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Strain engineering in graphene by laser irradiation

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We demonstrate that the Raman spectrum of graphene on lithium niobate can be controlled locally by continuous exposure to laser irradiation. We interpret our results in terms of changes to doping and mechanical strain and show that our observations are consistent with light-induced gradual strain relaxation in the graphene layer. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4907776]

Graphene, a recently discovered two-dimensional array of carbon atoms arranged in a honeycomb lattice,[1,2] has emerged as a technological material with properties that are expected to revolutionize a number of fields, such as electronics,[3] photonics,[4] and plasmonics.[5,6] One of the most attractive characteristics of graphene is the ability to control its electronic and optical properties through the charge carrier density. This can be achieved by chemical,[7] electronic,[1] optical,[8–10] or mechanical[11] means. Moreover, it has been suggested that the electronic and optical properties of graphene depend strongly on its strain distribution.[12] In fact, it has been predicted that high values of strain can dramatically change the electronic band structure of graphene and may even lead to the emergence of a bandgap.[11,13] Hence, the ability to control the mechanical properties of graphene is expected to facilitate the emergence of future electronics and photonics applications.

The properties of graphene are typically probed by Raman spectroscopy which is considered as a non-invasive method to retrieve information about strain and charge carrier concentration.[14,15] It has been demonstrated that laser irradiation even at low powers can lead to both reversible[8] and irreversible changes in graphene.[9,10] Typically, such changes are related either to charge carrier doping originating from the presence of charge traps in the substrate as in the latter case or they arise from hydrophilic/hydrophobic properties of the substrate as in the former case. Here, we study the effects of laser illumination on graphene deposited on lithium niobate and silicon oxide substrates. Whereas graphene on the latter shows increased hole doping upon prolonged laser exposure, we show that graphene on lithium niobate exhibits increasingly stronger Raman shifts that indicate relaxation of compressive strain. Our results provide an avenue towards spatial control of graphene's mechanical, and consequently optical and electronic, properties by light.

The substrate-induced changes in the properties of graphene were studied by Raman spectroscopy of graphene on high quality single crystal substrate ($LiNbO_3$). As control cases we employed suspended graphene as well as graphene deposited on silicon oxide on Si. In all cases, the graphene films were grown on polycrystalline Cu at temperatures up to 1000 °C by low pressure CVD process using a mixture of ethylene and hydrogen.[16] After the growth, the graphene-on-Cu samples were coated with poly-methyl methacrylate (PMMA) and the PMMA/graphene films were separated from the Cu foils by etching in an aqueous solution of iron nitrate. The PMMA/graphene films were then transferred on to the substrates and the PMMA was removed by acetone. We deposited graphene on three different types of substrates: lithium niobate, structured lithium niobate, and a standard SiO_2/Si substrate. The structured lithium niobate consisted of a series of long ridges fabricated by a combination of spatially selective ferroelectric domain inversion and wet etching.[17,18] The microstructured crystals used were etched to produce deep ($\sim 100 \mu m$) trenches, 0.5 mm long and $\sim 100 \mu m$ wide. The width of the trenches gradually reduced to a point at their extremes and it was on these locations where suspended graphene was observed over gaps of $\sim 10 \mu m$.

Measurements were performed in an INVIA Raman spectrometer. Input from a 532 nm laser was focused by 0.75 NA objective to a diffraction limited spot of roughly $\sim 1 \mu m \times 1 \mu m$. The input power of the laser beam was ~ 25 mW. A number (at least 10) of consecutive non-polarized measurements at a fixed location on the sample were performed to characterize the effects of laser irradiation on graphene. Each measurement lasted approximately 70 s. Here, graphene exposure and Raman spectral acquisition were performed simultaneously by employing a single laser beam. All Raman spectra were measured in ambient conditions.

In Fig. 1, we present a typical Raman spectrum of graphene on lithium niobate. A number of characteristic peaks can be discerned, superimposed on a background which becomes prominent at low wavenumbers. This background originates from the Raman peaks of lithium niobate and corresponds to the high wavenumber tail of these peaks.[19] In addition, lithium niobate exhibits a strong Raman peak at approximately 1740 cm^{-1} which is a signature of a two longitudinal optical phonon process.[19] The remaining four peaks can be attributed to the graphene monolayer: the lowest frequency peak (D) at around 1360 cm^{-1} is a defect activated
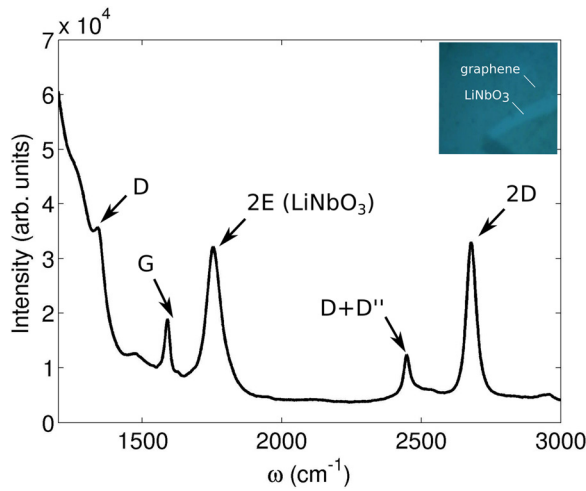
FIG. 1. Raman spectra of graphene on lithium niobate. The D, G, D + D″, and 2D peaks originate from the graphene monolayer, while the 2E peak is associated with the lithium niobate substrate. Inset: microscope photograph of a characteristic region on the sample, where part of the graphene has been peeled off revealing the lithium niobate substrate.

phonon process, the G peak at $1580 \, \text{cm}^{-1}$ corresponds to the main in-plane vibrational mode, whereas the 2D peak at $2700 \, \text{cm}^{-1}$ is the second overtone of the D-peak. Finally, the D + D″ peak at $2490 \, \text{cm}^{-1}$ occurs due to a combination of a phonon associated with the D-peak and a phonon from a longitudinal acoustic branch. The intensity ratio I_{2D}/I_G together with the narrow width of the 2D peak provides a reliable indicator for the number of graphene layers in the system.[15] Our measurements are consistent with the presence of a single graphene monolayer.

Figure 2 presents the effect of prolonged exposure on three Raman peaks for the graphene on lithium niobate sample: the G and 2D peaks of graphene, as well as the 2E lithium niobate peak. After 15 consecutive measurements (corresponding to a total exposure time duration of about 17 min), the G and 2D peaks of graphene shift by $\omega_G - \omega_G^{(0)} = 2.2 \, \text{cm}^{-1}$ and $\omega_{2D} - \omega_{2D}^{(0)} = 7.1 \, \text{cm}^{-1}$, respectively. In contrast, the 2E peak of lithium niobate remains unaffected. At the same time, both graphene peaks become narrower by $\gamma_G - \gamma_G^{(0)} = 2.2 \, \text{cm}^{-1}$ and $\gamma_{2D} - \gamma_{2D}^{(0)} = 7.1 \, \text{cm}^{-1}$, while the 2E peak retains its width.

The origin of the light-induced graphene-specific changes in the Raman spectrum is investigated further by comparing the response of graphene on different substrates. In Fig. 3(a), we show representative results of successive graphene exposures in terms of changes in the G and 2D peak Raman shifts for the graphene on lithium niobate samples (red triangles), as well as for the control samples of suspended graphene (blue circles), and graphene on silicon oxide (green squares). The most dramatic change occurs in the lithium niobate substrate case, where both the G and 2D peak shift gradually to higher frequencies. On the contrary, the SiO₂/Si sample exhibits a strong shift only for the G peak ($\omega_G - \omega_G^{(0)} = 2.87 \, \text{cm}^{-1}$), whereas the 2D peak retains its initial frequency position. Finally, the suspended graphene case presents very small shifts for both peaks.

The evolution of the graphene Raman peaks of Fig. 3(a) implies laser-induced changes in graphene that are specific
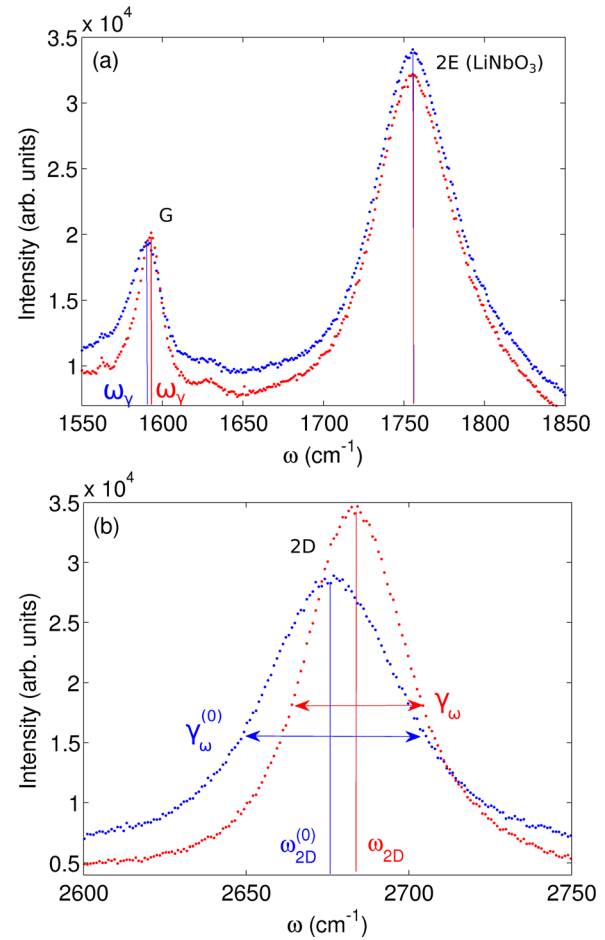

FIG. 2. Effects of laser illumination on the graphene G (a) and 2D (b) Raman peaks. Blue spectra correspond to the first exposure of a 15 exposures long set, whereas red to the last one. For comparison, (a) shows also the 2E peak of lithium niobate.

to and mediated by the substrate. In particular, the main mechanisms that can influence the Raman spectrum of graphene are modulation of the charge carrier density and changes in tensile/compressive strain. Recently, an elegant method has been suggested to distinguish between the effects of strain and doping on the graphene Raman spectra, based on the different dependence of the G and 2D peak positions to these factors.[20] In particular, changes in the Raman spectrum can be traced in the (ω_G, ω_{2D}) plane, where depending on the slope of this trace one can perform a vector decomposition of such changes to a strain-induced and a doping-induced component. More specifically, biaxial strain was associated with a slope of $d\omega_{2D}/d\omega_G = 2.2$, whereas hole doping was shown to result in a slope $d\omega_{2D}/d\omega_G = 0.70$.[20] These trends are represented by the two sets of parallel thin lines in Fig. 3(a) along which either strain or doping remains constant. Assuming that in pristine graphene the positions of its G and 2D peaks are $\omega_G^{(i)} = 1581 \, \text{cm}^{-1}$ and $\omega_{2D}^{(i)} = 2677 \, \text{cm}^{-1}$,[20] respectively, the initial peak positions of both the graphene on lithium niobate and graphene on silicon oxide samples indicate strong hole doping ($n \simeq 10^{13} \, \text{cm}^{-1}$) and compressive strain ($\epsilon \simeq 0.1\%$). In contrast, suspended graphene presents a behaviour close to that of pristine graphene with negligible strain, but a residual hole doping ($n = 4 \times 10^{12} \, \text{cm}^{-2}$).
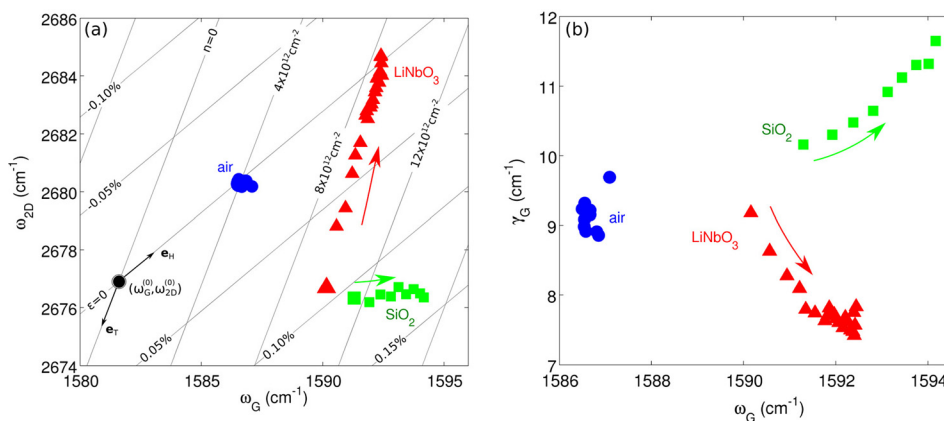
FIG. 3. Evolution of the 2D and G Raman shifts (a) and corresponding linewidths (b) of graphene on lithium niobate (red triangles), graphene on SiO_2 (green squares), and graphene suspended over ridges in lithium niobate (blue circles). Markers correspond to consecutive measurements, while the arrows show the chronology of the experiments. Straight lines in (a) represent lines of constant strain (ϵ) and doping (n), with slopes of $d\omega_{2D}/d\omega_G = 2.2$ and $d\omega_{2D}/d\omega_G = 0.75$, respectively.

Applying a vector decomposition in our measurements, we observe that the graphene on lithium niobate trace is parallel to the lines of constant doping, while strain reduces to zero. On the other hand, laser irradiation of graphene on silicon oxide leads to a horizontal shift, consistent with an increase in hole doping as well as in compressive strain, in agreement with recent experiments performed by laser pulses.[9,10] This interpretation is also supported by the behaviour of the linewidth of the G peak, presented in Fig. 3(b), where a substrate-dependent response was observed. Whereas illumination of graphene on lithium niobate leads to substantial narrowing, in the case of the silica substrate, the opposite trend is observed. The opposite trends for the lithium niobate and silicon oxide samples can be attributed mainly to changes in strain, as doping-induced changes in the G peak linewidth saturate at moderate doping levels.[21] Indeed, strain anisotropy leads to splitting of the G peak,[22,23] which in our measurements would manifest as an effective broadening with increasing strain due to the low strain levels. Finally, as expected, illumination of suspended graphene has limited effect on the peak linewidth.

The results presented here indicate that laser irradiation can be employed in order to control locally the strain in graphene monolayers. Such effects may arise due to a complex interaction of optical, mechanical, thermal, and electrostatic nature between graphene and substrate. Due to the slow, cumulative nature of the effect, we argue that the changes are mediated by absorption-induced heating of graphene and the ferroelectric substrate. However, our observations cannot be attributed directly to heating of the graphene layer as this would lead to a red shift of the Raman peaks,[24] in contrast to the non-volatile blue shifts reported here. Based on the different behaviours of graphene on different substrates, we trace the origin of the observed effects to the thermal properties of the substrate and the graphene layer. In particular, graphene has a negative thermal expansion of the order of about -8×10^{-6} K^{-1},[25] whereas in the case of lithium niobate the thermal expansion coefficient is $7.5-15 \times 10^{-6}$ K^{-1} (depending on orientation).[26] We argue that it is the high values and difference in sign of the thermal expansion coefficients for the two materials that leads to strain relaxation upon heating. This is also corroborated by the fact that in the case of the silica substrate, where the expansion coefficient is an order of magnitude smaller than that of lithium niobate,[27] no strain relaxation is observed.

Another mechanism that appears plausible involves electrostatic forces between the graphene layer and the substrate. Such forces could arise due to the accumulation of charges in the illuminated area of the sample in the graphene and/or lithium niobate substrate. In fact, lithium niobate has strong pyroelectric properties and hence an increase in temperature will lead to the accumulation of surface charges.[28] Such charges can also be generated through the activation of defects close to the surface of lithium niobate. However, in both cases, we would expect that accumulation of charges in lithium niobate would lead to changes in the charge carrier density of graphene. This stands in contrast with the experimental measurements of graphene on lithium niobate, where changes in doping are negligible. We attribute the absence of doping to the low density of defect states in the lithium niobate single crystal and its low absorption of the incident light. Although we argue that electrostatic interactions play only a minor role in our experiments, we expect such mechanisms to become particularly important in doped ferroelectric crystals (i.e., Fe:LiNbO$_3$), where a significant contribution from photoinduced charges is expected.[29]

In conclusion, we have demonstrated that the strain of graphene on lithium niobate can be controlled at the microscopic scale by laser irradiation. We argue that the observed effect is mainly due to the large thermal coefficient mismatch between the graphene and the substrate leading to relaxation of intrinsic strain. Further studies will focus on determining the localization extent of the effect and on demonstrating more complex spatial variations of strain.

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