Scanning Tunnelling Microscopy of Suspended Graphene

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Abstract. We have obtained for the first time atomic resolution STM images of free-standing graphene, and have found UHV high temperature annealing conditions to controllably achieve atomically clean surfaces. This is an important premise for fundamental studies of the interaction of pristine graphene with foreign atom species, in particular metals.

1. Introduction

Graphene, just one atom layer thick, has spurred a flurry of investigations into its structural properties, morphology and chemistry via number of different experimental techniques and instruments [1-3]. One of them is scanning tunnelling microscopy (STM), which has been used to investigate the atomic-scale topography of graphene. However, the graphene used in all such studies is supported by substrates [4, 5] and no observations for suspended graphene have been made [6]. Our experience of suspended graphene is based on transmission electron microscopy (TEM) studies and invasiveness of the electron beam in TEM has prompted us to investigate suspended membranes via STM as an alternative method [7, 8]. We have obtained for the first time atomic resolution STM images of free-standing graphene, and have found UHV high temperature annealing conditions to controllably achieve atomically clean surfaces. This is particularly important for probing the interaction of foreign species, e.g., metal with the pristine graphene surface, since TEM revealed poor adhesion. All reports of graphene-impurity interaction, graphene dosing, doping and functionalisation so far have been made without proof of the presence of a pristine surface- all graphene in previous studies either has an abundance of contaminants or is presented on substrates. The interaction between metal atoms and graphene is of great interest because metals, e.g. gold, chromium etc. are used in macroscopic electrical transport measurements of graphene as electrodes. We will give an account of new cleaning procedures and of our progress in observing atomic structure of suspended graphene at room temperature.
2. Experimental

Two different techniques for the preparation of graphene membranes have been used, which are micromechanical cleavage from HOPG (highly ordered pyrolytic graphite) [3] and CVD growth of films on Cu-substrates [9]. The graphene membranes are transferred to a TEM grid (400 mesh lacey carbon copper) after several chemical treatments [10] and finally dried in a critical point dryer to avoid possible damage. Identification of the graphene layer number has been done via electron diffraction patterns by comparing first and second ring intensities and via high angle annular dark field (HAADF) imaging in conjugation with ultra-high spatially resolved electron energy loss spectroscopy (EELS) [8]. Later, the graphene on the TEM grid is transferred to the STM chamber for analyses.

Initial verification of the existence of monolayer graphene and its coverage on the grid has been obtained in a TEM, a Tecnai F-30. An Omicron low-temperature UHV system (residual pressure $10^{-10}$ mbar) and electrochemically etched tungsten tips were used for the STM experiment. Standard tip cleaning and forming procedures were carried out in UHV. All STM data were taken at room temperature (300 K). Sample-tip bias voltages used were typically in the range of 0.5-1.5 V and tunneling currents were between 0.1 nA and 1.0 nA. The tip performance has been checked on gold on mica and graphite (HOPG) samples as measurement references. To make sure that we are tunneling on suspended parts and not on grid bars, we have systematically taken images at small spatial separation across entire grid squares (each square ~40 micron), with all high quality images yielding similar results.

3. Results and Discussion

We have started the STM measurements to establish annealing condition for suspended graphene (by stepwise increase of the temperature) because TEM studies of suspended graphene have revealed that only few tens of nm$^2$ clean surface (free from the contamination) can be obtained; these clean patches are surrounded by contamination (hydrocarbon), shown in figure 1a). Perfectly clean surface is required to be able to obtain stable tunneling from graphene in the STM. Our first attempt to image suspended graphene has been after degassing the sample at ca. 50 °C for a few hours, shown in figure 1b). This resulted in unstable tunneling behavior, characterized by diffuse images with poor reproducibility, which indicates that the surface was not clean enough for imaging with the STM tip. After annealing at ca. 100 °C for 1 h, the images showed improved stability although large amounts of contamination remained. Annealing at ca. 270 °C for 4 hours, and subsequently to ca. 300 °C for 18 hours further improved the image stability; however residual surface contamination still remained. An additional annealing step at ca. 550 °C for 15 minutes produced a clean surface, shown in figure 1c), and showed stable tunneling with smooth line profiles.

![Figure 1](image-url)

Figure 1. a) TEM image of suspended graphene. (b) STM image after initial degassing at 50°C for 4 hours. (c) Annealing at 550°C for 15 minutes. All images are raw.
By further exploring the annealing regimes in terms of time and temperature it was found that annealing the pristine sample for 24 hours ~400 °C is usually sufficient to remove almost all contamination, and with a well formed tip we were able to obtain atomic resolution images, shown in figure 2. A clear honeycomb monolayer structure was observed and the average bond length of 1.42 Å is consistent with literature values. This cleaning procedure allowed us to acquire atomic resolution graphene images at almost every probing position on the suspended layer.

![Figure 2. STM high resolution monolayer graphene (a) raw (b) Magnified area of square in a). Hexagonal monolayer structure is observed and one hexagon ring is overlaid in white in (b). The images represent raw data.](image)

In some areas of the sample both hexagonal and triangular structures were observed in a single image frame, corresponding to monolayer and bilayer graphene respectively. Figure 3 shows such mono- and bi-layer regions. Magnified mono- and bi-layer region in squares 1 and 2 in figure 3a) are shown in figures 3b and 3c, respectively.

![Figure 3. (a) STM high resolution mono- and bi-layer regions (b) magnified monolayer region, square 1 in a). (c) magnified bi-layer region, square 2 in a). One hexagon ring is overlaid in white in (b), and a white triangle in (c). The images represent filtered data.](image)

4. Conclusions
Suspended, i.e., free-standing graphene has been imaged at atomic resolution in the STM for the first time. Cleaning and annealing conditions have been established that enabled us to observe large monolayer (hundreds of nm²) and also some bilayer regions (tens of nm²). The cleaning and imaging
conditions reported here should make further development and application of UHV STM imaging and spectroscopy of suspended graphene possible.

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