

Tip-enhanced Raman Spectroscopic study of local structures of epitaxial graphene grown on SiC

(Kwansei Gakuin University) Sanpon Vantasin, Toshiaki Suzuki, Yasunori Kutsuma, Koji Ashida, Tadaaki Kaneko, Yukihiro Ozaki

Epitaxial graphene synthesized by sublimation of silicon atom from SiC has been considered as a promising material for electronic applications. It has many astonishing properties such as unique band gap, high charge mobility, and large graphene sheet. However, local structures on graphene sheet such as ridges and cliffs can greatly affect these properties. In this study, we used atomic force microscopy (AFM) and tip-enhance Raman spectroscopy (TERS) to investigate these local nanostructures. TERS is a technique that utilizes interaction between laser and metal tip to give near-field enhancement of Raman signal. With spatial resolution surpassing the diffraction limit of excitation laser, graphene local nanostructure can be precisely studied.

The graphene samples used in this study were synthesized by heating C-terminated 4H-SiC(000 $\bar{1}$) to 1800 °C for 15 minutes. TERS measurement were done with top-illumination top-collection setup using bulk Ag tip (~75 nm tip radius) and 514 nm excitation laser.

AFM images of synthesized epitaxial graphene show ridge and cliff nanostructures with height up to ~10 nm. In the areas apart from these structures, graphene sheet is extremely flat (< 1 nm height variation). The non-flat

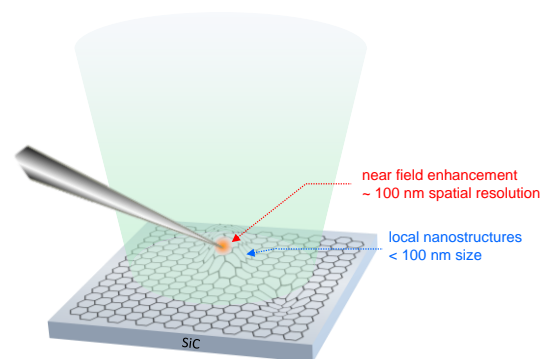


Fig. 1 Schematic illustration of TERS measurement on graphene local nanostructures.

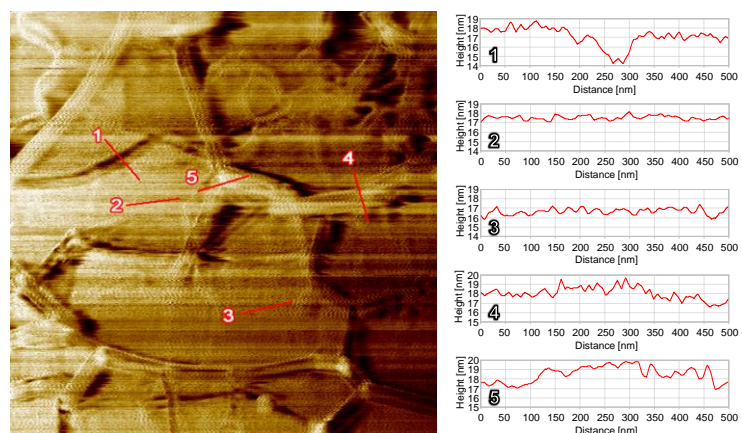


Fig. 2 AFM image of graphene grown on SiC and line profiles with corresponding paths.

structures arose from unequal shrinkage between SiC and graphene while cooling down from synthesizing temperature to room temperature [1]. This is due to the difference in thermal expansion coefficient between SiC and graphene [2].

Fig. 3 demonstrates series of TERS measurements on graphene ridge nanostructure. Since all G' peaks of TERS spectra has Gaussian shape and FWHM in $17 - 28 \text{ cm}^{-1}$ range, we can determine that graphene over this nanostructure is single layer. For the points on ridge structure, the position of G' peaks in TERS spectra clearly shifts ($\sim 9 \text{ cm}^{-1}$) to lower wavenumber. This denotes tensile strain of graphene at those points [3]. In Raman spectra this shift is far less obvious, because the distance between each point is too small for normal Raman to resolve. Thus, signal from nearby area is averaged out as the spatial resolution is not enough. We also studied other sub-micrometer size and nanometer size structures using this scheme. The results are similar, as TERS can specifically probe each structure while normal Raman only provides average spectra of the area.

From these results, we demonstrate that graphene grown on SiC has inhomogeneous strain even in nanoscale and TERS is a powerful tool to investigate this characteristic.

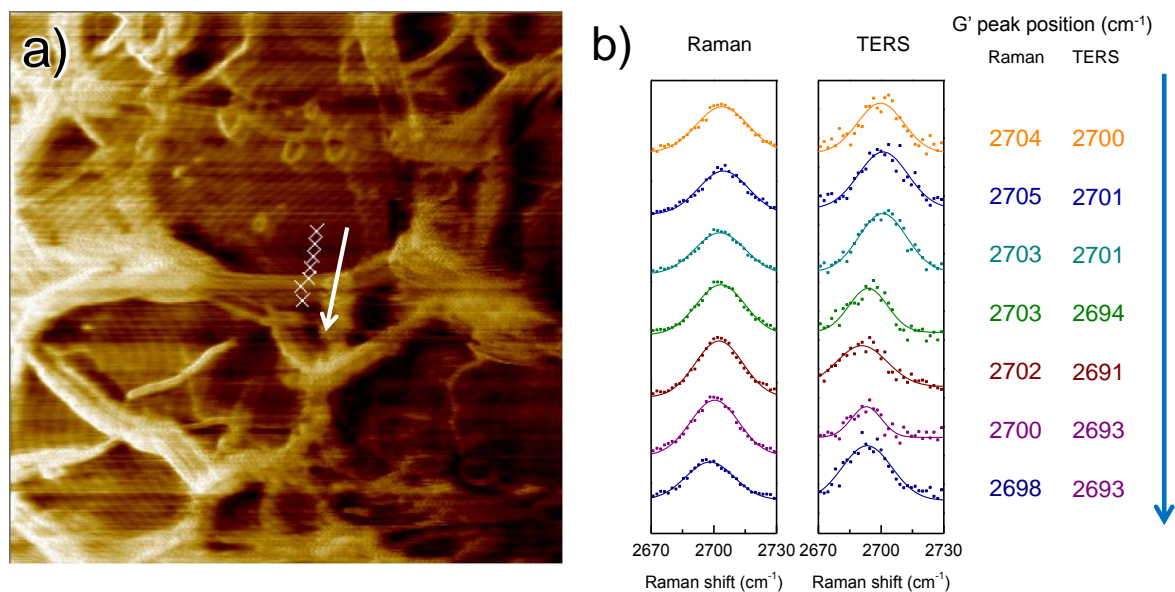


Fig. 3 (a) TERS measurement points shown in AFM image. (b) G' peak of Raman and TERS spectra acquired from points in (a).

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