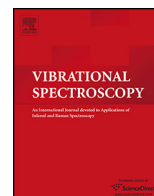




Contents lists available at ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

STM tip-enhanced Raman spectroscopy and the investigation of doped graphene

Jan Rogalski, Kai Braun, Anke Horneber, Marius van den Berg, Johannes Uihlein, Heiko Peisert, Thomas Chassé, Alfred J. Meixner, Dai Zhang*

Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen, Germany

ARTICLE INFO

Article history:

Received 3 June 2016

Received in revised form 26 September 2016

Accepted 27 September 2016

Available online xxx

Keywords:

Graphene

Tip-enhanced optical spectroscopy

Raman spectroscopy

Photoluminescence spectroscopy

ABSTRACT

In this manuscript, we report the integrating a home-built scanning tunneling microscopy runner into a parabolic mirror assisted confocal optical microscope for performing high tip-enhanced Raman spectroscopy on graphene. To achieve an optimized optical excitation of the tip, a radially polarized laser beam is focused at the tip apex via a parabolic mirror. Graphene flakes grown on Cu foil are investigated. A decrease in the 2D peak intensity and increase of the G peak position indicate n-doping of the graphene flakes. The ultraviolet photoemission spectroscopy experiment shows that the underlying Cu foil induces a slight n-doping by raising the Fermi level by about 0.29 eV as compared to the free-standing graphene. An increased electron concentration of about $0.6 \times 10^{13} \text{ cm}^{-2}$ can be derived from the tip-enhanced Raman spectra. A possible origin for the n-doping observed in the tip-enhanced Raman experiments, for example through the transfer of hot electrons from the excited Au tip to the graphene flake, is discussed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Graphene attracts great interest due to its unique band-structure and high mechanical stability. Its potential applications have been suggested in transparent electrodes, ultrafast photodetectors, solar cells etc. [1–4]. Graphene shows extraordinary optical properties, the most notable among them is the broad absorbance in the visible to near-infrared region of the electromagnetic spectrum [5–7]. Graphene also possesses fascinating intrinsic plasmonic properties, which can be tuned by electrostatic gating or doping [8–11]. Furthermore, as compared to plasmons in noble metals, graphene plasmons exhibit smaller Ohmic losses and can be confined to tighter regions [12,13]. Over the years different methods have been developed to create graphene flakes of varying quality. For example through chemical vapor disposition (CVD) on metals [14], reduction of graphene oxide (GO) [15] or via epitaxial growth on silicon carbide substrates [16]. One of the easiest methods has been established by Novoselov and Geim via the micromechanical exfoliation of graphite with adhesive tape [4].

The properties of graphene-based devices are highly related to the quality of the graphene sheets. For example, lattice defects or

disorders have been reported to have an impact on the graphene band gap [17–20]. Therefore, a variety of analytical methods is utilized to characterize the material properties of graphene. For example atomic force microscopy (AFM) [21], scanning tunneling microscopy (STM) [22], electron microscopy (EM) [23], and etc. Overall, Raman spectroscopy is one of the most widely used methods for studying the bonding structure of carbon films due to its non-destructive nature and ease of use [24–26]. The quantitative index $I(D)/I(G)$ ratio is often used to evaluate the disorder of carbon materials, such as in diamond-like carbon [27]. Here $I(D)$ is the scattering intensity of the D-peak which originates from the A_{1g} breathing mode of the aromatic ring structures, while the G-peak results from the E_{2g} stretching vibrations of both aromatic and olefinic molecules [27]. In addition, the positions and the peak width of the D and G bands give valuable information about the number of graphene layers, and doping properties [28]. Despite the rich information that can be collected by Raman spectroscopy, its optical resolution is diffraction-limited, which lies in the range of hundreds of nanometers using visible laser excitation.

Tip-enhanced spectroscopy methods, such as tip-enhanced Raman spectroscopy (TERS) and tip-enhanced fluorescence spectroscopy (TEFS), have demonstrated their exceptional sensitivity and resolution by e.g. optically imaging a single molecule on a single crystal surface or generating enhanced luminescence from organic semiconductor films [29–36]. Both techniques can simultaneously achieve high spatial resolution by

* Corresponding author.

E-mail address: dai.zhang@uni-tuebingen.de (D. Zhang).

collecting scanning probe microscopy (SPM) images and derive chemical information with a nanometer resolution from optical signals. An essential component of such techniques is a sharp metallic tip acting as an optical antenna. Collective oscillations of the free electron density (plasmons) can be excited at the metal-dielectric interface upon laser illumination. Combined with the lightening rod effect, the plasmon oscillation produces a strong evanescent electrical near-field at the tip apex. This strongly confined near-field can be used as a scanning probe, locally probing light-matter interaction at the sample surface. The optical resolution often roughly corresponds to the diameter of the tip apex; however, it can be greatly influenced by the tip-sample distance, and the sample properties [30,33,37,38]. TERS has already been used to collect Raman spectra from graphene flakes in 2008 by Hoffmann et al. [39]. Additionally a systematic analysis of a graphene flake has been reported by Saito et al. [40], where the edge boundaries and the number of stacking layers of the flake were successfully estimated. Moreover, nanoscale chemical imaging of single layer graphene using TERS has been reported by Stadler et al. [41].

As even a single layer of graphene is able to produce a detectable Raman spectrum with a certain integration time, the advantage of using TERS to study graphene is not centered on enhancing the Raman signal itself. It rather serves as an integrated platform which allows for the study of synergy effects of different processes in one run. For example, operating TERS with a tapping mode AFM allows to resolve the local stress distribution produced in graphene due to the pressure applied by the tip [42]. Due to the high optical resolution offered by TERS, it is also possible to map a strained region with a radius of about 85 nm on a graphene flake [43].

In this paper we demonstrate that combining a home-built STM runner with a parabolic mirror (PM) assisted confocal optical microscope allows us to study local doping effects in graphene using TERS measurements. The characteristic Raman peaks of graphene are closely monitored regarding their peak intensity and position. The doping of the graphene sheet through the underlying substrate is studied using ultraviolet photoemission spectroscopy (UPS). A possible origin for the doping effect observed in the TERS measurements, for example through transfer of hot electrons from the excited Au tip to the sample, is discussed.

2. Material and methods

The basic configuration of the setup used for performing the TERS and TEFS experiments is a confocal optical microscope. A continuous wave diode laser (636 nm) is used as excitation source. A laser line filter and neutral density filters are employed to purify the laser lines and to adjust the output power. Afterwards, the beam is expanded via two telescopes in order to achieve a beam diameter matching the open aperture of a PM. The PM focuses the incoming laser beam onto the sample and collects the emitted optical signals. As compared to the conventional focusing scheme using an objective lens. The PM allows us to achieve a high numerical aperture (NA) of nearly 1 in air [44], to minimize the chromatic aberrations and to be free of the restriction of needing a transparent sample. The elastically and inelastically scattered light from the sample can be collected via the PM and be delivered through the beam splitter to the detection path. After the third telescope, the diameter of the beam is reduced and the elastic scattered light is selectively blocked by two optical notch filters (12 optical densities in total). The spectrally red-shifted optical signal is delivered simultaneous to an avalanche photodiode (Single Photon Counting Module SPCM-AQR-14; Perkin Elmer) for optical imaging, and a CCD camera coupled to a spectrometer (Spectra Pro 300i; Acton Research) for spectroscopy.

For the TERS experiments, the Au tips are made by electrochemical etching of a gold wire (99.99% purity, ChemPur, Germany) in concentrated hydrochloric acid (Riedel de Haen, Germany). The counter electrode is a platinum ring. During the etching process, 8 V pulses with a length of 30 μ s and a square wave form are used. The Au tips are characterized by a scanning electron microscope (SEM) before use and some typical tips used for the TERS experiments are shown in Fig. S1 in the Supplementary information. Tips with very large cone angle (blunt tip) or very thin shaft are abandoned to ensure high-resolution imaging capability, mechanical stability, and a large enough volume of metal inside the focus. In addition, spectra were recorded for each tip before the TERS experiment to check if it is contaminated with carbonaceous species. Those with typical Raman spectra from amorphous carbon are discarded.

The graphene flakes used for this study are grown via chemical vapor deposition (CVD) according to [45] on a 20 μ m thick copper foil and are commercially available (Graphene Laboratories Inc., Calverton, USA).

The photoemission measurements were performed in an ultra-high vacuum (UHV) vessel with a base pressure of 4×10^{-10} mbar equipped with an Omicron EA 125 hemispherical analyzer. A He gas discharge lamp (UVS 10/35) is used as the source for UPS.

3. Results and discussions

3.1. TERS setup

To perform the tip-enhanced optical measurements, the Au-tip is inserted through a small hole at the top of the PM into the laser focus, as shown in Fig. 1a). A positive bias voltage is applied between the Au tip and a conductive substrate. If not otherwise specified, a bias of 500 mV was applied and the tunneling current was set to 1 nA, which corresponds to a tip-sample distance of about 1 nm. As shown in Fig. 1b), the optical resolution of our setup operating as a confocal optical microscope is diffraction-limited to about 300 nm laterally [44]. For the tip-enhanced near-field optical microscope, the optical resolution comes down to about 10 nm [46]. An illustration comparing the optical resolutions of these two techniques is shown in Fig. 1b).

The precise and stable positioning of the tip into the laser focus is a prerequisite for achieving high optical enhancement in a TERS experiment. A two-stage movement system allowing for a coarse and a fine positioning of the tip is used. This is performed using a home-built tip runner based on piezo ceramics [47]. The coarse positioning of the tip in the x, y and z directions is achieved by three 'slip-stick' motors. They consist of stacked piezo shear plates, which are driven by a saw tooth voltage signal. The amplitude of the saw tooth determines the step size of the movement. In our case a step size of smaller than 100 nm and a fast movement over a large range of up to 3 mm can be achieved. At the fine tuning stage, a four-segment piezo tube is used to position the tip precisely into the focus. This piezo tube has a resolution down to tens of picometers which is also used for tip-scanning in a TERS experiment.

An optimized optical excitation of the tip is another prerequisite in TERS experiments to achieve a high near-field enhancement. In our case a radially polarized cylindrical vector beam is used to selectively excite the tip apex longitudinally. This polarization is obtained by delivering the linearly polarized laser beam through a mode converter; a disc that is composed of four pieces of $\lambda/2$ waveplates [48]. The electric field distribution of a radially polarized laser beam that is focused by the PM is calculated using 'PM Calc', a modified program based on the "focused fields" method published in [49]. As shown in Fig. 2a), the laser focus possesses a dominant electric field along the z-axis (perpendicular

Download English Version:

<https://daneshyari.com/en/article/5141876>

Download Persian Version:

<https://daneshyari.com/article/5141876>

[Daneshyari.com](https://daneshyari.com)