

Thermal expansion coefficient of single-layer graphene measured by Raman spectroscopy

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Graphene is attracting much interest due to potential application as next generation electronic material as well as its unique physical properties. In particular, its superior thermal and mechanical properties, including high thermal conductivity and extremely high mechanical strength that exceeds 100 GPa, make it a prime candidate material for heat control in high-density, high-speed integrated electronic devices. For such applications, knowledge of the thermal expansion coefficient (TEC) as a function of temperature is crucial, but so far few reliable measurements on the TEC have been reported [1]. Several authors have calculated the TEC using various models [2-6]. Mounet *et al.* estimated the TEC of graphene as a function of temperature by using a first-principles calculation and predicted that graphene has a negative TEC at least up to 2500 K [6]. Bao *et al.* experimentally estimated the thermal coefficient in the temperature range of 300 – 400 K by monitoring the miniscule change in the sagging of a graphene piece suspended over a trench and found that it is negative only up to ~350 K [1]. It is not yet clear whether this discrepancy between theory and experimental data is caused by uncertainties in the accuracy of the experimental measurements or limitations in the theoretical calculation. Since precise knowledge of the TEC in the temperature range around room temperature is crucial in designing graphene-based devices and heat management systems, more precise measurements are needed. In this work, we analyze the temperature-dependent shift of the Raman G band of monolayer graphene on SiO₂ to estimate the TEC of graphene. We find that the data can be explained in the temperature range of 200 – 400 K with the help of the calculated temperature dependence of the Raman G band of free standing graphene.

When the temperature of a graphene sample fabricated on a SiO₂/Si substrate is raised, two effects should be considered: the temperature dependence of the phonon frequencies and the modification of the phonon dispersion due to strain caused by mismatch of the TEC'ss of the substrate and graphene. The Raman frequency shift of the G band of free standing graphene as a function of temperature has been estimated by first-principles calculations [7]. Since most graphene samples are fabricated on SiO₂ substrates or over a trench held at the edges, the pure effect of temperature change on the Raman spectrum cannot be measured directly and compared with the theory. The discrepancy between the experimentally measured Raman frequency shift and the theoretical prediction can be reconciled by accounting for the TEC mismatch between the substrate and graphene.

Graphene samples used in this work were prepared on silicon substrates covered with a 300-nm-thick SiO₂ layer by mechanical exfoliation of natural graphite flakes. The number of graphene layers was determined by inspecting the line shape of the Raman 2D band. Temperature-dependent Raman spectra of graphene and graphite were obtained while cooling and heating the samples in a microscope cryostat where the temperature could be controlled between 4.2 K and 475 K. The 514.5-nm line of an Ar ion laser was used as the excitation source, and low power (< 0.3 mW) was used to avoid unintentional heating. A long-working-distance microscope objective (40x, 0.6 N.A.) was used to focus the laser beam onto the sample and collect the scattered light. The Raman scattered light signal was dispersed by a Jobin-Yvon Triax 550 spectrometer (1800 grooves/mm) and detected with a liquid-nitrogen-cooled CCD detector. The spectral resolution was ~0.7 cm⁻¹.

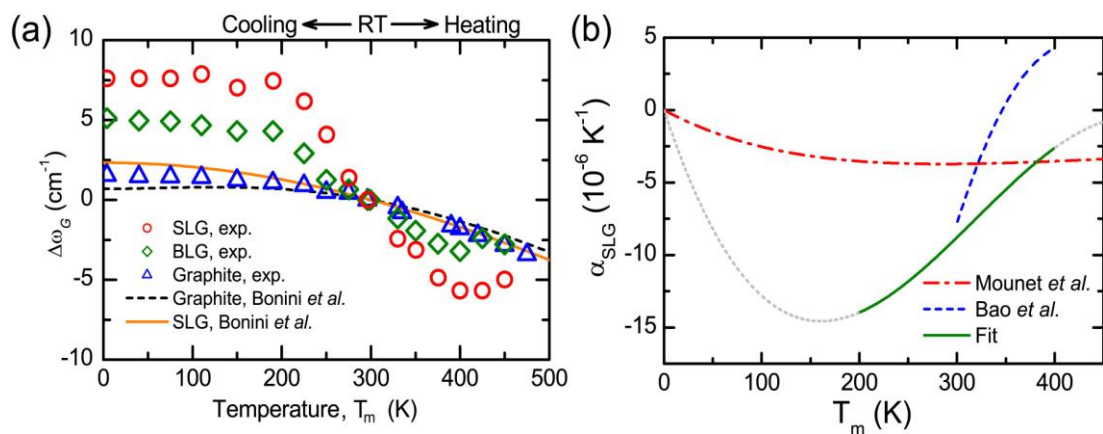
Figure (a) shows the frequency shifts of the Raman G band of single-layer graphene (SLG), bilayer graphene (BLG), and graphite samples as functions of temperature. The Raman peaks redshift as temperature rises and blueshift as temperature falls from room temperature. The Raman peak shift of SLG as a function of temperature is largest. Temperature-dependent Raman shift is commonly attributed to thermal expansion of the lattice and an anharmonic effect which changes the phonon self-energy. As the temperature rises, the SiO₂ layer expands whereas the graphene sheet contracts. This TEC mismatch would induce a biaxial tensile strain on the graphene sample. When the sample is cooled, a compressive strain is induced instead. In order to interpret our data correctly, we should consider the effect of strain on graphene induced by the TEC mismatch between the SiO₂ layer and the graphene sheet.

We estimated the TEC by fitting our data to the theoretical prediction [7] of temperature dependence of the Raman G band of *free standing* graphene. Figure (b) shows the temperature dependent TEC obtained from the fitting. TEC at room temperature is estimated to be $-9 \times 10^{-6} \text{ K}^{-1}$, which is similar to the previous experimental value of $-7 \times 10^{-6} \text{ K}^{-1}$ [1].

References

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Figures



(a) Raman frequency shifts of graphene and graphite as functions of temperature. (b) Thermal expansion coefficient of single layer graphene that gives the best fit between data and theoretical estimate.