

NANO EXPRESS

Open Access

Probing substrate influence on graphene by analyzing Raman lineshapes

Chen-Han Huang¹, Hsing-Ying Lin¹, Cheng-Wen Huang², Yi-Min Liu², Fu-Yu Shih³, Wei-Hua Wang³ and Hsiang-Chen Chui^{2,4*}

Abstract

We provide a new approach to identify the substrate influence on graphene surface. Distinguishing the substrate influences or the doping effects of charged impurities on graphene can be realized by optically probing the graphene surfaces, included the suspended and supported graphene. In this work, the line scan of Raman spectroscopy was performed across the graphene surface on the ordered square hole. Then, the bandwidths of G-band and 2D-band were fitted into the Voigt profile, a convolution of Gaussian and Lorentzian profiles. The bandwidths of Lorentzian parts were kept as constant whether it is the suspended and supported graphene. For the Gaussian part, the suspended graphene exhibits much greater Gaussian bandwidths than those of the supported graphene. It reveals that the doping effect on supported graphene is stronger than that of suspended graphene. Compared with the previous studies, we also used the peak positions of G bands, and I_{2D}/I_G ratios to confirm that our method really works. For the suspended graphene, the peak positions of G band are downshifted with respect to supported graphene, and the I_{2D}/I_G ratios of suspended graphene are larger than those of supported graphene. With data fitting into Voigt profile, one can find out the information behind the lineshapes.

Keywords: Substrate influence; Graphene; Raman lineshapes; Voigt fitting

Background

Graphene has many unique and novel electrical and optical properties [1-3] because it is the thinnest sp^2 allotrope of carbon arranged in a honeycomb lattice. Recent studies indicate that the remarkable carrier transport properties of suspended graphene with respect to supported graphene include temperature transport, magnetotransport, and conductivity [4-6]. The phonon modes of graphene and their effects on its properties due to the dopants and defects' effects are also different between suspended and supported graphene. These effects on its properties can be studied by Raman spectroscopy [7-9]. Raman spectroscopy has been extensively used to investigate the vibration properties of materials [10-13]. Recently, characterizing the band structure of graphene and the interactions of phonons has been applied as the powerful study method [14-18]. With the different effects

influenced by doping and substrate, charged dopants produced by residual photoresist in the fabrication process are possibly induced by the deposition and also affect the substrate. According to relevant studies [19,20], the properties of metallic particles on graphene used as an electrode in graphene-based electronic devices can be understood clearly and suspended graphene is suitable to use to understand the effect of charged dopants on the substrate. In our previous works [21,22], we used polarized Raman spectroscopy to measure the strain effect on the suspended graphene. We fitted the spectra with triple-Lorentzian function and obtained three sub-2D peaks: $2D_+$, $2D_-$, and $2D_0$. In another work, we observed three sub-G peaks: G_+ , G_- , and G_0 . The property of intensity of G_+ , G is similar as $2D_+$ and $2D$ peaks. The linewidth analysis with data fitting into pure Lorentzian and Voigt profiles had been applied two-photon transitions in atomic Cs [23,24], because of its elastic motion of atomic structures. The Voigt profile, a convolution of a Lorentzian and a Gaussian, is used to fit these Raman spectra of graphene.

In this work, the supported and suspended graphene were both fabricated by micromechanical cleavage, and

* Correspondence: hcchui@mail.ncku.edu.tw

²Department of Photonics, National Cheng Kung University, Tainan 70101, Taiwan

⁴Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan

Full list of author information is available at the end of the article

then, they were identified as monolayer graphene by Raman spectroscopy and optical microscopy. The Raman signals of suspended and supported graphene can be measured and analyzed by probing the graphene surface which contains them. The peak positions of G band, the I_{2D}/I_G ratio, and bandwidths of G band fitted with Voigt profile are obtained with the Raman measurements. Under our analysis, details about the effects of charged impurities on the substrate can be realized. About the strain effect or doping effect on graphene, some possible broadening mechanisms may still be responsible for deforming it, so we considered the Gaussian profile necessary.

Methods

Suspended graphene was fabricated by mechanical exfoliation of graphene flakes onto an oxidized silicon wafer, and the illustration of that is shown in Figure 1a. First, ordered squares with areas of $6\ \mu\text{m}^2$ were defined by photolithography on an oxidized silicon wafer with an oxide thickness of 300 nm. Reactive ion etching was then used to etch the squares to a depth of 150 nm. Micromechanical cleavage of highly ordered pyrolytic graphite was carried out using scotch tape to enable the suspended graphene flakes to be deposited over the indents. The thickness of the monolayer graphene is about 0.35 nm. The optical image of suspended graphene, atomic force microscopy (AFM) image, and its cross section are shown in Figure 1b,c. The surface of suspended graphene is like a hat, and the top of graphene surface can reach 100 nm high with respect to supported graphene. To identify the number of graphene layers and their properties, a micro-Raman microscope (Jobin Yvon iHR550, HORIBA Ltd., Kyoto, Japan) was utilized to obtain the Raman signals of monolayer graphene. A 632-nm He-Ne laser was the excitation light source. The polarization and power of the incident light were adjusted by a half-wave plate and a polarizer. The laser power was monitored by a power meter and kept constant as the measurements were made.

The experimental conditions for Raman measurement were as follows. In order to avoid the local heating effect, the excited laser power on the graphene surface was 0.45 mW and the integration time was 180 s. The laser beam was focused by a $\times 50$ objective lens (NA = 0.75) on the sample with a focal spot size of about $0.5\ \mu\text{m}$, representing the spatial resolution of the Raman system. Finally, the Raman scattering radiation was sent to a 55-cm spectrometer for spectral recording.

To understand the unique properties of graphene surface covering on the different substrates, the Raman signals of G and 2D bands of graphene were obtained in these measurements. According to previous study [25], the I_{2D}/I_G ratios and peak positions of G and 2D bands were various as graphene surface was doped by depositing silver nanoparticles on its surface. The I_{2D}/I_G ratios and peak positions can be related to the doping, and the I_{2D}/I_G ratio is more sensitive to the doping than is the peak shift. A lower I_{2D}/I_G ratio is associated with a larger amount of charged impurities in graphene. Therefore, peak positions of G band and I_{2D}/I_G ratios by integrating their respect band, G and 2D band, are obtained in Figure 2a,b. The horizontal axis is expressed as the positions of the focused laser which scanned across the graphene surface in the Raman measurement. The interval of line mapping points is set as $0.5\ \mu\text{m}$. Obvious frequency shift can be found at the G band peak positions between the suspended and supported graphene. The peak positions of G band of suspended and supported graphene are around $1,575$ and $1,577\ \text{cm}^{-1}$, and the I_{2D}/I_G ratios of suspended and supported graphene are around 3.9 and 2.1. The upshift of the G band reflects doping with charged impurities. The peak position of the G band of the suspended graphene is redshifted comparing to that of supported graphene, consistent with the above expectations.

The examination on G-band peak positions and the I_{2D}/I_G ratios for monolayer graphene flake covering on different substrates can provide information of substrate

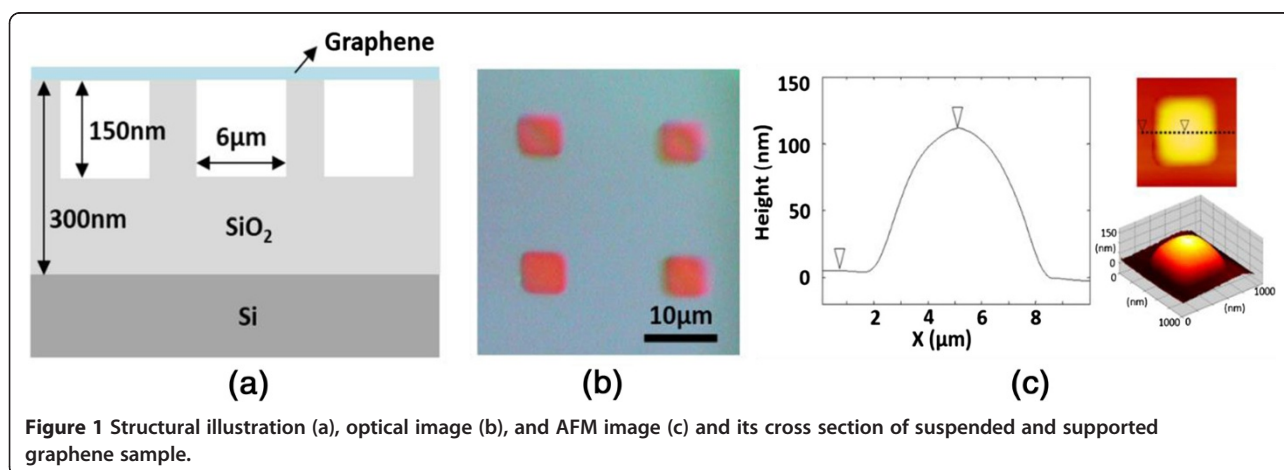
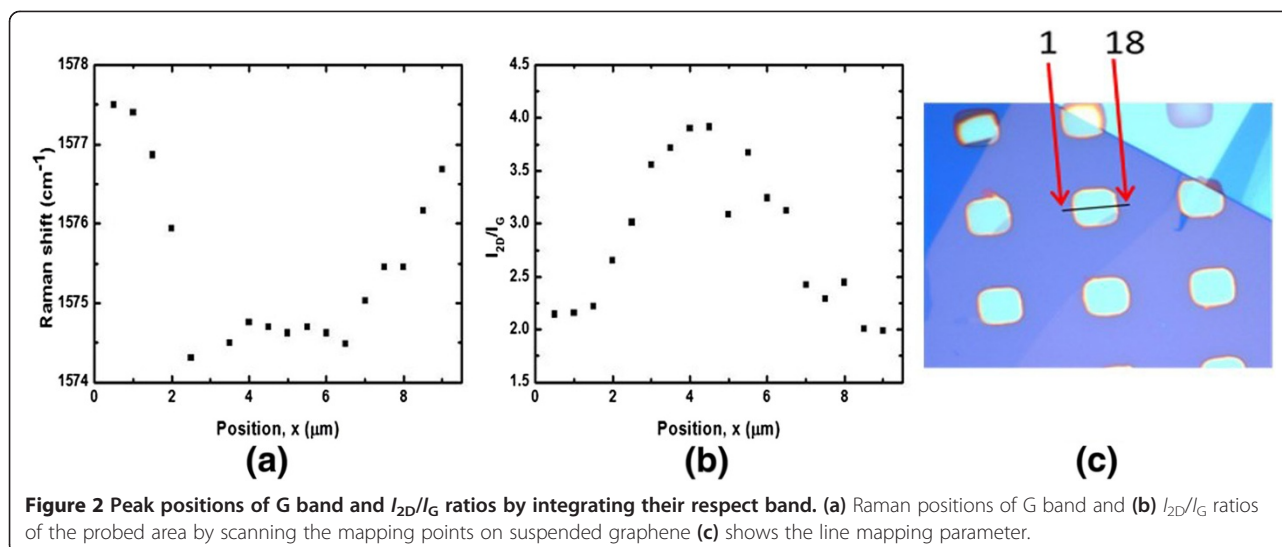


Figure 1 Structural illustration (a), optical image (b), and AFM image (c) and its cross section of suspended and supported graphene sample.



effect. In the previous reviews, the bandwidths of G and 2D bands were usually fitted by Lorentzian function [26-29], because it just related to the lifetime broadening between the levels. However, the bandwidth broadening of G bands was clearly observed and deserved worth to be investigated. Here, we introduced that the Voigt profile, a convolution of a Lorentzian and a Gaussian, is suitable for fitting the transition linewidth and expressed [30-32] as

$$V(\omega, \Gamma, \gamma) = L(\omega, \Gamma) * G(\omega, \gamma) = \frac{\Gamma}{2\pi\gamma\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\exp\left(-\frac{x^2}{2\gamma^2}\right)}{(\omega-x)^2 + \frac{\Gamma^2}{4}} dx, \quad (1)$$

where the Gaussian profile and Lorentzian profile are expressed as $G(\omega, \gamma)$ and $L(\omega, \Gamma)$, and γ and Γ are their bandwidths. In Figure 3a, the typical Raman spectrum (black line) of graphene was shown with the Lorentzian-fitted profile (blue line) and the Voigt-fitted profile (red line). The related fitting parameter of the Raman spectrum was showed in Figure 3b.

The bandwidth of Raman band was usually fitted and understood the situation of background of material by Gaussian function. Therefore, the G bands of supported and suspended graphene were fitted by Voigt profiles that give the Gaussian and Lorentzian profiles. The fitting results of Raman spectra of supported ($x = 0.5 \mu\text{m}$) and suspended ($x = 4.5 \mu\text{m}$) graphene by Voigt profile are shown in Figure 4a,b.

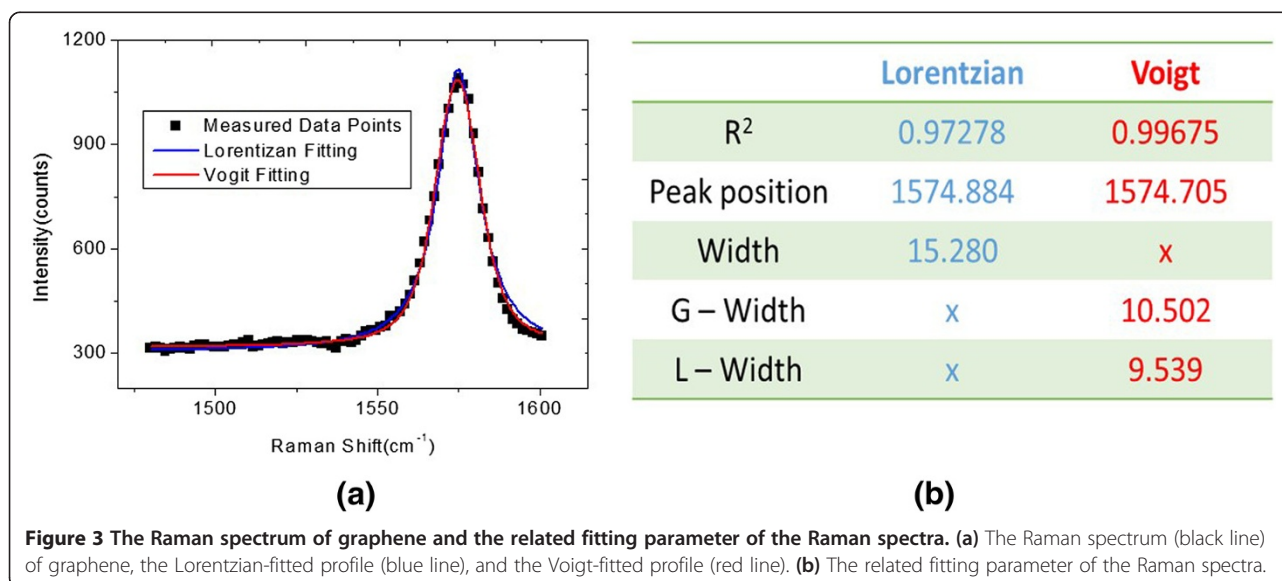


Figure 3 The Raman spectrum of graphene and the related fitting parameter of the Raman spectra. (a) The Raman spectrum (black line) of graphene, the Lorentzian-fitted profile (blue line), and the Voigt-fitted profile (red line). (b) The related fitting parameter of the Raman spectra.

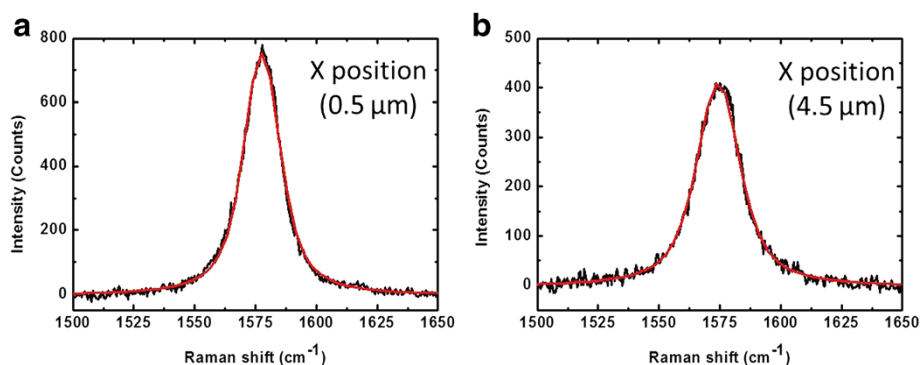


Figure 4 Raman spectra (black line) of (a) supported and (b) suspended graphene fitted by Voigt function (red line).

Results and discussion

Based on the data fitting results, the analysis of measured point across the graphene surface, the bandwidths of Gaussian profiles and Lorentzian profiles given by Voigt fitting is presented in Figure 4a,b. The horizontal axis is expressed as the mapping points of the area which contains supported (edge area) and suspended graphene (center area).

The Lorentzian bandwidths on the suspended and supported graphene are kept as $12.09 \pm 0.76 \text{ cm}^{-1}$. The Lorentzian bandwidth is mainly contributed by the natural linewidth and partly from the uncertainty of data fitting (0.3 cm^{-1}) and instrumental uncertainty (0.9 cm^{-1}). The natural linewidth is just linked with the phonon lifetimes between interaction levels. On the other hand, the Gaussian bandwidths of the suspended graphene exhibit a much higher than those of the supported graphene. Some

mechanisms resulted in the Gaussian bandwidth broadening and the curve is consistent with the deformation of graphene surface. Other broadening mechanisms are related to the substrate effect and the local heating effect (Figure 5).

Conclusions

Spectroscopic investigation on graphene of the interaction between phonons and electrons with the dopant or the substrate reveals a rich source of interesting physics. Raman signals of supported and suspended monolayer graphene were obtained. The peak positions of G bands, and I_{2D}/I_G ratios, and bandwidths of G bands fitted with Voigt profiles were obtained under our analysis, and their different performances of suspended and supported graphene can be used to demonstrate the substrate influences and doping effects on graphene. The Gaussian bandwidths of those separated from Voigt profiles provide a new method to study the influence of the substrate and doping effect on graphene.

Competing interests

National Science Council, Taiwan under contact no. NSC 101-2112-M-006-006 and NSC 102-2622-E-006-030-CC3.

Authors' contributions

CHH, HL, and CWH carried on the experimental parts: the acquisition of data, and analysis and interpretation of data. YL took the analysis and interpretation of data, and also had been involved in revising the manuscript. FS and WW (Institute of Atomic and Molecular Sciences, Academia Sinica) prepared the samples, suspended graphene using by micromechanical method, and captured the OM and AFM images. HC, the corresponding author, had made substantial contributions to conception and design, and had been involved in drafting the manuscript and revising it critically for important intellectual content. All authors read and approved the final manuscript.

Acknowledgments

We wish to acknowledge the support of this work by the National Science Council, Taiwan under contact no. NSC 101-2112-M-006-006 and NSC 102-2622-E-006-030-CC3.

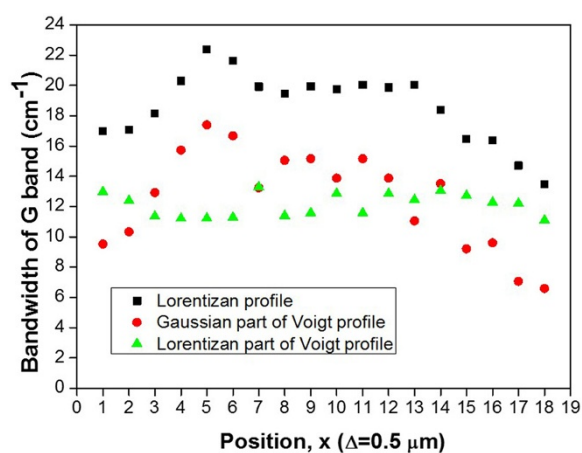


Figure 5 Bandwidths of G band of the probed area by scanning the mapping points on suspended graphene. By fitting with Voigt function contained (green triangle) Lorentzian part and (red circle) Gaussian part.

Author details

¹Center for Nano Bio-Detection, National Chung Cheng University, Chiayi 621, Taiwan. ²Department of Photonics, National Cheng Kung University, Tainan 70101, Taiwan. ³Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan. ⁴Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan 70101, Taiwan.

Received: 14 November 2013 Accepted: 19 January 2014

Published: 7 February 2014

References

- Novoselov KS, Geim AK, Morozov SV, Jiang D, Zhang Y, Dubonos SV, Grigorieva IV, Firsov AA: **Electric field effect in atomically thin carbon films.** *Science* 2004, **306**(5696):666–669.
- Geim AK, Novoselov KS: **The rise of graphene.** *Nat Mater* 2007, **6**(3):183–191.
- Geim AK: **Graphene: status and prospects.** *Science* 2009, **324**(5934):1530–1534.
- Bolotin KI, Sikes KJ, Hone J, Stormer HL, Kim P: **Temperature-dependent transport in suspended graphene.** *Phys Rev Lett* 2008, **101**:9.
- Chen SY, Ho PH, Shiue RJ, Chen CW, Wang WH: **Transport/magnetotransport of high-performance graphene transistors on organic molecule-functionalized substrates.** *Nano Lett* 2012, **12**(2):964–969.
- Rouhi N, Wang YY, Burke PJ: **Ultrahigh conductivity of large area suspended few layer graphene films.** *Appl Phys Lett* 2012, **101**:26.
- Compagnini G, Forte G, Giannazzo F, Raineri V, La Magna A, Deretzis I: **Ion beam induced defects in graphene: Raman spectroscopy and DFT calculations.** *J Mol Struct* 2011, **993**(1–3):506–509.
- Sahoo S, Palai R, Katiyar RS: **Polarized Raman scattering in monolayer, bilayer, and suspended bilayer graphene.** *J Appl Phys* 2011, **110**(4):044320.
- Cancado LG, Jorio A, Ferreira EHM, Stavale F, Achete CA, Capaz RB, Moutinho MVO, Lombardo A, Kulmala TS, Ferrari AC: **Quantifying Defects in graphene via Raman spectroscopy at different excitation energies.** *Nano Lett* 2011, **11**(8):3190–3196.
- Wang JK, Tsai CS, Lin CE, Lin JC: **Vibrational dephasing dynamics at hydrogenated and deuterated semiconductor surfaces: symmetry analysis.** *J Chem Phys* 2000, **113**(12):5041–5052.
- Wang HH, Liu CY, Wu SB, Liu NW, Peng CY, Chan TH, Hsu CF, Wang JK, Wang YL: **Highly Raman-enhancing substrates based on silver nanoparticle arrays with tunable sub-10 nm gaps.** *Adv Mater* 2006, **18**(4):491.
- Liu CY, Dvoynenko MM, Lai MY, Chan TH, Lee YR, Wang JK, Wang YL: **Anomalous enhanced Raman scattering from longitudinal optical phonons on Ag-nanoparticle-covered GaN and ZnO.** *Appl Phys Lett* 2010, **96**(3):033109.
- Huang CH, Lin HY, Chen ST, Liu CY, Chui HC, Tzeng YH: **Electrochemically fabricated self-aligned 2-D silver/alumina arrays as reliable SERS sensors.** *Opt Express* 2011, **19**(12):11441–11450.
- Ferrari AC, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, Piscanec S, Jiang D, Novoselov KS, Roth S, Geim AK: **Raman spectrum of graphene and graphene layers.** *Phys Rev Lett* 2006, **97**(18):187401.
- Malard LM, Pimenta MA, Dresselhaus G, Dresselhaus MS: **Raman spectroscopy in graphene.** *Phys Rep* 2009, **473**(5–6):51–87.
- Gao LB, Ren WC, Liu BL, Saito R, Wu ZS, Li SS, Jiang CB, Li F, Cheng HM: **Surface and interference coenhanced Raman scattering of graphene.** *ACS Nano* 2009, **3**(4):933–939.
- Schedin F, Lidorikis E, Lombardo A, Kravets VG, Geim AK, Grigorenko AN, Novoselov KS, Ferrari AC: **Surface-enhanced Raman spectroscopy of graphene.** *ACS Nano* 2010, **4**(10):5617–5626.
- Wu D, Zhang F, Liu P, Feng X: **Two-dimensional nanocomposites based on chemically modified graphene.** *Chem-Eur J* 2011, **17**(39):10804–10812.
- Casiraghi C, Pisana S, Novoselov KS, Geim AK, Ferrari AC: **Raman fingerprint of charged impurities in graphene.** *Appl Phys Lett* 2007, **91**:23.
- Ni ZH, Yu T, Luo ZQ, Wang YY, Liu L, Wong CP, Miao JM, Huang W, Shen ZX: **Probing charged impurities in suspended graphene using Raman spectroscopy.** *ACS Nano* 2009, **3**(3):569–574.
- Huang CW, Lin BJ, Lin HY, Huang CH, Shih FY, Wang WH, Liu CY, Chui HC: **Observation of strain effect on the suspended graphene by polarized Raman spectroscopy.** *Nanoscale Res Lett* 2012, **7**(1):533.
- Huang CW, Shiue RJ, Chui HC, Wang WH, Wang JK, Tzeng YH, Liu CY: **Revealing anisotropic strain in exfoliated graphene by polarized Raman spectroscopy.** *Nanoscale* 2013, **5**(20):9626–9632.
- Lee YC, Chui HC, Chen YY, Chang YH, Tsai CC: **Effects of light on cesium 6S-8S two-photon transition.** *Opt Commun* 2010, **283**(9):1788–1791.
- Lee YC, Chang YH, Chen YY, Tsai CC, Chui HC: **Polarization and pressure effects in cesium 6S-8S two-photon spectroscopy.** *J Phys B-At Mol Opt* 2010, **43**:23.
- Lee J, Novoselov KS, Shin HS: **Interaction between metal and graphene: dependence on the layer number of graphene.** *ACS Nano* 2011, **5**(1):608–612.
- Frank O, Mohr M, Maultzsch J, Thomsen C, Riaz I, Jalil R, Novoselov KS, Tsoukleri G, Parthenios J, Papagelis K, Kavan L, Galotias C: **Raman 2D-band splitting in graphene: theory and experiment.** *ACS Nano* 2011, **5**(3):2231–2239.
- Yoon D, Son YW, Cheong H: **Strain-dependent splitting of the double-resonance Raman scattering band in graphene.** *Phys Rev Lett* 2011, **106**:15.
- Mohiuddin TMG, Lombardo A, Nair RR, Bonetti A, Savini G, Jalil R, Bonini N, Basko DM, Galotias C, Marzari N, Novoselov KS, Geim AK, Ferrari AC: **Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Gruneisen parameters, and sample orientation.** *Phys Rev B* 2009, **79**:20.
- Ni ZH, Yu T, Lu YH, Wang YY, Feng YP, Shen ZX: **Uniaxial strain on graphene: Raman spectroscopy study and band-gap opening.** *ACS Nano* 2008, **2**(11):2301–2305.
- Chuev MA: **An efficient method of analysis of the hyperfine structure of gamma-resonance spectra using the Voigt profile.** *Dokl Phys* 2011, **56**(6):318–322.
- Pagnini G, Mainardi F: **Evolution equations for the probabilistic generalization of the Voigt profile function.** *J Comput Appl Math* 2010, **233**(6):1590–1595.
- Asthana BP, Kiefer W: **Deconvolution of the Lorentzian linewidth and determination of fraction Lorentzian character from the observed profile of a Raman line by a comparison technique.** *Appl Spectrosc* 1982, **36**(3):250–257.

doi:10.1186/1556-276X-9-64

Cite this article as: Huang et al.: Probing substrate influence on graphene by analyzing Raman lineshapes. *Nanoscale Research Letters* 2014 **9**:64.

Submit your manuscript to a SpringerOpen® journal and benefit from:

- Convenient online submission
- Rigorous peer review
- Immediate publication on acceptance
- Open access: articles freely available online
- High visibility within the field
- Retaining the copyright to your article

Submit your next manuscript at ► springeropen.com