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Tailoring the thermal expansion of graphene via controlled defect creation

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ABSTRACT

Contrary to most materials, graphene exhibits a negative thermal expansion coefficient (TEC), i.e it contracts when heated. This contraction is due to the thermal excitation of low energy out–of–plane vibration modes. These flexural modes have been reported to govern the electronic transport and the mechanical response of suspended graphene. In this work, we systematically investigate the influence of defects in the TEC of suspended graphene membranes. Controlled introduction of low densities of mono-vacancies reduces the graphene TEC, up to one order of magnitude for a defect density of 5×10^{12} cm^{-2}. Our molecular dynamics simulations reproduce the observed trend and show that TEC reduction is due to the suppression of out–of–plane fluctuations caused by the strain fields created by mono-vacancies in their surrounding areas. These results highlight the key role of defects in the properties of "real-life" graphene, and pave the way for future proposals of electronic and mechanical defect engineering.

1. Introduction

Graphene exhibits intrinsic out–of–plane thermal fluctuations that have dramatic effects on its conformation [1], electronic [2,3] and thermal transport properties [4], and on its elastic response [5]. One of the most prominent consequences of the presence of these flexural modes is the graphene large negative thermal expansion coefficient (TEC) [6–14]. The amplitude of these very soft acoustic ZA phonons rapidly increases with temperature and translates into an actual contraction of the material.

The thermodynamical theory of membranes predicts that out–of–plane thermal fluctuations should renormalize the elastic constants of graphene, making it softer as the amplitude of the fluctuations grows [5,15]. Lopez-Polin et al. [16] reported an increase in the Young's modulus of graphene for a dilute density of single–atom vacancies. In order to address this counterintuitive result, these authors suggested, without further proof, that the induced defects ironed the thermal fluctuations out, unveiling the bare (non-renormalized) Young's modulus of graphene. This scenario implies that, not only the Young's modulus, but all the elastic constants should be affected by the presence of defects.

Graphene TEC is an ideal candidate to explore the interplay between intrinsic thermal vibrations and defects, and to confirm or reject the conjecture made in Ref. [16]. Moreover, this interaction is key to understand the physics underlying many temperature effects in real-life graphene, from the behavior of nanoresonators [17] to the diffusion of water nanodroplets on graphene [18]. However, measuring graphene TEC is a challenging task since conventional experimental techniques designed for bulk materials cannot be applied to such thin membranes, and the anchoring of one–atom–thick membranes brings out technological difficulties [19]. Therefore only few experimental works are available in literature [6,8].

Here, we showed that the graphene TEC can be significantly reduced by the controlled introduction of low densities of single-atom (mono-) vacancies. Our novel approach measures the TEC

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by the determination of the stress induced in a suspended graphene sheet due to the mismatch with the substrate TEC during annealing–cooling cycles. This stress was determined from nanoindentations performed with the tip of an atomic force microscope (AFM) on monolayered graphene drums. Our molecular dynamics (MD) simulations reproduced the observed trend, and revealed that TEC reduction is due to the quenching of out-of-plane fluctuations caused by the strain fields created by mono-vacancies.

2. Results and discussion

Experiments were performed on samples prepared by mechanical exfoliation of natural graphite on SiO_2/Si substrates with predefined circular wells with diameter of 1–2 μm (see Supplementary Information). Only monolayered graphene was selected for this study. Suspended circular membranes were tested by indenting the tip at the center of the clamped area with an AFM probe. This situation can be modeled as a circular membrane with a central point load where the force versus indentation curves behave as [20]:

$$F(\delta) = \pi\sigma_0\delta + \frac{E_{2D}}{a^2}\delta^3 \quad (1)$$

where F is the loading force, δ is the indentation at the central point, a is the drumhead radius, E_{2D} is the two-dimensional elastic modulus of the membrane, and σ_0 is the stress of the membrane (both in N/m). Our $F(\delta)$ curves fitted correctly Eq. (1) (see Supplementary Fig. 2a) and our measured values in more than 10 drumheads for E_{2D} (350 ± 30 N/m) and σ_0 (0.2 ± 0.1 N/m) are in agreement with previous works [21,22]. The initial σ_0 reflects a small prestress accumulated in the sheet during the sample preparation procedure.

Towards thermo–mechanical characterization of graphene suspended layers, sample temperature was varied between 10 and 75° C and consecutive $F(\delta)$ curves were acquired at intermediate temperatures. Upon annealing, graphene tends to contract while the SiO_2 substrate shows negligible expansion [8]. This difference in behavior leads to an effective increase in the stress of the suspended graphene area that can be measured through the value of $\sigma_0(T)$ (see Fig. 1a and Fig. S2b). The use of the linear coefficient in Eq. (1) is indeed an experimental novelty since so far that equation was used to determine the Young's modulus of 2D materials through the coefficient of the cubic term. Green dots in Fig. 1b represent our measured σ_0 as a function of sample temperature for a representative pristine graphene drumhead. As expected, it displays an increasing stress with temperature. The two dimensional TEC (α_{2D}) of graphene can be directly calculated from this graph using:

$$\alpha_{2D} = -\left(\frac{\partial\varepsilon}{\partial T}\right)_V = -\frac{1}{E_{2D}}\left(\frac{\partial\sigma_0}{\partial T}\right)_V, \quad (2)$$

where ε is the strain induced by temperature. Our measured mean value for the room temperature TEC in 7 pristine membranes, $(-7\pm1)\times10^{-6}$ K^{-1}, agrees with previous experimental reports [6,8] and supports the validity of our technique for the characterization of thermo-mechanical properties of suspended 2D materials.

In order to measure the variation of the graphene TEC in the presence of defects, a controlled density of point defects was then introduced in the membranes by irradiating the samples with a known dose of Ar^+ with incoming energy of 140 eV in high vacuum. As reported in previous works by our group and others this technique allows the creation of controlled densities of carbon mono-vacancies [16,23]: we carefully characterized the induced defect type and density by Raman spectroscopy and Scanning Tunneling Microscopy (STM) in ambient conditions as described in Ref. [16] and Section SI3 in the Supplementary Information: Both the ratio of the intensity of the I_D and $I_{D'}$ peaks [24,25] in the Raman spectra (Fig. S3), and the characteristic $\sqrt{3}\times\sqrt{3}$ pattern observed in the atomically resolved STM images [23] (Fig. S4) pointed towards clean single vacancies without sp^3 hybridization. The I_D/I_G relation was used to determine the vacancy density. Consecutive low dose irradiations enable systematic study as a function of vacancy density.

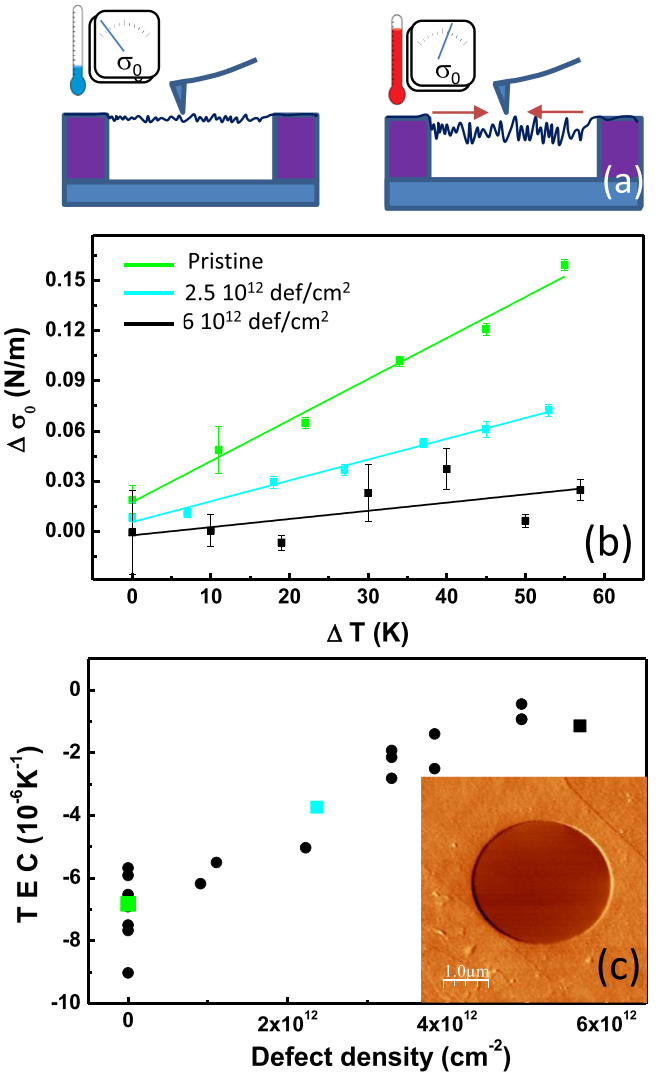

Fig. 1. Experimental measurements of graphene TEC. (a) Sketch of the experimental set-up. **(b)** Plot of measured stress as a function of sample temperature. Each color corresponds to a drumhead with a different defect density. Green: pristine. Blue: 2.5×10^{12} cm^{-2}. Black: 6.0×10^{12} cm^{-2}. **(c)** Experimentally measured TEC of different membranes as a function of the induced defect density. Inset: AFM image of a representative graphene drumhead. (A colour version of this figure can be viewed online.)

Mechanical testing by indentation experiments was performed after each ionic dose with the same AFM probe and in the same conditions described above. The $F(\delta)$ curves in defective membranes displayed also excellent fitting to Eq. (1) allowing accurate determination of σ_0 (see Fig. S5). Fig. 1b illustrates our results for pristine and defective membranes. The stress of irradiated membranes do not increase as much as that of pristine membranes with