Defects in graphene: a Raman spectroscopic investigation

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Graphene, the one monolayer thick flat graphite, has been attracting much interest since it was firstly reported in 2004. Graphene has many unique properties which make it an attractive material for fundamental study as well as for potential applications. Raman spectroscopy has been extensively used to study graphene, i.e. identify graphene layer numbers; probe electronic band structure; determine type of edges (zigzag or armchair); measure the concentration of electron and hole dopants. Here, we present our results on the Raman spectroscopic investigation of defects in graphene.

The Raman D peak (~1345 cm⁻¹) is commonly used to estimate the amount of defects in graphitic materials. However, no such peak has been reported for pristine cleaved graphene, this seems suggest that pristine cleaved graphene is a perfect crystal without defects (or defects are undetectable). Here, we point out that, although small and usually unnoticed under the noise level, the D peak is generally present in cleaved graphene and, typically, reaches ~1.5% in amplitude with respect to the G peak.[1] This small D peak could be due to a certain concentration of sp³ adsorbates and vacancies in graphene (in other words, defects), and such resonant scatters can effectively limit the carrier mobility in graphene. By comparing the amplitude of D peak and carrier mobilities obtained in transport measurement; we show that the observed small D peak is sufficient to account for the limited mobilities (~2 m²/Vs) currently achievable in graphene on a substrate.

We have also monitored graphene sheets with defects that are introduced during insulator layer (such as SiO_2 , HfO_2) deposition using different methods (Sputtering, PLD, E-beam evaporation), and our results show that defects were introduced in graphene during deposition and the amounts of defects increase as the graphene thickness decreases. After annealing, the defects in graphene can be greatly reduced.[2] In addition, we also studied the defects in epitaxial graphene grown on SiC substrate [3] and graphene treated by plasma (H₂ and Ar) and electron beam.

Reference:

- 1. Ni ZH, Ponomarenko LA, Nair RR, Yang R, Anissimova S, Grigorieva IV, Schedin F, Shen ZX, Hill EH, Novoselov KS, Geim AK **Nano Letters** 10, 3868-3872 (2010)
- 2. Ni ZH, Wang HM, Ma Y, Kasim J, Wu YH, Shen ZX *Tunable stress and controlled thickness modification in graphene by annealing* **ACS Nano** 2, 1033 (2008)
- 3. Ni ZH, Chen W, Fan XF, Kuo JL, Yu T, Wee ATS, Shen ZX Raman spectroscopy of epitaxial graphene on a SiC substrate Physical Review B 77, 115416 (2008)

Figures



Fig. 1. Raman spectra for pristine and defected graphene (red and blues curves, respectively). In the latter case, the defects were induced by exposure to atomic H. The curves are normalized with respect to the G peak amplitude and shifted for clarity. The inset zooms into the D band region. In our experience, such small D peaks are universally present in Raman spectra of cleaved graphene.



Fig. 2. (a) Raman spectra of single layer graphene before and after the 5 nm SiO_2 deposition. (b) Raman spectra of graphene with different thicknesses as well as that of bulk graphite after 5 nm SiO_2 deposition. Raman images of graphene sheets before SiO_2 deposition generated from the intensity of the D band (c) and G band (d). Raman images of graphene sheets after 5 nm SiO_2 deposition using the intensity of D band (e), and G band (f). The thinner graphene sheets have stronger D band, hence they contain more defects.