Biaxial Compressive Strain Engineering in Graphene/Boron Nitride Heterostructures

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Strain engineered graphene has been predicted to show many interesting physics and device applications. Here we study biaxial compressive strain in graphene/hexagonal boron nitride heterostructures after thermal cycling to high temperatures likely due to their thermal expansion coefficient mismatch. The appearance of sub-micron self-supporting bubbles indicates that the strain is spatially inhomogeneous. Finite element modeling suggests that the strain is concentrated on the edges with regular nano-scale wrinkles, which could be a playground for strain engineering in graphene. Raman spectroscopy and mapping is employed to quantitatively probe the magnitude and distribution of strain. From the temperature-dependent shifts of Raman G and 2D peaks, we estimate the TEC of graphene from room temperature to above 1000K for the first time.

Results

In this work, we utilize the different TEC of graphene and BN to engineer the strain in GBN heterostructures. After thermal cycling, large amount of triangular and polygonal graphene bubbles appear partly due to mechanical buckling under biaxial compressive strain. Finite element mechanical simulations show good agreement with experiments and reveal the strain distribution in the bubbles, which is further supported by Raman mapping. The spatially inhomogeneous strain distribution in graphene may be interesting for electronic device applications. Experimentally, Bao et al. formed 1D ripple textures in suspended graphene17, while Yoon et al. achieved a uniform compressive strain ~0.05% in graphene on SiO2 by thermal cycling. However, the strain distribution in these systems were not well understood, which hinders the rational design of strain-based electronic devices.

Atomic force microscopy characterizations of GBN samples. Single-layer GBN structures were made by a commonly used mechanical transfer technique (Fig. 1a, S1, the experimental details are described in Supplementary Information). We annealed the GBN in Ar atmosphere and employed atomic force microscopy (AFM)
Figure 1 | (a) Optical image of a single-layer GBN sample on 300nm SiO₂. (b) Schematics of the proposed formation process of graphene bubbles and ridges on BN. (c) A representative AFM image of GBN bubbles and ridges after thermal annealing. Angles between the adjacent ridges are indicated. (d) Distribution of the angles between neighboring ridges showing a peak around 120 degree.

Figure 2 | (a) Raman spectra of the same GBN before and after 300°C annealing. The inset compares the Raman peak of BN before and after annealing. The shifts in G and 2D peaks are not caused by system error as the BN peaks line up nicely for the two scans. We also carefully calibrated the spectrometer for each measurement. (b) Averaged G and 2D peaks positions of seven GBN samples as a function of annealing temperature. Solid lines are linear fittings of the data. The ratio between the linear temperature coefficient of 2D and G peak is 2.67. (c) A Raman mapping of 2D peak position near a graphene bubble with a 514 nm laser excitation. The bubble forms after annealing at 100°C. Inset shows the AFM of the bubble, sharing the same scale bar with (c). (d) The averaged Raman spectra taken at the bubble center and surrounding area from (c).
to characterize the samples. After annealing, we observed a large number of graphene bubbles, typically covering \( \approx 5\% \) of the total area (Fig. 1c). The bubbles were interconnected by 1D ridges to form many 2D domains in the GBN. Statistical study showed that the average size and height of the bubbles were \( \sim 300 \) nm and \( \sim 23 \) nm respectively (Fig. S2), much larger than graphene bubbles observed on metal surface\(^{10,19}\). As a result, typical triangular bubbles in GBN introduced a much smaller pseudo-magnetic field on the order of 1T (Ref. 16). The angle distribution between the neighboring ridges peaked at 120 degree (Fig. 1d), which is likely due to the symmetric nature of the interaction between the hexagonal graphene and BN lattices. Previous studies have demonstrated that van der Waals interaction between two parallel hexagonal lattices shows triangular symmetry, with three energy minima forming 120 degree angles\(^{20,21}\).

**Raman spectroscopic study of GBN samples.** Raman spectroscopy is a powerful tool to investigate the mechanical and thermal properties of graphene\(^2\). For the as-made single layer GBN samples, three characteristic peaks appeared in the Raman spectrum ranging from 1300 cm\(^{-1}\) to 2900 cm\(^{-1}\), namely BN peak (\( \sim 1366 \) cm\(^{-1}\)), graphene G peak (\( \sim 1580 \) cm\(^{-1}\)) and 2D peak (\( \sim 2640 \) cm\(^{-1}\)), without any defect-related peaks (Fig. 2a). We then gradually increased the annealing temperature of the GBN samples from 100 °C to 900 °C and did Raman mapping after each thermal cycling. Fig. 2a shows the typical Raman spectra of the same GBN as-made and after annealing at 300 °C, with clear blue shifts of G and 2D peaks after annealing. Such measurements were repeated on seven samples (Fig. 2b). In order to minimize the effect of inhomogeneous strain distribution within the GBN\(^7\), each data point in Fig. 2b represented the average G or 2D peak position from a Raman mapping (typically a few hundred curves). We observed a linear temperature evolution of the peak positions, with different slopes for G and 2D peaks.

Two possible explanations for the peak evolution are compressive strain and charge doping\(^22\)–\(^26\). However, we rule out the possibility of charge doping because 2D peak shift is less sensitive to doping than G peak\(^22\), which contradicts our data. In addition, BN has been shown to introduce negligible charge doping to graphene\(^*,\) which is not likely to shift the 2D peak by \( \sim 30 \) cm\(^{-1}\) (Fig. 2b, Ref. 25). On the other hand, under biaxial strain \( \gamma_{\text{biax}} \), Raman peaks shift linearly as

\[
\Delta \omega_{G(2D)} = -2 \gamma_{\text{biax}} \omega_0 G_{G(2D)} \gamma_{\text{biax}}.
\]

where \( \gamma_{\text{biax}} \) is the Grüneisen parameter and \( \omega_0 \) is the unstrained peak position\(^21\). In the literature, the reported values of \( \gamma_{\text{biax}} \) show variations up to \( \sim 40\%\)\(^22\). We adopted the values from \textit{ab-initio} calculations in Ref. 27 (\( \gamma_{\text{biax}} = 1.8 \), \( \gamma_{\text{biax}} = 2.7 \)) for quantitative analysis because they agreed well with experiments\(^29\) and other calculations\(^29\). We fit the peak evolution in Fig. 2b with linear function and obtained the linear coefficient

\[
\frac{\Delta \omega_{G(2D)}}{\Delta T} = -2 \gamma_{\text{biax}} \omega_0 G_{G(2D)} \gamma_{\text{biax}} \frac{\Delta \omega_{G(2D)}}{\Delta T} = \beta_{2D} \frac{\Delta \omega_{G(2D)}}{\Delta T}.
\]

to be 0.0138 cm\(^{-1}\)/K and 0.0369 cm\(^{-1}\)/K for G and 2D peaks respectively. The ratio between the slopes (\( \beta_{2D} = 2.7 \)) is in excellent agreement with the expected ratio of the pre-factors due to compressive strain

\[
\frac{\beta_{2D}}{\beta_{G}} = \frac{2 \gamma_{\text{biax}} \omega_0 G_{2D} \gamma_{\text{biax}}}{\gamma_{\text{biax}} \omega_0 G_{G}} \approx 2.7.
\]

Therefore, we attributed the Raman peak evolution to compressive strain in the GBN after thermal cycling\(^23\). As expected, the strain was biaxial in nature as we did not observe any peak splitting over the entire temperature range\(^23\).

**Discussion**

Bubbles were observed previously in GBN\(^7,12\), but the origin was still under debate. Possible explanation included trapped hydrocarbons\(^3,36\), gas bubbles\(^28,36\) and pre-existing strain in graphene\(^4\). Recently, Haigh et al. brought direct evidence of hydrocarbons under graphene bubbles\(^39\). Although we cannot rule out the possibility of hydrocarbons in our case, our Raman and finite element modeling suggest the biaxial compressive strain in graphene is also important in the formation of the bubbles (the detailed discussion of possible bubble formation mechanism is in supplementary information). Fig. 1b describes the possible formation process of the bubbles. Because of the weak interaction between graphene and BN, during heat-up, the graphene contracted and slided relative to the BN substrate due to TEC mismatch. During cool-down, the graphene expanded and experienced a biaxial compressive stress\(^37,38\). The bending stiffness of graphene (\( \sim 1.4 \) eV)\(^39\) is so small that slight
compressive stress can cause graphene to buckle and delaminate away from the substrate at weak interfacial interaction locations, forming nano-scale bubbles and ridges. For such buckling mechanism under a constant strain, linear correlation between the height and size of the bubbles (Fig. S2c) is expected. We also carried out in situ AFM at elevated temperatures to study the bubbles at different temperatures. Fig. S5 shows the AFM of the same area during 50°C and 100°C annealing in ambient respectively. Many bubbles became smaller or even disappeared at higher temperatures, presumably due to contraction of graphene relative to BN. We note that the bubbles observed here are distinct from those owing to trapped gas on SiO2 substrate28,36,37, where the round-shaped bubbles form without any thermal treatment and experience tensile strain. It is well known that BN has a negative in-plane TEC from room temperature to 770°C34. Therefore, the appearance of the bubbles indicates that graphene also has a negative TEC over a broad temperature range29,35, which is confirmed by molecular dynamics (MD) simulation (Fig. S4a, the details are in Supplementary Information).

The strain induced by TEC mismatch \( \Delta_e^{\text{TEC}}(T) = \frac{\Delta \alpha_{\text{BN}}(T)}{2\alpha_{\text{BN}}(0)} \) could be estimated from Fig. 2b, where \( \Delta \alpha_{\text{BN}}(T) \) is the Raman peak shift relative to the room temperature value. This can minimize the effect of pre-existing strain in graphene25. In Fig. 4a, we plot the temperature-dependent \( \Delta e^{\text{TEC}} \) derived from 2D peak evolution in Fig. 2b (G peak evolution gave similar results). In the case of small strain,

\[
\Delta e^{\text{TEC}}(T) = \int_{RT}^{T} [\alpha_{\text{BN}}(T) - \alpha_{\text{BN}}(T)]dT
\]

The linear temperature dependence of \( \Delta e^{\text{TEC}}(T) \) up to 900°C (Fig. 4a) suggested a constant difference in the TEC of graphene and BN throughout the studied temperature range. Using the well-documented value of \( \alpha_{\text{BN}}(T) \) by X-ray diffraction (up to \( \sim 800^\circ\mathrm{C} \))34, we can numerically derive that

\[
\alpha_{\text{G}}(T) \approx -6.6 \times 10^{-6} + 3.8 \times 10^{-9}T
\]

as plotted in Fig. 4b. We note that Eq. (3) has two hidden assumptions. First, at the highest temperature of each thermal cycling, graphene is unstrained, which is valid if graphene were completely decoupled from the substrate. Second, the strain is not released during cool down. However, the finite (although small) interaction of graphene and BN and partial release of strain makes the derived TEC a lower bound. Even then, \( \alpha_{\text{G}} \approx -5.5 \times 10^{-6}/\mathrm{K} \) at room temperature, well within the range of experimental values measured from suspended and supported graphene17,18, which suggest that Eq. (3) is still qualitatively valid in our analysis. However, the earlier experiments were unable to measure the TEC of graphene beyond \( \sim 400K \). Our derived \( \alpha_{\text{G}}(T) \) shows a much weaker temperature dependence than the previous experimental results17,18 and agrees well with the first-principle calculations by Mounet et al. over a wide temperature range25. In addition, we did MD simulations with Tersoff empirical bond order potential38 to calculate the bond length of graphene up to 600K. The calculated bond length agrees well with both the first-principle calculations25 and Eq. 4 (Fig. S4b). Possible sources of error in our analysis are discussed in the Supplementary Information.

In summary, we combined AFM, Raman spectroscopy and mapping, and mechanical modeling to study the biaxial compressive strain formation and distribution in GBN samples. Nano-scale bubbles appear partially as a result of mechanical buckling, creating interesting strain engineered graphene structures. Based on the strain evolution in GBN, we obtain the TEC of graphene over a wide temperature range.
temperature range, which agrees well with first-principle and MD calculations.

Methods

Fabrication and AFM characterization of GBN. We exfoliated single crystal BN flakes (∼10 nm thick, ∼100 µm in size) and single-layer graphene (Grade 300 Kish graphite, Graphene Laboratories, Inc.) onto separate 300 nm SiO2/Si substrates (Fig. S1a and S1b). The BN samples were annealed at 700 °C in 5% H2 in Ar atmosphere to remove possible organic contaminants. Optical microscopy, Raman spectroscopy and AFM were used to confirm single-layer nature of graphene. After a brief baking step at 80 °C, PMMA was spin coated onto graphene samples and subsequently baked at 180 °C for half an hour. Then we carefully pasted a piece of Scotch transparent tape (200 µm thick, 10 mm × 10 mm, 183–191 µm area, 3M) onto separate 300 nm SiO2/Si substrates (Fig. S1b). Then the graphene/PMMA/tape sample was align-transferred onto the prepared BN graphite membranes. AFM of the GBN samples was carried out in a Bruker Multimode 8 microscope under tapping mode.

Raman spectroscopy and mapping of GBN. Raman spectroscopy and mapping was done on a Horiba Jobin-Yvon HR800 confocal Raman microscope with a 633 nm He-Ne laser excitation and a liquid-nitrogen-cooled CCD detector (data from Fig. 2a and 2b in the main text). For each GBN sample, we usually mapped a 3 µm × 3 µm area with a 0.1 or 0.2 um steps. The mapping data in Fig. 2c and d was done using a 514 nm laser excitation. To avoid excessive heating effect on graphene, 2 mW laser power was used for all Raman measurements. We did AFM before and after Raman mapping to confirm that the bubbles were not damaged by the laser heating during Raman mapping.

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Author contributions
X. W., Y. S. and W. P. conceived the project. W. P., J. Z. and Z. N. carried out the experiments. J. X. did the finite element mechanical modeling. C. Y. and G. Z. did the molecular dynamics simulations. K. W. and T. T. provided the BN samples. W. P., J. X., Y. S. and X. W. co-wrote the paper. All authors reviewed and commented on the manuscript.

Additional information
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