Deformation Behavior and Mechanical Properties of Suspended Double-Layer Graphene Ribbons Induced by Large Atomic Force Microscopy Indentation Forces

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1. Introduction

The exceptional mechanical properties and robustness of graphene and its derivatives[1–3] make it a promising material in nanoelectromechanical systems (NEMS) applications such as resonators,[4] accelerometers,[5–7] pressure sensors,[8,9] and switches,[10–12] as well as a reinforcement additive in composite materials.[13,14] Nanoindentation experiments[15–18] and thin-film bulge tests[19–21] are commonly used to measure the elastic properties of graphene. For example, by using nanoindentation experiments based on atomic force microscopy (AFM), the Young’s modulus of defect-free single-layer graphene was measured to be ≈1 TPa.[15,20,22] Large ranges of Young’s moduli of double-layer graphene have been experimentally measured[5,16,20,21,23,24] and theoretically simulated.[25–28] For instance, based on nanoindentation experiments and thin-film bulge tests, the Young’s modulus of double-layer graphene was measured to be similar to that of single-layer graphene.[20,24] By contrast, Lee et al.[21] found that in their experiments, the Young’s modulus of double-layer graphene was lower than that of single-layer graphene. Likewise, different molecular dynamics simulations also estimate the Young’s modulus of double-layer graphene to be either comparable to[25] or lower than that of single-layer graphene.[26,27] However, the reasons for the large variation in reported Young’s moduli of double-layer graphene have been less studied and are still under investigation. Furthermore, although the AFM technique can be used to characterize the mechanical and electromechanical properties of graphene ribbons thanks to the convenient force and displacement measurements with an AFM tip,[29] doubly clamped graphene ribbons typically can only withstand small ranges of AFM indentation forces (typically tens of nanonewtons). [5,16,17,30] To the best of our knowledge, AFM indentation measurements with large indentation forces and the resulting deflections of the graphene ribbons have not yet been experimentally studied.

In this article, we utilized double-layer graphene ribbons with a Si mass attached to their center position to explore the mechanical characteristics of suspended double-layer graphene ribbons when exposed to consecutive loading–unloading cycles of a wide range of AFM indentation forces. We found that our graphene ribbons with an attached Si mass can withstand AFM indentation forces of up to 6800 nN. We used an analytic model of the structures to analyze the experimental results and extract the strain, Young’s modulus, and buckling of the graphene ribbons. We found that when using deflection–force curves with large AFM indentation forces (e.g., larger than 3000 nN) for extracting the Young’s modulus of double-layer graphene ribbons, the

Atomic force microscopy (AFM) indentation experiments are commonly used to study the mechanical properties of graphene, such as Young’s modulus and strength. However, applied AFM indentation forces on suspended graphene beams or ribbons are typically limited to several tens of nanonewtons due to the extreme thinness of graphene and their sensitivity to damage caused by the AFM tip indentation. Herein, graphene ribbons with a Si mass attached to their center position are employed, allowing us to introduce an unprecedented, wide range of AFM indentation forces (0–6800 nN) to graphene ribbons before the graphene ribbons are ruptured. It is found that the Young’s modulus of double-layer graphene ribbons decreases as the applied AFM indentation force is larger than ≈3000 nN, which indicates that the stiffness of double-layer graphene ribbons remains constant before exposing them to AFM indentation forces larger than ≈3000 nN.

1 TPa.

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2. Results and Discussion

For our experiments, we fabricated double-layer graphene ribbons suspending a Si mass in their center position and
performed a series of deflection–force measurements by applying AFM indentation forces at the center of the Si mass of the graphene ribbon of the evaluated devices (Figure 1a). Different deflection–force measurements were performed by sequential loading and unloading cycles of the AFM indentation forces on the device in which the dimensions of the Si mass were $20 \times 20 \times 16.4 \, \mu m$, the lengths of the suspended graphene ribbons were $2 \times 4 \, \mu m$, and the width of the ribbons was $10 \, \mu m$ (Figure 1b,c). When the maximum applied AFM indentation force in each sequential loading–unloading cycle was gradually increased from 1.5 to 4890 nN, the maximum displacement of the Si mass in each loading cycle increased from 1.75 to 52.4 nm (Figure 1d) and the corresponding average uniaxial strain in the double-layer graphene ribbons increased from $9.6 \times 10^{-8}$ to $8.6 \times 10^{-3}$ (Figure 1e). The average strain was approximated by using the relation $\varepsilon = \frac{Z^3}{L^3}$, where $Z$ is the resulting displacement at the center of the ribbon, $L$ is the total length of the ribbon, and $\varepsilon$ is the strain of the ribbon.

To elucidate the deflection of the suspended double-layer graphene ribbons of the device in Figure 1c during consecutive loading cycles with increasing maximum AFM indentation forces for each cycle, we plotted the deflection–force measurement data of 15 loading cycles in which the applied AFM indentation forces ranged from 196 to 4968 nN (Figure 1f). Larger deflections of the ribbons at the same indentation force of subsequent loading cycles started to appear as the maximum applied AFM indentation force of the previous loading cycle reached values larger than 3377 nN, i.e., after the loading cycles had maximum AFM indentation forces of more than 2984 nN, we selectively used various ranges of the force data for the loading cycles with increasing applied AFM indentation force to Equation (1). As the applied maximum AFM indentation force was increased to 2984 nN in the sequential loading cycles (Figure 2e), the quality of the curve fitting to the measured AFM deflection–force data started to degrade, with an associated decrease of the extracted Young’s modulus (Figure 2a). As the applied AFM indentation force in subsequent loading cycles was further increased to values beyond 2984 nN, i.e., to 3377 and 3787 nN, the quality of the curve fitting to the deflection–force data continued to degrade and the extracted Young’s moduli continued to decrease (Figure 2a,f and Figure S2d, Supporting Information). As shown in Figure 2a, as the applied AFM indentation force was larger than 2984 nN, the Young’s moduli extracted by curve fitting decreased from about 0.6 to 0.569, 0.512, and 0.429 TPa with an increasing applied maximum AFM indentation forces in sequential indentation cycles. It should be noted that the reliability of quantitative estimation of Young’s modulus of graphene is reduced when the quality of curve fitting to the deflection–force data degrades. However, the visible decrease of Young’s moduli extracted by curve fitting still indicates that there is an overall softening of double-layer graphene ribbons. The gradual deterioration of the curve fitting to the deflection–force data for the loading cycles with increasing applied maximum AFM indentation forces larger than 2984 nN may indicate possible geometrical dislocations, distortions, delamination of graphene ribbons away from the SiO$_2$ surface of the Si mass or the trench edges, and/or crack formation in the double-layer graphene ribbons.

To explore if the change of the deflection–force behavior of the double-layer graphene ribbons in the device in Figure 1c was permanent or recoverable after exposing it to AFM indentation forces of more than 2984 nN, we selectively used various ranges of the deflection–force data of the different cycles of the AFM indentation experiments for curve fitting with Equation (1). For example, we first focused on seven subsequent loading cycles with applied maximum AFM indentation forces ranging from 1988 to 4968 nN. In all curve fittings based on each of these seven loading cycles, we used only the data in the force range between 0 and 1988 nN for the curve fitting (Figure 3a,b). In this case, we found that the extracted Young’s modulus values (0.615, 0.614, 0.615, and 0.61 TPa) using the data from the first four loading cycles (i.e., with applied maximum indentation forces of 1988, 2385, 2984, and 3377 nN, respectively) were constant and the fitting quality was good (Figure 3c,d and Figure S3a,b, Supporting Information). However, based on the data from the subsequent three loading cycles (i.e., with applied maximum indentation forces of 3787, 3981, and 4968 nN, respectively) the extracted Young’s modulus values progressively decreased (0.562, 0.52, and 0.47 TPa) with the gradual degradation of the fitting quality after the graphene ribbons had previously been exposed to an
Figure 2. Curve fittings (Matlab function: nlinfit) using Equation (1) and the measured AFM deflection–force data of the device in Figure 1c at different applied maximum AFM indentation forces during sequential loading cycles. a) Comparison of extracted Young’s moduli of double-layer graphene based on the measurement data at different applied maximum AFM indentation forces. b–f) Curve fittings using the measured AFM deflection–force curves with applied maximum indentation forces of 1584, 1988, 2385, 2984, and 3377 nN, respectively, including the extracted Young’s modulus and built-in stress values.
Figure 3. Curve fittings (Matlab function: nlinfit) using Equation (1) and the deflection–force data of the device in Figure 1c in the force range of 0–1988 nN. a,b) Extracted Young’s modulus and built-in stress values based on the deflection–force data in the force range of 0–1988 nN from sequential loading cycles with applied maximum AFM indentation forces ranged from 1988 to 4968 nN. c–f) Curve fittings to the deflection–force data in the force range of 0–1988 nN of the loading cycles with applied maximum AFM indentation forces of 2984, 3377, 3787, and 3981 nN, respectively.
AFM indentation force equal to or larger than 3377 nN (Figure 3e,f and Figure S3c, Supporting Information). Likewise, we used deflection–force data only in the force range of 0–495 nN for curve fitting from the loading cycles with applied maximum AFM indentation forces that ranged from 495 to 4968 nN (Figure S4, Supporting Information), and in the force range of 0–998 nN for curve fitting from the loading cycles with applied maximum AFM indentation forces that ranged from 998 to 4968 nN (Figure S5, Supporting Information). The results of this analysis indicate that the elastic stiffness of the double-layer graphene ribbons started to soften when the applied maximum AFM indentation force reached around 2984 nN. After the maximum AFM indentation force reached around 3377 nN, the softening of the double-layer graphene ribbons was permanent and did not recover to the original values. In addition, as the applied AFM indentation forces were larger than 3377 nN, the fitting quality in the force ranges of both 0–495 nN and 0–998 nN for the curve fitting is better than the fitting quality in the force range of 0–1988 nN for the curve fitting (Figure 3 and Figures S3–S5, Supporting Information), which indicates that the reliability of the extracted lower Young’s modulus is better when the lower force ranges (0–496 nN or 0–998 nN) are used for the curve fitting.

Further, the gradual degradation of the fitting quality (Figure 2e,f and Figure S2d, Supporting Information) and the decrease of the extracted built-in stresses (Figure 3b) resulting from the loading cycles with applied maximum AFM indentation forces of 3787, 3981, and 4968 nN indicate that the double-layer graphene ribbons suffered further permanent changes. These could be geometrical dislocation, distortion, possible delamination of graphene ribbons away from the SiO2 surface of the Si mass or the trench edges, and/or crack formation by which the built-in stress of the graphene ribbons was relaxed to some extent. Analysis of additional AFM indentation data of the device in Figure 1c further confirmed these trends (Figure S6, Supporting Information).

3. Conclusion

Taken together, we demonstrated that our double-layer graphene ribbons suspending a Si mass can withstand AFM indentation force up to about 6800 nN without catastrophic device failure, which is significantly larger than the forces introduced by AFM indentation on other graphene membranes,15,19,22,23,31,32 graphene ribbons, or beams5,16,30,33,34 This is because, in our case, the AFM tip is introduced on the Si mass and not on the suspended graphene areas, which allows for substantially larger AFM indentation forces without causing damage to the suspended graphene ribbons by the AFM tip. The largest uniaxial strain we introduce to our double-layer graphene ribbons is at least one order of magnitude larger than the highest values obtained for graphene ribbons in previous reports.16,30,33,34 Our graphene ribbons suspending a Si mass enable the use of a larger range of AFM indentation forces to investigate the elastic stiffness of graphene ribbons. As the applied AFM indentation forces were larger than 3000 nN, the elastic stiffness of our double-layer graphene ribbons softened. Possible reasons for the softening of the elastic stiffness include large AFM indentation force-induced interlayer sliding between graphene layers,35–38 larger AFM indentation force-induced geometrical dislocation and distortion of graphene ribbons, delamination of graphene ribbons away from the SiO2 surface of the Si mass or the trench edges, and crack formations in the graphene ribbons.

In conclusion, we have shown that suspended double-layer graphene ribbons with a Si mass attached to the center position of the ribbons are excellent mechanical systems for studying the mechanical properties (e.g., Young’s modulus, built-in stress, and strain), deformations, and behavior of double-layer graphene ribbons using an unprecedented, wide range of AFM indentation forces (e.g., 0–5000 nN). The elastic stiffness of double-layer graphene ribbons during the indentation processes was impacted by the gradual increase of the values of applied AFM indentation forces.

4. Experimental Section

For the device fabrication, we used a thermally oxidized silicon-on-insulator (SOI) wafer with a thickness of the device layer, BOX layer, and handle layer being 15, 2, and 400 μm, respectively. A 1.4 μm thick thermal SiO2 layer was grown on the surfaces of the SOI wafer. Next, trenches were etched in the device layer of the SOI wafer with the SiO2 layer on top, by reactive ion etching (RIE) and deep reactive ion etching (DRIE), while the backside of the SOI wafer was etched in the handle layer of the SOI wafer by RIE and DRIE. Commercially available chemical vapour deposited (CVD) single-layer graphene films on copper (Graphenea) were used to obtain a double-layer graphene stack on copper by using a poly (methyl methacrylate) (PMMA)-support wet transfer approach. The double-layer graphene on copper was then transferred from the copper substrate to the prefabricated SOI substrate by a PMMA-support wet transfer approach. The PMMA layer was removed by placing the device substrate in acetone, followed by placing it in isopropanol. Next, the double-layer graphene was etched into ribbons using lithography and O2 plasma etching. Finally, the device substrate was placed in acetone after placing it in isopropanol to dissolve the photoresist residues. To freely suspend the Si masses on the double-layer graphene ribbons, the BOX layer (a 2 μm thick SiO2) of the SOI substrate was removed by RIE dry etching, followed by vapor hydrogen fluoride (HF) etching. For more details of the fabrication process of double-layer graphene ribbons with a Si mass attached to their center position, the reader is referred to our previous publication.17

Optical microscopy was used to observe and characterize the morphology of the devices during and after device fabrication. AFM indentation experiments were performed by using an AFM (Dimension Icon, Bruker) tool with a cantilever (Olympus AC240TM) and an AFM tip (tip radius: 15 nm). The spring constant of the AFM cantilever was calibrated to be 5.303 N m−1. A series of AFM indentation force loads from small to large values were applied at the center of the Si mass of the evaluated device (Figure 1c) attached to the suspended graphene ribbons during subsequent loading/unloading cycles to measure deflection–force data and find the maximum force that the suspended graphene ribbons can withstand without rupture. It should be noted that the applied AFM indentation force was removed (0 nN) after each loading/unloading cycle and was stepwise increased from 0 nN to the maximum desired value in the subsequent loading cycle. In all experiments, the AFM tip was placed at the same positions at the center of the suspended Si mass of the device in Figure 1c, respectively. The time interval between each sequential loading–unloading cycle during the AFM indentation experiments was less than 1 min.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.
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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

AFM indentation, elastic stiffness, graphene ribbons, interlayer sliding, Young’s modulus

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