

# Tip-enhanced Raman Spectroscopy for Suspended Graphene Integrated with Silicon Nanowire Array

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## Summary

Local chemical and mechanical properties of suspended graphene structure integrated with an array of silicon nanowires (SiNW) are investigated by employing Tip-Enhanced Raman Spectroscopy (TERS). Clear difference in the shift of the major graphene peak positions is observed between Raman spectra without the tip and TERS spectra across the graphene located on the edge of the SiNW underneath. Localised defects that might be induced by the graphene transfer on the array are identified with the spatial resolution of approximately 100nm by the analysis of the peak intensity ratio. The results suggest that TERS is a promising technology for further improvement of graphene-based nanoelectromechanical device fabrication processes.

## Introduction

To investigate mechanical and chemical properties of nanoscale devices from Raman signal, it is required to improve spatial resolution of Raman spectroscopy beyond a physical limit of wavelength. Tip-Enhancement Raman Spectroscopy (TERS) is a technique to realize higher spatial resolution by using near field induced by metal coated on the top of the Atomic Force Microscopy (AFM) cantilever tip. The spatial resolution of approximately 25 nm has been reported for single wall carbon nanotube [1]. On the other hand, graphene has been attracting much attention to be applied nanoelectromechanical systems (NEMS) as well as nanoelectronic device [2]. In particular for future large area graphene NEMS application, novel fabrication technology of suspended graphene structures and possible integration technology with silicon device are key things to be explored.

This study focuses on graphene on a silicon nanowires array fabricated by the transfer-last process developed in Ref. [3]. Chemical and mechanical properties of the nanostructure are investigated by various nano imaging tools such as helium ion microscopy (HIM), AFM and TERS.

## Method/Materials

Graphene on silicon nanowire (SiNW) structures shown in Fig. 1(a) were fabricated as follows. Firstly, approximately 50 nm of amorphous Si film was deposited on SiO<sub>2</sub> by plasma-enhanced chemical vapor deposition. The amorphous Si film was patterned by EB-lithography to be an array of SiNW with 200-300nm in width of the nanowires and with 100-200nm of the gaps in between. Then a single layer graphene grown by chemical vapor deposition was transferred on the SiNW array by wet process. By using transfer-last process, 100  $\mu\text{m}^2$  of uniform suspended graphene areas were obtained [3]. TERS was conducted by using MV4000 (Nanonics Imaging Ltd.) integrated with inVia Raman spectrometer (Renishaw, plc). A schematic of the TERS measurement is also shown in Fig. 1 (a). The diameter of the gold particle on the top of the tip used in this study is around 500nm. Two spectra were taken at a position to extract TERS signal; one is Raman spectrum with the tip contacted and the other is with the tip retracted. Subtraction of the spectrum with the tip retracted from that with tip contacted gives a TERS result where the surface signal is enhanced by the near field. Figure 1(b) shows typical Raman spectra with the tip contacted and with the tip retracted for the sample as well as the TERS result, the difference after subtraction. Four clear peaks are identified at the Raman shift of around 520, 1348, 1582, and 2689 cm<sup>-1</sup>, corresponding to Si substrate and SiNW structures, D peak coming from defects in graphene layer,

G and 2D peaks from honeycomb carbon structure in graphene sheet, respectively. In the TERS result, enhancement of Si peak, G peak and D peak is confirmed, while 2D peak intensity is quite weak, suggesting whether the enhancement takes place or not depends on individual peaks [4].

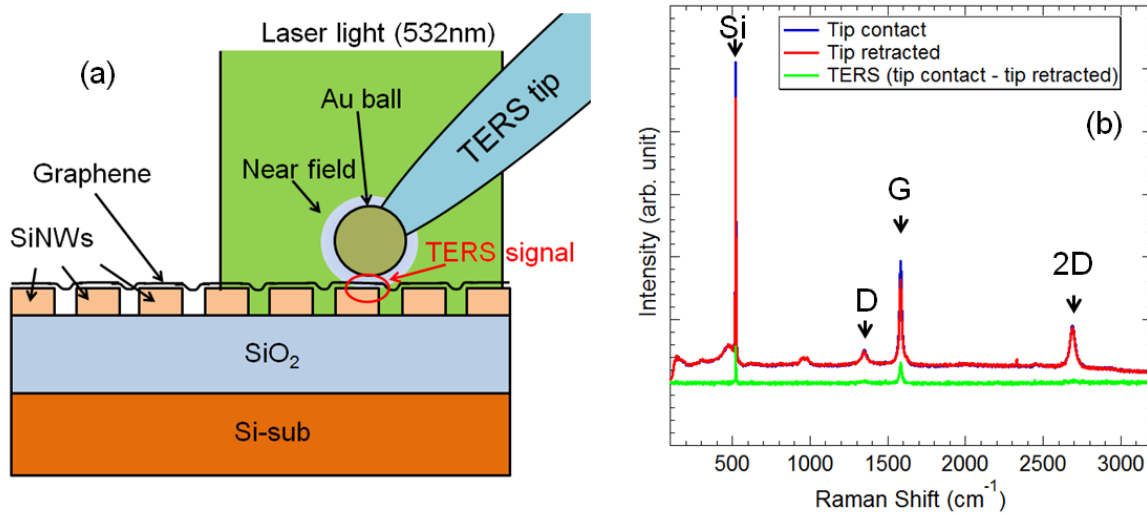


Figure 1. (a) A schematic image of the suspended graphene sample and TERS measurement. (b) Typical Raman spectra taken in TERS measurements.

## Results and discussion

The HIM image and AFM image of the sample are shown in Fig. 2(a) and 2(b), it is clear that the graphene on the gap between the nanowires is suspended. The AFM profile along the trace in Fig. 2(b) is shown in Figure 2(c), suggesting the maximum displacement of the suspended graphene is about 25 nm.

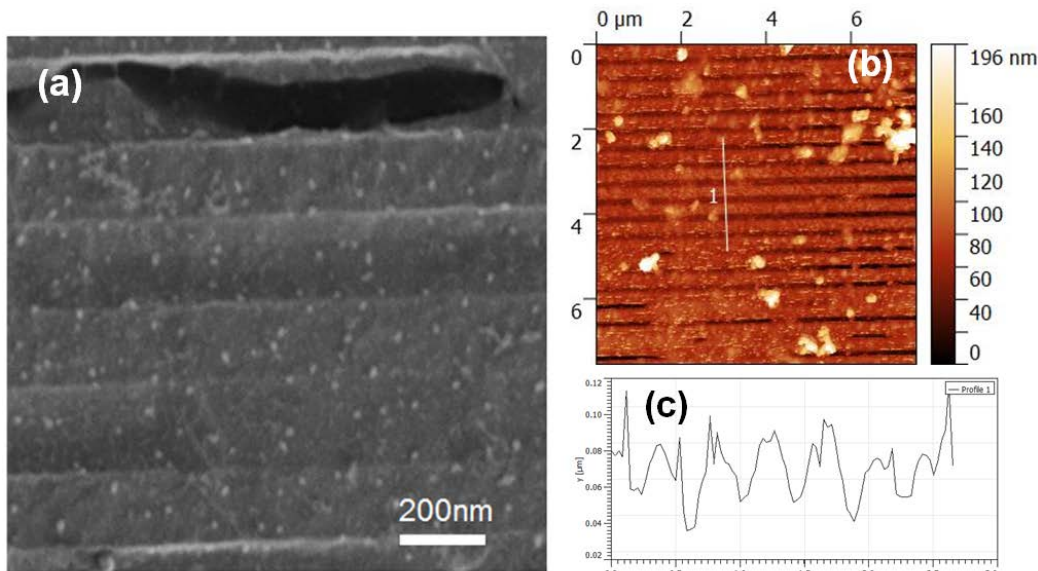


Figure 2. Surface structure of suspended graphene. (a) He ion microscopy image. (b) AFM image. (c) Cross section diagram of AFM image.

An AFM image taken by the tip for TERS is shown in Figure 3(a). A set of Raman spectra with the tip retracted and that of TERS spectra are shown in Fig 3(b) and 3(c) respectively. The spectra were taken along the white trace in Fig. 3 (a) from point A to B (every 50 nm steps). While the Raman spectra without the tip do not show any significant changes from point to point, we can see the difference of the TERS spectra, particularly for the D peak around  $1348 \text{ cm}^{-1}$  that is only identified at the certain points.

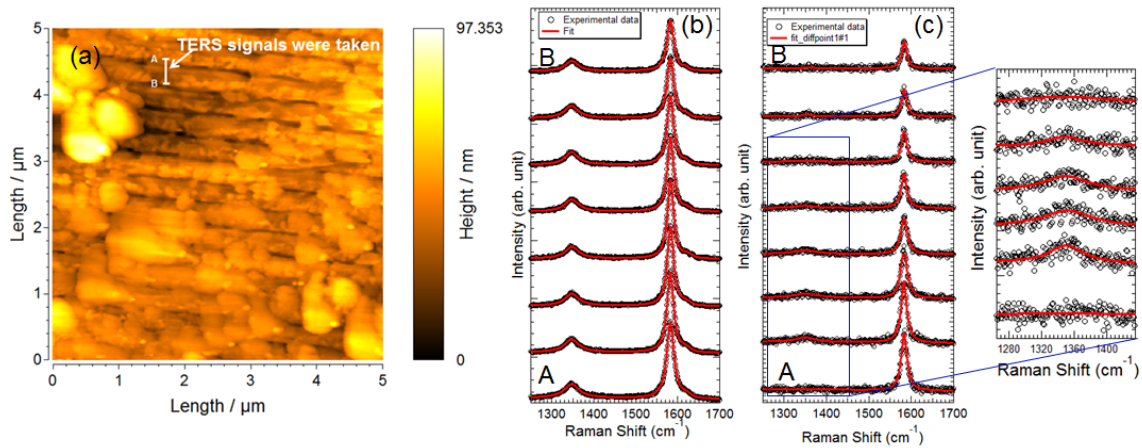


Figure 3. Results of TERS measurement. (a) AFM image obtained by TERS tip. (b) A set of Raman signal with tip retracted. (c) A set of TERS signals.

The Raman and TERS spectra in Fig. 3 are analysed and the peak position of the D peak and G peak is plotted along the scan in Fig. 4(a) and 4(b), respectively. While the peak positions in the Raman spectra without the tip are not changing, emergence and disappearance of the D peak and the shift of the G peak position are observed clearly in the TERS spectra. These changing in peak position of D and G peak might be caused by nanoscale chemical or mechanical interaction from SiNW underlayer. For further analysis, the ratio of the areal intensity of the D peak to that of the G peak  $I(D)/I(G)$  is extracted to evaluate the quality of graphene [5] and plotted from point A to B in Fig. 4(c). Again, there is no significant change in Raman spectra without the tip, whereas  $I(D)/I(G)$  of TERS spectra is localized in the middle of the scanned trace in from the 2<sup>nd</sup> to 5<sup>th</sup> points from Point A, corresponding to the edge of the SiNW. The result is consistent with an idea that defects are possibly induced at the edge of SiNW due to the contact between the graphene and the surface of the SiNWs after the transfer process.

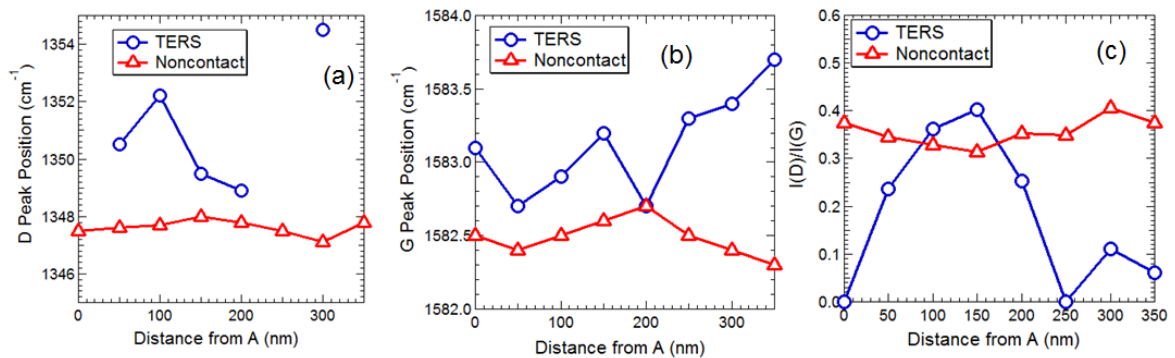


Figure 4. Peak parameters of Raman and TERS spectra. Point A and B in figure 3(a) is correspond to 0 nm and 350 nm in lateral axis of figures. (a) D peak position. (b) G peak position. (c)  $I(D)/I(G)$ .

## Conclusion

TERS was used to investigate local chemical and mechanical properties of suspended graphene integrated with a SiNW array. While there was no significant shift of the major graphene peak position in the Raman spectra without the tip, the shift was observed in the TERS spectra for the graphene located across the edge of the SiNW underneath. Furthermore, localized defect at the edge of SiNW was observed in  $I(D)/I(G)$  distributions with the spatial resolution of approximately 100 nm. TERS is appeared to be helpful for further improvement of graphene-based nanoelectromechanical device fabrication.

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## 5. References

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