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Helium diffraction and acoustic phonons of graphene grown on copper foil

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ABSTRACT

We report helium diffraction from graphene grown by chemical vapour deposition (CVD) using copper foil. This method reveals acoustic phonons, which are physically important to thermal conductance as well as a sensitive probe of graphene's interactions with the underlying substrate. Helium diffraction is made possible by the high quality of graphene produced by a recently reported "peel-off method". The graphene lattice parameter was found to remain constant in the temperature range between 110 and 500 K. The measured parabolic dispersion of the flexural mode along $\overline{\Gamma}\,\overline{M}$ allows determining the bending rigidity $k = (1.30 \pm 0.15)$ eV, and the graphene–Cu coupling strength $g = (5.7 \pm 0.4) \times 10^{19}$ N/m^3. Unlike analytics employing atomic resolution microscopy, we obtain information on the atomic-scale quality of the graphene over mm length scales, suggesting the potential for Helium atom scattering to become an important tool for controlling the quality of industrially produced graphene.

1. Introduction

Graphene's high carrier mobility [1–3] and thermal conductivity [4] promise breakthrough applications in future electronic devices [5]; however, producing mm-to cm-size samples in industrially useful amounts remains a challenge. Graphene grown by chemical vapour deposition [CVD] on copper foils is a potential solution [6–9]; unfortunately, its properties are typically degraded compared to exfoliated μm-sized single crystal graphene flakes [10–13]. Degraded electrical properties may arise from chemical contamination [13], polycrystallinity, graphene interactions with its substrate [14], or reduced flatness [15]. These properties are usually examined only over length scales of 1–50 μm with methods like STM, SEM and LEEM. For samples produced in industrial quantities, techniques sensitive to defect concentration, crystallinity and substrate interactions over larger length scales are urgently needed.

In this study, we report the first helium diffraction from CVD grown graphene. This method probes flatness, defect density and crystallinity over mm length scales and, furthermore, provides the material's flexural phonon spectrum, the fundamental property determining graphene's thermal conductivity [16,17] and a sensitive probe of graphene substrate interactions. We compare two graphene samples produced with modern CVD technique on two different Cu-substrates and demonstrate that a nearly ideal form of quasi-free-standing graphene can be formed on a Cu foil by CVD using a recently reported "peel-off" technique [18].

Helium atom scattering (HAS) is an established means of investigating the structure and dynamics of insulating as well as conducting surfaces in a completely nondestructive manner [19]. HAS diffraction provides direct information on surface crystallinity; inelastic HAS provides high-resolution (0.5 meV) spectral information in the acoustic phonon region (0–50 meV) and HAS specular scattering is highly sensitivity to surface flatness and defect density [20]. This imposes strong limitations to the samples to be studied by HAS, which are usually limited to single-crystal surfaces.

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Since He beams used in HAS are typically 1 mm in size, the method easily provides information over a macroscopic region, which is potentially useful for nanotechnology applications like optimization of CVD graphene growth. While research aimed at improving CVD conditions for graphene is rapidly advancing; unfortunately, the HAS method's extreme sensitivity to surface defects has so far prevented detection of He diffraction from any CVD produced graphene.

In this work we show that strong HAS signals can be obtained from CVD grown graphene and that HAS data provides useful information on its quality. Specifically, we employed two new CVD methods, both of which aimed at producing improved copper catalysts [18,21,22]. In the first method, graphene was grown on an epitaxial Cu(111) foil using a recently developed "peel-off" scheme [18]. In the second method, thin (~ 100 nm) epitaxial copper films grown on $\alpha - Al_2O_3(0001)$ (c-axis sapphire) are used directly as catalysts [21,22], producing graphene–Copper-Sapphire "sandwich" structures. This work shows that helium diffraction can become an important structural and morphological tool for industrially produced graphene.

2. Experimental

2.1. Sample preparation

Samples were prepared in Göttingen and then transported by courier to Madrid for HAS experiments. We have used two different Cu surfaces for graphene growth. In the first one, an epitaxial Cu(111) film (500 nm) was grown on C-plane sapphire by using electron beam evaporation method (0.3 nm/s). The second sample was a peeled-off epitaxial Cu(111) foil, which was obtained by additional Cu electroplating and peeled-off from a sapphire substrate, as reported in our previous study [18]. The graphene growth process was different on the two Cu samples used. To make a high-quality graphene on peeled-off epitaxial Cu(111) foil, we used same growth procedure as in our previous study [18]. However, the temperature should be lower than 1000° C to make a flat graphene on epitaxial Cu(111)/sapphire samples. Otherwise, due to Cu evaporation and migration, the surface morphology of the Cu film was found to be too rough for HAS. Cu migration and evaporation can be reduced at 850° C (see also supplementary information in Ref. [18]), but this leads to reduction of carbon solubility as well, resulting in small size of graphene. As a result, a compromise was found by preparing the graphene at 850° C by CVD, and doing additional ethylene annealing in UHV to get a high HAS signal. A typical growth process of graphene is as follows. First, the pressure in the growth chamber is pumped down to 3 mTorr using a mechanical pump. Second, a 40 sccm flow of hydrogen gas is introduced into the chamber at 950 mTorr. Third, the sample was heated to 850° C over 50 min. Fourth, 6 sccm flow of methane gas with 20 sccm hydrogen is introduced into the chamber for 3 min with a total pressure of 460 mTorr for graphene synthesis; after growth, the furnace was cooled down within 1 h to room temperature under a 20 sccm flow of hydrogen.

2.2. Experimental setup

The samples were characterized by a set of Helium Atom Scattering (HAS) and time-of-flight (TOF) measurements which were conducted in the Surface Science Laboratory in Universidad Autónoma de Madrid (LASUAM). The experiments have been carried out in two different systems, both having ultrahigh-vacuum (UHV) chambers with base pressures in the low 10^{-10} mbar range. The first system was a He-scattering apparatus that enables determination of absolute diffraction reflectivities by measuring directly the incident beam intensity [23]. The thermal attenuation (Debye–Waller) measurements reported in the text have been performed using this system. The second chamber was a high-resolution He-scattering machine with a time-of-flight arm and a fixed angle of 105.7° between the incident and outgoing beam [24,25]. In both HAS machines, the helium beam is generated by introducing the helium gas from an 80 bar reservoir into a high vacuum chamber (10^{-6} mbar) via a 10 μm platinum nozzle; the skimmer diameter is 0.6 mm. The beam energy can be varied by changing the nozzle temperature. The beam energies used in the current work were between 17.2 meV and 65.7 meV, with the corresponding energy spread varying from 1.5% to 5%, respectively.

The samples have been mounted between a disc (back) and a ring (front) made of tantalum, and were heated by electron bombardment of the disc on the back. The temperature has been measured using a K-type thermocouple, spot-welded to the ring, touching the sample surface. At high temperatures, the sample temperature was also measured using an infrared pyrometer.

2.3. Raman spectra

The Raman spectra were obtained with a LabRAM HR 800 (HORIBA Yvon GmbH) spectrometer under the following conditions: excitation wavelength of the laser: He–Ne 633 nm, spot size of the laser beam: 5 μm in diameter, measurement time: 20 s. The Raman spectrum of graphene grown on peeled-off epitaxial Cu(111) foil (Fig. 1) shows typical well-constructed monolayer graphene, namely an intensity ratio of the 2D and G lines between 2 and 3 as well as a symmetric 2D band. For the case of graphene grown on epitaxial Cu(111)/sapphire sample, we had to reduce the growth temperature to block Cu evaporation during graphene growth. Although we can get the Raman signal of monolayer graphene (CH_4 source, 1000° C, 10 min), the intensity is very small (compared to the graphene on peeled-off Cu surface) due to Cu evaporation. If we use ethylene (C_2H_4) as carbon source gas for graphene growth in CVD chamber (as we used for healing of graphene in HAS study) we were able to get a clear 2D line. These results show that C_2H_4 is a compatible carbon source for graphene healing at relatively low temperatures. This phenomenon is very likely due to the relatively low carbon dissociation energy of C_2H_4 compared to CH_4. The first C–H bond energy in C_2H_4, is analogous to the first two bonds in CH_4, which is expected since there is little

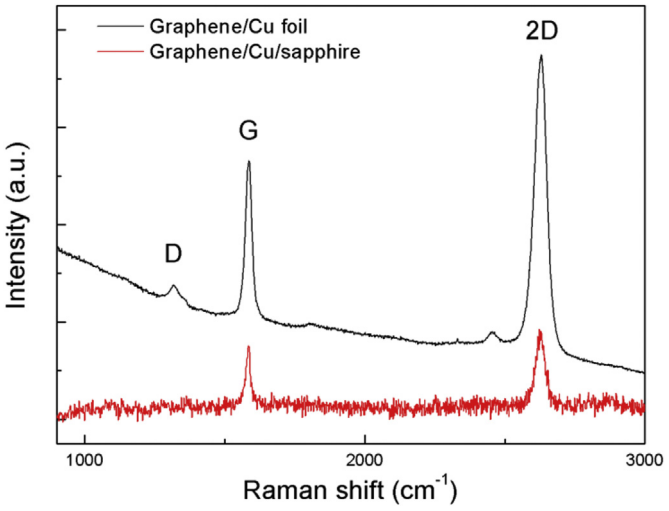

Fig. 1. Raman spectra of graphene grown with methane at 1000° C on the two samples used in the present work. Black curve: "Peel-off" graphene; red curve: "sandwich" graphene. (A colour version of this figure can be viewed online.)