Tip-Enhanced Raman characterization of He-ion-irradiated CVD graphene channels

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Graphene has been attracting significant attention for various types of device applications due to its unique properties emerging from the atomically-thin 2-dimentional layer. In particular for micro- and nanoscale device applications, how to control defects in graphene and how to observe the effects of defects are some of the most important issues to understand mechanisms behind device operation and to gain more flexibility in designing device structures [1,2]. While oxygen plasma, ion bombardment and focused ion beam (FIB) have been employed to introduce defects [1-3], helium ion irradiation via Helium Ion Microscope (HIM) is an attractive method because of excellent spatial resolution and position controllability. Effects of He ion irradiation on graphene have been investigated via Raman spectroscopy [4] and transport properties [5]. However to study the edge and boundary between the irradiated and non-irradiated regions, advanced tools with higher spatial resolution would be useful. In this work we have applied Tip-Enhanced Raman Spectroscopy (TERS) for He-ion-irradiated graphene for the first time to study effects of irradiation in details, in particular focusing on the boundary of the irradiated regions.

A sample fabrication process is shown in Fig. 1 (a). A commercial single layer CVD graphene on Si/SiO_2 was used as a substrate. The electrode was pattered by E-beam lithography and then Au/Ti was deposited. After lift-off, the second E-beam pattering is to define the graphene channel with the dimensions of 20 µm in length and 2 µm in width. The sample was irradiated with He ion using a Zeiss Orion He Ion Microscope with an acceleration voltage of 30 kV and with the dose level of 4.46 x 10^{14} ions/cm^2. As shown in a HIM image of the graphene channel in Fig. 1(b), the right-hand-side half of the channel was irradiated. Fig. 2 shows the electrical drain current (I_d) vs. back-gate voltage (V_{bg}) characteristics of the graphene channel before and after the irradiation. P-type nature of the channel and reduction of conductivity after irradiation have been confirmed.

A Nanonics MV4000 integrated with a Renishaw inVia Raman spectrometer was used for TERS measurements. A schematic setup of TERS is shown in Fig. 3. In TERS measurements, the probe tip is moved to a position of interest and then two Raman spectra with tip-retracted and with tip-contacted are taken there. Figure 4(a) shows both the spectra and subtracted TERS spectrum taken at an irradiated region. The strong D peak intensity and the D’ peak shoulder observed in the spectra suggest that introduction of defects was successful. After fitting of a series of spectra with tip-retracted, equivalent to the far-field Raman spectra, and TERS spectra, I(D)/I(G), G peak position and 2D peak position are plotted as a function of the position along the graphene channel in Fig. 4 (b), (c), and (d), respectively. The ratio of the D peak intensity to the G peak intensity, I(D)/I(G) is a well-known index of the amount of the defects in graphene. The clear changes in the I(D)/I(G) and G peak position in the scanned range clearly suggest that the probe scanned across the edge of an irradiated region. Note that the slope of the changes of the I(D)/I(G) and G peak position across the edge region is much steeper for the results from the TERS, suggesting higher spatial resolution has been achieved with TERS. The transition region is roughly estimated to be about 1000 nm in between 2500-3500 nm from the I(D)/I(G) change in TERS. Recently Iwasaki *et al* has determined the change of doping concentration across wrinkle-like defect structures from the analysis of TERS spectra. In the case of the edge of an irradiated area, characteristic features are (1) G peak position is clearly changed while the 2D peak position is not, and (2) a relatively larger red-shift of the G peak position at the edge in TERS. Not only change of doping concentration but also induction of strain by swelling may need to be taken into account for the artificially induced edges.

In summary, we have succeeded in taking TERS spectra across the edge of a He-ion-irradiated region on graphene for the first time, confirmed higher spatial resolution in TERS and found characteristic peak position shifts at the edge of the He-ion irradiated region.

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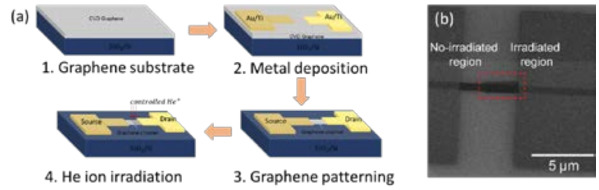

Figure 1 (a) A schematic diagram of He-ion irradiated graphene channel fabrication process flow. (b) Helium Ion Microscope (HIM) image of a graphene channel after fabrication.

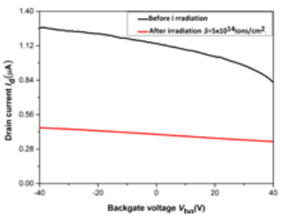

Figure 2 Electrical characteristics of the graphene channel before and after irradiation.

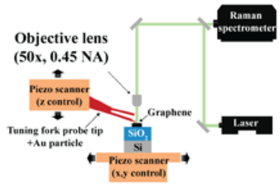

Figure 3 A schematic of the TERS measurement setup with top-illumination.

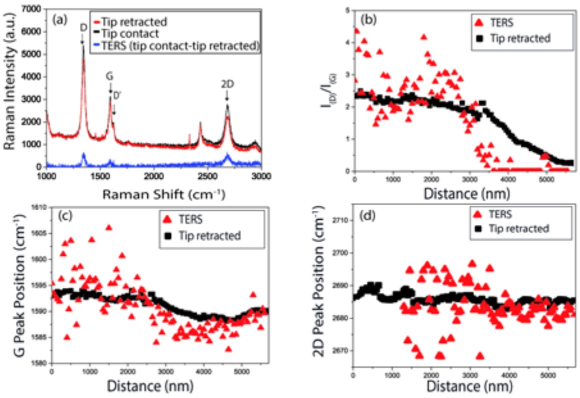

Figure 4. (a) Spectra with tip-contacted and with tip-retracted, and subtracted TERS spectrum taken from the irradiated region. The extracted data from the fitting of the far-field and TERS spectra, I(D)/I(G), G peak position and 2D peak position are plotted along the position on the graphene channel in (b), (c), and (d), respectively.