Stress-transfer at the nanoscale in simply-supported and embedded monolayer graphene/ polymer systems

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Efficient stress transfer in two-phase composites is central to the attainment of satisfactory mechanical performance. In polymer matrix composites, the compliant polymer surrounds the reinforcing phase, which is either in the form of dispersed micro- particles of high rigidity or in the form of micro-fibers. Recently, graphene is introduced as an ideal candidate for reinforcing polymer composites, due to its extraordinary physical and mechanical properties.

In this work, we examined the mechanical behavior of simply-supported and embedded graphene flakes on polymer substrates (such as PMMA, SU8), using the cantilever beam approach in tandem with Raman spectroscopy in order to record the stress/ strain transfer mechanism. Particularly, the cantilever frame was placed above a Melles Griot three – axis nanopositioning stage. At each deflection level, the stage was moved every 50 nm, from the edges until a distance up to 4μm (bulk), collecting simultaneously Raman spectra and allowing to perform a detailed mapping across a specific line on 1LG flakes. Raman spectra are measured at 785 nm & 514.5 nm using a MicroRaman (InVia Reflex, Rensihaw, UK) spectrograph, monitoring the profiles of 2D and G peak.

In the case of simply-supported flake, systematic shifts of the ω_{2D} are obtained as one move at steps of 100 nm from the edge of the flake towards the middle. These systematic shifts are evident at all strain levels but also in the as-received material. At 0% applied strain, there is almost a constant distribution of ω_{2D} Raman wavenumbers starting from ~2600 cm^{-1} at the edge up to a distance of 1.5μm and then moving to lower values at greater distances (~2580 cm^{-1}). It is a shift of almost 20 cm^{-1}, which cannot only be attributed to strains induced by the exfoliation procedure. The ω_{2D} phonon frequencies are sensitive to electrostatic interactions (in our case probably emanating from the substrate) causing its shifting to higher or lower values depending on doping. At the same time, the corresponding ω_G profile fluctuates between a much narrower range (from 1578 cm^{-1} to 1583 cm^{-1}), which indicates that the ω_G is not affected to the same extent, due to the much lower sensitivity of this phonon to electrostatic interactions . The above mentioned fluctuations at the edges, which are more intense at lower levels, are present in all applied strain levels, implying the presence of additional influences, such as doping that occurs via contact with the substrate.

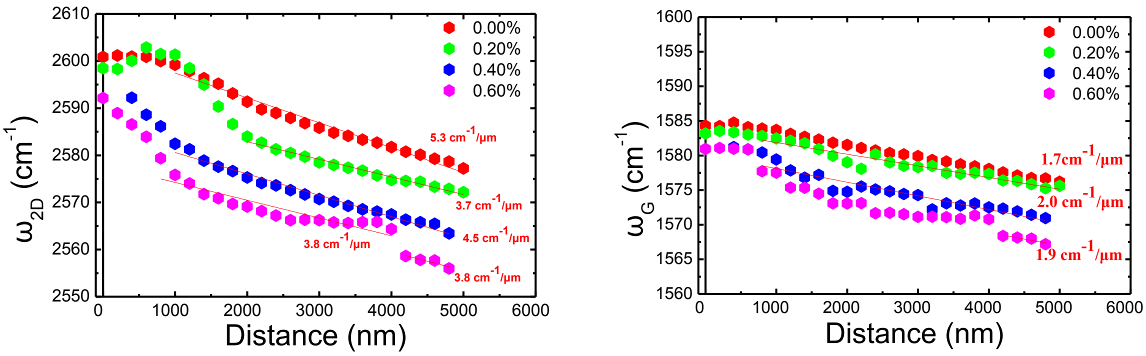

Figure 1. The ω_{2D} (left) and ω_G (right) distributions for various levels of strain are shown along a sampling line

For distances > 1.0 μm it seems that ω_{2D} has almost the same slope for all the applied strains (~ -4.7 cm^{-1}/μm), while the ω_G follows a similar linear profile with almost half strain sensitivity (~ -2.0 cm^{-1}/μm). Both values are indicating an adequate stress transfer from the substrate to the bulk of the graphene flake. In Figure 2, we plot on the same graph the values of the two phonons for the various strain levels. As has been well established previously, slope values higher than 2.5 normally indicate the presence of chemical doping in the regions of sampling. Indeed in this case some values marginally greater than 2.5 appear at low strains for which the observed significant shift of both phonons due to tensile loading is minimal. Provided that there is no severe doping at the edges, there is an efficient stress transfer through the edges into the "bulk" of the graphene flake as it is presented on Fig. 3

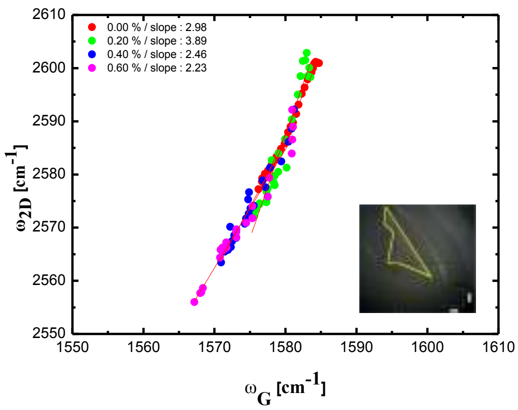

Figure 2: The correlation of ω_{2D} as a function of ω_G distributions for various levels of strain for a simply-supported flake .The measurements took place using a 785 nm excitation laser

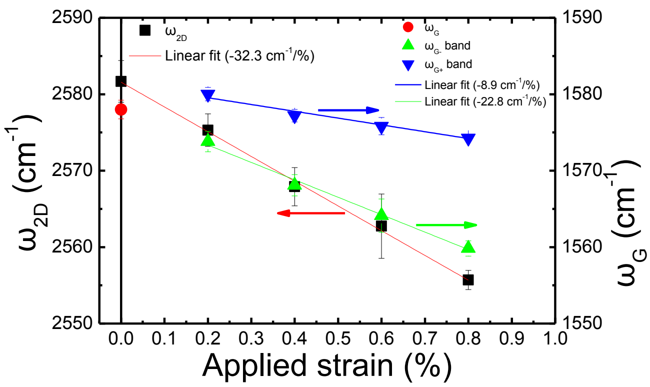

Figure 3: The linear relation of ω_{2D} and the splitting of ω_G phonon in the case where there is a sufficient stress transfer

In the embedded case, the experimental data of the position of the ω_{2D} as a function of distance from the free end are plotted in Fig. 4 for the as-received condition but also at various increments of tensile strains. As it seems in Figure 4, ω_{2D} shifts from the edge towards the middle, indicating stress transfer from the substrate to the graphene. Close to edges (< 1.5 μm) fluctuations of the ω_{2D} values are more intense at lower levels, implementing the presence of additional influences similar to the simply-supported case.

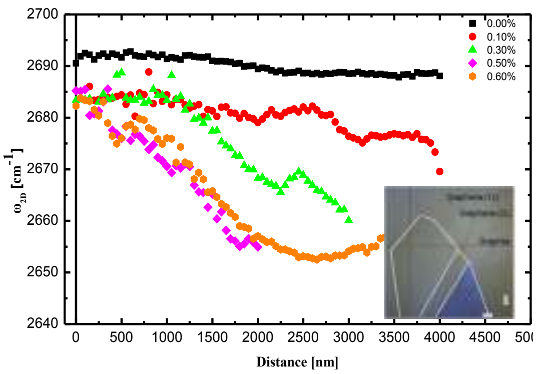

Figure 4. The ω_{2D} distributions for various levels of strain are shown along a sampling line in a embedded flake.

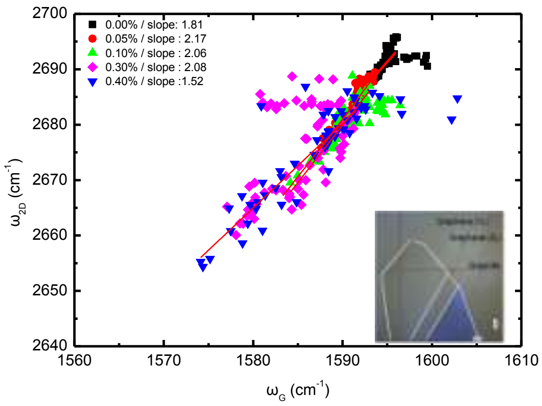

Figure 5. The correlation of ω_{2D} as a function of ω_G distributions for various levels of strain for an embedded flake .The measurements took place using a 514 nm excitation laser

In case of nanocomposite materials, the additional influence at the edges are more intense. However, if good adhesion is succeeded, there is sufficient stress transfer through the edges into the bulk area. It seems that the edges completely define how the stress is transferred at the bulk area. Therefore in the case of embedded sample, where the edge influences are less intense, there is an adequate stress transfer to graphene causing not only the shifting of ω_{2D} & ω_G but also the splitting of the latter to ω_{G+} and ω_{G-} components with the uniaxial applied strain. The obtained strain sensitivity for the embedded samples is presented in the following graph below.

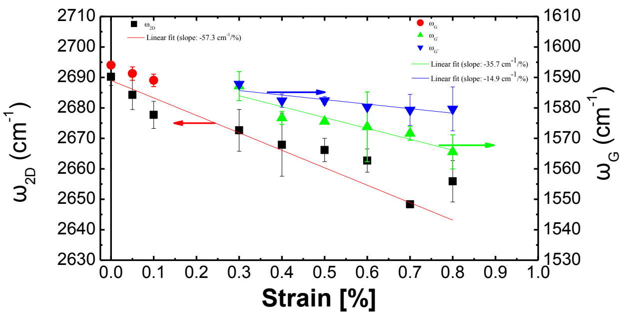

Figure 6. The ω_{2D} & ω_G peak positions for an embedded graphene in polymer beam in tension, where the edge influences are less intense

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