Imaging of Sub-nanometer Strain Variations in Monolayer Defect-Free Graphene using Tip-Enhanced Raman Spectroscopy

Maria Vanessa Balois[1], Norihiko Hayazawa[1,2,3], Satoshi Yasuda[4], Katsuyoshi Ikeda[5], Bo Yang[2], Emiko Kazuma[2], Yasuyuki Yokota[2], Yousoo Kim[2], and Takuo Tanaka[1,3,6]

[1] Innovative Photon Manipulation Research Team, RIKEN Center for Advanced Photonics, [2] Surface and Interface Science Laboratory, RIKEN Cluster for Pioneering Research, [3] National Institute of Physics, University of the Philippines, [4] Japan Atomic Energy Agency, [5] Nagoya Institute of Technology, [6] Metamaterials Laboratory, RIKEN Cluster for Pioneering Research
E-mail: mariavanessa.balois@riken.jp

1. Introduction

Strain can alter the electronic properties of graphene [1] and even local strain fluctuations can affect the maximum carrier mobility in high quality graphene [2]. So far, strain fluctuations have not been directly observed through imaging due to the diffraction limit and are mainly inferred through the broadening of the spectral width of the *2D* peak measure via micro-Raman [2]. These fluctuations, however, could be directly imaged through our scanning tunneling microscope-based tip-enhanced Raman spectroscopy (STM-TERS) system capable of sub-nanometer spatial resolution [3, 4]. TERS is a super-resolution technique that breaks the diffraction limit by merging scanning probe microscopy and Raman spectroscopy to simultaneously obtain chemical and structural information at the nanoscale. Recently, our team surpassed the highest spatial resolution of 1.7 nm for STM-TERS in ambient conditions [5] and can now attain sub-nanometer spatial resolution of 0.7 nm [3]. Thus, paving the way to analyze the local properties of graphene with sub-nanometer precision.

2. Results and Discussion

We conducted TERS experiments on defect-free monolayer graphene grown via atmospheric pressure chemical vapor deposition on an Au(111) single crystal substrate [6]. An area was scanned with a sharp Au tip illuminated by a 632.8 nm laser. Figures 1(a) – 1(c) show the spectroscopic images based on the *2D* band. Variations of ω_{2D} can be attributed to the inhomogeneity of the interaction between graphene and the Au(111) substrate and are clustered into nano-sized domains, which are labeled as 1, 2, and 3 with ω_{2D} decreasing from domain 1 to domain 3. To determine whether strain and/or doping is dominant, a correlation plot between the ω_{2D} and ω_G was made, which is similar to the data analysis technique developed by Lee, *et al*. that optically separates the effects of strain and doping [7]. Their data, however, is based on micro-Raman data while we used TERS data that is plotted in Fig. 1(d). The blue star indicates the deduced experimental micro-Raman peak values for unstrained and undoped single layer graphene on an SiO_2/Si substrate illuminated by a 632.8 laser (ω^0_G=1583 cm^{-1}; ω^0_{2D}=2646 cm^{-1}) [8]. The pink dashed line with a slope ($\partial\omega_{2D}/\partial\omega_G$) of 2.2 corresponds to the rate of change of ω_{2D} and ω_G under pure strain [9]. Pure strain is a combination of both biaxially isotropic and biaxially anisotropic strain for strains below 1%. Compared to (ω^0_G, ω^0_{2D}), the Raman modes are up-shifted implying compressive strain is present in all three domains. Collectively, the sub-nanometric domains exhibit a linear trend with $\partial\omega_{2D}/\partial\omega_G$ of 1.2 ± 0.2 (black line, Fig. 1(d)). This slope deviates from the pure strain slope of 2.2, meaning both strain and slight p-doping are influencing the detected shift of the Raman peaks.

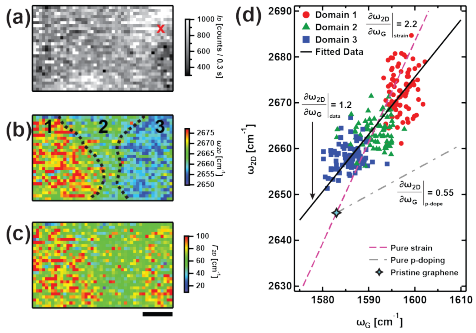

Figure 1. STM image STM-TERS spectroscopic imaging of area A1 (23 × 14 nm^2; 0.5 nm/pixel) of 2D band **(a)** integrated intensity, (I_{2D}), **(b)** Raman shifts (ω_{2D}) and **(c)** spectral width (Γ_{2D}). Domains are indicated as 1, 2, and 3 in (b). **(d)** Correlation plot of ω_{2D} vs. ω_G of domains 1 (red circles), 2 (green triangles), and 3 (blue squares) from TERS data of scanned area [3].

3. Conclusions

We have successfully imaged and analyzed sub-nanometer strain variations using STM-TERS in ambient. Through this work, high resolution materials characterization of the as-fabricated local properties, such as strain, of graphene and other two-dimensional nanomaterials is now possible.

References

[1] V. Pareira, et. al, Phys. Rev. Lett. **103** (2009) 046801.
[2] N.J.G. Couto, et. al, Phys. Rev. X **4** (2014) 041019.
[3] M.V. Balois, et. al, NPJ 2D Mater. Appl. **3** (2019) 38.
[4] M.V. Balois, et. al, Jpn. J. Appl. Phys. **58** (2019) SI0801.
[5] C. Chen, et. al, Nat. Commun. **5** (2015) 3312.
[6] S. Yasuda, et. al, J. Phys. Chem. Lett. **6** (2015) 3403-3409.
[7] J.E. Lee, et. al, Nat. Commun. **3** (2012) 1024.
[8] N.S. Mueller, et. al, 2D Mater. **5** (2018) 015016.
[9] G. Fröelicher, et. al, Phys. Rev. B **91** (2015) 205413.