Nucleation and growth studies of large-area deposited WS$_2$ on flexible substrates

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Abstract

Transition metal dichalcogenides (TMDCs) such as tungsten disulfide (WS$_2$) are studied for advanced electronic and optical devices because of their unique and versatile electrical, optical and mechanical properties. For the use of TMDC films in next-generation flexible electronics, large-area bottom-up synthesis on flexible substrates needs to be mastered, understood and controlled. In this study, we performed a detailed study on the nucleation and growth of WS$_2$ layers deposited by metalorganic chemical vapor deposition (MOCVD) on crystalline van-der-Waals material muscovite mica as a model substrate and on the alkali-metal free flexible glass AF $32^\circ$ eco. The deposition of the WS$_2$ layers was performed using an all nitrogen-coordinated bis-imido-bis-amido tungsten based precursor in combination with elemental sulfur as the co-reactant. On both substrates, crystalline growth of WS$_2$ at a moderate growth temperature of 600 $^\circ$C was verified by Raman spectroscopy and X-ray diffraction (XRD). However, the growth mode and nucleation density differ significantly. On mica, an initially planar growth of WS$_2$ triangular islands is observed, whereas untreated glass reveals an out-of-plane growth. Detailed XRD and Raman analysis show tensile strain in the WS$_2$ films on both substrates, indicating a strong interaction from CVD grown TMDC films with the underlying carrier material. In order to avoid such substrate-semiconductor interaction, a substrate pre-treatment is required. A plasma pre-treatment prior to the deposition leads to a planar growth even on amorphous glass substrates.

1. Introduction

Since the first successful exfoliation of graphene, 2D materials have attracted considerable interest from both the research community and industry. Especially flexible electronics with smart materials are playing a key role to meet market demands of future technologies in the major driving applications of the Internet of things (IoT), wearable electronics, healthcare and electronic skins (e-skins) [1, 2]. For flexible electronics based on transition metal dichalcogenides (TMDCs) to be implemented in future technological devices, large-scale growth on various surfaces including flexible substrates must be mastered and tailored. So far, large-area growth on 2D materials is still in its infancy [3].

Among the several hundreds of 2D materials, Group VI transition metal dichalcogenides (TMDCs) such as MoS$_2$ and WS$_2$ are widely studied regarding their potential in advanced electronics. Their semiconducting polymorphs have a considerable band gap [4] and exhibit high electron mobility [3]. WS$_2$ is a layered material with strong in-plane bonds and weaker interactions between two adjacent layers. The mobility is theoretically even higher for WS$_2$ than for MoS$_2$ [5] and is therefore in the focus of this study. To gain insight into the material properties, most of the studies were done on mechanical exfoliated flakes. However, exfoliation is not a scalable
technique. Thus, to close the gap between laboratory research and industrial implementation, large-scale deposition techniques need to be investigated, understood and developed. The common approaches for obtaining large-area TMDC films are atomic layer deposition (ALD) [6–8], chemical vapor deposition (CVD) [9–13], physical vapor deposition (PVD) [14, 15] and thermal vapor sulfurization on a metal or metal oxide [16–18]. ALD processes are very attractive for flexible electronics because of the low deposition temperatures, but the resulting films often show poor crystallinity [8, 19, 20].

Therefore, among the bottom–up approaches, 2D material growth by CVD prevail as the most promising technique so far. During the WS2 film growth the substrate has a significant impact concerning the film quality and topography. Most of the studies have been performed on amorphous SiO2 [21, 22], sapphire model substrates [23–27] and graphene/HOPG [28, 29]. Recently, on W–Au alloy substrate Wang et al demonstrated a strategy for preferentially forming antisite defects during WS2 growth [30]. Nevertheless, the high growth temperatures required for CVD processes prevent mostly the use of flexible substrates, especially polymer substrates. A further difficulty in the large-area growth of TMDCs is the undesirable formation of vertical 3D structures composed of out–of–plane layers [31]. Since basal and edge–plane oriented TMDCs exhibit highly anisotropic properties [32], suppressing the vertical growth of TMDC films is of critical importance for microelectronic devices.

To get rid of the trade–off between high crystallinity and low temperatures, which are demanded by the flexible substrates, new precursor chemistries with higher reactivity at moderate temperatures are necessary. During gas phase deposition processes, several reactions can take place simultaneously. How the material starts to cover the surface depends on the interplay between the reaction kinetics of surface, gas phase reaction (in case of CVD growth), deposition temperature, reactor pressure, surface states and the reactivity of the surface. The nucleation primarily depends on the amount and reactivity of the chemical sites at the surface. Three strategies can be distinguished to improve the controllability of CVD growth of TMDCs: (a) temperature triggering, (b) precursor choice and (c) substrate engineering [33].

In this study the WS2 films were grown using an all nitrogen–coordinated bis-imido-bis-amido precursor namely [W(N′Bu)2(N′Pr2)2] and elemental sulphur. The deposition procedure followed was similar to that recently reported for WS2 on Si substrates, where the suitability of the precursor for processes at moderate temperatures has been demonstrated as crystalline film growth below 700 °C was observed [34]. Thus, the process temperature, the precursor source and co-reactants are fixed according to the optimized deposition process for [W(N′Bu)2(N′Pr2)2] and here we focus exclusively on the influence of the substrate on the growth process. Substrates could for example introduce scattering centers, dopants and roughness, which may affect the intrinsic properties of the WS2 layer. This work deals with the growth and nucleation of WS2 on flexible substrates based on analyses of topography, morphology and structure of the WS2 with respect to the deposition time. Understanding the TMDC-substrate interaction will provide crucial information for selecting suitable substrates for future flexible electronics. Controlling the crystallinity, structure and morphology of TMDC layers is even less trivial at low deposition temperatures, as required for flexible substrates. But this is important for the development of an advanced process for integrating 2D materials on a chip-scale level, as required for commercial products. The task for the coming years must be to gain a deeper understanding of large-area growth on flexible substrates as well as the flexible substrate-TMDC interface, as this will form the basis for future strategies of substrate engineering.

Within the scope of this work, we combine atomic force microscopy (AFM), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM), XRD, Raman spectroscopy and contact angle measurements to gain insight into the growth of WS2 on muscovite mica and alkali-free glass (Schott AF 32° eco). The nucleation of the TMDC film determines the crystallinity and morphology and its analysis can provide an insight on how to tailor the material properties and desired growth towards specific applications. The primary aim of CVD growth is to maximize the grain size and surface coverage, minimizing the grain boundaries and making crystals large enough that a device can operate within a single domain. The integration of dissimilar materials underlies most functional devices, which implies in 2D electronics the dominance of interfaces in performance or that they are ‘still the device’ [35].

2. Choice of flexible substrates

Polymer substrates are attractive for flexible electronics due to their low cost; however, their low temperature budget, high surface roughness, and high oxygen transmission rate currently prevent their efficient use in 2D technology. In contrast, flexible amorphous glasses allow temperatures up to 700 °C, have low surface roughness and an oxygen and water transmission rate that is close to zero. This means that the preparation of complex barrier layers is not necessary and saves process steps, materials and time. For this purpose, glass substrates are the better choice. To reduce the grain boundaries within the 2D layer, crystalline substrates such as sapphire and
Thermal expansion coefficient

Substrate sizes: Currently only small synthetic mica substrates available.
Temperature stability: Up to 700 °C.
Roughness: Atomically flat cleavage.

Crystal structure:

Property
Muscovite mica
Flexible glass (Schott AF 32° eco)

| Property                      | Muscovite mica                                      | Flexible glass (Schott AF 32° eco) |
|-------------------------------|-----------------------------------------------------|-------------------------------------|
| Crystal structure             | Crystalline substrate, \(a = 0.519, b = 0.901, c = 1.996 \text{ nm}\) | Amorphous, < 1 nm                   |
| Roughness                     | Atomically flat cleavage                            |                                     |
| Temperature stability         | Up to 700 °C                                       | Up to 650 °C                        |
| Substrate sizes               | Currently only small synthetic mica substrates available (\(d < 10 \text{ cm}\)) | Up to 12 inch available             |
| Thermal expansion coefficient | \(9 \cdot 10^{-6} \cdot 36 \cdot 10^{-6} \text{ K}^{-1}\) | \(3.2 \cdot 10^{-6} \text{ K}^{-1}\)  |

Muscovite mica (\(\text{KAl}_3\text{Si}_3\text{O}_10(\text{OH})_2\)) are often used. Higher-quality 2D layers are therefore expected to be formed on the model substrate mica and it is the long-term goal to produce 2D layers with similar layer quality on the industrially relevant glass substrate. This is the reason why we decided to make a comparative growth study on amorphous glass and crystalline mica. In a next step, the growth on glass must be controlled and influenced by for e.g. a specific surface pretreatment. The occurrence of only weak van-der-Waals (vdW) interactions between the 2D film and the substrate instead of strong covalent and ionic bonding enables the growth of epitaxial films of materials with dissimilar lattice constants or even different crystal structures than the substrate without build-up of strain in the film. Mica, a silicate-based mineral, has been used as a substrate for the growth of various materials [36]. It does not exhibit dangling bonds on its clean surface, and is therefore one of the preferred substrates for vdW epitaxy, which allows the formation of heterostructures composed of materials with a large lattice mismatch [37]. A critical feature of such an approach is the weak interaction between the films and the muscovite substrate due to the nature of vdW epitaxy. Similar thermal expansion coefficients can potentially solve the problem. MICATronics, or vdW epitaxy on mica, is expected to have a significant impact on high-performance flexible electronics, sensors, energy-harvesting devices, etc [36]. In covalent heteroepitaxy, similarity in crystalline symmetry, lattice parameters, and thermal expansion coefficients between the substrate and the epitaxial crystalline overlayer is required to suppress elastic strain and the nucleation of defects in the crystal. Although the lattice constant of mica is larger than that of most TMDCs, high quality MoSe₂ [38] and SnS₂ [39] layers have been successfully grown on muscovite by vdW epitaxy. In this study, we also use the layer-structured muscovite mica (figure S1) as a substrate to study the CVD growth process on a crystalline, flexible substrate. The layer structure of muscovite mica is shown in figure S1. Within each layer, the atoms are connected by strong covalent silicon–oxygen and aluminum–oxygen bonds, whereas the basal layers are only held together by electrostatic and weaker vdW forces [40]. The negatively charged aluminosilicate sheets are electrostatically bound to alternating layers of K⁺ ions. The freshly cleaved surface of muscovite mica is expected to be free of dangling bonds as adjacent layers are connected by vdW attraction instead of chemical bonds and is therefore suitable for the demonstration of crystalline growth of TMDC films. Nevertheless, up to now synthetic mica substrates are not available in large scale and can therefore only serve as a model substrate. For industrial applications, it must be the goal to establish a growth process on amorphous flexible substrates, which are commercially available in large formats. We selected Schott AF 32° eco glass in our study, as it has a low coefficient of thermal expansion similar to a silicon wafer (table 1). With its high thermal stability, high optical quality, excellent dielectric properties and very low roughness (< 1 nm), it suits a broad range of applications. Moreover, the glass is alkali-free and made without antimony and arsenic, making it compatible with the requirement profile of many clean rooms in the semiconductor industry. Additionally, the glass substrates are available up to a 12-inch wafer format. The prominent properties of both substrates, which are in the focus of this study are summarized in table 1. The glass substrates were cleaned with solvents before deposition and the muscovite mica substrates were freshly cleaved. The cleaved crystalline mica substrate is almost entirely chemically inert [41] and the basal plane [001] of the cleaved muscovite mica surface is a hexagonally arrayed pattern of oxygen atoms. In contrast, the amorphous glass surface exhibits more active surface sites, which leads to a higher amount of absorbed hydrocarbons.

3. Results and discussion

3.1. Contact angle measurements

Wettability of a substrate is an indicator for its free surface energy, which decisively determines the nucleation density of the film [43]. Thus, contact-angle measurements were performed first, which are summarized in table 2. The corresponding contact angle images for droplets of water and diiodomethane on both substrates can be found in the supporting information (figure S2). Freshly cleaved mica is extremely hydrophilic, resulting in smaller contact angles, compared to the corresponding angles on glass. Consequently, the surface free energy determined using the Owens-Wendt-Rabel-Kaelble model [44–46] is significantly higher on mica. Under
ambient conditions, the contact angle of a cleaved mica substrate increases slightly [47]. It is widely-known, that the wettability of a surface is influenced by the surface topography [48]. When particles come into contact with the substrate, they bind mainly to crystallographic defects, e.g. steps. Therefore, AFM measurements on the glass and mica substrate were performed (figure S3) and revealed a root-mean-square roughness of 0.28 nm and 0.07 nm, respectively. The high surface energy of mica enables a good absorption of other molecules to which it is exposed to [49] and should reduce nucleation density and promote planar growth. This consideration is verified in the following based on AFM measurements.

### 3.2. Topographical film analysis

To evaluate the dependency of the crystallite growth on the substrate and deposition time, atomic force microscopy was conducted. Figure 1 displays exemplarily the atomic force micrographs of WS2 films on top of mica and glass substrates for 2 min, 6 min and 8 min deposition time (table 3). The complete topographical analysis for deposition times between 2 min and 20 min can be found in the supplementary information figure S4 (on mica) and figure S5 (on glass). On glass substrates, uncoordinated and possibly out-of-plane growth was observed, while there is triangular nucleation on muscovite mica. Additionally, the WS2 features on mica are more flat compared to the WS2 on top of glass, which is directly evident by the height scale. For deposition times below 4 min the WS2 films on mica have a flatter surface compared to WS2 on glass. Also, at the beginning of the growth the grain size of the WS2 crystallites is larger on mica than on glass. The analysis of the nucleation density revealed a lower density on mica compared to glass substrate for short deposition times (table 3). For deposition times of 2 min the nucleation density of WS2 is more than twice as high on glass than on mica and for deposition times of 3 min it is even 5 times larger. This significantly lower nucleation density of WS2 on mica is a promising indicator for larger crystallites, which should be verified by XRD and Raman measurements. Correspondingly, the grain sizes of WS2 flakes on mica are also larger when compared to those on glass. These findings suggest a more in-plane growth on the mica substrates and a more pronounced out-of-plane growth on the glass substrates for the first monolayers. Therefore, an additional roughness analysis was performed. The root-mean square roughness with respect to the deposition time on both substrates are summarized in figure S6. For longer deposition times the roughness of the WS2 films rises extremely, which indicates a possible onset of an out-of-plane growth mode. To evaluate the assumptions regarding crystallite size and growth-mode further characterization of the films is necessary. For that reason, we performed Raman spectroscopy in order to get more information about the quality of the deposited films. To estimate the nucleation density and grain size AFM images were processed using the software gwyddion. For this purpose, corresponding areas were marked that belong to individual grains. For the segmentation of the nucleation islands, the watershed algorithm [50] was used. The distribution of the island diameters was evaluated by statistical analysis of the raw data and illustrated by histograms. The samples exhibit a unimodal distribution that was fitted by a Gaussian peak. The average flake size and the FWHM of the size distribution were determined on mica as well as on glass substrates as illustrated in figures 1(g) and 1(h).

### 3.3. Raman analysis

Raman spectroscopy is a unique and powerful tool to investigate layer numbers [51], strain effects [52, 53], doping [54, 55] and morphology [56] in WS2 based on molecular vibrations and has also been used to interpret TMDC substrate interactions [57, 58]. Most of these studies are done on exfoliated WS2 flakes. Raman scattering on large-area deposited WS2 films remains largely unexplored especially for multilayer WS2 inhibiting in-plane and out-of-plane layers. The presence of the characteristic $E_{2g}^{1}$ peak (in-plane vibration), the 2LA (M) peak (second-order logitudinal acoustic mode) and $A_{1g}$ peak (out-of-plane vibration) in Raman analysis indicate the successful deposition of crystalline WS2 on mica as well as on glass substrates (figure 2(a)). Figure 2(b) displays exemplary the Raman spectra of WS2 on both substrates for a deposition time of 6 min. The peak position located around 353 cm$^{-1}$ ($E_{2g}^{1}$) and 420 cm$^{-1}$ ($A_{1g}$) are in relative accordance with literature values for exfoliated bulk layer WS2 [59]. The position of the $E_{2g}^{1}$ is red-shifted for WS2 films on both substrates compared to exfoliated films. The $E_{2g}^{1}$-peak is known to be extremely sensitive to in-plane strain, which leads to a

| surface | contact angle (°) | surface free energy (mJ/m²) |
|---------|------------------|-----------------------------|
|         | DI-water         | diiodomethane               |
| mica    | 2.7              | 34.5                        |
| glass   | 29.7             | 48.8                        |

Table 2. Contact angles and surface free energies of freshly cleaved mica and Schott AF 32° eco glass.
strain-induced red-shift. Thus, for a more detailed analysis a Lorentzian fit of the overlaying modes of WS$_2$ was carried out. The diagrams in figure 3 show the resulting peak-positions for WS$_2$ films on mica (red) and glass (blue). The positions shown are mean values with their respective standard deviation obtained from six measurements at different locations on the specimen. The high-frequency phonons $E_{2g}^1$ and $A_{1g}$ are mainly caused by relative vibrations of atoms in the adjacent sublayers with the restoring force of covalent type and are thus very insensitive to sample-substrate interaction with applying the force of vdW type. Since the shift of the $E_{2g}^1$ peak with respect to the deposition time is higher for mica (2.25 cm$^{-1}$) than for glass (1.65 cm$^{-1}$), a higher uniaxial strain for WS$_2$ on mica is observed, when compared to WS$_2$ on glass (figure 3(a)). For exfoliated TMDC films the out-of-plane $A_{1g}$ mode is insensitive to in-plane strain.

| Deposition time | Nucleation density ($\mu$m$^{-2}$) |
|----------------|----------------------------------|
| Muscovite mica | Glass substrate                  |
| 2 min          | 176                              | 387                           |
| 3 min          | 69                               | 333                           |
| 4 min          | 131                              | 264                           |
for planar films [52] and is significantly affected by doping. Here we observe a distinct blue-shift of the $A_{1g}$ peak on mica for deposition times of 5 min, 6 min, 12 min and 20 min. For two-dimensional flat TMDC sheets, an increase of layer numbers would increase the vdW force that stiffens atom vibration, causing a blue shift of the $A_{1g}$ mode [59, 60]. Therefore, with increasing deposition time a continuous blue-shift of the $A_{1g}$ peak should be the expected, contrary to our results. Since doping can be excluded, the $A_{1g}$ shift may also be a signature of strain.

In the studies of Wang et al on three-layer walled WS$_2$ nanotubes, they demonstrated that the inter-layer mode $A_{1g}$ of WS$_2$ nanotubes with small diameters is significantly affected by curvature strain [61]. Unlike exfoliated films, the CVD-grown TMDC films are not planar and different orientations of the crystallites occur. Thus, on the nanoscale the deformation of a CVD grown TMDC layer on a given substrate is a mixture of strained, unstrained, uniaxially and biaxially, as well as curvature strained regions, all averaged by the large laser spot. Since in our case the blue shift of the $A_{1g}$ peak is not continuous and corresponds to a significant increase of the roughness on mica substrates we assign the position of the $A_{1g}$ peak of a signature to the beginning of out-of-plane growth. The curvature energy becomes dominant over the van der Waals force, causing an abrupt blue shift of $1.5 \text{ cm}^{-1}$ for $A_{1g}$ mode, as shown in figure 3(b). With the $D-A_{1g}$ (405–415 cm$^{-1}$) peak, there is a direct defect peak, similar to the D-peak in graphene. Causes of structural disorder could be the misalignment of SWS stacks, strain, or local intra layer defects like dislocations or atoms with dangling bonds. We observe a blue shift of the $D-A_{1g}$ peak of $5 \text{ cm}^{-1}$ for WS$_2$ deposited on mica substrates (figure 3(c)), while the $I_{A_{1g}}/I_D$ peak intensity decreases from 4 to 1.5 (figure 4(b)). On glass, neither parameter is significantly affected in terms of deposition times. Krause et al demonstrated in their work that the disorder-induced $D-A_{1g}$ Raman line intensity for WS$_2$ implies a correlation with the number of interlayer defects [56] similar to that known for the $I_{D}/I_G$ ratio in disordered graphite [62]. From the measurement, it can be deduced that in the early stages of WS$_2$ growth on mica a lower number of interlayer defects occur than in later stages.

### 3.4. XRD analysis

Apart from the Raman spectra, crystalline growth of WS$_2$ is also verified using XRD. Figure 5 shows the XRD spectra (a) of WS$_2$ on muscovite mica for varied deposition time (1 min $\leq t \leq 20$ min), (b) of muscovite mica (c) of WS$_2$ on glass for varied deposition time (1 min $\leq t \leq 20$ min) and (d) of WS$_2$ derived from the crystal
structure [63]. A diffraction reflex is present in the pattern of WS$_2$ on glass as well as on mica, at $2\theta$ of 14.16°; this reflex corresponds to the (002) plane of hexagonal WS$_2$, indicating the growth of crystalline WS$_2$ with a preferential orientation of the (00l) series. Figure S7 depicts a detail view of the XRD spectra of the WS$_2$ films on mica (a) as well as on glass (b) near to the (002) reflection of hexagonal WS$_2$. The slightly decreased 20 reflection compared to its natural position, which is slightly more pronounced for glass, indicates tensile strain for WS$_2$ on both substrates. The position of the (002) reflection as well as the FWHM are elevated by a Lorentzian fit of the measurements and summarized in figure 6. The larger FWHM values of the TMDC film on glass compared to those obtained on mica correspond to smaller WS$_2$ crystallites on glass than on mica. The size of the crystallites were calculated using the Scherrer equation and revealed sizes up to 6 nm (4 nm) on mica (glass). The larger tensile strain in WS$_2$ grown on glass may be a result of the cooling process after the film deposition, caused by the distinct thermal expansion coefficients of WS$_2$ and the substrate. The thermal expansion coefficient (TEC) of mica (glass) amounts to $9 \cdot 10^{-6}$–$36 \cdot 10^{-6}$ K$^{-1}$ ($3.2 \cdot 10^{-8}$ K$^{-1}$) [64]. The in-plane TEC of WS$_2$ was determined as $1.01 \pm 0.06 \cdot 10^{-5}$ K$^{-1}$ for freestanding bulk WS$_2$ [65]. Huang et al determined a significantly larger TEC of the out-plane mode than that of the in-plane mode for monolayer WS$_2$ above room temperature [66].

Figure 4. $I_{A1g}/I_{E2g}$ peak intensity ratio (a) and $I_{A1g}/I_{D}$ peak intensity peak ratio (b) on mica (red) and glass (blue) in dependence of the deposition time.

Figure 5. XRD pattern of (a) WS$_2$ on mica substrate (b) muscovite mica (c) WS$_2$ on glass and (d) WS$_2$ derived from the crystal structure of WS$_2$ [62].
the WS2 nanostructures have been briefly discussed for MoS2 in previous CVD studies [31, 68], nevertheless, a comprehensive understanding of the formation is still missing. Comparable to the studies of Li et al for MoS2, we observe laterally expanding grains following Volmer Weber growth. All grains have their basal planes parallel to the mica surface. TEM measurements on the glass substrate reveal no planar growth and no layered structure of WS2 on mica: the reposition of the WS2 film is close to the natural position, which means that in these cases the impact of the underlying substrate can be neglected. While Raman spectra are sensitive to strain within the TMDC interface, CVD grown TMDC interacts much stronger with the underlying substrate, and hence the CVD grown TMDC films appear to be more strained and less n-doped compared to exfoliated films, possibly due to the intercalated water film [67].

3.5. SEM and TEM analysis

Finally, SEM and HRTEM measurements were performed, to get further insight into the morphology. Prior to the measurements, the samples were covered with Cr and C, respectively. On the SEM images of WS2 deposited on mica, cracks are visible (figure 7(a)), which are not observed for WS2 deposited on glass. Crack induced delamination is a signature of high tensile stress within the WS2 film on the mica substrate. Bright fin-like structures on the scanning electron micrographs correspond to out-of-plane WS2 crystallites. The number density of the vertical layers is significantly higher for WS2 layers on glass (figure 7(d)) than on mica (figure 7(c)) and the lateral dimension of the vertically grown WS2 layers are smaller on glass. For a longer deposition time of 20 min the surface topography appears very different (figure 8). While the vertical layers are still observable on glass and the fins remain thin, WS2 on mica substrates possesses much wider planar flakes and the cracks within the WS2 film on mica remain. Since scanning electron microscopy gives just a rough idea of the morphology of the WS2 film, HR-TEM gives us the opportunity to have a closer look at the buried WS2 layers especially at the interface. From the cross-sectional HR-TEM images the atomic structure at the interface between the mica substrate and the first layers of the WS2 films reveal the initial basal-plane oriented horizontal layers. After the initial horizontal growth of up to 10 layers, out-of-plane growth occurs. For the muscovite mica substrate the aluminosilicate interlayer spacing were measured to be 1 nm (figure 9(a)) and the interlayer spacing of the WS2 film amounts to 0.67 nm for the in-plane layers and 0.78 nm for the out-of-plane layers (figure 9). The regions where these values were determined are marked in figure 9(a). The determined layer distances within the WS2 film and mica are in good accordance to values found in literature. Formation mechanism of vertical nanostructures have been briefly discussed for MoS2 in previous CVD studies [31, 68], nevertheless, a comprehensive understanding of the formation is still missing. Comparable to the studies of Li et al for MoS2, we observe laterally expanding grains following Volmer Weber growth. All grains have their basal planes parallel to the mica surface. TEM measurements on the glass substrate reveal no planar growth and no layered structure was observed possibly due to a phase transition of the TMDC layer during the FIB cleavage process, which was performed at 30 kV [69]. Formation of out-of-plane growth depends on several factors e.g. minimization of surface energy, relaxation of accumulated strain, defect-mediated growth at vacancies and grain boundaries. Vertical growth can also originate directly from defects and contamination on the substrate [70]. Interestingly some layers are protruding out of the film. In other positions an exclusively planar growth is observed (figure 9(b)).
4. Discussion

Crystalline growth of WS$_2$ on the two flexible substrates alkali-free glass and muscovite mica was verified for our WS$_2$ process by Raman Spectroscopy and XRD. In both cases the crystallite sizes are still too small to use in high-performance 2D microelectronics. Although on both substrates the determined crystallite sizes do not differ significantly, very different growth modes take place. On freshly cleaved muscovite mica, the first monolayers of WS$_2$ grow with a planar orientation. From Raman and XRD measurements, it is evident that the WS$_2$ undergoes significant tensile strain resulting in a crack induced delamination of the film, as shown in SEM images. XRD measurements also reveal a compressive strain within the mica substrate, when WS$_2$ is deposited. Although muscovite mica is a vdW material, we observe a WS$_2$ mica substrate coupling, which is rather typical.

Figure 7. Scanning electron micrographs of 6 min deposited WS$_2$ films on top of mica (a), (c) and glass (b), (d).

Figure 8. Scanning electron micrographs of 20 min deposited WS$_2$ films on top of mica (a), (c) and glass (b), (d).
for conventional epitaxy, which is dominated by covalent bonds. On air-cleaved mica substrates the presence of carbon and hydrocarbon impurities has been detected [71] and is likely the cause for the rather high nucleation density of WS₂ on mica. The nucleation density and grain size of an UHV-cleaved mica-surface are of interest for further studies, since the presence of water vapour is necessary for the formation of carbonaceous species on the surface [72]. Additionally, randomly distributed potassium ions appear to also have a major effect on surface epitaxy. Ostendorf et al demonstrated the formation of potassium carbonate following the interaction of a cleaved mica surface with ambient air [73]. For deposition times above 6 min out-of-plane growth occurs, which was visualised by TEM measurements. Therewith, the roughness of the film increases significantly (figure S4) and the curvature strain leads to a blue-shift of the A₁g peak within the Raman spectrum (figure 4(b)). Simultaneously, the defect peak of the WS₂ Raman spectrum shifts to higher wavenumbers and the Iₐ₁₉/I₃ peak intensity peak ratio on mica decreases significantly. These features indicate higher amounts of defects within the WS₂ film during the beginning out-of-plane growth. The XRD reflection of WS₂ is also broadened for growth times of 6 and 8 min, indicating the significantly increased disorder and/or strain effects, respectively. Presumably, both effects play a role in these films, since in the XRD spectra of the crystalline Mica substrate broaden significantly and split into two peaks (figure S8). Figure 10 shows a schematic diagram of the growth mode on mica and in which areas tensile, compressive and curvature strain appears. For the amorphous, flexible glass substrate a higher roughness is detected at the beginning of the deposition process and no triangular features or planar growth was observed. The higher amounts of adsorbed hydrocarbons [49] on the more active surface sites of the flexible glass may be responsible for the vertical growth mode on glass. To evaluate this assumption, we prepared alignment marks on cleaved mica, subsequently cleaned the substrate analogous to the glass substrate, and then deposited WS₂. Contaminations such as resist residuals and hydrocarbons lead to a higher number of nuclei on the substrate, resulting in a WS₂ film with lower grain size and a higher nucleation density. The surface energy an important factor to control the film orientation and surface coverage and a higher surface energy is preferable for promoting in-plane layers. In fact, through an Ar sputter step prior to the WS₂ deposition, we were also able to achieve a planar growth on the flexible glass substrates (figure S10). Based on these observations, we can conclude that tuning the substrate determines the growth of WS₂ layers with different orientations and thus allows controlling the texture of nanostructured WS₂ during its growth. It demonstrates a strategy for achieving large-scale growth on commercially available 12-inch scale flexible amorphous substrates. To verify this, further detailed analysis of the growth in relation to the surface treatment is required and will be the focus of our next studies. Thereby, it should be investigated, how to tailor the wettability/surface energy by using different pre-treatment methods and seed layers to achieve a desired crystalline growth. The surface free energy of the substrate depends on pre-treatment and temperature conditions. Here we could clearly correlate the higher surface energy of mica with a reduced nucleation density when compared to the nucleation density of glass. The overall goal of a low nucleation density and a large-area coverage is not achieved yet, but we were able
to determine a method. Further strategies for pre-treatment and deposition without vacuum loss are needed, in order to avoid undesired carbon hydrogen species hampering large-area growth and simultaneously increasing the surface energies.

5. Conclusions and outlook

We performed a comparative study on the growth of WS$_2$ on crystalline muscovite mica and amorphous flexible glass. The analysis comprises AFM, contact angle measurements, XRD measurements, Raman spectroscopy, HR-TEM and SEM measurements. For both substrates a crystalline growth of WS$_2$ in a bottom-up approach was successfully achieved even at a proceeding temperature of 600 °C. We observe an initial planar growth of WS$_2$ triangular islands on top of the vdW material muscovite mica, whereas the growth on untreated alkali free glass reveals an out-of-plane growth. With detailed Raman analysis, we observed tensile strain in the WS$_2$ films on both substrates, but only on mica the high tensile strain within the planar layers leads to a crack induced delamination. Despite the atomically flat vdW material a strong substrate-semiconducting film interaction is detected by XRD measurements, which we attribute to potassium carbonate. On glass substrates a plasma treatment prior to the WS$_2$ growth also leads to planar growth and indicates that the presence of hydrocarbon or potassium carbonate species on the surface are critical for WS$_2$ growth on flexible substrates. To avoid such nucleation centers and thus achieve a reduction of the substrate-semiconductor interaction, substrate pre-treatment is required, ideally directly in a system where deposition of the TMDC film can take place without vacuum loss. For further applications interface engineering in wafer scale technology of flexible substrate is of great significance.

6. Experimental

WS$_2$ samples were grown on 1 cm × 1 cm muscovite mica and flexible glass AF 32° eco substrates in a homebuilt CVD reactor as reported in previous work [34]. The muscovite mica substrates were freshly cleaved instantly before the deposition and the glass substrates, were cleaned with acetone and isopropanol before the WS$_2$ growth. Atomic force microscopy (AFM) measurements were performed using a Nanoscope Multimode V microscope from Digital Instruments, operating in tapping mode. The Raman spectra were measured with a Renishaw InVia microscope (532 nm) with a laser power < 2 mW and an exposure time of 1 s to prevent the samples from heating up. XRD measurements were conducted on a Bruker AXS D8 Advanced diffractometer in $\theta$–$2\theta$ geometry with CuK$_\alpha$ (1.5418 Å) radiation in the range from $2\theta = 10^\circ$ to $2\theta = 60^\circ$. High-resolution transmission electron cross-section micrographs of selected samples were prepared using a dual-beam FEI...
Helios G4 CX focused ion beam (FIB) instrument operated at 30 kV. To protect the samples from damage caused by the ion beam, carbon was sputtered on the layers in advance. TEM imaging were performed using a FEI Tecnai F20 instrument operated at 200 kV. Contact angles of drops have been measured using a drop shape analyzer DSA25 from Krüss GmbH and a circular fitting algorithm. Two probe liquids of known polar and dispersive interactions (deionized water and diiodomethane) were dosed automatically onto the horizontally arranged substrate surfaces. The profile determination of more widely spread droplets were performed by both automatic and manual circle-fitting. Based on these measurements, the surface energy was calculated by using the Owens-Wendt-Rabel-Kaelble model (OWRK).

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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