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Raman spectroscopy is an ideal tool for the characterization of strained graphene. Biaxial strain, in particular, allows for more reliable calculation of the Grüneneisen parameters than uniaxial strain. However, the application of biaxial strain is rather difficult to achieve experimentally, so all previous studies reported on graphene subjected to relatively small biaxial strains (0.1%–1%), in contrast to uniaxial strain above 10%. Here, we report a simple fabrication technique to produce pressurized and stable graphene membranes that can support differential pressures up to 14 bar, corresponding to a reversible strain up to ~2%. We find that the Grüneneisen parameters remain constant even for the largest strains achieved, in agreement with the theoretical predictions. However, for strains above 1%, a distinctive broadening of both the G and 2D peaks was observed for biaxial strain. We attribute this to the nanoscale variations of strain in the membrane within an area comparable with the laser spot size. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4952972]

Raman spectroscopy is a fast, non-destructive, and well-established technique for the investigation of carbon nanostructures.1–4 It proved to be particularly useful for investigating the properties of graphene: it is able to distinguish monolayer and bilayer graphene from graphite and few-layer graphene,5 identify superlattice effects,6,7 atomic arrangement at the edges,8 and to probe the amount of doping,9 disorder,10–12 and strain.13,14

Strain is of particular importance because nanoscale variations of strain strongly affect the carrier mobility in graphene15,16 and the electronic and optical properties of heterostructure-based devices.7,17 The possibility to apply controlled strain is also very attractive, as this would allow simple tuning of the electronic and optical properties of graphene.18–20 However, most of the Raman studies focused on graphene under small strain, especially for the biaxial configuration that allows for more reliable measurements of the Grüneneisen parameters compared to uniaxial strain.13,21 Studies of the effect of biaxial strain on graphene are typically performed in the range 0.1%–1% of strain,14,22–27 while uniaxial strain above 10% was reported.28 Only one study29 claims to achieve biaxial strains up to 20%. However, the corresponding Raman spectra show a shift of the 2D peak of just 10–20 cm−1, which does not appear compatible with such a large strain. It is therefore important to find better ways to apply biaxial strain in order to study the Raman spectrum of graphene under larger strain.

In our previous work, we used pressurized membranes to study the Raman spectrum of a bilayer under a biaxial strain up to ~1%.14 However, under our configuration, membranes made of monolayer graphene were not strong enough to sustain larger strains. Here, we present an improved fabrication technique that allowed us to measure highly pressurized (up to ~14 bar, compared to 2 bar as previously reported) graphene membranes by Raman spectroscopy. This allowed us to study the Raman spectrum of strained graphene up to 2% of biaxial strain. The deformation of the membrane was completely reversible, i.e., the membrane could be depressurized to 0% strain and pressurized to different strains repeatedly before becoming damaged. This was confirmed by performing Raman spectroscopy on the membrane after releasing the pressure. No difference in the Raman peak positions was observed between the measurements taken at zero pressure and on the released membrane (Figure 1). Note that although the membranes can be repeatedly pressurized and depressurized several times, the Raman measurements are challenging as the setup has to be inserted under the optical microscope and connected to the piping

![FIG. 1. Raman spectra of a graphene membrane measured before pressurizing and after depressurizing the chamber. The Raman spectrum shows no damage of the membrane after pressurization.](http://dx.doi.org/10.1063/1.4952972)
line, and has to be perfectly stable during the measurements—the laser spot needs to be in the center of the membrane to achieve biaxial strain conditions. The measurements also require rather long time due to the use of low power (to avoid damage) and the long-distance objective.

Figure 2(a) shows a schematic of the setup used in this work. To fabricate the suspended graphene membrane, a double coated Si/SiN_x wafer is first etched to obtain a 500 nm thick, free standing SiN_x membrane of typically 70 × 70 μm^2 in area. Then, a circular aperture (5–10 μm in diameter) is drilled into the SiN_x membrane and the back side of the devices is covered with a reinforcing metal layer of ~100 nm thickness (10 nm Cr and 90 nm Au or Cu). Finally, a micro-mechanically exfoliated single-layer graphene is transferred from silicon and suspended over the circular aperture with the AFM tip. However, this method can be applied only at very low pressure; higher pressures break the membrane, hence, the need to use a different geometry, as shown in panel (a). (c) SEM micrograph of the same membrane.

FIG. 2. (a) Experimental setup. Monolayer graphene is suspended over a circular aperture (10 μm diameter) etched into a Si/SiN_x substrate. The substrate is covered with a metallic layer (~100 nm thickness) to improve the mechanical stability. The device is used to seal a chamber containing pressurized He gas. The Raman spectrum is monitored at several differential pressures ranging from 0 to 14 bar. (b) AFM image of a pressurized membrane (~1 bar). Note that this measurement was performed by applying the pressure from the back side (opposite of what shown in panel (a)) due to the difficulty of approaching the membrane through the aperture with the AFM tip. However, this method can be applied only at very low pressure; higher pressures break the membrane, hence, the need to use a different geometry, as shown in panel (a). (c) SEM micrograph of the same membrane.

FIG. 3. Raman spectra of a graphene membrane measured at unpressurized and pressurized (~2% strain) membrane. The Raman peaks are strongly down-shifted when the strain is applied: the G peak position moves from ~1586 cm^{-1} to ~1476 cm^{-1}, while the 2D peak moves from ~2679 cm^{-1} to ~2441 cm^{-1}. This is in agreement with the Raman spectrum of graphene under tensile strain. We note that the G and 2D peak positions of unstrained graphene do not correspond to those expected for suspended graphene. A likely reason for this is that the membrane becomes slightly doped and...
also strained during fabrication, which can explain the relatively high values observed for both the G and 2D peak positions without any applied pressure. The small contribution of strain and doping, however, do not strongly affect the relative changes of the peak positions with strain ($\Delta\omega/c$), Figure 4. Note that the uncertainties in strain values shown in the figure are mostly originating from the uncertainty in pressure measurements. Moreover, for low differential pressures, the strain is likely to be over-estimated due to the difficulty of controlling a very small differential pressure inside the chamber. The average rates of change of the Raman shift with the strain for G and 2D peaks are $\Delta\omega(G)/c = -62\,\text{cm}^{-1}/\%$ and $\Delta\omega(2D)/c = -138\,\text{cm}^{-1}/\%$, respectively. This is in very good agreement with the calculated $\Delta\omega(G)/c$ and $\Delta\omega(2D)/c$ for biaxial strain under 5%, which has been reported in the range of $-59\,\text{cm}^{-1}/\%$ and $-144\,\text{cm}^{-1}/\%$, respectively.\textsuperscript{13,21} Also, the ratio between the rates is 2.225, in excellent agreement with a ratio of 2.2, as experimentally and theoretically reported in Refs. 35 and 36.

Because our fabrication technique allows straining graphene over a large range, we can now investigate if and how the Raman spectrum changes from small to large strains. Calculations have shown that the Grüneisen parameters of graphene can change with strain: under large biaxial strain either compressive or expansive, $\Delta\omega(G)/c$ is expected to be significantly different than that for small strains, being smaller in the case of compressive strain and larger in the case of expansive strain.\textsuperscript{13} Our data are in very good agreement with the calculations of Ref. 21 that reports a G peak Grüneisen parameter of 1.8 in the range of strain investigated in our work. This implies that a higher strain, possibly above 5%, is needed to change the fundamental properties of graphene.\textsuperscript{21}

However, a clear change in the Raman spectrum is observed for strain beyond 1%: both the G and 2D peaks appear broader, Figure 2. The full width at half maximum (FWHM) strongly increases above 1% strain, Figure 5: FWHM(G) increases from $\sim 13\,\text{cm}^{-1}$ to $23\,\text{cm}^{-1}$, while FWHM(2D) increases from $\sim 22\,\text{cm}^{-1}$ to $45\,\text{cm}^{-1}$. Broadening of the 2D peak has been observed previously for uniaxial strain\textsuperscript{13} but not for biaxial strain, as the latter configuration does not affect the reciprocal position of the Dirac cones; so it is not expected to affect the resonant activation mechanism of the 2D peak.\textsuperscript{37} As this change becomes clear only above 1% strain, the broadening could be related to a loss of the biaxial configuration. However, in this case, we would expect to see the splitting of the G peak, as in any type of strain configuration that is not biaxial.\textsuperscript{13} Considering that the strain we were able to achieve is rather large, the splitting should be clearly visible: under uniaxial strain, for example, the splitting is already visible at $\sim 0.6\%$ strain.\textsuperscript{13} Therefore, the peak broadening does not look like an artifact.

A recent work\textsuperscript{38} reported broadening of the G and 2D peak, when measured under a magnetic field of 8 T. The high magnetic field suppresses any effect from doping on the width of G peak; therefore, the broadening has been attributed to a local variation of strain within the laser spot size. Indeed, broadening is clearly observed whenever significant nanometer-scale strain variations are present, i.e., next to wrinkles, bubbles, etc. The ratio between FWHM(2D) and FWHM(G) reported in Ref. 38 is $\sim 2.2$. Following this reasoning, we also calculated the ratio between FWHM(2D) and FWHM(G) at different strains and found it to be $\sim 2.3$ on average, similar to Ref. 38. Therefore, the broadening observed at high biaxial strain could be explained by assuming that such a large strain starts deforming locally graphene, by producing “strain-puddles” over an area comparable with the laser spot size ($\sim 500\,\text{nm}$).

In summary, we have introduced a simple technique for the fabrication of pressurized and stable graphene membranes that can hold up to 14 bar and $\sim 2\%$ strain. Compared
to previous studies, our device offers controllable, reversible application of biaxial strain on single-layer membranes. No changes in the Grüneisen parameters are observed in the range of strains investigated. However, broadening of the G and 2D peak is observed at strains above 1%. This has been attributed to large nanometer-scale strain variations produced within the laser spot size.

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