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Full Length Article

Low-energy electron point projection microscopy/diffraction study of suspended graphene

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ABSTRACT

In this work, we present our study of suspended graphene with low-energy electrons based on a point projection microscopic/diffractive imaging technique. Both exfoliated and chemical vapor deposition (CVD) graphene samples were studied in an ultra-high vacuum chamber. This method allows imaging of individual adsorbates at the nanometer scale and characterizing graphene layers, graphene lattice orientations, ripples on graphene membranes, etc. We found that long-duration exposure to low-energy electron beams induced aggregation of adsorbates on graphene when the electron dose rate was above a certain level. We also discuss the potential of this technique to conduct coherent diffractive imaging for determining the atomic structures of biological molecules adsorbed on suspended graphene.

1. Introduction

Graphene has received much attention owing to its outstanding electrical and mechanical properties [1–5]. It is also considered to be a model system of two-dimensional (2D) materials. Suspended graphene provides true 2D graphene without the substrate effect. In addition, suspended graphene is a good supporting substrate for observation of nano-objects, including organic molecules and bio-molecules [6,7], in electron microscopy because of its atomic-level thickness, extended structure, good electrical conductivity and high transparency. However, defects, impurities, and contaminants on graphene may complicate the image interpretation of nano-objects supported by graphene [8]. Therefore, preparation of clean graphene samples and characterization of defects and adsorbates on graphene are highly desirable.

Preparation of suspended graphene usually requires the transfer of graphene sheets from a solid substrate to a perforated membrane. Polymer-assisted transfer methods have been extensively used because of the convenience of handling and processing [9–11]. Several procedures have been developed to clean graphene samples, but polymer residues often remain on the graphene surface [12,13]. Polymer-free transfer methods have been reported [14–17], but contaminants or adsorbates may still be present on graphene. Raman spectroscopy has been widely used to characterize the cleanliness of the graphene surface [18,19]. However, the technique is not sensitive enough to detect small amounts of residual adsorbates or contaminants on graphene, and the spatial resolution is at best sub-micron. Transmission electron microscopy (TEM) is a general instrument used to investigate 2D materials down to the nanometer or atomic scale. However, conventional TEMs operate at an electron energy of 100 keV or higher, and thus the image contrast of graphene and organic contaminants is relatively poor. In addition, radiation damage to the sample is apparent under the exposure to high-energy electrons [20,21]. Recently, TEMs with electron energies down to 20–60 keV have been used to image graphene [21–24]. However, the instruments are very expensive and not easily available for most research laboratories. Besides, a beam-induced chemical etching effect has been observed on graphene samples with the electron beam energy of 20–80 keV [24].

In recent years, suspended CVD-graphene has been studied with low-energy electron point projection microscopy (PPM) [25–28], which may be the simplest type of electron microscopy to image suspended graphene. In PPM, a biased metal nanotip is brought close to a grounded sample. Field-emitted electrons from the sharp tip are transmitted through the thin sample and projected on to an electron-detection screen placed a certain distance behind the

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sample, resulting in a magnified projection image on the screen [29]. The magnification of the image is equal to the ratio of the tip-screen distance to the tip-sample distance. By bringing the tip to the sample to within a separation of 1 μm, the magnification can easily reach 10^5 or higher. PPM offers several other advantages over conventional TEM and scanning transmission electron microscopy (STEM) techniques. First, it is a lensless technique, so does not suffer from spherical aberration. Second, the radiation damage is small. Typical electron energies used in PPM range from 40 to 500 eV, considerably lower than those used in modern high-voltage electron microscopes. This allows repeated imaging of graphene for an extended period of time. Third, the scattering cross sections for low-energy electrons are large, and thus the image contrasts for material thickness and individual adsorbates are very high [30,31]. Previous studies have demonstrated that PPM can easily distinguish between different graphene layers with an opacity of 26–27% per graphene layer for low-energy (50–200 eV) electrons [26,28]. Those studies also show images of defects and adsorbates on CVD-graphene samples. The best resolution of PPM is 1–2 nm [32].

In this work, we studied suspended graphene samples using a low-energy electron point projection microscopic/diffractive imaging technique. The instrument is almost identical to a PPM. In addition to PPM imaging, our setup allows adjustment of the sample-screen distance to record high-angle diffraction patterns, which provide the periodicity and lattice orientation of graphene sheets and other information such as graphene rippling. Such an instrument has a potential to become a powerful new tool for characterizing free-standing graphene and small adsorbed molecules.

2. Experimental setup

Our imaging of suspended graphene samples was carried out in an ultra-high vacuum (UHV) chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. A schematic of our setup is shown in Fig. 1a. During operation of the PPM, the sample was grounded and an electron emitter (a sharp tip) was negatively biased to extract electrons from the tip end. The electron beam illuminated the sample and the transmission pattern was projected on a screen consisting of a micro-channel plate (MCP, Hamamatsu F2226-24PGFX, 75 mm in diameter) and a phosphor plate. A CCD camera (ANDOR Neo 5.5 sCMOS, 2560 pixels × 2160 pixels, 16-bit dynamic range) adapted with a camera head (Nikon AF Micro-Nikkor 60 mm f/2.8 D) was placed behind the screen and outside the UHV chamber to record the images on the screen. The magnification of the image is equal to the ratio of the source-screen distance $(D+d)$ to the source-object distance (d), i.e. magnification $M=(D+d)/d$ (Fig. 1a). The emitter was mounted on a three-axis piezo-driven nano-positioner (Unisoku, Japan) with a travel distance of 5 mm in each direction. When d was large, the projection image on the screen had a large field of view and a small magnification. When the emitter was moved close to the sample, the magnification increased with a decrease in the field of view. In typical PPM, D is fixed at a distance of ~10 cm and the screen size is usually 7.5 cm in diameter. The unique design of our setup in Fig. 1a is that the screen was mounted on a rail such that D could be changed from 30 mm to 132 mm. We could record high-magnification projection images when D was large and high-angle diffraction patterns when D was small. In particular, high-order diffraction patterns reveal the lattice structures, such as periodicity, orientations, and ripples of 2D materials, which cannot be detected with typical PPM.

The sample holders we used were gold-coated Si_3N_4 membranes containing periodic holes [33]. A PPM image of a sample holder is shown in Fig. 1b. Both exfoliated graphene sheets and CVD-grown graphene sheets were transferred onto the membranes to be used as samples. To prepare an exfoliated graphene sample, a piece of graphene sheet was mechanically exfoliated from a highly oriented pyrolytic graphite (HOPG) (lateral sizes of 12 mm × 12 mm, ZYB; Momentive) on a SiO_2(300 nm)/Si substrate [34]. The exfoliated graphene sheet was then transferred onto a Si_3N_4 membrane using the polymer-assisted transfer method [9]. The sample was then annealed at 400 °C in Ar/H_2(10%) forming gases for 4 h to remove resist residues and contaminations. To prepare a suspended CVD-graphene sample, we transferred a CVD-grown graphene sheet (ACS material, single layer graphene on a Cu foil, 4 inch × 2 inch) onto the Si_3N_4 membranes using a polymer-free transfer technique [14]. These samples were then annealed up to 200 °C on a hot plate with a heating rate of 1 °C/sec to remove the remaining moisture. Raman spectroscopy of a CVD-graphene sample prepared in this way (Supplementary Fig. S1) showed the absence of the D peak at around 1350 cm^{-1}, which is generally considered to be an indication of a clean graphene sample. As will be shown later with our imaging under UHV, graphene samples prepared with this method still contain many adsorbates.

We used noble metal-covered W(111) single-atom tips (SAT) [35–38] as the electron emitters. A W(111) wire was first etched into a tip with a radius of 20–40 nm [39], and then electroplated with a thin Ir film [38]. The emitter was placed in an UHV chamber and annealed at ~1100 K until a pyramidal SAT formed. The formation process can be monitored by observing the electron field emission (FE) pattern on the screen. Previous studies have established the relationship between the FE pattern and the corresponding field ion microscopy (FIM) image of a SAT [37,40]. The electron beam emitted from this emitter exhibited a Gaussian intensity profile with a full divergence angle of 2–6° [37,40,41]. The PPM image shown in Fig. 1b also reflects such an intensity profile. This electron source has been demonstrated to possess full spatial coherence [41], i.e. the coherence width is larger than the beam width. The whole system was kept at room temperature during electron emission.

3. Results and discussion

Fig. 2a shows an optical image of a piece of exfoliated graphene, lying on a Si substrate covered with a 300 nm thick SiO_2 film. Single-layer graphene can be identified at a lower edge of the thicker film (indicated by a blue arrowhead). The graphene sheet was transferred to a gold-coated Si_3N_4 membrane as described in the experimental section. Fig. 2b shows a PPM image of the transferred graphene sample on the membrane. Several open holes of the Si_3N_4 membrane are evident as bright regions. There was a dark region at the center, corresponding to the multi-layer graphene which is not transparent to the low-energy electron beam. At the bottom edge of the dark region, some holes appeared semi-transparent, corresponding to single-layer graphene. The blue arrow indicates a region of a single-layer graphene corresponding to the region shown in Fig. 2a.

Fig. 3 shows our higher-resolution study of the region indicated by the blue arrow in Fig. 2b. The image on the left of Fig. 3a is a projection image of graphene spanning across a hole. The outer region is totally dark because the low-energy electron beam cannot penetrate the gold-coated Si_3N_4 membrane. The upper part of the holed region exhibited a darker contrast relative to the lower part, indicating a thicker layer for the upper region. Dark point defects, probably caused by adsorbates on the graphene, were evident. Similar defects have been reported in previous PPM imaging of graphene samples [26,28,31]. In addition, there were narrow stripes (from tens to 200 nm in width) with slightly darker and brighter contrasts extending from the upper left to the lower right of the thin graphene layer. We then moved the screen closer to the sample from $D=131.8$ mm to $D=34.5$ mm. The position of the tip