



Plasma-based chemical modification of epitaxial graphene with oxygen functionalities [☆]



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ABSTRACT

Epitaxial graphene is promising material for future graphene-based applications including high frequency devices and chemical/biological sensors. Modifying the surface chemistry of graphene allows one to control its properties and thus provides a promising route towards further broadening the device application space for this unique material. Herein, we demonstrate the use of electron beam generated plasmas as a route towards controlled oxygen doping of epitaxial graphene. X-ray photoelectron spectroscopy, Raman spectroscopy and electrical measurements are used to track the oxygen incorporation and its influence on the structural and electrical properties of epitaxial graphene.

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1. Introduction

Graphene has attracted enormous attention due to its exceptional properties and its potential as the next-generation material in electronics, energy conversion, spintronics, and biological/chemical sensing applications [1–7]. Of the various synthesis routes available [8–12], epitaxial growth of graphene, derived from the sublimation of Si from SiC substrates [13,14], is capable of producing high-quality, wafer-scale [15] continuous graphene sheets and holds promise for large-scale, uniform production [16–19]. While there are many applications for graphene, manipulating its surface chemistry can allow one to tailor its properties and thus broaden the potential. For example, the lack of a band gap has yielded poor current saturation in graphene transistors with ON–OFF ratios of ~ 10 [20], but the use of fluorinated-graphene has produced ON–OFF switching ratio of $\sim 10^5$ [21].

Approaches aimed at chemical modification [22–35] have demonstrated significant modulation in electronic properties [36] and chemical reactivity and will likely play a vital role in realizing graphene's

potential in electronics [1–7,37,38] and sensing applications [39,40]. Electron-beam generated plasmas are one such approach. They are capable of imparting a variety of functional group types over a controlled range of coverages with minimal damage to the carbon back bone because of their inherently low ion energies and as such, offer a unique approach for large area uniform chemical processing of graphene films [41–44]. It should be noted that there are significant differences between the various forms of graphene (e.g. exfoliated, CVD-derived, epitaxial), particularly when including the substrate on which they reside in terms of materials characteristics, surface morphology and resulting electrical properties. As such, detailed attention is paid here to the changes in the material properties as a result of oxygen incorporation as measured by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and electronic properties. Linking these changes provides not only practical information on processing but also insight about the influence of oxygen on epitaxial graphene.

2. Materials and methods

2.1. Graphene growth

Epitaxial graphene samples were grown by Si sublimation on the Si-face of 8×8 mm² semi-insulating 6H-SiC substrates (II-VI, Inc.) in a commercial Aixtron/Epigress VP508 chemical vapor deposition reactor. Prior to growth, samples underwent an in situ H₂ etch to remove any

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surface damage thus producing a uniform stepped surface. Graphene growth followed at temperatures ranging from 1620 to 1650 °C, in an argon atmosphere for 1–3 h at various pressures as described elsewhere [19,37]. In this work, graphene films are typically 1–3 monolayers (ML).

2.2. Plasma processing

Pulsed, electron-beam generated plasmas were produced by applying a -2 kV pulse to a linear hollow cathode. The emergent beam passes through a slot in a grounded anode and terminates at a second grounded anode located further downstream. The resulting electron beam is magnetically confined to minimize spreading, producing a sheet-like plasma in mixtures of argon and oxygen. The system base pressure was maintained at $\sim 1 \times 10^{-6}$ Torr prior to processing by a turbo molecular pump. For this work, the operating pressure was varied between 50 and 90 mTorr, by controlling by the total gas flow rate (100–180 sccm). For all conditions, the reactive gas (O_2) was introduced at 5% of the total flow rate with argon as the remainder. Plasma processing was conducted for 60 s using a 2 ms electron beam pulse at a duty factor of 10%. EG samples were placed on a processing stage adjacent to the plasma at a distance of 2.5 cm from the electron-beam axis. All processing experiments were performed at room temperature.

2.3. Surface characterization

Ex-situ surface diagnostics were performed before and immediately after plasma processing to determine the starting material quality and chemistry and the changes resulting from plasma treatment. Chemical analysis was carried out by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha spectrometer with a monochromatic Al-K α source with a spot size of 400 μ m. The graphene thickness was determined by comparing the ratio of the integrated area of the silicon to carbon signal of the high-resolution spectra. The total oxygen content was determined by the ratio of the integrated area of the oxygen and carbon content. Raman characterization was performed with an InVia Raman microscope (Renishaw) equipped with a 50 \times objective lens and a 514.5 nm diode laser excitation on 1800-line grating; analysis was performed at a set power of 20 mW at the source with a spot size of 5 μ m. Hall-effect characteristics were measured at room temperature using large area van der Pauw configuration. Four point contact measurements were performed using copper clips over sample areas of 8 \times 8 mm², applied currents of 1 and 5 μ A, and an external magnetic field of 2 kGs. Resistance vs. temperature data were obtained with a measuring current of 0.01 mA in a Quantum design PPMS using the van der Pauw method.

3. Results and discussion

Chemical changes and resulting bonding characteristics in epitaxial graphene (EG) due to plasma processing were tracked by X-ray photo-electron spectroscopy (XPS). Shown in Fig. 1 are the XPS survey spectra of as-grown and plasma processed samples. Following plasma exposures, the presence of oxygen is clear (O1s) and increases with increasing operating pressure, going from 3.6 at.% at 50 mTorr to 11.7 at.% at 90 mTorr.

A better understanding can be developed by comparing the high-resolution C1s spectra of graphene before and after processing for each plasma processing condition. The results are shown in Fig. 2. The C1s peaks for untreated EG was deconvoluted into three components centered at about 283.6 eV, 284.6 eV and 285.4 eV which correspond to the silicon carbide (Si-C) substrate, the graphene film (C–C), and the interfacial layer between the SiC and epitaxial graphene, respectively [45]. Here the graphene peak with sp^2 bonding is labeled as EG, the interfacial layer is labeled as IR, and the silicon carbide signal is referred to as SiC. The spectra presented in Fig. 2 have been shifted to the

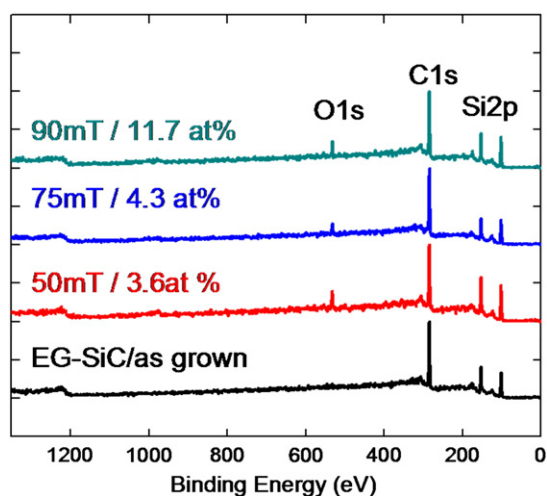


Fig. 1. XPS survey spectra of oxygen functionalized epitaxial graphene at increasing operating pressure.

intensity of the substrate (Si-C) peak at ≈ 283.6 eV. Differences in the intensities within the C1s spectra between the (Si–C) and the (C–C) peaks of the samples (before plasma processing) reflect minor differences in the amount of graphene layers/surface coverage [45–47]. Following plasma treatment, the C1s spectra shows the incorporation of oxygen functionalities which are assigned to carbon bonding involving ethers or alcohols (C–O–C, C–O, or C–OH) and carbonyl bonds ($=O$) located at ≈ 286.4 eV and ≈ 287.1 eV, respectively.

Due to the strong silicon-carbide contribution to the C1s spectra, the oxygen functionalities can be further understood by deconvoluting the O1s high-resolution spectra shown in Fig. 3. Before plasma processing, the O1s scans generally show little to no signal, indicating no oxygen present on the samples. After plasma processing, features on the O1s spectra arise at three different locations corresponding to carbonyl groups (C=O) bonding at ≈ 534.3 eV, ethers or alcohols (C–O–C, C–O, or C–OH) at ≈ 533.3 eV and silicon oxide (Si–O) at ≈ 532.2 eV. The deconvoluted O1s spectra show pressure dependence in terms of the amount and type of carbon–oxygen bonds formed after O_2/Ar plasma treatment. To understand this, first note that increasing the pressure in the system increases the production of charged particles and reactive neutrals and thus the delivery of these species to the surface [48]. Then, consider that upon initial exposure, single (σ) bonds will form between the oxygen species and graphene. These functionalized sites are now less sp^2 in character which alters the charge of its surrounding C atoms, lowering the adsorption energy for subsequent adsorbates near that defect [49]. Thus, at low pressures, the formation of single (σ) bonds between oxygen and EG is expected. Additional reactive oxygen species available in the plasma will be attracted to these locations making the formation of π -bonds more favorable. At the higher pressures, there is a larger amount of reactive oxygen species available, therefore accelerating the σ to π bond formation rate. The observed increase in total oxygen incorporated coupled with larger fraction of π -bonded oxygen functionalities at elevated pressures is in reasonable agreement with this scenario.

Raman spectroscopy is powerful for identifying the number of layers, disorder and doping of graphene. The Raman spectra of as-grown and plasma processed EG samples are shown in Fig. 4. Before processing there is a G peak (≈ 1600 cm^{-1}) and a 2D peak (≈ 2730 cm^{-1}), and no detectable D peaks (indicative of EG disorder) for all EG samples (black curves in Fig. 4) [50]. The G peak is convoluted with the background contribution of SiC, which was not subtracted in Fig. 4a, and can be difficult to observe. However, the 2D was easily distinguishable from the background. After plasma treatment, the Raman spectra of the same sample at approximately the same location, showed an increase in the disorder induced D peak and decreases in both the

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