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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Intercalation, Adsorption and Reaction of Molecules on Graphene/Ru(0001)

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Physics

by

Tianbai Li

March 2018

Dissertation Committee:

Dr. Jory Adam Yarmoff, Chairperson

Dr. Ward Beyermann

Dr. Nathaniel Gabor

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2018

The Dissertation of Tianbai Li is approved:

Committee Chairperson

University of California, Riverside

Acknowledgements

Getting a Ph.D. degree is not just completing the courses and passing the exams. You need to be self-motivated and conquer those expected and unexpected troubles scientific study. Fortunately, I am not alone. There have been many people who have walked alongside me during the last four years. First, I would like to express my deepest gratitude to my advisor, the committee chair, Professor Jory A. Yarmoff for his insightful, expert, and generous guidance. Four years ago, when I first joined the Yarmoff group, I do not have much knowledge about the vacuum techniques and surface science. It is Prof. Yarmoff that helped me with the operation of the equipment and passed on his own valuable experience on the research. He was always patient when I got stuck in the projects and his encouraging words and professional advices undoubtedly helped me to overcome those difficulties. He sets an example for us that we should always keep strict, conscientious and enthusiastic on the research. He also did me a great favor on the scientific writing. Through his guidance, I gradually improved my understanding of science and become a skilled researcher. I could not have finished my PhD program fruitfully without his help.

I would also like to thank to the other members of my committee, Prof. Ward P Beyermann and Prof. Nathaniel Gabor, for their valuable suggestions and thoughtful questions on the dissertation. I really appreciate their attendance of my defense. I also express my gratitude to my oral committee members: Prof. Marc W Bockrath and Prof. Jianlin Liu.

I am also very grateful to the previous and current members in Prof. Yarmoff's group who I have worked with along the way. The senior students: Weimin Zhou and Alex Arjad gave me a lot of suggestions on the problems I encountered, which accelerate the completion of my projects and extend my surface science knowledge. I really appreciate Christopher Salvo, Haoshan (Shawn) Zhu and Joshua Raimist for their assistance on the project, helpful discussions and precious friendship. I want to thank the undergraduates, Dani`el Ryan, Josiah Keagy and Bradley Erwin. They assisted me a lot generously as well.

Thanks to my colleagues and friends during the past six years. Without them, the off-school life would be boring. I really enjoyed the time spent with them: Bowen Yang, Mingyue Liu, Hua Wei, Liankun Zou, Yunqiu Luo, Xiang Tong, Chaoping Zhu, Tiancong Zhu, Chi Tang, Shaolong Chen, Supeng Ge, Zhishen Lin, Yanmeng Shi, Yi Wu, Changtong Hou, and Yadong Xu.

Last but not least, I want to dedicate my work to my parents. They tried their best to give me a high-quality life and education. And, it is their patience and love that encouraged me to overcome the difficulties in such a long and challenging PhD program. Highest gratitude is also given to my grandparents. Those precious memories with them is the biggest treasure in my life.

The text of this dissertation, in part or in full, is a reprint of the material in *Phys. Rev. B.* 96, 155441-October (2017), and in material submitted to *Surf. Sci.*. The coauthor Jory A. Yarmoff listed in those publications directed and supervised the research which forms the basis for this dissertation.

This material is based upon work partially supported by the National Science Foundation under CHE - 1611563.

ABSTRACT OF THE DISSERTATION

Intercalation, Adsorption and Reaction of Molecules on Graphene/Ru(0001)

by

Tianbai Li

Doctor of Philosophy, Graduate Program in Physics
University of California, Riverside, March 2018
Dr. Jory A. Yarmoff, Chairperson

Graphene has attracted great interest in many fields due to its outstanding electronic and chemical properties. Among them, its surface inertness and high thermal stability makes graphene a promising candidate as a protective material for transition metal surfaces. Recent studies show, however, that small molecules, such as O₂, CO and H₂O, intercalate between a graphene film and a metal substrate at particular temperatures.

The intercalation of O₂ between graphene and Ru(0001) is studied with 3 keV helium ion scattering and low energy electron diffraction. It is shown that O₂ intercalates between the graphene and the Ru(0001) substrate at a temperature of 650 K and does not adsorb onto the graphene surface. Nevertheless, the graphene layer efficiently avoids both intercalation and adsorption of oxygen at room temperature. It is also found that the intercalated oxygen thermally desorbs from the surface after it is heated to 800 K. Such a desorption is not, however, observed for oxygen dissociatively adsorbed on a bare Ru(0001) surface until 1200 K. It is thus inferred that the oxygen intercalated between graphene and

Ru(0001) is in a molecular form. In addition, part of the graphene overlayer is etched by a chemical reaction during the thermal desorption of oxygen.

The role of the defects on the graphene layer is also studied. Defects are introduced by 50 eV Ar^+ sputtering, which creates single vacancies with a quick sputtering or larger open areas of substrate following a prolonged sputtering. It is found that oxygen molecularly adsorbs at single carbon vacancies even at room temperature, which does not occur on a complete graphene layer. Following post-annealing to 600 K, it is observed that such adsorbed oxygen diffuses to become intercalated between graphene and Ru(0001). Oxygen dissociatively adsorbs in the large open areas of exposed substrate by forming strong oxygen-metal bonds. It is also found that the presence of defects facilitates the intercalation of oxygen and improves the etching efficiency of the graphene during the desorption of oxygen.

In addition, CO intercalation is investigated for graphene/Ru(0001). Here, isotopically enriched ^{13}CO is used to distinguish the intercalates from the carbon atoms in graphene. It is observed CO intercalates between the graphene and Ru(0001) at room temperature, although with an extremely low efficiency. The intercalated graphene has an orientation in which the CO is vertical with the oxygen atoms pointing up. Following heating to a temperature of 363 K, some of the CO desorbs and the geometry of the remaining intercalated CO changes such that the molecules are tilted or lying flat.

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Chapter 1 Introduction

1.1 Motivation

Graphene (Gr) is a fascinating 2D material consisting of a single layer of carbon atoms in hexagonal honeycomb structure. The electronic and chemical properties of graphene are outstanding so that it attracts great interest in many fields [1-3]. The unique electronic properties of graphene originate from its special carbon lattice structure, which is shown in Fig. 1.1.

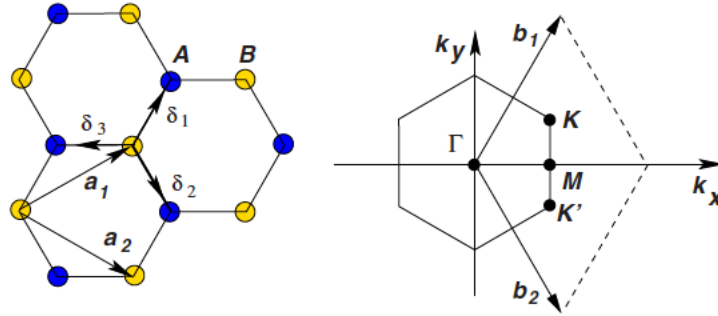


Figure 1.1 Honeycomb lattice (left) and Brillouin zone (BZ) (right) [4]. (Reprinted figure with permission from Castro Neto et al. Copyright (2009) by the American Physical Society.)

This structure can be seen as a triangular lattice with a basis of two atoms per unit cell. The lattice vectors and the reciprocal vectors can be written as:

$$a_1 = \frac{a}{2}(3, \sqrt{3}), \quad a_2 = \frac{a}{2}(3, -\sqrt{3}); \quad b_1 = \frac{2\pi}{3a}(1, \sqrt{3}), \quad b_2 = \frac{2\pi}{3a}(1, -\sqrt{3})$$

where $a \approx 1.42\text{\AA}$ is the carbon-carbon distance. In this honeycomb structure, one s-orbital and two p-orbitals forms the sp^2 hybridization leading to the formation of a stable σ band,

which contributes to the high stability of carbon lattice. Meanwhile, the unaffected p_z orbital perpendicular to the planar structure forms the π band ensuring the significant electronic properties of graphene [4].

The particular importance of graphene in physics are related to the two points K and K' , shown at the corners of the graphene BZ in the right part of Fig 1.1, which are also known as Dirac points. From the tight-binding reported in Ref. [5], the energy bands derived from the Hamiltonian considering nearest-neighbor hopping and next nearest-neighbor hopping are given as:

$$E_{\pm}(\vec{k}) = \pm t \sqrt{3 + f(\vec{k})} - t' f(\vec{k})$$

with

$$f(\vec{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{\sqrt{3}}{2}k_x a\right)$$

where the “ $\pm$ ” sign denotes the upper (π^*) and lower (π) bands, respectively, t is the nearest-hopping energy, and t' is the next-nearest-hopping energy. It is clear that the band structure is symmetric around 0 if the next-nearest-hopping is ignored ($t' = 0$). For finite values of t' shown in the Fig 1.2, the electron hole symmetry is broken, and the π and π^* bands become asymmetric. The linear dispersion can be obtained by expanding the full band structure near the Dirac point ($\vec{k} \approx \vec{K}$) as $E_{\pm}(\vec{k}) = \pm \hbar v_F |\vec{k}|$ [5], where the Fermi velocity $v_F \sim 1 \times 10^6$ m/s. That results in the most striking difference between graphene and common semiconductors that the Fermi velocity around the Dirac point does not depend on the momentum or energy in contrast to the usual case ($v = k/m$), which provides the carriers in graphene with high mobility.

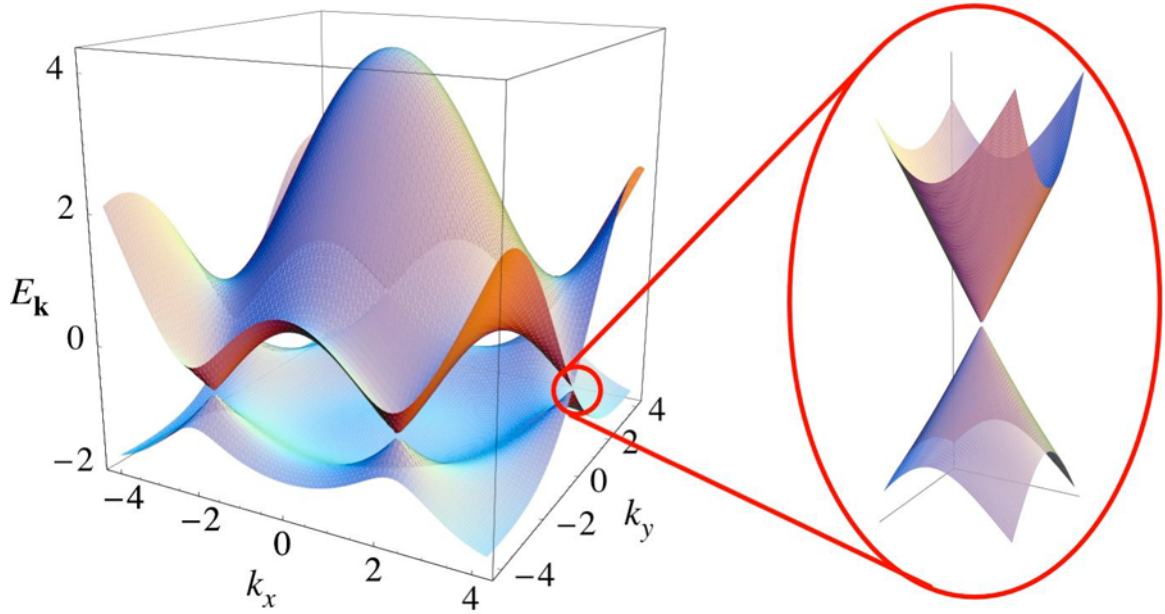


Figure 1.2. Band structure of graphene. Left: Energy spectrum (in units of t) for finite values of t and t' , with $t = 2.7$ eV and $t' = -0.2 t$. Right: Zoom in of the energy bands close to one of the Dirac points [4]. (Reprinted figure with permission from Castro Neto et al. Copyright (2009) by the American Physical Society.)

Graphene is also well-known for its chemical inertness and thermal stability, which lead to its proposed use as a protection layer, especially for transition metals, to avoid oxidation and corrosion [6,7]. For example, oxygen immediately adsorbs on most transition metal surfaces, even at room temperature, due to the low dissociation energy of around 0.05-0.3 eV [8-10]. The presence of a graphene overlayer, however, prevents the substrate from oxidation at low temperature by elevating the dissociation energy barrier [11].

Graphene has been produced through microcleaving or chemical vapor deposition (CVD). As a facile and efficient method, microcleaving is widely used in the fabrication of graphene-based devices [1,12]. The epitaxial growth of graphene via CVD, however,

offers more advantages when pursuing uniform and large areas of graphene deposited onto a substrate with excellent quality, as is needed in many large-scale applications [13-16]. In the CVD process, the interface of graphene with other materials is a key part of controlling the large-scale graphene growth [17,18].

During the transferring or cleaning of graphene-based devices, some defects are introduced on the surface. The scattering of electron waves at defects has an enormous influence on the electrical conductivity. Weaker bonds around defects affect the thermal conductivity and reduce the mechanical strength. Thus, those defects deteriorate the performance of graphene [19]. Such a deviation from perfect graphene film can, however, be used to tailor the local properties of graphene, which can be helpful in many applications [20,21].

1.2 Low Energy Ion Scattering

Low Energy Ion Scattering (LEIS) is the main surface analysis tool used in this dissertation. LEIS is an extremely surface sensitive technique that provides important and unambiguous information about the surface structure, and it has been previously applied to the study of the Gr surface [22].

1.2.1 Binary Collision Approximation (BCA)

The analysis of LEIS is well modeled classically and with the binary collision approximation (BCA). The beam energy used in most low energy ion scattering is between 500 eV and 10 keV. Thus, the de Broglie wavelength is so small that the wave properties

can be neglected and the scattering process can be interpreted with classical mechanics. In addition, because the incident energy of the ions is much larger than the interatomic bonding energies the surface can be considered as composed of isolated unbound target atoms located at their lattice sites. Because the scattering cross sections are smaller than the interatomic spacings, it can further be assumed the projectiles interact with only one target atom at a time [23]. Then, the entire scattering process can be described as a series of binary collisions between the ions and isolated surface atoms, which is the BCA.

Based on the conservation of energy and momentum in classical mechanics, the scattered energy E_f of an ion with mass m_i in a single collision is given by [24]:

$$E_f = E_0 \left(\frac{\cos\theta \pm \sqrt{m_t^2/m_i^2 - \sin^2\theta}}{1 + m_t/m_i} \right)$$

where E_0 and E_f are the kinetic energies of the incident ion and scattered ions respectively, m_t is the mass of the target atom, m_i is the mass of the projectile, and θ is the scattering angle. The “ $\pm$ ” sign becomes addition, “+”, when $m_2/m_1 > 1$, which is necessary for backscattering. It can be inferred from this equation that the scattered energy of the ions during each collision is dependent only on the target/projectile mass ratio and the scattering angle. When the entire trajectory consists of only a single collision in the solid that leads to a projectile that backscatters from the surface, then E_0 is the incident beam energy.

It should be noted that this simple equation ignores some quantum effects that slightly decrease the energy of scattered projectiles, such as the phonon and plasmon

excitations of the solid target. Nevertheless, it is widely applied in the analysis of LEIS energy spectra.

1.2.2 Single Scattering and Multiple Scattering

During the scattering process from a solid target, as illustrated in Fig. 1.3, some incident ions only experience one collision before escaping the surface, which is called a single scattering event. Similarly, multiple scattering refers to those ions that experience more than one collision in the scattering process.

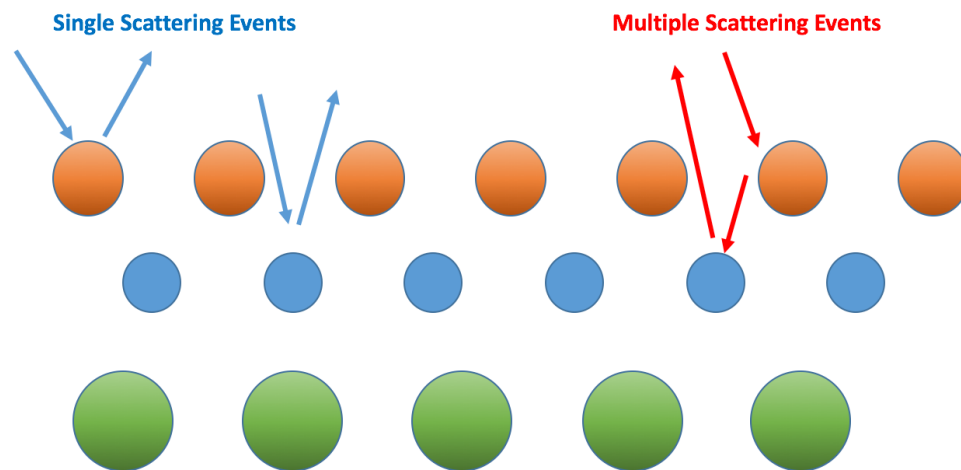


Figure 1.3. A schematic diagram illustrating single and multiple scattering.

Each atomic species on the surface that is directly visible to both the incoming ion beam and the detector will produce a single scattering peak (SSP) in a LEIS energy spectrum. Therefore, by measuring the locations of the SSPs, the elemental composition

can be identified. It is noted that each SSP rides on a background of multiple scattered ions, which is larger on the low energy side of each SSP due to reionization [25]. For example, the O SSP (375 eV) and the Ti SSP (700 eV) are shown in the spectra collected from clean TiO_2 shown in Fig. 1.4. It is also noted the oxygen intensity becomes completely attenuated when additional Ti is grown on the surface.

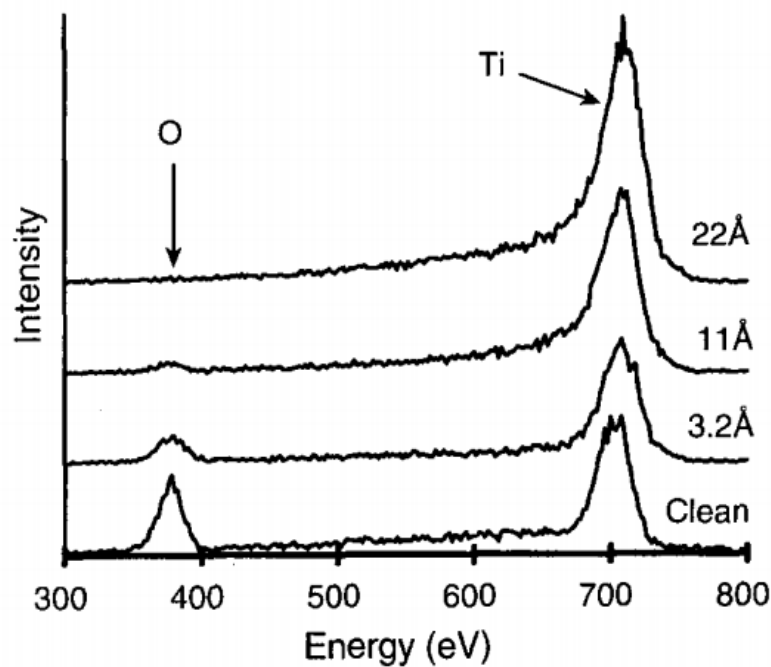


Figure 1.4. LEIS spectra collected using 1 keV He^+ ions scattered from TiO_2 with various Ti coverages [26]. (Reprinted figure with permission from Mayer et al. Copyright (1995) by the Elsevier.)

1.2.3 Scattering Angle

LEIS is an efficient surface-sensitive technique partly due to shadowing. The repulsive potential acting between the projectile and target atoms forms an angular region behind the target that restricts further penetration of the incoming ions.

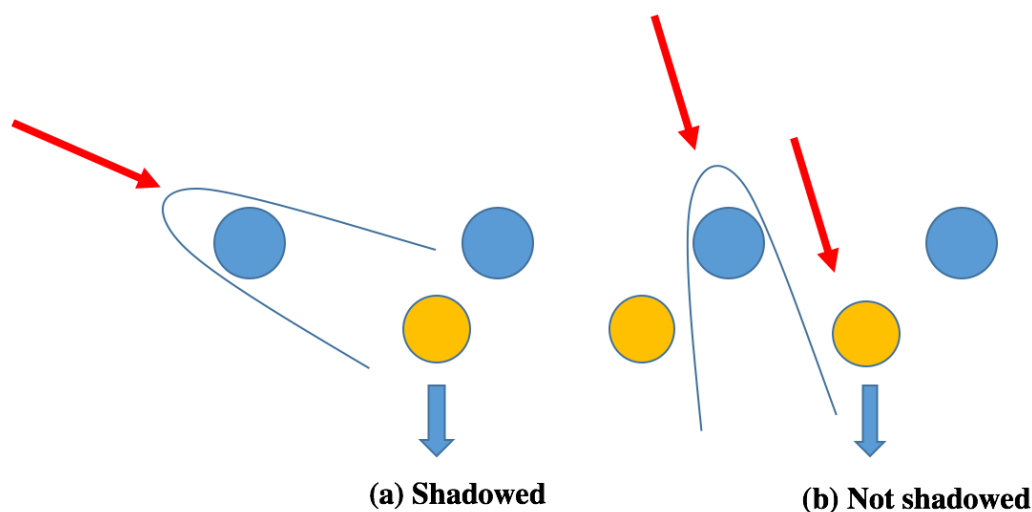


Figure 1.5. A schematic side-view diagram illustrating the shadowing effect in the scattering. The 1st layer atoms are colored blue, while the 2nd layer atoms are colored yellow. In case (a), the 2nd layer atoms are shadowed by the 1st layer; in case (b), the 2nd layer atoms are visible to the incoming ion beam.

The choice of the scattering angle is therefore important as means for the study of surface structure. At a grazing incidence angle, as shown in the case (a) of Fig. 1.5, the majority of the signal consists of single scattering from outermost atomic layer because the deeper lying atoms fall within the shadow cones of the surface atoms. A shadow cone is the region behind an atom from which the incident ions are excluded due to scattering. For case (b) in Fig. 1.5, a larger scattering angle is used so that the trajectories are closer to the surface normal, which allows penetration to the 2nd or 3rd atomic layers thus making single scattering from deeper lying atoms possible.

1.2.4 Auger Neutralization and Resonant Neutralization

In the ion scattering process, there are ion-surface interactions that involve quantum mechanical charge exchange between the projectiles and the target. This leads to some of the incoming ions becoming neutralized. Neutralization can be classified into two different charge transfer mechanisms that depend on the electronic structure of the projectile and target: Auger neutralization [27,28] and resonant neutralization [29].

Auger neutralization (AN) occurs when the incident ion's ionization level is much larger than the target's conduction band, as shown in Fig. 1.6(a). The charge transfer process in AN is a relaxation of the excited atom-surface system that involves two or more electrons. As the ion is approaching to the surface, its deep empty ionization level is filled by an electron from a higher conduction band of the surface. The energy dissipated due to the transition between the levels will then excite another electron in the conduction band. The excited electron usually gains enough energy to overcome the work function and escape from the surface. Auger de-excitation (AD) is associated with the excited state of the projectile, which can be classified with indirect de-excitation (the solid arrow in Fig. 1.6(c)) and direct de-excitation (the dashed arrow in Fig.1.6(c)). In indirect AD, after capturing an electron from the target conduction band, the projectile decays by emitting an outer atomic level electron into the vacuum. Alternatively, the electron can fill the vacancy of the projectile from an outer level while another electron in the conduction band is excited, which is termed as direct de-excitation. Unlike AN, AD does not change the charge state of the projectile, however, the energy released during the transferring can excite a surface plasmon [30].

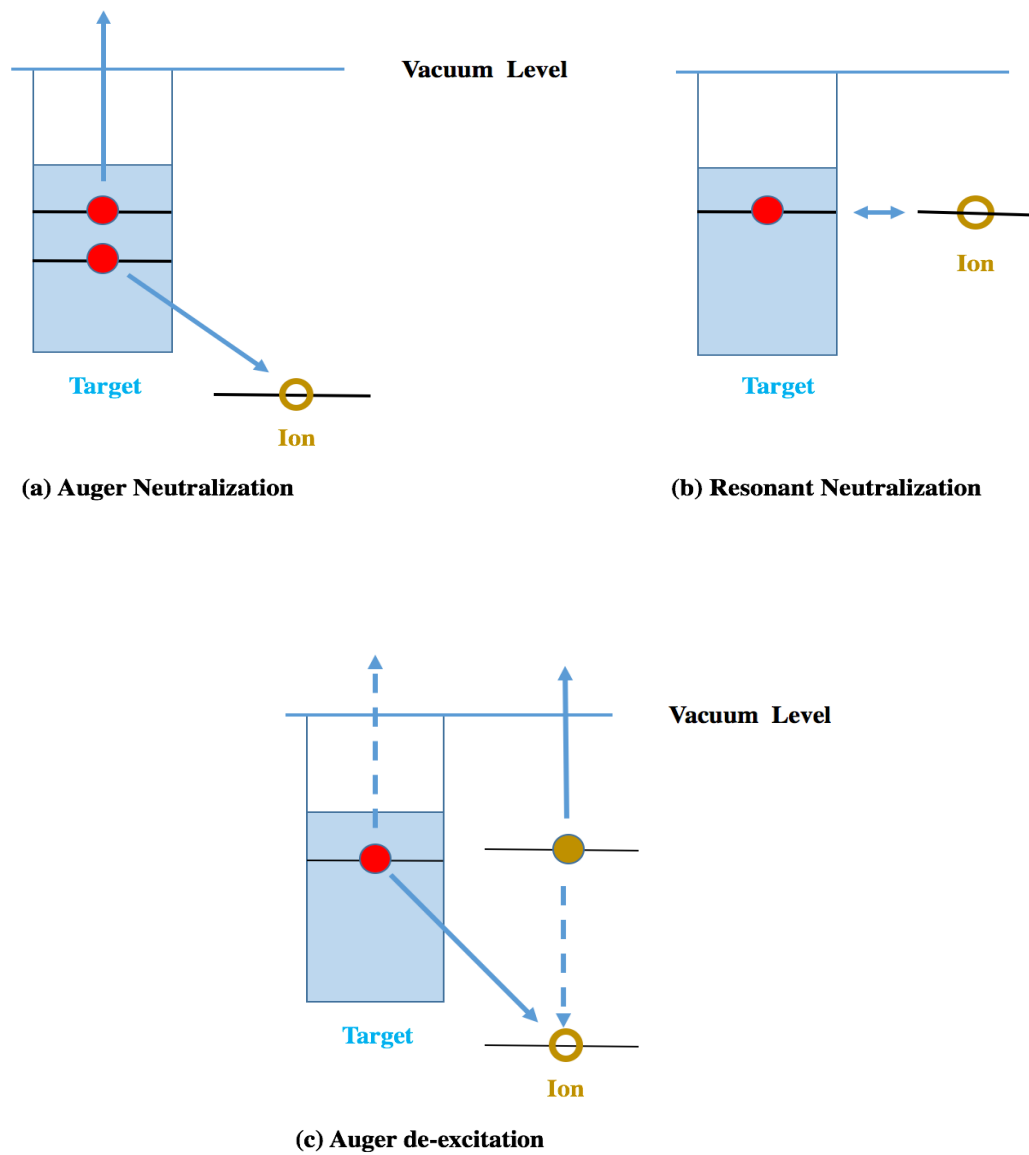


Figure 1.6. Schematic diagrams for (a) Auger neutralization, (b) resonant neutralization (c) Auger de-excitation.

AN is expected to dominate when an empty level of the ion lies deep below a surface band, which is generally seen in the scattering of noble gas ions [31]. It is important

to note that the Auger charge transfer mechanism is irreversible [32] leading to a high neutral fraction, although some reionization can occur during a hard collision.

It should be noted on some certain projectile-target combination, such as He^+ scattered from Ge, In, Pb and graphene [33,34], the neutral fraction of positive ions exhibits as an oscillation as a function of primary beam energy. This phenomenon is caused by quasi-resonant neutralization (qRN), which occurs on the target with a narrow band nearly resonant with the unperturbed He 1s-level. qRN is a highly efficient process leading to the ion yields two orders of magnitude lower than in system where an Auger process is the primary operative neutralization mechanism.

The semi-classical explanation of qRN has been established by Tolk in Ref. [35] as a quantum interference effect. When a He^+ ion approaches a surface atom X, quasi-resonant charge exchange can occur at a distance r smaller than a certain ‘mixing distance’ r_m . At $r < r_m$, a coherent mixed state $\text{He}^+ + \text{X}$ and $\text{He} + \text{X}^+$ evolves. The potential difference between the $\text{He}^+ + \text{X}$ and $\text{He} + \text{X}^+$ is labeled as ΔE . The intensity of backscattered ions I^+ can be written as:

$$I^+ = A^+ + \beta^+ \sin^2(\Delta\varphi/2),$$

where $\Delta\varphi = \frac{1}{\hbar} \int \frac{\Delta E(R)}{v(R)} dR$ is a phase difference depending on the ΔE and $\bar{v}$, which denotes the mean projectile velocity. The integral boundary corresponding to the points when the projectile passes through the distance of r_m on the inbound and outbound parts of the trajectory. The coefficients A^+ and B^+ are slowly varying functions of the ion energy.

Resonant charge transfer (RCT) is the process that typically occurs when the energy of the unoccupied projectile level is close to the target’s Fermi level, which is common for

alkali and other ions (e.g., Li, Na, Ga, Cl, O), as depicted in Fig. 1.6(b). In scattering that involves RCT, the electron transfer is in both directions: resonant ionization (RI) and resonant neutralization (RN). RI occurs when an occupied atomic level is above the Fermi energy. In contrast, the RN process will be present if the atomic level is empty and below the Fermi level. During scattering, both RN and RI occur simultaneously.

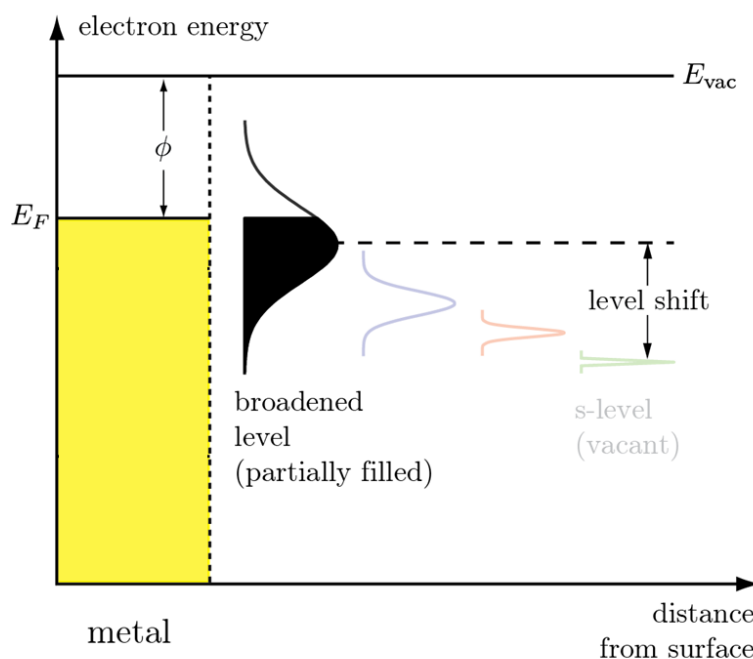


Figure 1.7. A diagram illustrating resonant charge transfer between alkali ion and a metal surface.

The model of the RCT involves the tunneling of electrons between the projectile and target, which has been well established in previous studies [32,36]. When an atom is approaching a metal surface, an image charge is induced. The potential due to the presence of the image charge increases as the ion moves toward the surface leading to a bending of

the ionization level. Meanwhile, the orbital wave function of the incoming ion overlaps with surface states, causing a broadening of the ionization level as shown in Fig. 1.7.

1.3 Experimental Techniques

The experiments are conducted in an ultra-high vacuum (UHV) chamber with a base pressure between 3×10^{-10} and 6×10^{-10} Torr.

1.3.1 Ultra-high vacuum

Most surface science experiments need to be performed under UHV. Here, UHV corresponds to a vacuum regime normally below 10^{-9} Torr. At such a low pressure, the mean free path of a gas molecule is about 40 km, ensuring the transmission of electron and ions.

In addition, operating under a UHV pressure efficiently reduces the number of unwanted adsorbates on the sample. As a good assumption, gaseous molecules or atoms inside the UHV chamber can be regarded as ideal gases, which follow the Maxwell-Boltzmann distribution. The average velocity can be written as:

$$\bar{v} = \sqrt{8RT/\pi\mu}$$

where $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant, T is the temperature, and μ is the molecular weight of the gas. Thus, the collision frequency with the unit area in the chamber can be computed as $\Gamma = \frac{PN_A}{\sqrt{2\pi\mu RT}}$, where P is the pressure and $N_A = 6.02 \times 10^{23}$ is Avogadro's number. Considering a chamber with a pressure of 1×10^{-9} Torr and supposing the background gas in the chamber is CO, there will be 1.4×10^{15} collisions between CO

and a 1 cm^2 sample surface in an hour based on the collision frequency. The atom density for a crystal surface is about $\sim 10^{15} \text{ cm}^{-2}$. Thus, it can be assumed that every surface atom on the sample collides with one background molecule each one hour at a pressure of 1×10^{-9} Torr. Assuming that the sticking efficiency is 10%, then a considerable portion (10%) of the sample will be contaminated. A pressure of $\sim 10^{-10}$ Torr, however, efficiently reduce the contamination speed by a factor of 10, which helps to maintain the cleanliness of surfaces before re-preparation of the sample is needed. Therefore, a UHV environment is essential to research that requires chemically clean sample surfaces [37].

An ion pump is used to acquire a UHV pressure. An ion pump ionizes gas within the vessel it is attached to by employing a strong electrical potential (3–10 keV), which accelerates the ions and captures them in a solid chemically active electrode. In addition, system is usually heated above the 100°C for 20–40 hours (“baking”) to remove water and trace gases that remain on the walls of the chamber. A titanium sublimation pump (TSP) is normally used to further lower the pressure. When current is run through a TSP filament, a thin reactive titanium coating is formed on the chamber surface. The residual gas inside the chamber reacts with the titanium coating to form a solid product, leading to a decrease of the pressure. In a well-baked UHV chamber, the major remaining gas is primarily CO.

1.3.2 Chamber and Experimental Setup

Fig. 1.8 depicts the UHV chamber used in our experiments. The main techniques used in the experiments are LEIS and low energy electron diffraction (LEED).

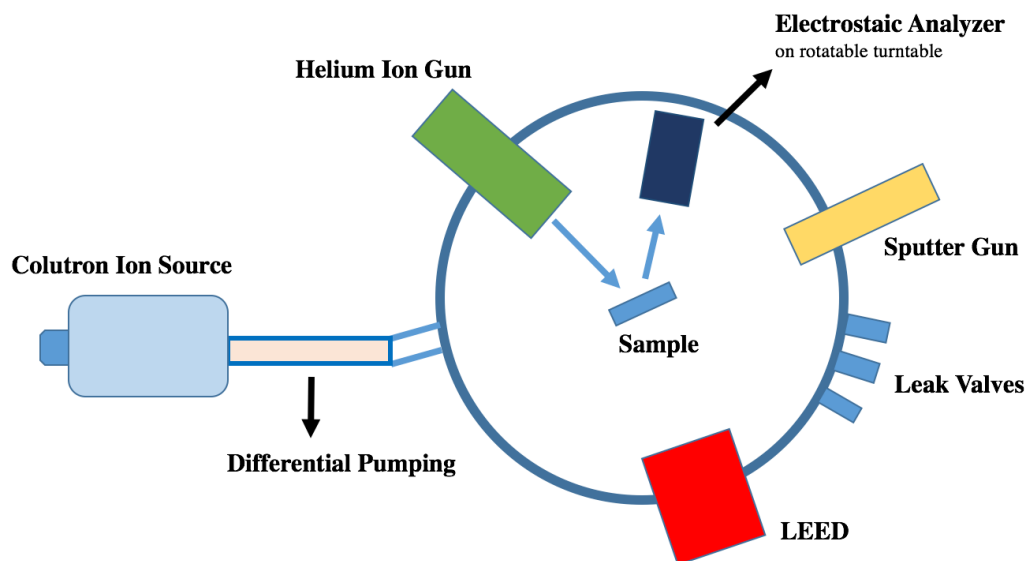


Figure 1.8. Schematic diagram of the UHV chamber and the equipment installed in it.

The chamber is equipped with a sputter gun (Varian), a LEED optics (Varian), a differentially pumped ion gun (PHI 04-303), a Comstock electrostatic analyzer (ESA) mounted on a rotatable turntable, 3 sapphire leak valves and a differentially pumped beamline connected to a Colutron ion source.

The sputter gun is used to clean the sample surface and introduce defects. LEED is employed to ascertain the surface order. The differentially pumped ion gun generates He^+ ions used for LEIS measurements and the ESA collects the scattered charged ions. The leak valves are used to introduce gases for different purposes. The Colutron system can be used to produce alkali, noble gas and other more exotic ions.

The sample is mounted on a holder (VG) attached to the foot of a manipulator (Thermionics) that enables x-y-z motions and rotations about both the polar and azimuthal

angles. The sample holder contains an e-beam heater that uses a rhenium-coated filament floated at a high voltage with respect to the sample. The temperature of the sample is monitored with K-type thermocouples that are spot-welded in the vicinity of the sample.

1.3.3 LEED

LEED is a technique used for the determination of the surface crystallinity. LEED utilizes the wave properties of electrons, which was first proposed by de Broglie [38]. In LEED measurements, a low energy electron beam (20-200 eV) is incident normally on the target and the diffraction pattern is recorded on a fluorescent screen. The resultant LEED pattern provides the crystallinity, orientation and the symmetry of the surface [37,39,40]. LEED can also be used in quantitative way, in which the intensities of diffracted beam are recorded as a function of the incident electron beam energy to generate the I-V curves. By comparison with theoretical calculations for a given surface structure, the atomic positions at the sample surface can be determined.

LEED is a diffraction technique that occurs as electrons elastically scatter from the surface lattice, so that the pattern observed is a reciprocal of the real-space surface unit cell. As shown in the Ewald's sphere in Fig. 1.9, the intersections between the Ewald's sphere and the reciprocal lattice rods define the allowed diffraction beams, which form dots on the screen. The size of the Ewald's sphere is dependent on the electron beam energy.

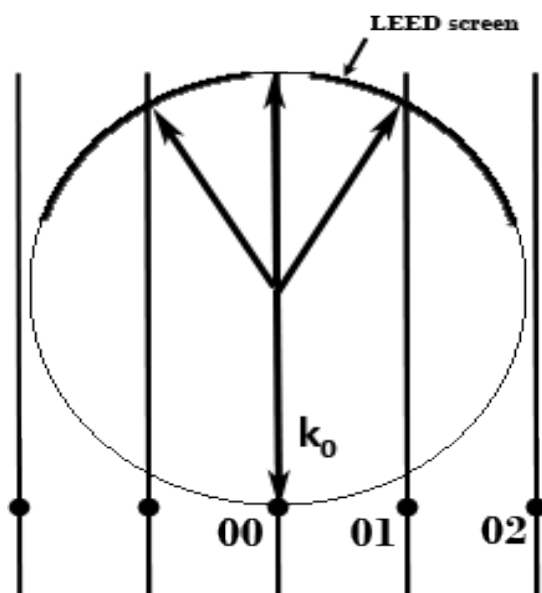


Figure 1.9. Ewald's sphere construction for the case of the normal incidence of the primary electron beam.

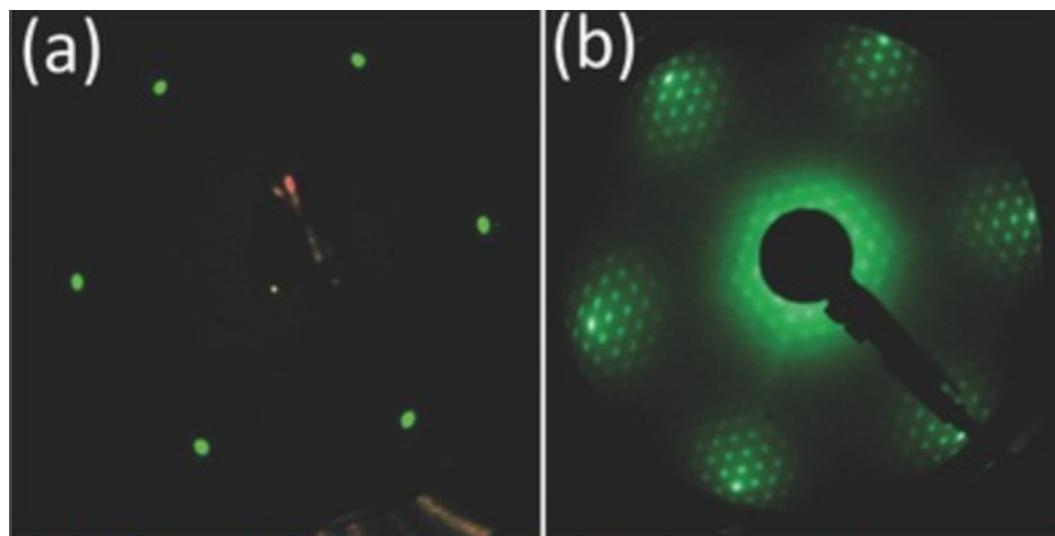


Figure 1.10. LEED patterns of (a) Ru(0001) and (b) graphene/Ru(0001) [41]. (Reprinted figure with permission from Pan et al. Copyright (2014) by the John Wiley and Sons.)

As an example, a LEED pattern of clean Ru(0001) is presented in the Fig. 1.10(a). The sharp hexagonal dots confirm the cleanliness and the hcp geometry of the surface. It is noted that a Moiré pattern is formed on the Fig. 1.10(b) after the growth of a graphene overlayer, which is caused by the superlattice induced by the slightly different lattice parameters of the graphene layer and the Ru crystal. The major hexagonal pattern represents the geometry of the graphene layer, while the satellite dots are attributed to the presence of the Gr-Ru superlattice, as shown in the Fig 1.11 [42,43].

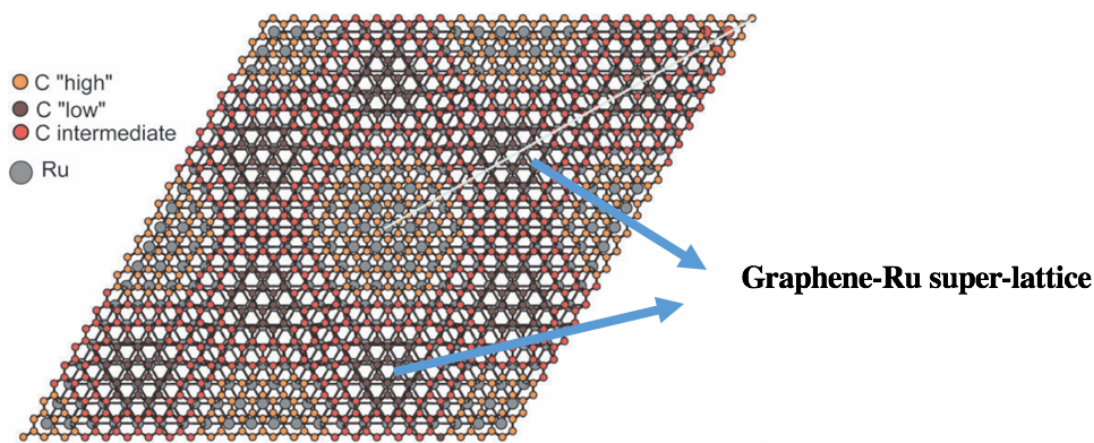


Figure 1.11. Schematic diagram of Graphene-Ru super-lattice [42]. (Reprinted figure with permission from Wang et al. Copyright (2008) by the Royal Society of Chemistry.)

1.3.4 Helium ion gun

The PHI C04-303 differentially pumped ion gun is used to produce helium ions for the LEIS measurements. The gas to be ionized enters ionization chamber, and ions are created through electron impact and then accelerated through condenser, objective and

deflection lenses. The maximum beam energy available is 5 keV. The condenser lens set focuses the ions from the first aperture plate to the second, allowing an arrangement for differential pumping using a turbo-molecular pump between the ionization chamber and the main chamber. During the operation, the main chamber's pressure is maintained between 1×10^{-9} to 1×10^{-8} Torr, which is much less than the pressure in the ionization region of the gun and helps to reduce the exposure of the specimen to the gas. In this case, contamination is not an issue, however, as He is a non-reactive gas.

1.3.5 ESA

In the experiments, the LEIS spectra are collected with a Comstock hemispherical ESA. Scattered ion enters the entrance of the analyzer and are focused by an Einzel lens mounted at the analyzer entrance. The main body of the analyzer consists of two hemispherical parallel plates that have a potential difference applied to them, which allows the passage of ions with a certain kinetic energy. There is a dual microchannel plate (MCP) array mounted at the exit of the ESA that collects the charged particles that pass through the analyzer. The final signal is recorded by a pre-amplifier/discriminator mounted outside the chamber that sends TTL pulses to a data acquisition (DAQ) board in the computer.

The ESA is operated in a constant pass energy mode, which means that the particles that can pass through the analyzer have the same kinetic energy. This pass energy can be adjusted by varying the potential difference between the curved plates. For the Comstock model, it is $E_{pass} = 2.254\Delta V$, where E_{pass} is the pass energy and ΔV is the potential difference between the inner and outer hemisphere plates. The factor of 2.254 is determined

by the geometry of the analyzer. In the measurements, a ramping voltage is applied on the entire analyzer through an external power supply controlled by the DAQ board. The actual kinetic energy $E_{kinetic}$ of the passed ions is therefore the sum of the pass energy E_{pass} and the contribution of the ramp voltage V_{ramp} :

$$E_{kinetic} = E_{pass} + eV_{ramp}$$

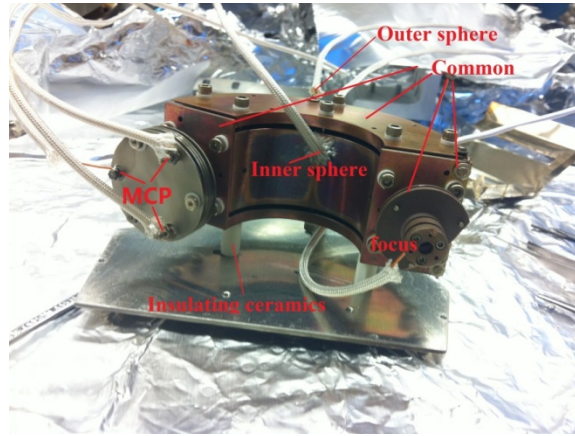


Figure 1.12. A photo of the Comstock electrostatic analyzer.

1.4 Outline of the Dissertation

Chapter 2 uses 3 keV helium ion scattering to investigate oxygen intercalated between a deposited graphene film and the Ru(0001) substrate. Following exposure to O₂ at 650 K, oxygen becomes intercalated and does not adsorb atop of the graphene surface. It is further shown that the intercalated oxygen desorbs from the surface when it is heated to 800 K, while the temperature required for complete desorption of oxygen from bare Ru(0001) is 1200 K. These differences in the thermal stability of the oxygen infers that the

intercalated oxygen is molecular. In addition, part of the graphene is etched during the desorption of the intercalated oxygen. The products of this etching reaction likely include O_2 , CO and/or CO_2 , and the ratio of the products changes as a function of the amount of the intercalated oxygen.

Chapter 3 investigates the role of the defects of graphene on the adsorption of oxygen. The defects are introduced with a light 50 eV Ar^+ sputtering. By controlling the sputtering time, either isolated single carbon vacancies are created or larger open areas of the Ru substrate are revealed. It is shown that oxygen molecularly adsorbs at single carbon vacancies even at room temperature, even though no adsorption or intercalation occurs below 450 K on a completely intact graphene [44]. For large area defects, oxygen dissociates and chemically bonds directly to the metal substrate. That indicates the defects activate new adsorption sites on graphene/Ru(0001) that are not present on intact graphene, and the stability and bonding of the adsorbates is affected by the size of the defects.

Chapter 4 reveals how defects in graphene affect the oxygen intercalation and the etching of the graphene during the oxygen desorption. It is shown that those defects improve the efficiency of oxygen intercalation and increase the rate of the etching reaction between graphene and the intercalated oxygen during the desorption process. This can be attributed to the better reactivity of the carbon atoms located near the defects as compared to those ones in the intact graphene layer.

Chapter 5 studies the CO intercalation between Gr/Ru(0001). The geometry of intercalated CO and of CO directly bonded on Ru(0001) is upright with the O end on the top, although it may be tilted at a small angle. At elevated temperature, however,

intercalated CO molecules lie down or tilt at a large angle, as demonstrated with LEIS. In addition, the temperature needed for the thermal desorption of intercalated CO is 383 K, which is the temperature needed for the thermal desorption of intercalated CO is 383 K, which is 80 K higher than is needed for CO to desorb from bare Ru(0001).

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Chapter 2 Intercalation and desorption of oxygen between graphene and Ru(0001) studied with helium ion scattering

2.1 Introduction

Graphene (Gr) has attracted interest in many fields due to its special properties as a single sp^2 carbon layer [1-3]. Among them, its chemical and thermal stability suggest its use as a protection layer, especially on transition metal surfaces, to avoid oxidation or corrosion when working in an ambient environment [4,5]. Moreover, graphene is highly regarded as a promising candidate for carbon-based electronic devices [6]. During the preparation of devices with suspended graphene, the material is typically pre-annealed in vacuum to obtain better quality materials and performance [7]. Presumably, this annealing removes adsorbed contaminant species that modify the Gr electronic structure. Recent studies show, however, that small molecules, such as O_2 , CO and H_2O , intercalate between a graphene overlayer and a metal substrate, rather than adsorb on the surface [8-11]. The contrasting claims of adsorption vs. intercalation of contaminants provide the motivation for studying the reaction between O_2 and Gr grown on a metal substrate, in this case Ru (0001), to see where the O_2 sticks and how oxygen exposure and removal affects the quality of the graphene.

This chapter contains material published to T. Li, J. A. Yarmoff, Intercalation and desorption of oxygen between graphene and Ru(0001) studied with helium ion scattering, *Phys. Rev. B* **96**, 155441 (2017)

The present study uses helium (He) low energy ion scattering (LEIS), which is well known for its extremely high surface sensitivity [12] and has been previously applied to measure impurities in Gr overlayers [13]. LEIS directly reveals the elemental composition and structural parameters of the outermost atomic layers. Helium ions experience Auger neutralization (AN) during scattering, which leads to a high neutralization probability that is proportional to time spent interacting with the surface leading to a strong surface sensitivity when detecting only the scattered ions. In addition, it is possible to probe either the 1st or the 1st and 2nd atomic layers by adjusting the scattering angle, which provides a useful tool to explore the reaction of O₂ with Gr/Ru(0001). The LEIS results physically confirm that the O₂ intercalates between the Gr and the Ru substrate at 600 K and does not adsorb on top of the Gr, in agreement with Refs. [9,14]. Note that oxygen does not react with Gr/Ru(0001) at room temperature. It is also found that oxygen thermally desorbs from the sample at a relatively low temperature, suggesting that it remains as a molecule when intercalated. Furthermore, it is demonstrated that some of the Gr is etched during the desorption process.

2.2 Experimental Procedure

The experiments are carried out in an ultra-high vacuum (UHV) chamber with a base pressure of 4×10^{-10} Torr. The chamber is equipped with an ion sputter gun (Varian) for sample cleaning, low energy electron diffraction (LEED) optics (Varian) and the instrumentation needed for LEIS.

The sample is mounted on a x-y-z manipulator that enables rotation about both the polar and azimuthal angles. The sample holder (VG) contains an e-beam heater that uses a rhenium-coated tungsten filament held at -650 V with respect to the sample. The temperature of the sample is measured by type K thermocouples attached to the sample plate.

The Ru(0001) substrate is cleaned using a standard ion bombardment and annealing (IBA) approach, as reported in the literature [14,15]. This involves 500 eV Ar^+ ion sputtering for 30 min with a spot size of $3 \times 3 \text{ cm}^2$ and a flux of $4 \times 10^{13} \text{ ions/sec} \cdot \text{cm}^2$, annealing under 4×10^{-8} Torr of O_2 at 1100 K for 8 min followed by a flash annealing at 1300 K for 2 min under UHV. The reaction with O_2 is used to remove carbon contamination from the Ru substrate. Normally, this process is repeated several times to acquire a clean and well-ordered surface. The quality of the clean surface is verified with LEIS and LEED.

The graphene layer is prepared by a chemical vapor deposition (CVD) method in which the 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 [14]. This growth cycle is repeated several times until the surface is fully covered by a single, continuous graphene layer. The presence and quality of the Gr overlayer is confirmed by LEIS and LEED.

The O_2 exposures of the Gr/Ru(0001) samples are performed at a pressure of 1.5×10^{-6} Torr with the sample held at 600 K. Exposures are reported in units of Langmuirs (L), where $1 \text{ L} = 1 \times 10^{-6} \text{ torr sec}$. The sample is cooled to room temperature before the O_2 is evacuated from the chamber.

Helium ions for the LEIS measurements are generated by a differentially pumped ion gun (PHI model 04-303). The 3 keV incident ion beam has a diameter of 1.6 mm, and the current measured on the sample is 1.5 nA. The scattered ions are collected by a Comstock AC-901 160° hemispherical electrostatic analyzer (ESA) that has a radius of 47.6 mm. The ESA is mounted on a rotatable platform inside the chamber that allows the scattering angle to be adjusted. For the data collected here, a specular geometry is always used such that the incident and exit angles are equal with respect to the surface normal as the scattering angle is varied.

Note that ion scattering is an inherently destructive process, so it is important to verify that beam damage does not affect the results. To test whether beam damage plays a role in the present measurements, five spectra were collected successively from the same spot of a sample. Note that the sample was exposed to small amounts of O₂ between spectra, but this does not affect the size of the C peak because the oxygen is positioned below the Gr, as discussed below. It was found that the intensity of the carbon peak did not decrease during the test, which verifies that the amount of beam damage that occurs during the collection of 5 spectra is negligible. In the measurements reported here, the surface is re-prepared after every 4 spectra are collected to negate any effects of beam damage.

2.3 Results

For the 3 keV low energy ions used in these experiments, the de Broglie wavelength is so small that their wave properties can be neglected and the scattering process can be analyzed with classical mechanics. In addition, because the scattering cross sections are

smaller than the interatomic spacings, it can be assumed the projectile interacts with only one target atom at a time, which is known as the binary collision approximation (BCA) [16]. In low energy ion scattering energy spectra, the most significant features are the single scattering peaks (SSPs) which correspond to projectiles that experience one hard, elastic collision with a target atom that causes the projectile to backscatter directly into the detector. The position of a SSP is determined primarily by the projectile/target mass ratio and the scattering angle, although continuous inelastic losses due to interaction with substrate electrons can slightly reduce the energy of the scattered projectile [12]. Since carbon and oxygen are both light elements, a very light projectile, such as helium, is needed to easily observe single scattering from these species.

The high probability for neutralization of scattered He ions is the main reason for the surface sensitivity of He LEIS. The ions are neutralized by an AN process in which electrons transfer from the sample to the projectiles with the neutralization probability being generally proportional to the amount of time the projectile spends in the near-surface region [12]. AN is an irreversible process in this case because the He ionization level is positioned well below the conduction band of metals and reionization of the projectiles is limited [17]. The spectra thus consist primarily of single scattering events from the outermost atomic layers, since most of the He projectiles that penetrate deeply or experience multiple scattering spend enough time interacting with the sample to be neutralized and are thus not detected by the ESA.

There is, however, a strong matrix effect in He LEIS from graphitic carbon leading to an extremely high neutralization probability for scattered ions, as reported in Refs.

[13,18,19]. This effect is very prominent for incoming ions with kinetic energies of 2500 eV or below making it difficult to detect any scattered ions. For example, Mikhailov *et al.* found no C SSP in scattering from a graphitic monolayer on clean Re with 1000 eV He⁺ ions [18]. According to the calculation carried out by Himpsel, et al. [20], the C 2s and C 2p_z states are less bound by about 8 eV in carbidic than in graphitic carbon and the bottom of the sp valence band of graphite is very close to the ground state of Helium 1s (24.6 eV). Thus, the He ions undergo a quasi-resonant neutralization in conjunction with AN in scattering from graphitic carbon [21] leading to an enhancement of the neutralization probability. Therefore, to avoid the matrix effect and provide a detectable signal from C in the graphene layer, 3000 eV He⁺ projectiles are employed here.

Figure 2.1 shows ion scattering spectra collected with 3000 eV He⁺ at a scattering angle of 115° from clean Ru(0001), Gr-covered Ru, and Gr-covered Ru after an O₂ exposure, along with an inset that shows the LEED pattern for Gr/Ru(0001). C, O and Ru SSPs can be clearly seen in the various LEIS spectra. Analysis of these SSPs positions and areas as a function of O₂ exposure and scattering angle is used to determine how O₂ molecules interact with the Gr/Ru(0001) surface. Each SSP rides on a background of multiple scattered projectiles, which is larger on the low energy side of each SSP due largely to reionization [17]. The area of each SSP is computed by integrating the peaks after subtracting the multiple scattering baseline. The baseline is found by fitting the shape of the background surrounding the SSP to a polynomial. The area under the baseline is then subtracted from the total area under the curve to determine the intensity of the SSP itself.

When comparing the intensity of SSPs due to different elements, a normalization based on the relative differential cross sections is employed [12,22].

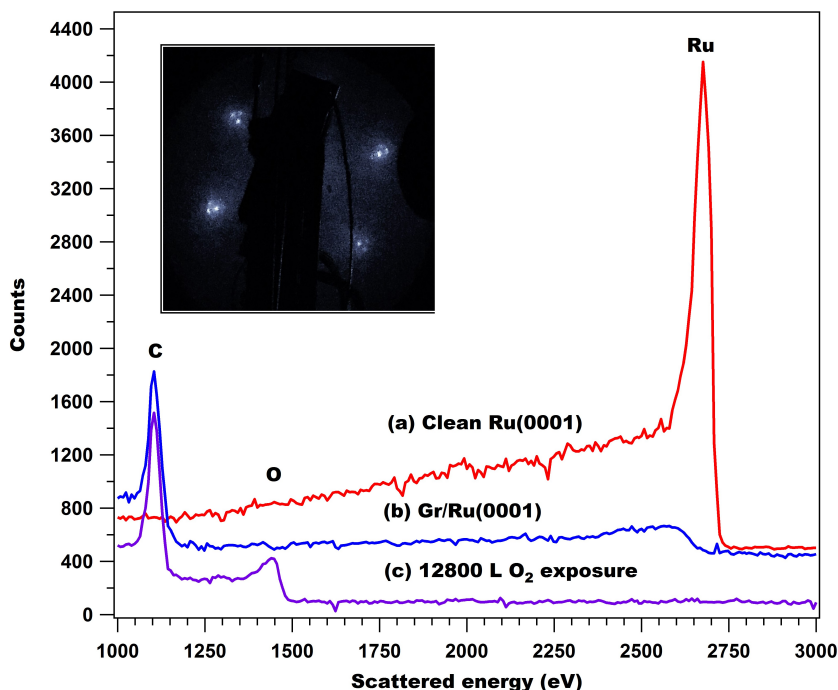


Figure 2.1 3.0 keV He⁺ ion scattering spectra collected at a 115° scattering angle from (a) clean Ru(0001), (b) Gr/Ru(0001) and (c) Gr/Ru(0001) exposed at 600 K to 12800 L O₂. The carbon, oxygen and Ru SSP positions are labeled. The y-axes are offset for clarity. The inset is the LEED pattern collected from Gr-covered Ru(0001) using an electron energy of 74 eV.

Spectrum (a) in Fig. 2.1 was collected from a clean Ru(0001) surface prepared using several cycles of IBA. A clear Ru SSP at 2600 eV and a sharp hexagonal 1×1 LEED pattern are observed after the cleaning procedure. The shoulder to the left of the Ru SSP is attributed to multiple scattering. Those ions that experience multiple scattering have a higher probability for neutralization and lose more energy than singly scattered ions, which

is why their intensity is low compared to that of the Ru SSP. The absence of any other SSPs confirms that the surface is clean. The observation of a sharp 1x1 LEED pattern confirms that the surface is well-ordered.

Spectrum (b) was collected from a sample covered with a monolayer of graphene. After growth of the graphene layer, the Ru SSP is replaced by the C SSP at 1150 eV, which indicates that the surface is covered by a complete Gr layer. The Ru SSP is reduced for two reasons. First, the relatively high neutral fraction of AN means that He ions colliding with the underlying Ru atoms are more likely to be neutralized. Second, in this geometry, most of the Ru atoms are shadowed by the Gr overlayer which precludes single scattering. The small bump around 2600 eV represents a small amount of scattering from sub-surface Ru as the Gr atoms don't line up exactly with the atoms in the substrate and therefore don't completely shadow them.

The fact that the C atoms in Gr and the Ru substrate atoms don't line up, despite both being single crystals, leads to a Moiré LEED pattern for Gr/Ru(0001), as shown in the inset to Fig. 2.1. The Moiré pattern is caused by the different lattice parameters of the graphene layer (2.46 Å) and the Ru crystal (2.30 Å) and indicates a weak interaction between the Gr and the Ru substrate and the formation of a supercell [23,24].

Spectrum (c) in Fig. 2.1 was collected from Gr/Ru(0001) after a 12800 L exposure to O₂. The existence of the O SSP at 1418 eV indicates the presence of oxygen. The exposure to O₂ does not change the intensity of the C SSP, but the Ru signal becomes almost undetectable because of additional shadowing of Ru by oxygen. Furthermore, the Moiré pattern disappears following O₂ exposure, which shows that the oxygen decouples

the interaction between Gr and the Ru substrate and breaks up the super-lattice structure, as was observed for O₂ and CO reactions with Gr/Ru(0001) [25-27].

The scattering angle is used here as means for locating the oxygen atoms. At the larger scattering angles, such as the 115° angle used in collecting the spectra shown in Fig. 1 and illustrated on the left side of Fig. 2.2, the trajectories are close to the surface normal so that the incoming ions can penetrate more deeply and single scattering from deeper lying atoms is possible. If a more grazing angle is used, such as the 45° scattering angle trajectory shown on the right side of Fig. 2.2, the projectiles are better shadowed from reaching below the outermost Gr layer and do not experience single scattering from the second layer. Thus, the single scattering signal from atoms below the outermost atomic layer is very weak at such small scattering angles.

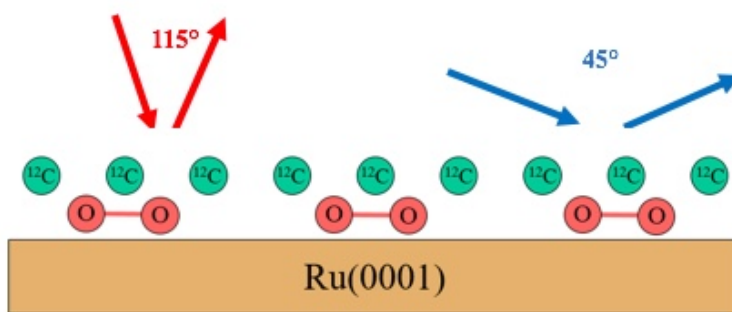


Figure 2.2 A schematic diagram of helium ions scattered from oxygen intercalated Gr/Ru(0001) to show how larger scattering angles can interrogate more deeply below the surface.

Figure 2.3 shows He^+ LEIS spectra collected from Gr/Ru(0001) after a 12800 L exposure to O_2 using different scattering angles. As the scattering angle decreases, the area of the O SSP becomes smaller until it disappears completely at a scattering angle of 45° , where only a C SSP is observed. As mentioned above, for a smaller scattering angle, it is more difficult for the incoming ions to reach the sub-surface target atoms so that only the signal from the outermost Gr layer is detected. Comparing the spectra measured at 45° and 115° , it can be concluded that the oxygen is present below the Gr overlayer and none is adsorbed on top of the Gr, i.e., the oxygen is intercalated between the Gr and the Ru substrate. Note that the increased AN for He projectiles scattered from the second layer O atoms can lead to a reduction of the O SSP intensity relative to that of the C SSP so that the areas of the C and O SSPs cannot be quantitatively compared to each other.

In Fig. 2.4, the intercalation of oxygen is monitored as a function of O_2 exposure using 3 keV He^+ ion scattering at a scattering angle of 115° , in which the intensity of the O SSP is indicative of the concentration of oxygen in the second atomic layer. Exposures of high purity O_2 are performed at a pressure of 1.5×10^{-6} Torr with the sample held at 600 K. The oxygen SSP first appears after a 1600 L exposure and increases with additional exposure.

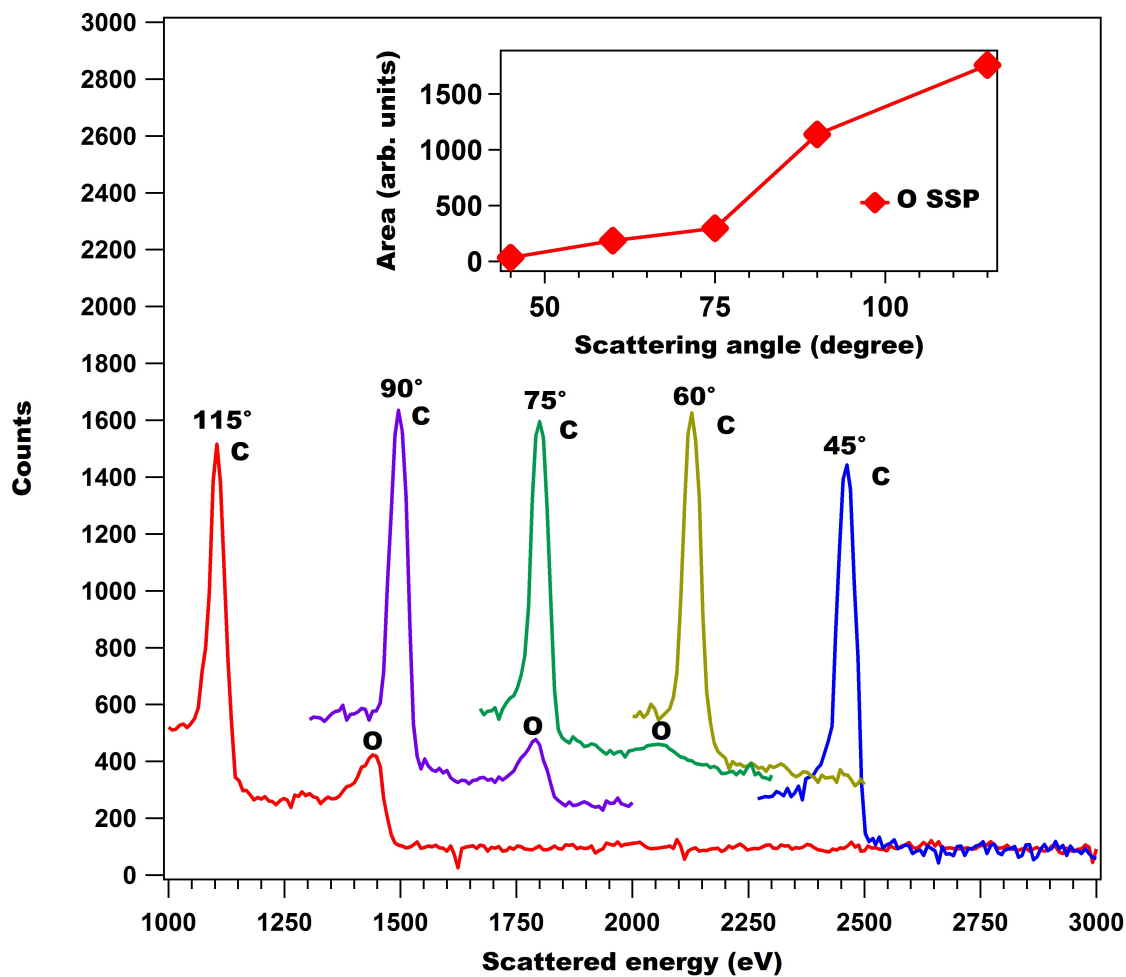


Figure 2.3 3.0 keV He⁺ LEIS spectra, collected from Gr/Ru(0001) exposed at 660 K to 12800 L of O₂, at the indicated scattering angles in a specular configuration. The spectra are offset vertically from each other for clarity. The inset shows the O SSP area as a function of the scattering angle.

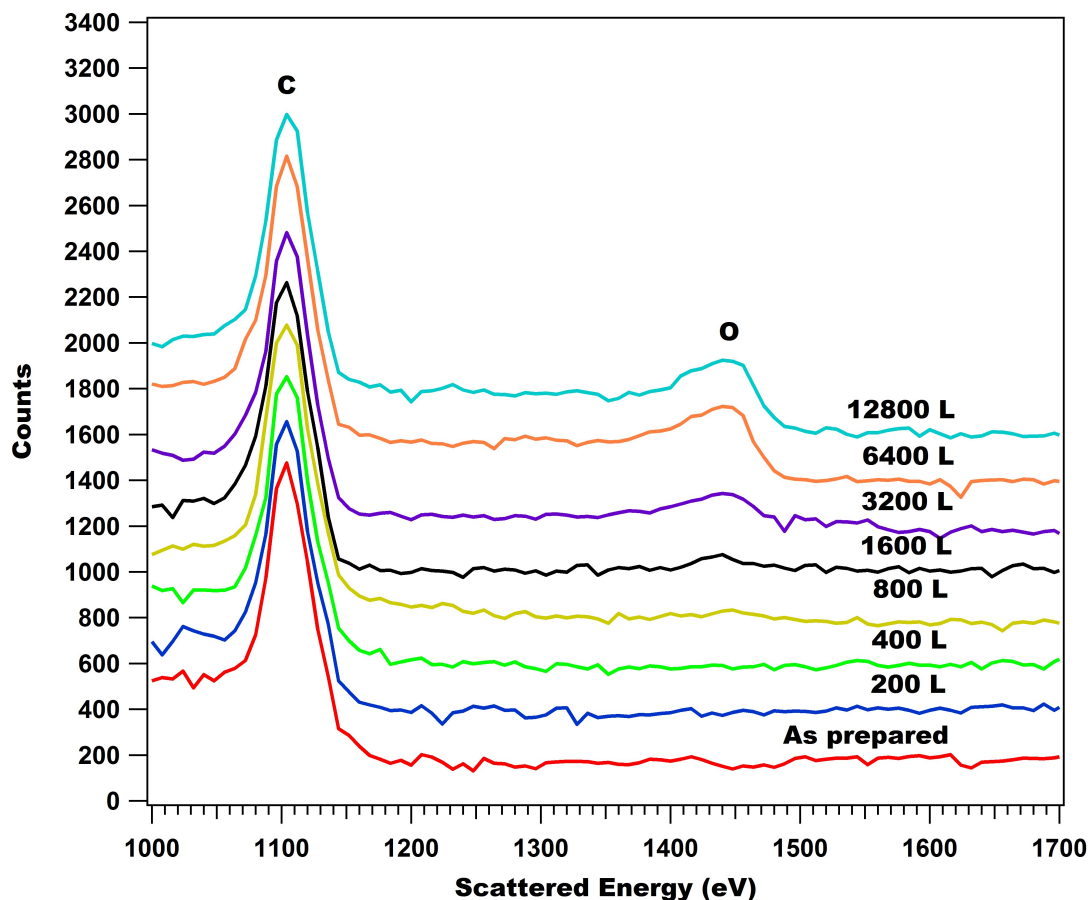


Figure 2.4 3.0 keV He⁺ LEIS spectra collected at a scattering angle of 115° from Gr/Ru(0001) with the indicated O₂ exposures.

Figure 2.5 shows the areas of the carbon and oxygen SSPs as a function of O₂ exposure. The area of the C SSP during the O₂ exposures remains nearly constant, which indicates that the Gr layer is not covered by oxygen following reaction with 1.5×10^{-6} Torr of O₂ at 600 K. The oxygen SSP area increases until an exposure of about 7000 L, at which point it saturates. This result is more obvious in the O to C ratio, also shown in Fig. 2.5, which indicates that the amount of oxygen present is initially small, but grows until it

maximizes after a 7000 L O₂ exposure. Also, note that the Moiré spots in the LEED pattern disappear by the time that the sample is saturated with O₂.

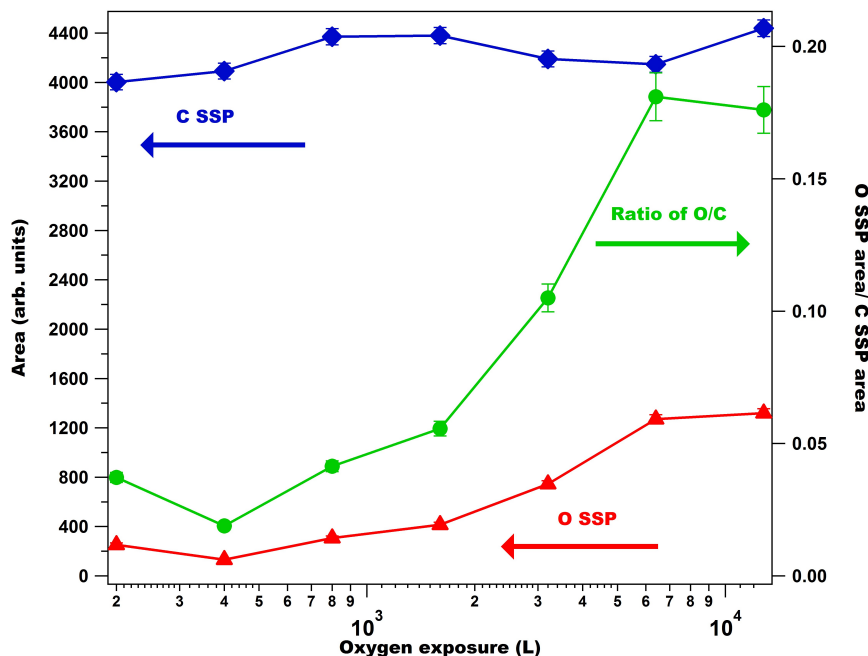


Figure 2.5 The C SSP, O SSP areas and their ratio for O₂-exposed Gr/Ru(0001) shown as a function of O₂ exposure on a log scale. The ratio curve was produced by dividing and SSP areas and then normalizing by their respective differential scattering cross sections.

To further understand the Gr/O₂/Ru(0001) system, experiments are performed in which oxygen is desorbed by annealing, with the results shown in Fig. 2.6. The upper spectrum in Fig. 2.6 was collected from the fully saturated sample prior to annealing. Following annealing at temperatures up to 600 K, the spectra do not change. A small decrease of the oxygen SSP starts to occur at 700 K and it keeps decreasing at higher annealing temperatures. After being heated to 800 K, the oxygen peak is absent, suggesting

that the desorption process is complete. Note that the characteristic Moiré LEED pattern recovers along with the complete desorption of oxygen. The inset to Fig. 2.6 shows how the oxygen and carbon SSP areas change with annealing temperature. One thing to note is that both the C and O SSP areas decrease during the desorption process.

To compare the behavior of intercalated oxygen to that of oxygen adsorbed onto Ru(0001), the bare Ru surface was exposed to O₂ and then subjected to a series of anneals to induce desorption, as shown in Fig. 2.7. It is understood that O₂ reacted with a bare metal will adsorb dissociatively [28,29]. The temperature needed to desorb this atomic oxygen from the bare Ru(0001) surface is about 1200 K, which is 500 K higher than for oxygen intercalated between Gr and Ru(0001).

In Fig. 2.8, the decrease of the C and O SSPs and how their relationship changes during the desorption process is shown as a function of O₂ exposure. The Gr/Ru(0001) sample is prepared with various oxygen exposures at 600 K. After cooling to room temperature, the sample is then annealed to 1000 K for 5 min to accomplish a complete desorption of the intercalated oxygen. The decrease in the carbon and oxygen SSP areas are then computed and shown as a function of O₂ exposure in the figure. These decreases represent the amount of C and O lost during the desorption process. The amount of oxygen lost represents the entire amount that was intercalated. The data indicate that with sufficient O₂ exposure, there is a concurrent loss of C, presumably due to an etching reaction between the oxygen and Gr. With increasing oxygen exposure, the absolute values of the loss of the oxygen and carbon SSP areas both increase. The ratio of lost C to lost O, also shown in the figure, decreases quickly with the magnitude of the O₂ exposure.

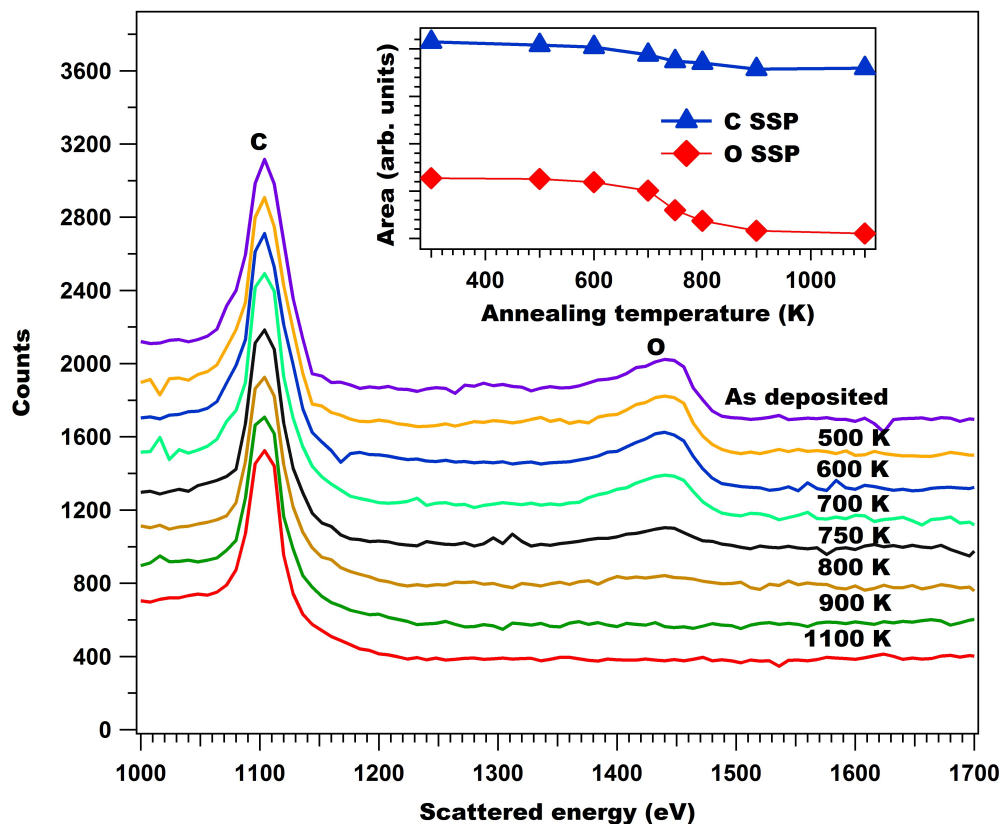


Figure 2.6 LEIS spectra of 3.0 keV He⁺ collected at a scattering angle of 115° from Gr/Ru(0001) exposed to 12800 L of O₂ at 600 K followed by an additional annealing at the indicated temperature for 5 min. The upper curve in the figure is the as-prepared Gr/O₂/Ru(0001). The spectra are offset for better clarity. The inset shows how the C SSP and O SSP areas change with annealing temperature.

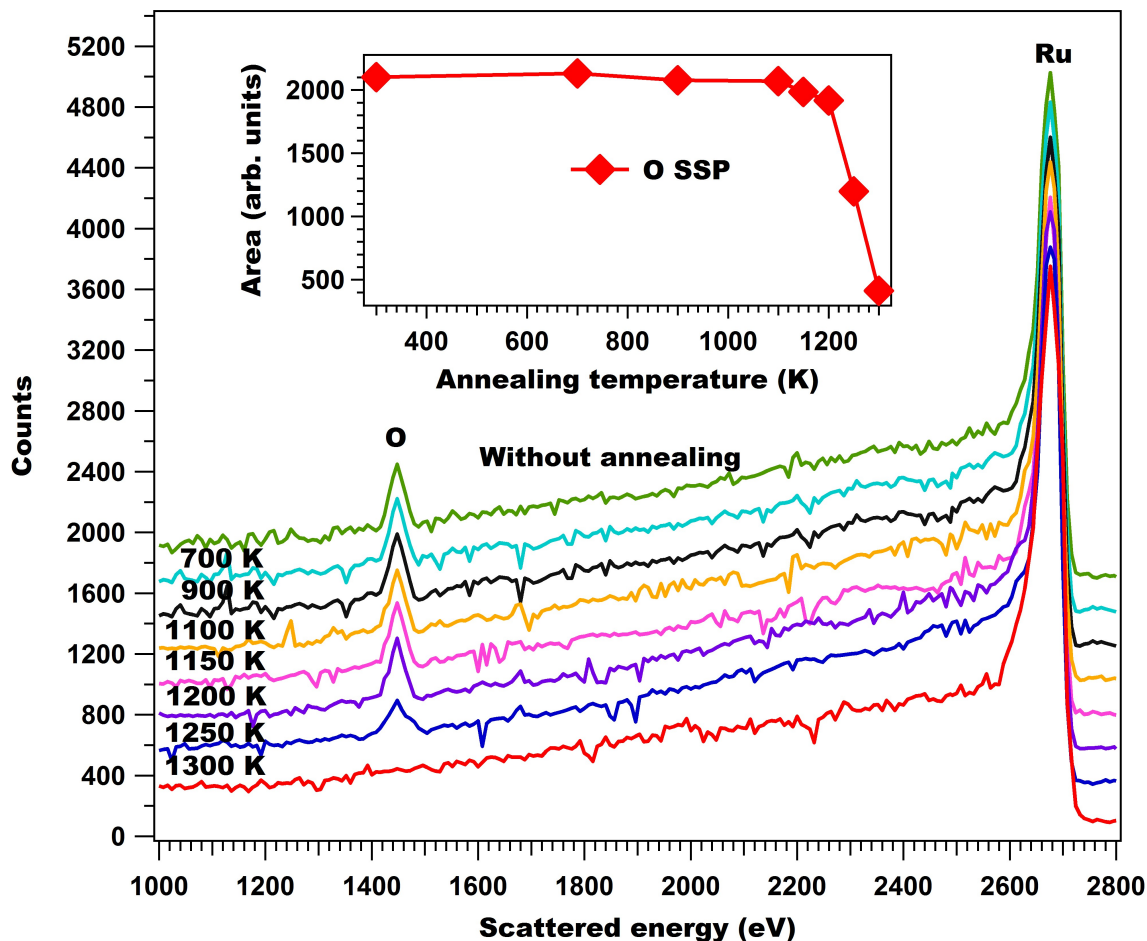


Figure 2.7 LEIS spectra of 3.0 keV He⁺ collected at a scattering angle of 115° from Ru(0001) exposed to 3000 L of O₂ at 400 K, followed by a 5 min annealing at the indicated temperature. The spectra are offset from each other for better clarity. The inset shows how the O SSP area changes with annealing temperature.

2.4 Discussion

Oxygen adsorbed onto bare Ru(0001) starts to desorb around 1200 K, as seen in Fig. 2.7, which is 500 K higher than the temperature needed to remove oxygen intercalated between graphene and Ru(0001), as shown in Fig. 2.6. This indicates that the oxygen adsorbed on bare Ru is more strongly bound than the oxygen intercalated between Gr and

Ru. This suggests that the intercalated oxygen is molecular, while oxygen adsorbed on bare Ru is atomic, as intercalated molecules would be significantly less strongly bound than chemisorbed atomic oxygen adatoms.

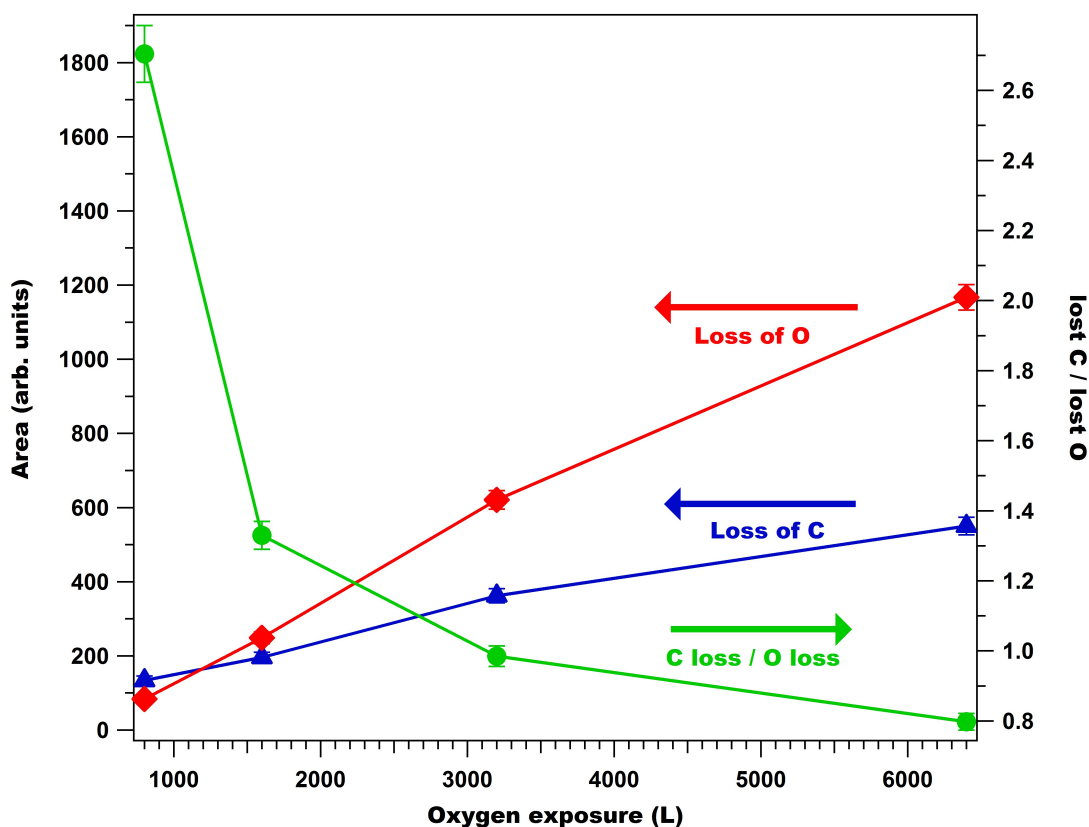


Figure 2.8 The decrease of the oxygen and carbon SSPs during the desorption process as a function of the initial O₂ exposure. The Gr/Ru(0001) sample was held at 600 K during the exposures. After cooling, desorption was performed at 1000 K for 5 min. Also shown is the ratio of the decrease of the C to the decrease of the O SSP after normalization by the differential cross sections.

In recent work, the Gr/O₂/Ru(0001) system was studied by XPS [30]. In this experiment, the O 1s level was found to have two components and the Ru 3d level showed

a component that indicated bonding of oxygen to Ru. The O₂ pressure used in ref. [30] was 0.5 Torr, however, which is much higher than in the present experiment, and the XPS data was collected under ambient conditions, both of which could lead to the formation of Ru-O bonds. In addition, ref. [30] reported that the oxygen is removed at a lower temperature (750 K) than in the present experiment (800 K), but in this measurement the temperature was continuously increased at a slow enough heating rate so that the sample was effectively annealed for a longer time than the 5 min used here, which likely accounts for the lower temperature needed to remove the oxygen. In addition, there could be some small differences in the reported temperatures that are related to calibration of the absolute surface temperature. Thus, the XPS data of ref. [30] are not inconsistent with the conclusion that the intercalated oxygen is molecular under the present conditions that involve lower exposures and measurements in UHV.

Another possible contribution to the differences of the thermal stabilities between oxygen intercalated in Gr/Ru(0001) and adsorbed onto bare Ru(1000) is that the confinement effect of the graphene overlayer destabilizes the bond between O and Ru, as discussed in ref. [9]. DFT calculations had demonstrated a similar confinement effect for CO intercalated between Gr/Pt(111) where the annealing temperature needed to remove CO from Pt(111) is 50 K higher than the temperature needed to desorb CO intercalated between Gr/Pt(111) [26]. In their calculation, the adsorption energy of CO decreases by 0.4 eV as the distance between the Gr overlayer and the Pt substrate drops from 5.91 Å of fully relaxed graphene to 5.3 Å showing that the distance decreases due to the Gr-substrate interaction. The calculation confirms that the CO adsorption energy on Pt(111) is weakened

by the Gr overlayer. It can be inferred that the smaller the nanospace, the weaker the molecular adsorption. Nevertheless, the difference in desorption temperature of 500 K observed here is much greater than 50 K, suggesting that there is something aside from a confinement effect that is primarily responsible for the increased thermal stability of O chemisorbed directly onto Ru. Since CO adsorbs as a molecule on Pt group metals and Ru [25,31], while oxygen adsorbs dissociatively, this is a reasonable interpretation.

Meanwhile, the possibility cannot be ruled out that it is the reaction of carbon in Gr with the intercalated oxygen that causes desorption at a lower temperature, regardless of the form of the intercalated oxygen. In fact, both the C SSP and O SSP areas decrease after being heated to 600 K, which indicates some etching of the graphene overlayer. Figure 8 shows the loss of carbon during the removal of O₂ by annealing, which suggests the products of the desorption are not solely O₂, but also include carbon-containing molecules such as CO or CO₂. In addition, the ratio of lost C to lost O drops with the amount of oxygen intercalation, showing that the etching reaction has a higher rate at low O₂ coverages, even though the absolute amount of C removed increases with O₂ exposure.

It is significant to realize that graphene is typically considered as an inert 2D material that can be used as a protection layer. This was investigated here by exposing an as-prepared Gr/Ru sample to 10000 L of O₂ at room temperature (data not shown). This surface shows no detectable oxygen SSP with LEIS, confirming that Gr acts as protection layer at room temperature. When the temperature is raised, however, small molecules such as O₂ do intercalate between a graphene overlayer and substrates such as Ir(111) and

Ru(0001) [8,30,32]. Then, further heating can lead to a substantial number of the intercalated oxygen atoms reacting with the carbon atoms thereby etching the Gr.

In addition, the presence of intercalated oxygen molecules decouples the graphene-metal interaction [8,10,26,27]. This decoupling effect is significant for those transition metals on which Gr is weakly bonded through van der Waals forces. This explains the disappearance of the Moiré pattern of Gr/Ru(0001) after oxygen intercalation. Similar phenomena were observed with scanning tunneling microscopy (STM) for Gr/Ru(0001) [27], electron energy loss spectroscopy (EELS) for CO intercalation between Gr and Pt(111) [26] and XPS and LEED for Gr on SiC [33]. For Gr/Pt(111), it was found that the characteristic loss feature (4-7 eV) due to the collective excitation of π electrons in freestanding graphene [34] is not observed on the Gr/Pt(111) surface [26]. The absence of this feature is believed to be caused by an electronic interaction between graphene and the Pt substrate that disrupts the π band structure, and the presence of intercalated CO causes the loss feature to return [26]. Thus, results from the literature indicate that the graphene decouples from the substrate and behaves more like a freestanding layer in the presence of intercalates.

2.5 Conclusions

Helium low energy ion scattering is a very useful tool for the study of molecules intercalated between graphene and a substrate. It has already been reported that small molecules, such as O₂, intercalate between graphene and a substrate using XPS and microscopy techniques [8-11]. The work presented here, however, unambiguously

demonstrates that oxygen is intercalated and not adsorbed, as it is based on a physical technique that directly measures the location of the oxygen, rather than relying on chemical information or images to infer that location. It is further shown that the intercalated oxygen fully desorbs from the surface when the sample is annealed to 800 K, while it takes 1200 K to remove oxygen from bare Ru. It is thus concluded from this large difference in the stability of the reacted oxygen that the intercalated oxygen is molecular. In addition, some of the graphene is etched along with the thermal desorption of oxygen. The products of this desorption likely include O_2 along with CO and/or CO_2 , and the ratio of the products depends on the amount of intercalated oxygen. This implies that special attention is required when heating graphene-based devices in air or low vacuum, where a significant amount of oxygen is present, to avoid etching that could result in degradation of the quality of the graphene material. Also, the property that the graphene can ease the desorption of adsorbates from certain substrates might have a potential use in catalysis.

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Chapter 3 Defect-induced oxygen adsorption on graphene films

3.1 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].

This chapter contains material submitted to T. Li, J. A. Yarmoff, Defect-induced oxygen adsorption on graphene films, *Surf. Sci.*

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 SiO₂ [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 O₂ in the presence of defects. For example, O₂ has been shown experimentally to molecularly chemisorb at two types of adsorption sites on TiO₂ 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 MoS₂ and doped boron nitride surfaces, which are two-dimensional materials that have similar structures as Gr, are active sites that enable the uptake of O₂ and Cl₂ 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 O₂ 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 O₂ molecules intercalate between the Gr overlayer and the Ru(0001) substrate when exposed to O₂ 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 O₂. Although a complete graphene layer is inert to adsorption at room temperature, it is found that O₂ 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 the vacancies are large enough to produce open areas of exposed substrate, however, then O₂ dissociates to form strong O-Ru metal bonds.

3.2 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 the 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 end of the manipulator foot for accurately measuring the ion beam sizes and fluxes.

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 $\text{sec}^{-1} \text{cm}^{-2}$ with a beam size of $3 \times 3 \text{ cm}^2$. 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 $6.7 \times 10^9 \text{ ions sec}^{-1} \text{ cm}^{-2}$. 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 $1.2 \times 10^{12} \text{ ions cm}^{-2}$. Considering that the lattice constant of free-standing graphene at room temperature is about 2.45 Å [28], it is estimated that 1 out of 167 Gr carbon atoms, or 0.6% of the surface carbon, is impacted during this light sputtering. The second defect formation involves a 1-hour sputtering, which corresponds to a fluence of $2.4 \times 10^{13} \text{ ions cm}^{-2}$, so that 1 out of every 8 Gr carbon atoms is impacted.

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 ($1 \text{ L} = 1 \times 10^{-6} \text{ torr sec}$). Additional post-annealing under UHV is also performed after the exposures.

The helium low energy ion scattering is performed with a differentially pumped ion gun (PHI model 04-303) that produces a beam diameter of 1.6 mm with a total sample current 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 always 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.

3.3 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 small. In addition, due to the small ratio between the scattering cross sections and 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 surface atom at a time [29]. The most significant features in LEIS spectra are the single scattering peaks (SSP) that represent projectiles that experience one hard collision with a single target atom before scattering from the surface [21]. The position 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 [21,30]. 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 [22,31,32]. 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 [33]. 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.

Figure 3.1 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 only probes 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 [23,34], which indicates that the overlayer is a single crystal that forms a superlattice with

substrate due to their different lattice parameters. These data indicate that a complete Gr film covers the surface without a measurable number of defects.

Spectrum (b) in Fig. 3.1 was collected after the sample was sputtered by 50 eV Ar⁺ for 3 min, which is the “light” sputtering that corresponds to a fluence of 1.2×10^{12} ions cm⁻². The spectrum displays a small Ru SSP at around 2920 eV, as well as the C SSP, which indicates a small number of carbon vacancies that reveal the Ru substrate. The LEED pattern observed after the 3 min sputtering does not change, signifying that the small number of defects created is insufficient to affect the alignment between the Gr overlayer

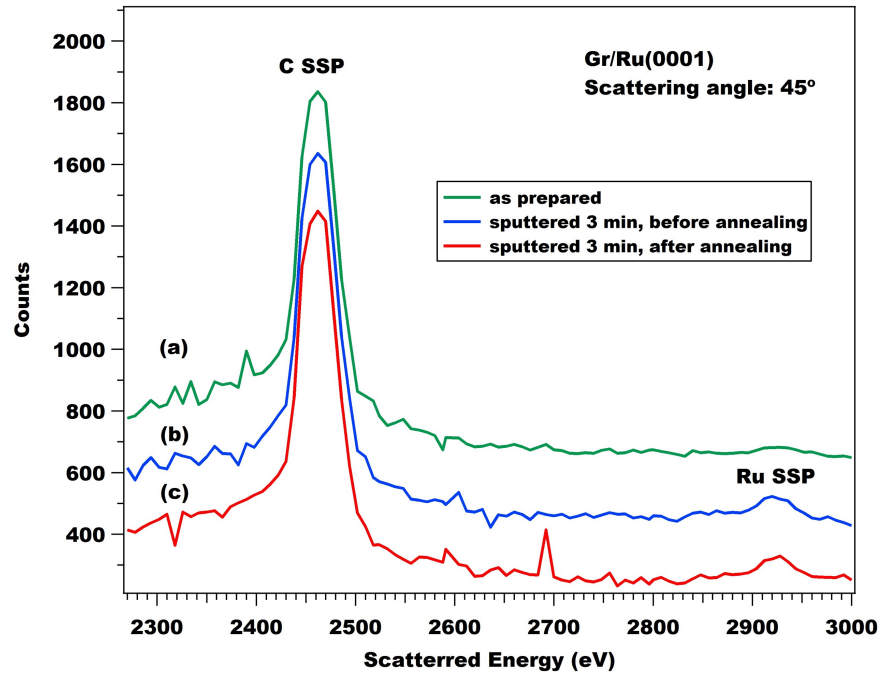


Figure 3.1 3000 eV He⁺ LEIS spectra collected at a 45° scattering angle from (a) as prepared Gr/Ru(0001), (b) Gr/Ru(0001) pre-sputtered for 3 min (fluence = 1.2×10^{12} ions/cm²), and (c) after an additional annealing to 1000 K for 5 min. The relevant SSP's are indicated and the y-axes are offset from each other for clarity.

and the Ru substrate. The cross section for 3000 eV He^+ scattering from Ru is about a factor of 16 larger than for scattering from C [35], so that the relative changes of the Ru SSP area are much larger than those of the C SSP and the number of revealed Ru atoms is rather small. If it is assumed that each defect reveals a single Ru substrate atom and that the neutralization probability is the same for scattering from C and Ru, the ratio of the Ru SSP to the C SSP, after correction for the cross section difference, implies that approximately only 0.4% of the C atoms are removed by the “light” sputtering. This number is similar to the estimate that 0.6% of the C atoms were impacted by Ar^+ , and thus suggests that approximately one defect is formed by each impact. The small number of missing C atoms is consistent with the notion that the light sputtering creates isolated, single vacancy defects that are randomly positioned across the surface [24,25].

The sputtered surface was then annealed at 1000 K for 5 min, and spectrum (c) in Fig. 3.1 was collected. It is seen that the areas of the C and Ru SSPs do not change with annealing, which infers that the vacancies induced by the light sputtering of Gr/Ru(0001) do not recover on their own. Thus, any possible restoration of the graphene lattice caused by post-annealing can be neglected.

After exposure to O_2 , 3000 eV He^+ LEIS spectra were collected at a 45° scattering angle to probe the outermost Gr layer and any possible adsorbates, as shown in Fig. 3.2. Spectrum (a) was collected from fully-covered Gr/Ru(0001) after an 8000 L oxygen exposure with the sample at room temperature. The only visible peak in the spectrum is the C SSP, which indicates that oxygen does not adsorb on top of the carbon atoms in a continuous graphene layer. Spectrum (b) was collected from Gr/Ru(0001) after a 3 min

light sputtering followed by a 1500 L O₂ exposure at room temperature. A new peak appears at 2580 eV that represents the O SSP, while the area of C SSP does not change. A small Ru SSP also appears, but it is smaller than the Ru SSP from the sputtered surface prior to O₂ exposure shown in Fig. 3.1(b). It is thus inferred that randomly distributed single vacancies on the graphene surface enable the adsorption of oxygen, even at room temperature, and that the adsorbed oxygen initially sits on or near the defects so that some of the underlying Ru is shadowed. The sample was then annealed to 600 K for 10 minutes and re-measured to produce spectrum (c) of Fig. 3.2. It is found that annealing causes the oxygen peak to disappear and the Ru signal to increase. This indicates that the adsorbed oxygen either desorbs from the surface or diffuses underneath the Gr after heating so that the Ru sites near the carbon vacancy defects are less shadowed.

To further study oxygen adsorption on Gr/Ru(0001) with isolated C vacancies, the above LEIS measurement was repeated at a 120° scattering angle, as shown in Fig. 3.3. A larger scattering angle enables some ions to pass through the graphene layer making it possible to detect both the surface atoms and those that have intercalated beneath the Gr overlayer. Note that the SSPs occur at lower energies than in Figs. 3.1 and 3.2 because of the larger scattering angle. From spectrum (a) in Fig. 3.3, it is found that no O₂ intercalates underneath a pristine Gr film at room temperature, in contrast to what it does at elevated temperature [23,36]. Note that the small Ru SSP is caused by the He⁺ ions that can penetrate the overlayer and backscatter at this angle. Similar to spectrum (b) in Fig. 3.2, spectrum (b) in Fig. 3.3 shows both O and Ru SSPs after a 1500 L room temperature oxygen exposure. After the additional annealing to 600 K, however, the oxygen peak in Fig. 3.3(c) decreases

but does not disappear as it did in Fig. 3.2. This indicates that the oxygen has diffused from the previous adsorption site at a carbon vacancy to a new position that is between the Gr overlayer and Ru substrate, i.e., most of the oxygen intercalates when annealed rather than desorbs. The small decrease in the O SSP area is likely due to the neutralization probability being larger for He^+ scattered from buried oxygen.

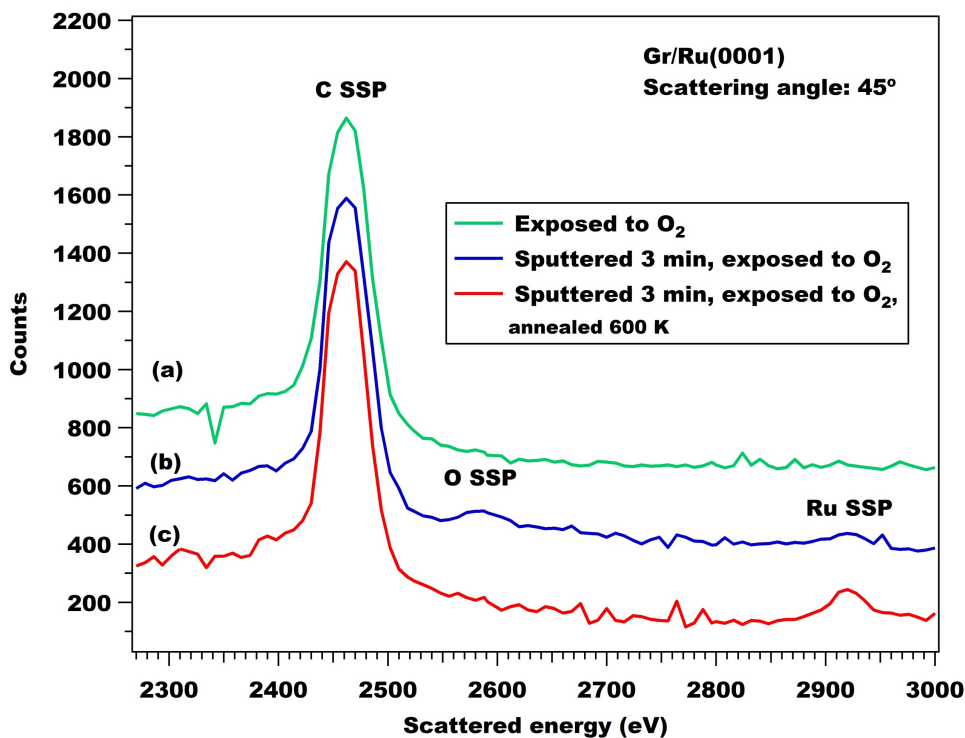


Figure 3.2. 3000 eV He^+ LEIS spectra collected at a scattering angle of 45° from (a) as-prepared Gr/Ru(0001) exposed to 8000 L of O_2 at 300 K, (b) Gr/Ru(0001) pre-sputtered for 3 min and then exposed to 1500 L of O_2 at 300 K, and (c) after an additional annealing at 600 K for 10 min.

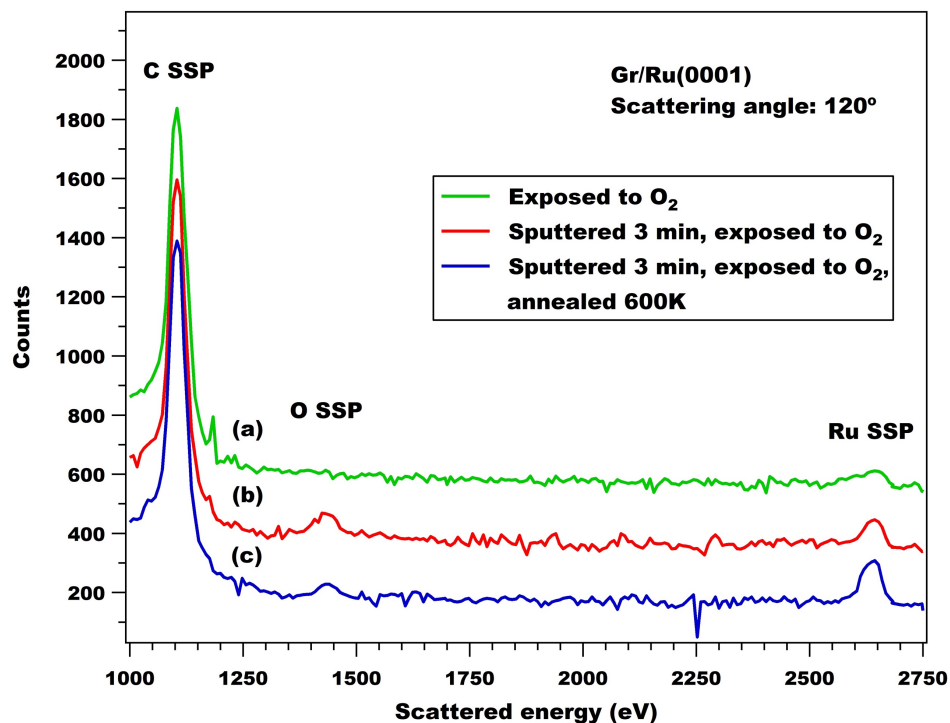


Figure 3.3. 3000 eV He⁺ LEIS spectra collected at a scattering angle of 120° from (a) as-prepared Gr/Ru(0001) exposed to 8000 L of O₂ at 300 K, (b) Gr/Ru(0001) pre-sputtered for 3 min and then exposed to 1500 L of O₂ at 300 K, and (c) after an additional annealing at 600 K for 10 min. The relevant SSP's are indicated and the spectra are offset from each other for clarity.

To explore the relationship between the oxygen adsorption and defect size, further measurements are performed in which larger defects are produced by using a longer sputtering time. Figure 3.4 shows spectra collected from a Gr/Ru(0001) sample that was sputtered for 1 hour, and then exposed to O₂ at room temperature and subsequently annealed. The LEIS spectra are collected at a 45° scattering angle so that any intercalated oxygen buried beneath the graphene layer is not visible. Spectrum (a) was collected from the Gr/Ru(0001) sample following the 1 hour sputtering. The Ru SSP is much larger than

that in Fig. 1(b) indicating that more Ru target atoms are visible to the incoming ions due to the larger vacancy defects. An analysis of the C/Ru SSP ratio suggests that approximately 2.3% of the carbon is removed by the 1 hour sputter. In addition, the Moiré pattern of Gr/Ru(0001) becomes blurry after the 1 hour sputtering indicating that the superlattice structure is partially destroyed. The LEIS data collected after the sputtered sample is exposed to 1500 L of O₂ at room temperature are shown in spectrum (b). The presence of the oxygen peak, the unchanged intensity of the carbon peak and the decrease of the size of the Ru peak suggest that oxygen adsorbs in the large defects and partially shadows the Ru underneath. As seen in spectrum (c), after annealing the sample to 600 K, both the O and the Ru SSPs do not change intensity, which is in contrast to the behavior after the 3 min sputtering seen in Fig. 3.2. Considering that oxygen chemisorbed on bare Ru(0001) is very stable and does not desorb until being heated to 1200 K [23,36], it can thus be inferred that most of the O₂ dissociatively chemisorbs as atomic oxygen to bare areas of the Ru substrate produced by the prolonged sputtering, and does not react with the Gr film.

3.4 Discussion

An implicit assumption in this analysis is the intrinsic stability of the single C vacancy defects on Gr/Ru(0001), which is based on the data shown in Fig. 1 after annealing. Indeed, free-standing graphene is able to reconstruct its lattice in the presence of defects under certain conditions [8]. As a good example, the Stone-Wales intrinsic defect (4 hexagons are transformed into 2 pentagons and 2 heptagons) can occur without any

removed or added C atoms after heating graphene over 1000 K or through mechanical strain [8,37]. For a single vacancy in graphene, the formation of this reconstruction is not

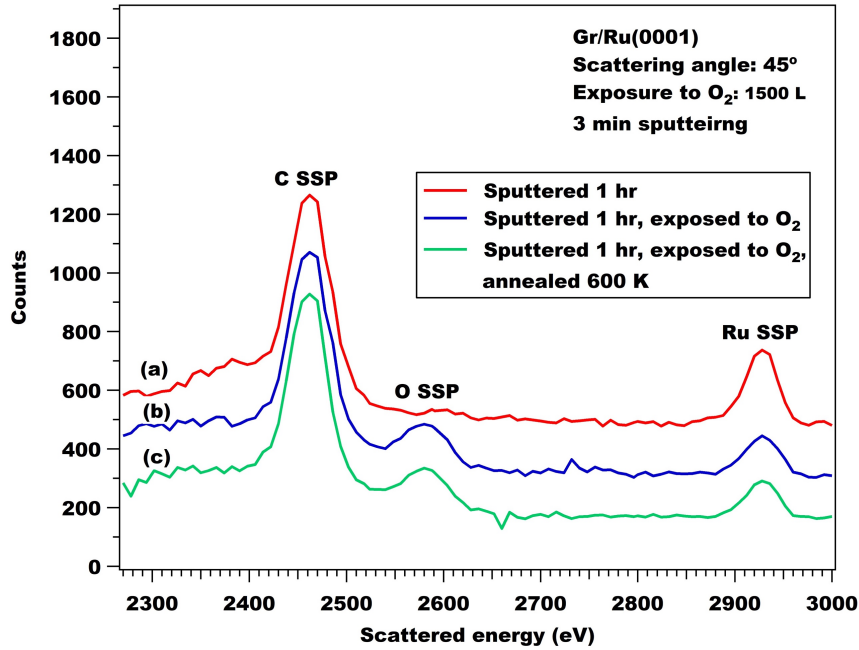


Figure 3.4. 3000 eV He⁺ LEIS spectra collected at a scattering angle of 45° from (a) Gr/Ru(0001) sample after a 1 hour sputtering, (b) the sputtered sample after exposure to 1500 L of O₂ at 300 K, and (c) after an additional annealing at 600 K for 10 min. The relevant SSP's are indicated and the spectra are offset from each other for clarity.

easy, however, as the energy required has a calculated value of 7.5 eV [8,38], which is much higher than the vacancy formation energy of many other materials [39,40]. Once a single vacancy is formed by rapid quenching from high temperature, collision or irradiation, one carbon atom is permanently lost which can lead to the formation of 5-membered and 9-membered rings [25,41]. That structure is very stable so that the restoration of the single vacancy does not occur, as is suggested by the spectra of Fig. 3.1. Nevertheless, migration

of single vacancies is possible when heated. As reported in Ref. [38], the calculated migration energy is about 1.3 eV, which should allow migration at temperatures slightly above 200°C. This migration of the defects cannot be detected in the LEIS spectra of Fig. 1 after annealing, however, because of the much larger scale of the beam size (1.6 mm) compared to the graphene lattice, and because the diffusion of the single vacancies is completely random.

When a large number of C atoms are removed from the surface by sputtering, a reconstruction could occur that involves bending and warping of the Gr layer due to its reduced surface area and the formation of open regions that have unsaturated bonds around their circumference, as occurs for free standing Gr [8]. For Gr films on a substrate treated with a lengthy Ar^+ sputtering, it is likely that the carbon vacancies migrate and coalesce after many C atoms are removed, even at room temperature, due to the instability of the film when it is missing too many carbon atoms, which leads to the formation of continuous areas that are void of Gr within an otherwise crystalline Gr overlayer. Such a case was observed in the aberration-corrected TEM images of monolayer graphene after a prolonged irradiation to a high energy electron beam [42], where 11% of the carbon was removed and continuous defects formed. The estimate above from the LEIS data is that about 2.3% of the surface consists of large areas that are void of carbon in which the bare Ru(0001) substrate is revealed. It is thus shown in this paper that the size of the vacancies on Gr/Ru(0001) makes a difference in the adsorption and subsequent diffusion of the oxygen. To systematically compare how the defect size affects the adsorption of oxygen, the Ru SSP areas collected at 45° from the clean surface and following the sputtering, oxygen

adsorption and annealing steps are plotted in Fig. 3.5. The triangles (a) correspond to the 1 hour pre-sputtering, and the circles (b) correspond to the 3 min pre-sputtering. It is observed that the areas of both of the Ru SSPs increase after the pre-sputtering due to the removal of C atoms, but the increase is larger following the longer sputtering time, as expected. Following a 1500 L oxygen exposure at room temperature, both Ru SSP areas decrease, but the magnitude of the decrease is different for the two sputtering times. This could be attributed to the number of available adsorption sites being different for the two cases or that the efficiency of oxygen adsorption at the different sites is not the same. After an additional annealing at 600 K for 10 min, little change of the Ru peak area is observed in (a), but the Ru SSP area in curve (b) rises close to what it was right after the pre-sputtering, suggesting that the isolated vacancy sites are void of oxygen following annealing.

The likely explanation for the behavior of lightly sputtered Gr/Ru(0001) is that the oxygen remains molecular when attached at a single carbon vacancy site. The adsorption of O₂ in molecular form on surface defects has been demonstrated previously [17,19,20]. For example, it has been shown from STM images that molecular oxygen species adsorbs at two different defect sites on rutile TiO₂ at a temperature as high as 230 K [17]. Such a temperature is much higher than it is needed to maintain molecular adsorption on the perfect TiO₂ surface (60 K). In Ref. [19], two stable configurations of O₂ adsorption on MoS₂-V_s (with one sulfur vacancy) and MoS₂-V_{s2} (with two sulfur vacancies) were proposed using first principles DFT calculations. The corresponding adsorption energies are -1.822 eV and -1.687 eV, respectively, thus producing a more stable structure than the

perfect MoS₂ surface. Additionally, a similar molecular adsorption of O₂ was proposed for doped boron nitride with adsorption energies ranging from -1.13 eV to -5.677 eV, depending on the type of dopant [20]. The adsorption energy for molecular oxygen on pristine boron nitride is only -0.008 eV, however, making it difficult to occur except at extremely low temperatures [20]. Thus, it can be inferred that single C vacancy defects in Gr activate a new adsorption site that stabilizes O₂ molecules.

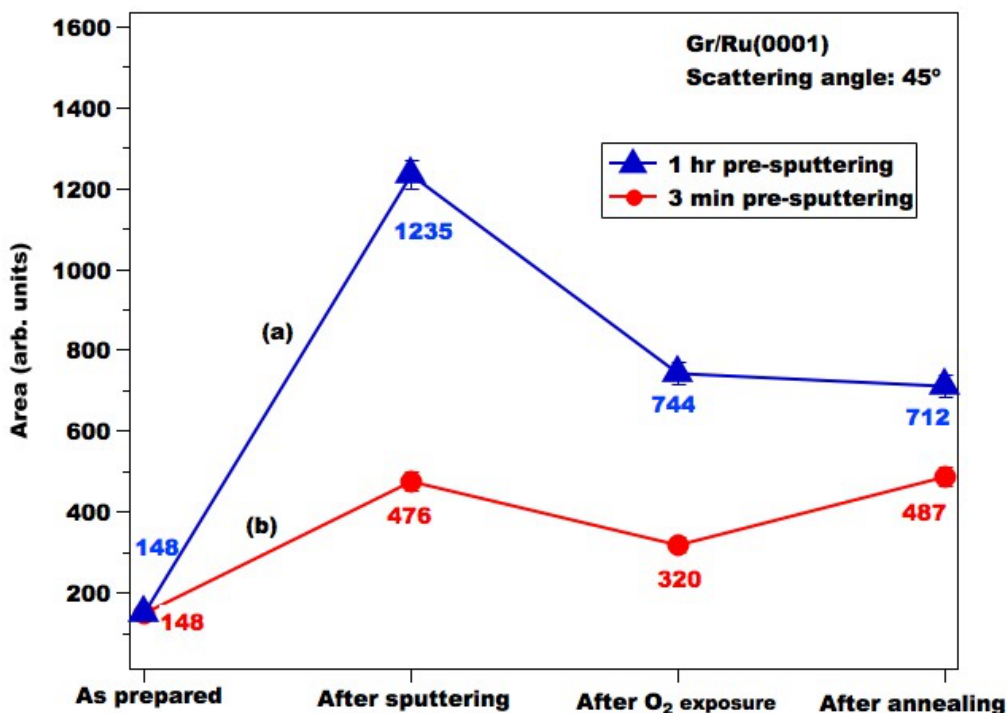


Figure 3.5. The Ru SSP areas of (a) 3 min pre-sputtered Gr/Ru(0001) and (b) 1 hour pre-sputtered Gr/Ru(0001) following the indicated treatments. The O₂ exposures are 1500 L, the annealing temperature is 600 K, and the 3000 eV He⁺ LEIS spectra are collected at a 45° scattering angle.

A question to be addressed is whether these conclusions concerning the adsorption of species at defect sites for Gr films can be extended to free graphene. For example, the adsorption of molecular oxygen at single C vacancy sites could involve only bonding to other carbon atoms while the Ru substrate has no effect. The adsorption energy of molecular oxygen on free-standing graphene is, however, much affected by the type of defect per the DFT calculations of Refs. [43,44]. The energy of molecular oxygen adsorption on a Stone–Thrower–Wales defect is -0.17 eV, which should only be observed at very low temperatures [43]. Molecular adsorption at a divacancy site of free-standing graphene, however, has an adsorption energy about -8.48 eV, which should survive even above room temperature [44]. Thus, in the present case, the Ru(0001) substrate might affect the stability of the adsorbates at single vacancy defects. In addition, the difference of lattice sizes between the substrate and deposited graphene leads to a corrugation of the overlayer [45], so that those carbon vacancies residing at different sites with respect to the substrate might not be equivalent. This suggests that information about adsorption at single C vacancy sites on Gr films may not transfer to free-standing Gr, and more work is needed to determine whether or not this is the case.

In the present experiment, the intercalated oxygen that diffuses at 600 K from single carbon vacancy adsorption sites on Gr/Ru(0001) to become intercalated completely desorbs when the sample is heated to 1000 K for 10 min. This indicates that the intercalated oxygen is molecular as, according to the analysis in Ref. [23], atomic oxygen chemisorbed on Ru doesn't desorb until 1200 K. It can therefore be inferred that the O₂ molecules are initially physically adsorbed at the vacancy sites before the post annealing and that such a

physical bond is so weak that when the sample is gently heated to 600 K, the physisorbed O₂ molecules migrate to find more stable sites as intercalates. Certainly, some oxygen could also desorb from the surface during the annealing, but the spectra in Fig. 3.3 do not show a significant change in the size of the O SSP after annealing.

A one hour pre-sputtering of Gr/Ru(0001) leaves larger open areas of the substrate. The oxygen adsorbed on these exposed substrate areas is more stable and does not diffuse even after being heated to 600 K. As is well known, the dissociative adsorption of O₂ occurs readily on transition metals at room temperature [10,11]. For Ru(0001), this dissociative adsorption only requires an energy of about 0.15-0.19 eV, which is obtained at room temperature [46]. On the graphene overlayer, however, the dissociation energy of O₂ is 2.71 eV [47], making graphene a good protective layer for transition metals at temperatures below 700 K [6,7]. Thus, it is likely that O₂ easily dissociates to form strong O-Ru bonds in the open areas of bare Ru(0001) and does not attach to directly to, or intercalate beneath, the Gr.

3.5 Conclusions

Gr films on transition metal substrates are an important class of carbon-based materials. Uniform and completely covered graphene layers can be used to prevent O₂ from reacting with transition metals. It is shown here that O₂ does not adsorb on the top of Gr/Ru(0001) nor does it intercalate between the Gr and the substrate at sample temperatures below 450 K [36]. Oxygen can, however, adsorb at Gr carbon vacancy defects even at room temperature. For isolated C vacancies, the oxygen adsorbs molecularly. If the

defects are large enough, then oxygen dissociates and chemically bonds directly to the revealed areas of bare metal substrate. This indicates that defects activate new adsorption sites on Gr/Ru(0001) that are not present on pristine graphene and that the adsorption sites of the oxygen and the stability of the adsorbates are very much affected by the size of the defects. These results demonstrate that it is necessary to maintain a complete graphene overlayer when it is being used as a protection layer, or in devices for which the Gr is part of a heterostructure.

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Chapter 4 The role of defects in the etching of graphene by intercalated oxygen

4.1 Introduction

Graphene (Gr), an atomically thin sheet of sp^2 bonded carbon, is regarded as a promising material for future carbon-based device architectures due to its particular electronic properties [1-3]. The interface of graphene with other materials is a key part of developing large-scale graphene growth and forming conventional device contacts [4-6]. Moreover, graphene can also be used as a protection layer on metal surfaces to avoid oxidation or corrosion due to its chemical and thermal stability [7,8]. It is reported, however, that small molecules, such as O_2 , CO and H_2O , intercalate between a deposited graphene overlayer and the metal substrate when exposed above room temperature or in the presence of defects [9-12].

In previous work [13], helium (He) low energy ion scattering (LEIS) was used to investigate the intercalation of oxygen underneath a Gr film deposited onto a Ru(0001) substrate. It was shown that the O_2 intercalates when exposed at 650 K and that it remains in molecular form. It was further shown that the intercalated O_2 desorbs from Gr/Ru(0001) when it is annealed to 800 K and, in doing so, etches away some of the graphene. The intercalation process extends progressively from the edge of the graphene layer towards

This chapter contains material submitted to T. Li, J. A. Yarmoff, The role of defects in the etching of graphene by intercalated oxygen, *J. Vac. Sci. Technol. A*

the center and a post-annealing at 823 K leads to a rapid etching of the graphene edge, as shown in Ref. [10], which implies that the edge of the graphene film is more reactive than the intact areas of the film. Note that calculations have also suggested the atoms in the vicinity of a carbon vacancy defect also have a high reactivity [14]. It is thus important to study how the defects in deposited graphene layers, which commonly occur during fabrication and cleaning procedures, affect the intercalation of small molecules and the consequent etching reaction when the material is heated to remove the intercalates. In this paper, small defects are induced by a low fluence Ar^+ sputtering of Gr/Ru(0001), and the results show that the defects facilitate both the intercalation of oxygen and the etching of the graphene during the thermal desorption.

The major tool used in this experiment is LEIS, which is well known for its extremely high surface sensitivity [15], and LEIS has been previously applied to measure impurities in Gr overlayers [16]. The surface sensitivity is high when detecting the projectiles that scatter as ions because the Auger neutralization of He^+ ions during the scattering process causes most of the ions that experience multiple scattering to be neutralized. By adjusting the scattering angle, a configuration can be obtained that probes only the Gr layer and any adsorbates, or the Gr layer along with any intercalates and revealed areas of the substrate.

4.2 Experimental Procedure

The experiment was conducted in an ultra-high vacuum (UHV) chamber that has a base pressure of 4×10^{-10} Torr and is equipped with an ion bombardment gun (Varian) for

sputtering, low energy electron diffraction (LEED) optics (Varian) and the equipment needed for the LEIS experiments, as described below. The 1 cm diameter sample is mounted on the foot of a manipulator that allows for rotations about both the polar and azimuthal angles. The manipulator foot contains an e-beam heater that uses a rhenium-coated tungsten filament that is floated at a high negative voltage to heat the sample up to 1400 K. The temperature is measured by K-type thermocouples spot welded to the sample plate.

A standard procedure is used for the preparation of a clean and well-ordered Ru(0001) surface, as reported in the literature [17,18]. The approach includes both ion bombardment and annealing (IBA) and a chemical reaction. First, a 30 min 500 eV Ar⁺ ion sputtering is performed using a flux of 4×10^{13} ions sec⁻¹ cm⁻². The spot size of the sputtering beam is 3×3 cm², as measured by a Faraday cup mounted near the sample holder, to ensure that the entire sample is uniformly bombarded. After sputtering, the sample is annealed under 4×10^{-8} Torr of O₂ at 1100 K for 8 min followed by a flash annealing at 1300 K for 2 min under UHV to remove the carbon contaminants via chemical reaction with oxygen, as well as any oxygen residue. To acquire a sufficiently clean and well-ordered surface, this process is normally repeated several times. The cleanliness and crystallinity of the sample surface is verified with LEIS and LEED.

The graphene layer is prepared by a chemical vapor deposition (CVD) method as reported in the literature [18]. This involves annealing the Ru(0001) sample to 900 K under 1.5×10^{-7} Torr of ethylene for 5 min, followed by a flash annealing under vacuum at 1200 K and then cooling to 450 K for another 5 min. Repeating this growth cycle 3 or 4 times is

generally required to get a fully-covered, single and continuous graphene layer on the Ru(0001) surface. The quality of the graphene layer is monitored with LEIS and LEED.

Carbon vacancy defects are produced via Ar^+ sputtering performed on the as-prepared Gr/Ru(0001) sample, as detailed in Ref. [14]. To remove only a few carbon atoms from Gr, a light sputtering is performed by defocusing the beam and setting the ion energy to 50 eV. As measured by the Faraday cup, the average beam density is 10 pA mm^{-2} and two different sputtering times (1 min and 3 min) are employed. The total fluences of the 1 min and 3 min sputtering treatments are $4 \times 10^{11} \text{ ions cm}^{-2}$ and $1.2 \times 10^{12} \text{ ions cm}^{-2}$, respectively. The lattice constant for free-standing graphene at room temperature is about $2.45 \text{ \AA}$ [19] so that there are about $2 \times 10^{14} \text{ C atoms within each cm}^2$. As a good approximation, only 1 out of 167 Gr carbon atoms is impacted during the 3 min light sputtering. Considering the low energy and flux of the Ar^+ ions, it is assumed that such a light sputtering leads to randomly distributed and isolated single carbon vacancies.

After introduction of defects in Gr/Ru(0001), O_2 exposures are performed at a pressure of $1.5 \times 10^{-6} \text{ Torr}$ with the sample held at 650 K to produce intercalated oxygen. The location of the oxygen beneath the Gr layer is confirmed with 3 keV He^+ ion scattering using the method reported in Ref. [13]. Exposures in this paper are reported in units of Langmiurs (L), where $1 \text{ L} = 1 \times 10^{-6} \text{ torr sec}$. The sample is held at 650 K until the O_2 is evacuated from the chamber.

A differentially pumped ion gun (PHI model 04-303) is used for the He^+ LEIS measurements. The incident He^+ ion beam has a diameter of 1.6 mm and a total sample current of 1.5 nA. The scattered ions are collected by a Comstock AC-901 hemispherical

electrostatic analyzer (ESA) that is mounted on the rotatable platform inside the UHV chamber, which allows for the scattering angle to be adjusted. The data collected in this paper uses a specular geometry in which the incident and outgoing angles are always equal with respect to the surface normal as the scattering angle is varied.

To test for the occurrence of any beam-induced surface damage, five spectra were collected successively from the same spot of a Gr-covered Ru sample, and it was found that the C LEIS peak intensity did not change. To completely avoid beam damage, the samples used in the present experiments are re-prepared after the collection of three spectra.

4.3 Results and Discussion

LEIS data are normally analyzed classically and with the binary collision approximation (BCA) [20] due to the small de Broglie wavelength of the incoming ions and the small ratio between the scattering cross section and the interatomic spacings, respectively. In the BCA, the scattering process is considered as a series of interactions of the projectile with one atom in the crystal at a time. The ions that experience only one hard collision with a surface atom that is visible to both the incoming ion beam and the detector produce a sharp single scattering peak (SSP) in a LEIS spectrum. The kinetic energy of the scattered projectiles in a SSP are determined primarily by the projectile/target mass ratio and the scattering angle, basically providing a mass spectrum of the surface composition [15]. To study defected and oxygen exposed Gr/Ru(0001), the areas of the C, O and Ru SSPs are computed by integration after subtracting the baseline of multiply scattered ions, which is modeled via a polynomial fit of the shoulder of the SSPs. When computing the

ratio of SSP areas between different elements, a normalization based on the relative differential cross sections is employed [15,21].

In order to backscatter from light target atoms, such as C and O, a light projectile is required, such as helium. Another advantage of using He^+ for ion scattering is its high surface sensitivity due to Auger neutralization (AN) [15,22]. In AN, most of the projectiles that collide with multiple target atoms are neutralized due to the relatively large He ionization level compared to the size of the surface conduction band. Thus, the signal captured by the ESA consists primarily of single scattering events from the outermost atomic layers. In addition, there is a strong matrix effect when helium ions are scattered from graphitic carbon [16,23,24]. This effect involves a quasi-resonant neutralization in conjunction with AN, which leads to a very high neutral fraction for primary incident beam energies below 2500 eV [25]. Therefore, to avoid the matrix effect and provide a strong signal of scattered He^+ , an incident beam energy of 3000 eV is used here.

The experiments are performed using a specular geometry in which the incident and exit angles are equal with respect to the surface normal, and a scattering of angle or either 45° or 115° is employed [26]. At 45° , the incident and exit angles are grazing enough that only the outermost Gr layer and any adatoms adsorbed on it are probed. At the larger 115° angle, the ions penetrate the overlayer so that the spectra also probe any intercalates and some of the underlying substrate.

The cleanliness of the Ru(0001) surface and the growth of graphene onto it are verified with He^+ LEIS and LEED. The clean Ru(0001) surface shows only a Ru SSP in LEIS spectra and a 1×1 LEED pattern. After producing a clean surface, LEIS at a scattering

angle of 45° is used to monitor the outermost surface after the growth of graphene. Spectrum (a) in Fig. 4.1 shows only a C SSP, which indicates that the graphene overlayer completely covers the substrate. Since the cross section for the scattering from Ru is about 16 times larger than for scattering from C, this is a very sensitive measurement of the completeness of the overlayer. In addition, LEED images collected from this surface show a Moiré pattern due to the formation of a superlattice between the Gr film and the Ru(0001) substrate, as reported previously [27,28].

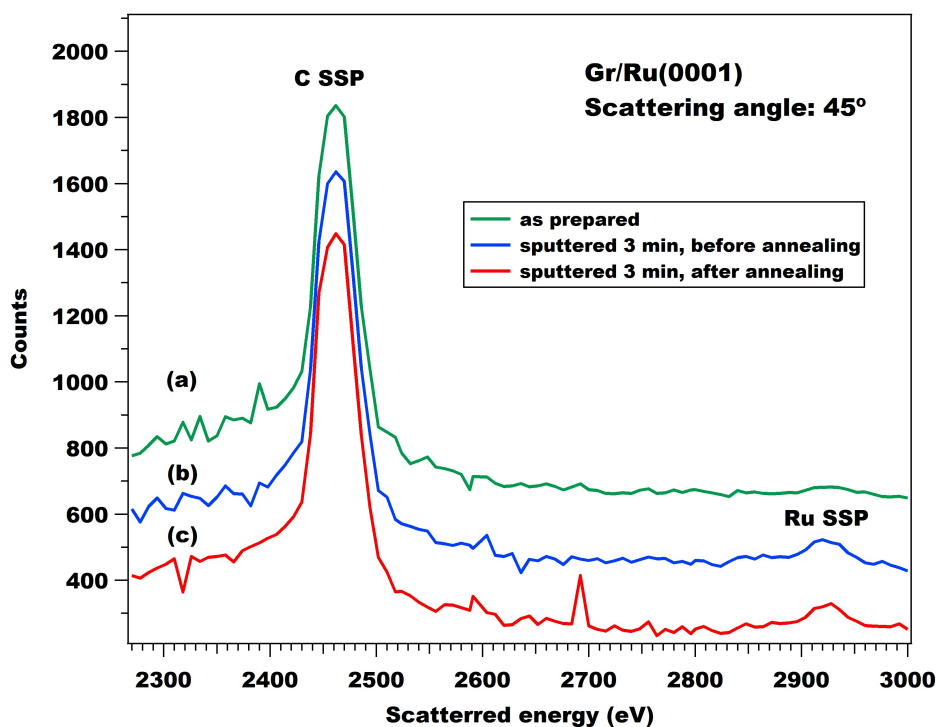


Figure 4.1. 3.0 keV He^+ ion scattering spectra collected at a 45° scattering angle from (a) as prepared Gr/Ru(0001), (b) after a 3 min light sputtering, and (c) after post-annealing at 1000 K. The y-axes of the spectra are offset for clarity.

A. The Role of Defects in Intercalation

The defects on Gr/Ru(0001) are introduced by a 3 min 50 eV Ar^+ sputtering, and 3 keV He^+ ion scattering spectra collected at a 45° scattering angle are used to monitor any changes to the surface, as shown in spectrum (b) of Fig. 4.1. The sharp C SSP is still clearly seen in LEIS and the LEED Moiré pattern remains sharp, which indicate that the structure of the graphene overlayer is not overtly affected by the light sputtering. There is a small Ru SSP in the spectrum, which indicates that a small number of C vacancy defects are introduced by the light sputtering that reveal a small part of the substrate. This low fluence of Ar^+ sputtering produces isolated single carbon vacancy defects, as described elsewhere [26].

Because the sample is annealed when investigating the intercalation of oxygen and the reaction of intercalated oxygen with graphene below, the sputtered surface is annealed here as a control prior to oxygen exposure. The LEIS spectrum collected after the lightly sputtered sample is annealed to 1000 K is shown in spectrum (c) of Fig. 4.1. It is seen that the areas of the C and Ru SSPs do not change and the Moiré LEED pattern is retained after the annealing, which implies that the defects on Gr/Ru(0001) are themselves stable, at least for annealing under 1000 K.

In addition, as shown in our recent work [26], oxygen molecules can physically absorb onto isolated carbon vacancy defects, even at room temperature, and the adsorbed oxygen diffuses and intercalates between graphene and Ru(0001) when the sample is heated to 600 K. To avoid the influence of oxygen attached to defect sites in the present measurements, the samples are held at 650 K during the O_2 exposures so that the all of the

molecules intercalate. To confirm the location of oxygen after exposure of defective Gr/Ru(0001), a He^+ ion scattering spectrum is collected at 45° after a 3 min sputtering followed by a 6400 L O_2 exposure at 650 K, as shown in Fig. 4.2. In this case, only the C SSP and a small Ru SSP are observed, which indicates that any adsorbed oxygen is intercalated below the Gr overlayer and none is present atop the Gr or at defect sites following O_2 exposure at elevated temperature.

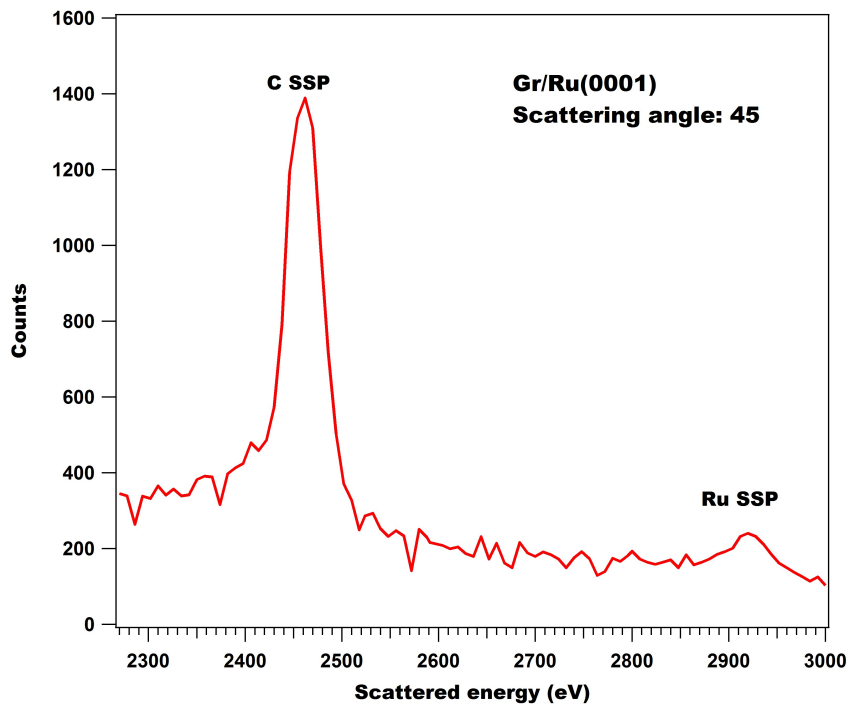


Figure 4.2. 3.0 keV He^+ ion scattering spectrum collected at a 45° scattering angle from Gr/Ru(0001) after a 3 min light sputtering followed by exposure to 6400 L of O_2 at 650 K.

To explore how the oxygen intercalation efficiency is affected by the isolated carbon vacancies produced by a light pre-sputtering, an O_2 exposure of 900 L at 650 K is

performed on the as-prepared Gr/Ru(0001) and on Gr/Ru(0001) with 1 min pre-sputtering and 3 min pre-sputtering, and the subsequent LEIS spectra are shown in Fig. 4.3. During the exposure, the sample is held at 650 K, and the spectra are collected at a 115° scattering angle to probe beneath the Gr film after the sample has cooled to room temperature. The figure shows that the areas of C SSPs do not change, but the areas of O SSPs increase with sputtering time. It is thus inferred that the oxygen intercalates easier on Gr/Ru(0001) as the concentration of C vacancy defects increases.

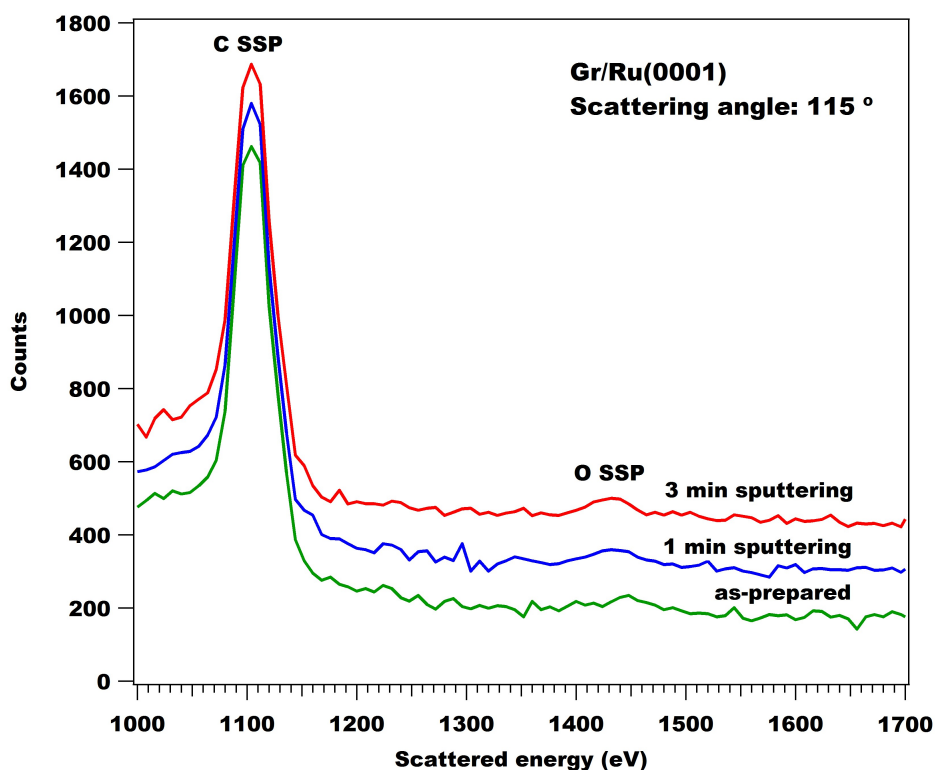


Figure 4.3. 3.0 keV He^+ LEIS spectra collected at a scattering angle of 115° from Gr/Ru(0001) exposed to 900 L of O_2 at 650 K following the indicated amounts of pre-sputtering. The spectra were collected after the sample cooled to room temperature.

In fact, it is shown in the LEEM images of Ref. [10] that the oxygen intercalates from the edges of graphene flakes on a Ru substrate. This suggests that it is energetically favorable for oxygen to adsorb at the edge of the graphene film and to then diffuse to become intercalated if the surface temperature is high enough to enable the diffusion. The mechanism is very similar in the presence of defects. As proposed in previous reports [29-33], the defects and dopants on 2D materials, such as MoS₂, boron nitride or graphene, act as active sites for molecular adsorption even at room temperature. In particular, our previous study of defects on Gr/Ru(0001) [26] showed that the oxygen adsorbs molecularly, even at room temperature, on single vacancy defects created by light sputtering and then diffuses between the graphene film and Ru(0001) substrate when annealed to 600 K. It is thus reasonable to assume that when defect containing Gr/Ru(0001) is exposed to O₂ at elevated temperature, the defect sites behave as transition stations for the intercalation process, in which they keep adsorbing and transferring the adsorbates to the more stable sites beneath the graphene overlayer. This process increases the intercalation rate as compared to that of the original intact graphene layer. This indicates that defects further degrade the quality of graphene films on metal substrates, beyond the presence of the defects themselves, by increasing the probability and rate of intercalation. This effect will be particularly critical in applications in which graphene materials are exposed to an ambient environment and/or prepared at an elevated temperature.

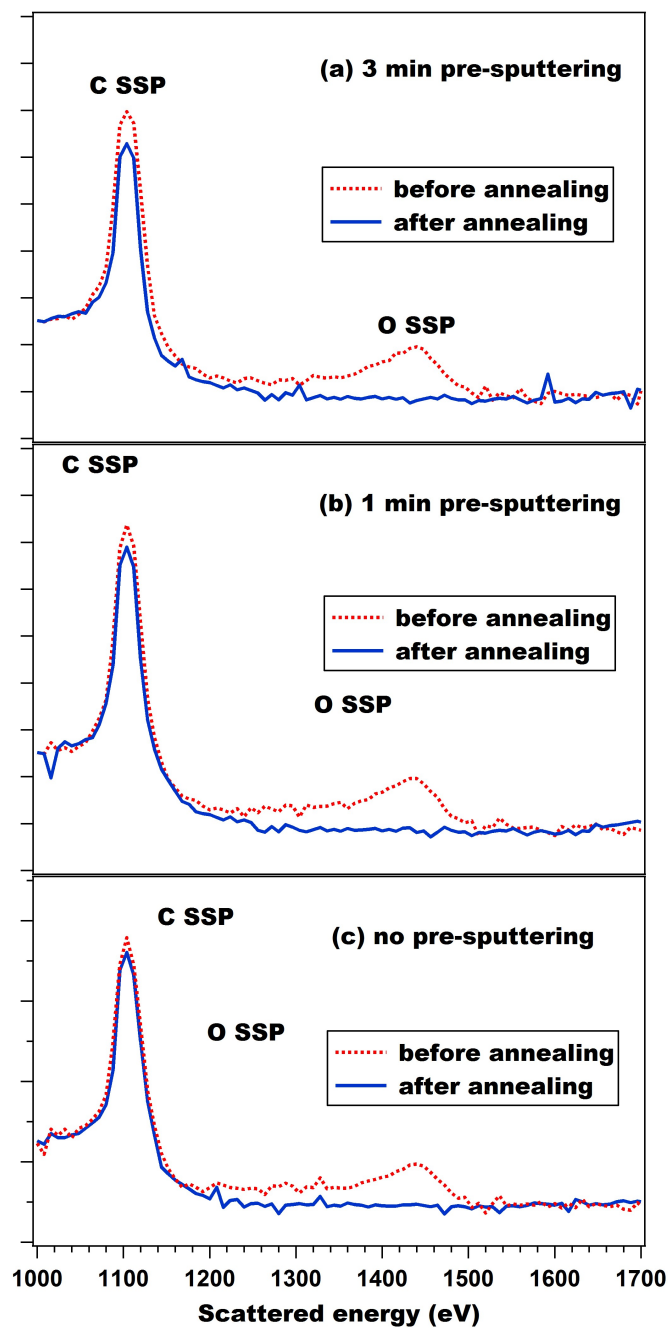


Figure 4.4. 3.0 keV He⁺ LEIS spectra collected at a scattering angle of 115° from Gr/Ru(0001) exposed to 6400 L of O₂ at 650 K (a) after a 3 min sputtering, (b) after a 1 min sputtering, and (c) without sputtering. The dashed lines show spectra collected right after the oxygen exposure, while the solid lines show spectra collected after an additional annealing at 1000 K for 10 min.

B. The Role of Defects in the Etching Reaction

It has been reported that oxygen intercalated between Gr and Ru(0001) starts to desorb from the sample and react with the graphene overlayer when annealed to 750 K or above [13,34]. The annealing leads to both the removal of molecular O₂ and the etching of some of the graphene, presumably through the formation of gaseous CO or CO₂.

To explore how this etching is affected by carbon vacancy defects, spectra collected from the as-prepared Gr/Ru(0001) are compared to those collected from the defect-containing samples in Fig. 4.4. The as-prepared Gr/Ru(0001) samples and those pre-sputtered for 1 min and 3 min are exposed to 6400 L of O₂ while being held at 650 K. Following the O₂ exposures, an additional 10 min post-annealing at 1000 K is employed to force the complete desorption of the intercalated oxygen. Each panel of Fig. 4.4 shows He⁺ ion scattering spectra collected from the O₂ exposed samples both before (dashed lines) and after (solid lines) the post-annealing. The spectra are all collected at 115°, so that the intercalated oxygen is detected. It is seen in Fig. 4.4 that the oxygen SSPs are absent after the annealing, confirming that the desorption process is complete after annealing to 1000 K. The etching of graphene during the desorption process is indicated by the decrease of the C SSPs following annealing. It is clearly seen that magnitude of the decrease of the C SSP area increases with the fluence of the pre-sputtering treatment.

In Fig. 4.5, the absolute amounts of C in the graphene film and intercalated O before and after the annealing are plotted, along with the ratio of C to the O decrease following the desorption process, as a function of sputtering time. The amount of C was calculated

from the LEIS data shown in Fig. 4.4 by assuming that the as-grown sample represents a full ML of Gr, and that the C SSP area is proportional to the Gr coverage. The oxygen coverage was calculated by normalizing the O SSP area to that of the C SSP after correcting for the differential cross section. Note that the O coverage may be an underestimate, as the He ions scattered from intercalated oxygen may be more prone to neutralization than those scattered from the Gr film, and some of oxygen may also be shadowed by the surface Gr. Nevertheless, the data in the figure does correctly show the trends in how the oxygen coverage and the ratio of lost C to lost O change.

It is clearly seen that the amount of oxygen decreases to the same level after the post-annealing for all sputtering times. Since the intercalation efficiency depends on the number of defects on the surface, as discussed above, it is reasonable that a longer pre-sputtering time leads to a slightly larger amount of oxygen intercalation even though the exposures are the same, which can be seen in the data of Fig. 4.5. Thus, the decrease of the amount of intercalated oxygen during the desorption process increases with pre-sputtering time because there is more oxygen that can be removed.

Meanwhile, the decrease in the amount of surface carbon following annealing is much more affected by the number of surface defects. Although it may be expected that the C coverage would not decrease in the absence of defects, the data show a loss of 0.066 ML of C when the as-prepared sample is heated, as was reported previously [13]. The data further show, however, that with increased sputtering time, the absolute decrease in the amount of C and the ratio of lost C to lost O during desorption both increase. That indicates

that the defects introduced by the sputtering treatment improve the etching efficiency of the graphene layer.

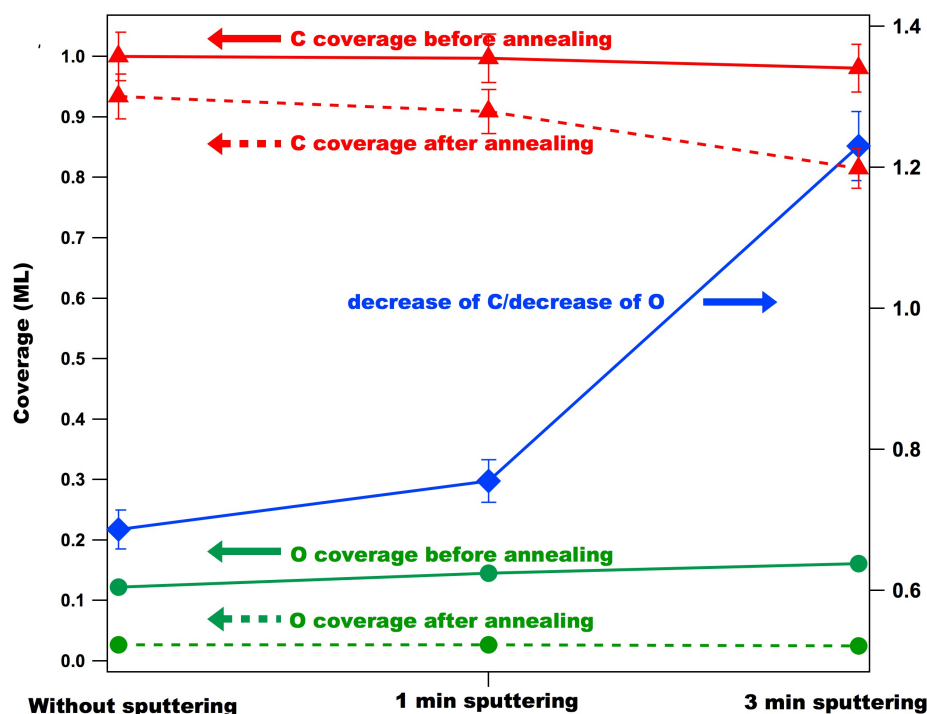


Figure 4.5. The left axis is used to show the amount of C and O on the surface before and after a 10 min annealing at 1000 K, based on the data from Fig. 4.4, and are shown as a function of the amount of pre-sputtering before the O₂ exposure. The right axis is used to indicate the ratio of the decrease of C coverage to the decrease of O coverage during the oxygen desorption. The ratio calculation includes a normalization of the SSP areas by the respective differential cross sections for He scattering from C and O.

A reasonable explanation for how the defects created by the pre-sputtering ease the etching of graphene by intercalated oxygen is that the C atoms in the vicinity of the defects are more active in contrast to their inert behavior when intercalated beneath a complete graphene layer. As reported in Ref. [14], single carbon vacancies are introduced on Gr/Pt(111) by 140 eV Ar⁺ sputtering, which is also a weak graphene-metal interacting

system similar to Gr/Ru(0001). In their DFT simulations, a 6×6 unit cell (4 cells of the 3×3 Gr/Pt(111) Moiré) was used. It was found that two of the three undercoordinated C atoms that surround a single C vacancy move closer to each other and form a pentagonal ring, becoming weakly bonded so that they could be etched first during the desorption process. In addition, the third atom and one of its neighbors moves out of the initial graphene plane towards the Pt substrate (distance decreases from 3.27 Å to 1.97 Å), forming two new chemical bonds with Pt atoms. This likely further improves the etching efficiency as the carbon-metal bond is easier to break than the carbon-carbon bond in defect-free graphene. It is also noted that the average distance between the graphene overlayer and the Pt(111) substrate decreases by 0.1 Å due to the presence of the C vacancies, which could also enhance the etching reaction at the edges of the Gr films.

4.4 Conclusions

Small molecules, such as O₂, can intercalate between a graphene film and the substrate and the intercalated oxygen will etch the graphene overlayer when the sample is annealed to remove the intercalated oxygen [9,10,13,34]. To further study the factors that affect the oxygen intercalation and the etching of Gr during the thermal desorption of oxygen, a light sputtering of the Gr/Ru(0001) surface was performed before the O₂ exposures to create single carbon vacancy defects. The data show that those defects improve the efficiency of oxygen intercalation. This implies that it is necessary to maintain the completeness of a graphene overlayer when storing graphene-based devices, as defects will cause the devices to degrade more quickly, especially when heating or fabricating them

in air or low vacuum. Furthermore, it is shown that etching of the Gr film during the desorption of intercalated oxygen is more efficient in the presence of defects. It is thus concluded that the C atoms located near the defects or edges of the Gr film are less stably bonded and can thus more easily react with intercalated oxygen to form the gaseous etching products.

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Chapter 5 The intercalation and orientation of CO between graphene and Ru(0001)

5.1 Introduction

Graphene (Gr), a two-dimensional, single-layer sheet of sp^2 hybridized carbon atoms, has attracted world-wide attention owing to its exceptional properties, such as high electronic conductivity and good chemical and thermal stability [1-4]. Chemical vapor deposition (CVD) on transition metal substrates can be used to produce large-scale, monocrystalline graphene with good quality [5-9]. CVD-grown graphene overlayers can protect transition metal substrates from being oxidized or corroded due to its chemical inertness [4,10]. Recent studies also show that small molecules, such as O_2 and CO, intercalate between the Gr film and Ru(0001) and Pt(111) substrates even at room temperature, rather than adsorb on top of the graphene layer [11,12]. In the past decade, the interaction between CO molecules and transition metal substrates has also been well studied, including binding geometries [13,14], vibrational properties [15], and the kinetics of adsorption and desorption [16-18]. The interaction of CO with the metal substrate beneath a Gr overlayer has, however, rarely been reported.

Here, CO intercalation between Gr/Ru(0001) is studied with helium low energy ion scattering (LEIS), using the methodology developed in our previous study of O_2 intercalation [19]. LEIS is well known as a surface science technique and it has been previously applied to measure impurities in graphene [20]. Helium ions are used as projectiles, as this leads to a high surface sensitivity because most of the He^+ that

experiences multiple scattering become neutralized and are thus not detected. By adjusting the scattering angle, as shown in Ref. [19], the intercalated atomic species can be distinguished from those of the Gr layer and any adsorbates. To distinguish the ^{12}C species in graphene from any intercalated or adsorbed molecules, isotopically enriched ^{13}CO is used here. It is found that ^{13}CO molecules intercalated between Gr and Ru(0001) change their geometry when heated to 343 K and starts to desorb from the surface at 383 K. The desorption of ^{13}CO from bare Ru(0001) starts at room temperature, however, which indicates that the Gr/metal system could be a good nano-container for certain gas molecules under vacuum. In addition, the ability to adjust the orientation of intercalated molecules can provide a means for altering the curvature, and thus the electronic transport properties [21-23], of the Gr, as well as a means for data storage in nanoelectronic systems.

5.2 Experimental procedure

The experiment was performed in an ultra-high vacuum (UHV) chamber with a base pressure of 4×10^{-10} Torr. The chamber is equipped with an ion bombardment gun (Varian) for sample cleaning, low energy electron diffraction (LEED) optics (Varian) and the instruments needed for the LEIS experiments, as described below.

The 1 cm diameter sample is mounted on the foot of a x-y-z manipulator that enables rotations about both the polar and azimuthal angles. An e-beam heater containing a rhenium-coated tungsten filament floated at -650 V is used to heat the sample up to 1400 K. The temperature of sample is measured by type K thermocouples attached to the sample plate.

The Ru(0001) sample is cleaned with a standard ion bombardment and annealing (IBA) approach along with an oxygen treatment, as reported in the literature [24,25]. A 30 min 500 eV Ar⁺ ion sputtering is first employed using a flux of 4×10^{13} ions sec⁻¹ cm⁻² with a beam size of 3×3 cm², as measured by a Faraday cup attached below the sample holder. The ion bombardment is followed by annealing under 4×10^{-8} Torr of O₂ at 1100 K for 8 min to remove carbon contaminants via chemical reaction and then a flash annealing under UHV at 1300 K for 2 min to remove the oxygen residue. This growth cycle is normally performed several times to acquire a sufficiently clean and well-ordered surface. The quality of sample surface is monitored with LEIS and LEED.

The graphene layer is grown through a CVD process, as reported in Ref. [25]. This procedure consists of heating the Ru(0001) sample to 900 K under 1.5×10^{-7} Torr of ethylene for 5 min, a flash annealing under vacuum at 1200 K for 1 min, and a slow cooling down to 450 K for another 5 min. This process is repeated 3 or 4 times to get a fully-covered, single and continuous graphene layer on the Ru(0001) substrate. The presence and the quality of the graphene layer is verified with LEIS and LEED.

After the growth of graphene, exposures of isotopically enriched ¹³CO are conducted at a pressure of 4×10^{-3} Torr on Gr/Ru(0001) and 1×10^{-5} Torr on bare Ru(0001), respectively, with the sample at room temperature. Exposures in this paper are reported in units of Langmuirs (L), where 1 L = 1×10^{-6} torr sec.

A differentially pumped ion gun (PHI model 04-303) is used to create 3 keV He⁺ for LEIS measurements. The incident He⁺ ion beam has a diameter of 2 mm and a flux of 7.5×10^{12} ions sec⁻¹ cm⁻². The scattered ions are collected by a Comstock AC-901

hemispherical electrostatic analyzer (ESA) mounted on the rotatable platform inside the UHV chamber, which enables adjustment of the scattering angle. A specular geometry is used for the spectra shown in this paper, in which the incident and exit angles are set to be equal with respect to, but on opposite sides of, the surface normal as the scattering angle is varied.

To test the possible beam-induced damage during the LEIS measurements, five spectra were collected successively from the same spot of a Gr/Ru(0001) sample. Each spectrum takes about 85 sec to collect. It is found that the C signal intensity in these five spectra does not change as a function of ion bombardment time. Thus, it is reasonable to assume the beam damage during the collection of five spectra is negligible. The samples used in the present measurements are re-prepared after collecting every four spectra to completely avoid any effects of beam damage.

5.3 Results

LEIS data can be analyzed with the binary collision approximation (BCA), which assumes the projectile interacts with only one surface atom at a time, as the scattering cross sections are smaller than the interatomic spacings [26]. The most significant features in LEIS spectra are single scattering peaks (SSP), which correspond to projectiles that experience only one hard collision with a target atom before escaping the surface and being collected by the detector. The SSPs ride atop a small background of multiple scattered ions. The energy loss during a single collision is determined primarily by the ratio of the projectile mass to that of the target and the scattering angle, as the interactions can be treated

classically because the de Broglie wavelength of low energy ions is very small [27]. Therefore, by measuring the kinetic energy and intensity of the SSPs, the elemental composition of the near-surface region can be determined.

A light projectile, such as helium, is used in these experiments in order to enable single scattering at a large angle from relatively light C and O atomic species on the surface. Additionally, helium ion scattering has an extremely high surface sensitivity due to Auger neutralization (AN), which is an irreversible process that dominates the charge transfer between noble gas projectiles and solid targets. In the process of AN, most of the projectiles that undergo multiple collisions and collide with deeper lying target atoms are neutralized and thus not detected by the ESA [27,28].

In addition, there is a strong matrix effect that occurs for helium ions scattered from graphitic carbon [20,29,30]. This matrix effect is due to a quasi-resonant neutralization of helium ions in scattering from certain substrates in conjunction with AN, which makes the neutralization of scattered ions a strong function of the primary beam energy. For He^+ ions scattering from graphitic carbon with a kinetic energy below 2.5 keV, the neutralization is almost complete [31]. Thus, to avoid the matrix effect and guarantee the detection of scattered ions, a 3.0 keV He^+ beam energy is employed here.

The cleaning of the sample and the growth of graphene are conducted as discussed above and presented previously [19]. LEIS spectra collected from Gr/Ru(0001) show only a sharp ^{12}C SSP, which indicates the formation of a complete graphene overlayer. LEED displays satellite spots that indicate the presence of a Moiré pattern on the surface formed by a superlattice between the Gr film and the Ru(0001) substrate [19,32].

After cleaning, the Gr/Ru(0001) sample is exposed to 1×10^9 L of ^{13}CO at room temperature, and the LEIS spectra collected at 45° and 115° are shown in Fig. 5.1(a). The different scattering angles are used here as means for locating the ^{13}CO molecules after exposure. At a small scattering angle, such as 45° used here, the incident and exit beams are near the surface planes so that atoms positioned below the graphene overlayer are completely shadowed and only the ^{12}C species of the graphene film and any adsorbates attached to it are detected. For a larger scattering, such as 115° , the trajectories are closer to the surface normal, so that the incoming ions can penetrate the surfaces more deeply and reach atoms below the Gr overlayer [19].

It is observed in the spectrum collected at 45° in Fig. 5.1(a) that only a ^{12}C SSP is visible after the ^{13}CO exposure. For the 115° scattering angle, however, an additional ^{16}O peak is present. It can thus be concluded that the ^{13}CO is intercalated beneath the Gr film and does not adsorb on top of the overlayer. In addition, no ^{13}C signal is detected in the spectrum collected at 115° , which indicates that the intercalated ^{13}CO is oriented vertically beneath the graphene layer with the oxygen pointing up so that the ^{13}C atoms are completely shadowed by the O atoms.

Spectra collected after ^{13}CO exposure of bare Ru(0001) are shown in Fig. 5.1(b). Only ^{16}O and Ru SSPs are observed in spectra collected at both 45° and 115° . This indicates that ^{13}CO adsorbed on Ru(0001) shares the same geometry as the ^{13}CO intercalated between Gr/Ru(0001), in which the CO molecule is also adsorbed vertically with the O end point straight up, consistent with reports in the literature [33].

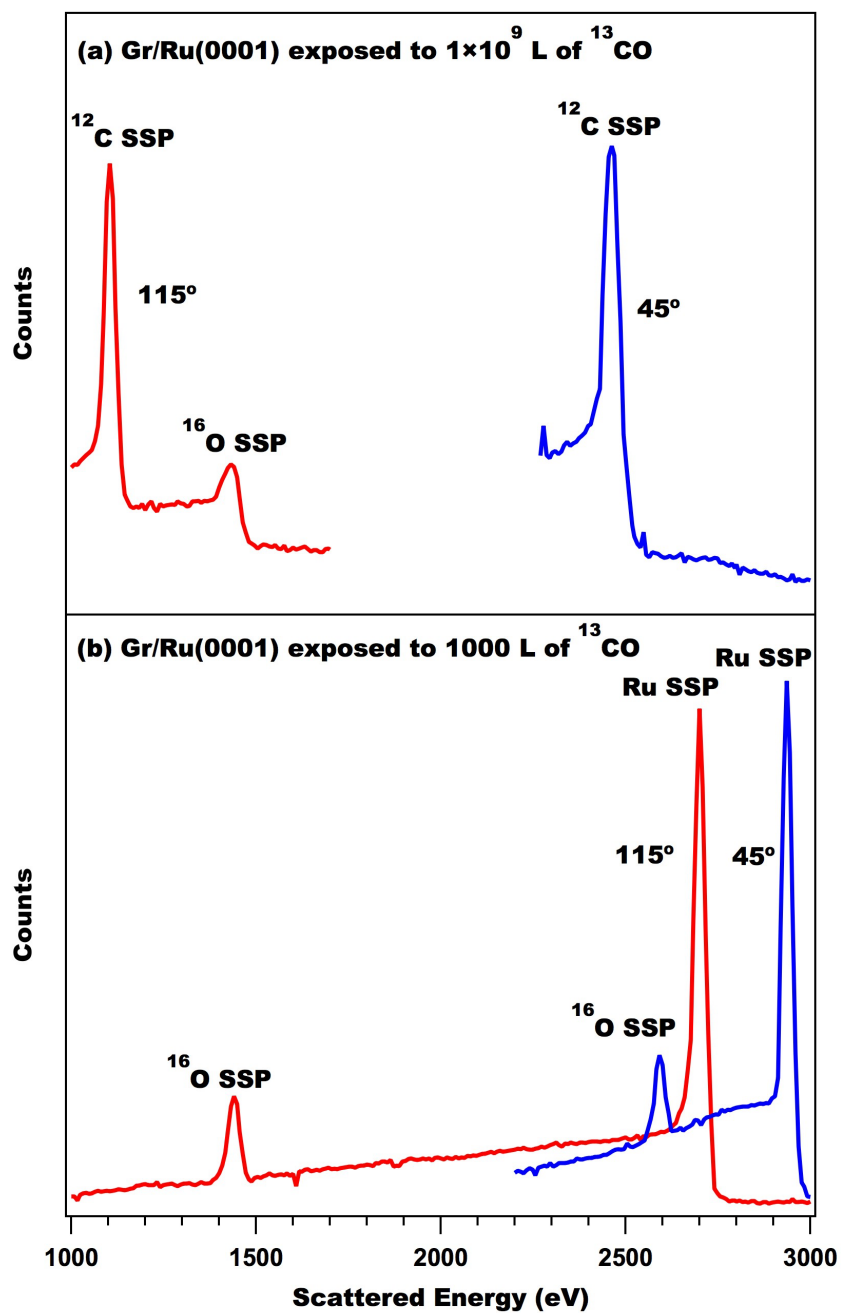


Figure 5.1. 3.0 keV He⁺ LEIS spectra collected at scattering angles of 45° and 115° from (a) Gr/Ru(0001) exposed to 1×10^9 L of ^{13}CO and (b) bare Ru(0001) exposed to 1000 L of ^{13}CO .

Figure 5.2 shows how the concentration of intercalated ^{13}CO changes as a function of exposure using 3 keV He^+ ion scattering at an angle of 115° . The exposures are performed at a pressure of 4×10^{-3} Torr at room temperature. It is found that the oxygen SSP does not appear until a rather large exposure of 1×10^8 L, which shows that the efficiency of the intercalation of ^{13}CO at room temperature is very low. The ^{13}CO concentration then increases with additional exposure until it saturates around 1×10^9 L.

The inset of Fig. 5.2 shows the change of oxygen coverage as a function of exposure amount. Here, and in the following figures, the coverage of O is calculated from the ratio of the areas of the ^{16}O to the ^{12}C SSP by assuming that the as-grown sample represents a full ML of graphene and the SSP area is proportional to the coverage. In the calculation of the area of an SSP, the integration is performed after subtracting the multiple scattering background, which is modeled using a polynomial fit of the region surrounding the SSP. In addition, the ratios are normalized by the differences in the differential cross sections for He scattering from C and O to obtain the oxygen coverage in units of ML. Note that the O coverage might still be underestimated, however, because some O atoms are shadowed by the C atoms in the graphene overlayer and the neutralization probability in scattering from buried O is likely to be larger than the neutralization from the surface C in graphene. Nevertheless, the trend of how the oxygen coverage evolves with CO exposure is correct.

To further study the Gr/CO/Ru(0001) system, spectra are collected as a function of surface temperature, as shown in Fig. 5.3. The uppermost solid line in Fig. 5.3 (2nd spectrum from the top) shows the LEIS spectrum collected from the as-prepared

Gr/Ru(0001) sample after it is first exposed to 1×10^9 L of ^{13}CO at 300 K. This spectrum shows an ^{16}O SSP and a ^{12}C SSP similar to the data in Fig. 5.2. The spectra shown below the one from the as-prepared sample were collected while the sample was held at the indicated temperature for at least 120 sec. It is seen that a small ^{13}C peak begins to appear at a temperature of 333 K, reaches its maximum intensity at 363 K and then decreases at higher temperatures. The ^{16}O SSP intensity also decreases with heating temperature. In addition, an Gr/Ru(0001) sample exposed to ^{13}CO at room temperature is annealed to 353 K, and LEIS was measured after cooling the sample back to room temperature, as shown by the uppermost dashed spectrum in Fig. 5.3. It is seen that this spectrum is similar as the one collected before heating.

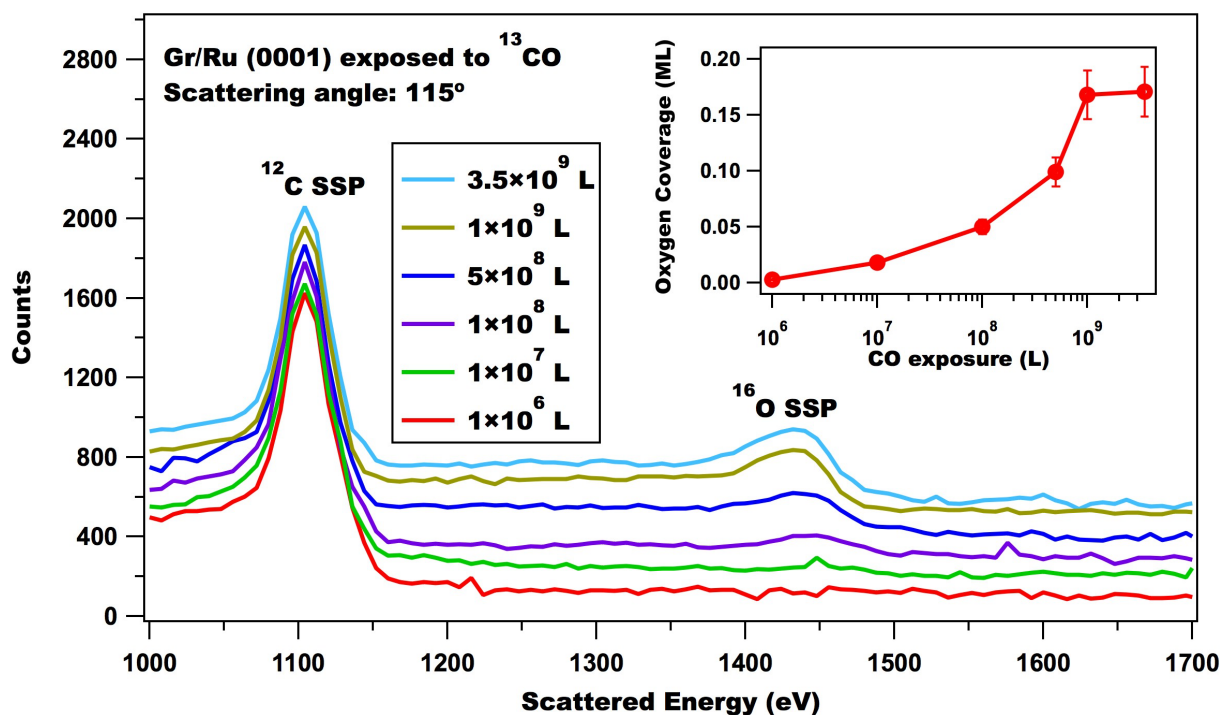


Figure 5.2. 3.0 keV He^+ LEIS spectra collected at a scattering angle of 115° from Gr/Ru(0001) following the indicated ^{13}CO exposures. The inset shows the oxygen coverage as a function of ^{13}CO exposure.

The inset of Fig. 5.3 shows the coverages of ^{13}C and O as a function of temperature. The O coverage shows a stepwise decrease during the desorption process. The first decrease is observed at ~ 340 K, which corresponds with the appearance of the ^{13}C peak. This is interpreted as resulting from a change in the geometry of the ^{13}CO molecules with temperature that reveals the underlying ^{13}C atoms. In this case, the ^{13}CO molecules are likely tilting or lying flat instead of binding perpendicular to the Ru(0001) substrate. Meanwhile, the spectrum collected at room temperature after annealing to 353 K shows that this change in the geometry of intercalated ^{13}CO molecules is reversible. The second change of the slope of the O coverage vs. temperature occurs at 383 K when both SSPs begin to disappear. When the temperature reaches 393 K, the SSPs are completely gone, indicating the thermal desorption of the intercalated ^{13}CO .

The desorption of ^{13}CO from bare Ru(0001) is also studied using helium ion scattering at 115° , with the spectra shown in Fig. 5.4. The Ru(0001) sample is exposed at room temperature to 1000 L of ^{13}CO , followed by heating at different temperatures. The spectra show only the ^{16}O SSP and no ^{13}C peak at any time during the adsorption and desorption process, which is consistent with the CO molecules sitting upright on the metal surface. The inset shows the change of the O coverage with annealing temperature. It is clear that the O coverage decreases gradually with complete desorption occurring at 430 K, unlike the stepwise decrements observed in Fig. 5.3 for intercalated ^{13}CO .

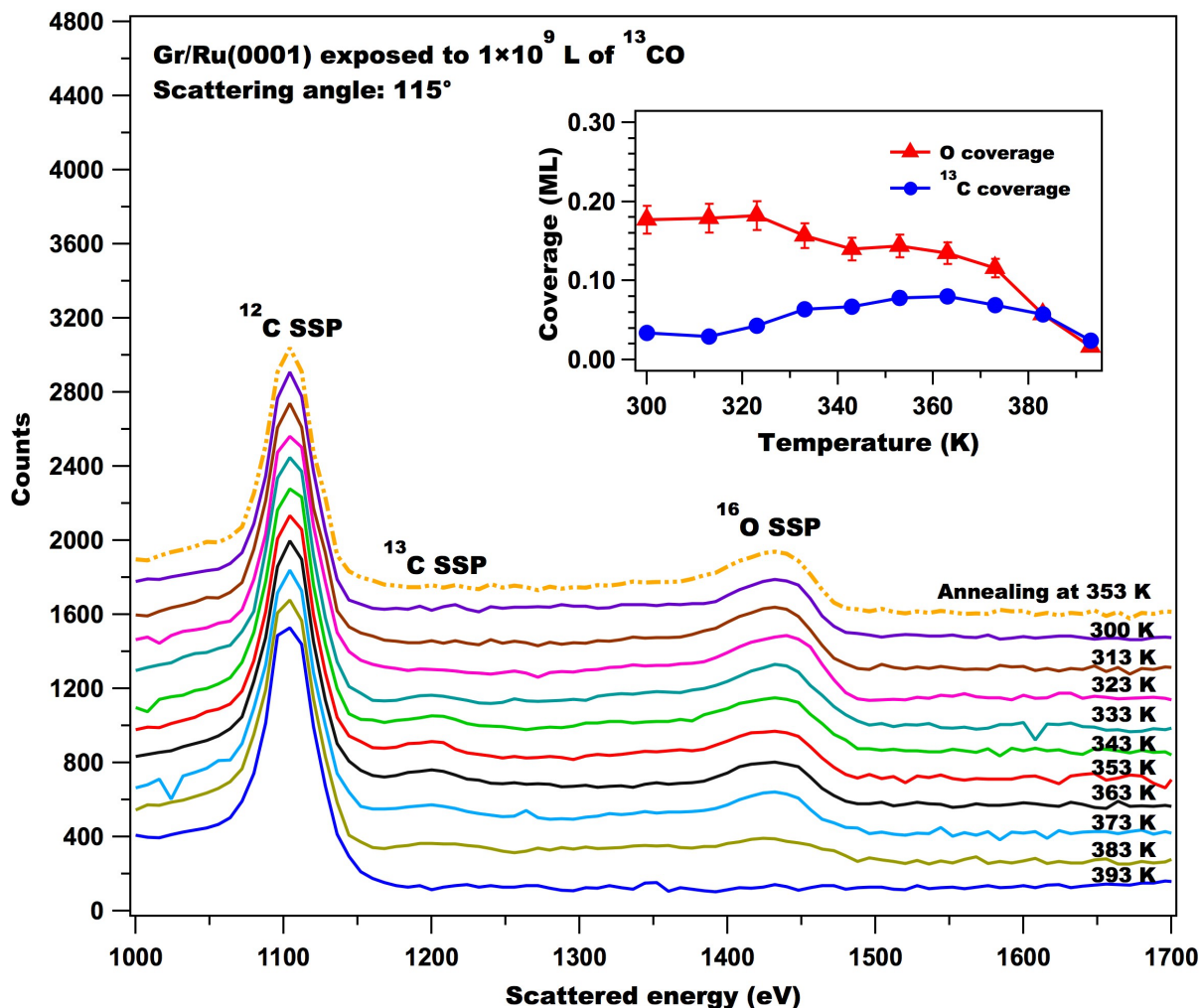


Figure 5.3. The solid lines show 3.0 keV He^+ LEIS spectra collected at a scattering angle of 115° from Gr/Ru(0001) exposed to 1×10^9 L of ^{13}CO at room temperature and then heated to the indicated temperatures for at least 120 sec before collecting the spectra. The uppermost spectrum shown by the dashed curve was collected from Gr/ ^{13}CO /Ru(0001) after annealing at 353 K and then cooling back to 300 K. The spectra are offset from each other for better clarity. The inset shows the ^{13}C and ^{16}O coverages as a function of the sample temperature.

IV. Discussion

CO adsorption on transition metal surfaces normally occurs with the carbon atom bonding to the substrate and the oxygen atoms pointing up with the bond perpendicular to

the surface plane, as suggested by angular UV photoemission spectra (UVS) and electron stimulated desorption ion angular distribution (ESDIAD) [13,34,35]. This is because polarization of the CO molecule leads to a net negative charge on the carbon end [36], which forms a relatively stable chemical bond when attached to a metal surface.

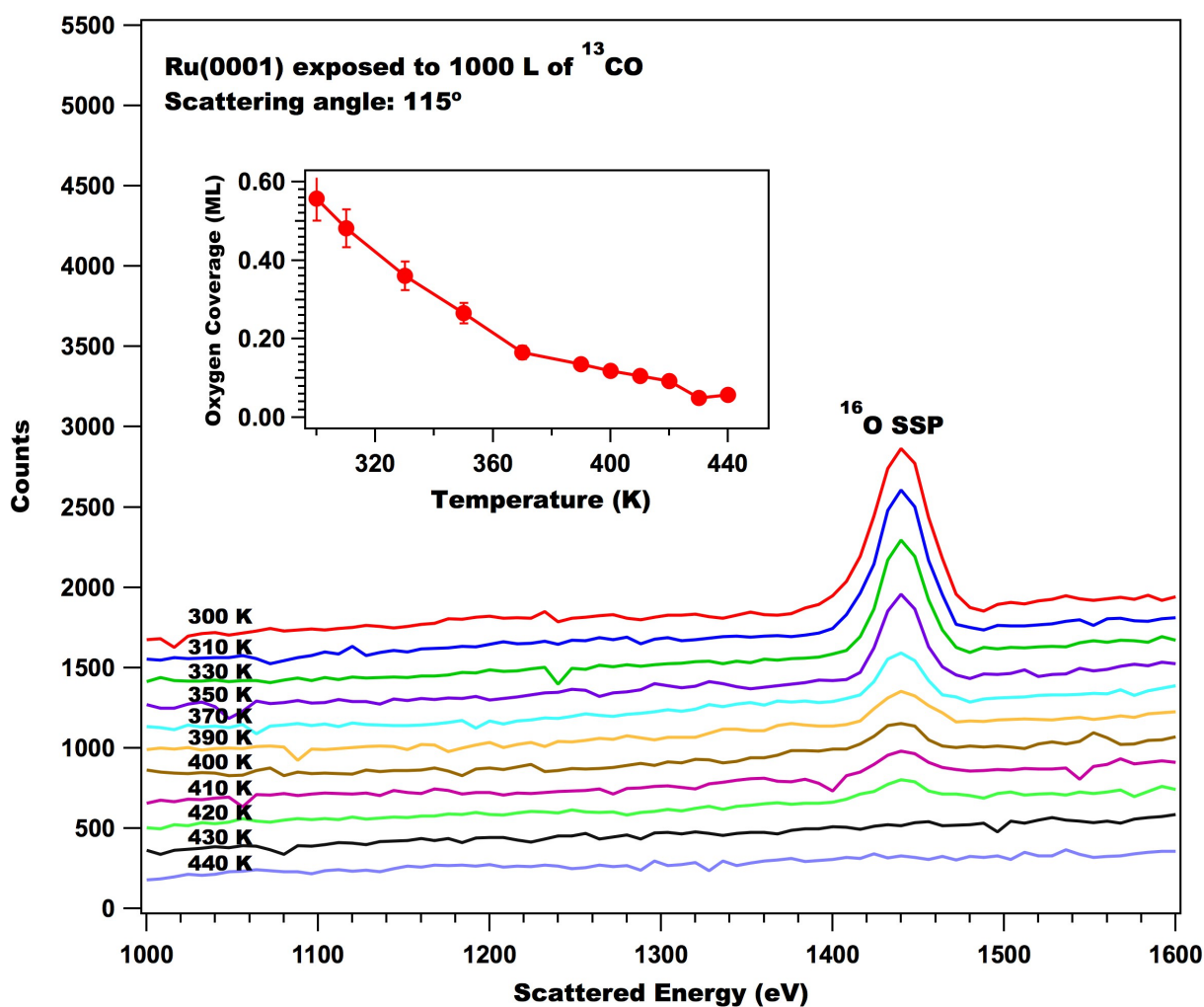


Figure 5.4. 3.0 keV He^+ LEIS spectra collected at a scattering angle of 115° from Ru(0001) exposed to 1000 L of ^{13}CO at room temperature and then heated to the indicated temperatures for at least 120 sec before collecting the spectra. The spectrum shown by the uppermost curve was collected from the as-prepared $^{13}\text{CO}/\text{Ru}(0001)$. The spectra are offset from each other for better clarity. The inset shows oxygen coverage as a function of the sample temperature.

For CO adsorbed on Ru(0001), it has been shown that the normal upright configuration occurs at low coverages (<0.33 ML) with the CO attached at atop sites. At higher coverages, STM images and DFT calculations indicate that a fraction of molecules adsorbs at hollow sites with a slight tilt that increases with coverage up to the approximately 0.6 ML that saturates the surface [16,33]. In the present study, 0.52 ML of ^{13}CO is initially present on the bare Ru(0001) sample, as shown in the Fig. 4, which should lead to some tilting of the adatoms. The tilting of the CO molecule is not, however, detected with LEIS for ^{13}CO directly adsorbed on Ru(0001). That is likely because the tilt angle of CO adsorbed on bare Ru(0001) is in the range of 13.9° to 15° [13,33], which is small enough that the underlying ^{13}C atom is still shadowed by the O atom. According to a calculation based on the formula in Ref. [37], considering a C-O bond distance of $1.13 \text{ \AA}$ and an impact parameter of $0.0175 \text{ \AA}$ for 3.0 keV He^+ scattered from O at 115° , the smallest tilt angle that would uncover the ^{13}C atom is 58.7° [37].

For ^{13}CO molecules intercalated between Gr and Ru(0001), however, a large change in the orientation of ^{13}CO is detected with low energy helium ion scattering when heated to 343 K. It is thus suggested that the ^{13}CO intercalated between Gr/Ru(0001) lies down, or at least tilts at an angle larger than 59° with respect to the surface normal, so that the both the ^{16}O and the ^{13}C atoms are visible to the incident helium ions and detector.

One possible explanation is that some CO molecules lie flat as a precursor to dissociation after being heated, as suggested in the literature for CO that lies flat on Cr surfaces [38,39]. Dissociation of the CO does not appear to occur, however, as the formation of free O atoms would lead to some etching of the Gr overlayer, as has been

observed in experiments that probe the intercalation of oxygen in Gr/Ru(0001), while no loss C from the Gr is observed here. Thus, dissociation of CO is not very likely unless the C and O atoms recombine and completely recover their molecular form in the cooling procedure as the dashed spectrum in Fig. 5.3 indicates that the geometry change of the intercalated molecules is completely reversible.

A more reasonable explanation involves the cause of the tilting that some adsorbed CO molecules are less stably bonded to the substrate and easier affected by the repulsion between the nearest neighboring adsorbates, as suggested in Ref. [16]. Note that in the literature [12], a confinement effect is reported that the graphene overlayer destabilizes the bond between intercalated adsorbates and the metal substrates. Thus, it is reasonable to propose that the presence of graphene layer combined with the thermal vibration during the heating largely weakens the bond between intercalated CO molecules and Ru(0001) substrate so that they are lying down or tilted at an angle, at least larger than 59° , to become detectable in the LEIS measurement.

In addition, it is found from Fig. 5.4 that the ^{13}CO starts to desorb from Ru(0001) even at room temperature. The Gr/Ru(0001) system, however, can keep the intercalated ^{13}CO under vacuum until being heated to 383 K, as shown in Fig. 5.3, although the desorption process is abrupt. This provides the Gr/Ru(0001) system the potential to retain small molecules on the surface.

V. Conclusions

The work presented here use helium low energy ion scattering to unambiguously show that CO molecules intercalate between a Gr film and a Ru(0001) substrate at room temperature, and do not adsorb to the Gr. The intercalation efficiency is, however, extremely low compared to the sticking probability on bare Ru(0001). The geometry of intercalated CO and of CO directly bonded on Ru(0001) is upright with the O end on the top, although it may be tilted at a small angle. The configuration of the intercalated CO changes with temperature, however, as demonstrated with LEIS. The intercalated CO molecules lie down or tilt at a large angle when heated to 343 K. In addition, the temperature needed for the thermal desorption of intercalated CO is 383 K, which is 80 K higher than is needed for CO to desorb from bare Ru(0001). This suggests the use of a Gr/metal system as nano-container in vacuum, or to use the orientation of intercalates as a means to store information in a nano-device.

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