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The orientation of CO intercalated between graphene and Ru(0001)

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ABSTRACT

^{13}CO molecules are intercalated under a single layer graphene film on Ru(0001) and interrogated with helium low energy ion scattering. Single scattering is used to determine the mass distribution of atomic species visible to the ion beam and detector, and the scattering angle is varied to distinguish adsorbed from intercalated molecules. At room temperature, CO intercalates as molecules that sit upright with the O end on top, as on clean Ru. When the temperature is raised, the intercalated CO tilts more than it does on clean Ru. This is presumably due to increased vibrational amplitudes combined with the confining effect of the graphene film.

Graphene (Gr), a two-dimensional, single-layer sheet of sp^2 hybridized carbon atoms, has attracted wide attention owing to its exceptional properties, such as high electronic conductivity and chemical and thermal stability [1–5]. Chemical vapor deposition (CVD) of Gr on transition metal substrates produces large-scale, monocrystalline films with good quality [6–10] and CVD-grown films can protect transition metal substrates from oxidation or corrosion due to their chemical inertness [4,11].

Small molecules, such as O_2 and CO, intercalate between Gr films and metal substrates, rather than adsorb on top of the graphene layer [12–14]. The molecules generally adsorb at the edge of the film or at defects and then diffuse beneath the film to become intercalated at a sufficiently high surface temperature [15]. Thus, intercalation normally requires a warm sample, but it can occur at room temperature for some molecules, including CO [12]. The intercalates can act to increase the spacing between the Gr film and the substrate, decouple the film from the substrate, and modify the morphology of the Gr layer [12,16–18]. Previous work has detailed much about intercalation beneath Gr films but, to our knowledge, the orientation of the intercalated molecules has not been addressed.

CO intercalation between Gr and Ru(0001) is studied here with helium low energy ion scattering (LEIS) [19,20]. The methodology for investigating intercalation was developed in our prior study of O_2 exposure to Gr/Ru(0001), which found that oxygen intercalates and does not adsorb, that intercalated oxygen is less stable than oxygen chemisorbed on clean Ru, and that it desorbs and etches some of the graphene when annealed [21]. The present experiments use shadowing and blocking to determine the orientation of intercalated CO molecules in a manner not achievable with other techniques, and find that the CO is oriented vertically with the oxygen end pointing up but the geometry changes when the sample is heated.

The experiments are performed in an ultra-high vacuum (UHV) chamber (base pressure = 4×10^{-10} Torr) that contains an ion bombardment gun for sample cleaning, low energy electron diffraction (LEED) optics and the equipment needed for LEIS. The 1 cm diameter sample is mounted on the foot of an x-y-z manipulator that enables rotations about the polar and azimuthal angles. An e-beam heater filament is located behind the sample and the temperature is measured by type K thermocouples.

The Ru(0001) is cleaned with ion bombardment and annealing (IBA) plus an oxygen treatment [22,23]. A one-hour 500 eV Ar^+ ion sputtering at a flux of 4×10^{13} ions s^{-1} cm^{-2} is followed by annealing under 4×10^{-8} Torr of O_2 at 1100 K for 8 min to chemically remove carbon contaminants and then a flash annealing at 1300 K under UHV for 2 min to remove the oxygen residue. This cleaning cycle is performed several times to acquire a clean and well-ordered surface, as monitored with LEIS and LEED.

The graphene layer is grown via CVD by heating the Ru(0001) sample to 900 K under 1.5×10^{-7} Torr of ethylene for 5 min, flash annealing under vacuum at 1200 K for 1 min, and slow cooling down to 450 K for another 5 min [23]. The process is repeated until a fully-covered, single and continuous graphene layer is formed, as verified with LEIS and LEED.

After graphene growth, exposures of ^{13}CO are conducted at pressures of 8×10^{-2} Torr on Gr/Ru(0001) and 1×10^{-5} Torr on bare Ru (0001) with the samples at room temperature. Exposures are reported in Langmiurs (L), where 1 L = 1×10^{-6} Torr s.

A differentially pumped ion gun creates a beam of 3.0 keV He^+ for LEIS that has a diameter of approximately 2 mm and a flux of 1.9×10^{11} ions s^{-1} cm^{-2}. Scattered ions are collected by a hemispherical

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electrostatic analyzer (ESA) mounted on a rotatable platform, which enables adjustment of the scattering angle. A specular geometry is used in which the incident and exit angles are equal with respect to, but on opposite sides of, the surface normal. Each spectrum is collected for 86 s, which leads to a fluence that is equivalent to about 1.6% of a monolayer (ML). Although spectra collected successively from the same Gr-covered sample show no changes due to beam damage, the samples used here are re-prepared after collecting each spectrum to be certain [21].

LEIS data can be analyzed with the binary collision approximation (BCA), which assumes that the projectile interacts with only one target atom at a time [24]. The target atoms are considered unbound, as the projectile kinetic energy is much higher than bonding energies in a solid. The main features in LEIS spectra are single scattering peaks (SSPs), which correspond to projectiles that experience one hard collision with a target atom before escaping the surface and reaching the detector. The SSPs ride atop a small background of multiply scattered ions. The energy loss during a single collision is determined primarily by the target to projectile mass ratio and the scattering angle [19]. Thus, the kinetic energy and intensity of the SSPs provide the elemental composition of the near-surface region. For the data shown here, the SSPs for ^{12}C, ^{13}C, ^{16}O and Ru have the expected kinetic energies as calculated using the BCA and those energies change with scattering angle accordingly.

Helium projectiles are used to enable single scattering at a large angle from the relatively light C and O atomic species. Helium also has an extremely high surface sensitivity due to Auger neutralization (AN), which is an irreversible process that dominates charge transfer between noble gas projectiles and solid targets. Most of the projectiles that experience multiple collisions or collide with deeper lying target atoms undergo AN and are thus not detected [19,25]. There is also a matrix effect for He^+ scattered from graphitic carbon due to a quasi-resonant process in conjunction with AN that leads to nearly complete neutralization for ions with kinetic energies below 2.5 keV [26–28]. To avoid the matrix effect and guarantee the detection of scattered ionic projectiles, 3.0 keV He^+ incident ions are employed here.

Helium LEIS spectra collected from as-grown Gr/Ru(0001) show only a sharp ^{12}C SSP and no Ru SSP [21], which indicates the formation of a complete graphene overlayer. LEED patterns display satellite spots that are induced by the superlattice formed between the Gr film and the substrate [18,21].

Shadowing and blocking are unique features of LEIS [19] that can be used to distinguish intercalated atomic species from those of the Gr layer and any adsorbates [21]. Shadowing occurs when a surface atom sits above a deeper lying atom so that it cannot be directly impacted by incoming ions. A shadow cone is the region behind an impacted atom inside of which other atoms cannot be hit directly by the incident ion beam. Blocking is a similar phenomenon that prevents ions scattered from deeper lying atoms from reaching the detector because a surface atom is positioned above it. Fig. 1 shows the sizes and orientations of the shadow cones formed at the two scattering angles used here. The size of the shadow cones was calculated using the formula in Ref. [20]. At the smaller angle of 45°, the incident and exit trajectories are close to the surface plane causing any atoms below the graphene overlayer to be completely shadowed so that He can only singly scatter from ^{12}C in the graphene film and any adsorbates attached atop of it. For the larger 115° scattering angle, the trajectories are closer to the surface normal so that the ions penetrate more deeply and can singly scatter from atoms below the Gr overlayer.

Shadowing and blocking are used here to determine the orientation of intercalated CO molecules. To distinguish the ^{12}C species in graphene from carbon in intercalated molecules, isotopically enriched ^{13}CO is used. LEIS spectra collected from Gr/Ru(0001) exposed to 1×10^9 L of ^{13}CO are shown in Fig. 2(a), with the different scattering angles used to locate the ^{13}CO molecules [21]. In the spectrum collected at 45°, only the ^{12}C SSP from Gr is visible, which leads to the conclusion that ^{13}CO

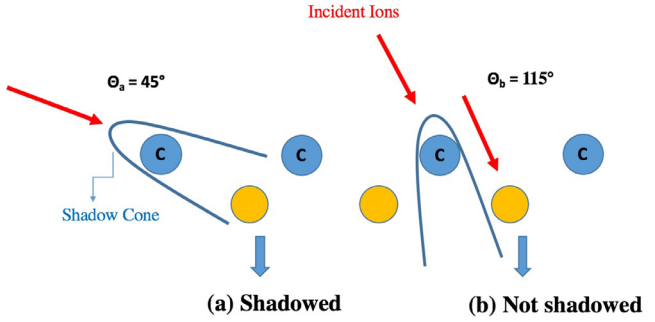

Fig. 1. Schematic diagram illustrating shadowing during ion scattering from a graphene film at scattering angles of (a) 45° and (b) 115°. In (a), all of the atoms underneath the graphene overlayer are within the shadow cone produced by the Gr atoms and therefore cannot be directly impacted by the incident ions. In (b), atoms in the second layer are not shadowed so that the incident ions can impact intercalated molecules and the substrate.

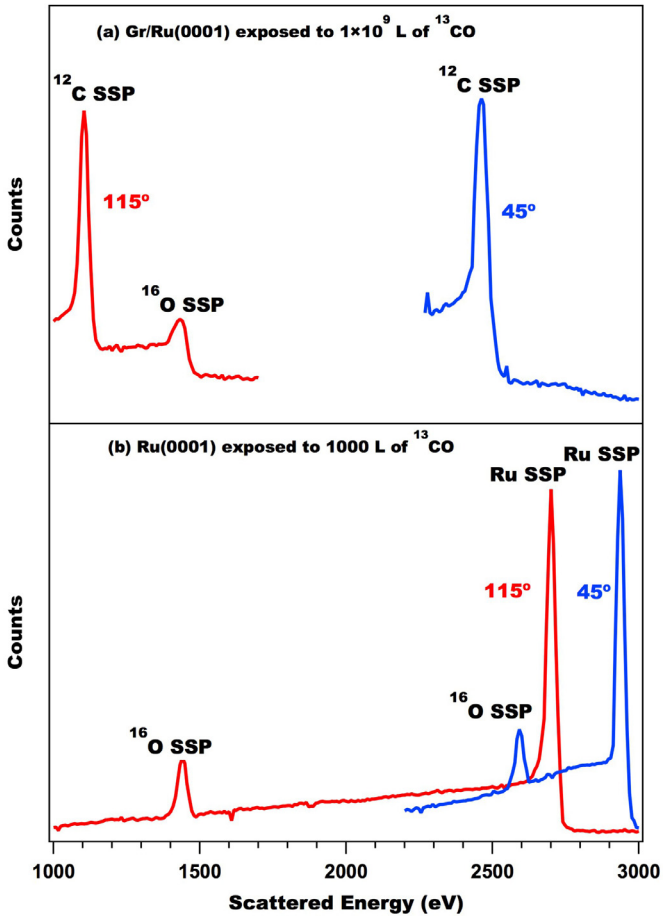

Fig. 2. 3.0 keV He^+ LEIS spectra collected at scattering angles of 45° and 115° from (a) Gr/Ru(0001) exposed to 1×10^9 L of ^{13}CO and (b) bare Ru(0001) exposed to 1000 L of ^{13}CO.

intercalates beneath the Gr film and does not adsorb atop the overlayer. At the 115° scattering angle, however, an additional ^{16}O peak is present and no ^{13}C is detected. This indicates that the ^{13}CO is intercalated but is oriented vertically with the oxygen atoms on top such that they shadow the ^{13}C.

Spectra collected from a saturation coverage of 0.6 ML of ^{13}CO on bare Ru(0001) are shown in Fig. 2(b). Only ^{16}O and Ru SSPs are observed at both scattering angles. The absence of a ^{13}C SSP at 115° indicates that ^{13}CO adsorbed on Ru(0001) is also adsorbed vertically with