

Substrate-Induced Variances in Morphological and Structural Properties of MoS₂ Grown by Chemical Vapor Deposition on Epitaxial Graphene and SiO₂

Jakub Sitek,* Janusz Plocharski, Iwona Pasternak, Arkadiusz P. Gertych, Clifford McAleese, Ben R. Conran, Mariusz Zdrojek, and Wlodek Strupinski

Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 45101–45110

Read Online

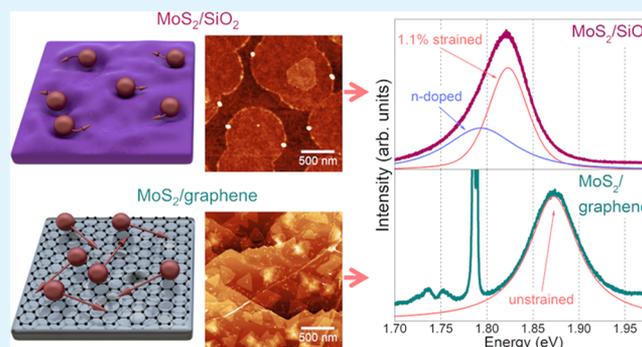
ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: In this work, we report the impact of substrate type on the morphological and structural properties of molybdenum disulfide (MoS₂) grown by chemical vapor deposition (CVD). MoS₂ synthesized on a three-dimensional (3D) substrate, that is, SiO₂, in response to the change of the thermodynamic conditions yielded different grain morphologies, including triangles, truncated triangles, and circles. Simultaneously, MoS₂ on graphene is highly immune to the modifications of the growth conditions, forming triangular crystals only. We explain the differences between MoS₂ on SiO₂ and graphene by the different surface diffusion mechanisms, namely, hopping and gas-molecule-collision-like mechanisms, respectively. As a result, we observe the formation of thermodynamically favorable nuclei shapes on graphene, while on SiO₂, a full spectrum of domain shapes can be achieved. Additionally, graphene withstands the growth process well, with only slight changes in strain and doping. Furthermore, by the application of graphene as a growth substrate, we realize van der Waals epitaxy and achieve strain-free growth, as suggested by the photoluminescence (PL) studies. We indicate that PL, contrary to Raman spectroscopy, enables us to arbitrarily determine the strain levels in MoS₂.

KEYWORDS: MoS₂, graphene, CVD, van der Waals heterostructures, photoluminescence, surface diffusion



INTRODUCTION

Two-dimensional (2D) semiconductors are currently of interest to the research community as they are foreseen to be important building blocks for beyond-silicon electronics. MoS₂, a transition-metal dichalcogenide (TMDC), is the most researched representative of 2D semiconductors due to the presence of a direct band gap, which changes to indirect with an increasing number of layers,¹ and due to widespread material availability. It can be used in a variety of applications, including transparent photodetectors,² field-effect transistors,³ photoresponsive memory devices,⁴ and quantum well light-emitting diodes.⁵ There are two main methods to obtain MoS₂ monolayers: mechanical exfoliation⁶ and chemical vapor deposition (CVD).⁷ Mechanical exfoliation, despite yielding high-quality flakes, is not scalable and repeatable, whereas CVD is much more controllable and is suitable for industrial-scale production. There are numerous modifications of CVD; however, in the context of MoS₂ growth, only two methods are relevant, namely, metal–organic chemical vapor deposition (MOCVD)⁸ and thermal vapor deposition (TVD).⁹ While MOCVD is an industrially proven technique to produce high-

quality crystals,¹⁰ TVD is a perfect platform for proof-of-concept studies at the laboratory scales. Additionally, the knowledge gained during TVD growth can be directly transferred to industrial-scale reactors, as in the case of graphene.¹¹

One of the most important variables in the growth of MoS₂ is the substrate. There are several suitable platforms for MoS₂ growth, with SiO₂ and sapphire being the most widely used due to their affordability.¹² Alternatively, graphene can also be used as a growth platform for MoS₂.³ Additionally, the use of a 2D material as a substrate for the growth of other 2D materials results in the creation of van der Waals (vdW) heterostructures.¹³ These heterostructures are superior to the classical heterostructures as the epitaxial layer is bound only

Received: April 3, 2020

Accepted: September 15, 2020

Published: September 15, 2020



by weak van der Waals forces, so extreme lattice mismatches can be accommodated (e.g., graphene and MoS₂ have mismatch equal to 28%).¹⁴ Interestingly, despite the weak interaction between materials, the grown material follows the crystallographic orientation of the substrate, which should result in perfect alignment and strain-free growth.¹⁵

Recently, research interest in MoS₂-graphene vdW heterostructures is increasing; however, the majority of the articles are presenting the structures created with at least one transfer step.^{16–19} Still, several scientific papers are reporting all-CVD growth of MoS₂/graphene vdW sandwich,^{20–22} suitable for the industrial implementation. It has to be noted, however, that most of these stacks are grown on a metallic substrate, preventing full exploitation of the potential of graphene-based heterostructures. There are only a handful of reports showing van der Waals epitaxy of MoS₂ on graphene synthesized on insulating substrates.^{23–27} These works are presenting the fundamental research on these vdW heterostructures, focused mainly on the electronic behavior of the materials. For instance, the application of semi-freestanding epitaxial graphene on SiC as a growth platform allowed the electronic structure of the MoS₂/graphene heterostructure to be revealed.²⁵ Also, the structural properties have been characterized, and it was proved that MoS₂ is commensurate to epitaxial graphene, growing with two preferential domain orientations.²⁶ While these investigations are valuable, still more research is needed to understand the CVD-grown MoS₂/graphene system. A convincing explanation of how the epitaxial graphene is influencing the growth of MoS₂ is still lacking, especially in the context of arbitrary substrates like SiO₂ or sapphire. Also, a more thorough analysis of the impact of the MoS₂ growth on graphene quality is yet to be presented. Moreover, the strain state of MoS₂ on graphene is still under discussion, and various works are presenting different, contradictory conclusions.^{18,26}

In this article, we present a direct comparison between MoS₂ grown on graphene, SiO₂, and sapphire, and we explain how the obtained layers are affected by the growth platform. In particular, we show that the morphology of MoS₂ grains on graphene is unusually stable and practically unchanged by the modification of the growth conditions. Furthermore, we present a viable kinetics-based explanation for the observed effects. In addition, for the first time, we present a method to obtain circular MoS₂ domains on SiO₂ and sapphire, complemented by the possible growth model. The results are supported by thorough Raman and photoluminescence (PL) analyses, showing how graphene is affected by the growth. We also indicate PL as a method that enables us to arbitrarily determine the strain levels in MoS₂, and we show that MoS₂ grown on graphene follows van der Waals epitaxy, resulting in unstrained growth.

EXPERIMENTAL SECTION

CVD Growth of Graphene and Substrate Preparation. The detailed graphene growth procedure was presented elsewhere.¹¹ Polycrystalline graphene was grown in an experimental AIXTRON reactor. As a substrate, 2-in. single-side-polished *c*-plane sapphire wafers were used. The process was carried out for 4 min at 1560 °C, and methane was used as a carbon precursor.

For the MoS₂ growth, we used three types of substrates: SiO₂/Si (*n*-type, 285 nm thick thermal oxide), sapphire (*c*-plane), and graphene/sapphire. SiO₂, graphene, and sapphire were manually cleaved into 8 × 8 mm² pieces. Except for argon flushing, no additional cleaning procedure was applied for all substrates.

CVD Growth of MoS₂. CVD growth of MoS₂ was carried out in a tube furnace (Figure 1). As a work tube, we used a 1200 mm 2-in.

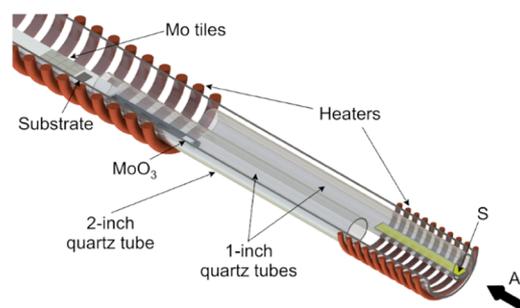


Figure 1. Scheme of tube furnace used for the growth of MoS₂.

quartz tube. To limit parasitic reactions, we used two 1-in. quartz tubes, and in each, we placed one precursor. As precursors, we used MoO₃ (Alfa Aesar, 99.95%) and sublimated sulfur (Chempur, pure p.a.), and Ar served as a carrier gas. Metallic Mo tiles (99%) with a naturally formed oxide layer were used as an additional source of molybdenum oxide. The substrates were placed on a quartz rod, approximately 8 mm above the bottom of the work tube, and 10 and 40 cm from Mo and S precursors, respectively, to increase the uniformity across samples. An additional custom-made heater was added to the system to enable better control of the sulfur temperature. To ensure the process repeatability, the substrates, precursors, quartz elements, and sulfur heater between the growth runs were placed in the same positions with an accuracy of ±1 mm. All of the measurements were performed in the centers on the samples to reduce the effects of the disturbed gas flow at the edges of the substrates. The standard growth parameters are presented in Table 1.

Table 1. Standard Growth Run Parameters

| parameter | value |
|--------------------------------------|---------------------|
| substrate temperature | 770 °C |
| MoO ₃ temperature | 687 ± 15 °C |
| S temperature | 115 °C |
| weight of MoO ₃ | 50 mg |
| weight of S | 125 mg |
| evaporation area of MoO ₃ | 0.5 cm ² |
| evaporation area of S | 10 cm ² |
| pressure | 930 mbar |
| Ar flow | 100 sccm |
| growth time | 15 min |

Characterization. To determine the morphology of the obtained MoS₂ layers, we used a Bruker Dimension Icon atomic force microscope (AFM). The topography of samples was measured in tapping and PeakForce modes using standard (tip radius ~10 nm) and supersharp (tip radius ~1 nm) probes, respectively. Scanning electron microscopy (SEM) images were taken in RAITH eLINE plus electron-beam lithography SEM with an in-lens detector.

The as-grown samples were characterized by means of Raman spectroscopy and photoluminescence. For this purpose, we used a Renishaw inVia Qontor Raman spectroscope in a backscattering configuration equipped with *xyz* stage with a resolution of 100 nm. All measurements were done with 532 nm laser, 50× objective, 1800 lines/mm grating, and 8 mW laser power. To exclude laser-induced effects, we minimized laser power density on the sample using a relatively large laser beam spot size approximately 4 μm in diameter. Circularly polarized light was used to eliminate any symmetry-based phenomena. A detailed explanation and discussion about this measurement condition can be found in our previous work.²⁸ Statistical measurements were obtained in the form of square

Raman maps over an area of $40 \times 40 \mu\text{m}^2$ with 196 points distributed at $3 \mu\text{m}$ steps in both x and y directions.

RESULTS AND DISCUSSION

Direct Comparison between MoS₂ Grown on SiO₂, Sapphire, and Graphene. The initial investigation was focused on achieving individual MoS₂ grains on three substrates to compare their morphology. AFM images of MoS₂ grown on SiO₂, sapphire, and graphene are shown in Figure 2, accompanied by height profiles. The height profiles

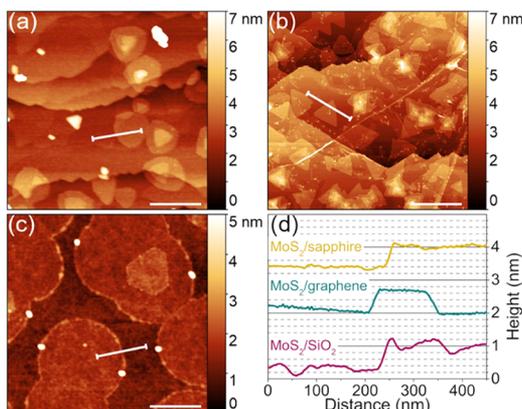


Figure 2. AFM images of MoS₂ grown on: (a) sapphire, (b) graphene, (c) SiO₂, and (d) corresponding height profiles. The samples have been grown with standard growth conditions. The scale bars are 500 nm.

on each substrate show MoS₂ layers approximately 0.7 nm thick, proving the monolayer nature of these as-grown nuclei. The MoS₂ grain morphology, however, is different on each substrate. MoS₂ on SiO₂ and sapphire tends to form circular domains, whereas on graphene, these grains are triangular. The largest domains and smallest nucleation density were achieved on SiO₂.

To confirm the chemical composition and presence of MoS₂ on the substrates, we conducted simple Raman characterization, shown in Figure 3. MoS₂ E_{2g} and A_{1g} peaks are present on all three samples, and the peak separations are small, that is, 19, 21.3, and 22.1 cm⁻¹ for SiO₂, graphene, and sapphire, respectively, indicating the presence of monolayer MoS₂. Additionally, on graphene and sapphire substrates, the A_{1g} peak of sapphire can also be noted. The MoS₂ peaks are positioned differently on each substrate, which will be discussed later.

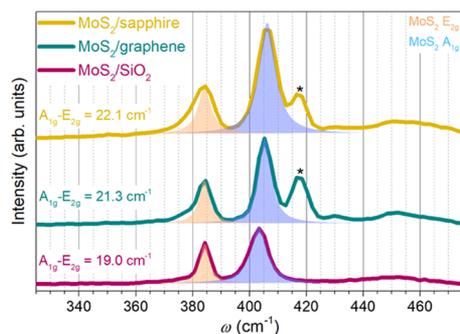


Figure 3. Raman spectra of discrete MoS₂ islands on three substrates. Raman spectra are normalized to MoS₂ E_{2g} peaks. The sapphire A_{1g} peaks were marked with asterisks.

After establishing the standard growth parameters, we focused on the detailed investigations of the MoS₂ synthesis on graphene. For a reference substrate, we chose only SiO₂, which was then always inserted into the reactor chamber alongside graphene. As we were modifying several variables, that is, substrate temperature (770–900 °C), the flux of sulfur (modified by its temperature in the range of 115–180 °C), precursor evaporation area and weight, the distance between the precursors, and growth time (15–60 min), we observed only minor changes in MoS₂ morphology on graphene samples, namely, slight variations in grain size and nucleation density (Figure 4d–f). On the contrary, the morphology of MoS₂ grains on SiO₂ was much more diverse, changing from higher coverage to circles with a higher number of adlayers and to truncated triangles (Figure 4a–c).

Chemistry of CVD Synthesis of MoS₂. The unusual stability of MoS₂ growth on graphene needs more attention. Before we explain the observed differences of MoS₂ morphology on different substrates, it is necessary to introduce several theoretical aspects of CVD growth. First of all, it has to be determined how the MoS₂ synthesis occurs. The most accepted route for the formation of MoS₂ from MoO₃ and S is as follows²⁹



In fact, the synthesis of MoS₂ during CVD growth does not involve single MoO₃ and S species. Instead of atomic sulfur, sulfur molecules, S_{*n*}, with *n* between 2 and 8, are present in the gaseous form, and S₈ is the most abundant.³⁰ Similarly, also no single MoO₃ molecule reacts in the vapor, but rather Mo_{*n*}O_{3*n*} polymeric species with $3 \leq n \leq 5$, and Mo₃O₉ constitutes 70% of the vapor.³¹ The more adequate chemical reaction, therefore, should involve S₈ and Mo₃O₉ rather than atomic S and MoO₃. Currently, no reports are discussing whether MoS₂ in the gaseous form is a single molecule or a cluster. Still, as the structure of Mo₃O₉³² is similar to the structure of MoS₂, Mo₃S₆ clusters might be present in the vapor.

There are two hypotheses discussing where the reduction of Mo-containing species occurs: in the first, the reaction is occurring purely in the gas phase,³³ while the second advocates that the partially reduced MoO_{3-*x*} is adsorbed on the substrate and is further reduced by sulfur on-site.²⁹ The driving force for the CVD growth is the local supersaturation of a metastable phase at a surface. The three chemical species present during the growth have distinctly different vapor pressures, indicating the different abilities to form supersaturated medium. The equilibrium vapor pressures of MoO₃ and S at the standard growth temperature are easy to compute and are equal to 4.2 mbar³⁴ and 21.4 bar,³⁵ respectively.

However, there are no reports showing the value of MoS₂ vapor pressure at high temperatures. Extrapolating the evaporation rate of MoS₂ obtained by Bisson to 770 °C,³⁶ the calculated value of MoS₂ vapor pressure is approximately 0.1 mbar, which is significantly lower than the vapor pressure of MoO₃ and S. Since the growth occurs and MoS₂ has the lowest vapor pressure among the three compounds, it is likely that the growth is driven by the adsorption and coalescence of gaseous MoS₂ molecules synthesized in the vapor phase rather than on-site reduction of MoO₃. Furthermore, if MoO₃ and S adsorb on the substrate, their presence should be visible in Raman spectroscopy measurements. It is not the case as except MoS₂ and substrate peaks, no more chemical compounds are present.

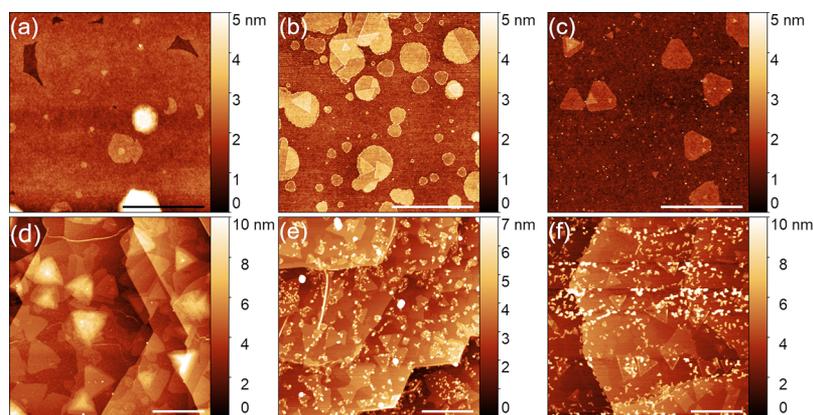


Figure 4. MoS₂ grain morphologies observed in modified growth conditions on SiO₂ (a–c) (scale bars 2 μm) and on graphene (d–f) (scale bars 500 nm). The growth conditions were modified as follows: (a, d): the growth time was increased to 60 min; (b, e) the substrate temperature was increased to 900 °C; (c, f) the S flux was increased approximately 20-fold, and it was achieved by changing S weight to 1000 mg and increasing the S temperature to 180 °C.

Surface Kinetics and Thermodynamics of CVD Growth. Since growth conditions were the same for all substrates, the apparent differences in MoS₂ layer properties originate solely from the growth platforms. Indeed, one can enumerate several differences between the three substrates, including crystallinity or surface energy. However, the ability of a substrate to create bonds with the synthesized layer is arguably the most important feature in the context of CVD growth of 2D materials. Carbon atoms forming the graphene layer cannot create any new chemical bonds, which is also characteristic of any layered 2D material, including MoS₂. Therefore, only very weak interactions between adsorbed species and graphene can be expected, which is the main prerequisite for the van der Waals epitaxy.^{37,38}

The ability of the substrate to create bonds significantly influences the dynamics of adsorbates at the substrate surface, especially the surface diffusion mechanism. In typical three-dimensional (3D) materials, that is, with unsaturated bonds on the surface, including SiO₂ or sapphire, the mechanism of surface diffusion is described by a hopping model in which adsorbed species are localized at high-energy-binding sites on the surface,³⁹ for example, active hydroxyl groups on SiO₂⁴⁰ (Figure 5). The movement of the species is allowed only

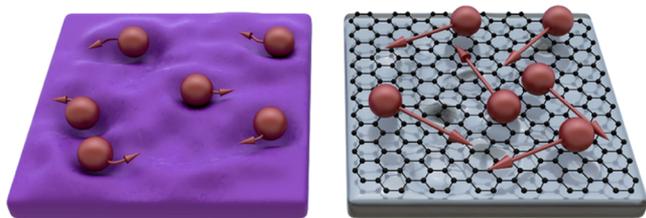


Figure 5. Schematic representations of the movement of the adsorbed MoS₂ species (red balls) on SiO₂ (left) and graphene/sapphire (right). The valleys on the SiO₂ surface represent high-energy binding sites. The schematic is not to scale.

between these binding sites. These hydroxyl groups can also become nucleation sites for MoS₂ growth as the predicted activation energies of R₃–Si–O–MoS₂ from R₃–Si–OH are similar to the thermal energy of gas molecules at the growth temperature, that is, 156 and 135 meV, respectively.⁴⁰

It has to be noted, however, that the hopping mechanism is not valid for some materials. There are studies of gas

movement on weakly interacting surfaces, for example, Xe, Kr, CH₄, or NO on graphite,⁴¹ that showed the surface diffusion should be rather described as a so-called mobile diffusion.⁴² In this mechanism, the gas molecules are forming a 2D gas directly above the surface and are no longer bound to the high-energy sites, moving virtually unrestricted over the substrate surface. Importantly, strikingly similar behavior has been theoretically predicted for graphene, on which the surface diffusion is governed by a gas-molecule-collision-like mechanism.⁴³

It is commonly known that for the hopping mechanism, the surface mean free path⁴⁴ and the residence time^{44,45} of adsorbed molecules are decreasing with an increase of temperature. Currently, there are no studies showing the impact of elevated temperatures on the mean free path of adsorbed gases on graphene. However, in the ideal gas case, the energy of molecules as well as the distance traveled are increasing at higher temperatures. As the surface diffusion on graphene is similar to the ideal gas, it is likely that the mean free path will also increase. On the other hand, in the ideal gas approximation, the residence time is shorter at elevated temperatures, similarly to the hopping mechanism.

Besides surface kinetics, also the ratio of available chemical species as a part of the growth thermodynamics has to be discussed to describe a wide range of MoS₂ morphologies. As theoretically predicted by Cao et al.,⁴⁶ a S-rich environment drives the growth of the triangular domains. When decreasing the amount of available sulfur, the domains are becoming truncated triangles and hexagons. In a Mo-rich environment, the domains should take the form of dodecagons. Interestingly, almost every predicted domain shape has been obtained experimentally,^{47,48} except dodecagons, which we will discuss later.

Explanation of the Observed Differences in MoS₂ Grain Morphology. We suggest that the observed differences in the various substrates can be explained in terms of the different surface diffusion mechanisms. On graphene, the surface diffusion manifests as the gas-molecule-collision-like mechanism (shown schematically in Figure 5), and the adsorbed MoS₂ can travel at significant distances to find the energetically favorable sites. As a result, the kinetics is not limiting the growth, and the domains tend to form thermodynamically favorable shapes. Furthermore, one can

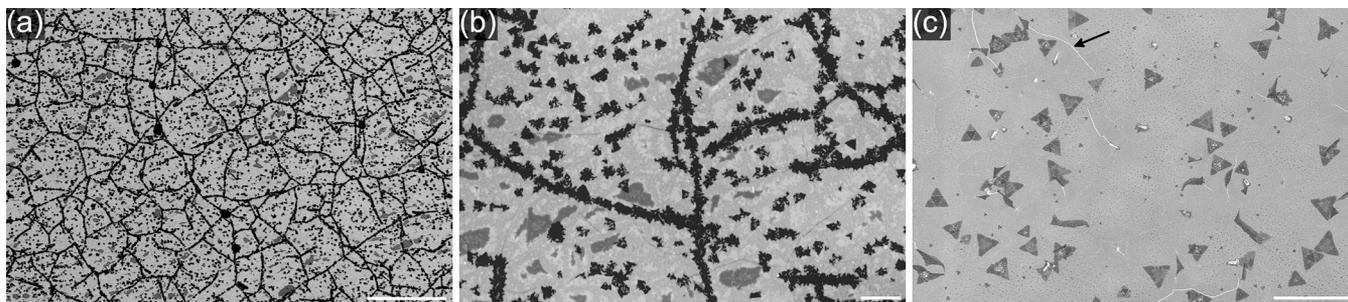


Figure 6. SEM micrographs in in-lens contrast of continuous layer of MoS₂ on: (a) graphene (scale bar, 10 μm), (b) graphene, with visible bi- and multilayers as black areas (scale bar, 1 μm), and (c) SiO₂, with a crack marked with a black arrow (scale bar, 10 μm).

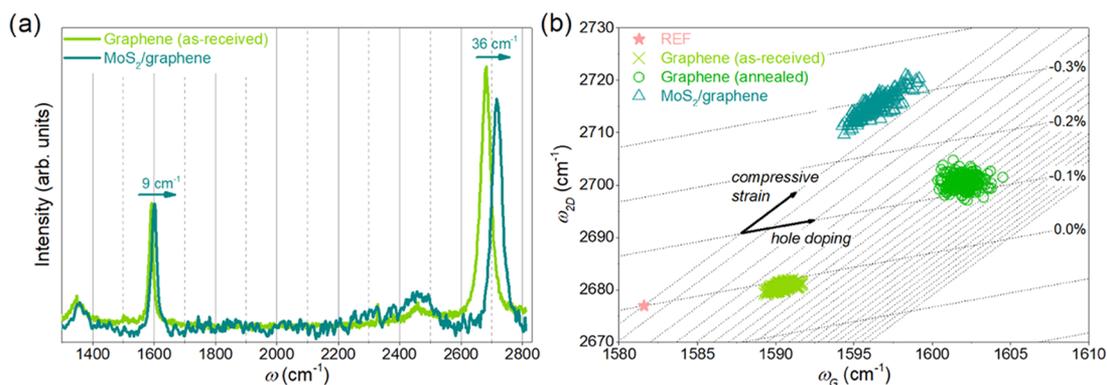


Figure 7. (a) Raman spectra of graphene before and after the growth on MoS₂. Raman spectra are normalized to G peak, and the background has been subtracted. (b) Strain doping relation in as-received graphene, annealed graphene, and graphene with MoS₂ layer grown on top of it.

observe second-layer domains on SiO₂ in Figures 2c and 4b. Contrary to the first MoS₂ layer, the adlayers are angular, taking the form of triangles and truncated triangles. In this case, the first layer serves as a van der Waals substrate; hence, the surface diffusion mechanism should be similar to the case of graphene. As a result, the growth of the first MoS₂ layer is limited by the SiO₂, while the growth of the second MoS₂ layer is analogous to the growth of MoS₂ on graphene.

The explanation for the formation of circular domains on SiO₂ should be based both on the growth kinetics and thermodynamics. Instead of theoretically predicted dodecagons, it was more favorable for MoS₂ domains to form circles. The typical growth run was conducted at a very low sulfur flux, which is the limiting growth process factor. Moreover, carrier gas flow and growth temperature were also relatively low. SiO₂ and sapphire have unsaturated bonds, and the surface diffusion is moderated by hopping mechanism, which results in a short surface mean free path of adsorbed MoS₂ at growth temperatures. Hence, the adsorbed MoS₂ species are binding to the existing nuclei at random sites rather than energetically favorable ones, as a result forming circles. Still, with an increase of S flux, resulting in the change of the thermodynamic conditions, it is possible to obtain angular shapes at different growth temperatures, confirming the limiting nature of the Mo/S ratio.

Another hypothesis, assuming that the circular domains are amorphous, should not be treated as valid as it can be seen in Figure 4b that different adlayer nuclei grown on individual first-layer domains are rotated only at two preferential angles, that is, 0 and 60°. If the hypothesis of amorphous islands would be valid, the domains would have been rotated randomly as the first layer on SiO₂ in Figure 4c. Interestingly,

Zhang et al.⁴⁹ also presented circular domains very similar to our results, and transmission electron microscopy (TEM) and selected area electron diffraction (SAED) proved the monocrystalline nature of these domains. These observations strongly suggest that the surface diffusion is low enough to allow the formation of circular domains but high enough to allow the adsorbates to rotate, forming a monocrystal. In the case of sapphire, the formation of circles is less pronounced, as on the crystalline substrate, the movement of the adsorbed species is less restricted, leading to the formation of rounded triangles.

We conclude that on SiO₂, the surface diffusion realized by a hopping mechanism drives the MoS₂ growth, as a result forming a variety of domains, including circles. Simultaneously, MoS₂ growth on graphene is probably close to thermodynamic equilibrium due to the gas-molecule-collision-like mechanism, and it can explain the relatively low responsiveness to the change of the growth conditions. Also, we want to note that by using 2D material as a growth platform we only can extend the technological window for MoS₂ growth, and for more extreme growth conditions, the growth of angular crystals might not be possible.

Impact of a Continuous MoS₂ Layer on Graphene. To thoroughly investigate MoS₂ on graphene, we synthesized a continuous layer. It has been achieved by a modification of the thermodynamic conditions, namely, by placing the substrates significantly closer to the precursors. The SEM image of a continuous layer on graphene is presented in Figure 6a. It is possible to see that besides monolayer, also bi- and multilayers have been grown (Figure 6b). Interestingly, these adlayers are forming a network without any particular direction, and it is caused by the fact that MoS₂ tends to grow on defects,⁵⁰ in this

case, on graphene wrinkles. For comparison, also the SEM image of a continuous layer on SiO₂ is presented in Figure 6c. Several cracks of the layer can be seen, and a notable number of adlayers is visible but still lower than that in the case of graphene.

The achievement of a continuous layer enabled the statistically oriented characterization of both MoS₂ and graphene. Further analyses were performed on samples with similar morphologies, as presented in Figure 6. First, we investigated changes in the structural properties of graphene induced by MoS₂ growth. To confirm that graphene withstood the growth process, we have measured its Raman spectrum prior to and after the process (Figure 7a). Surprisingly, the graphene layer is virtually intact after the growth, with only changes in G and 2D peak positions, that is, approximately 9 and 36 cm⁻¹, respectively, along with a small decrease in 2D peak amplitude. The changes in positions of graphene peaks can be used to determine strain and doping levels in graphene, according to Lee et al.⁵¹ However, at this point, it has to be noted that the absolute values of strain and doping cannot be established on a dielectric substrate, and only the relative change can be determined. It is due to dielectric screening, which reduces the electron–phonon coupling, manifested as an upshift of graphene 2D peak.⁵²

The analysis of the graphene Raman peaks position is presented in Figure 7b. When MoS₂ is synthesized on graphene, it can be noted that both strain and doping components are significantly changed, with higher compressive strain and lower doping. To determine the reason for these changes, we annealed the as-received graphene sample by placing the substrate in the growth chamber and applying the same growth parameters as in the standard growth run, except that we did not introduce precursors to the growth chamber.

After annealing, the graphene layer is in an intermediate strain state with slightly higher doping. One possible explanation of doping change is that during reactor heating up, moisture and other impurities desorb from graphene, which restores it to the pristine nondoped state.⁵³ This state, however, reverts closely to the doping of the as-received graphene when exposed again to dopants from the ambient atmosphere. On the other hand, when MoS₂ is grown on graphene, it acts similarly to hexagonal boron nitride (hBN)⁵⁴ and encapsulates the nondoped state. As a result, graphene with MoS₂ on top is low doped.

Therefore, we can conclude that the graphene layer is well preserved after the growth of the MoS₂ layer. The change of the graphene doping determined *via* shifts of G and 2D peak positions can be explained by both thermal treatment and MoS₂ encapsulation.

Raman Characterization of Continuous MoS₂ on SiO₂ and Graphene. Investigations of the strain level in MoS₂ layers are of increasing interest as they provide insight into the tunability of the band gap of the 2D semiconductor.⁵⁵ There are two main methods to characterize the strain levels in TMDCs, that is, Raman spectroscopy⁵⁶ and photoluminescence.⁵⁷ Several factors can impact the shift and separation of Raman peaks. Besides strain, stacking order,⁴⁸ number of layers, and doping can also influence the position of the peaks. With a higher number of layers, the peak separation is increasing.⁶ Doping predominantly influences the A_{1g} peak, shifting it toward higher wavenumbers with larger hole doping,⁵⁸ and increase in compressive strain results mostly in the increase of E_{2g} peak position. However, similar to graphene

on a dielectric substrate, it has been shown that it is not possible to determine the absolute values of strain and doping in MoS₂, and it has to be stressed that only the relative changes between two samples can be established.⁵⁹

Still, the peak positions derived from Raman mapping can be used to determine the relative change in these properties. The MoS₂ peak positions are presented in Figure 8. The average

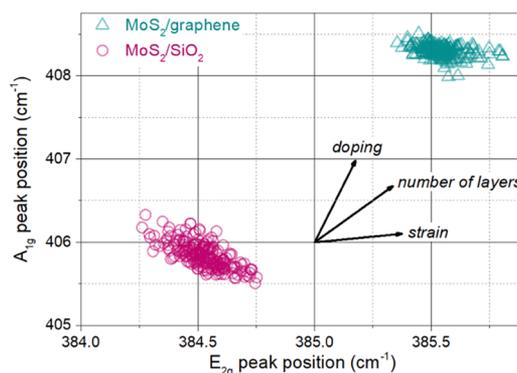


Figure 8. Position of MoS₂ Raman peaks on graphene and SiO₂.

MoS₂ peak separation on graphene is higher, reaching 22.7 cm⁻¹, while on SiO₂, this value is equal to 21.3 cm⁻¹. As shown in Figure 6, there is a significant number of adlayers, especially in the case of the graphene sample. The spectra were collected in a statistically oriented manner with a defocused laser beam; hence, the adlayers contributed to the peak separation. Nevertheless, even if we assume a complete bilayer on graphene and a monolayer on SiO₂, the contribution of adlayers does not explain the observed shift of the peaks. Therefore, also strain and doping affect the peak positions, suggesting higher tensile strain and electron doping in the SiO₂ sample.

Interestingly, the higher wavenumber of MoS₂ peaks on graphene is also reported by other groups.²⁶ Furthermore, the standard peak separation in monolayer MoS₂ on SiO₂ is approximately 19 cm⁻¹,⁵⁷ while the lowest reported separation for MoS₂ on graphene is 20.9 cm⁻¹,²⁶ and other groups achieved 21.3⁶⁰ and 21.5 cm⁻¹.²⁴ It suggests that MoS₂/graphene heterostructures behave differently from MoS₂/SiO₂, which is consistent with our hypothesis of the impact of the growth substrate.

Quantitative Determination of Strain Levels in Continuous MoS₂ on SiO₂ and Graphene *via* PL. As the Raman analysis cannot be used to arbitrarily determine the structural and electronic properties of MoS₂, we measured the photoluminescence spectra of MoS₂ on both samples. The PL intensity on graphene is significantly suppressed due to the photoluminescence quenching effect. It is explained by an electronic coupling between MoS₂ and graphene, which results in transferring the photogenerated carriers to graphene before they recombine.¹⁷ As a result, the PL signal on graphene is much weaker, and to achieve similar intensity to the signal, we exposed the graphene sample to laser light 45 times longer than the SiO₂ substrate. Any temperature-related effects have been suppressed by the defocused laser beam.

Notably, in our samples, there are multiple PL peaks, and three excitons, namely, A, B, and I, can be distinguished (Figure 9). The A and B excitons originate from the direct transitions between valence and conduction bands at the K point,⁷ and I is directly associated with an indirect transition

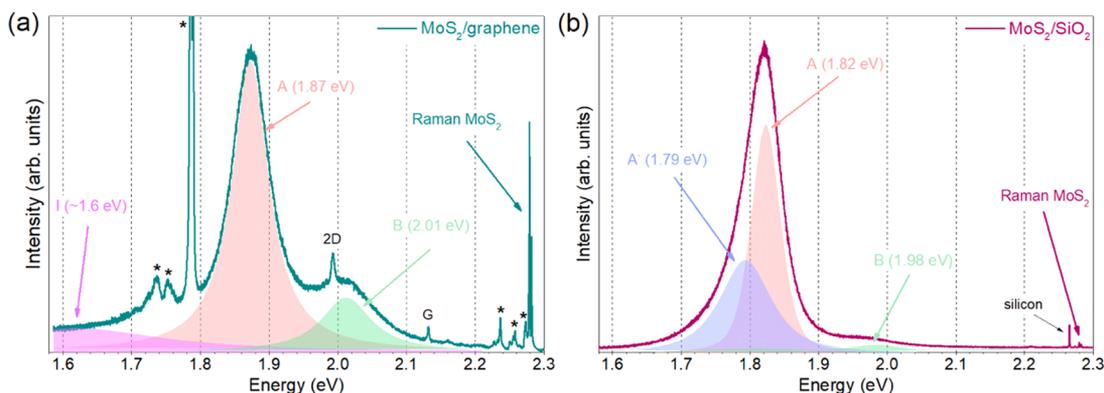


Figure 9. Photoluminescence spectra of continuous MoS₂ layer on (a) graphene and (b) SiO₂. Sapphire peaks were marked with asterisks. To achieve comparable intensity, the MoS₂/graphene sample was irradiated 45 times longer.

from K to Γ in bilayer MoS₂.⁵⁷ Additionally, also a negative trion, A⁻,⁶¹ can be observed.

The presence of I exciton in our graphene sample is caused by a significant number of adlayers. Furthermore, the presence of A⁻ trion in the SiO₂ sample might indicate n-doping or a relatively strong MoS₂-substrate interaction.^{18,63} As the trion is not present in the graphene sample, it indicates that the doping is at a low level caused by the lack of dopants in graphene. Simultaneously, we used n-doped SiO₂, which induced electron doping of MoS₂.

Finally, we observed that the position of exciton A is substantially shifted toward lower energy on SiO₂. Contrary to Raman peaks, the position of the main photoluminescence peak is virtually unaffected by the number of layers,⁶² and the contribution of doping manifests as the presence of trions. Additionally, temperature can shift the PL peak position; however, this change is small compared to strain,⁶⁴ and the majority of the research groups are measuring PL at room temperature. As a consequence, the only variable substantially influencing the exciton peak position is strain.

Numerous works are showing the impact of strain on the photoluminescence peak position.^{55,57,63,65,66} Interestingly, in the case of MoS₂ on SiO₂, the reported A exciton energy of the unstrained MoS₂ is varying from 1.8⁵⁵ to 1.9 eV,⁶⁶ and the theoretical value for the band gap in MoS₂ is predicted to be 1.9 eV.⁶² Nevertheless, in the case of MoS₂ on graphene, the reported energy of A exciton is in a much narrower range, between 1.86²¹ and 1.88 eV.⁶⁰ Similar values of A exciton position were also measured for freestanding MoS₂ monolayers, in which the influence of substrate is negligible.⁶⁷

Combining all of the literature data and our observations, a clear conclusion is drawn. First of all, the van der Waals epitaxy is by definition a strain-free growth method, and the work of Liu et al.²⁶ confirms that MoS₂ grown on graphene has the same lattice constant as bulk MoS₂, indicating a strain-free layer. Second, the exceptional stability of A exciton energy in MoS₂/graphene systems highlights the unusual structural similarity between samples produced at different groups. Therefore, we conclude that MoS₂ grown by van der Waals epitaxy on graphene is, in fact, strain-free, and the band gap energy of monolayer MoS₂ is in a narrow range between 1.86 and 1.88 eV.

We also remind that the graphene layer under MoS₂ is compressed, and it results directly from the epitaxial growth. Graphene on sapphire is presumably partially covalently bound to sapphire, as it is in the case of epitaxial graphene on SiC and

due to similarity of the growth processes.^{68,69} Therefore, chemical bonds restrict the adaption of graphene to the substrate. MoS₂, however, is bound only by the weak van der Waals forces, which enable better accommodation to the underlying layer. Similar observations were made by Verhagen et al.,⁷⁰ who showed that the top layer of bilayer graphene is more relaxed as it can slip over the bottom graphene layer.

We also suggest that PL can be used to arbitrarily determine the strain level in MoS₂. According to the work of Conley et al.,⁵⁷ the value of A exciton response to strain is 45 meV/%. The thermal expansion coefficient of SiO₂ is $0.5 \times 10^{-6} \text{ K}^{-1}$,⁷¹ while that of MoS₂ is $17.4 \times 10^{-6} \text{ K}^{-1}$.⁷² In our case, the difference between growth and PL measurement temperature is 750 K; therefore, the calculated strain difference between MoS₂ on graphene and SiO₂ is approximately 1.27%. Simultaneously, the difference resulting from A exciton shift is 1.11%, which is in excellent agreement. The small difference between these values can be explained by the cracks of MoS₂ on SiO₂, partially releasing strain. It proves that the PL-based determination of strain is a viable and accessible method to establish strain levels in MoS₂.

CONCLUSIONS

The direct comparison of MoS₂ grown by TVD on SiO₂, sapphire, and graphene showed that the growth on these substrates is governed by different surface diffusion mechanisms. On 3D substrates, it can be described as hopping between high-energy sites, while on graphene, it is characterized by the gas-molecule-collision-like mechanism. The synthesis on SiO₂, as controlled by the low surface diffusion, is sensitive to even slight variations in the growth conditions. This explains the differences between results achieved by different research groups using apparently identical growth conditions. Moreover, the nature of the growth on 3D substrates can even manifest as the formation of circular domains in unfavorable thermodynamic conditions, *i.e.*, low sulfur flux, low temperature, and low carrier gas flow.

At the same time, on graphene, the surface diffusion mechanism results in thermodynamically driven growth, leading to the formation of triangular domains only. The MoS₂ growth on graphene is unusually stable and practically unaffected by the change of the growth conditions, which may be favorable for industrial-scale growth. Interestingly, graphene is virtually unchanged by the growth process, further suggesting the industrial capability of graphene as the growth platform. Also, the application of graphene as the growth

substrate resulted in the realization of van der Waals epitaxy; therefore, the MoS₂ layer is strain-free. The strain-free nature of MoS₂ on graphene is confirmed by PL studies and supported by the literature data, and we settle the ongoing discussion of the strain levels in MoS₂ on graphene. We also suggest that PL can be used to arbitrarily determine strain levels in MoS₂, as we showed for MoS₂ on SiO₂.

Still, there is some uncertainty in several aspects of the MoS₂ growth, including whether MoS₂ molecules or clusters are present in the vapor phase or what is the impact of these particular species on the actual surface diffusion mechanism on a CVD graphene. To address these concerns, further theoretical research on the growth of van der Waals heterostructures is necessary.

AUTHOR INFORMATION

Corresponding Author

Jakub Sitek – Faculty of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland; orcid.org/0000-0001-6777-2839; Email: jakub.sitek@pw.edu.pl

Authors

Janusz Plocharski – Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland

Iwona Pasternak – Faculty of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland; orcid.org/0000-0002-3393-4593

Arkadiusz P. Gertych – Faculty of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland; orcid.org/0000-0002-7740-9651

Clifford McAleese – AIXTRON Ltd., Swavesey CB24 4FQ, United Kingdom

Ben R. Conran – AIXTRON Ltd., Swavesey CB24 4FQ, United Kingdom

Mariusz Zdrojek – Faculty of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland

Wlodek Strupinski – Faculty of Physics, Warsaw University of Technology, 00-662 Warsaw, Poland

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsami.0c06173>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the support of the EU Graphene Flagship funding (Grant Graphene Core3 no. 881603). This work was also partially supported by the CHARMING project (EOS 30467715), funded by Research Foundation—Flanders (G0F6218N). The research leading to these results has received funding from the PROM PW project, financed by the European Social Fund under the Operational Program Knowledge Education Development (POWR.03.03.00-00-PN13/18). The research was realized as a part of two PRELUDIUM projects (UMO-2019/33/N/ST5/01414 and UMO-2016/21/N/ST5/03332), funded by the Polish National Science Centre.

REFERENCES

(1) Han, S. W.; Kwon, H.; Kim, S. K.; Ryu, S.; Yun, W. S.; Kim, D. H.; Hwang, J. H.; Kang, J. S.; Baik, J.; Shin, H. J.; Hong, S. C. Band-Gap Transition Induced by Interlayer van der Waals Interaction in

MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2011**, *84*, No. 045409.

(2) Zhang, W.; Chuu, C.-P.; Huang, J.-K.; Chen, C.-H.; Tsai, M.-L.; Chang, Y.-H.; Liang, C.-T.; Chen, Y.-Z.; Chueh, Y.-L.; He, J.-H.; Chou, M.-Y.; Li, L.-J. Ultrahigh-Gain Photodetectors Based on Atomically Thin Graphene-MoS₂ Heterostructures. *Sci. Rep.* **2015**, *4*, No. 3826.

(3) Yu, W. J.; Li, Z.; Zhou, H.; Chen, Y.; Wang, Y.; Huang, Y.; Duan, X. Vertically Stacked Multi-Heterostructures of Layered Materials for Logic Transistors and Complementary Inverters. *Nat. Mater.* **2013**, *12*, 246–252.

(4) Roy, K.; Padmanabhan, M.; Goswami, S.; Sai, T. P.; Ramalingam, G.; Raghavan, S.; Ghosh, A. Graphene-MoS₂ Hybrid Structures for Multifunctional Photoresponsive Memory Devices. *Nat. Nanotechnol.* **2013**, *8*, 826–830.

(5) Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tartakovskii, A. I.; Novoselov, K. S. Light-Emitting Diodes by Band-Structure Engineering in van der Waals Heterostructures. *Nat. Mater.* **2015**, *14*, 301–306.

(6) Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700.

(7) Van Der Zande, A. M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y.; Lee, G. H.; Heinz, T. F.; Reichman, D. R.; Muller, D. A.; Hone, J. C. Grains and Grain Boundaries in Highly Crystalline Monolayer Molybdenum Disulphide. *Nat. Mater.* **2013**, *12*, 554–561.

(8) Kim, H.; Ovchinnikov, D.; Deiana, D.; Unuchek, D.; Kis, A. Suppressing Nucleation in Metal-Organic Chemical Vapor Deposition of MoS₂ Monolayers by Alkali Metal Halides. *Nano Lett.* **2017**, *17*, 5056–5063.

(9) Dumcenco, D.; Ovchinnikov, D.; Marinov, K.; Lazić, P.; Gibertini, M.; Marzari, N.; Sanchez, O. L.; Kung, Y. C.; Krasnozhan, D.; Chen, M. W.; Bertolazzi, S.; Gillet, P.; Funtcuberta i Morral, A.; Radenovic, A.; Kis, A. Large-Area Epitaxial Monolayer MoS₂. *ACS Nano* **2015**, *9*, 4611–4620.

(10) Nakamura, S.; Harada, Y.; Seno, M. Novel Metalorganic Chemical Vapor Deposition System for GaN Growth. *Appl. Phys. Lett.* **1991**, *58*, 2021–2023.

(11) Mishra, N.; Forti, S.; Fabbri, F.; Martini, L.; McAleese, C.; Conran, B. R.; Whelan, P. R.; Shivayogimath, A.; Jessen, B. S.; Buß, L.; Falta, J.; Aliaj, I.; Roddaro, S.; Flege, J. I.; Bøggild, P.; Teo, K. B. K.; Coletti, C. Wafer-Scale Synthesis of Graphene on Sapphire: Toward Fab-Compatible Graphene. *Small* **2019**, No. 1904906.

(12) Cun, H.; Macha, M.; Kim, H. K.; Liu, K.; Zhao, Y.; LaGrange, T.; Kis, A.; Radenovic, A. Wafer-Scale MOCVD Growth of Monolayer MoS₂ on Sapphire and SiO₂. *Nano Res.* **2019**, *12*, 2646–2652.

(13) Geim, A. K.; Grigorieva, I. V. Van der Waals Heterostructures. *Nature* **2013**, *499*, 419–425.

(14) Wan, W.; Li, X.; Li, X.; Xu, B.; Zhan, L.; Zhao, Z.; Zhang, P.; Wu, S. Q.; Zhu, Z. Z.; Huang, H.; Zhou, Y.; Cai, W. Interlayer Coupling of a Direct van der Waals Epitaxial MoS₂/Graphene Heterostructure. *RSC Adv.* **2016**, *6*, 323–330.

(15) Yue, R.; Nie, Y.; Walsh, L. A.; Addou, R.; Liang, C.; Lu, N.; Barton, A. T.; Zhu, H.; Che, Z.; Barrera, D.; Cheng, L.; Cha, P.-R.; Chabal, Y. J.; Hsu, J. W. P.; Kim, J.; Kim, M. J.; Colombo, L.; Wallace, R. M.; Cho, K.; Hinkle, C. L. Nucleation and Growth of WSe₂: Enabling Large Grain Transition Metal Dichalcogenides. *2D Mater.* **2017**, *4*, No. 045019.

(16) Ago, H.; Endo, H.; Solís-Fernández, P.; Takizawa, R.; Ohta, Y.; Fujita, Y.; Yamamoto, K.; Tsuji, M. Controlled van der Waals Epitaxy of Monolayer MoS₂ Triangular Domains on Graphene. *ACS Appl. Mater. Interfaces* **2015**, *7*, 5265–5273.

(17) Azizi, A.; Eichfeld, S.; Geschwind, G.; Zhang, K.; Jiang, B.; Mukherjee, D.; Hossain, L.; Piasecki, A. F.; Kabius, B.; Robinson, J. A.; Alem, N. Freestanding van der Waals Heterostructures of Graphene and Transition Metal Dichalcogenides. *ACS Nano* **2015**, *9*, 4882–4890.

- (18) Chen, T.; Zhou, Y.; Sheng, Y.; Wang, X.; Zhou, S.; Warner, J. H. Hydrogen-Assisted Growth of Large-Area Continuous Films of MoS₂ on Monolayer Graphene. *ACS Appl. Mater. Interfaces* **2018**, *10*, 7304–7314.
- (19) Pierucci, D.; Henck, H.; Naylor, C. H.; Sediri, H.; Lhuillier, E.; Balan, A.; Rault, J. E.; Dappe, Y. J.; Bertran, F.; Fèvre, P. L.; Johnson, A. T. C.; Ouerghi, A. Large Area Molybdenum Disulfide-Epitaxial Graphene Vertical van der Waals Heterostructures. *Sci. Rep.* **2016**, *6*, No. 26656.
- (20) Shi, Y.; Zhou, W.; Lu, A.-Y.; Fang, W.; Lee, Y.-H.; Hsu, A. L.; Kim, S. M.; Kim, K. K.; Yang, H. Y.; Li, L.-J.; Idrobo, J.-C.; Kong, J. Van der Waals Epitaxy of MoS₂ Layers Using Graphene As Growth Templates. *Nano Lett.* **2012**, *12*, 2784–2791.
- (21) Shi, J.; Liu, M.; Wen, J.; Ren, X.; Zhou, X.; Ji, Q.; Ma, D.; Zhang, Y.; Jin, C.; Chen, H.; Deng, S.; Xu, N.; Liu, Z.; Zhang, Y. All Chemical Vapor Deposition Synthesis and Intrinsic Bandgap Observation of MoS₂/Graphene Heterostructures. *Adv. Mater.* **2015**, *27*, 7086–7092.
- (22) Wan, W.; Chen, L.; Zhan, L.; Zhu, Z.; Zhou, Y.; Shih, T.; Guo, S.; Kang, J.; Huang, H.; Cai, W. Syntheses and Bandgap Alterations of MoS₂ Induced by Stresses in Graphene-Platinum Substrates. *Carbon* **2018**, *131*, 26–30.
- (23) Lin, M.-Y.; Chang, C.-E.; Wang, C.-H.; Su, C.-F.; Chen, C.; Lee, S.-C.; Lin, S.-Y. Toward Epitaxially Grown Two-Dimensional Crystal Hetero-Structures: Single and Double MoS₂/Graphene Hetero-Structures by Chemical Vapor Depositions. *Appl. Phys. Lett.* **2014**, *105*, No. 073501.
- (24) Chen, H. A.; Chen, W. C.; Sun, H.; Lin, C. C.; Lin, S. Y. Scalable MoS₂/Graphene Hetero-Structures Grown Epitaxially on Sapphire Substrates for Phototransistor Applications. *Semicond. Sci. Technol.* **2018**, *33*, No. 025007.
- (25) Miwa, J. A.; Dendzik, M.; Grønberg, S. S.; Bianchi, M.; Lauritsen, J. V.; Hofmann, P.; Ulstrup, S. Van der Waals Epitaxy of Two-Dimensional MoS₂-Graphene Heterostructures in Ultrahigh Vacuum. *ACS Nano* **2015**, *9*, 6502–6510.
- (26) Liu, X.; Balla, I.; Bergeron, H.; Campbell, G. P.; Bedzyk, M. J.; Hersam, M. C. Rotationally Commensurate Growth of MoS₂ on Epitaxial Graphene. *ACS Nano* **2016**, *10*, 1067–1075.
- (27) Liu, X.; Balla, I.; Bergeron, H.; Hersam, M. C. Point Defects and Grain Boundaries in Rotationally Commensurate MoS₂ on Epitaxial Graphene. *J. Phys. Chem. C* **2016**, *120*, 20798–20805.
- (28) Judek, J.; Gertych, A. P.; Czerniak, K.; Zdrojek, M. Temperature Dependence of Phonon Properties in CVD MoS₂ Nanostructures – a Statistical Approach. *Phys. Chem. Chem. Phys.* **2018**, *20*, 15486–15495.
- (29) Ji, Q.; Zhang, Y.; Gao, T.; Zhang, Y.; Ma, D.; Liu, M.; Chen, Y.; Qiao, X.; Tan, P. H.; Kan, M.; Feng, J.; Sun, Q.; Liu, Z. Epitaxial Monolayer MoS₂ on Mica with Novel Photoluminescence. *Nano Lett.* **2013**, *13*, 3870–3877.
- (30) Steudel, R.; Steudel, Y.; Wong, M. W. Speciation and Thermodynamics of Sulfur Vapor. *Elemental Sulfur and Sulfur-Rich Compounds I*; Steudel, R., Ed.; Springer: Berlin, Heidelberg, 2003; pp 117–134.
- (31) Berkowitz, J.; Inghram, M. G.; Chupka, W. A. Polymeric Gaseous Species in the Sublimation of Molybdenum Trioxide. *J. Chem. Phys.* **1957**, *26*, 842–846.
- (32) Fialko, E. F.; Kikhtenko, A. V.; Goncharov, V. B.; Zamaraev, K. I. Molybdenum Oxide Cluster Ions in the Gas Phase: Structure and Reactivity with Small Molecules. *J. Phys. Chem. A* **1997**, *101*, 8607–8613.
- (33) Yu, Y.; Li, C.; Liu, Y.; Su, L.; Zhang, Y.; Cao, L. Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-Layer MoS₂ Films. *Sci. Rep.* **2013**, *3*, No. 1866.
- (34) Stull, D. R. Inorganic Compounds. *Ind. Eng. Chem.* **1947**, *39*, 540–550.
- (35) Rau, H.; Kutty, T. R. N.; Guedes de Carvalho, J. R. F. High Temperature Saturated Vapour Pressure of Sulphur and the Estimation of Its Critical Quantities. *J. Chem. Thermodyn.* **1973**, *5*, 291–302.
- (36) Bisson, E. E. *Lubrication and Bearing Problems in the Vacuum of Space*; NASA Lewis Research Center Cleveland, 1966.
- (37) Walsh, L. A.; Hinkle, C. L. Van der Waals Epitaxy: 2D Materials and Topological Insulators. *Appl. Mater. Today* **2017**, *9*, S04–S15.
- (38) Koma, A. Van der Waals Epitaxy – a New Epitaxial Growth Method for a Highly Lattice-Mismatched System. *Thin Solid Films* **1992**, *216*, 72–76.
- (39) Ehrlich, G.; Stolt, K. Surface Diffusion. *Annu. Rev. Phys. Chem.* **1980**, *31*, 603–637.
- (40) Kataria, S.; Wagner, S.; Cusati, T.; Fortunelli, A.; Iannaccone, G.; Pandey, H.; Fiori, G.; Lemme, M. C. Growth-Induced Strain in Chemical Vapor Deposited Monolayer MoS₂: Experimental and Theoretical Investigation. *Adv. Mater. Interfaces* **2017**, *4*, No. 1700031.
- (41) Dash, J. G.; Ruvalds, J. *Phase Transitions in Surface Films*; Dash, J. G., Ruvalds, J., Eds.; Springer US: Boston, MA, 1980.
- (42) Oura, K.; Katayama, M.; Zotov, A. V.; Lifshits, V. G.; Saranin, A. A. *Surface Science: An Introduction*; Advanced Texts in Physics; Springer: Berlin, Heidelberg, 2003.
- (43) Sun, C.; Bai, B. Gas Diffusion on Graphene Surfaces. *Phys. Chem. Chem. Phys.* **2017**, *19*, 3894–3902.
- (44) Persson, M.; Andersson, S. Physisorption Dynamics at Metal Surfaces. *Handbook of Surface Science*; Elsevier, 2008; Vol. 3, pp 95–139.
- (45) Suzanne, J.; Gay, J. M. The Structure of Physically Adsorbed Phases. *Handbook of Surface Science*; Elsevier, 1996; Vol. 1, pp 503–575.
- (46) Cao, D.; Shen, T.; Liang, P.; Chen, X.; Shu, H. Role of Chemical Potential in Flake Shape and Edge Properties of Monolayer MoS₂. *J. Phys. Chem. C* **2015**, *119*, 4294–4301.
- (47) Wang, S.; Rong, Y.; Fan, Y.; Pacios, M.; Bhaskaran, H.; He, K.; Warner, J. H. Shape Evolution of Monolayer MoS₂ Crystals Grown by Chemical Vapor Deposition. *Chem. Mater.* **2014**, *26*, 6371–6379.
- (48) Shinde, S. M.; Dhakal, K. P.; Chen, X.; Yun, W. S.; Lee, J.; Kim, H.; Ahn, J.-H. Stacking-Controllable Interlayer Coupling and Symmetric Configuration of Multilayered MoS₂. *NPG Asia Mater.* **2018**, *10*, e468–e468.
- (49) Zhang, J.; Yu, H.; Chen, W.; Tian, X.; Liu, D.; Cheng, M.; Xie, G.; Yang, W.; Yang, R.; Bai, X.; Shi, D.; Zhang, G. Scalable Growth of High-Quality Polycrystalline MoS₂ Monolayers on SiO₂ with Tunable Grain Sizes. *ACS Nano* **2014**, *8*, 6024–6030.
- (50) Wan, W.; Zhan, L.; Xu, B.; Zhao, F.; Zhu, Z.; Zhou, Y.; Yang, Z.; Shih, T.; Cai, W. Temperature-Related Morphological Evolution of MoS₂ Domains on Graphene and Electron Transfer within Heterostructures. *Small* **2017**, *13*, No. 1603549.
- (51) Lee, J. E.; Ahn, G.; Shim, J.; Lee, Y. S.; Ryu, S. Optical Separation of Mechanical Strain from Charge Doping in Graphene. *Nat. Commun.* **2012**, *3*, No. 1024.
- (52) Forster, F.; Molina-Sanchez, A.; Engels, S.; Epping, A.; Watanabe, K.; Taniguchi, T.; Wirtz, L.; Stampfer, C. Dielectric Screening of the Kohn Anomaly of Graphene on Hexagonal Boron Nitride. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *88*, No. 085419.
- (53) Tsukamoto, T.; Yamazaki, K.; Komurasaki, H.; Ogino, T. Effects of Surface Chemistry of Substrates on Raman Spectra in Graphene. *J. Phys. Chem. C* **2012**, *116*, 4732–4737.
- (54) Banszerus, L.; Schmitz, M.; Engels, S.; Dauber, J.; Oellers, M.; Haupt, F.; Watanabe, K.; Taniguchi, T.; Beschoten, B.; Stampfer, C. Ultrahigh-Mobility Graphene Devices from Chemical Vapor Deposition on Reusable Copper. *Sci. Adv.* **2015**, *1*, No. e1500222.
- (55) Hui, Y. Y.; Liu, X.; Jie, W.; Chan, N. Y.; Hao, J.; Hsu, Y.-T.; Li, L.-J. J.; Guo, W.; Lau, S. P. Exceptional Tunability of Band Energy in a Compressively Strained Trilayer MoS₂ Sheet. *ACS Nano* **2013**, *7*, 7126–7131.
- (56) Rice, C.; Young, R. J.; Zan, R.; Bangert, U.; Wolverson, D.; Georgiou, T.; Jalil, R.; Novoselov, K. S. Raman-Scattering Measurements and First-Principles Calculations of Strain-Induced Phonon Shifts in Monolayer MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, *87*, No. 081307.

(57) Conley, H. J.; Wang, B.; Ziegler, J. I.; Haglund, R. F.; Pantelides, S. T.; Bolotin, K. I. Bandgap Engineering of Strained Monolayer and Bilayer MoS₂. *Nano Lett.* **2013**, *13*, 3626–3630.

(58) Chakraborty, B.; Bera, A.; Muthu, D. V. S.; Bhowmick, S.; Waghmare, U. V.; Sood, A. K. Symmetry-Dependent Phonon Renormalization in Monolayer MoS₂ Transistor. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, No. 161403.

(59) Michail, A.; Delikoukos, N.; Parthenios, J.; Galiotis, C.; Papagelis, K. Optical Detection of Strain and Doping Inhomogeneities in Single Layer MoS₂. *Appl. Phys. Lett.* **2016**, *108*, No. 173102.

(60) McCreary, K. M.; Hanbicki, A. T.; Robinson, J. T.; Cobas, E.; Culbertson, J. C.; Friedman, A. L.; Jernigan, G. G.; Jonker, B. T. Large-Area Synthesis of Continuous and Uniform MoS₂ Monolayer Films on Graphene. *Adv. Funct. Mater.* **2014**, *24*, 6449–6454.

(61) Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J. Tightly Bound Trions in Monolayer MoS₂. *Nat. Mater.* **2013**, *12*, 207–211.

(62) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 2–5.

(63) Dubey, S.; Lisi, S.; Nayak, G.; Herziger, F.; Nguyen, V.; Le Quang, T.; Cherkez, V.; González, C.; Dappe, Y. J.; Watanabe, K.; Taniguchi, T.; Magaud, L.; Mallet, P.; Veuillen, J.-Y.; Arenal, R.; Marty, L.; Renard, J.; Bendiab, N.; Coraux, J.; Bouchiat, V. Weakly Trapped, Charged, and Free Excitons in Single-Layer MoS₂ in the Presence of Defects, Strain, and Charged Impurities. *ACS Nano* **2017**, *11*, 11206–11216.

(64) Tongay, S.; Zhou, J.; Ataca, C.; Lo, K.; Matthews, T. S.; Li, J.; Grossman, J. C.; Wu, J. Thermally Driven Crossover from Indirect toward Direct Bandgap in 2D Semiconductors: MoSe₂ versus MoS₂. *Nano Lett.* **2012**, *12*, 5576–5580.

(65) Castellanos-Gomez, A.; Roldán, R.; Cappelluti, E.; Buscema, M.; Guinea, F.; Van Der Zant, H. S. J.; Steele, G. A. Local Strain Engineering in Atomically Thin MoS₂. *Nano Lett.* **2013**, *13*, 5361–5366.

(66) Niehues, I.; Blob, A.; Stiehm, T.; Schmidt, R.; Jadriško, V.; Radatović, B.; Capeta, D.; Kralj, M.; de Vasconcelos, S. M.; Bratschitsch, R. Strain Transfer across Grain Boundaries in MoS₂ Monolayers Grown by Chemical Vapor Deposition. *2D Mater.* **2018**, *5*, No. 031003.

(67) Scheuschner, N.; Ochedowski, O.; Kaulitz, A. M.; Gillen, R.; Schleberger, M.; Maultzsch, J. Photoluminescence of Freestanding Single- and Few-Layer MoS₂. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2014**, *89*, No. 125406.

(68) Emtsev, K. V.; Speck, F.; Seyller, T.; Ley, L.; Riley, J. D. Interaction, Growth, and Ordering of Epitaxial Graphene on SiC{0001} Surfaces: A Comparative Photoelectron Spectroscopy Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, No. 155303.

(69) Strupinski, W.; Grodecki, K.; Wyszomolek, A.; Stepniewski, R.; Szkopek, T.; Gaskell, P. E.; Grüneis, A.; Haberer, D.; Bozek, R.; Krupka, J.; Baranowski, J. M. Graphene Epitaxy by Chemical Vapor Deposition on SiC. *Nano Lett.* **2011**, *11*, 1786–1791.

(70) Verhagen, T. G. A.; Drogowska, K.; Kalbac, M.; Vejpravova, J. Temperature-Induced Strain and Doping in Monolayer and Bilayer Isotopically Labeled Graphene. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *92*, 1–9.

(71) Tada, H.; Kumpel, A. E.; Lathrop, R. E.; Slanina, J. B.; Nieva, P.; Zavracky, P.; Miaoulis, I. N.; Wong, P. Y. Thermal Expansion Coefficient of Polycrystalline Silicon and Silicon Dioxide Thin Films at High Temperatures. *J. Appl. Phys.* **2000**, *87*, 4189–4193.

(72) Peng, B.; Zhang, H.; Shao, H.; Xu, Y.; Zhang, X.; Zhu, H. Thermal Conductivity of Monolayer MoS₂, MoSe₂, and WS₂: Interplay of Mass Effect, Interatomic Bonding and Anharmonicity. *RSC Adv.* **2016**, *6*, 5767–5773.