Carbon 112 (2017) 192–200

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Defects of clean graphene and sputtered graphite surfaces characterized by time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy

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ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form
31 October 2016
Accepted 1 November 2016
Available online 4 November 2016

ABSTRACT

Clean surface of graphene was obtained at 500 °C and characterized by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). In the XPS C1s spectrum of graphene, besides an asymmetric sp^2 carbon peak and a π-π^* shake-up peak appeared, an additional sp^3 carbon peak representing sp^3 defects was also present. In the ToF-SIMS positive ion spectrum of graphene, a series of $C_xH_2^{+\bullet}$ ions originated from the defects of graphene was found. To determine the origin of the $C_xH_2^{+\bullet}$ ions, defects were created on the surface of nearly defect-free highly oriented pyrolytic graphite (HOPG) by bombarding it with a Cs^+ ion beam at various sputtering doses. A detailed examination of the positive ion spectra of ion-bombarded HOPG surfaces reveals the presence of the $C_xH_2^{+\bullet}$ ions, confirming that these $C_xH_2^{+\bullet}$ ions, which came from the defects created on the sputtered HOPG surfaces, are similar to the defects present on graphene surface. A sp^3 carbon peak at 285.3 eV, representing sp^3 defects appeared in the XPS spectra of sputtered HOPG samples, confirms that the surface of the sputtered HOPG is similar to that of graphene. Fragmentation mechanisms of selected ions in the ToF-SIMS spectra of graphene and HOPG were proposed.

1. Introduction

Graphene, a single layer of graphite [1], has been produced by chemical vapor deposition (CVD) on a variety of metal substrates such as Cu and Ni [2,3]. During the preparation process, graphene domains with various orientations on the surface of a Cu foil are first formed under a carbonaceous atmosphere at high temperatures. As the growth time increases, these graphene domains expand and aggregate into graphene sheets [4]. However, defects in the gaps between graphene domains disturb the delocalization of the sp^2 carbons in the graphene aromatic structure. Those defects can exist in the form of sp^3 carbons with more or less than six carbon atoms in a ring [5]. Usually, one or two H atoms are attached to the sp^3 carbons. The presence of defects on graphene, which can change its electrical, mechanical and magnetic properties, can have significant impact on the performance of graphene-based devices [6,7]. The defects on the graphene surface can also enhance its surface chemical reactivity, which allows chemical functionalization for different chemical applications [6]. On the other hand, highly oriented pyrolytic graphite (HOPG) consists of stacked carbon layers with sp^2 hybridized carbons and is considered defect-free [8]. HOPG is formed by pyrolysis of a carbonaceous gas at high temperatures, which can easily generate a new graphite surface *via* simple tape cleavage [9,10]. Compared to graphene, the surface of HOPG is smooth and almost defect-free. The defects in graphene can be detected from an X-ray photoelectron spectroscopy (XPS) C1s spectrum [11,12]. Furthermore, XPS C KLL spectra can also be used as fingerprints for identification of the form of the carbons at the surface of diamond and graphite [13]. The distance between the most positive maximum and most negative minimum of the first derivative of a C KLL spectrum is referred to as the D

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http://dx.doi.org/10.1016/j.carbon.2016.11.002
0008-6223/

parameter, which can be used to estimate the ratio of sp^3 to sp^2 carbons. For HOPG, this value varies from 21.2 to 23.1 eV [14–16]. However, XPS cannot detect H, thus it is difficult to identify the structure of the defects. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is an extremely surface-sensitive technique with a sampling depth of approximately 1 nm. This technique provides surface chemical composition and detailed molecular information of the surface of a sample [17]. A combination of these two techniques can give a fuller picture of graphene and HOPG surfaces.

Poly(methyl methacrylate) (PMMA), which is used to transfer graphene from Cu foil to other substrates, has been shown to remain on the surface of graphene [18,19]. Efforts have been made to produce a clean graphene surface by annealing it at high temperatures under high vacuum [20,21]. In our previous work [22], we found that clean surfaces of graphene and HOPG can be obtained by annealing the samples at 500 °C in an ultra-high vacuum chamber without creating any additional defects. In this work, XPS and ToF-SIMS were used to characterize the clean surfaces of graphene and HOPG. The XPS and ToF-SIMS spectra of clean graphene and HOPG showed many similar features. The major difference was the presence of a series of $C_xH_2^{+\bullet}$ ions ($x = 1, 2, 3 \ldots$) in the ToF-SIMS positive ion spectrum of the clean graphene. We suspect that the $C_xH_2^{+\bullet}$ ions came from the defects in graphene. A common way to create defects on the surface of graphite is using an ion beam to bombard its surface [23,24]. Assuming that the defects created on the HOPG surface by an ion beam are similar to those present on the graphene surface, we created defects on the surface of HOPG by bombarding it at 500 °C with a Cs^+ ion beam at various doses with the objective of determining the origin of these $C_xH_2^{+\bullet}$ ions. ToF-SIMS spectra of ion-bombarded HOPG surfaces were analyzed and compared with those of graphene. In addition, we created defects on the surface of HOPG by bombarding it at 500 °C with an Ar^+ ion beam at various doses with the objective of monitoring the evolution of the sp^3 carbon peaks by XPS. The energies of the Cs^+ and Ar^+ ion beams were kept low at 1 and 2 keV, respectively, to minimize damages induced on the sputtered HOPG surfaces. Fragmentation mechanisms of selected ions in the ToF-SIMS spectra of graphene and HOPG were proposed.

2. Experimental section

2.1. XPS experiments

HOPG (Grade SPI-1, 10 mm × 10 mm × 2 mm) was purchased from SPI Supplies. The surface of HOPG was prepared by peeling ten times using an adhesive tape. Graphene on a SiO_2/Si wafer (10 mm × 10 mm) was purchased from Graphenea, Spain. In order to remove the residual PMMA on the surface of graphene, the graphene was immersed in acetone at 25 °C for 3 h before the experiments.

An X-ray photoelectron spectrometer (Axis Ultra DLD system, Kratos Analytical, UK) equipped with a 150 W monochromatic Al Kα X-ray source (1486.6 eV) was adopted for the analysis. Take-off angles of 20 and 90° were used with a spot size of 2 mm × 1 mm under the electrostatic mode. Survey scan spectra were collected at binding energies ranging from 0 to 1400 eV with a step size of 1 eV and a pass energy of 160 eV. High-resolution C1s spectra were obtained at a step size of 0.1 eV and a pass energy of 20 eV. Ten scans were taken for each spectrum with 100 s per scan. Sputtering of the HOPG surface was achieved with an Ar^+ ion gun at 500 °C. The energy of the Ar^+ ion beam was 2 keV. The sputtering current and rate, which were 0.6 μA and 4.2×10^{13} ions cm^{-2} s^{-1}, respectively, were kept constant during sputtering. The sputtering area was 3 mm × 3 mm. Survey and C1s spectra of sputtered HOPG surfaces were obtained with sputtering times of 10, 30 and 120 s and at 500 °C to prevent adsorption of hydrocarbons. The corresponding sputtering doses were 4.2×10^{14}, 1.3×10^{15} and 5.0×10^{15} ions cm^{-2}, respectively. XPS C KLL spectra of HOPG were obtained at a step size of 0.3 eV and a pass energy of 40 eV under the hybrid mode at 25 and 500 °C. Twenty and ten scans were taken for each spectrum with 200 s per scan for C KLL spectra obtained at the take-off angles of 20 and 90°, respectively. The first derivative spectra were obtained using a 15 point Savitzky-Golay, quadratic polynomial differentiation method. The pressure inside the chamber during the experiment was kept to approximately 10^{-8} Torr.

It is known that C1s spectra of HOPG are asymmetric [25,26]. The asymmetry is due to the low energy electron-hole pair excitation as the valence electrons respond to the presence of the core hole. Two empirical approaches have been used to curve fit this asymmetric line shape. The first approach used an asymmetric Doniach-Sunjic function, which was originally developed for analyzing the asymmetric line shapes of metals [27], while the other considered HOPG as a neutral alternant hydrocarbon and fitted its C1s spectrum with five symmetric components [28–30]. We used the Doniach-Sunjic function to curve fit the asymmetric C1s spectrum in this work because it has been widely used in literature to empirically fit the C1s spectra of carbonaceous materials [25,26]. The C1s spectrum of the HOPG sample after annealing at 500 °C for 2 h was used as a reference spectrum for a defect-free surface [22], which only has delocalized sp^2 carbons. An asymmetric fitting function with a combination of Doniach-Sunjic and Gaussian-Lorentzian functions was used in the curve-fitting analysis of the C1s spectrum of HOPG to determine the asymmetric parameter, which was 0.035 [22]. The binding energy of delocalized sp^2 carbons in the C1s spectrum of HOPG was centered at 284.5 eV. The full-width-at-half maximum (FWHM) of the peak was set to 0.7 eV. The peak representing the π-π^* shake-up was set to 290.9 eV with its FWHM varied until the best fit was obtained. For symmetric components, a Gaussian-Lorentzian fitting function was used. A Shirley background was subtracted in the curve-fitting analysis.

The FWHM of its C1s spectra of sputtered graphite became broader and more asymmetric in the line shape at the high-binding-energy side of the peak [31,32] due to the disorder of its delocalized sp^2 structure and the development of the sp^3 component [11,33]. The sp^3 carbon peak is related to defect structures in the sputtered graphite. As more defects are generated on the graphite surface, the intensity of the sp^3 carbon peak increases. In our curve-fitting of the C1s spectra after Ar^+ sputtering of the surface of HOPG, the FWHM of delocalized sp^2 carbons increased, keeping the same asymmetric parameter as that of the non-sputtered HOPG. Sputtering the surface of HOPG can also introduce localized sp^2 carbons to the surface. The binding energy of the localized sp^2 carbons is about 284.7 eV [34], close to that of the delocalized sp^2 carbons in HOPG (284.5 eV). As a result, we did not differentiate between localized and delocalized sp^2 carbons. Besides, a symmetric peak centered at 285.3 ± 0.1 eV was assigned to represent sp^3 carbons [12,33,35–38]. The FWHM of the sp^3 carbon peak was 1.0 eV. The software used for peak fitting was CasaXPS.

2.2. ToF-SIMS experiments

ToF-SIMS (ToF-SIMS V spectrometer, ION-TOF GmbH, Munster, Germany) spectra were acquired using a Bi_3^+ beam operating at 25 keV. The scanning area was 200 μm × 200 μm with an acquisition time of 40 s. A Cs^+ ion gun was used for HOPG sputtering at four doses — 4.4×10^{13}, 8.8×10^{13}, 17.6×10^{13} and 52.7×10^{13} ions cm^{-2}. The energy of Cs^+ ion beam was 1 keV. The sputtering area was 800 μm × 800 μm. ToF-SIMS negative ion spectra were taken