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#### ABSTRACT

The defects created by scanning probe lithography (SPL) under ambient conditions in CVD grown graphene were investigated using atomic force microscopy, micro-Raman ( $\mu$ -RS) and micro-X-ray photoelectron spectroscopy ( $\mu$ -XPS). Topographically, both protrusion and depression structures with distinguishable tribological properties were produced simultaneously. However, the key aspects of the spectroscopy were similar for the two topographies.  $\mu$ -RS revealed that the ratio of the defect Raman peaks ( $I_D/I_D$ ) and the effective distance between defects (LD) had similar magnitude and dependence on the applied bias voltage.  $\mu$ -XPS revealed no evidence of the generation of sp<sup>3</sup>-type defects. The small amplitude of the C–O peak and absence of C=O and C–OH peaks, suggested a complete absence of graphene oxide in the defect areas. Our results indicate that similar defects are present in both depressions and protrusions and suggest that a common active mechanism, namely bond reconstruction, is responsible for both structures.

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# 1. Introduction

The electronic and optical properties of a crystalline material can be substantially modified with a minute amount of defects [1,2]. Graphene, as a unique two dimensional (2D) honeycomb lattice consisting  $sp^2$  bonded carbon atoms, is not immune to defects. On the one hand, the presence of defects can be seen as detrimental to the electrical performance of graphene, e.g., lowering electron mobility due to scattering [3–5], and thus something to be avoided. On the other hand, defects can be employed to tailor the electrical

and chemical properties of graphene. Band gap opening and reactivity modification by functionalization with foreign atoms or structural defects are good examples of the utilization of defects in graphene [6,7]. As a sp<sup>2</sup> bonded 2D crystal, each carbon atom has three nearest neighbors in a perfect 2D honeycomb network. Defects can be created by either rotating bonds, losing one or two of neighboring atoms, reconstructing bonds to accommodate more neighbors, or forming additional out of plane bonds with foreign atoms. Defects have been categorized as Stone–Thrower–Wales (STW), vacancy, and sp<sup>3</sup> type of defects [8–10]. The defect

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creation energy barrier for each type of defects is vastly different and ranges from 1.5 eV to  $\sim 10 \text{ eV}$  [11]. The formation energy of a STW type defect is  $\sim$ 5 eV and thus can be initiated by electron or ion irradiation under room temperature [12]. Vacancy generation requires ~7.5 eV of formation energy but is subject to bond reconstruction under room temperature due to its relatively low migration energy barrier (~1.3 eV) [13]. Ion bombardment with electrons or ions can result in vacancy like defects [14]. The energy barrier for creation of sp<sup>3</sup> type defects is about 2–3 eV, and can be achieved by bonding with interstitial atoms or chemical treatment [15,16]. The stability of sp<sup>3</sup> type defects depends on the bond strength between carbon and foreign atoms. For weaker bonds, unstable chemically bonded defects may result in dangling bonds in graphene and subsequent bond reconstruction around the defects resulting in a deviation from 2D sp<sup>2</sup> bonding when the number of neighboring atoms becomes larger than three [17]. Such bond reconstruction (at room or elevated temperature), can then produce a distortion of bonds or even an out of plane structure [18]. For stronger sp<sup>3</sup> bonds, clustering of defects occurs and patches of low conductivity appear [19].

Scanning probe lithography (SPL) is a mask-less technique that enables nanometer scale patterning on metallic or semiconducting substrates. Under ambient conditions, a water meniscus forms between the substrate surface and atomic force microscope (AFM) probe tip. When there is a strong bias between tip and substrate, water molecules decompose under the strong vertical electrical field and interact with surface atoms to form an oxide. SPL is a complex physical-chemical process that sensitively depends on tip bias, humidity, substrate surface hydrophobicity, tip writing speed, and substrate/probe work function [20-23]. SPL on graphene has been demonstrated recently with both protrusion and depression topographies reported under similar SPL conditions. Conventionally, the SPL process on graphene is attributed to an electrochemical process involving C-O bond formation between graphene and decomposed OH<sup>-</sup> ions in the water meniscus that forms between tip and sample surface [24-29]. The protrusion (depression) topography is usually explained in terms of non-volatile (volatile) oxidation of the carbon atoms in graphene [24-26]. The above scenario implies that sp<sup>3</sup> (vacancy) type defects dominate in the protrusion (depression) structures. Nevertheless, to date, no direct experimental support for this intuitive scenario has been presented.

In this work we employ micro-Raman spectroscopy ( $\mu$ -RS) and scanning micro-X-ray photoelectron spectroscopy  $\mu$ -XPS) to investigate the structural and chemical natures of these two defect structures. Raman spectroscopy was chosen as it has been shown to be a powerful tool for probing structural information of graphene [30–32]. Typical Raman fingerprints of graphene include G (~1580 cm<sup>-1</sup>) and 2D (~2680 cm<sup>-1</sup>) bands since Raman selection rules are always satisfied. Defects result in the appearance of the additional Raman forbidden D (~1350 cm<sup>-1</sup>) and D' (~1620 cm<sup>-1</sup>) bands as the defect provides the missing momentum to satisfy momentum conservation in the Raman scattering process. Namely, the D (D') band represents processes activated by a defect assisted single-phonon inter-valley (intra-valley) scattering processes [33]. Recently, Raman spectroscopy has been used to probe the nature of defects in graphene by measuring the ratio of the D and D' intensities  $(I_D/I_{D'})$  [34,35]. Due to lower activation of the intra-valley transition for sp<sup>3</sup> type defects compared to vacancy type defects,  $I_D/I_{D'}$  can be used to distinguish the defect type in graphene.

The chemical bond profile was probed with X-ray photoelectron spectroscopy. 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. This method has in the past been used for the identification of PMMA residue, fluorination and other functionalization of graphene [36–38]. By focusing the intense X-ray beam down to <0.1  $\mu$ m by a zone plate, and scanning the sample with a motorized stage, the chemical bond profile of the SPL defects was obtained with submicrometer resolution [39].

#### 2. Experimental

#### 2.1. Growth of monolayer graphene

Monolayer graphene was grown on 25  $\mu$ m thick copper foil in a quartz tube furnace system using chemical vapor deposition (CVD) involving methane and hydrogen gases [40,41]. Under vacuum conditions of 10 mTorr and at a temperature of 1000 °C, H<sub>2</sub> was introduced (flow rate = 2 sccm) for 40 min, followed by methane (35 sccm) for 15 min. Quick cooling was then applied (300 °C/min) under continuous methane and hydrogen gas flows. Films were then transferred to 100 nm thick oxide buffered SiO<sub>2</sub>/Si wafers through polymethylmethacrylate (PMMA) coating and iron (III) nitrate etching. The film's monolayer characteristics and film quality were then verified using  $\mu$ -RS. Films exhibited the characteristic monolayer signature ( $I_{2D}/I_G > 2$  and symmetric 2D band) [42,43].

# 2.2. Defect generation and characterization methods

SPL was conducted using a contact mode AFM (Bruker Innova) equipped with a custom implemented external bias source to allow for the application of bias ranging between ±15 V, with tunable step <0.1 V using a conductive AFM probe (Pt/Ir coated point-probe series, Nanosensor) [29]. The relative humidity was kept at  $RH \sim 55\%$  throughout the SPL process in a sealed chamber. Patterns or lines were drawn using the built-in software (Nanoplot, Bruker) to enable exact positioning (down to nanometer scale). After patterning, topographical and lateral force information was acquired using the same tip. For more refined structural detail, tapping mode AFM with a sharp probe (SSS series, Nanosensor) was employed to avoid image distortion. After AFM characterization, the spectroscopy of the samples was observed using µ-RS and µ-XPS. µ-RS was acquired using a confocal micro-Raman spectrometer (Lab Ram HR, Horiba) employing a  $\lambda$  = 532 nm DPSS laser for excitation. A100X, NA = 0.9 objective lens, and a motorized stage (step size =  $0.5 \,\mu$ m) were employed to achieve a spatial resolution of  ${\sim}1\,\mu\text{m}.$   $\mu\text{-XPS}$  was acquired on the soft X-ray (photon energy 380 eV) beam line (SPEM end station, 09A1) of the

National Synchrotron Radiation Research Center (NSRRC, Hsinchu, Taiwan). A spatial resolution of 100 nm was achieved using a Fresnel zone plate, and a peizo-controlled motorized stage.

# 3. Result

# 3.1. Quality of chemical vapor deposition grown graphene

The quality of the graphene films (outside the region of SPL modification) was first checked using μ-RS, as it is well known that unlike pristine graphene flakes acquired by exfoliation, CVD grown graphene always contains defects, at least at grain boundaries [44]. The transfer and chemical process can further introduce defects into the 2D sp<sup>2</sup> lattice [45]. The defect density of as-grown CVD graphene was found to be reasonably low. Typically,  $I_D/I_G < 0.05$  resulting in  $L_D > 50$  nm using  $(L_D^2(nm^2) = (1.8 \pm 0.5) \times 10^{-9} \lambda_D^4 (I_D/I_G)^{-1})$  (cf Fig. 2(a) and (b) for typical micro-Raman spectra of the films) [46]. Unfortunately, not all defects are Raman active [30]. Therefore, despite the absence of significant D and D' bands in the Raman spectra, there still may be structural or chemical defects that could contribute to a difference in defect generation at the subsequent defect introduction process, compared to its exfoliated counterpart.

## 3.2. AFM characterization of SPL generated defects

Fig. 1 illustrates the patterning process (a) and typical topographical (AFM) and lateral force microscopy (LFM) images at bias voltages of -6V (b) and -12V (c). In the LFM images the frictional interaction in the SPL region provides strong contrast indicating that the material properties have been modified by the SPL process. The topographical images (see cross-sections) indicate that this LFM contrast results from both protrusions with a height of <1 nm, and depressions with a depth of <1 nm. Both categories of patterns can be created with bias voltages (Vbias) ranging from -14 V to -6 V. Above  $|V_{\text{bias}}| > 15$  V, the tip becomes unstable, resulting in tip deformation and subsequent image distortion. Below |V<sub>bias</sub>| < 6 V, patterns have low reproducibility, indicating a threshold for the SPL process. Both positive and negative bias voltages can be employed in creating SPL patterns but we found empirically that negative voltages are more reliable. Moreover, in order to compare to previous works that attributed structure to local anodic oxidation, the data presented in following discussion are restricted to negative V<sub>bias</sub> cases. We did not find any evidence for a higher tendency for generating depression patterns under higher bias voltages. Rather, depression (protrusion) patterns can be created at low as well as high bias. Note that the SPL generated patterns do not necessarily start at sample edges as has been previously found for exfoliated graphene [24,25,27]. Rather they are generated at various locations on the same continuous graphene film. The existence of intrinsic defects in CVD grown graphene may explain why the SPL barrier is much lower than in exfoliated pristine graphene.

#### 3.3. µ-RS characterization of SPL generated defects

Fig. 2 summarizes the key µ-RS results. Two obvious signatures can be found for SPL produced defects. First, a significant increase in D and D' band intensities, can be found, indicating an SPL induced generation of defects in graphene. Second, there is a significant decrease in the intensity of the G and 2D bands for the depression patterns, while no obvious change in the intensity of these two bands occurs for the protrusion patterns (Fig. 2(a) and (b)). The effective distances between defects ( $L_D$ ) as measured through  $I_D/I_G$  for each case are presented in Fig. 2(c).  $L_D$  decreases significantly down from >50 nm before SPL processing to <10 nm for all cases, indicating the creation of defects through the SPL process. For bias voltages above 7 V, a widening of the characteristic bands occurs, and  $L_D$  drops from 5 nm ( $|V_{bias}| = 6 V$ ) to <1 nm. Above 7 V,  $L_D$  is approximately constant. The similar magnitude and dependence of  $L_D$  on bias voltage for both protrusions and depressions indicates a similar rate of defect generation and suggests that the defects generated may be similar in nature for the two cases. As to the nature of the drop at bias voltages above 6 V, previous work has shown that the evolution of defect generation involves two distinct stages [34]. In stage 1, the activation of D and D' bands increases as the defect density increases. In stage 2, the density of defect sites becomes so high that the cross-section of defect related Raman active bands become smaller, and thus the intensity of D and D' bands becomes lower and broader. In our case, by increasing electron energy through increasing |V<sub>bias</sub>|, a transition from stage 1 to 2 is expected. In our experimental data, this transition appears to occur around  $|V_{\rm bias}|\sim 7$  V. Not altogether unsurprisingly, the Raman spectra indicates that protrusions, in general, exhibit larger I<sub>G</sub>/I<sub>Go</sub> (ratio of G band intensity before (IGo) and after SPL (IG)) than depressions (Fig. 2(d)). This difference is most pronounced at low V<sub>bias</sub> (i.e. stage 1 growth) but tends to converge at higher bias voltage (i.e. stage 2 growth). Further information on the nature of defects can be obtained from the ratio  $I_D/I_{D'}$ . In Fig. 2(e) the data is summarized by plotting  $I_D/I_G$  vs.  $I_{D'}/I_G$ . As seen in the figure, the data lies on one of two lines. The ratio  $I_D/I_{D^\prime}$  is dependent only on bias voltage, i.e. is independent of topographic structure, suggesting that the same type of defect is created in both structures. Defects, for both protrusion and depression topography, are vacancy like ( $I_D/I_{D'} \sim 6.0$ ) at lower  $|V_{\rm bias}|,$  and become boundary-like ( $I_{\rm D}/I_{\rm D'}\sim2.2$ ) at elevated  $|V_{\text{bias}}|$  [34,35]. Note that since the sp<sup>3</sup> type defect gives rise to much lower  $I_{D'}$ , ( $I_D/I_{D'} \sim 13$ ), the absence of  $I_D/I_{D'} > 10$  indicates that, even for protrusion defects, out of plane sp<sup>3</sup> bonds between C and O are not a dominate factor [34-36].

In summary, the Raman spectroscopy results are: (1) consistent with previous models of depressions formed under low bias being due to volatile oxidation of the carbon atoms in graphene, (2) inconsistent with previous intuitive models invoking a non-volatile oxidation mechanism to explain the protrusion topography under all biases [24–26], and (3) suggestive of a common bias dependent mechanism for all defects. In the following sections, we will argue that at least at higher voltage biases and probably all voltage biases, the



Fig. 1 – Patterns formed by SPL under ambient conditions (a) schematic diagram of the SPL setup; topography and lateral force images of SPL patterns produced at (b)  $V_{\text{bias}} = -6 \text{ V}$  and (c)  $V_{\text{bias}} = -12 \text{ V}$  respectively. Cross-sections are shown as insets in Fig. 1(b) and (c). (A color version of this figure can be viewed online.)

common active mechanism involves bond reconstruction for both topographic structures.

#### 3.4. μ-XPS characterization of SPL generated defects

To further clarify the above pictures,  $\mu$ -XPS was used to characterize the chemical bonding profiles in the SPL defects. Fig. 3 presents the C1S mapping of SPL patterned CVD grown graphene supported on the SiO<sub>2</sub>/Si template (a) along with the  $\mu$ -XPS recorded at various points in the film (b–d). In Fig. 3(a), Channel 1 (monitors the convoluted C–C and C–O bond strengths while Channel 2 monitors the C=C bond strength. Protrusions and depressions, as identified by AFM, appear brighter (darker) in the Channel 1 (2) image (Fig. 3a). In non-SPL processed areas of the film (defect-free graphene) the typical graphene feature: a narrow and asymmetric C=C peak at 284.5 eV is observed. A small amplitude C-O bond related peak is also present and is attributed to low amount of C-O bonding formed between ambient oxygen and dangling carbon bonds due to intrinsic defects in the CVD grown graphene [36]. In the depression spectra the C=C peak is significantly lower and slightly blue shifted and additional C-C and C-O peaks around 285.5 and 288 eV respectively, are present. Similar additional peaks can be found for the protrusion, but with



Fig. 2 – Micro-Raman spectroscopy of the SPL patterns. Typical Raman spectra for (a)  $V_{\text{bias}} = -6$  V and (b)  $V_{\text{bias}} = -12$  V. The upper (lower) column represents protrusion (depression) patterns; (c) estimation of  $L_D$  from  $I_D/I_G$  for various applied biases. (d) Changes in  $I_G$  intensity after the SPL processes; (e)  $I_D/I_G$  versus  $I_D/I_G$ . Fittings of curves shown in dashed lines. In (c)  $L_D$  for protrusions and depressions are overlap at 6 V and 12 V bias. (A color version of this figure can be viewed online.)



Fig. 3 – (a)  $\mu$ -XPS microscopy image of CVD grown graphene with SPL fabrication at moderate bias voltage (V<sub>bias</sub> = -10 V) (a) Intensity maps for two different energy ranges. (b)–(d) Spectra recorded at locations D (depression), P (protrusion) and R (reference spectra) marked in (a). Locations of the depressions and protrusions were determined with AFM by identifying a nearby marker. (A color version of this figure can be viewed online.)

stronger C–C and weaker C–O peaks. Most importantly, the drop in C=C peak intensity is much less in the case of protrusions than for depressions. The above spectra are consistent with the Raman results and imply several important messages. First, the small amplitude of the C–O related peak

and absence of C=O and C-OH peaks, the fingerprints of graphene oxide, suggests that the protrusion pattern is not constructed by non-volatile graphene oxide generation. Second, the lower C=C peak height in the depression case suggests that reconstructions of bonds after the SPL process

result in a lower density for the honeycomb lattice, consistent with the pronounced decrease in the G band observed in the Raman Spectra. A more subtle aspect in the XPS spectra is the difference in ratio between C–C and C–O bonds related peaks for protrusion and depressions which is much higher in the case of protrusions (1.97) than for depressions (0.66): a result that is consistent with bond reconstruction being the active mechanism in both cases. According to the bond reconstruction model, in the protrusion case there will be less room for C–O bonding since out of plane defective C–C bonding limits the density of remaining dangling C bonds available for C–O bonding. The slight blue shift in C=C peak indicates bond distortion in both topographies [36].

# 4. Discussion

Both the Raman and XPS results indicate that non-volatile oxidation is not responsible for defects in the protrusion geometry, but rather indicate a common mechanism, i.e., bond reconstruction after volatile oxidation, is responsible for defect generation in both topographies. In particular, we find that the protrusion topography is not result of sp<sup>3</sup> C–O bonding and stacking as previously thought. Considering the relatively long time scale of SPL processes (typically micro-seconds, many orders longer than chemical reactions) and stability of C-O related bonds (C-O, C=O, C-OH) [47], we propose that the intense electric field between tip and sample surface induces repeating cycles of water decomposition into H<sup>+</sup> and OH<sup>-</sup>, followed by formation of C–O related bonds, subsequent dissociation of these C-O related bonds, volatile desorption of CO<sub>x</sub> molecules leaving behind dangling bonds on carbon atoms, and finally bond reconstruction of carbon atom in the 2D lattice. Once clustering of reconstructed bonds occurs, the dissociation energy of such cluster could become much higher [19], resulting in a higher stability of such structure relative to non-volatile C-O related bonds. In this case, it is energetically favorable to have reconstructed bonds and their clustering as the final result under such repeating bonding-dissociation cycles. Protrusion structures could then be formed if patches of out-of-plane clustering occur while depression structures could be formed if volatile generation of C-O dominates. The issue of which of these processes dominate is likely related to local structure prior to SPL process (such as local intrinsic defect density, defect types). In the future we hope to correlate initial conditions and final defect generation with similar methodology employed in this work. In addition, atomic resolution measurement on the defect structures with methods such as ultra-high vacuum scanning tunneling microscopy could further provide information to be compared with atomistic calculation. Overall speaking, this work provides an understanding on the defect generation mechanism in CVD grown graphene but not necessarily explains all the defects observed in graphene prepared by other means.

# 5. Conclusion

In conclusion, the defects created by SPL under ambient conditions in CVD grown graphene were investigated using AFM,  $\mu$ -RS and  $\mu$ -XPS. While, topographically, both protrusion and depression structures with distinguishable tribological properties were produced simultaneously, the key aspects of the spectroscopy were similar for both topographies.  $\mu$ -RS revealed that  $I_D/I_{D'}$  and  $L_D$  had similar magnitude and dependence on the applied bias voltage for both topographies.  $\mu$ -XPS revealed no evidence of the generation of sp<sup>3</sup>-type defects and the small amplitude of the C–O peak and absence of C=O and C–OH peaks, suggest a complete absence of graphene oxide in the defect areas. Our results indicate that similar defects are present in both depressions and protrusions and suggest that a common active mechanism, namely bond reconstruction, is responsible for both structures.

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