



## Novel gold cantilever for nano-Raman spectroscopy of graphene

Valentinas Snitka\*, Raul D. Rodrigues, Vitas Lendraitis

Research Center for Microsystems and Nanotechnology, Kaunas University of Technology, Studentu 65, Kaunas LT-51369, Lithuania

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### ABSTRACT

This paper presents the simultaneous topographical and tip-enhanced Raman imaging of single layer and multilayer graphene flakes. The probe tips suitable for tapping mode atomic force microscopy (AFM) and tip-enhanced Raman spectroscopy have been fabricated by flattening Au microwires. The flattened part of the probe provides a flexible cantilever suitable to work in a tapping mode as a force sensor and the electrochemically etched tip works as an optical antenna. The enhancement up to  $10^6$  of the D and G band of graphene has been observed while control of the tip sample pressure produced the shift in G band wavelength. The peak fluctuation in the 2D band also suggests the local stress distribution produced due to graphene–tip interaction. The number of layers and stress analysis in 2-D imaging allows nondestructive identification of graphene layers critical for the evaluation of this material in future device applications.

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### 1. Introduction

The interest in graphene is continuously rising among science and business communities. Applied physicists, new material designers and nanotechnology engineers are attracted by its unique properties such as electrical and thermal conductivity. Fundamental physicists are enchanted by the possibility of exploring quantum relativistic phenomena on 2-D crystals that have an unusual electronic spectrum [1]. In order to manipulate a single-atom-thin structure, reliable high precision tools have to be developed. In this regard Raman spectroscopy has taken a new boost in recent years thanks to the development of tip-enhanced Raman spectroscopy (TERS) [2]. In a TERS experiment a metallic tip is brought in close proximity to the laser illuminated region of the sample. Enhancement is produced by the excitation of localized surface plasmons at the tip apex and its coupling with Raman modes of the sample. The Raman signal generated is further amplified by the tip acting also as a nano-antenna resulting in an overall fourth power increase of the initial electromagnetic field. Besides enhancement, another interesting effect that arises in TERS is the increase in spatial resolution which would extend far beyond the optical diffraction limit giving the possibility to explore the physical and chemical properties of materials at the nanoscale level. This has made of TERS one of the hottest emerging research topics in recent time [3,4]. However, one of the major difficulties of TERS is the low reproducibility of the Au or Ag-vapor coated tip. The gold or silver nanoparticles are randomly positioned at the apex of the

tip, leading to only 10–20% on average of excellent TERS tips which provide high Raman signal enhancements at the excitation wavelength. Additionally, even if the coated AFM tip is working in non-contact mode (intermittent mode), the tip can be worn during the measurement or crash into the sample. As a result, the Au or Ag particle deposited at the end of the tip can be removed, or get damaged and/or contaminated with sample material. The enhancement factor and the spatial resolution are both determined by the choice of material and the size and shape of the tip, the smaller the tip radius the better the spatial resolution and the higher the enhancement [5,6]. TERS has the potential to achieve atomic resolution for the tips of 1 nm radii [7], however the only few experimental TERS works of graphene were published until now [8,9]. Obtaining tips with such small radii from metal-coated cantilevers is unrealistic as most of those tips have radius of  $\sim 20$  nm. Bulk gold tip is one of the best candidates for TERS; in contrast to silver, gold chemical stability is not compromised by oxidation.

Moreover, gold acting as a nanoscattering center provides the highest enhancement in the near infrared region which is the most suitable spectral range to study biological samples [10]. Bulk gold tips can be obtained by electrochemical etching of a microwire showing radii less than 30 nm [11]. However these tips can only be used in a scanning tunneling microscope (STM) or a shear force microscope setup [12,13]. STM has proven an outstanding experimental technique in nanosciences but its application is limited to conductive samples and even operation conditions may require ultrahigh vacuum which is not ideal for most organic samples. Shear force probe microscopy has a great disadvantage for biosciences which is the often unavoidable sample damage induced by the oscillating tip. Because of the soft interaction with the sample, AFM in tapping mode has become the operation mode of choice for

\* Corresponding author. Tel./fax: +370 37451588; mobile: +370 68642705.  
E-mail address: [vsnitka@ktu.lt](mailto:vsnitka@ktu.lt) (V. Snitka).

imaging of soft samples and nanomaterials with high spatial resolution [14].

We demonstrate in this work the use of bulk gold cantilevers to be operated in tapping mode for TERS experiments on graphene.

## 2. Experimental

A highly oriented pyrolytic graphite (HOPG) sample purchased from Goodfellow Inc. was used to obtain the graphene samples. A piece of HOPG was cleaved and gently rubbed on a glass cover slip. Cantilever fabrication procedure was similar to the one adopted by Macpherson et al. [15]. A gold micro wire purchased from Goodfellow was flattened against two flat silicon surfaces producing the cantilever force sensor. One of the extremities of the wire, left without being flattened, was bent at 90° resulting in the future tip. This cantilever was glued to a standard silicon chip, equal to the ones used to hold commercial cantilevers. The tip extremity was both shortened and sharpened by electrochemical etching. The etching solution was prepared by adding 10 mL of saturated CaCl<sub>2</sub> to 30 mL of ultrapure water. Etching was performed in a 30 μL drop of a CaCl<sub>2</sub> solution deposited on an aluminum foil connected to the negative pole of the circuit. The cantilever was connected to the positive pole. The obtained cantilever, shown in Fig. 1, had a length of 250 μm, average thickness of 33 μm and average width of 75 μm.

Confocal Laser Imaging, micro-Raman and TERS measurements have been performed on the glass cover slip placed on a Nikon inverted optical microscope equipped with an x–y positioning piezoelectric controlled stage from NT-MDT Inc. An oil immersed objec-

tive with 100× magnification and numerical aperture NA = 1.49 was used for focusing the laser on the sample and collection of the Raman signal. The Raman spectrometer optically coupled to the inverted microscope was a NTEGRA from NT-MDT powered by a He–Ne laser with  $\lambda = 632.8$  nm and power of 350 μW. Scheme of the experimental setup is shown in Fig. 2. Confocal imaging was performed by detecting on a photomultiplier the back reflected laser beam from the sample while it was raster scanned. For Raman measurements a cooled (−40 °C) CCD camera was used to detect the Raman signal. The exposition time varied from 30 s in the case of conventional Raman, to fractions of seconds, in the case of TERS. TERS experiments were done using an AFM head from NT-MDT Inc. mounted on top of the inverted optical microscope. The gold cantilever was mounted on the holder of the AFM and driven at its resonance frequency around 310 kHz for tapping mode. The very end of the tip was aligned with the center of the laser spot on the sample using micrometric positioning screws and with visual aid from an external telescope and the inverted microscope itself. TERS was turned on when the tip was engaged on the sample. Further control of tip pressure on the sample was accomplished by tuning the amplitude set point of the vibrating cantilever.

## 3. Results and discussion

AFM topography and confocal microscopy image of graphene sample is shown in Fig. 3.

The obtained Raman spectrum of graphene flake is presented on Fig. 4. The peak around 2700 cm<sup>−1</sup> in Fig. 4b is the so-called 2D band (or G' band) and is observed in all graphitic structures; it is a second order, double resonance process which is quite sensitive to lattice perturbations affecting the vibration and electronic properties of graphene. Its position depends on the excitation energy (dispersive) but the shape of this peak gives information about the thickness of graphene [16]. Relatively strong peaks at 2450 cm<sup>−1</sup> and two peaks between 2800 and 3200 cm<sup>−1</sup> in the second order frequency region is the double resonance Raman scattering process [17]. It has been demonstrated that 2D band can be used as a signature of the number of carbon layers on graphene [18]. If the 2D band appears as a single peak then the thickness of the graphene corresponds to one monolayer (Fig. 4a). If there is a shoulder that appears at lower wave number of the shifted 2D main peak then it can be deduced that the graphene sheet is comprised of more than one layer; ultimately the number of layers can be deduced by analyzing the shape of the peak [16]. In this way the graphene sheet indicated by the arrow in Fig. 3a, with spectra shown in Fig. 4b, was identified as a single layer flake and was used to perform the micro-Raman and TERS measurements. As shown in Fig. 5, the Raman spectrum of graphene displays some characteristic peaks in the range 1000–1800 cm<sup>−1</sup>. The first one, around 1333 cm<sup>−1</sup> is known as D peak (disorder-induced), it requires of a defect to be active [18]. It is a double resonance process and it is the first order of the 2D band discussed above. Its position depends on the energy of the laser excitation but contrary to the 2D band, the D band does not depend on the number of layers present on graphene, but depends on the amount of the disorder. The lateral size of the graphene flake is about 400 nm, given that the size of the laser spot is larger (>2 μm) than the size of the flake then the measured intensity is maximal because all the phonons at the edges of the flake are excited and contribute to the Raman spectra shown in Fig. 4 increasing the amplitude of D band. The other characteristic peak appears around 1576 cm<sup>−1</sup>, it is the so-called G band which is universal to all graphitic forms and carbon structures having sp<sup>2</sup> hybridization. The G band is sensitive to strain induced defects on the flat graphene sheet. The ratio between the intensity of D and G bands is often used to quantify

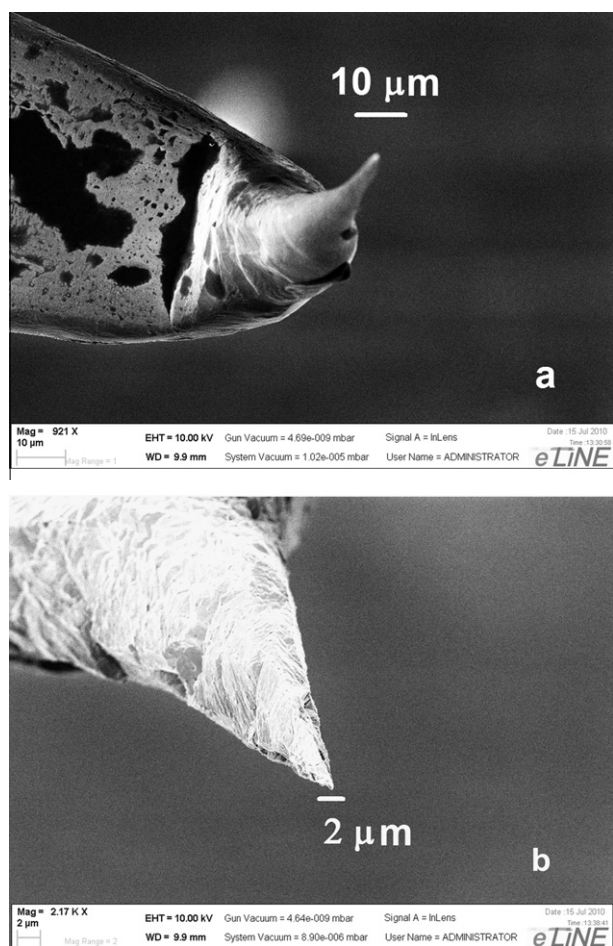


Fig. 1. SEM image of the gold cantilever (a), an apex (b).

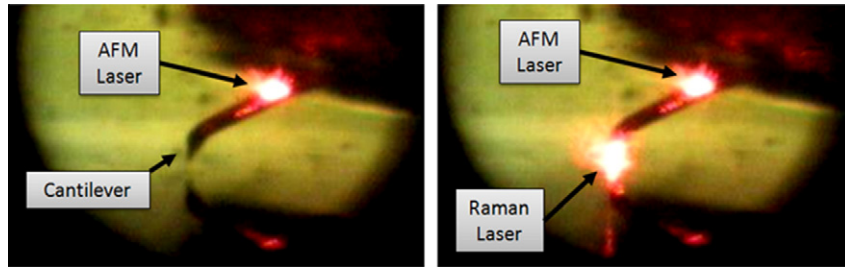


Fig. 2. Optical image of tip-enhanced Raman spectroscopy set-up: AFM gold cantilever (a) and lasers adjustment (b).

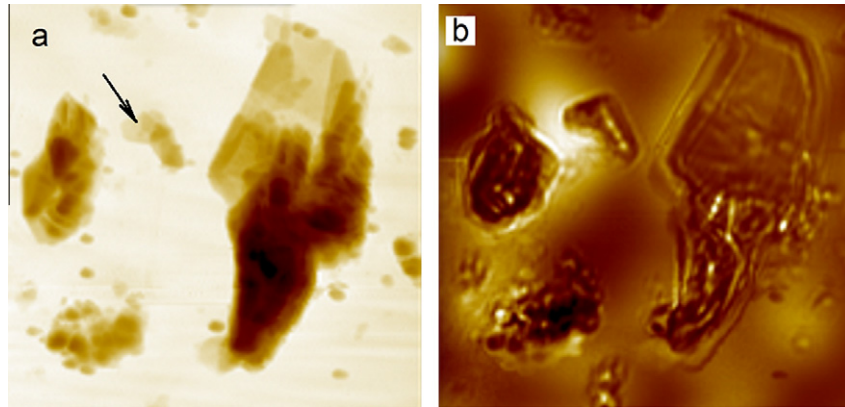


Fig. 3. AFM topography image (a) and scanning laser confocal microscopy image of graphene flakes (b). Image scan area: (25 × 25) microns. The height of single graphene layer measured by AFM was 0.4 nm. An arrow indicates the spatial location of the spot of micro-Raman and tip-enhanced Raman spectra shown in Fig. 4.

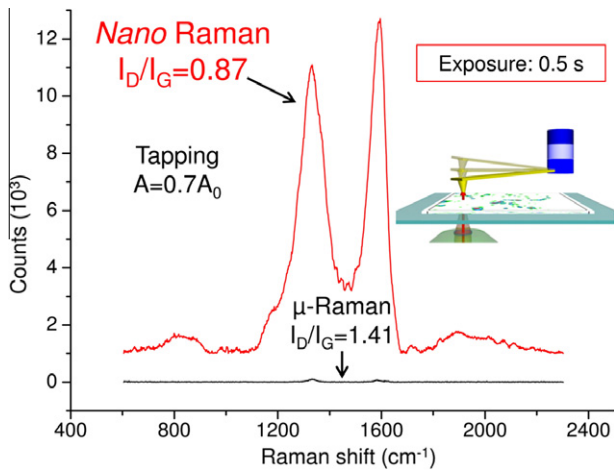


Fig. 4. Micro-Raman spectra of graphene flake spot marked on Fig. 3 by arrow.

the amount of defect in graphitic materials and it can be related to the average distance between defects using the Tuinstra–Koenig relation or a recent phenomenological model proposed by Lucchese et al. [19] The decrease in D band amplitude in the case of TERS can be explained in localization of active excitation area by gold tip and as a result, the decrease of graphene flake edge area defects influence on scattered Raman signal.

TERS and micro-Raman spectra at the same intensity scale are shown in Fig. 5. Large exposition times would have risked the CCD camera while measuring in TERS mode, thus for the sake of comparison between tip-enhanced and micro-Raman the exposition time was limited to 0.5 s. It is seen from the results presented

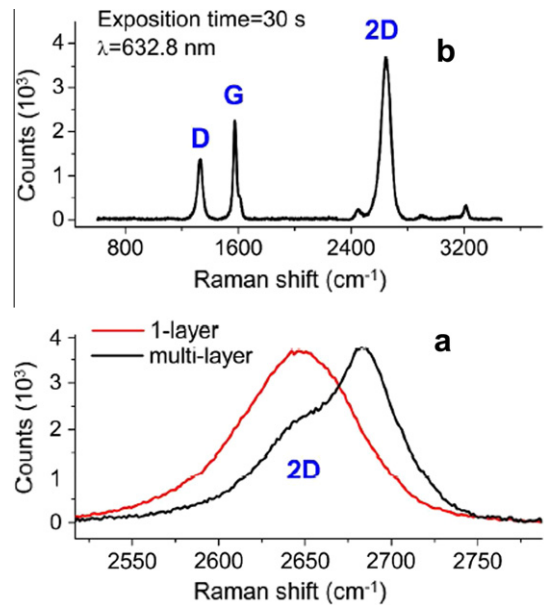


Fig. 5. TERS of graphene obtained with bulk gold cantilever in a tapping mode.

in the Fig. 5 that the high enhancement was induced by the gold tip. Enhancement factors (EF) were calculated for the G and D band. First the contrast was determined using the formula:  $C = \frac{I_{TERS} - I_0}{I_0}$  where  $I_0$  and  $I_{TERS}$  represent the intensity of the Raman signal with the tip away and in contact with the sample, respectively. Then the EF are calculated using the expression:  $E_F = C \cdot \frac{d_L^2}{d_{tip}^2}$  where  $d_L = 2.8 \mu\text{m}$  and  $d_{tip} = 0.016 \mu\text{m}$  are the diameters of laser spot and tip, respectively. Notice that only the area



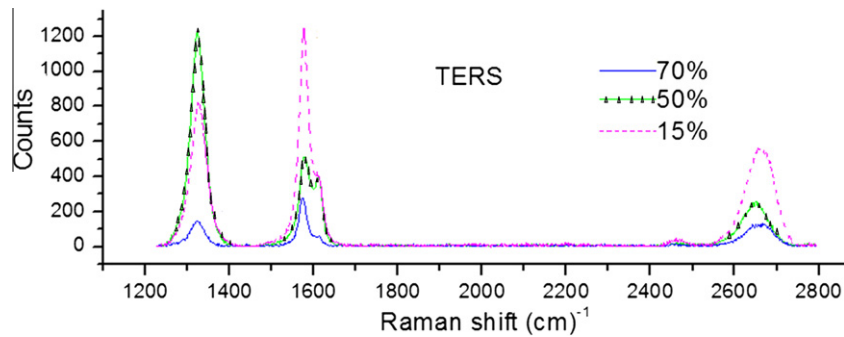


Fig. 6. Tip-enhanced Raman spectra at different distance between the tip and graphene surface.

is considered in the calculation of the EF and not the volume because the extension of the irradiated region perpendicular to the graphene sheet is much larger than its thickness. Contrast factors calculated are  $C(D) = 102$  and  $C(G) = 171$  with  $I_{\text{TERS}}(D) = 11,083$ ,  $I_0(D) = 105$ ,  $I_{\text{TERS}}(G) = 12,724$  and  $I_0(G) = 74$ . Determination of enhancement factors gives  $3 \times 10^6$  and  $5 \times 10^6$  for the D and G band, respectively. Enhancement factors obtained here are comparable to the highest values reported in a TERS experiment using a side illumination setup and a SERS-like substrate [20]. Kharintsev et al. [12] made a comparison between TERS using AFM and shear force microscopes for analysis of carbon nanotubes. They found enhancement factors three orders of magnitude larger with shear force than with AFM. Such difference may be largely attributed to the tip used in each case, while a metalized silicon cantilever was used for AFM a bulk gold tip was employed in shear force. Our results confirm the superior performance of bulk cantilevers for electromagnetic enhancement in tapping mode AFM.

The influence of the gold tip pressure on a single layer graphene Raman spectra was investigated changing the distance between the tip and graphene surface. The distance was controlled by changing AFM feedback set-point from  $A_0$  to  $0,2A_0$ , where  $A_0$  is free cantilever vibration amplitude. The research results presented on Fig. 6.

We found in our experiment that applying a high pressure between the tip and the sample the shift in Raman spectra peaks occur, as it has been reported on carbon nanotubes [18]. Changing the AFM feedback set-point from free oscillation amplitude  $A_0$  to  $0,2A_0$  the magnitude of the Raman 2D peak was shifted up on the scale about  $10 \text{ cm}^{-1}$  and the G band has not shown any shift. The more detail investigation of the phenomena is on the way. The important point that we want to highlight in this section, as illustrated in Fig. 6, is the possibility to control the degree of interaction (pressure) with the sample using bulk gold cantilevers in AFM tapping mode just by changing the cantilever amplitude set point. In this way, in addition to an impressive enhancement and the possibility to conduct pressure-assisted TERS with ultra-high resolution, controlled experiments can also be performed in order to investigate the effect of external mechanical perturbations induced by the tip on the phonon and electronic structure of a sample [21].

#### 4. Conclusions

In this work Raman enhancement  $>10^6$  in graphene has been demonstrated using a bulk gold cantilever in a tapping mode atomic force microscopy setup. The bulk gold AFM cantilever allows to investigate biological samples under native conditions and fast Raman imaging can be achieved without the need of specialized ultrasensitive detectors. The aspect ratio and tip sharpness can be tailored by changing the electrochemical conditions of the etching procedure. The possibility of tailoring the cantilever geometry

is also a great advantage for the implementation of side/top illumination-collection setups which can be used for imaging opaque samples and can also yield impressive enhancement when coupled with SERS.

In our work it is shown for the first time that Raman mode of graphene is shifted when strain is induced by the gold tip in a TERS experiment. The study of strain induced effects on graphene by tapping mode TERS, and understanding on how it changes graphene electronic properties, open new possibilities to study performance of this promising material for future applications. There is no doubt that improvement of traditional probes and development of new ones is essential steps in order to achieve the ultimate resolution in Raman spectroscopy and imaging.

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