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# Local oxidation and reduction of graphene

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Mass production of graphene can be achieved through CVD or reduction of graphene oxide. Whereas CVD grown

graphene is basically a poly-crystalline film with low defects,

substantial variation in the structure and chemical properties

of reduced graphene oxide have been widely reported [3]. Variations in the oxygen coverage have been attributed to

differences in starting materials, i.e., the graphite oxide

source, or reduction protocol. The above issue has resulted in

ambiguity in even the definition of 'graphene oxide' itself,

hampering its potential for industrial standardization and

application. It is still unclear whether oxygen coverage of

graphene oxide increases incrementally or abruptly over a

threshold condition. In most cases, oxidation of graphene

involves not only oxygen incorporation or formation of oxide

groups in into the graphene network, but also generation of

defects. Is defect generation a pre-requirement for effective

oxidation? Can oxidation directly occur for pristine defect free graphene? To fully understand the mechanisms involved in the oxidation processes and the reasons for its variation, it

is imperative to study the issue using a starting material with

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#### Abstract

Micrometer sized oxidation patterns were created in chemical vapor deposition grown graphene through scanning probe lithography (SPL) and then subsequently reduced by irradiation using a focused x-ray beam. Throughout the process, the films were characterized by lateral force microscopy, micro-Raman and micro-x-ray photoelectron spectroscopy. Firstly, the density of grain boundaries was found to be crucial in determining the maximum possible oxygen coverage with SPL. Secondly, the dominant factor in SPL oxidation was found to be the bias voltage. At low voltages, only structural defects are formed on grain boundaries. Above a distinct threshold voltage, oxygen coverage increased rapidly, with the duration of applied voltage affecting the final oxygen coverage. Finally, we found that, independent of initial conditions, types of defects or the amount of SPL oxidation, the same set of coupled rate equations describes the reduction dynamics with the limiting reduction step being  $C-C \rightarrow C=C$ .

Keywords: graphene, defects, scanning probe lithography, Raman spectroscopy, photoelectron spectroscopy

(Some figures may appear in colour only in the online journal)

#### 1. Introduction

Defect generation in a two dimensional crystal is not only an intriguing fundamental issue [1], but also of practical concern —all commercially viable preparation techniques for 2D materials result in defects. For instance, chemical vapor deposition (CVD) grown graphene unintentionally acquires defects through generation of grain boundaries and vacancies both during the nucleation and growth period, as well as the subsequent transferring processes [2]. It is thus important to study the dynamics of defect generation (and recovery) in a controllable and systematic way in order to gain practical understanding in the management of defects in 2D materials. A study of graphene and graphene oxide, as a model 2D materials, can offer insight into defect generation mechanism in other 2D materials.

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well-defined chemical and structural properties, along with controlled oxidation, reduction and characterization methodologies.

In previous work we employed scanning probe lithography (SPL), a mask-less technique that enables nanometer scale patterning on metallic or semiconducting substrates [4], to control the oxygen coverage. A number of groups, including our own, have previously demonstrated the feasibility of this technique to locally oxidize and generate defects in a graphene sheet [5–10]. We previously demonstrated local reduction of oxidized graphene through prolonged irradiation of focused x-rays and showed that a set of coupled rate equations is able to describe the reduction dynamics of oxidized graphene prepared under a fixed oxygen coverage condition [11]. In this work, we investigate the effect of differences in initial oxygen coverage of oxidized graphene on the reduction dynamics and final physical-chemical properties of the reduced graphene.

#### 2. Experiment

#### 2.1. Sample preparation

A 10 mm  $\times$  10 mm silicon chip with 300 nm SiO<sub>2</sub> and a monolayer of CVD grown graphene was purchased from Graphenea Inc. Electrical contact was made on graphene through application of conductive silver paint (Ted Pella Inc.). A local region (~mm) in the CVD-grown monolayer graphene sample was used to prepare oxidized patterns. SPL was conducted with a Bruker Innova AFM using a conductive AFM probe (Pt/Ir coated point-probe series, Nanosensor) at room temperature in a sealed chamber in which the relative humidity was maintained at ~55%. A custom implemented external bias source allowed for bias application between  $\pm 50$  V, with a tunable step <0.1 V. A. Contact mode AFM was used for SPL due to better pattern continuity and reproducibility. Square patterns of about  $1.5 \,\mu\text{m} \times 1.5 \,\mu\text{m}$ were drawn by using the built-in software (Nanoplot, Bruker) with closed loop function to enable exact positioning down to nanometer scale precision.

#### 2.2. Characterization

Optical images were acquired through an upright microscope (BX-51, Olympus). Topographical and lateral force information (LFM) were acquired immediately before and after SPL using the same conductive AFM probe. For more refined structural detail, tapping mode AFM was employed to avoid probable image distortion. Structure was characterized by a home-made micro-Raman spectroscopy ( $\mu$ -RS) with a 532 nm laser with a spot size  $\sim 1 \,\mu m$  [12]. Typical Raman fingerprints of graphene including G ( $\sim 1580 \,\mathrm{cm}^{-1}$ ) and 2D ( $\sim 2680 \,\mathrm{cm}^{-1}$ ), and the defect related D ( $\sim 1350 \,\mathrm{cm}^{-1}$ ) and D' ( $\sim 1620 \,\mathrm{cm}^{-1}$ ) bands were observed. The defect density was quantified through ratio of the D and G band intensities ( $I_{\rm D}/I_{\rm G}$ ) using the equations

$$L_{\rm D}(\rm nm) = 2.4 \times 10^{-10} \lambda^4 (I_{\rm G}/I_{\rm D}). \tag{1}$$

for lower defect density (stage 1), and

$$L_{\rm D}^{2}(\rm nm^{2}) = 2.6 \times 10^{-9} \lambda^{4} (I_{\rm D}/I_{\rm G})$$
<sup>(2)</sup>

for higher defect density (stage 2) [13, 14]. The nature of defects in graphene was determined using the ratio of D and D'-band intensities  $(I_D/I_{D'})$  [15].

The chemical bond profile was probed with micro-photoelectron spectroscopy ( $\mu$ -XPS) [16]. Chemical bonds associated with modification of the sp<sup>2</sup> bond and functionalization with carbon were identified by taking the carbon 1s spectra around photoelectron energy at 284.5 eV [17]. By focusing the intense x-ray beam down to  $<0.1 \,\mu\text{m}$  by a zone plate, and scanning the sample with a motorized stage, the chemical bond profile of the SPL defects was obtained with sub-micrometer resolution [16]. While the x-rays involved in taking the spectrum, did not change the spectrum of the pristine graphene, repeated exposure of the SPL treated samples resulted in significant changes in the C1s spectra after each round (20 s) of acquisition. Thus only the first spectrum taken at each point was used to represent initial chemical bonding condition of SPL treated patterns prior to reduction. The XPS signal collected from each scanned spot was used to produce chemical mapping images (scanning photoelectron microscopy, SPEM).

#### 3. Results

#### 3.1. Characterization of pristine graphene

Before any SPL treatment, the graphene was first characterized. Figure 1(a) provides a typical  $\mu$ -RS (sum of ten positions) of the CVD grown graphene in a local region  $(200 \,\mu\text{m} \times 200 \,\mu\text{m})$ . The  $\mu$ -RS indicated that the CVD grown graphene was monolayer ( $I_{2D}/I_G > 2$ , symmetric and single peak 2D band), and had low defect density (low D band,  $L_{\rm D} \sim 300$  nm) figure 1(b) shows the corresponding  $\mu$ -XPS spectra acquired from this region. It shows that the XPS are mainly composed of sp<sup>2</sup> related carbon-carbon bonds (C=C+C-C > 90%), and a low amount of C-O related bonds. There is no indication of PMMA residue in the graphene sheet. Structural defects, unintentional airborne hydrocarbon contaminants, or encapsulated hydrocarbon residue during the transfer process may be responsible for the observed >20% C–C bonds in the monolayer graphene [18]. While it has been reported that thermal annealing (by up to several hundred of degrees Kelvin) or exposure to UV ozone can effectively remove the airborne hydrocarbon contaminants, it also results in side effects such as generation of defects or oxidation of the substrate [18]. In our case, to avoid unwanted changes to the SPL patterns, we opted to avoid additional processing.

#### 3.2. Characterization of SPL treated (oxidized) regions

SPL was applied with voltage biases ( $|V_{\text{bias}}|$ ) ranging from 5 to 10 V and writing speeds ranging from 0.15 to 1.2  $\mu$ m s<sup>-1</sup>.



**Figure 1.** Typical (a) micro-Raman and (b) micro-x-ray photoelectron spectra acquired at the region of CVD grown graphene prior to SPL treatment. Each spectrum is the average of ten positions randomly measured across a local area of 200  $\mu$ m × 200  $\mu$ m in the film.

Prior to SPL, a rough scanning of the region of interest is usually needed in order to 'clean' the surface. Protruded lines can be seen at the boundaries of the first rough AFM scan. This probably reflects a scratching off of weakly attached surface contaminants by the contact mode AFM operation. The optical contrast, topography and tribology of the SPL treated patterns are shown in figure 2. Faint contrast can be seen between the SPL treated patterns and surrounding graphene in the optical image (figure 2(a)), indicating some changes in the optical/material properties. As seen in figure 2(b), all AFM images were characterized by protrusion patterns of about 1 nm height. Topology was independent of SPL parameters. (Note that we have previously investigated the nature of defects created through SPL under ambient condition and found that both protrusion and depression patterns with similar chemical and structural properties are possible [6].) Overall speaking, the SPL pattern surface appears to be rougher than the surrounding graphene surface. Tribological features are more sensitive to SPL treatment than topographical ones, as seen by the better contrast found in lateral force microscopy images (LFM) (figure 2(c)). The LFM signal was independent of both  $|V_{\text{bias}}|$  and writing speed indicating similar roughness.

Figure 3 presents the results of Raman spectroscopy in the region of interest. A micro-Raman map  $(I_G/I_D)$  within the investigated region is presented in figure 3(a). The SPL treated patterns appear to be darker due to deterioration of local sp<sup>2</sup> order (lower G band), and stronger defect related excitation (higher D band). Roughly speaking, patterns with higher  $|V_{\text{bias}}|$  appear to be darker. On the other hand, no significant dependence of  $I_G/I_D$  on writing speed is observed. Figure 3(b) shows the typical  $\mu$ -RS spectra for SPL patterns prepared with various  $|V_{\text{bias}}|$  conditions at the same writing speed. Under low  $|V_{\text{bias}}|$ , the intensity of D band increases as  $|V_{\text{bias}}|$  increases. Under high  $|V_{\text{bias}}|$ , the intensity of D band decreases while the width increases. Varying writing speed does not make significant difference in Raman signature (figure 3(c)). Figures 3(d) and (e) summarize the dependence of  $I_{\rm D}/I_{\rm G}$  and the corresponding converted  $L_{\rm D}$  on  $|V_{\rm bias}|$  and writing speed, respectively. Two equations (equation (1) for stage 1 for 5–7 V, and equation (2) for 8–10 V) are needed to maintain the continuity of  $L_{\rm D}$  value.  $I_{\rm D}/I_{\rm G}$  ( $L_{\rm D}$ ) first slightly increases (decreases) as  $|V_{\rm bias}|$  increases under lower  $|V_{\rm bias}|$ , and saturates at a threshold  $|V_{\rm bias}|$  of 8 V. No dependence of  $I_{\rm D}/I_{\rm G}(L_{\rm D})$  on writing speed is evident (figure 3(e)).  $I_{\rm D}/I_{\rm D'}$ remains between 2.5 and 3.5 as  $|V_{\rm bias}|$  or writing speed varies (figures 3(f) and (g)) indicating that this ratio is largely independent of SPL conditions.

The work of Casiraghi et al [15] provides insight into the nature of the defects being generated. For defect generation at stage 1, sp<sup>3</sup> defects are characterized by a significantly higher value of  $I_{\rm D}/I_{\rm D'}$  (typically ~ 12) than either vacancy-like (~6) or boundary-like defects ( $\sim$ 2). As can be seen in figure 3(f), the stage 1  $I_{\rm D}/I_{\rm D'}$  data acquired ( $|V_{\rm bias}|$  < 8 V) are all lower than 4, suggesting that under  $|V_{\text{bias}}| < 8 \text{ V}$ , defect generation occurs mainly along grain boundaries, i.e., more bombardment related defect that lead to connected vacancies with unpaired edges, with no significant oxidation occurring [15]. The above reasoning does not apply over a threshold  $|V_{\rm bias}| > 8$  V, as this region is described by stage 2 defect generation. At this higher voltage, complex defects that involve damage of local honeycomb order (drop in  $I_{\rm G}$  and broadening of G and D bands) are generated.  $I_D/I_{D'}$  remains low despite the possibility of C-O related sp<sup>3</sup> like bonding after SPL treatments.

Comparing this result with our previously reported work [6] using a more defective graphene ( $L_D \sim 34$  nm) provides insight into the role the pristine substrate plays. Despite identical SPL processing, the value of  $I_D/I_{D'}$  is significantly different, having a value of  $I_D/I_{D'} \sim 6$  ( $|V_{\text{bias}}| \sim 6$  V) indicating that initial conditions play a crucial role in determining the type of defects. It is conjectured that the different  $I_D/I_{D'}$  are due to the fact that vacancy creation through direct knocking out of a C atom in a defected 2D graphene network is relatively easier than in the nearly perfect 2D crystals investigated in this work.



**Figure 2.** (a) Optical image of the SPL treated film. The bias voltage  $|V_{\text{bias}}|$  increases from left to right, and writing speed increases from top to bottom. AFM images of the SPL treated film. (b) Topography (tapping mode). The green/pink curve besides the image shows cross sectional height data along the varying  $|V_{\text{bias}}|$  and writing speed direction, respectively. (c) Lateral force images. The red/blue curve besides the image shows cross sectional lateral force signal along the varying  $|V_{\text{bias}}|$  and writing speed direction, respectively.

Figure 4(a) presents the scanning photoelectron microscopy images of the SPL patterned samples before reduction. The upper/lower panel of figure 4(a) shows the mapping of the C1s  $\mu$ -XPS spectra taken at 286 eV (C–O)/284.4 eV (sp<sup>2</sup> C=C). The bright/dark areas reflect defected graphene in the SPL patterns, indicating a substantial increase/decrease in the number of C–O/C=C bonds in SPL-processed regions. From figure 4(b), we can see there is no significant C–O related bonds created under low  $|V_{\text{bias}}|$  condition, while oxygen coverage increases significantly under high  $V_{\text{bias}}|$  conditions. While varying writing speed does not make great difference in oxygen coverage under low  $|V_{\text{bias}}|$ , Under high  $|V_{\text{bias}}|$ , a slight decrease in oxygen coverage is found as writing speed increases (figure 4(c)). Figures 4(d) and (e) shows the peak area of each bond fitted from  $\mu$ -XPS data versus  $|V_{\text{bias}}|$  and writing speed, respectively. Figures 4(f) and (g) plots the concentration of C–C and C–O related bonds versus  $|V_{\text{bias}}|$ . A transition-like behavior for C-O related bond concentration versus  $|V_{\rm bias}|$  can be found. SPL with low  $|V_{\rm bias}|$  (<8 V) results in smooth concurrent decrease of C=C and increase of C-C bonds, with no significant increase for C-O and C=O bonds. At  $|V_{\text{bias}}| = 8$  V, an abrupt drop in C=C bonds and increase in C–O bonds is found. At  $|V_{\text{bias}}| > 8$  V, C–C drop abruptly and C–O increase significantly. At  $|V_{\text{bias}}| = 10 \text{ V}$ , most of the C=C and C-C bonds are converted to C-O related bonds ( $\sim$ 85%), with  $\sim$ 65% of C=O and  $\sim$ 20% of C-O. On the contrary, only weak changes can be seen as writing speed varies. The above observations are summarized in the 3D contour graph (figure 4(h)). Whereas the density of structural defects is low ( $|V_{\text{bias}}| < 8 \text{ V}$ ), oxidation of graphene through formation of sp<sup>3</sup> C–O related bonding is difficult due to lacks of unpaired carbon bonds, thus longer SPL duration (low writing speed) cannot contribute to more significant oxidation. On the contrary, when the density of structural defect is high ( $|V_{\text{bias}}| > 8 \text{ V}$ ), oxidation becomes easier, thus at longer SPL duration (low writing speed) results in higher oxygen coverage. Combining the facts that (1) low oxygen coverage is found at low  $|V_{\text{bias}}|$ , and (2) writing speed only plays a role in determining oxygen coverage at high  $|V_{\text{bias}}|$ suggest that structural defect creation has taken place prior to oxidation. Furthermore, the data suggests that structural defect creation in graphene through SPL is a fast and direct process while SPL oxidation of graphene is a comparatively slower and more indirect one.

#### 3.3. Reduction dynamics of SPL treated regions

Finally, we discuss the reduction dynamics of the SPL treated regions. With prolonged irradiation of focused x-ray on the SPL treated patterns, reduction occurs with a decrease of C-O related bonds and an increase of C-C related bonds. The reduction dynamics is recorded in situ by taking multiple high resolution C1s XPS (acquisition time = 20 s) with continuously irradiation of x-ray irradiation at target spots for 270 s (located according to the contrast shown in SPEM acquired immediately prior to high resolution XPS acquisition). Figure 5(a) shows the SPEM images taken before and after 270 s irradiation at each SPL-treated area (from left to right). As can be seen in comparing the images before and after irradiation, the intensity at 284.4 eV in each of the irradiated areas has almost recovered to the level of pristine graphene indicating an almost complete recovery of C=C bonds, probably due to low energy photo-electrons generated from both graphene and the underneath SiO<sub>2</sub> by the absorption of x-ray radiation. It is expected that these low energy photo-electrons could result in mild bombardment in the irradiated area and locally break the chemical bonds. The mechanism of the x-ray induced reduction is not fully understood at the moment. We can estimate the upper limit of heating effect induced by the x-ray irradiation. Consider a



**Figure 3.** (a) Micro-Raman mappings ( $I_G/I_D$ ) of the SPL treated region. The bias voltage  $|V_{\text{bias}}|$  increases from left to right, and writing speed increases from up to down. (SPL treated areas appear darker in the images.) Typical Raman spectra for various conditions: (b)  $|V_{\text{bias}}|$ , with fixed writing speed = 0.15  $\mu$ m s<sup>-1</sup>, and (c) writing speed, with fixed  $|V_{\text{bias}}| = 10$  V. Further information extracted from Raman spectra. Defect density information:  $I_D/I_G$ , and  $L_D$  (converted from  $I_D/I_G$ ) versus (d)  $|V_{\text{bias}}|$  and (e) writing speed. Defect type information:  $I_D/I_{D'}$  versus (f)  $|V_{\text{bias}}|$  and (g) writing speed.

micron-sized defective graphene with thermal conductivity  $\sim 400 \text{ W mK}^{-1}$  [19], irradiated by a focused x-ray with  $\sim 640 \text{ KW m}^{-2}$ , with  $\sim 1.8 \times 10^{13}$  photon s<sup>-1</sup> (assuming only 1% of irradiance remained after attenuation by focusing devices) [20]. Using Fourier equation  $q = KA\Delta T/s$ , where q is the heat transferred, K is thermal conductivity, A is the heated area,  $\Delta T$  is the temperature difference, and s is the thickness, we can calculate the temperature rise in the irradiated graphene. Putting all assumed parameters, the rise in temperature in a defective graphene is merely about 1.6  $\mu$ k. Therefore, local joule heating is not expected to be the cause

for reduction. What has been confirmed at the moment is that the reduction rate can be vastly changed when using substrates with different binding energy, i.e., different photoelectron yield upon the same x-ray irradiation [21]. Our work suggests that photoelectrons are mainly responsible for the observed reduction of oxidized graphene but no detailed mechanism can be established due to a lack of information on the exact value of x-ray flux and photoelectron yield. Figures 5(b) and (c) show the *in situ* acquired  $\mu$ -XPS waterfall spectra measured at SPL pattern generated at low (7 V) and high (10 V)  $|V_{\text{bias}}|$ , respectively. For low  $|V_{\text{bias}}|$ , the



**Figure 4.** (a) Scanning photo-electron microscopy images.  $|V_{\text{bias}}|$  increases from left to right, and writing speed increases from up to down. The map in the upper panel shows the C–O intensity (binding energy = 286 eV). The map in the lower panel shows the C=C intensity (284.4 eV). (b) Evolution of XPS under various (b)  $|V_{\text{bias}}|$  and (c) writing speed, with fitted curves included. (d) Peak area of each bond fitted from XPS data versus (e)  $|V_{\text{bias}}|$  and (d) writing speed. (e) C–C (black)/C–O (red) related bond concentration versus (f)  $|V_{\text{bias}}|$  and (g) writing speed. (h) The 3D color contour summarizing the effect of  $|V_{\text{bias}}|$  and writing speed on oxygen related bond concentration.

spectrum recovers to almost pristine like feature after one or two irradiation session, while the high  $|V_{\text{bias}}|$  case needs longer time to fully recover. The difference in the recover duration can be seen more clearly in the color contour figures shown in figures 5(d) and (e).

Based on the above observations, we propose an empirical model to describe the reduction dynamics. Five coupled rate equation set involving reduction sequence of C–OOH  $\rightarrow$  C=O  $\rightarrow$  C-OH  $\rightarrow$  C-C  $\rightarrow$  C=C is proposed to

empirically describe the observed reduction dynamics.

$$\frac{\mathrm{d}N_{\mathrm{C-OOH}}}{\mathrm{d}t} = -k_1(N_{\mathrm{C-OOH}} - N_{\mathrm{C-OOH}}'),\tag{3a}$$

$$\frac{\mathrm{d}N_{\mathrm{C=O}}}{\mathrm{d}t} = +k_1((N_{\mathrm{C-OOH}} - N_{\mathrm{C-OOH}}')) - k_2(N_{\mathrm{C=O}} - N_{\mathrm{C=O}}'),$$
(3b)

$$\frac{\mathrm{d}N_{\mathrm{C-OH}}}{\mathrm{d}t} = +k_2(N_{\mathrm{C=O}} - N_{\mathrm{C=O}}') - k_3(N_{\mathrm{C-OH}} - N_{\mathrm{C-OH}}'),$$
(3c)

$$\frac{\mathrm{d}N_{\mathrm{C-C}}}{\mathrm{d}t} = +k_3(N_{\mathrm{C-OH}} - N_{\mathrm{C-OH}}') - k_4(N_{\mathrm{C-C}} - N_{\mathrm{C-C}}'),$$
(3d)

$$\frac{dN_{C=C}}{dt} = +k_4(N_{C=C} - N'_{C=C}),$$
(3e)

where Ns represent the respective bond densities, ks represents the corresponding empirical rate constants for the bond dissociation/creation and N's are constants related to their corresponding steady state bond concentrations at the end of the reduction process obtained from experimental data. The major aim of the above model is to provide a picture of the probable dynamics. So far we have no further evidence to prove the proposed model and cannot identify the detailed intermediate states involved in the process. The proposed model only serves as an auxiliary scenario that may help to comprehend the experimental observations. Furthermore, note that for chemically prepared graphene oxide which contains a high concentration of oxide groups in a low structural order network, the reduction dynamics is usually more complicated than the step-by-step reduction dynamics found here. In most cases, the reduced graphene oxide would still contain significant concentration of oxide groups, due to formation of highly stable carbonyl and ether groups that hinder its complete reduction to graphene [22]. In contrast, for our case only insignificant oxide groups can be found after the x-ray reduction process. Furthermore, it has been observed that spontaneous oscillation redox reactions (oscillation in concentration between high and low binding energy bonds) can also occur in reduced graphene oxide under oxygen rich environment [23]. Therefore, it is difficult to comprehend the reduction dynamics of reduced graphene oxide in light of lowest energy configuration consideration. The above facts mark the major difference between our oxidized graphene and conventional reduced graphene oxide.

Figures 6(a) and (b) show the typical fitted time dependent curves for all involved chemical bonds in a SPL pattern fabricated with low (7 V) and high  $|V_{\text{bias}}|$  (10 V), respectively. A characteristic reduction time  $\tau$  is defined as the duration between the starting of x-ray irradiation to the time when C=C bond density recovered back to 95% of the final concentration, as depicted in figure 6(a). For each  $|V_{\text{bias}}|$  condition, data point shown in figure 6(c) is the averaged values of four writing speed conditions. It is found that  $\tau$  increases monotonically as  $|V_{\text{bias}}|$  increases, indicating a more complex bond reconstruction processes are involved as oxygen coverage increases (figure 6(c)). Larger error bar for  $|V_{\text{bias}}|$  is



**Figure 5.** (a) SPEM images taken before and after 270 s irradiation at each SPL-treated area (from left to right). The SPL patterns enclosed in red (purple) column are before (after) reduction. Waterfall diagram illustrating the gradual changes in  $\mu$ -XPS as a SPL pattern fabricated with (b)  $|V_{\text{bias}}| = 7 \text{ V}$  and (c)  $|V_{\text{bias}}| = 10 \text{ V}$  is gradually reduced by focused x-rays. Success curves are taken 27 s apart. (d) Color contour of the reduction process for SPL pattern fabricated with (d)  $|V_{\text{bias}}| = 7 \text{ V}$  and (e)  $|V_{\text{bias}}| = 10 \text{ V}$ .

natural consequence of slightly different starting condition with respect to writing speed. As shown in figure 6(d), the value of reduced rate  $\frac{k_3}{k_4}$  (the rate ratio of C–OH  $\rightarrow$  C=C to C–C  $\rightarrow$  C=C) is rather insensitive to  $|V_{\text{bias}}|$ . The average value of  $\frac{k_3}{k_4}$  is ~1.47  $\pm$  0.3. Comparing this with our previous work [11] involving

Comparing this with our previous work [11] involving SPL patterns on defective graphene one finds that (1) the value of  $\frac{k_3}{k_4}$  is the same (~1.46,  $|V_{\text{bias}}| = 10 \text{ V}$ ) [11] and (2) were described by a set of four coupled rate equations, i.e.

equation (3*a*) was not necessary. The above observations demonstrate that although different characteristic reduction duration  $\tau$  is needed for oxidized graphene with different oxygen coverage, the limiting step for reduction is still C-C  $\rightarrow$  C=C. The above results also show that the step-by-step reduction dynamics model is valid over a wide range of oxygen coverage and initial graphene conditions.



**Figure 6.** Fitted time dependent curves for all involved chemical bonds in a SPL pattern fabricated with (a) low (7 V) and (b) high  $|V_{\text{bias}}|$  (10 V). A characteristic reduction time  $\tau$  is defined as the duration between the starting of x-ray irradiation to the time when C=C bond density recovered back to 95% of the final concentration. (c)  $\tau$  versus  $|V_{\text{bias}}|$ . (d) The rate ratio of C–OH  $\rightarrow$  C=C to C–C  $\rightarrow$  C=C  $\frac{k_3}{k_4}$  versus  $|V_{\text{bias}}|$ .

#### 4. Conclusion

In summary, we have presented a comprehensive study in controlled micro-oxidation and reduction of graphene under ambient conditions. Making use of  $\mu$ -RS and  $\mu$ -XPS characterizations, we have shown that the dominant factor in SPL oxidation is  $|V_{\text{bias}}|$ . Writing speed only matters at high  $|V_{\text{bias}}|$ . In particular, there is a sharp transition in defect density and oxygen coverage at  $|V_{\text{bias}}| = 8$  V. Below this, only structural defects are formed around grain boundaries. Above this threshold an abrupt increase in oxygen coverage is found, indicating easier bonding between oxygen related radicals to the already defected C-C network. Reduction of the oxidized areas through prolonged irradiation of focused x-ray can be fitted using 5 rate equations. The limiting step of reduction is C–C  $\rightarrow$  C=C, for all  $|V_{\text{bias}}|$  cases, and the rate ratio between C–OH  $\rightarrow$  C=C and C–C  $\rightarrow$  C=C processes is about 1.47. The time required for reduction was found to be directly proportion to the degree of oxidation. Finally, in combining the results reported here with those in [6, 11] for more defective graphene, we have shown that while the initial state of the graphene substrate affects the type of defects produced in SPL, identical rate equations, with the same limiting step and ratio of rate constants being similar. This finding suggests that the proposed coupled rate equation set is widely applicable and the step by step reduction mechanism is valid for a wide range of oxygen coverage and broad range of initial graphene defect conditions.

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