

A high-reflectivity, ambient-stable graphene mirror for neutral atomic and molecular beams

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We report a He and H₂ diffraction study of graphene-terminated Ru(0001) thin films grown epitaxially on c-axis sapphire. Even for samples exposed for several weeks to ambient conditions, brief annealing in ultrahigh vacuum restored extraordinarily high specular reflectivities for He and H₂ beams (23% and 7% of the incident beam, respectively). The quality of the angular distributions recorded with both probes exceeds the one obtained from *in-situ* prepared graphene on Ru(0001) single crystals. Our results for graphene-terminated Ru thin films represent a significant step toward ambient tolerant, high-reflectivity curved surface mirrors for He-atom microscopy. © 2011 American Institute of Physics. [doi:10.1063/1.3663866]

Electromagnetic and electrostatic lenses and mirrors allow the facile manipulation of beams of charged particles (electrons, ions). The focusing of neutral particle (atom, molecule) beams is significantly more challenging, but it can in principle be accomplished by either refractive (Fresnel) or reflective optics (surface mirrors). Efficient focusing of neutral He beams would establish a foundation for realizing scanning He atom microscopy.^{1,2} Using focused beams of neutral, low-energy (~ 50 meV) He atoms for imaging, this technique could avoid issues due to electrical charging and beam damage inherent in higher energy electron- or ion microscopy, and thus provide unprecedented insight into the nanoscale structure of biological materials, polymers, ceramics, and other insulators.

While the focusing of He atom beams to $\sim 2 \mu\text{m}$ spots has been demonstrated using Fresnel zone plates^{2–5} and surface mirrors,^{1,6,7} both approaches entail challenges that need to be resolved before sub- μm focusing can be achieved. Free-standing zone plates for high-transmission focusing of neutral beams are fragile, require complex fabrication processes, and suffer from chromatic aberrations. Mirror optics—inherently achromatic—provide a possible alternative. The main obstacle to using atom-focusing mirrors has been the requirement for atomically smooth surfaces with high specular reflectivity, which can remain long-term stable in vacuum and are easily recovered following exposure to ambient conditions. Initial work has employed mirrors of H-passivated Si(111) with specular reflectivities of $\sim 1\%$ and limited stability in ambient air.¹ Quartz mirrors, appealing for their simplicity, also have low reflectivity except under grazing incidence.⁶ Quantum-stabilized Pb films on Si(111)⁸ and Pb($\sqrt{3} \times \sqrt{3}$)R30/Si(111) surfaces⁹ provide high specular He reflectivity ($\sim 15\%$) but are only stable in ultrahigh vacuum (UHV). We have recently shown that monolayer gra-

phene (MLG) on Ru(0001) single crystals can provide an inert surface^{10,11} with high reflectivity for thermal He and H₂ beams.¹² However, a path toward using such surfaces in curved mirrors has not been demonstrated so far.

Curved MLG/Ru focusing elements may be realized by using polycrystalline Ru thin films conformally coating a shaped amorphous substrate (e.g., fused silica),¹⁰ but surface roughness could limit the achievable He spot sizes. An alternative avenue, previously employed with Si(111) mirrors,¹ is based on the deformation of a thin substrate ($\sim 100 \mu\text{m}$) prepared with a high-reflectivity surface. Here, we report a step toward the realization of this approach using Ru(0001) thin films grown epitaxially on c-axis sapphire (Al₂O₃(0001)).¹³ Epitaxial Ru(0001) films have extremely low surface roughness comparable to Ru(0001) single crystals, and a graphene monolayer can be grown with very low defect density on these thin film metal templates. Using diffraction experiments, we demonstrate a very high specular reflectivity of MLG/Ru/Al₂O₃ for neutral He and H₂ beams, and this high reflectivity is easily recovered even after extended (~ 1 month) exposure to ambient conditions. Thus, MLG/Ru/Al₂O₃ represents a promising system for producing high-reflectivity, ambient-stable focusing mirrors for scanning He atom microscopy.

Samples were prepared and characterized by scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) at Brookhaven National Laboratory (USA) and then transported to Madrid (Spain) for He and H₂ diffraction measurements. Epitaxial Ru films with 50 nm thickness were grown on α -Al₂O₃(0001) substrates by RF magnetron sputtering of a Ru target (99.95% purity), at a substrate temperature of 650 °C and 0.06 nm/s growth rate. The Ru films were annealed in UHV for 15 min at 850 °C, followed by graphene growth by exposure to ethylene at 950 °C and slow cooling in UHV.^{13–16} This process leads to full coverage of the sample with a uniform graphene monolayer. The morphology of the MLG/Ru films was

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investigated *in-situ* by STM and *ex-situ* by cross-sectional TEM in an FEI Titan 80–300 microscope equipped with a CEOS Cs-corrector. Following long-term exposure to air (~ 1 month), the samples were introduced into a separate UHV chamber, which is part of a high-resolution atomic and molecular beam diffraction apparatus.^{16,17} In this system, the angular distribution of scattered beams is measured with a quadrupole mass spectrometer mounted on a two-axis goniometer. After brief *in-situ* annealing (100°C for 10 min), He and H_2 diffraction experiments were carried out. Absolute diffraction intensities were determined by normalization with the measured intensity of the incident beam for given incidence conditions.

Figure 1 shows the structure and morphology of the as-grown MLG/Ru/ Al_2O_3 thin film heterostructures. The Ru films are monocrystalline ([0001] oriented) and epitaxial with aligned $[10\bar{1}0]$ in-plane axes of the Ru and Al_2O_3 lattices.¹³ TEM (Fig. 1(a)) shows a flat, sharp interface between film and substrate, low defect density in the film, and—important for He scattering—suggests very low roughness at the MLG/Ru surface. A smooth, well-ordered surface of alternating atomically flat terraces and mostly monolayer steps is confirmed by STM, performed *in-situ* following graphene growth (Fig. 1(b)). Large-scale STM imaging shows the surface completely covered by a graphene layer exhibiting the characteristic moiré structure of MLG/Ru(0001).^{14,17,18} The MLG/Ru(0001) moiré shows no detectable defects over very large areas, and we found no gaps in the moiré structure, which would indicate either incomplete graphene coverage or patches of bilayer graphene.¹⁶

The as-grown MLG/Ru/ Al_2O_3 samples were exposed to air for ~ 1 month, before being introduced into the scattering chamber for He and H_2 diffraction. Following a brief

(10 min) UHV anneal to 100°C , diffraction experiments were carried out and the results compared with MLG-terminated Ru(0001) bulk single crystals prepared *in-situ*. Both thin film and bulk samples were aligned with their $[11\bar{2}0]$ directions along the direction of the incident beam. The diffracted intensity was measured as a function of final angle (θ_f) for fixed angle of incidence (θ_i) of the He beam. Measurements at different azimuths, ϕ , allowed mapping different portions of reciprocal space: sections through the specular (0, 0), first-order $(-1, -1)$ and $(1, 1)$, and moiré diffraction spots $[\phi = 0^\circ]$; through the additional moiré spots near (0, 0) $[\phi = 1.4^\circ]$; and through the remaining first-order spots, $(-1, 0)$ and $(0, 1)$ $[\phi = 16^\circ]$. Figure 2 summarizes the results of these experiments. While the overall features appear similar for the two types of samples, the He-diffraction peaks are generally more intense for the MLG/Ru/ Al_2O_3 surface than for the MLG/Ru(0001) prepared *in-situ*, which attests to the extremely high quality of surface ordering and cleanliness of the epitaxial MLG/Ru/ Al_2O_3 thin films. The thin film samples show clear 2nd order moiré spots, which are not detected on the single crystal. This indicates that the density of defects (steps, bubbles, dislocations) of the Ru single-crystal film grown on sapphire is smaller than the one of a sputtered and annealed Ru(0001) single-crystal. The measured absolute reflectivity of He atoms at this incident energy and angle exceeds 20% for both surfaces (at 120 K) and reaches a maximum of 23% for $\theta = 50^\circ$ and 28 meV energy of the He beam. Importantly, the intense diffraction and very high He reflectivity of the MLG/Ru/ Al_2O_3 surface were achieved following extended exposure to ambient conditions and only brief, low-temperature annealing in

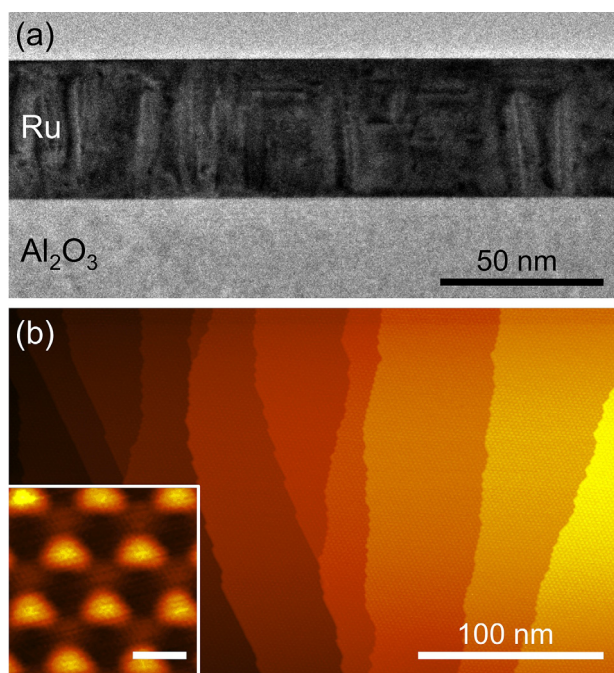


FIG. 1. (Color online) Microstructure and surface morphology of epitaxial MLG/Ru/ Al_2O_3 . (a) Low-magnification bright-field cross-sectional TEM image. (b) Large-scale STM image, showing a defect-free MLG/Ru moiré structure throughout. Inset: Atomic-resolution STM image of several moiré unit cells on the MLG/Ru/ Al_2O_3 sample. Scale bar: 2 nm.

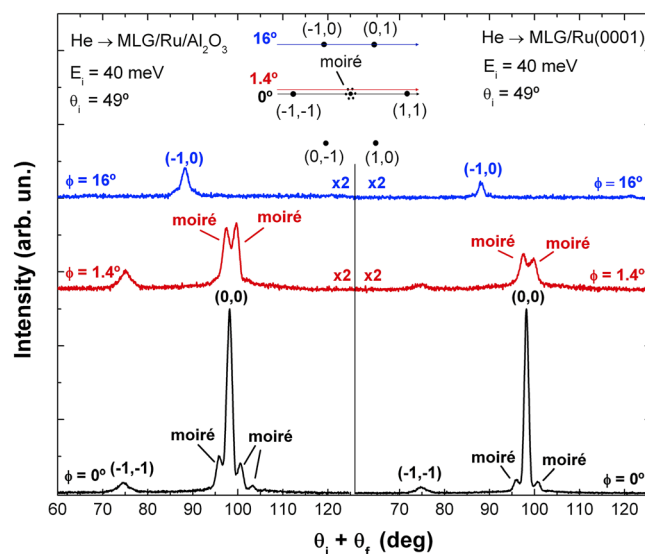


FIG. 2. (Color online) Angular distributions of He atoms scattered off MLG/Ru/ Al_2O_3 prepared *ex-situ* (left) and *in-situ* grown MLG on a Ru(0001) single crystal (right) under the same incidence conditions (along $[11\bar{2}0]$). The inset illustrates the two reciprocal lattices: the moiré superstructure lattice (small hexagon) and the graphene atomic lattice (large hexagon). The azimuthal angle, ϕ , is defined with respect to the $[11\bar{2}0]$ direction. In-plane scans ($\phi = 0^\circ$; black) show moiré diffraction peaks close to the specular peak and first-order peaks of the graphene lattice. Out-of-plane scans at ($\phi = 1.4^\circ$; red) show two peaks near the specular position, due to the first out-of-plane order of the moiré superstructure. Finally, the out-of-plane first-order peaks of the graphene atomic lattice are visible for $\phi = 16^\circ$ (blue curves). Sample temperature: 120 K.

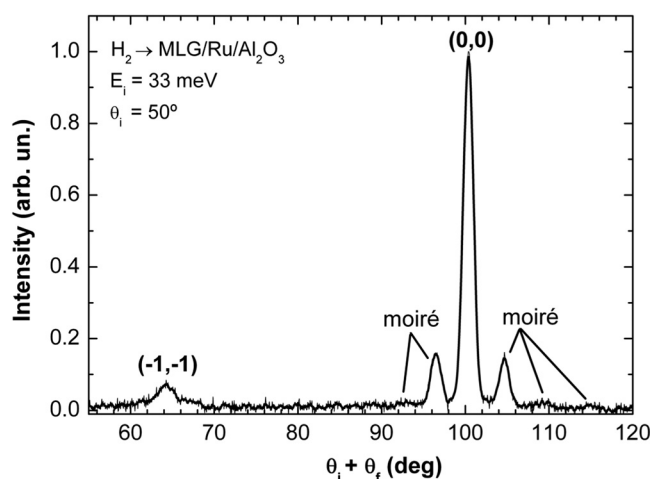


FIG. 3. In-plane ($\phi=0^\circ$) angular distribution of H_2 molecules scattered from MLG/Ru/ Al_2O_3 . The moiré peaks are very well resolved. The reflectivity of H_2 molecules at this incident energy and angle is about 7% of the incident beam. Sample temperature: 120 K.

UHV. Our findings not only confirm the excellent reflectivity of the MLG/Ru/ Al_2O_3 heterostructures, a prerequisite for their use as He mirrors, but also demonstrate their extremely low chemical reactivity and the ability to easily recover pristine surfaces—as judged from He scattering—following long-term ambient exposure. The MLG/Ru/ Al_2O_3 structures thus fulfill key requirements—high reflectivity of low-energy neutral He beams, good long-term stability and tolerance to air, and facile recovery of the reflecting surface—of a practical mirror for scanning He atom microscopy.

To further explore the properties of the MLG/Ru/ Al_2O_3 heterostructures as mirrors for neutral particles, we have measured their diffraction of thermal beams of H_2 molecules (Fig. 3). Similar to our He diffraction experiments, a low-energy (tens of meV) molecular H_2 beam was formed by supersonic expansion of H_2 , diffracted off the MLG/Ru surface, and detected as a function of the final angle for a fixed angle of incidence of the beam. The characteristics of the H_2 diffraction patterns closely follow those in He scattering: a high specular reflectivity ($\sim 7\%$), indicative of a smooth, contaminant free surface; and resolved moiré peaks up to 3rd order, consistent with a well-ordered MLG/Ru moiré structure. Hence, MLG/Ru/ Al_2O_3 can be used in reflective optics for manipulating neutral beams of molecular species, with potential applications in lithography, atomic physics, quantum information processing, etc.

In conclusion, by measuring the diffraction of neutral, low-energy atomic (He) and molecular (H_2) beams on graphene-terminated Ru(0001) thin films grown epitaxially on sapphire substrates, we have demonstrated properties that qualify this thin film system as a promising candidate for focusing mirrors in scanning He atom microscopy and other applications requiring manipulation of neutral atomic or molecular

beams: (i) high specular reflectivity, reaching 23% for He and 7% for H_2 , respectively, at high incidence angles around 50° and (ii) a remarkable stability under ambient conditions and easy recovery of highly reflective surfaces in vacuum. Different from single crystal surfaces, which offer no path toward curved reflectors, the sapphire-based thin films provide several possible avenues for fabricating focusing mirrors. Growing MLG/Ru(0001) on thin (flexible) sapphire substrates, for instance, should provide structures suitable for either fixed deformation or reconfigurable electrostatic bending.^{1,7} Alternatively, graphene-terminated thicker (few μm) Ru(0001) films, which we have already grown with similar crystal quality, could be isolated from the sapphire substrates to produce free-standing foils with high surface reflectivity, which can be incorporated into focusing optics for neutral beams.

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