12]. Most structural models of graphite oxide also include an epoxide group (C–O–C), which should have a C1s binding energy similar to C–OH [13]. However, it is possible that there is a larger than expected chemical shift in the C–O–C emission into the range of the C=O emission. Further measurements with techniques that are sensitive to the vibrational modes of the functional groups are indicated. The C1s spectra in Figs. 4a and 5a have a main peak at 285.1 eV, and there is another peak at 287.8 eV that can be fit to peaks at 286.4, 287.8 and 288.9 eV and thus assigned to C–OH, C=O, and O=C–OH species, respectively. An attempt was made to fit the “expected” [11,12] peaks at 286.6, 287.6, 289.1 but the mean square error for such a fit was much larger. There is a small peak at 289.7 eV after the 1000 °C treatment in Argon, and we do not

know what functional group to assign to this peak. The large full width at half maximum (FWHM) and the broad tail towards higher binding energy indicate that contributions of a variety of different carbon bonding configurations are superimposed. The peaks contributing at 285.1 eV become broader and reduced in intensity for the higher temperature heat treatments. The peaks contributing at 287.7 eV disappeared after the 1000 °C treatment in Argon, Fig. 4a, and are significantly reduced after the 1000 °C treatment in Argon and Hydrogen, Fig. 5a. The atomic ratio of carbon to oxygen (area of the C1s peak divided by area of the O1s peak, multiplied by the ratio of the photoionization cross sections) was calculated from the XPS survey spectrum after each treatment and the calculated results are shown in Table 1.

The assignment of peaks in the O1s spectra is of interest, as there are some conflicting assignments of the “carbon–oxygen” functional groups in the literature [13–15]. Information provided by analysis of the O1s spectra can complement the information provided by analysis of C1s spectra. Because the O1s photoelectron kinetic energies are lower than those of the C1s, the O1s sampling depth is smaller, and therefore the O1s spectra are slightly more surface specific. By reference to the C1s peak changes, we have assigned the O1s peak at 530.6 eV to contributions from C=O and O=C–OH groups and



**Fig. 5** – XPS spectra for Graphene Oxide films on  $\text{Si}_3\text{N}_4$ -on Si substrate after exposures to 200, 500, and 1000 °C in flowing Argon and Hydrogen: (a) comparison of C1s peaks, (b) comparison of O1s peaks, and (c). Raman spectra of D and G band, with inset showing the 2-D band.

**Table 1** – The values of C1s/O1s (atomic ratios) obtained by XPS survey spectra

	200 °C	500 °C	700 °C	900 °C	1000 °C
As-deposited film	$2.8 \pm 0.1$				
Heat treatment in Ar	$3.9 \pm 0.1$	$6.8 \pm 0.2$			$11.36 \pm 0.3$
Heat treatment in Ar and $\text{H}_2$	$3.9 \pm 0.1$	$7.3 \pm 0.2$			$12.4 \pm 0.3$
UHV heat treatment		$8.9 \pm 0.2$	$13.2 \pm 0.3$	$14.1 \pm 0.3$	
Hydrazine treatment	$8.8 \pm 0.2$				

that at 533 eV to C–OH groups. After annealing to 200 °C and 500 °C, the peak at 530.6 eV shifts to lower binding energy (ranging from 529.6 to 529 eV, depending on the thermal treatment), which indicates a conversion of the C=O and O=C–OH groups to a new chemical species. Whereas, the peak at 533 eV does not appear to shift appreciably at these anneal temperatures. The complete disappearance of all peaks other than the 533 eV peak after the 1000 °C treatment indicates loss of oxygen (and possibly carbon) during the high temperature treatments. The remaining peak at 533 eV indicates that C–OH groups are still present. It is perhaps of interest that the authors of theoretical calculations reach the conclusion that the reduction of remaining C–OH groups in a reduced graphene oxide is very difficult, although reduction of some initial fraction of the C–OH groups in the as-prepared graphene oxide

is more facile [16]. It is noted that a slight shift of 0.25 eV to lower binding energy is observed for the peaks of both the C1s and O1s spectra after the 1000 °C anneal, which indicates that there was some sample charging in the spectra for GO and the lower temperature anneals.

### 3.1.2. Micro-Raman spectroscopy

Raman spectra (obtained with a micro-Raman instrument as mentioned above) of the film for each stage of processing are shown in Figs. 4c and 5c. The Raman spectrum of the as-deposited graphene oxide film displays a D-band at  $1340 \text{ cm}^{-1}$  and a broad G-band at  $1580 \text{ cm}^{-1}$ , the latter corresponding to the first-order scattering of the E<sub>2g</sub> mode [17]. The prominent D peak is from the structural imperfections created by the attachment of hydroxyl and epoxide groups on the carbon

basal plane. The intensity of the overtone 2D-band with respect to the D and G peaks is small. After the heat treatment, there is a small peak shift for the 2D-band and no obvious shift for the D-band or the G-band. The 2D-band peak is centered at 2688, 2690, and 2694  $\text{cm}^{-1}$  after 200, 500, and 1000 °C heat treatments in Argon, respectively, while the 2D-band peak is centered at 2690, 2693, and 2693  $\text{cm}^{-1}$  after 200, 500, and 1000 °C heat treatments in Argon and Hydrogen, respectively. The shift of the peak position of the 2D-band and reduction in its magnitude (Table 2 shows the ratio of the area of the 2D-band to the G band obtained in each Raman spectrum) is, given the XPS results, indicative of reduction of the graphene oxide film. To our knowledge this is the first use of the overtone region in Raman spectroscopy to ascertain the degree of reduction of graphene oxide films. In contrast

to the overtone region, the almost identical I(D)/I(G) ratio does not seem to offer any insights about the chemical changes that are evidently (per the XPS results) occurring, in marked contrast to XPS.

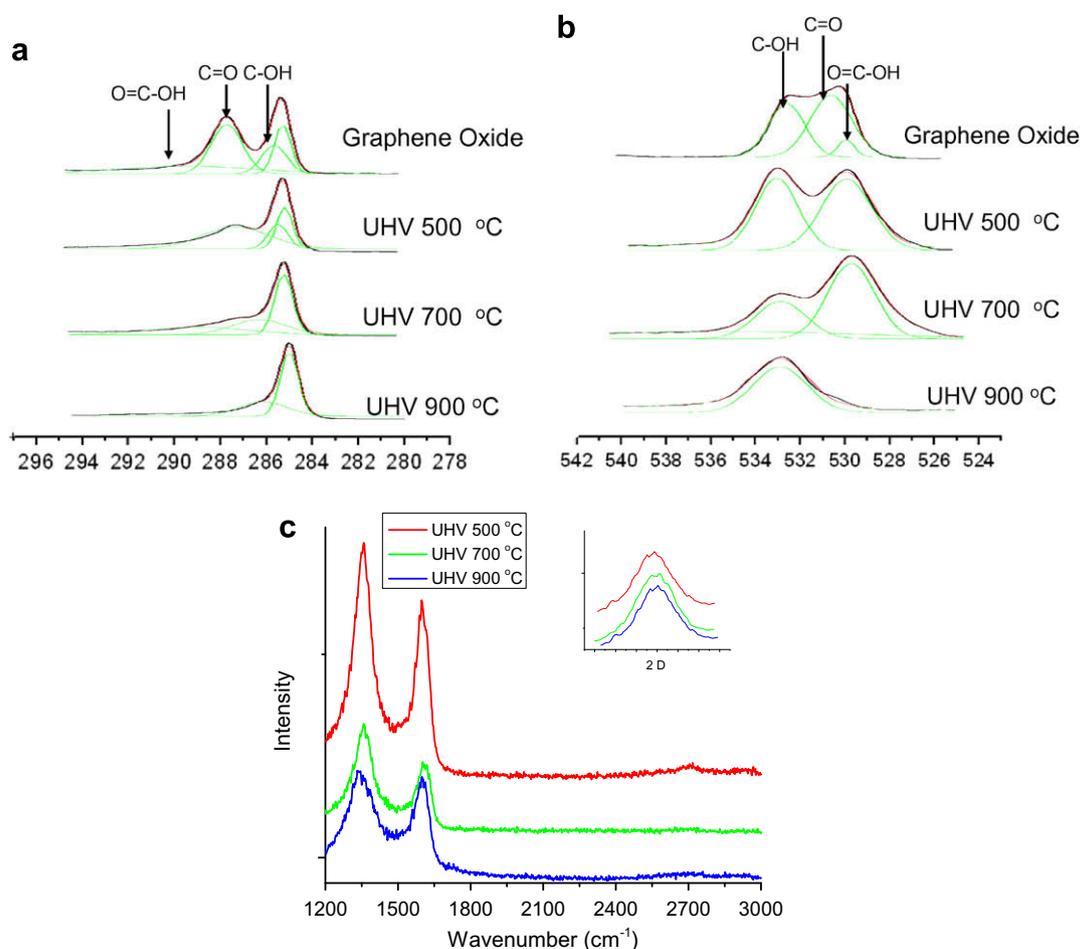
### 3.2. Heat treatment in ultra high vacuum

#### 3.2.1. X-ray photoelectron spectroscopy

The C1s and O1s XPS spectra are shown in Fig. 6a and b, respectively, of a graphene oxide film on  $\text{Si}_3\text{N}_4$ -on-Si after 500, 700 and 900 °C treatments for 15 minutes in UHV. The C1s peak at 287.7 eV decreased in intensity following the 500 °C treatment, almost disappeared after the 700 °C treatment, and completely disappeared after the 900 °C treatment. The O1s peak at 530.6 eV is observed at 529.2 eV after both the

**Table 2 – The percentage values of I(2D)/I(G) ratios obtained by Raman spectroscopy**

	200 °C	500 °C	700 °C	900 °C	1000 °C
As-Deposited film	3.3 ± 0.2				
Heat treatment in Ar	1.8 ± 0.1	2.5 ± 0.1			1.7 ± 0.1
Heat treatment in Ar and H <sub>2</sub>	2.6 ± 0.2	2.9 ± 0.2			2.3 ± 0.1
UHV heat treatment		2.3 ± 0.1	1.9 ± 0.1	1.8 ± 0.1	
Hydrazine treatment	1.5 ± 0.1				



**Fig. 6 – XPS spectra for Graphene Oxide films on  $\text{Si}_3\text{N}_4$ -on Si substrate after 500, 700 and 900 °C treatment in UHV: (a) comparison of C1s peaks, (b) comparison of O1s peaks and (c). Raman spectra of D and G band, with inset showing the 2-D band.**

500 °C and 700 °C treatments, again indicating a chemical conversion of the C=O and O=C–OH groups to a new chemical species. After the 900 °C treatment, this peak disappears. The decrease of these peaks indicates loss of oxygen and possibly carbon.

The O1s/C1s ratio obtained from the XPS survey spectra thus decreases after each of the nine high-temperature treatments (three under Argon, three under Argon with Hydrogen, and three at UHV), which also indicates a partial reduction of the graphene oxide film samples heated at temperatures even as low as 200 °C.

### 3.2.2. Micro-Raman spectroscopy

A Raman spectrum (acquired in ambient after each stage of processing) of each film treated in UHV is shown in Fig. 6c. There is a shift of the overtone 2D-band ( $2691\text{ cm}^{-1}$  after the 500 °C heat treatment,  $2697\text{ cm}^{-1}$  after 700 °C heat treatment and  $2698\text{ cm}^{-1}$  after 900 °C heat treatment) and the latter is closer to the graphite 2D band ( $2700\text{ cm}^{-1}$ ) than the case of the sample exposed to tube furnace at, e.g., 1000 °C, which suggests more significant structural changes towards ‘graphite’ in UHV. A small but perceptible decrease of the I(D)/I(G) ratio is perhaps also an indication of ‘graphitization’.

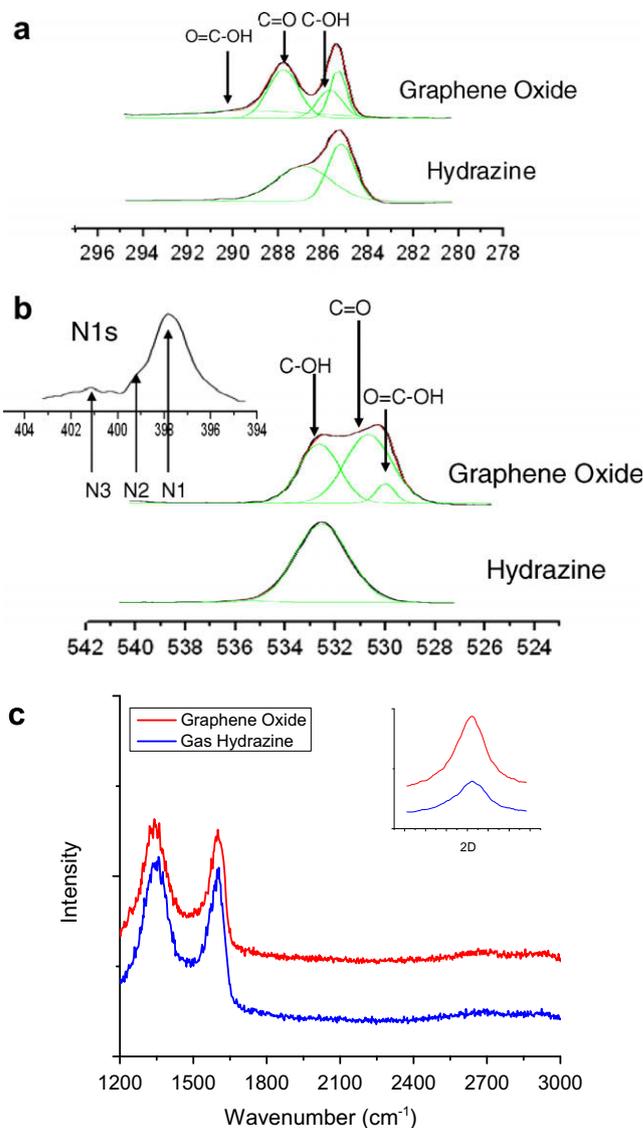
## 3.3. Chemical treatment

### 3.3.1. X-ray photoelectron spectroscopy

The C1s and O1s XPS spectra for as-deposited graphene oxide and after the exposure to gas-phase hydrazine are shown in Fig. 7a and b, respectively. (We note that we have not explicitly verified that hydrazine is present in the gas phase; as stated above, we have a container holding hydrazine-monohydrate at room temperature, and are exposing a heated thin film sample to the vapor emanating from the hydrazine-monohydrate.) The fraction of carbon participating in C–O single bonds, in carbonyl bonds, and in carboxylic groups, are all reduced after this exposure and new C–N peaks compared to the as-deposited graphene oxide film also appear, as shown in the inset of Fig. 7b. The N1s envelope contains three peaks at 397.8, 398.9, and 400.9 eV, which can be assigned to N–N, N–sp<sup>3</sup>C, and N–sp<sup>2</sup>C, respectively [18–20]. The intensity of the N1s peaks is very small and indicates a minor amount of N was introduced. It should be noted that N–O bonds should be at about 404.0 eV [21]; therefore, there is no bonding of O with N. The remaining O1s peak at 533 eV after hydrazine treatment indicates the presence of C–OH together with the C–N bond (from N1s peaks). Moreover, the FWHM of the peak attributed to C–N appears quite larger than all other C components. This may be due to the persistence of oxygen-carbon bonds.

### 3.3.2. Micro-Raman spectroscopy

The Raman spectra for the as-deposited graphene oxide film on silicon nitride-on-silicon, and after exposure to the ‘hydrazine’ gas in equilibrium with the liquid hydrazine monohydrate held at room temperature and the sample at 70 °C, are shown in Fig. 7c. After the ‘hydrazine’ exposures, there is a small shift of the 2D-band peak (from  $2687\text{ cm}^{-1}$  of graphene oxide to  $2691\text{ cm}^{-1}$ ). The I(D)/I(G) intensity ratio is slightly increased, which suggests a possible decrease in the average



**Fig. 7 – XPS spectra for graphene oxide films on Si<sub>3</sub>N<sub>4</sub>-on Si substrate after ‘hydrazine monohydrate’ gas treatment: (a) comparison of C1s peaks, (b) comparison of O1s peaks with inset of N1s after hydrazine treatment, and (c). Raman spectra of D and G band, with inset showing the 2-D band.**

size of the sp<sup>2</sup> domains. This can be explained, if new ‘graphene-like’ domains were created that are smaller in size than the ones present in the films before exposure to hydrazine, but more numerous in number. The reduction in the magnitude of the I(2D)/I(G) ratio in Table 2 is also a possible indication of ‘graphitization’. (The most significant change in reduction in the magnitude of the I(2D)/I(G) ratio is for the hydrazine treatment compared to the thermal treatments.)

## 4. Conclusions

Several nanometer-thick films consisting of overlapping graphene oxide platelets deposited on silicon nitride-on-silicon substrates were studied using AFM, XPS, and micro-Raman spectroscopy. AFM was used to assess film thickness and variation of thickness, and it was found that a typical film

has regions that are monolayer and other regions that are bilayer and trilayer. Nine different heat treatments (three under Argon, three under Argon and Hydrogen, and three under UHV) at different final temperatures, and also a protocol of exposing a sample held at 70 °C to vapor from hydrazine monohydrate, were used to study the possible reduction of films composed of graphene oxide. Significant reduction of such films was observed by X-ray photoelectron spectroscopy, with the largest extent of reduction obtained at high temperature, and with heating under UHV looking particularly advantageous. With the XPS spectra as a key in assigning the degree of reduction, it was possible to correlate changes in the overtone region of the Raman spectrum as indicative of reduction. This is the first time, to our knowledge, that the overtone region has been used to “fingerprint” changes in the extent of reduction of graphene oxide films, and that samples have been heated to elevated temperatures in UHV.

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