

Comparative study between the fracture stress of poly- and single-crystalline graphene using a novel nanoelectromechanical system structure

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Graphene is a two-dimensional carbon material with extraordinary mechanical properties. However, recent studies have found that the presence of grain boundaries significantly decreases fracture stress of graphene, warranting further investigation. This work reports the development of a new method to measure the fracture stress of monolayer graphene with a novel nanoelectromechanical system (NEMS) structure. Suspended graphene ribbon devices with a range of geometries were electrostatically actuated while the graphene sheet was pinned down with various nail structures. By recording the electromechanical responses at fracture and using finite element simulations, the fracture stress was calculated. Using this novel NEMS structure, the fracture stress of polycrystalline graphene grown using conventional chemical vapour deposition (CVD) and single-crystalline graphene grown using local feeding CVD were found to be ~30 and ~90 GPa, respectively.

1. Introduction: Graphene is a two-dimensional (2D) carbon allotrope with exceptional physical properties. At room temperature, it's known to have high electrical conductivity and is impermeable to gases, including helium [1–3]. Due to these extraordinary properties, graphene has a wide range of potential applications including its use in medical devices, electronics, energy storage, and water filtration [4–6].

Graphene is also known for its astonishing mechanical properties. Pristine monolayer single-crystal graphene (SCG) is one of the strongest materials known today with Young's modulus of ~1 TPa and can be stretched up to about 20% of its original length [7]. However, large area pristine SCG is difficult to grow. Currently, the prominent method for producing large area monolayer graphene is chemical vapour deposition (CVD) [8]. However, this method grows polycrystalline monolayer graphene (PCG) with grain sizes that depend on the growth parameters [8]. Unfortunately, some studies have found the mechanical properties of PCG to be inferior to SCG, particularly the fracture stress [9, 10]. The number of experimental studies on this topic has been low and warrants further investigation.

In this Letter, a new method of measuring the fracture stress of monolayer graphene using a novel nanoelectromechanical system (NEMS) structure is presented. Suspended graphene ribbon devices are fabricated, and then measurements investigating their electromechanical responses are made by actuating the ribbons using an applied bias. By using finite element simulations and the experimentally obtained data, the stress required to fracture PCG and SCG was calculated and is reported.

2. Methodology

2.1. Suspended graphene ribbon device: Fig. 1 shows a schematic of the suspended graphene ribbon device. The device is a two-terminal mechanical switch consisting of a graphene ribbon suspended above a heavily p-doped (p++) Si floor separated by an air gap. The two terminals (a cathode, K; and an anode, A) are the graphene ribbon and the p++ Si floor, respectively, with two metal pads connected to the graphene ribbon.

The physical mechanism governing actuation of the graphene ribbon is the microelectromechanical pull-in phenomenon. When a bias is applied between the two terminals, there is an

electrostatic force that pulls the ribbon down towards the floor; however, there is also a mechanical restoring force that fights against it. At low voltages, the mechanical restoring force is able to balance the electrostatic force, and graphene remains suspended. However, at a threshold called the pull-in voltage ($V_{\text{pull-in}}$), the mechanical restoring force is no longer able to balance the electrostatic force, causing graphene to collapse and make contact with the floor. $V_{\text{pull-in}}$ is dependent on the device geometry and whose equation is given by [11, 12]

$$V_{\text{pull-in}} \sim \left(\frac{Et^3d^3}{\epsilon_0 L^4} \right)^{1/2} \quad (1)$$

where E is the Young's modulus, d is the distance of the air gap at zero bias, t is the thickness of graphene, ϵ_0 is the free space electrical permittivity, and L is the length of the ribbon.

This device's capability of electrostatic actuation has been demonstrated and confirmed through DC and transmission line pulse testing for electrostatic discharge protection [12–14].

Stress on the graphene sheet can be introduced and even tuned during pull-in. Nails were implemented where the graphene makes contact with the metal pads (see Fig. 1) in such a way that they act as rigid bodies pinning down graphene. During pull-in, the nails obstruct graphene's movement, causing stress at the points of contact. At sufficiently high stress, the graphene sheet fractures. The ribbon becomes less suspended with each subsequent pull-in, resulting in a decrease in the pull-in voltage (see (1)). Therefore, stress which initiates a pull-in voltage decrease fractures graphene.

The four nail structures chosen for the study are shown in Fig. 2. The logic in choosing them is as follows. Multiple nails were expected to distribute stress better than single nail. Furthermore, triangular nails were expected to distribute stress differently than square nails because of the difference in their arrangement of stress concentration points, or corners. Therefore, in choosing these structures, a variety of stresses can be produced.

2.2. Pull-in I - V curve measurements: To measure the $V_{\text{pull-in}}$ of a device, I - V curve measurements were done by applying a DC

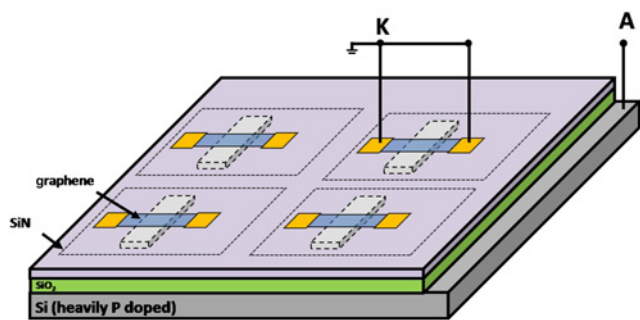


Fig. 1 Schematic of the suspended graphene ribbon device used for fracture stress measurements

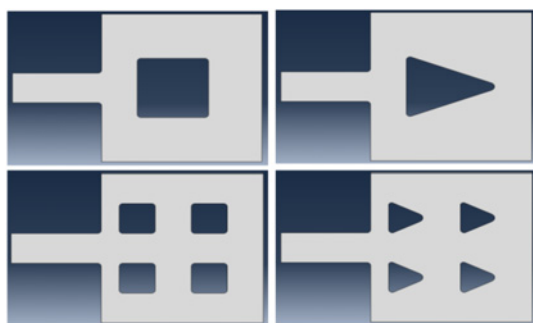


Fig. 2 Illustration of nail structures used to induce stress on the graphene sheet during pull-in

bias across the top and bottom terminals. At low V , the ribbon remains suspended and the current is low. However, when $V > V_{\text{pull-in}}$, the ribbon collapses to the floor, resulting in a low-resistance path connecting the terminals and a sharp increase in the current. By observing where this sharp increase occurs, the $V_{\text{pull-in}}$ of a device is measured. Repeated DC I - V curve measurements were made to record the electromechanical responses of the devices.

2.3. Finite element simulations: The stresses on the graphene sheet were calculated using finite element simulations on Abaqus for the four different nail structures. Nails were modelled as rigid bodies with a fixed location, the mesh density was increased at the stress concentration points for better accuracy, and the corners were rounded to avoid any singularities.

2.4. Device fabrication: PCG used in this Letter was grown using conventional CVD on Cu foil (Alfa Aesar #46365). Growth was carried out at 1050°C with a CH_4/H_2 gas mixture flowing at 200/70 sccm with a total pressure of ~ 1 Torr for 30 min in a Lindberg Blue Tube CVD furnace. Using this growth method, a continuous film was achieved fully covering the Cu foil with graphene grains on the order of a few microns in size.

SCG used in the study was provided by Professor Tianru Wu at the Chinese Academy of Sciences. The SCG sample was grown using their local feeding CVD method [15], with typical grain sizes of ~ 5 – 10 mm achieved (Fig. 3a). An optical microscope image of a single SCG grain is shown in Fig. 3b. The grain is hexagonal in shape, indicating the grains are indeed single crystal.

Fig. 4 illustrates the process flow for fabricating the suspended graphene ribbon devices. First, a SiO_2 layer of desired thickness was thermally grown on p++ Si substrate (resistivity ~ 0.001 – $0.005 \Omega \text{ cm}$). Then, a 100 nm thick SiN layer was deposited using plasma-enhanced CVD (Fig. 4a). The sample was then annealed for 1 h at 1100°C in air, increasing the SiO_2 and SiN

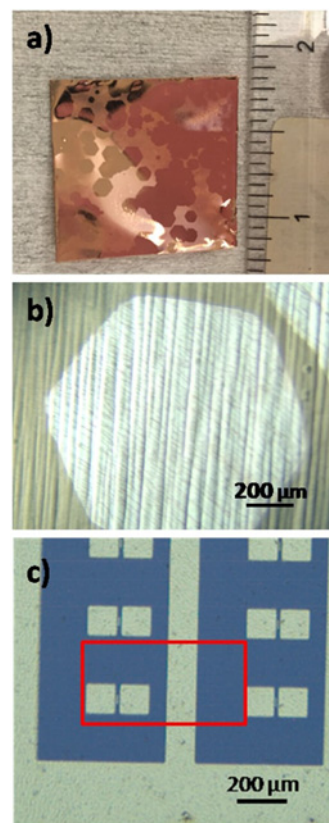


Fig. 3 Photos and optical microscope images for SCG and SCG devices
a Photo of SCG grown by local feeding CVD on Cu-Ni alloys with grain sizes of 5–10 mm
b 5 $\times$ optical microscope image of a single SCG grain
c Top view 5 $\times$ optical microscope image of finished device with area of separating one device from the others outlined in red

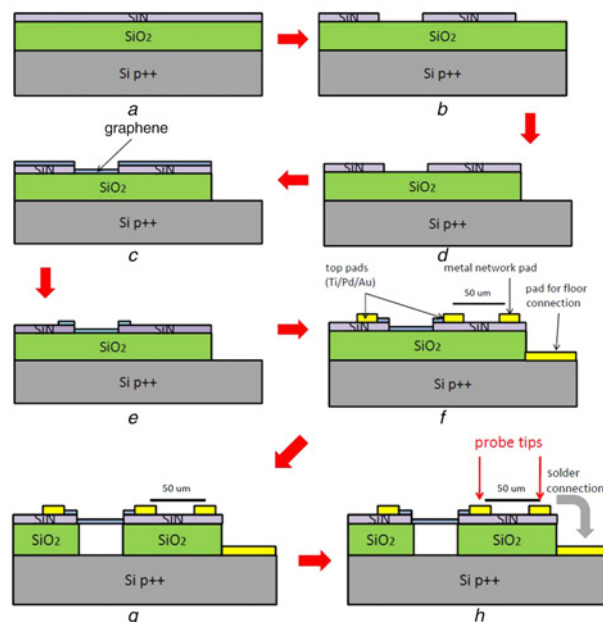


Fig. 4 Process flow illustrating the fabrication of suspended graphene ribbon devices with nail structures

film quality and releasing strain at the SiO_2 -SiN interface. Photolithography and reactive-ion etching were then done to pattern and etch the SiN, opening up the trench, holes for the

nails, and exposing the perimeter of the chip (Fig. 4b). Next, another step of photolithography and hydrofluoric acid-buffered oxide etching was done to remove SiO₂ along the perimeter of the chip (Fig. 4c). Next, graphene was wet transferred using poly (methyl methacrylate) as a structural support and FeCl₃ as a metal etchant, as described in [16] (Fig. 4d). At this step, PCG and SCG mentioned earlier were transferred onto different substrates, making different batches of devices. Next, photolithography and O₂ plasma etching were done to pattern the graphene ribbon, creating an array of ribbons with different lengths and widths (Fig. 4e). A final step of photolithography and electron beam metal deposition was done to deposit a layer of Ti/Pd/Au (5/30/120 nm) for the metal pads and the metal network (Fig. 4f). The metal network consists of runners that are 50 µm away from the metal pads, allowing pull-in *I-V* curve measurements to be done more easily. Furthermore, during deposition, metal fills up the holes in the SiN, creating nails to pin down the graphene sheet. Then, the exposed SiO₂ region was HF vapour etched to create the trench (Fig. 4g). Finally, a connection is soldered so that the metal network is connected to the floor (Fig. 4h). The locations where probe tips are placed for pull-in *I-V* curve measurements are indicated in Fig. 4h.

The area separating one device from the others (~500 × 300 µm²) is orders of magnitude smaller than the size of a typical grain from the SCG sample (~5–10 mm). This area is shown in Fig. 3c and outlined in red. Assuming a 5 mm hexagonal SCG grain occupies an area of 65 mm², about 433 devices can be made from that one grain. Therefore, the probability of a device made with graphene containing a grain boundary is <1%, ensuring that devices made using SCG do not contain grain boundaries. On the other hand, devices made with PCG are sure to contain grain boundaries because the PCG grain size is on the order of a few microns.

Furthermore, SEM and Raman spectroscopy were conducted on the finished devices to ensure proper fabrication.

Devices were designed and made with different lengths ($L = 3, 5, 7, 10, 15$, and $20 \mu\text{m}$), widths ($w = 3, 5, 7$, and $10 \mu\text{m}$), trench depths ($d = 100, 200$, and 500 nm), and the four nail structures, yielding a variety of stresses imposed on graphene during pull-in. These dimensions were achieved through careful lithography and etching outlined during the fabrication in Fig. 4. The methodology to measure the fracture stress of graphene using these devices is elaborated in Section 2.5.

2.5. Fracture stress measurement: To calculate the stress experienced by graphene, the forces acting on the ribbon at pull-in need to be considered. When $V > V_{\text{pull-in}}$ is applied between a top pad and the floor, an electrostatic force, F_{ES} , is uniformly distributed across the ribbon and pulls it downward. A free-body diagram of this is shown in Fig. 5a. F_{ES} is given by [17]

$$F_{\text{ES}} = \frac{\epsilon_0 A V_{\text{pull-in}}^2}{2d^2} \quad (2)$$

where A is the area of the graphene ribbon. At pull-in, the mechanical restoring force is insignificant compared to the electrostatic force [11] and is neglected in our analysis.

The force acting at the end of the ribbon, F_{end} , was calculated by analysing half of the ribbon. Because F_{ES} is uniformly distributed across the entire ribbon, the electrostatic force is then $F_{\text{ES}}/2$ acting on the midpoint of half of the ribbon, as shown in Fig. 5b. F_{end} is then given by

$$F_{\text{end}} = \frac{F_{\text{ES}}}{2\cos(\theta)} \quad (3)$$

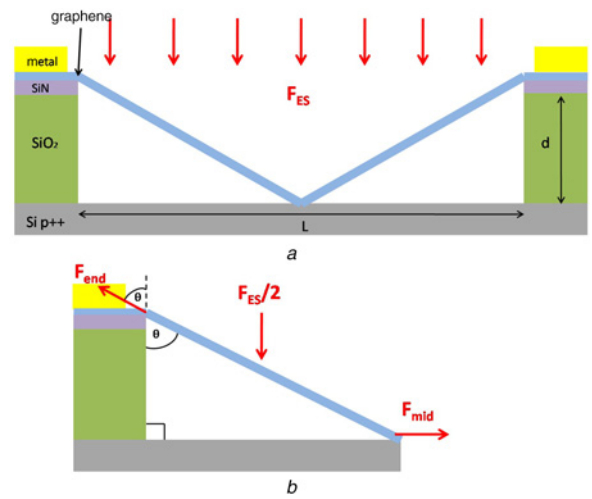


Fig. 5 Free-body diagram of graphene ribbon device at pull-in

where θ is the angle formed between the ribbon and wall at pull-in and is determined by the device geometry.

The pull-in stress on the ribbon is then given by

$$\sigma = \frac{F_{\text{end}} \sin(\theta)}{wt} \quad (4)$$

where w is the width of the ribbon and t is the thickness of graphene.

Taking into consideration the effect of the nail structures, the maximum stress on the graphene sheet at pull-in, σ_{max} , is

$$\sigma_{\text{max}} = R\sigma \quad (5)$$

$$\sigma_{\text{max}} = R \left(\frac{\epsilon_0 L V_{\text{pull-in}}^2 \tan(\theta)}{4d^2 t} \right) \quad (6)$$

where R is the ratio of the maximum stress to pull-in stress ratio calculated using the finite element simulations explained in Section 2.3. R is dependent on the nail structure used, and the results for values of R are presented in Section 3.2.

PCG and SCG devices were tested using electrical measurements, and the $V_{\text{pull-in}}$ needed to cause fracture was observed. Then, by plugging in $V_{\text{pull-in}}$ observed; A , d , w , t , and θ obtained from the device geometry; and R obtained from the finite element simulations into (6), the fracture stress of PCG and SCG was calculated.

3. Results and discussion

3.1. SEM and Raman spectroscopy results: Fig. 6 shows a top view SEM image of a finished device fabricated using the method described in Section 2.4.

Figs. 7a and b show the Raman spectrum of PCG and SCG, respectively, prepared with the growth methods mentioned in Section 2.4. Graphene's characteristic peaks (the D, G, and 2D peaks) can easily be seen. The G peaks' relative intensity to the 2D peaks indicates that the PCG and SCG are indeed monolayers. The D peak originates from a disorder in graphene's crystal structure; greater D peak intensity indicates a greater density of broken C–C bonds [18]. Because the PCG sample has a higher area density of grain boundaries, more broken C–C bonds contribute to the Raman signal, resulting in greater D peak intensity compared to SCG's Raman spectrum.

3.2. Simulation results: Fig. 8 shows the finite element simulation results described in Section 2.3, and Table 1 summarises the values of interest from these results. The pull-in stress of 30 GPa

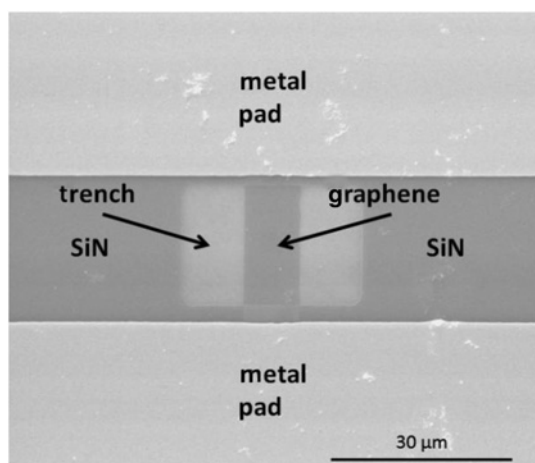


Fig. 6 SEM image of fabricated suspended graphene ribbon device ($L = 20 \mu\text{m}$, $w = 10 \mu\text{m}$)

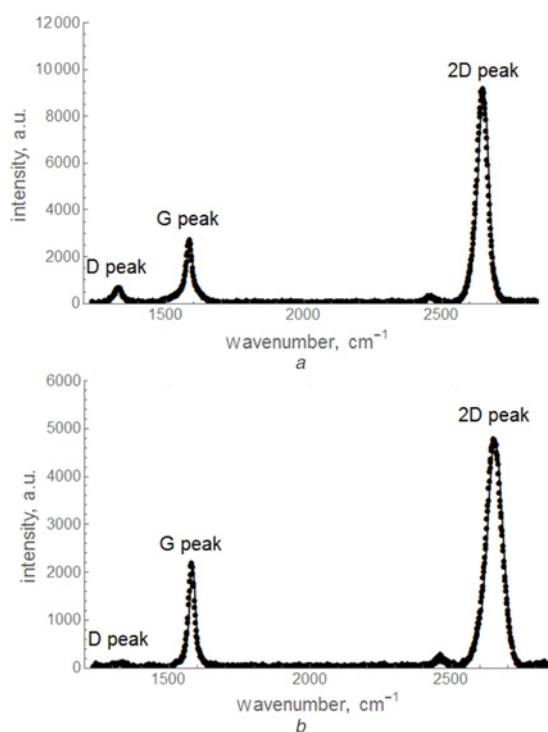


Fig. 7 Raman spectrum of
a PCG and
b SCG prepared by conventional CVD and local feeding CVD, respectively. Raman spectra were obtained using a 633 nm laser with a 3 s acquisition time

was used for all simulations, and the maximum stress on each scale bar was set to 49.02 GPa (the maximum stress concentration of the four triangular nails simulation). This allows the difference in the simulation results among the different nail structures, providing an easier comparison. To characterise each nail structure's force distribution ability, the maximum stress to pull-in stress ratio, R , was calculated and is presented in Table 1. A greater R indicates more stress concentration; an R closer to 1 indicates less concentration, with 1 being the best achievable. From Table 1, a trend can be seen: the four triangular nails structure has the least stress concentration, and the single triangular nail structure has the most stress concentration, with $R=1.634$ and 3.186, respectively. The square nail structures lie somewhere in between.

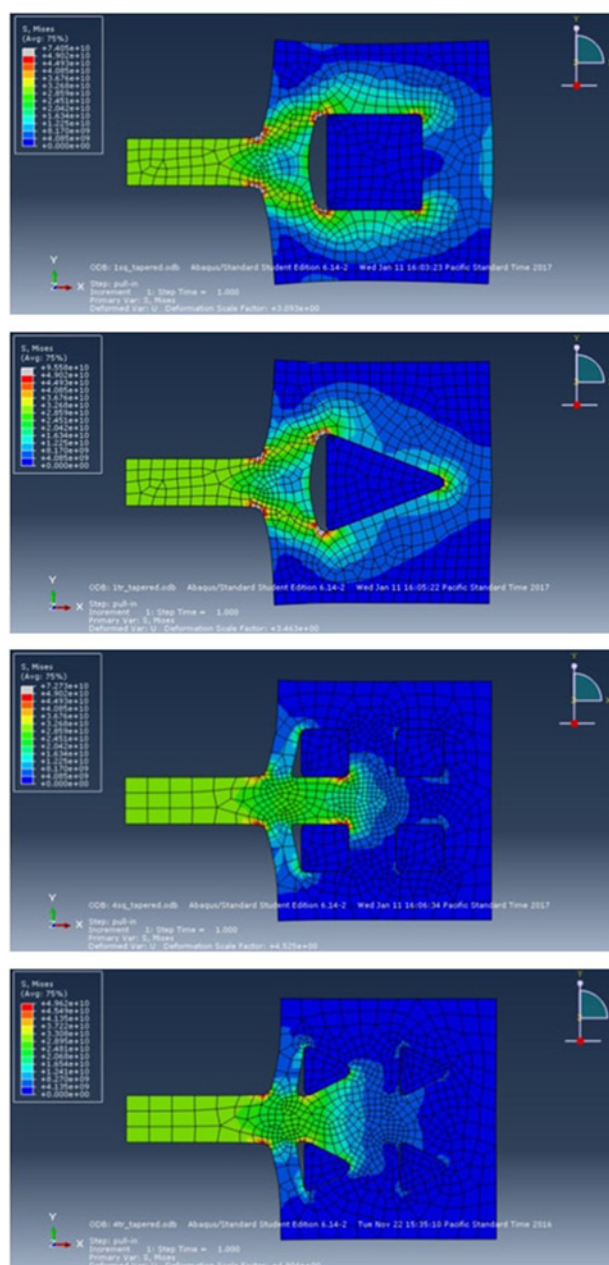


Fig. 8 Finite element simulation results modelling pull-in for the nail structures investigated

Table 1 Maximum stress and maximum stress to pull-in pressure ratio for the four nail structures

Nail structure	Value of interest	
	Maximum stress, GPa	Maximum stress to pull-in stress ratio
one square nail	74.05	2.468
one triangular nail	95.58	3.186
four square nails	72.73	2.424
four triangular nails	49.02	1.634

3.3. I - V curve measurement results: I - V curve measurements described in Section 2.2 were made on the fabricated devices. Sufficiently high voltages were applied to repeatedly actuate the ribbons to pinpoint the device geometry leading to graphene

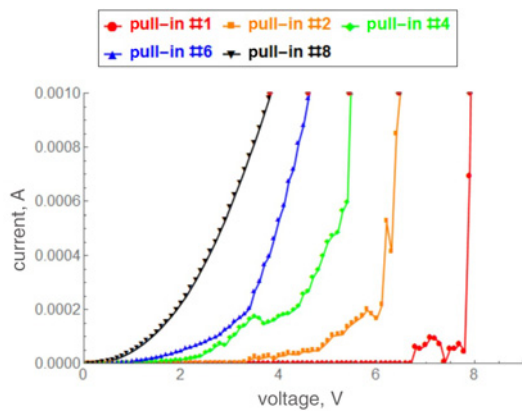


Fig. 9 Repeated pull-in I - V curves for PCG square nail device ($L = 15 \mu\text{m}$, $w = 3 \mu\text{m}$, and $d = 100 \text{ nm}$)

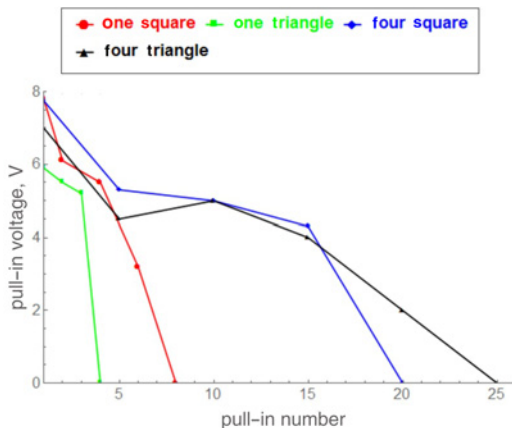


Fig. 10 Plot of the pull-in voltage against pull-in number for PCG devices with different nail structures ($L = 15 \mu\text{m}$, $w = 3 \mu\text{m}$, and $d = 100 \text{ nm}$)

fracture. An example of this is presented using a PCG square nail device ($L = 15 \mu\text{m}$, $w = 3 \mu\text{m}$, and $d = 100 \text{ nm}$), as shown in Fig. 9. There is abrupt pull-in behaviour with the first measurement. However, due to fracture in the graphene sheet, the ribbon becomes less suspended, resulting in a decrease in the pull-in voltage with each subsequent measurement (see (1)). Eventually, the ribbon is no longer suspended, resulting in resistor-like behaviour on the I - V curve due to a permanent connection between the top and bottom terminals. This behaviour indicates that graphene is indeed fracturing.

This was done for each of the four nail structure PCG devices. The pull-in voltage was plotted against the pull-in number for each device and is shown in Fig. 10. The trend in the pull-in voltage decrease matches the trend observed in the simulation results. That is, nail structures indicated by the simulations to have greater stress concentration also exhibit a faster decrease in the pull-in voltage and vice versa, as expected. This suggests that the I - V curve measurements and simulations were done are sound. The SCG devices exhibit a similar behaviour and are not shown here for brevity.

3.4. Fracture stress measurement results: The methodology outlined in Section 2.5 was used to calculate the fracture stress of PCG and SCG. It was found that PCG fractures at values as low as $\sim 30 \text{ GPa}$ and were found using a PCG one triangle nail device ($L = 10 \mu\text{m}$, $w = 3 \mu\text{m}$, $d = 200 \text{ nm}$, and $V_{\text{pull-in}} = 14.4 \text{ V}$). Reported values for pristine SCG are 130 GPa [7]; however, measuring the fracture stress of PCG by applying force using an AFM tip, Huang *et al.*

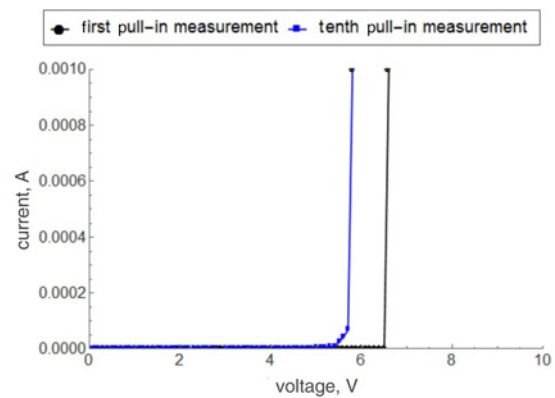


Fig. 11 Repeated pull-in I - V curve measurements were done on an SCG square nail device ($L = 15 \mu\text{m}$, $w = 3 \mu\text{m}$, and $d = 100 \text{ nm}$). The first and tenth pull-in I - V curve is shown

report values of $\sim 35 \text{ GPa}$ [9], very similar to the results observed in this Letter. The discrepancy in fracture stress values can be explained by the existence of grain boundaries in PCG. Huang *et al.* found that grains were ‘stitched together by a series of pentagons, heptagons, and distorted hexagons’ [9], resulting in imperfect bonding there. Graphene fractures at the grain boundary, resulting in PCG’s fracture stress being over three times less than pristine SCG [7, 9].

SCG’s fracture stress was also measured in this Letter. Fig. 11 shows the pull-in I - V curve for a square nail device with the same geometry as that shown in Fig. 9. I - V curve measurements were done repeatedly, with the first and tenth pull-in I - V curve shown. Instead of a gradual decrease as shown in Fig. 9, the SCG device I - V curves indicate that the pull-in voltage remains relatively stable. Without the presence of grain boundaries, the fracture stress was higher, as expected. Using this study’s methods, SCG was observed to fracture at $\sim 90 \text{ GPa}$ and was found using an SCG one square nail device ($L = 20 \mu\text{m}$, $w = 3 \mu\text{m}$, $d = 100 \text{ nm}$, and $V_{\text{pull-in}} = 5.0 \text{ V}$). The SCG’s fracture stress was found to be about three times greater than PCG’s, in alignment with other studies [7, 9]. Using this novel NEMS structure, this work adds to the limited amount studies in the literature on this topic. Furthermore, this work provides a starting point to make stress measurements with other 2D materials.

4. Conclusion: In this Letter, a new way of measuring the fracture stress of monolayer graphene was reported using a novel NEMS structure. Suspended graphene ribbon devices with a range of geometries were electrostatically actuated while the graphene sheet was pinned down with various nail structures, causing stress on the graphene sheet. The devices that led to graphene fracture were found. Then, using finite element simulations to model pull-in, the stress experienced by graphene for those devices was calculated. In this way, the fracture stress of PCG grown using conventional CVD and SCG using local feeding CVD were found to be ~ 30 and $\sim 90 \text{ GPa}$, respectively. Graphene’s fracture stress is an important mechanical property. This Letter adds to the limited amount of studies in the literature thus far and provides a starting point to make stress measurements with other 2D materials.

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