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Influence of Graphene Thickness and Grain Boundaries on MoS$_2$
Wrinkle Nanostructures

Seon Joon Kim $^{a,}$, Ohmin Kwon $^{b,}$, Dae Woo Kim $^{a,}$, Jihan Kim $^{b,c,}$, Hee-Tae Jung $^{*}$, $^{a,}$, $^{b,}$, $^{c}$

Controlling wrinkle nanostructures of two-dimensional materials is critical for optimizing the material properties and device performance. In this study, we demonstrated the in situ synthesis of large-area MoS$_2$ wrinkles on graphene by chemical-vapor-deposition-assisted sulfurization, and investigated the influence of graphene thickness and grain structures on the feature dimensions of MoS$_2$ wrinkle nanostructures. The height, width, and overall surface roughness of the MoS$_2$ wrinkles diminish as the number of graphene layers increases, which was further verified by determining the binding energy of graphene layers by density functional theory calculations. Furthermore, the feature dimensions of MoS$_2$ wrinkle nanostructures were also influenced by graphene domain boundaries because of the difference in graphene nucleation density. This may be attributed to the influence of the mechanical properties of graphene substrates on the overall feature dimensions of MoS$_2$ wrinkles, which are directly correlated with the interfacial adhesion energy. We believe that our findings may contribute toward the controllable synthesis of MoS$_2$ wrinkle nanostructures and other two-dimensional materials used for high-performance devices.

1. Introduction

Mechanical instability at the interface of two different layers causes the formation of wrinkles or ridges, which relieves the residual stress in a film$^{[1-3]}$. Wrinkles in nanomaterials offer a wide range of advantages for controlling the surface properties of thin films, such as surface adhesion$^{[4-6]}$, wettability$^{[7,8]}$, as well as for enhancing the performance of sensors$^{[9,10]}$, photovoltaics (such as organic solar cells)$^{[11]}$, and organic light-emitting diodes$^{[12]}$. Moreover, the structural morphology of wrinkles has been used to align nanowires$^{[13]}$ and block copolymers$^{[14]}$ over a long range. It is well known that controlling the nanostructures of two-dimensional (2D) materials generates favorable properties$^{[15–17]}$. Accordingly, wrinkle fabrication has been recently extensively applied to 2D materials. For example, wrinkled graphene films display enhanced optoelectrical efficiency in plasmonic sensors based on surface-enhanced Raman scattering$^{[18]}$ and in photodetectors$^{[19]}$. Graphene and MoS$_2$ wrinkles have been employed as high-performance platforms for energy storage$^{[20]}$ and electrocatalysis$^{[21]}$, respectively. Furthermore, optimized performance in biological applications was achieved by the precise control of wrinkle dimensions. For instance, the antibacterial activity of wrinkled graphene oxide (GO) films was the highest when the GO wrinkle roughness was made closer to the bacterial diameter$^{[22]}$. The highest activity in stem cell differentiation was observed on nanocrystalline graphitic films with the highest percentage of wrinkles$^{[23]}$.

Although various techniques are available for the synthesis of wrinkle nanostructures in 2D materials, only a few allow scalable control over wrinkle dimensions. First, the most common and accessible method for the synthesis and control of the wrinkle nanostructure of 2D materials is the deposition of 2D films on pre-strained elastomeric substrates$^{[24–26]}$, which has been employed to synthesize graphene and MoS$_2$ wrinkles. In this method, wrinkles are synthesized by relieving the strain in pre-strained substrates. The wrinkle dimensions are manipulated by controlling the intensity and axial direction of contraction during strain relief. A second approach for forming wrinkles in 2D materials is tuning the surface tension of the transfer media$^{[27]}$. Previous studies have shown that graphene sheets floating on water can be shrunk when transferred onto a water/ethanol mixture because of the reduced surface tension of the solution. In this method, wrinkle dimensions are simply controlled by adjusting the ethanol concentration. In a third technique, wrinkles are synthesized by integrating 2D materials onto pre-featured substrates$^{[28]}$. In this method, control over wrinkle dimensions can be achieved by tuning substrate architecture; however, the method lacks scalability because of its elaborate process.
Herein, we prepared controlled nanostructures of MoS$_2$ wrinkles over a large area by sulfurization of Mo precursor films on graphene grown by chemical vapor deposition (CVD)-. Ridge-like MoS$_2$ wrinkles were synthesized in situ during sulfurization, unlike in conventional methods in which post-synthesis processes are employed to synthesize wrinkles. We found that the graphene thickness and graphene domain boundaries play a significant role in determining the feature dimensions of MoS$_2$ wrinkles: tuning the number of graphene layers allowed the controlled synthesis of MoS$_2$ wrinkle nanostructures. To resolve the overall mechanism behind the control of MoS$_2$ wrinkle feature dimensions, the mechanical properties of graphene substrates were theoretically correlated with the interfacial adhesion energy, which was then compared with the experimental results. Furthermore, the adhesion energy of each graphene substrate was calculated by density functional theory (DFT) to support the theoretical correlations.

2. Experimental Methods

2.1. Preparation and transfer of monolayer and few-layer graphene

Cu foil pieces (25 μm thickness, Goodfellow) were placed in a 4-inch-diameter quartz tube in a chemical vapor deposition apparatus. H$_2$ at 8 sccm was introduced into a vacuum environment, and the chamber was heated to 1040°C for 1 hour. The carbon source, CH$_4$ at 50 sccm, was introduced for 10 minutes at a constant temperature to grow graphene. The furnace was rapidly cooled to room temperature while only H$_2$ flow was retained in the chamber. For the transfer process, graphene was coated with a poly(methyl methacrylate) (PMMA) support by spin coating and then annealed at 180°C to remove residual solvents. Cu was then dissolved using an iron(III) chloride (FeCl$_3$) solution, and the PMMA–graphene film was washed with distilled water before it was transferred onto a SiO$_2$ substrate. The PMMA layer was dissolved in acetone to expose the graphene film. Transfer cycles were repeated several times on a single target substrate for the preparation of bilayer, trilayer, and tetralayer graphene.

Graphene islands for the observation of nuclei were prepared by limiting the CH$_4$ injection duration to less than 30 seconds. For the clear observation of graphene nuclei, Cu foil samples with graphene islands were briefly heated at 200°C in air to oxidize the bare surface of uncovered Cu.

2.2 Preparation and transfer of graphite

Ni foil pieces (25 μm thickness, Goodfellow) were placed in a 4-inch-diameter tube, and then H$_2$ at 50 sccm and Ar at 300 sccm were introduced into the chamber. The total pressure inside the chamber was kept at 10 Torr while the temperature was elevated to 1040°C for 1 hour. CH$_4$ at 50 sccm was introduced for 20 minutes at a constant temperature to supply a carbon source for the Ni bulk. The furnace was rapidly cooled to room temperature to complete graphite growth. Prior to the transfer process, graphite grown on the back side of the Ni foil was etched with plasma so that only graphite from the front side was used. The remaining transfer processes of CVD-grown graphite films were the same method as that used for monolayer graphene.

2.3. Observation of graphene domains

4-Cyano-4’-pentylbiphenyl (SCB) was spin coated onto graphene transferred to SiO$_2$ substrates in order to fabricate a uniform liquid crystal thin film. Polarized optical microscopy (POM) was used to observe the graphene domains at room temperature (25°C), and a lambda plate was utilized to obtain color images.

2.4. Theoretical methods for calculating adhesion energy

DFT calculations were conducted using the Quantum-Espresso program. The initial structure of reconstructed SiO$_2$ system was obtained from a previous work. The initial unit cell of graphene was expanded to match the lattice parameters of the SiO$_2$ within a single unit cell. In the case of graphene with SiO$_2$ system, graphene was put on top of the SiO$_2$ surface and fully relaxed. There is a small lattice mismatch of less than 5% in the total unit cell due to different cell parameters between the SiO$_2$ and the graphene system. A vacuum spacing of more than 15 Å was used to avoid the artificial interaction between the cells. The 7 × 7 × 1 Monkhorst–Pack k-point grids were used in the calculation of graphene/SiO$_2$ systems, and the 7 × 7 × 5 grids were used in calculation of bulk graphite systems. The planewave kinetic energy cutoff for wavefunctions was set to 60 Ry (≈ 816 eV).

All of the energies are obtained from single point energy calculations and the adhesion energy was calculated using the following formulas:

- $\Delta E_{\text{SiO}_2-\text{graphene}} = \left( E_{\text{Graphene with SiO}_2} - \left( E_{\text{Monolayer graphene}} + E_{\text{SiO}_2} \right) \right) / \text{Area}$
- $\Delta E_{G-\text{graphene}} = \left( E_{\text{Bilayer graphene}} - 2 \times E_{\text{Monolayer graphene}} \right) / \text{Area}$
- $\Delta E_{G-\text{graphite}} = \left( E_{\text{Graphite}} - N \times E_{\text{Monolayer graphene}} \right) / \text{Area}$

(N: number of graphene layers in a graphite unit cell)

(G: graphene layers)

2.5. Equipment and characterization

The surface morphologies of graphene were analyzed using scanning electron microscopy (SEM, FEI Nova230), and topologies were measured using atomic force microscopy (AFM, Park Systems). Cross-sectional images were prepared by a focused ion beam (FEI Helios Nanolab 450 F1) and then observed by transmission electron microscopy (TEM, FEI Tecnai TF30 ST). The film properties of MoS$_2$ and graphene were also analyzed by Raman spectroscopy (Horiba Jobin Yvon ARAMIS), and grazing-incidence X-ray diffraction experiments were conducted at the Pohang Accelerator Laboratory (Pohang, Korea) using a beam size of 200 μm × 500 μm (Rayonix 2D MAR 165 detector). Liquid-crystal-coated graphene layers were observed under a polarized optical microscope (Nikon).
### 3. Results and Discussion

![Figure 1. Synthesis of large-area MoS$_2$ wrinkles on graphene. (a) Schematic illustration for synthesizing MoS$_2$ wrinkles on graphene. Polycrystalline graphene is grown by LPCVD on Cu, which is then transferred onto a SiO$_2$ substrate. The Mo precursor films are then deposited by e-beam deposition and then sulfurized into MoS$_2$ via CVD. (b) Image of MoS$_2$ wrinkles synthesized on a 1.5 × 1.5 cm$^2$ SiO$_2$ wafer. (c) Large-area and magnified (top inset) SEM images of synthesized MoS$_2$ wrinkles. The bottom inset shows the Raman spectrum of the MoS$_2$ wrinkled films.](image)

The schematic illustration for fabricating MoS$_2$ wrinkle nanostructures on graphene is displayed in Fig. 1a. Initially, monolayer graphene was grown on a Cu foil via low-pressure chemical vapor deposition (LPCVD) at an elevated temperature (1040°C). Because of the polycrystalline nature of the Cu catalyst substrate, graphene films with polycrystalline domain structures were obtained.$^{[32]}$ The graphene then was transferred onto pre-cleaned SiO$_2$/Si substrates by a conventional wet-transfer method with a PMMA support film. Transfer steps were repeated multiple times on a single substrate in order to obtain few-layer graphene films. The Raman spectrum of a transferred film was obtained in order to investigate the quality of graphene films (Fig. S1). A negligible D peak at 1355 cm$^{-1}$ and a small $I_d/I_G$ (intensity of D peak over that of G peak) ratio of 0.08 can be observed; these indicate the successful transfer of high-quality graphene films with few defects.$^{[33]}$ Afterward, a molybdenum (Mo) precursor film of 20 nm thickness was deposited on the graphene film via e-beam deposition. For the next step, Mo films on graphene were further converted to MoS$_2$ by rapid sulfurization via CVD. Here, a two-chamber setup was used to precisely control the operation temperature. Excess amounts of sulfur (S$_2$) powders were placed in the upstream chamber to ensure complete sulfurization, while the Mo deposited graphene substrates were placed in the downstream chamber. The temperature of the downstream chamber with Mo-graphene substrates was elevated to 770 °C under an Ar atmosphere, and the temperature of the upstream chamber with sulfur powders was elevated to 220 °C to begin sulfurization. Sulfurization was performed at 770 °C for 20 minutes, and then the chamber was cooled down to room temperature to complete the conversion of Mo films to MoS$_2$. The synthesized films consisted of edge-oriented MoS$_2$ layers (Fig. 2a), while the underlying graphene layer induced buckling of the MoS$_2$ film, creating wrinkles.$^{[21]}$

Since MoS$_2$ wrinkles were directly synthesized over the CVD-grown graphene substrate, wrinkles were synthesized over a very large area. Fig. 1b shows a photographic image of MoS$_2$ wrinkles synthesized on a 1.5 × 1.5 cm$^2$ SiO$_2$/Si substrate. Here, the light-scattering effect of wrinkles resulted in a matte surface. The SEM image in Fig. 1c shows that uniform wrinkles were present over a large area; the morphology of individual wrinkles is shown in the magnified SEM image in the top inset. Furthermore, the Raman spectrum of the synthesized MoS$_2$ film in the bottom inset of Fig. 1c displays two sharp peaks at 383 and 409 cm$^{-1}$, which correspond to the E$_{2g}$ and A$_{1g}$ peaks of MoS$_2$.$^{[18]}$ These indicate the synthesis of high-quality films.

Fig. 2 shows the change in MoS$_2$ wrinkled nanostructures as a function of graphene thickness. The graphene thickness was controlled by sequential transfer of monolayer graphene grown on Cu onto SiO$_2$ substrates, from which monolayer, bilayer, trilayer, and tetralayer graphene substrates were fabricated. The increasing number of graphene layers can be clearly seen in the Raman spectra (Fig. S3). Here, the intensity ratio ($I_d/I_G$) of the G peak at 1586 cm$^{-1}$ to the 2D peak at 2690 cm$^{-1}$ gradually increases from 0.7 (monolayer) to 1.5 (tetralayer). The low intensity of the D peak at 1355 cm$^{-1}$ also indicates high-quality graphene layers with few defects. Mo films of 20 nm thickness were then deposited on few-layer graphene and then converted into MoS$_2$ wrinkles by rapid sulfurization via CVD. We found that the feature dimensions of wrinkle nanostructures were significantly different in terms of the underlying graphene thickness. Fig. 2a–d shows that the largest wrinkles formed on monolayer graphene, while the feature dimensions of wrinkles gradually diminished as the graphene substrate became thicker. AFM measurements of each sample were conducted to precisely measure the feature dimensions of wrinkles, as shown in Fig. 2e–h. The average MoS$_2$ wrinkle heights were 0.86, 0.65, 0.39, and 0.28 μm on mono-, bi-, tri-, and tetralayer graphene, respectively, while the average MoS$_2$ wrinkle widths were 1.16, 0.49, 0.16, and 0.14 μm, respectively; this result shows the gradual decrement in MoS$_2$ wrinkle dimensions. The wrinkle density gradually also increased as the graphene substrate became thicker, as seen in the images. The surface roughness was also measured by calculating the surface area increment. The total increments relative to the geometric area were 20.4%, 15.3%, 14.3%, and 13.4% for MoS$_2$ synthesized on mono-, bi-, tri-, and tetralayer graphene, respectively (summarized in Fig. 2i). The overall trend clearly shows that the feature dimensions of MoS$_2$ wrinkled nanostructures gradually diminish as the graphene substrate becomes thicker. To further confirm this correlation, MoS$_2$ was synthesized on CVD-grown graphite corresponding to approximately 300 layers of turbostratically stacked graphene layers. Fig. 54 shows that after the growth of MoS$_2$ on the graphite substrate, MoS$_2$ wrinkles became unobservable, coinciding with the observed trend of diminishing wrinkles for thicker graphene substrates.

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In order to measure the residual stress in the wrinkles, the Raman spectra of MoS$_2$ synthesized on different layers of graphene were recorded, as shown in Fig. 2j and k. Interestingly, the peak positions of planar regions in MoS$_2$ films differed from those of wrinkled regions. Peak positions from a basal plane for all samples appeared at 383 and 409 cm$^{-1}$, which correspond to the E$^{1g}$ and A$^{1g}$ peaks of MoS$_2$; the peak positions obtained for the MoS$_2$ wrinkles on monolayer graphene red-shifted to 379 and 405 cm$^{-1}$. This type of peak shift indicates the presence of local stress in MoS$_2$ wrinkles [35], which typically appears on various types of wrinkled nanostructures. The peak shift gradually diminished for MoS$_2$ on thicker graphene substrates; the peak positions of MoS$_2$ wrinkles on tetralayer graphene appeared at 383 and 409 cm$^{-1}$ with no peak shift. The above results indicate that the feature dimensions of MoS$_2$ wrinkled nanostructures can be controlled by changing the thickness of the underlying graphene substrate. In other words, tunable MoS$_2$ wrinkle growth can be achieved on graphene with controlled thickness. To demonstrate tunable MoS$_2$ wrinkle growth, varying layers of mono-, bi-, tri-, and tetralayer graphene were prepared on a single SiO$_2$ substrate, and then MoS$_2$ wrinkles were synthesized accordingly. Fig. S5 shows that the synthesis of MoS$_2$ wrinkles with tunable feature dimensions at the desired regions, which can be precisely controlled through lithographic techniques.

In order to verify the adhesion energies of the graphene layers, we carried out DFT calculations. The interfacial adhesion energy largely influences the feature dimensions of wrinkles formed by buckle delamination, that is, weaker adhesion leads to larger wrinkles. Because of this phenomenon, the influence of graphene thickness on the feature dimensions of MoS$_2$ wrinkles was verified by calculating the interfacial adhesion energy of few-layer graphene sheets via DFT. Here, three different graphene models were investigated: monolayer graphene on SiO$_2$, bilayer graphene, and bulk graphite. For the case of monolayer graphene with SiO$_2$, a single configuration was used for calculation, as previous works have shown that the difference of binding energies from various positions of graphene on SiO$_2$ was small [36]. For bilayer graphene, the binding energy of freestanding graphene sheets without a SiO$_2$ layer and that of

Figure 2. Influence of the graphene thickness on the feature dimensions of MoS$_2$ wrinkles. (a–d) SEM images of large-area MoS$_2$ wrinkles synthesized on (a) monolayer, (b) bilayer, (c) trilayer, and (d) tetralayer graphene. (e–h) AFM images of MoS$_2$ wrinkles synthesized on (e) monolayer, (f) bilayer, (g) trilayer, and (h) tetralayer graphene. Graphs under each AFM image display representative height profiles. (i) Correlation of the number of graphene layers with the MoS$_2$ wrinkle dimensions (left, black) and surface area increment relative to the geometric area (right, blue). (j, k) Raman spectra of MoS$_2$ films on graphene at the (j) planar region and (k) wrinkle region. Insets in (j) and (k) represent the probed area.
Figure 3. DFT calculations for the adhesion energies of various graphene layers. (a–c) Layer configurations of (a) monolayer graphene on SiO$_2$, (b) bilayer graphene, and (c) bulk graphite. α-Quartz was used for the SiO$_2$ layer, and the number of graphene unit cells in the $xy$ direction was chosen to match the size of the SiO$_2$ unit cell. Graphene sheets were assumed to be AB-stacked. (d, e) Binding energies obtained from single point energy calculations according to various interlayer distances using (d) LDA and (e) vdW-DF2 for monolayer graphene (black) and bilayer graphene (red). (f) Minimum binding energies of monolayer graphene, bilayer graphene, and bulk graphite calculated using LDA and vdW-DF2.

to foil the interlayer distance in bulk graphite displayed a larger interlayer distance compared with LDA. 3.55 Å for vdW-DF2. In both cases, the vdW-DF2 functionals were used to calculate the exchange-correlation potential. The energy for monolayer graphene, according to previous studies on graphitic binding energies. In fact, the bilayer graphene used in experiments is closer to turbostratic graphene than AB-stacked graphene as they were prepared by sequential transfer of polycrystalline monolayer graphene. To obtain an estimate of the binding energy of such turbostratic graphene, we also calculated the binding energy of AA-stacked double-layer graphene, as previous works$^{109}$ have shown that the binding energy of turbostratic graphene lies in between those of AA- and AB-stacked graphene. As shown in Table S2, the minimum binding energy of AA-stacked bilayer graphene was -16.00 meVÅ$^{-2}$. Thus, we can expect that turbostratic double-layer graphene will have a binding energy in between -16.00 and -18.24 meVÅ$^{-2}$. Still, the entire range of binding energy for double-layer graphene is still above that of monolayer graphene (-14.05 meVÅ$^{-2}$), which suggests that values calculated for turbostratic graphene will still follow the trend of increasing adhesion for thicker graphene films. In overall, DFT calculations indicate that the interfacial adhesion energy increases for thicker graphene substrates, in agreement with the experimental results for smaller MoS$_2$ wrinkles synthesized on thicker graphene substrates.

Interestingly, we found that the graphene domain boundaries also influenced the feature dimensions of MoS$_2$ wrinkled nanostructures. To directly observe the correlation between graphene domain structures and MoS$_2$ wrinkles, both features were directly compared in the same region. In order to fully grow Cu grains for clear comparison, Cu substrates were annealed at 1040°C for 1 h prior to graphene growth$^{40,41}$. Pristine Cu substrates displayed a random grain orientation, while annealed substrates predominantly consisted of low-index crystal facets with a few high-index crystal facets in the form of twin crystals (see Fig. 57). The Cu grains became larger after annealing; the average grain sizes of pristine grains and those after annealing for 1 h were 8.3 and 150 μm, respectively. After annealing, monolayer graphene was grown by LPCVD and then transferred onto a SiO$_2$/Si substrate. In order to directly visualize the graphene domain structure over a large area, graphene films were spin-coated with a nematic liquid crystal (SCB) layer. The graphene quasi-domain boundaries were observed by the optical birefringence of the aligned liquid crystals$^{32}$; this is shown in the POM image in Fig. 4a. Graphene domains synthesized on high-index Cu crystal facets significantly differed from those synthesized on low-index Cu crystal facets, as evident from the difference in the color-induced degree of rotation of liquid crystal molecules. After the removal of liquid crystals, MoS$_2$ was sequentially synthesized on the graphene film (Fig. 4a). The optical image in Fig. 4b shows that MoS$_2$ wrinkles with a pattern identical to that of the graphene quasi-domain structure formed; this formation implies that the quasi-domain structure significantly influences the feature dimensions of MoS$_2$ wrinkles. Magnified images in the highlighted region (dotted box) of Fig. 4b obtained by SEM (shown in Fig. 4c) clearly display a difference in the wrinkle feature dimensions at the Cu crystal domain boundary. For quantitative...
comparison, wrinkle dimensions of both sides of the grain boundary were measured by AFM, as shown in Fig. S8. The average width and height of MoS$_2$ wrinkles originating from a high-index Cu crystal facet region were 2.02 and 1.18 μm respectively, while those for wrinkles from a low-index facet region were 1.16 and 0.86 μm respectively; this result shows that wrinkles with larger feature dimensions formed on graphene grown on high-index Cu crystal facets.

We assumed that the difference in feature dimensions of MoS$_2$ wrinkles on distinct graphene quasi-domains is due to the difference in mechanical strength of each quasi-domain with the same film thickness. Such mechanical strength of a quasi-domain is largely influenced by the internal density of graphene domain boundaries, which is in turn influenced by the initial nucleation density of graphene$^{[42]}$. Therefore, we investigated the difference in initial graphene nucleation behavior on distinct quasi-domains to estimate the variation in mechanical strength. The correlation between initial nucleation and graphene domain boundary is illustrated in Fig. 4d and e. Initially, carbon precursors rapidly bind to the Cu surface to initiate nucleation, which then laterally expands, resulting in full growth of graphene across the entire surface (Fig. 4d). As the lattice parameters of graphene do not completely match those of Cu$^{[43]}$, graphene domain boundaries form at each stitching site despite similar lattice orientation (Fig. 4e). The number of domain boundaries is proportional to the initial nucleation density.

In order to experimentally observe the initial graphene nucleation behavior, methane was briefly included to partially grow graphene islands on polycrystalline Cu. Fig. 4f displays the SEM image of graphene islands at the boundary between high-index and low-index Cu crystal facets. The graphene islands are clearly seen as black dots. Cu surfaces were slightly oxidized prior to SEM observation to clearly distinguish individual graphene islands. The surface image shows that the graphene nucleation density was substantially higher on high-index Cu facets in comparison with that on low-index Cu facets. We expected that the variation in graphene nucleation density for distinct crystal facets is due to the different binding energies of graphene precursors to each Cu facet$^{[44]}$. Previous studies have shown that Cu surfaces with a high-index crystal facet possess a precursor adsorption energy higher than that of low-index crystal facets, leading to favored graphene growth on high-index Cu facets$^{[45]}$. From these results, we can deduce that a higher density of graphene domain boundaries exists on high-index Cu crystal facets after graphene growth is complete. On the basis of our empirical results, we can conclude that a higher density of graphene domain boundaries leads to more severe buckling, leading to larger MoS$_2$ wrinkles.

To further verify the influence of graphene domains on MoS$_2$ wrinkle feature dimensions, MoS$_2$ wrinkles were synthesized on arbitrary graphene quasi-domains and compared. Fig. 59 shows the nucleation behavior of graphene in an arbitrary region of polycrystalline Cu, and Fig. 510 shows the correlation between feature dimensions of MoS$_2$ wrinkles with graphene quasi-domain structure in an arbitrary region. Fig. 59 indicates that the graphene nuclei density clearly differs on all Cu crystal facets. According to our assumption, such a universal difference may lead to distinct MoS$_2$ wrinkle dimensions in all regions and not only between high-index and low-index Cu crystal facets.
low-index Cu crystal facets. We can indeed observe in Fig. S10 that the pattern of MoS$_2$ wrinkles is identical to that of graphene quasi-domains in an arbitrary region, and that the MoS$_2$ wrinkle dimensions are significantly distinct in all regions. These results support our assumption that the graphene domain boundaries play a significant role in determining the feature dimensions of MoS$_2$ wrinkles.

As a result, the MoS$_2$ wrinkle feature dimensions are influenced by the graphene thickness and the density of graphene domain boundaries. Both parameters were correlated with the interfacial adhesion energy, which is influenced by mechanical properties. The interfacial adhesion energy ($\Gamma$) is known to be proportional to the stretching stiffness ($E_{2D}$) and the bending stiffness ($D$) of a buckled film.\(^{[46]}\) It is expressed as the following equation:

$$\Gamma = k_1 \cdot E_{2D} + k_2 \cdot D$$

where $k_1$ and $k_2$ are values dependent on the wrinkle dimensions.

First, the influence of graphene thickness in Fig. 2 was correlated with the bending stiffness ($D$) of graphene. Previous studies have shown that the bending stiffness of graphene sheets drastically increases as the number of layers increases; the stiffness of tetralayer graphene ($D = 12.50$ eV) is an order of magnitude higher than that of monolayer graphene ($D = 1.5$ eV)\(^{[47]}\). Because stretching stiffness is similar for monolayer and few-layer graphene\(^{[46]}\), we can deduce from the equation that the adhesion energy of few-layer graphene is considerably higher than that of monolayer graphene. Second, the influence of the graphene domain boundaries in Fig. 4 was correlated with the stretching stiffness ($E_{2D}$) of graphene. Graphene domain boundaries have mechanical strength lower than that of basal planes; indentation experiments have directly shown that graphene with a low density of domain boundaries possess mechanical strength ($E_{2D} = 339$ N/m) higher than that of graphene with a high density of domain boundaries ($E_{2D} = 328$ N/m)\(^{[49]}\). Assuming a similar bending strength for both types due to similar layer thickness, we can deduce from the equation that the adhesion energy of graphene with a higher density of grain boundaries is lower than that with large grains, eventually leading to larger MoS$_2$ wrinkles.

The equation above also implies that graphene domain boundaries influence the feature dimensions of MoS$_2$ wrinkles on both monolayer and few-layer graphene. Fig. 5 shows optical images of MoS$_2$ wrinkles synthesized on polycrystalline mono, bi-, tri-, and tetralayer graphene. These show that the distinct MoS$_2$ wrinkles along the graphene quasi-domain pattern are clearly distinguishable on the monolayer graphene, while the difference slowly fades with thicker graphene substrates. This phenomenon can be explained by the equation above; the second term ($k_2 \cdot D$) becomes much larger for few-layer graphene ($D_{2L/G}/D_{LL/G} \approx 8$), becoming the dominant term that determines the overall interfacial adhesion energy.

4. Conclusions

In conclusion, we synthesized and controlled MoS$_2$ wrinkle nanostructures on various graphene substrates through rapid sulfurization via CVD, and investigated the major factors influencing the feature dimensions of wrinkles. We demonstrated large influence of the graphene thickness and density of graphene domain boundaries on the feature dimensions of MoS$_2$ wrinkles. MoS$_2$ wrinkles on few-layer graphene gradually diminished as the graphene thickness increased; the wrinkles were not observed at all on thick graphite, and the controlled growth of MoS$_2$ wrinkles was achieved by precisely tuning the number of graphene layers prior to sulfurization. DFT calculations further support the influence of graphene thickness, revealing that the adhesion energy increased as the graphene substrate became thicker. We correlated the feature dimensions of MoS$_2$ wrinkles with the mechanical properties of graphene substrates. Here, we showed the contributions of graphene thickness and domain boundaries to the overall interfacial adhesion energy. We expect that our finding will pave a way toward tunable morphology control of MoS$_2$ and other 2D materials for enhanced properties and device performance.

Conflicts of interest

There are no conflicts to declare.

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References
In this work, the influence of the graphene grain structure and thickness on the MoS$_2$ wrinkle features were investigated.