Defect-induced oxygen adsorption on graphene films

Tianbai Li, Jory A. Yarmoff*

Department of Physics and Astronomy, University of California, Riverside, CA 92521, United States

ARTICLE INFO

ABSTRACT

Although defects on graphene can degrade electron transport and its ability for use as a protection layer, they can also be helpful to tailor the local properties or activate new sites for particular adsorbates. Here, carbon vacancy defects are formed in graphene films on Ru(0001) using low energy Ar^+ bombardment and the materials are then reacted at room temperature with oxygen (O_2). Helium low energy ion scattering shows that no oxygen attaches to the intact graphene layer. When isolated single carbon vacancy defects are present, oxygen adsorbs molecularly at the defect sites and intercalates beneath the graphene overlayer after post-annealing at 600 K. When the defects are large enough to consist of open areas of bare substrate, the oxygen dissociatively chemisorbs to the Ru. This work shows that the adsorption depends on the size of the surface vacancies, and that it is important to have defect-free graphene when using it as a protection layer.

1. Introduction

The epitaxial growth of uniform and large areas of graphene (Gr) with excellent quality is now routinely achieved by chemical vapor deposition (CVD) on transition metal surfaces [1–5]. The inertness and high thermal stability of graphene make it a good candidate for use as a protective layer, especially for transition metals [6,7]. Nevertheless, in the transferring of graphene or in the fabrication of devices, it is inevitable that some defects, most likely carbon vacancies, will be introduced. It can be expected that those defects will leave unoccupied sites at which contaminants can absorb and thus degrade the graphene's performance over a large scale. Such a deviation from a perfect graphene film can, however, be useful in some applications. For example, such defects can be used to tailor the local properties of graphene and achieve new functionalities [8]. Although defects in graphene have been well studied and widely used, the relationship between the defects and the adsorbates on the surface is still not clear.

One of the most important adsorbates is oxygen due to its high reactivity and abundance in the atmosphere. In general, at room temperature O_2 molecules adsorb dissociatively on metal surfaces forming chemical bonds to surface atoms [9–11]. Oxygen can adsorb molecularly via van der Waals forces at sufficiently low temperatures [11–14]. Molecular adsorption, however, can be observed at a relatively high temperature in some rare cases. For instance, a small amount of oxygen can adsorb in molecular form on certain Si surfaces at room temperature in which it serves as precursor for dissociative chemisorption during the process of forming fully oxidized SiO_2 [15] or as a minority

species after the initial formation of a surface oxide [16].

There are, however, many reports of the adsorption of molecular O_2 in the presence of defects. For example, O_2 has been shown experimentally to molecularly chemisorb at two types of adsorption sites on TiO_2 with oxygen vacancies at temperatures of 150 K and 230 K [17]. Also, when defects are created on Ag(111) by exposure to a high dose of chlorine, molecular oxygen can stick to those defects at room temperature [18]. In addition, DFT calculations have shown that defects on MoS_2 and doped boron nitride surfaces, which are also promising two-dimensional materials, are active sites that enable the uptake of O_2 and Cl_2 molecules with a much lower adsorption energy [19,20]. It is thus important to explore the possible adsorption of molecules on defected graphene at temperatures that are higher than those usually associated with physisorption on surfaces.

In this paper, the relationship between defects on graphene and adsorbed O_2 is studied with He^+ low energy ion scattering (LEIS) [21]. As a highly surface sensitive tool, LEIS has been previously applied to measure the impurities in graphene overlayers [22] and intercalation of molecules underneath the Gr overlayer [23]. In particular, by adjusting the scattering angle, LEIS spectra collected from Gr films can detect only the outermost atoms or can also detect intercalated species and uncovered substrate atoms [23]. In our previous study [23], a comparison of spectra collected at different scattering angles was used to show that O_2 molecules intercalate between the Gr overlayer and the Ru(0001) substrate when exposed to O_2 at 650 K, and that no oxygen adsorbs on the surface. Furthermore, by comparing the desorption temperature of the intercalated oxygen to that of oxygen chemisorbed

directly on Ru(0001), it was concluded that the intercalated oxygen remains in molecular form.

This work presented here details the role of carbon vacancies in promoting adsorption on Gr. As reported in Refs. [24,25], Ar^+ sputtering can create single carbon vacancies on Gr/Pt(111) and graphite, as confirmed by STM images. Here, defects are introduced on Gr/Ru (0001) by 50 eV Ar^+ pre-sputtering before the material is exposed at room temperature to O_2. Although a complete graphene layer is inert to adsorption at room temperature, it is found that O_2 does adsorb on pre-sputtered Gr/Ru(0001). In addition, it is observed that the size of the defects affects the form of the adatoms and their stability. For a light sputtering that generates isolated single C vacancy defects, oxygen adsorbs molecularly on the defect sites and diffuses to become intercalated between Gr and the Ru(0001) substrate following post-annealing at 600 K. If there are a sufficient number of vacancies to produce open areas of exposed substrate, however, then O_2 dissociates to form strong O-Ru metal bonds.

2. Experimental procedure

The experiments are performed in an ultra-high vacuum (UHV) chamber with a base pressure of 4×10^{-10} Torr. An Ar^+ ion sputter gun (Varian) is used to clean the Ru substrate and introduce defects into the Gr overlayer. Sapphire leak valves are used to introduce Ar gas for sputtering and other gasses for the growth of the Gr overlayer and the introduction of oxygen molecules. For the analysis of the surface and the confirmation of its cleanliness, the chamber is equipped with low energy electron diffraction (LEED) optics (Varian) and the LEIS setup, which is described below. The sample is mounted on a holder attached to the foot of a manipulator that enables x-y-z motion and rotation about both the polar and azimuthal angles. An e-beam heater filament is mounted behind the sample holder that can be floated at a negative high voltage to heat the sample up to 1400 K. The temperature of the sample is monitored with K-type thermocouples that are spot-welded in the vicinity of the sample. There is a Faraday cup with a 1 mm diameter entrance hole attached at the bottom of the manipulator foot for accurately measuring the ion beam size and flux.

The cleaning of the ~ 1 cm diameter Ru(0001) sample is performed using a standard IBA and chemical treatment, as reported in the literature [26,27]. A 30 min 500 eV Ar^+ ion sputtering is first applied to the Ru(0001) sample at a flux of 4×10^{13} ions s^{-1} cm^{-2} with a beam size of 3×3 cm^2. The sample is then annealed under 4×10^{-8} Torr of O_2 at 1100 K for 8 min to remove adsorbed carbon, followed by a flash annealing at 1300 K for 2 min under UHV to remove the remaining carbon-containing contaminants and residual oxygen. This IBA/chemical treatment is normally repeated several times to acquire a clean and well-ordered surface. The cleanliness and the periodicity of the surface are confirmed with LEIS and LEED, respectively.

The graphene overlayer is grown through a chemical vapor deposition (CVD) method [27]. The cleaned Ru surface is heated to 900 K and then exposed to 1.5×10^{-7} Torr of ethylene for 5 min, followed by annealing under vacuum at 1200 K for 1 min and then slowly cooling down to 450 K for another 5 min. This process is repeated until the surface is fully covered with a continuous monolayer of graphene, which typically requires about 4 cycles. The quality of the Gr/Ru(0001) overlayer is monitored with LEIS and LEED.

Defects are formed via Ar^+ sputtering of Gr/Ru(0001). To gently remove carbon from the graphene, a low beam energy (around 50 eV) is employed and the beam is defocused to produce an average flux of 6.7×10^{10} ions sec^{-1} cm^{-2}. To study the effects of defect size, two different sputtering times are used. For the "light" sputtering, the beam is applied for 3 min so that the total fluence is 1.2×10^{13} ions cm^{-2}. The second defect formation involves a 1 h sputtering, which corresponds to a fluence of 2.4×10^{14} ions cm^{-2}.

After the introduction of defects in Gr/Ru(0001), O_2 exposures are performed with the sample held at room temperature. Exposures are

given in units of Langmuirs (1 L = 1×10^{-6} torr sec). Additional post-annealing under UHV is performed after the exposures.

Helium low energy ion scattering is performed using a differentially pumped ion gun (PHI model 04–303) to produce a beam of 3000 eV He^+ ions with a diameter of 1.6 mm and a total current, as measured on the sample, of 1.5 nA. The scattered ions are collected by a Comstock AC-901 hemispherical electrostatic analyzer (ESA) mounted on a rotatable platform in the UHV chamber, which allows the scattering angle to be adjusted. The ESA collects only those projectiles that remain ionic after scattering. A specular geometry is used for all the spectra collected in this paper in which the incident and outgoing angles are equal with respect to the surface normal. No detectable damage of the Gr overlayer due to the He^+ ion beam occurs within the time it takes to collect 5 successive spectra [23]. Thus, to absolutely avoid effects of any beam damage during LEIS, the sample is re-prepared after the collection of every 3 spectra.

3. Results

The primary tool used for these experiments is LEIS [21]. The scattering process can be analyzed classically because the de Broglie wavelength of low energy ions (1–10 keV) is very small. In addition, due to the small size of the scattering cross sections with respect to the interatomic spacings, low energy ion scattering from a solid can be analyzed with the binary collision approximation (BCA) in which it is assumed that the projectile interacts with only one atom in the solid at a time [28]. The most significant features in LEIS spectra are the single scattering peaks (SSP) that represent projectiles that experience only one hard collision with a target atom before scattering from the surface [21]. The kinetic energy of a SSP depends on the mass of the target atom and the scattering angle, while the area is proportional to the number of target atoms that are directly visible to the incoming ions and the detector. In this experiment, the areas of the SSPs are computed by integrating the peaks after subtracting the background of multiply scattered projectiles, which is modeled as a polynomial by fitting the shape of the region surrounding the SSPs.

In the present measurements, a very light projectile, such as helium, is needed to enable backscattering from C and O surface species. Helium LEIS also has an extremely high surface sensitivity due to Auger neutralization (AN), which is an irreversible process that dominates for noble gas projectiles [21,29]. In the process of AN, most of the projectiles that collide with deeper layer atoms remain neutralized and are not detected by the ESA. Thus, the spectra consist primarily of single scattering events from the outermost few atomic layers. There is also, however, a strong matrix effect for helium ions scattered from graphitic carbon making it difficult to detect scattered He^+, as reported in the literature [22,30,31]. The reason is that He ions undergo a quasi-resonant neutralization in conjunction with AN when scattering from graphitic carbon that leads to a very high neutralization probability [32]. This effect is particularly significant for primary beam energies below 2500 eV. To avoid the matrix effect and provide a detectable signal, a 3000 eV He^+ beam energy is employed here.

Fig. 1 shows He^+ LEIS spectra collected from Gr/Ru(0001) at a 45° scattering angle after various treatments. At this small scattering angle, the incident and scattered ions are 22.5° from the surface plane so that atoms positioned below the graphene overlayer are completely shadowed by the overlayer, which leads to a signal that probes only the Gr surface and any adsorbates attached to it [23].

Spectrum (a) was collected from the clean, as-prepared Gr/Ru (0001) and shows only a single SSP at 2450 eV, which represents carbon in the Gr overlayer. In addition, the LEED pattern collected from this surface displays a Moiré pattern, as reported previously [23,33], which indicates that the overlayer is a single crystal that forms a superlattice with the substrate due to their different lattice parameters. These data indicate that a complete Gr film covers the surface without a measurable number of defects.