Suppression of Mirror Domains in the Epitaxial Growth of Single Layer WS$_2$

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The need for a versatile, scalable protocol to grow single layer transition-metal dichalcogenides (TMDCs) beyond exfoliation is an essential requirement for expanding the knowledge about the features of these materials and thus implementing devices based on them. However, TMDCs grown by bottom-up methods usually exhibit two mirror orientations, a condition that invalidates the possibility of applications in devices using the valley degree of freedom. We present herein a bottom-up approach to grow epitaxial single layer tungsten disulfide (WS$_2$) suppressing the growth of a detrimental mirror orientation. By means of fast X-ray photoelectron spectroscopy we show that a low W evaporation rate and high substrate temperature lead to crystalline islands with a single orientation, as demonstrated by photoelectron diffraction experiments. The morphology and size of the WS$_2$ domains were probed by employing low-energy electron microscopy. Our results can pave the way to the realization of valleytronic and optoelectronic applications based on single layer tungsten disulfide.
INTRODUCTION

Only a short time after the successful creation of graphene by mechanical exfoliation [1-3], it was realized that other two-dimensional materials could be obtained in a similar way from layered crystals, especially transition metal dichalcogenides (TMDCs) [4]. This has lead to an intense study of single layer (SL) TMDCs which, like graphene, show electronic properties that are remarkably different from those of their parent bulk compound. Initially, much attention had been given to the presence of a direct band gap in some of the semiconducting SL TMDCs [5, 6] and the possibility to exploit this property in electronic and opto-electronic applications [7, 8]. Later, it was suggested that these materials could be used for entirely new concepts in electronics because of their coupled spin [9] and valley [10-13] degrees of freedom [14], something that does not play a role in graphene where inversion symmetry prevents the lifting of the spin degeneracy.

The technological exploitation of the SL TMDCs will benefit from production by bottom-up growth, rather than exfoliation. Chemical vapor deposition and molecular beam epitaxy appear to be promising approaches to obtain a high degree of orientation and a closed layer [15-22]. An additional requirement for devices that shall make use of the valley degree of freedom, such as a valley filter [23], is to avoid the presence of mirror domains, a common defect in the growth of SL TMDCs [19]. The two mirrored versions of the SL TMDC unit cell have the same reciprocal lattice, with merely the K and -K points of the surface Brillouin zone inverted [24] and the same band structure, apart from an inverted spin polarization for the two mirror domains. The presence of mirrored domains is thus detrimental for both fundamental studies on the coupled spin and valley degrees of freedom and for the use of TMDCs in devices [13, 25].

There has been recent progress in the growth of single orientation two-dimensional materials, for example for SL BN on Ir(111) [26], as well as for SL MoS$_2$ on hexagonal boron nitride [21] and Au(111) [24]. Here we show that by careful tuning the growth parameters, this can also be achieved for SL WS$_2$, the material of choice for the investigation of the spin degree of freedom in TMDCs because of the very large spin splitting in the valence band [27]. We introduce two different growth procedures, characterize the outcome by X-ray photoelectron spectroscopy (XPS) and determine the structural parameters and the extent and orientation of the crystalline domains by combining low-energy electron diffraction (LEED) and microscopy (LEEM) with X-ray photoelectron diffraction (XPD). XPD measurements were able to conclusively prove that SL WS$_2$ can grow with a single orientation and determine the relative orientation of SL WS$_2$ with
respect to the Au(111) substrate. The acquisition of the W 4f and S 2p core levels with fast-XPS during the deposition of WS\textsubscript{2} was instrumental to determine the best growth parameters needed to obtain a SL with a single orientation.

**METHODS**

Growth and characterization experiments were carried out at the SuperESCA beamline\textsuperscript{[28]} of the Elettra Synchrotron radiation facility in Trieste, Italy, except for the LEEM data, which were acquired at the University of Bremen. The Au(111) substrate was cleaned by cycles of Ar\textsuperscript{+} ion sputtering at 2 keV and annealing up to 950 K. Cleanliness of the surface was checked by LEED and XPS, which did not detect traces of contamination. High-resolution S 2p and W 4f core level spectra were measured at room temperature in normal emission on the as-grown WS\textsubscript{2} single layer, using photon energies of 260 eV and 140 eV, respectively. The overall energy resolution was below 50 meV. Thanks to the combination of a high-flux beamline and a high-efficiency electron detector, it was possible to measure fast X-ray photoelectron spectroscopy (XPS) spectra during the growth, greatly aiding the optimization of growth parameters.

Each XPD pattern was measured by collecting XPS spectra for more than 1000 different polar (\(\theta\)) and azimuthal (\(\phi\)) angles, as defined in the diagram in Figure\textsuperscript{[2]} For each of these spectra, a peak fit analysis was performed (parameters of the analysis reported in Supplementary Information) and the intensity \(I(\theta, \phi)\) of each component resulting from the fit, \(i.e.\) the area under the photoemission line, was extracted. The resulting XPD patterns are the stereographic projection of the modulation function \(\chi\), which was obtained from the peak intensity for each emission angle (\(\theta, \phi\)) as

\[
\chi = \frac{I(\theta, \phi) - I_0(\theta)}{I_0(\theta)},
\]

where \(I_0(\theta)\) is the average intensity for each azimuthal scan at polar angle \(\theta\). The structural determination was performed by comparing measured XPD patterns to multiple scattering simulations for a trial structure. Such patterns were simulated using the program package for Electron Diffraction in Atomic Clusters (EDAC)\textsuperscript{[29]}. The presence of two mirror domain orientations was taken into account by an incoherent superposition of the calculated intensities, based on the well-funded \textsuperscript{[30] [31]} assumption of domain sizes that are sufficiently large to neglect boundary effects. The agreement between the simulations and the experimental results was quantified by computing the
reliability factor \( (R) \) \[32\]

\[
R = \frac{\sum_i (\chi_{\text{exp},i} - \chi_{\text{sim},i})^2}{\sum_i (\chi_{\text{exp},i}^2 + \chi_{\text{sim},i}^2)},
\]

(2)

where \( \chi_{\text{sim},i} \) and \( \chi_{\text{exp},i} \) are the simulated and the experimental modulation functions for each emission angle \( i \). The estimation of the accuracy of the quantities derived by means of R-factor analysis, i.e. lattice constant, layer thickness and percentage of mirror domains, was deduced from the R-factor confidence interval defined as \[33\]

\[
\Delta R_{\text{min}} = R_{\text{min}} \sqrt{\frac{2}{N}},
\]

(3)

where \( R_{\text{min}} \) is the minimum R-factor value and \( N \) is the number of well-resolved peaks in the XPD pattern \( (N \sim 350) \).

The LEED experiments were carried out using a commercial VG instrument installed at the experimental chamber of the SuperESCA beamline.

LEEM data were recorded using an ELMITEC LEEM III instrument at the University of Bremen. A sample was prepared at the SuperESCA beamline, transferred to Bremen through air and then annealed to 670 K after inserting it in the ultra-high vacuum (UHV) chamber. As a diffraction based method, LEEM can access either real space (imaging mode) or reciprocal space (diffraction mode) providing information on both surface morphology and atomic structure.\[34\] By constricting the illuminated area with an aperture in diffraction mode, information on the local atomic structure can be obtained from areas as small as 250 nm in diameter, an approach known as \( \mu \)LEED. In BF imaging contrast usually arises from differences in local atomic structure and composition. In DF-LEEM diffraction contrast is obtained since only regions contributing to this very beam will show up bright in the image. In LEEM, the \( I(V) \) curves were extracted from a stack of images, yielding individual \( I(V) \) curves for every image pixel, thus enabling structural identification on the nanoscale.\[35,36\]. The LEED calculations were performed using the AQuaLEED package, which is based on the Barbieri/Van Hove SATLEED package and on the layer stacking implementation by N. Materer \[37,39\]. The \( I(V) \) curves have been calculated considering SL WS\(_2\) with the structural parameters obtained from XPD stacked on the Au(111) substrate and stretching the Au(111) surface lattice constant to match that one of WS\(_2\).
RESULTS AND DISCUSSION

We have characterized SL WS\textsubscript{2} on Au(111) prepared according to two distinct growth procedures, hereinafter labeled as GR1, that led to the growth of a mixture of two mirror domains, and GR2, which resulted in the growth of SL WS\textsubscript{2} with a single orientation. In both growth methods, tungsten was dosed on Au(111) from a hot W filament in a background pressure of H\textsubscript{2}S. For GR1, the substrate temperature was 873 K and the W deposition rate, measured by means of a quartz microbalance, was $7.5 \times 10^{-3}$ ML/min, with 1 ML corresponding to the surface atomic density of the Au(111) surface. The H\textsubscript{2}S pressure was $1 \times 10^{-6}$ mbar. For GR2 the growth was performed at a higher sample temperature (923 K) while a more than two-times lower W deposition rate ($3.3 \times 10^{-3}$ ML/minute) was employed. H\textsubscript{2}S pressure was set to $1 \times 10^{-5}$ mbar. The growth was followed in real-time by fast-XPS, acquiring the W 4\textit{f} core level during the entire process. A full account of these measurements is presented in Supplementary Information.
High-resolution W 4f core-level spectra measured after GR1 and GR2 are shown in Figure 1a and b, respectively. For GR1, the main spin-orbit doublet, interpreted as stemming from SL WS$_2$ (blue component) [40], is accompanied by many small contributions (grey components) at lower binding energy (BE), attributed to incompletely sulfided W species of the form WS$_{2-x}$ (0 < x < 1) or metallic W clusters, as observed earlier for the same system [40–42]. For GR2, on the other hand, these additional components are entirely absent and the W 4f$_{7/2}$ spectrum shows a single peak at BE = 32.78 eV, characteristic of SL WS$_2$ [40], with its spin-orbit doublet separated by 2.14 eV. The line-shape parameters used for the spectral deconvolution are given in Supplementary Information.

In Figure 1c and 1d we show the S 2p spectra resulting from the two growth procedures. Two main components are visible in each of the spin-orbit peaks, indicated in light (S 2p$_{3/2}$ BE=162.45 eV) and dark (S 2p$_{3/2}$ BE=162.59 eV) orange: the latter has been assigned to S atoms from the ‘bottom’ (close to the Au(111) surface) while the former stems from the ‘top’ atoms in the S-W-S sandwich arrangement of WS$_2$. This interpretation follows the assignments for SL MoS$_2$ prepared on Au(111) [24], and it will be discussed in the XPD experiments aiming to determine the polytype of the SL (see Supplementary Information). Besides these two components we observed several extra peaks at lower binding energy for GR1, which are originating from species other than WS$_2$. On the contrary, the spectrum acquired on GR2 shows the spectral components associated with top and bottom sulfur only, indicating a better quality of the grown layer.

Figure 1e reports the LEED pattern acquired on the GR2 sample. The most intense spots corresponding to the reciprocal lattice of WS$_2$ are surrounded by moiré satellites, due to the lattice mismatch between WS$_2$ and the Au substrate [40]. The first order Au(111) diffraction spots also exhibit a hexagonal pattern, though slightly bigger in dimension due to a smaller lattice vector, and they are aligned with those of WS$_2$ (see dashed yellow line in Figure 1e and inset thereinto). By comparing the reciprocal lattice vectors of WS$_2$ with those of Au(111), we obtain a moiré periodicity of 3.19 ± 0.1 nm, in close agreement with literature [40]. This is indicative of the formation of a superstructure with a periodicity of (10 x 10)-WS$_2$ on (11 x 11)-Au unit cell configuration.

Furthermore, the LEED pattern acquired on GR2 displays a three-fold symmetry (as evidenced by the circular profile taken across the WS$_2$ spots in the pattern), which could indicate the presence, for this sample, of a single azimuthal orientation of the WS$_2$ crystalline domains. However, a conclusive answer about the orientation of the layers and about the absence of detrimental mirror domains can only be obtained by means of XPD experiments.
FIG. 2. (top-panel) Side view (left) of the trigonal prismatic (1H) structural phase of WS₂, and top view (right) of the main (Or1) and mirror (Or2) orientations used for XPD simulations. (a) XPD pattern acquired on sample GR2 for the W 4f₇/₂ component ($h\nu = 170$ eV) (in color) together with a simulation assuming a single orientation of the layer (in greyscale). (b) W 4f₇/₂ XPD pattern obtained on sample GR2, with $h\nu = 360$ eV. (c) Contour plot reporting the R-factor as a function of the layer thickness and lattice constant. (d) and (e) R-factor along the dashed lines in panel (c). (f) R-factor vs. percentage of mirror orientation admixture, obtained for layer thickness and lattice constant values corresponding to the minima of the R-factor shown in panels (d) and (e). The inset of (d), (e) and (f) panels shows a magnification of the graph around the minimum of the R-factor, with the vertical dashed arrow indicating the confidence interval $\Delta R_{\text{min}}$ and the horizontal arrow the uncertainty in the determination of the lattice constant, layer thickness and percentage of mirror orientation, respectively, as explained in Methods. The simulated pattern shown are those obtained employing the parameters deduced from the R-factor analysis.
In XPD, photoemission intensity modulations arise from the interference between the component of the photoelectron wave field that reaches the detector directly from the emitting atom and the components scattered by atoms surrounding the emitter. This makes XPD very sensitive to the local environment of the emitter \[32\], hence making this technique ideal to address questions about the polytype of the layer (trigonal prismatic or octahedral), the distribution of mirror domains and other structural parameters such as lattice constant and layer thickness.

We acquired XPD patterns from the W \(4f_{7/2}\) core level on the layer produced with GR2 using a photon energy \(h\nu = 170\) eV (photoelectron kinetic energy, KE\(~\sim\)137 eV), at which both forward and backward scattering contributions are significant, and at \(h\nu = 360\) eV (KE\(~\sim\)326 eV), enhancing the forward scattering and suppressing the backscattering\[32\]. The experimental XPD patterns (color sector in Figure 2a and b) were compared to simulations (greyscale) using the reliability factor (R-factor) analysis (see Methods). Simulated diffraction patterns were calculated for different structural phases and their corresponding structural parameters assuming, as initial guess, the trigonal prismatic (1H) phase (sketched in Figure 2), following the indications obtained earlier for this system \[40\]. The presence of two orientations in the SL can be modeled by assuming an incoherent superposition from the domains, such that the total photoemission intensity is

\[
I_{\text{tot}} = aI_0 + bI_{\text{mir}} \quad (b = 1 - a),
\]

where \(I_0\) is the contribution to the XPD pattern from the main orientation (Or1) and \(I_{\text{mir}}\) is the contribution from the mirror orientation (Or2), according to the models shown in top-right of Figure 2. The simulated XPD patterns for the two mirrored orientations stemming from W \(4f_{7/2}\) (KE\(~\sim\)326 eV) are reported in the Supplementary Information.

The three-fold symmetry of the simulated patterns for a single orientation matches the experimental data, which is a direct experimental indication of a dominant domain orientation and hints at a minor contribution from the mirror orientation. However, a conclusive determination of the layer orientation was achieved only through the R-factor analysis, as shown in the following. For the simulations of the photoemission intensity by multiple scattering calculations, the values for layer thickness (i.e. the vertical S-S distance), the lattice constant and the fraction of mirror domains in the SL, assuming the 1H phase, were changed independently, running an R-factor optimization in the three-dimensional parameter space, using the data sets of both Figure 2a and b. The analysis clearly reveals a global minimum for a single orientation structure (a maximum of 5% contribution of mirror domains), a lattice parameter of 3.17 ± 0.04 Å and a layer thickness of 3.17 ± 0.05 Å in
FIG. 3. (a) XPD experimental pattern (colored) and simulated pattern (greyscale) for the W 4f$_{7/2}$ photoemission intensity modulation from sample GR1. The XPD pattern was measured with a photon energy of 360 eV, corresponding to a kinetic energy of 326 eV. (b) R-factor vs percentage of mirror orientation admixture for sample GR1.

very good agreement with the values reported in literature [43]. The very low absolute value of the minimum R-factor ($R = 0.05$) indicates an excellent agreement between experiment and simulation. For the sake of simplicity, Figure 2c reports a two-dimensional plot of the R-factor as a function of lattice constant and layer thickness obtained for the single orientation ($b = 0$). Figures 2d and 2e are obtained by taking cuts along the dashed lines in panel (c) to highlight the R-factor trend around the absolute minimum, while Figure 2f clearly shows that a minimum of R-factor is observed when only a single orientation is present.

A similar analysis on the XPD patterns from S 2p$_{3/2}$ and W 4f$_{7/2}$ was performed assuming an octahedral (1T) polytype for the WS$_2$ SL. The simulations of the XPD patterns were performed using the same lattice constant and layer thickness determined earlier for the 1H polytype. The analysis returned higher values of the R-factor for the 1T phase, ruling out this structure. The details of this analysis are reported in the Supplementary Information.

To understand whether also GR1 leads to a singly-oriented SL WS$_2$, we carried out an R-factor analysis simulating XPD patterns with a different percentage of mirror domains and compared them with the experimental pattern obtained from the W 4f$_{7/2}$ peak belonging to WS$_2$ acquired on GR1 (Figure 3a). The other structural parameters, obtained from the analysis on GR2, remained unchanged. In this case, the absolute minimum of the R-factor (0.07) was found when including ~20% of mirror domains in the simulation, as shown in Figure 3b.
It is interesting to ask what physical mechanisms are responsible for the growth of the single orientation. The only element breaking the symmetry is the Au(111) substrate. While the first Au layer has a six-fold symmetry, considering deeper layers lowers the symmetry to three-fold, providing a suitable template for the growth of singly-oriented WS$_2$. However, this feature can only be exploited by an adequate choice of the growth parameters, in particular the W deposition rate, the substrate temperature and the H$_2$S partial pressure. Optimizing these does not only improve the quality of the resulting SL WS$_2$ but drives the formation of a single domain orientation. This could be favorable to achieve in GR2 because a higher temperature allows an enhanced surface diffusion of W atoms on the Au substrate while a lower W deposition rate, together with a higher H$_2$S background pressure, avoids the formation of partially sulfided species, as seen by XPS.

Having established that GR2 results in the growth of a single domain orientation, we used the XPD pattern from the W 4$f_{7/2}$ core-level component for GR2 to determine the orientation of the WS$_2$ layer with respect to the Au(111) substrate. In order to do this, we determined the orientation of the Au(111) substrate by measuring an XPD pattern stemming from the bulk component of Au 4$f_{7/2}$ on the clean Au sample, i.e. before the deposition of WS$_2$. Figure 4a shows the typical Au 4$f_{7/2}$ spectrum acquired on clean Au(111). This is part of the series used to determine the XPD pattern of the bulk component Au$_B$, which is shown (colored sector) in Figure 4b together with a simulated XPD pattern (grey sector) obtained using a 4 layer slab, bulk terminated Au(111) surface, with emitters in the second and deeper layers. A good agreement of the three fold symmetric pattern (corresponding to the fcc (111) crystal stacking) with the simulation (R-factor=0.2), returns the orientation of the Au crystal as given in Figure 4c. Details about this R-factor analysis are given in Supplementary Information. Figure 4d and 4e show the two possible orientations of the SL WS$_2$ on Au(111). We call these configurations W$_{fcc}$S$_{top}$ and W$_{hcp}$S$_{top}$, in analogy with the case of h-BN on Ir(111)[26]. In the former configuration the sulfur atoms at the left bottom corner are adsorbed in atop position and the W atoms adsorb in the fcc hollow sites, while in the latter W sits in hcp hollow sites. The comparison between the XPD patterns of the Au substrate and of the WS$_2$ overlayer unambiguously proves that the singly-oriented WS$_2$ sample assumes the configuration W$_{fcc}$S$_{top}$ shown in Figure 4d. In Figure 4e we show a sketch of the entire moiré unit cell consisting of the (10 × 10) WS$_2$ superstructure on the (11 × 11) Au unit cell for the W$_{fcc}$S$_{top}$ orientation. For the mixed domain growth produced with GR1, only 80% of domains are oriented with the W$_{fcc}$S$_{top}$ configuration, while the remaining 20% adopts the W$_{hcp}$S$_{top}$ orientation.

Details about the surface morphology and the size of the crystalline domains have been obtained
FIG. 4. (a) Au $4f_{7/2}$ core level acquired on clean Au(111) at $h\nu = 400$ eV. Surface (Au$_{S}$) and bulk (Au$_{B}$) components are indicated. (b) XPD pattern acquired at 400 eV photon energy (KE~316 eV), showing the XPD pattern (color) associated to the bulk component Au$_{B}$ in the Au $4f_{7/2}$ core level together with the multiple scattering simulation (grey) for the clean Au(111) sample. (b) Orientation of the Au sample derived from the comparison of the XPD experiment with the simulation. (d) and (e) Ball model of the adsorption geometry of WS$_{2}$ on Au(111) at the corner of the moiré unit cell with orientation Or1 (W$_{fcc}$S$_{top}$) and Or2 (W$_{hcp}$S$_{top}$), respectively. (f) Moiré unit cell for the configuration Or1 (preferred) with the regions of high local symmetry for WS$_{2}$ on Au(111).
FIG. 5. (a) Bright-Field LEEM image (field-of-view ∼ 5µm, electron primary beam energy = 15.2 eV) acquired on GR2, showing areas covered with SL WS$_2$ and bare Au surface. µLEED patterns acquired on regions with (b) bare Au substrate and (c) covered with SL WS$_2$.

from LEEM measurements, carried out on a SL WS$_2$ sample prepared ex-situ according to the GR2 procedure. In Figure 5a, a typical LEEM image of the surface is shown, acquired using the specular (00) LEED beam. This imaging condition is known as bright-field (BF) mode. The surface presents a distinct contrast, distinguishing bright and dark areas. Micro-LEED patterns recorded from a 1 micron large dark area show the diffraction pattern expected for bare Au substrate (yellow circle, Figure 5b) whereas the brighter areas are WS$_2$-covered regions (orange circle, Figure 5c) with the characteristic moiré, as seen in the large area LEED pattern in Figure 1e. The black areas in the center of the image can be related to surface contaminations due to transfer through air of the sample. Surface steps of the Au(111) substrate are also visible at these imaging conditions. It appears that WS$_2$ domains have grown on individual terraces and they stretch over several microns along the steps.

Figure 6a displays a BF image acquired at larger magnification. Again, the bright areas exhibit a LEED pattern with the moiré of WS$_2$ on Au(111) (Figure 6b). The use of a higher order LEED beam for imaging (dark-field imaging, DF), in this case the (10) beam, should allow for contrast between rotational domains of WS$_2$, given the three-fold symmetry of the LEED pattern at some energies, as already shown in the LEED pattern in Figure 1e. A DF image of the same surface
FIG. 6. (a) Bright field-LEEM reveals islands which are identified as WS$_2$ islands by their specific LEED pattern. (b) $\mu$LEED pattern obtained using an illumination aperture of 1 $\mu$m (illuminated area marked by a yellow circle in (a)). (c,d) Dark field LEEM images of area (a) using the (10) beam of the WS$_2$ LEED pattern (cf. (b)), evidencing contrast changes of different WS$_2$ domains at certain energies. The filled triangle points to a specific reference position in the image. (e) Bright field $I(V)$ curves from the regions marked with red and black circles. (f) Corresponding dark field experimental (filled) and simulated (dashed) $I(V)$ curves for the two domains observed in panel (c) and (d), respectively. The $I(V)$ curves are vertically shifted for sake of clarity.
area is presented in Figure 6c. The majority of the WS$_2$ domains show up bright at the chosen electron energy of 31 eV. Tuning the energy to 40 eV highlights other WS$_2$ islands, as can be seen in Figure 6d. We now show that the islands of different contrast correspond to opposite domain orientations. The dependence of the local LEEM intensity vs electron energy (so-called $I(V)$ LEEM [35]) at the points marked in red and black in figures 6c and 6d can be used to determine the local structure [36]. First, the $I(V)$ curves of the (00) LEED beam for the two domains are compared in Figure 6e, revealing almost no difference. This finding directly proves that the two WS$_2$ domains have virtually the same atomic structure [35, 36]. By contrast, the two $I(V)$ curves obtained for the (10) spot, i.e. for the DF-mode image (filled lines in Figure 6f), are indeed dissimilar for the two different domains. While at 40 eV one WS$_2$ domain shows intense back reflection, at 31 eV the same domain reflects only weakly while the other does more strongly.

In order to confirm the structural origin of these differences, we show calculated $I(V)$ curves (dashed lines in Figure 6f) for the two possible adsorption configurations of SL WS$_2$. A very good agreement between the experimental and calculated curves is found assigning the configuration W$_{fcc}$S$_{top}$ to the majority of WS$_2$ domains (red), while only a minor fraction of domains assumes the W$_{hcp}$S$_{top}$ (black). This interpretation is confirmed by $\mu$LEED patterns acquired in each of the two regions (see Supplementary Information). Thus, the different domain orientations can be spotted at the nanoscale because of their different $I(V)$-curve fingerprint. From an overall quantitative evaluation of the available DF images, we derive a fraction of less than 5% of the surface being covered by the minority domains, in agreement with the results of the R-factor analysis performed for the XPD experiments. Moreover, these mirror domains are not uniformly distributed on the surface but rather were only found near surface defects, such as scratches or contaminations. This outcome sets the LEEM as an ideal technique to investigate the growth and features of TMDCs at the nanoscale, helping to understand the role of the deposition parameters and the growth mechanism from a microscopic point of view.

**CONCLUSION**

In summary, by using a bottom-up approach, we have grown WS$_2$ single layers on Au(111) with a single orientation, i.e. preventing the formation of detrimental mirror domains. This achievement is crucial in view of a development of devices exploiting the spin-valley degree of freedom. Our investigation has shown that a low W deposition rate, a high partial pressure of H$_2$S and a high
substrate temperature during the growth yield a unique crystalline orientation of SL WS$_2$. We have provided a characterization of SL WS$_2$ highlighting the differences in the final outcome due to the growth conditions combining spectroscopy (XPS), diffraction (XPD) and microscopy (LEEM), thus returning a complete overview of the characteristics of the WS$_2$ layer.

Earlier studies about the growth of epitaxial SL TMDC layers did rarely explore the domain morphology and distribution in quantitative detail since most experimental techniques are only able to give laterally averaged information over a macroscopic surface area. However, there have been indications of a domain mixture different from 50% for WS$_2$ on Ag(111), as circular dichroism in the excitation of a valley polarization was observed for this system [44]. We envision that the approach outlined herein can be applied to a wide range of materials and TMDC/substrate combinations and should pave the way for the synthesis of large area, high-quality SL WS$_2$ for the exploitation of the spin and valley degrees of freedom. Moreover, the growth protocol depicted here could be combined with methods already successfully employed to transfer WS$_2$ from Au to other substrates.

ACKNOWLEDGEMENTS

This work was supported by the Danish Council for Independent Research, Natural Sciences under the Sapere Aude program (Grant No. DFF-4002-00029) and by VILLUM FONDEN via the Centre of Excellence for Dirac Materials (Grant No. 11744). We thank Jan Lachnitt for fruitful discussion about the LEED-$I(V)$ calculations and assistance with the AQuaLEED software package.
SUPPLEMENTARY INFORMATION

Lineshape of Core Levels

|                  | Au 4f_{7/2} (hν=136 eV) | L(eV) | α   | G(eV) | SCLS(eV) |
|------------------|--------------------------|-------|-----|-------|----------|
| Bulk (B)         |                          | 0.31  | 0.02| 0.09  | 0.0      |
| Surface (S_{clean}) |                          | 0.37  | 0.02| 0.23  | -0.33    |
| Au_{WS_2}        |                          | 0.37  | 0.02| 0.23  | -0.09    |

TABLE I. Line shape parameters for different components in the Au 4f_{7/2} spectrum acquired at 136 eV photon energy. L is the Lorentzian width, α is the asymmetry parameter and G is the Gaussian width.

|                  | W 4f (hν=140 eV) | L(eV) | α   | G(eV) | BE(eV) |
|------------------|-----------------|-------|-----|-------|--------|
| 4f_{7/2}         |                 | 0.13  | 0.01| 0.08  | 32.79  |
| 4f_{5/2}         |                 | 0.16  | 0.01| 0.09  | 34.93  |

TABLE II. Line shape parameters for different components for W 4f and S 2p spectra acquired at 140 eV and 260 eV photon energy, respectively, for growth GR2. L is the Lorentzian width, α is the asymmetry parameter and G is the Gaussian width. The main peaks for GR1 have the same lineshape and BE position.

Determination of the WS_2 Coverage

In figure 7, the high-resolution XPS spectra of the Au 4f_{7/2} core level are shown for the clean Au(111) (top) and after the growth of WS_2 for GR2. Table II presents the parameters of the peaks fitting. After the growth of SL WS_2 an extra component (Au_{WS_2}) appears and it is accompanied by the decrease in the intensity of the clean surface peak Au_S. This new peak can be attributed to the Au surface atoms in direct contact with the WS_2 layer. In order to calculate the WS_2 coverage we
FIG. 7. Au 4\(_{f_{7/2}}\) component measured for clean Au surface (top) and after growth GR2 (bottom). The photon energy was 136 eV.

considered the decrease of the Au\(_S\) component in the Au 4\(_f_{7/2}\) spectrum after WS\(_2\) growth for the sample prepared with GR2, where only the WS\(_2\) related XPS features are present. The coverage \(\theta\) can be extracted from

\[
\theta_{WS_2}(t) = 1 - \frac{I_{AuS}(t)}{I_{AuS}(t = 0)}, \tag{A.5}
\]

where \(I_{AuS}(t)\) indicates the intensity of the surface component of Au 4f at time \(t\). We find for GR2 a WS\(_2\) coverage of 45%. The same WS\(_2\) coverage was present at the end of uptake GR1 as found by comparing the intensity of the blue W 4\(_f\) components in Figure 9b and d.

**Orientation of the Au substrate**

The orientation of the Au(111) surface is necessary to identify the relative stacking of the WS\(_2\) layer on the substrate. This information was obtained performing XPD measurements of the Au 4\(_f_{7/2}\) core level for the clean sample, as mentioned in the main text. Figure 8a and 8c show the XPD patterns corresponding to the bulk (Au\(_B\)) and clean surface (Au\(_S\)) components (colored), respectively, measured at 400 eV photon energy (photoelectron kinetic energy \(\sim 316\) eV).
FIG. 8. XPD pattern acquired at 400 eV photon energy (KE~316 eV), showing the XPD pattern (color) associated to the bulk component Auₜ (a) and to the surface component Auₛ (c) of the Au 4f₇/2 core level together with the multiple scattering simulation (grey) for the clean Au(111) sample with the azimuthal orientation of 0° depicted in (b). (b) R-factor vs azimuthal angle for the XPD pattern associated to the bulk peak of the Au 4f₇/2.

The expected three-fold symmetry is observed for the XPD pattern of the bulk component, while the herringbone reconstruction returns an almost six-fold symmetric pattern for the 4f₇/2 surface component Auₛ. Therefore, the XPD pattern of the bulk peak was used to determine the orientation of the Au substrate. The pattern for the bulk component was simulated with a bulk-terminated surface, accounting for the high absolute value of the R-factor. The herringbone reconstruction was simulated by compressing the surface unit cell in the ⟨−110⟩ direction by 4.5%, averaging over the three 60° rotated domains, while three layers below the surface were considered as the bulk. In order to unambiguously identify the orientation of the substrate, we performed an R-factor analysis calculating the XPD patterns of the bulk peak for different azimuthal orientations of the Au(111) substrate. The analysis (Figure 8b) shows the absolute minimum of the R-factor (0.2) for the substrate orientation corresponding to an azimuthal angle of 0°, i.e. with the same orientation of the model depicted in Figure 8b.

Fast-XPS Characterization of WS₂ Growth

In Figure 9a and b, a fast-XPS intensity plot is shown together with the peak fit analysis of the last W 4f₇/2 core level spectrum of the fast-XPS spectral sequence for GR1. The growth of the peak at a binding energy (BE) BE=32.79 eV (blue) corresponding to WS₂ is accompanied by the
FIG. 9. (a) and (c) W 4f$_{7/2}$ fast-XPS intensity plot obtained for GR1 and GR2, respectively, together with the last W 4f$_{7/2}$ core level spectra of the fast-XPS series (b and d), showing the spectral contributions resulting from peak fit analysis. The photon energy is 140 eV. (e) Evolution of the WS$_2$ coverage in time for the two growths.

correction from various components at lower BE [40]. The presence of these components is consistent with the formation of incompletely sulfided species of the form WS$_{2-x}$, (with 0 < x ≤ 1), as observed for the same system in earlier literature [40,42]. In Figure 9c and d we show the results achieved on GR2. For this growth, only the component associated with WS$_2$ is observed.

The coverage of WS$_2$ ($\theta_{WS_2}$), which is proportional to the intensity of the main blue component
of the W 4f core level, is shown as a function of time for both uptakes in Figure 9c. θWS₂ was calculated from the intensity loss of the clean surface peak of the Au 4f₁/₂ XPS spectra after the growth of the WS₂ layer (Figure 7). In Figure 9c, we observe that the θWS₂ is an almost linear function of the W deposition time for GR2 (red curve) throughout the deposition, up to a WS₂ coverage of about 45%. This suggests that all the deposited W atoms react and form WS₂. On the contrary, the θWS₂ obtained for GR1 shows a deviation from the linear behavior, with a modification of the slope around a coverage of 25%. Moreover, the much higher W deposition rate for GR1 (more than double than that for Growth 2) is not reflected in a comparable increase of the WS₂ growth rate, as seen from the slope of the two curves in the initial stage of the growth. This is due to the formation of incompletely sulfided species right from the beginning which, as the coverage increases, prevent the formation of WS₂.

**Determination of the polytype**

X-ray photoelectron diffraction is an excellent tool to determine the polytype of the WS₂ monolayers on Au(111). This goal is achieved by measuring the XPD patterns from the bottom component of the S 2p₃/₂ core level, i.e. the component associated to S atoms in direct contact with the Au substrate, and choosing a photon energy (hv = 560 eV) tuned to enhance the forward scattering conditions. In this way, we can map the positions of the scattering atoms (mainly W), with respect to the S emitter. These experimental patterns are reported in Figure 10 together with simulated patterns sourcing from a trigonal prismatic (1H) structure (Figure 10a) and from octahedral (1T) structure (Figure 10b and c). Two distinct mirrored 1T structures were simulated, similarly to the two possible orientations that the 1H structure can assume. A sketch of the simulated structures is shown at the top of the figure. The results obtained performing a R-factor analysis (see the main text for details) are R=0.24 for the 1H structure and R=1.23 and R=0.66 for the two 1T structures. The minimum R-factor observed for the patterns shown in Figure 10a is clearly indicative of a 1H structure. The good agreement between simulations and experiments corroborates the fact that the component at higher BE observed for each of the spin-split peaks of the S 2p₃/₂ spectrum originates from the bottom sulfur layer. The higher absolute value of the R-factor obtained for the pattern of Sbottom –when compared to the case of W 4f₁/₂– depends on the small photoemission signal from the bottom sulfur atoms, worsening the statistics and signal-to-noise ratio of the measurement. On the other hand, the quality of the data is sufficient to observe
FIG. 10. Determination of the polytype of WS$_2$ layer. The XPD experimental patterns (colored sector) obtained for bottom S 2$p_{3/2}$ component (acquired at $h\nu = 560$ eV) are compared with simulations performed for the 1H (a) and for the two 1T polytypes (b and c), as depicted at the top of the figure. Similar results but W 4$f_{7/2}$ are displayed in the bottom row (acquired at $h\nu = 170$ eV). The green circles indicate the position of the forward-scattering peaks due to the W atoms.

Clearly the forward-scattering peaks due to the W scatterers in the layer.

A similar experiment and comparison has been carried out for the W 4$f_{7/2}$ core level, acquired with a photon energy of 160 eV, for which both forward and backward scattering processes are
FIG. 11. WS$_2$ atomic ball model for the main and mirror domains with the corresponding XPD simulations. As expected there is a mere rotation of 60° or, equivalently 180° between the two XPD patterns. Simulations performed by using the lattice parameters that minimize the R-factor in Figure 2 of the main text.

present. The R-factor minimization returns an R-factor of 0.059, 0.20 and 1.16, respectively, validating the outcomes observed for S 2p and showing unambiguously that WS$_2$ assumes the 1H polytype structure on the Au(111) surface.

### Simulated XPD Patterns for Mirror Orientation

An important information that can be extracted from XPD is the detection of mirror domains in the WS$_2$ layer. Some information about the domain orientation can be readily obtained from a mere inspection of the diffraction pattern without any need for simulations. If, for instance, there is an equal area covered by the two mirror domains, the diffraction pattern would be expected to show a six-fold symmetry. If, on the other hand, only one orientation is present, the symmetry should be three-fold. Such simple arguments are only valid when the (threefold) Au(111) substrate is neglected in the calculations but this turns out to be a valid approximation due to the absence of the same local arrangement of the WS$_2$ atoms with respect to the Au atoms because of the mismatch between the two lattices.

Figure 11(a) and (b) show simulated W 4$f_{7/2}$ XPD patterns for the two mirrored orientations
(labeled Or1 and Or2, respectively) for a free-standing WS$_2$ layer with 1H geometry as depicted in the ball-model at the top. These patterns are calculated for an electron kinetic energy (KE) of 326 eV. Since the Au(111) substrate is neglected in these simulations, the diffraction patterns are identical although mirrored.

**μLEED of WS$_2$ domains**

![μLEED patterns](image)

FIG. 12. μLEED patterns acquired on the main and mirror SL WS$_2$ domains, as labelled in the main text, for the same electron energy (40 eV).

As explained in the main text, we could identify the presence of a negligible amount of SL WS$_2$ domains assuming the mirror, W$_\text{hcp}$S$_\text{top}$ configuration, which are minority with respect to the main W$_\text{fcc}$S$_\text{top}$ configuration (see Figure 6c and 6d). The two orientations can be seen in a μLEED experiment, as shown in Figure[12]. The two patterns show a three-fold symmetry, which is reversed in between them. This indicates that the patterns are produced by mirrored structures.

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