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

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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, and due to widespread material availability. It can be used in a variety of applications, including transparent photodetectors, field-effect transistors, photoresponsive memory devices, and quantum well light-emitting diodes. There are two main methods to obtain MoS₂ monolayers: mechanical exfoliation and chemical vapor deposition (CVD). 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) and thermal vapor deposition (TVD). While MOCVD is an industrially proven technique to produce high-quality crystals, 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.

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. Alternatively, graphene can also be used as a growth platform for MoS₂. 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. These heterostructures are superior to the classical heterostructures as the epitaxial layer is bound only...
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 heterostructures is increasing; however, the majority of the articles are presenting the structures created with at least one.16−19 Still, several scientific papers are reporting all-CVD growth of MoS2/graphene vdW sandwich,20−25 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.24−27 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 graphene, 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.

**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 Qntor Raman spectroscopy 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
Focused on achieving individual MoS$_2$ grains on three substrates to compare their morphology. AFM images of MoS$_2$ grown on SiO$_2$, sapphire, and graphene are shown in Figure 2, accompanied by height profiles. The height profiles on each substrate show MoS$_2$ layers approximately 0.7 nm thick, proving the monolayer nature of these as-grown nuclei. The MoS$_2$ grain morphology, however, is different on each substrate. MoS$_2$ on SiO$_2$ and sapphire tends to form circular domains, whereas on graphene, these grains are triangular. The largest domains and smallest nucleation density were achieved on SiO$_2$.

To confirm the chemical composition and presence of MoS$_2$ on the substrates, we conducted simple Raman characterization, shown in Figure 3. MoS$_2$ 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 SiO$_2$, graphene, and sapphire, respectively, indicating the presence of monolayer MoS$_2$. Additionally, on graphene and sapphire substrates, the A$_{1g}$ peak of sapphire can also be noted. The MoS$_2$ peaks are positioned differently on each substrate, which will be discussed later.

RESULTS AND DISCUSSION

Direct Comparison between MoS$_2$ Grown on SiO$_2$, Sapphire, and Graphene. The initial investigation was focused on achieving individual MoS$_2$ grains on three substrates to compare their morphology. AFM images of MoS$_2$ grown on SiO$_2$, sapphire, and graphene are shown in Figure 2, accompanied by height profiles. The height profiles on all three samples, and the peak separations are small, 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 MoS$_2$ morphology on graphene samples, namely, slight variations in grain size and nucleation density (Figure 4d–f). On the contrary, the morphology of MoS$_2$ grains on SiO$_2$ 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 MoS$_2$. The unusual stability of MoS$_2$ growth on graphene needs more attention. Before we explain the observed differences of MoS$_2$ 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 MoS$_2$ synthesis occurs. The most accepted route for the formation of MoS$_2$ from MoO$_3$ and S is as follows:

$$7S + 2MoO_3 \rightarrow 2MoS_2 + 3SO_2$$  

(1) In fact, the synthesis of MoS$_2$ during CVD growth does not involve single MoO$_3$ and S species. Instead of atomic sulfur, sulfur molecules, S$_n$, with n between 2 and 8, are present in the gaseous form, and S$_8$ is the most abundant. Similarly, also no single MoO$_3$ molecule reacts in the vapor, but rather MoO$_3$$_n$ polymeric species with 3 ≤ n ≤ 5, and Mo$_x$O$_y$S$_z$ constitutes 70% of the vapor. The more adequate chemical reaction, therefore, should involve S$_8$ and Mo$_x$O$_y$S$_z$ rather than atomic S and MoO$_3$. Currently, no reports are discussing whether MoS$_2$ in the gaseous form is a single molecule or a cluster. Still, as the structure of Mo$_x$O$_y$S$_z$ is similar to the structure of MoS$_2$, Mo$_x$S$_y$ 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, while the second advocates that the partially reduced MoO$_3$$_{1-n}$ is adsorbed on the substrate and is further reduced by sulfur on-site. 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 MoO$_3$ and S at the standard growth temperature are easy to compute and are equal to 4.2 mbar$^{34}$ and 21.4 bar$^{35}$, respectively.

However, there are no reports showing the value of MoS$_2$ vapor pressure at high temperatures. Extrapolating the evaporation rate of MoS$_2$ obtained by Bisson to 770 °C,$^{36}$ the calculated value of MoS$_2$ vapor pressure is approximately 0.1 mbar, which is significantly lower than the vapor pressure of MoO$_3$ and S. Since the growth occurs and MoS$_2$ has the lowest vapor pressure among the three compounds, it is likely that the growth is driven by the adsorption and coalescence of gaseous MoS$_2$ molecules synthesized in the vapor phase rather than on-site reduction of MoO$_3$. Furthermore, if MoO$_3$ and S adsorb on the substrate, their presence should be visible in Raman spectroscopy measurements. It is not the case as except MoS$_2$ and substrate peaks, no more chemical compounds are present.
prerequisite for the van der Waals epitaxy.\textsuperscript{37,38} Therefore, only very weak interactions between adsorbed species and graphene can be expected, which is the main characteristic of any layered 2D material, including MoS\textsubscript{2}. Carbon atoms forming the graphene layer cannot create any new chemical bonds, which is also characteristic of any layered 2D material, including MoS\textsubscript{2}. Therefore, only very weak interactions between adsorbed species and graphene can be expected, which is the main prerequisite for the van der Waals epitaxy.\textsuperscript{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 SiO\textsubscript{2} 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,\textsuperscript{39} for example, active hydroxyl groups on SiO\textsubscript{2} (Figure 5). The movement of the species is allowed only between these binding sites. These hydroxyl groups can also become nucleation sites for MoS\textsubscript{2} growth as the predicted activation energies of R\textsubscript{3}—Si—O—MoS\textsubscript{2} from R\textsubscript{3}—Si—OH are similar to the thermal energy of gas molecules at the growth temperature, that is, 156 and 135 meV, respectively.\textsuperscript{40}

It has to be noted, however, that the hopping mechanism is not valid for some materials. There are studies of gas movements on weakly interacting surfaces, for example, Xe, Kr, CH\textsubscript{4}, or NO on graphite,\textsuperscript{41} that showed the surface diffusion should be rather described as a so-called mobile diffusion.\textsuperscript{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.\textsuperscript{43}

It is commonly known that for the hopping mechanism, the surface mean free path\textsuperscript{44} and the residence time\textsuperscript{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 MoS\textsubscript{2} morphologies. As theoretically predicted by Cao et al.,\textsuperscript{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,\textsuperscript{57,48} except dodecagons, which we will discuss later.

**Explanation of the Observed Differences in MoS\textsubscript{2} 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 MoS\textsubscript{2} 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

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**Figure 4.** MoS\textsubscript{2} grain morphologies observed in modified growth conditions on SiO\textsubscript{2} (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.

**Figure 5.** Schematic representations of the movement of the adsorbed MoS\textsubscript{2} species (red balls) on SiO\textsubscript{2} (left) and graphene/sapphire (right). The valleys on the SiO\textsubscript{2} surface represent high-energy binding sites. The schematic is not to scale.
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 dodeca-gons, 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 SiO$_2$ 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 MoS$_2$ 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 MoS$_2$ 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. 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 photothermal screening, which reduces the electron–phonon coupling, manifested as an upshift of graphene 2D peak.

The analysis of the graphene Raman peaks position is presented in Figure 7b. When MoS$_2$ 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. This state, however, reverts closely to the doping of the as-received graphene, which acts similarly to hexagonal boron nitride (hBN) and encapsulates the nondoped state. As a result, graphene with MoS$_2$ on top is low doped.

Therefore, we can conclude that the graphene layer is well preserved after the growth of the MoS$_2$ layer. The change of the graphene doping determined via shifts of G and 2D peak positions can be explained by both thermal treatment and MoS$_2$ encapsulation.

### Raman Characterization of Continuous MoS$_2$ on SiO$_2$ and Graphene

Investigations of the strain level in MoS$_2$ layers are of increasing interest as they provide insight into the tunability of the band gap of the 2D semiconductor. There are two main methods to characterize the strain levels in TMDCs, that is, Raman spectroscopy and photoluminescence. Several factors can impact the shift and separation of Raman peaks. Besides strain, stacking order, number of layers, and doping can also influence the position of the peaks.

With a higher number of layers, the peak separation is increasing. Doping predominantly influences the A$_{1g}$ peak, shifting it toward higher wavenumbers with larger hole doping, 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 MoS$_2$, and it has to be stressed that only the relative changes between two samples can be established.

Still, the peak positions derived from Raman mapping can be used to determine the relative change in these properties. The MoS$_2$ peak positions are presented in Figure 8. The average

![Figure 8. Position of MoS$_2$ Raman peaks on graphene and SiO$_2$.](image-url)
from K to Γ in bilayer MoS₂.\(^\text{57}\) Additionally, also a negative trion, \(\text{A}^{-}\),\(^\text{63}\) can be observed.

The presence of I exciton in our graphene sample is caused by a significant number of adlayers. Furthermore, the presence of \(\text{A}^{-}\) trion in the SiO₂ sample might indicate n-doping or a relatively strong MoS₂—substrate interaction.\(^\text{19,63}\) 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,\(^\text{65}\) 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,\(^\text{64}\) 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.\(^\text{55,57,65,66}\) Interestingly, in the case of MoS₂ on SiO₂, the reported A exciton energy of the unstrained MoS₂ is varying from 1.8\(^\text{65}\) to 1.9 eV,\(^\text{66}\) and the theoretical value for the band gap in MoS₂ is predicted to be 1.9 eV.\(^\text{62}\) Nevertheless, in the case of MoS₂ on graphene, the reported energy of A exciton is in a much narrower range, between 1.86\(^\text{61}\) and 1.88 eV.\(^\text{50}\) Similar values of A exciton position were also measured for freestanding MoS₂ monolayers, in which the influence of substrate is negligible.\(^\text{67}\)

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.,\(^\text{26}\) 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.\(^\text{68,69}\) 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.,\(^\text{70}\) 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.,\(^\text{57}\) the value of A exciton response to strain is 45 meV/%. The thermal expansion coefficient of SiO₂ is 0.5 \(×\) \(10^{-6}\) K\(^{-1}\),\(^\text{71}\) while that of MoS₂ is 17.4 \(×\) \(10^{-6}\) K\(^{-1}\).\(^\text{72}\) 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 platform...
substrate resulted in the realization of van der Waals epitaxy; therefore, the MoS$_2$ layer is strain-free. The strain-free nature of MoS$_2$ on graphene is confirmed by PL studies and supported by the literature data, and we settle the ongoing discussion of the strain levels in MoS$_2$ on graphene. We also suggest that PL can be used to arbitrarily determine strain levels in MoS$_2$, as we showed for MoS$_2$ on SiO$_2$.

Still, there is some uncertainty in several aspects of the MoS$_2$ growth, including whether MoS$_2$ 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.

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### Notes

The authors declare no competing financial interest.

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