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On the nature of defects created on graphene by scanning probe lithography under ambient conditions

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ARTICLE INFO

ABSTRACT

The defects created by scanning probe lithography (SPL) under ambient conditions in CVD grown graphene were investigated using atomic force microscopy, micro-Raman (μ-RS) and micro-X-ray photoelectron spectroscopy (μ-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. μ-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. μ-XPS revealed no evidence of the generation of sp^3-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^2 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^3 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 ~10 eV [11]. The formation energy of a STW type defect is ~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^3 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^3 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^2 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^3 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^- 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^3 (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 (μ-RS) and scanning micro-X-ray photoelectron spectroscopy μ-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^{-1}) and 2D (~2680 cm^{-1}) bands since Raman selection rules are always satisfied. Defects result in the appearance of the additional Raman forbidden D (~1350 cm^{-1}) and D′ (~1620 cm^{-1}) 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^3 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^2 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 μm 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 μm 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_2 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_2/Si wafers through polymethylmethacrylate (PMMA) coating and iron (III) nitrate etching. The film's monolayer characteristics and film quality were then verified using μ-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 ~ 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 λ = 532 nm DPSS laser for excitation. A100X, NA = 0.9 objective lens, and a motorized stage (step size = 0.5 μm) were employed to achieve a spatial resolution of ~1 μm. μ-XPS was acquired on the soft X-ray (photon energy 380 eV) beam line (SPEM end station, 09A1) of the