Surface roughness is a key parameter for judging the performance of a given material’s surface quality for its electronic application. A powerful tool to measure surface roughness is 3D laser scanning confocal microscopy (LSM), which will allow you to assess roughness and compare production and finishing methods, and improve these methods based on mathematical models.

Focus on creating high-conductivity electronic devices with minimal power loss using laser scanning microscopy is an effective tool to discern a variety of roughness parameters.
Controllable and Reproducible Growth of Transition Metal Dichalcogenides by Design of Experiments

Stefan Heiserer,* Peter Eder, Cormac Ó Coileáin, Josef Biba, Tanja Stimpel-Lindner, Cian Bartlam, Ulrich Rührmair, and Georg S. Duesberg*

1. Introduction

2D materials have gained an enormous interest in academic research due to their unique and tunable electrical and optical properties.[1,2] They have potential for numerous applications in sensing or photonic devices.[3–7] In the large family of semiconducting 2D materials, transition metal dichalcogenides (TMDs) such as tungsten disulfide (WS2) are promising candidates for future applications due to their outstanding optoelectronic properties.[8,9] Reliable and scalable fabrication of the material is thereby crucial for academic studies and applications.

Chemical vapor deposition (CVD) is largely regarded as the most promising platform for large-scale synthesis of 2D materials including TMDs.[8,10] During the CVD process, gas phase precursors undergo chemical reactions on and near a substrate surface at elevated temperatures, resulting in the deposition of material on the surface.[11] Thereby, a vast parameter space opens up, including different types of precursors, substrates, temperature, gas concentration, flow rate, pressure, process time, and many others.[12,13] Often single process parameters like temperature or carrier gas composition are varied to enhance the output quality.[12] Furthermore, the relationship between growth conditions and the resulting material deposition differs from setup to setup. Thus, reported process parameters cannot be simply copied for other setups and expected to yield the same results. Growth conditions have to be optimized carefully for each setup, and therefore benchmarking of the results is difficult. Regardless all these effort, growth control and reproducibility remains challenging as small changes in the growth conditions can have strong impact on the resulting deposition.[12,14–16]

Design of experiments (DoE) can create a set of experiments where the different input parameters are varied concurrently. This allows one to scan the parameter space within a finite set of growth processes in a more efficient and sophisticated way. Zhang et al. investigated the interaction between different process parameters in CVD growth of TMDs by modeling reported crystal morphologies with respect to corresponding growth settings. However, process settings, outputs, and their relations usually depend on the specific setup used and thus are hardly comparable.[17] Therefore, it is crucial to fix all settings which are not going to be optimized during DoE. Focusing
on 2D materials, optimization using DoE is only reported for graphene CVD synthesis.\[18,31] To the best of our knowledge, an experimental and consistent CVD growth optimization for TMDs based on design of experiments has not been reported.

Here we describe a study on the synthesis of WS\(_2\) which demonstrates how DoE statistical approaches can be exploited to optimize CVD growth of TMDs. As different process parameters interact with each other, it is not enough to simply optimize one at a time separately. Five input parameters were varied concurrently to design 29 processes covering the entire parameter space. The corresponding growth results fit a model describing the dependencies of the growth outputs on the process parameters. The established model is used to determine the influential input parameters and to predict the optimized settings needed to enhance growth for various applications. It was successfully tested by directing the growth toward certain crystal qualities like single monolayer crystals or large-area continuous films. In addition, the optimized processes show very good stability and reproducibility. Certainly, the technique presented can easily be applied to other CVD setups, with alternative key parameters, and any TMD material, providing an efficient and systematic method to optimize CVD growth of TMDs.

2. Results and Discussion

2.1. Prestudies: Precursor and Parameter Set

A schematic of setup used for WS\(_2\) growth is shown in Figure 1a. It features a microreactor containing a solid state precursor seed and a growth substrate in close contact.\[20] The patterned seed substrate shown in Figure 1b) is sputter-coated with oxidized tungsten and serves as metal precursor supply and has patterned and continuous WO\(_3\) areas to prestructure growth. This microreactor design allows the WO\(_3\) precursor to be only supplied locally and avoids potential contamination of the reactor, thus ensuring better run to run comparability. Sulfur, as the chalcogenide precursor, is carried by the Ar/H\(_2\) flow to the growth substrate. The two precursors are at different temperatures \(T_{\text{precursor}}\) for sulfur and \(T_{\text{growth}}\) for the microreactor. After preliminary studies, the process parameters and their range were selected according to Table 1 which defined the extent of the parameter space to be explored. As a fundamental principle for a successful DoE, other possible influencing factors were kept consistent and constant as far as possible during experiments.\[21] The selection of input parameters heavily depends on the setup and growth method used. Therefore, there is no complete list of input parameters for CVD processes. For example, temperature ramp, type of precursor, or the relative position of the precursor sources with respect to the growth substrate can be optimized.\[22,33]

2.2. Design of Experiments

To find optimized and stable growth conditions within the spanned parameter space, a D-optimal design of experiments was used. Optimal designs are commonly used in DoE as they allow versatile choice regarding the number of parameters and their values such that experimental constraints can be accounted for. In a D-optimal design the confidence ellipsoid is minimized to increase the precision of the fit coefficients and the predictions.\[24] The designed parameter sets then fractionally cover the entire parameter space within the selected model. Thereby, the vast number of possible combinations within the parameter space was reduced to only 29 processes. As further fundamental principles of DoE, they include repetitions and are in a random order.\[21] The details of the performed processes defined within the design can be found Table S1 (Supporting Information).

In the model applied, the output \(Y(x)\) depends on linear, quadratic, and interaction terms of the input parameters \(x_i\). In the formula

\[
Y(x) = a_0 + \sum_{i=1}^{p} a_i x_i + \sum_{i=1}^{p} a_i x_i^2 + \sum_{i=1}^{p} \sum_{j=1}^{p} a_{ij} x_i x_j (1)
\]

The table below shows the selected input parameters and their corresponding value range:

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temperature</td>
<td>800–900 °C</td>
</tr>
<tr>
<td>Precursor temperature</td>
<td>100–120 °C</td>
</tr>
<tr>
<td>(H_2) concentration</td>
<td>10%–50%</td>
</tr>
<tr>
<td>Process time</td>
<td>15–45 min</td>
</tr>
<tr>
<td>Pressure</td>
<td>2–50 mbar</td>
</tr>
</tbody>
</table>

The corresponding growth results fit a model describing the dependencies of the growth output on the process parameters. The confidence ellipsoid is minimized to increase the precision of the fit coefficients and the predictions.\[24] The designed parameter sets then fractionally cover the entire parameter space within the selected model. The vast number of possible combinations within the parameter space was reduced to only 29 processes. As further fundamental principles of DoE, they include repetitions and are in a random order.\[21] The details of the performed processes defined within the design can be found Table S1 (Supporting Information).
formed responses. Layer number remained untransformed.

$\alpha_0$ denotes the overall mean response, $\alpha_i$ is the main effect of factor $x_i$, and $\alpha_{ij}$ is two-way or quadratic interactions between the $i$th and $j$th factors.

### 2.3. Growth Evaluation

After performing the CVD processes, in-depth material characterization was performed using Raman spectroscopy, atomic force microscopy (AFM), and optical microscopy (Figure S1, Supporting Information). To fit the selected model, measurable outputs have to be defined. Therefore, the characterization results were combined to derive a consistent and efficient all-optical evaluation routine which takes four output parameters into account: surface coverage, single crystal size, film thickness, and film area.

**Figure 3** shows the adjusted response graph which illustrates the relationship between each process parameter and the different output variables. As the impact of the other input parameter is averaged out for each single plot, the graph helps provide a fundamental understanding how different process parameters influence CVD growth. In general, the surface coverage and film size exhibit similar trends. For example, both output values increase with increasing growth temperature until a plateau is reached. Single crystal size follows a similar trend with growth temperature. In contrast, the film thickness decreases at the same time, suggesting lateral growth is preferred at higher temperatures, which is often desired. The process pressure has the greatest influence on film thickness and surface coverage shows a maximum at around 25 mbar, but it has almost no influence on film size and single crystal size. Another input parameter $H_2$ concentration has a significant impact only on film thickness as it increases for both, high and low concentrations. Significantly, process time has no major effect on any of the responses. This finding was confirmed by a test process with a much longer process time of 90 min, which showed no significant change in output parameters and may be attributed to a simultaneous and self-limiting etch effect due to hydrogen in the carrier gas and limited metal precursor. The influence of precursor temperature seems to have the most complex trends as it depends heavily on the setting of other parameters. For example, there is a strong interaction between the precursor temperature and both the growth temperature and pressure (see Figure S3 in the

Table S2 (Supporting Information) shows the coefficients for each model as well as their significance values. The adjusted $R$-square values for the fits of surface coverage, film size, thickness, and single crystal size are 0.845, 0.913, 0.804, and 0.83, respectively. This indicates already a reliable data set and a correctly chosen model. Moreover, a proper residual analysis was made to ensure trustworthy data interpretation. Figure 2 shows the residual probability plots for all responses where residuals are plotted against theoretical values of normal probability distribution. Besides one obvious outlier, the residuals stay well within the $3\sigma$ range and follow the straight line of normal distribution which is desirable for confidence and significance calculations. Furthermore, this confirms that the model chosen is suitable and reliable conclusions and predictions can be made from it.

**Figure 2** shows residual probability plots showing a normal distribution of fit residuals.
Figure 3. Adjusted response graph for crystal size, layer number, film size, and surface coverage: The influence of each process parameter is shown in the corresponding box. The impact of the remaining input parameters is averaged out.

Supporting Information). The former can be related to maintaining the necessary ratio between metal and sulfur precursor during growth. The latter one confirms increased sulfur evaporation rate at lower pressure.\(^{[17]}\)

2.5. Successful Prediction and Growth Control

To achieve high-quality materials for the desired applications, process parameter sets can be predicted to optimize the material with respect to certain aims. These aims can be single or a combination of optimized output values. In our study, we show two examples of possible optimization scenarios: The first aim is single monolayer crystals where crystal size is maximized and layer number minimized at the same time. The second aim is to get samples with high yield of continuous material which is often desired for electrical device applications. Thereby, the two output parameters, film size and surface coverage, are maximized. The optimized process parameters shown in Table 2 are derived from the fit model to optimize the aim of large single monolayer crystals and or large-area continuous films, respectively. As predicted by the model, the processes using the optimized parameters resulted in enhanced output values. Table 2 compares the values for each objective before and after optimization starting from the best processes found by trial and error over 20 different processes. All values markedly increased, showing controlled growth and successful optimization.

2.6. Optimized Material Quality and Process Stability

To confirm the consistent high quality of the grown material, the optimized processes were performed multiple times. The resulting growth was characterized using Raman and photoluminescence (PL) spectroscopy (see Figure 4). In the scenario where the growth was optimized to produce a continuous monolayer film, there is additional bilayer growth which can be seen in optical contrast as well as in PL intensity. Furthermore, the grain boundaries of underlying monolayer film show a decreased signal in the PL intensity map (Figure 4c)). Figure 4d shows an optical micrograph of the sample optimized for single crystals featuring monolayer crystals. The PL map of a 23 μm monolayer single crystal

Table 2. Process parameters for optimized processes toward large monolayer crystals and continuous film.

<table>
<thead>
<tr>
<th>Aim</th>
<th>Single monolayer crystals</th>
<th>Large film size</th>
<th>Optimized parameters: ( \text{H}_2) conc., pressure, process time, growth temp., precursor temp.</th>
<th>25%, 2 mbar, 40 min, 870, 115 °C</th>
<th>30%, 26 mbar, 30 min, 850, 110 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average value before → after DoE percentage change</td>
<td>8 μm → 19 μm</td>
<td>120 μm → 950 μm</td>
<td>+137%</td>
<td>+690%</td>
<td></td>
</tr>
<tr>
<td>Standard deviation before → after DoE percentage change</td>
<td>48% → 34%</td>
<td>67% → 27%</td>
<td>−29%</td>
<td>−59%</td>
<td></td>
</tr>
</tbody>
</table>

Optimization led to significantly higher output values and lower interprocess standard deviations in both scenarios.
Figure 4. a,b) Optical images of a continuous monolayer film with additional crystalline bilayer regions. c) PL intensity map of WS$_2$ continuous film showing suppressed intensity along grain boundaries and in bilayer regions. d) Single monolayer (light brown) and bilayer (dark brown) crystals of WS$_2$. PL intensity map of a 23 μm flake (inset). e) Raman spectra and corresponding optical micrographs of monolayer and bilayer WS$_2$ single crystals.

(inset of Figure 4d) exhibits a slight intensity decrease along its symmetry axis which is often seen in CVD crystals and can be attributed to tungsten vacancies.\[^{32–34}\]

As shown in Table 2 not only did the desired output values increase, but moreover the interprocess fluctuations in the outputs, using the same recipe, drastically decreased to values of 34% and 27% standard deviation for the single crystal and film process, respectively. This confirms unique process stability and reproducibility of the CVD-grown material.

3. Conclusions

In summary, CVD growth of WS$_2$ was optimized by tuning the process parameters using DoE. The output was modeled with regards to surface coverage, film size, layer number, and crystal size to develop an understanding of the basic underlying growth kinetics. Furthermore, the model successfully provided predictions of parameter sets for different application scenarios including single monolayer crystals and large continuous films. For all of them, the predicted processes show optimized results and moreover enhanced stability due to drastically decreased interprocess fluctuations. Our technique offers a straightforward and coherent route to get controllable and stable growth which can be tuned for the desired application. Moreover, the technique is not limited to morphology evaluation. Electrical characteristics could be used as an output parameter to further refine and direct the growth or properties of the materials. We believe the approach can easily be adapted to broader application areas including different TMD materials and other CVD methods with different growth parameters. Thereby, mapping the scope of the parameter space through DoE may offer a route to realistically compare the materials produced in different CVD setups.

4. Experimental Section

Precursor Synthesis and CVD Growth: WO$_3$ seed substrates were prepared by patterned deposition of 10–20 nm of tungsten on silicon substrates and subsequent oxidation under low pressure O$_2$/Ar atmosphere at 550 °C for 10 h. Growth substrates (Si with 90/300 nm thermal SiO$_2$) were cleaned in acetone and IPA in an ultrasonic bath and placed face down on top of the WO$_3$ substrates. The microreactor design allows the WO$_3$ source substrates to be only supplied locally and avoids potential contamination of the reactor with excess materials, thus ensuring better run to run comparability. The WO$_3$ source substrates were replaced for each experiment with the same quantity and configuration of WO$_3$. The samples were placed in a ceramic boat within the hot zone of the quartz tube furnace. A second movable furnace was used to heat the sulfur powder placed within a boat upstream the tube. When the main furnace reached the set process temperature, the sulfur furnace was moved toward the main furnace heating the sulfur to the set precursor temperature. At the same time the process time started and 20 sccm of H$_2$ was added to the carrier gas. The argon flow was thereby adjusted with respect to the set H$_2$ concentration. After the process the H$_2$ flow was stopped and the precursor supply rapidly stopped by moving the sulfur furnace away from the precursor source.

Material Characterization: Photoluminescence and Raman spectra were recorded using a Witec alpha 300 R under 532 nm laser excitation. AFM was performed using a Jupiter XR Asylum Research from Oxford Instruments in tapping mode. For the growth output evaluation for the DoE
an all-optical method was developed using the optical mode of the Raman microscope with different magnifications. The layer number of the crystals was clearly identified by optical contrast. **Data Analysis:** For design of experiments the software Cornerstone 7.3 from CamLine GmbH was used. Input factors and responses were defined relating to the process parameters and measured output, respectively. A model was selected including linear, quadratic, and interaction terms. The process runs were then chosen using a D-optimal design.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

2D materials, chemical vapor deposition, design of experiments, growth optimization, transition metal dichalcogenides, tungsten disulfide

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