

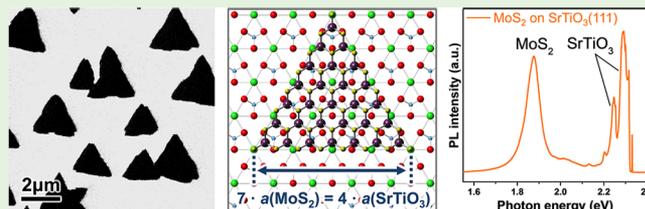
# Epitaxial Growth of Monolayer MoS<sub>2</sub> on SrTiO<sub>3</sub> Single Crystal Substrates for Applications in Nanoelectronics

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**ABSTRACT:** Monolayer molybdenum disulfide (MoS<sub>2</sub>) crystals grown on amorphous substrates such as SiO<sub>2</sub> are randomly oriented. However, when MoS<sub>2</sub> is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In this paper, we present the results from chemical vapor deposition growth of MoS<sub>2</sub> on three different terminations of single crystal strontium titanate (SrTiO<sub>3</sub>) substrates. On SrTiO<sub>3</sub>(111), the monolayer MoS<sub>2</sub> crystals form equilateral triangles with two main orientations, in which they align their  $\langle 2\bar{1}10 \rangle$ -type directions (i.e., the sulfur-terminated edge directions) with the  $\langle 1\bar{1}0 \rangle$ -type directions on SrTiO<sub>3</sub>. This arrangement allows near-perfect coincidence epitaxy between seven MoS<sub>2</sub> unit cells and four SrTiO<sub>3</sub> unit cells. On SrTiO<sub>3</sub>(110), the MoS<sub>2</sub> crystals tend to align their edges with both the  $\langle 1\bar{1}0 \rangle$  and  $\langle 1\bar{1}\bar{2} \rangle$  directions on SrTiO<sub>3</sub> because these both provide favorable coincidence lattice registry. This distorts the crystal shapes and introduces an additional strain detectable by photoluminescence. When triangular MoS<sub>2</sub> crystals are grown on SrTiO<sub>3</sub>(001), they again show a preference to align their edges with the  $\langle 1\bar{1}0 \rangle$  directions on SrTiO<sub>3</sub>. Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS<sub>2</sub> monolayers and SrTiO<sub>3</sub> is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this paper is that the vdW interaction between MoS<sub>2</sub> and SrTiO<sub>3</sub> substrates determines the supported crystal shapes and orientations by epitaxial relations. Controlled crystal orientations make the growth of large sheets of MoS<sub>2</sub> possible when there are multiple nucleation sites. This minimizes the number of grain boundaries and optimizes the electronic properties of the material, e.g., charge mobility, which is crucial for the application of monolayer MoS<sub>2</sub> in next-generation nanoelectronic devices.

**KEYWORDS:** MoS<sub>2</sub>, SrTiO<sub>3</sub>, van der Waals epitaxy, scanning tunneling microscopy, chemical vapor deposition, Raman spectroscopy, photoluminescence, 2D materials



## 1. INTRODUCTION

Monolayer MoS<sub>2</sub> has been extensively studied as the prototypical material of the family of transition-metal dichalcogenides (TMDCs).<sup>1</sup> It was discovered that the electronic properties of TMDCs are drastically affected by dimensionality: MoS<sub>2</sub> in its bulk form is a semiconductor with an indirect band gap of 1.2–1.3 eV, which transforms into a direct band gap of 1.8–1.9 eV when the material is as thin as a monolayer.<sup>2,3</sup> These band-gap energies span the visible and near-infrared range of the electromagnetic spectrum, and therefore MoS<sub>2</sub> is a promising candidate for optoelectronic applications.<sup>4</sup> Monolayer MoS<sub>2</sub> is also viewed as a two-dimensional (2D) semiconductor with great potential because of its high charge mobility of more than 200 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off current ratio of up to ~10<sup>8</sup>.<sup>5</sup> These properties make it competitive with graphene for use in novel low-power digital electronics.<sup>5</sup>

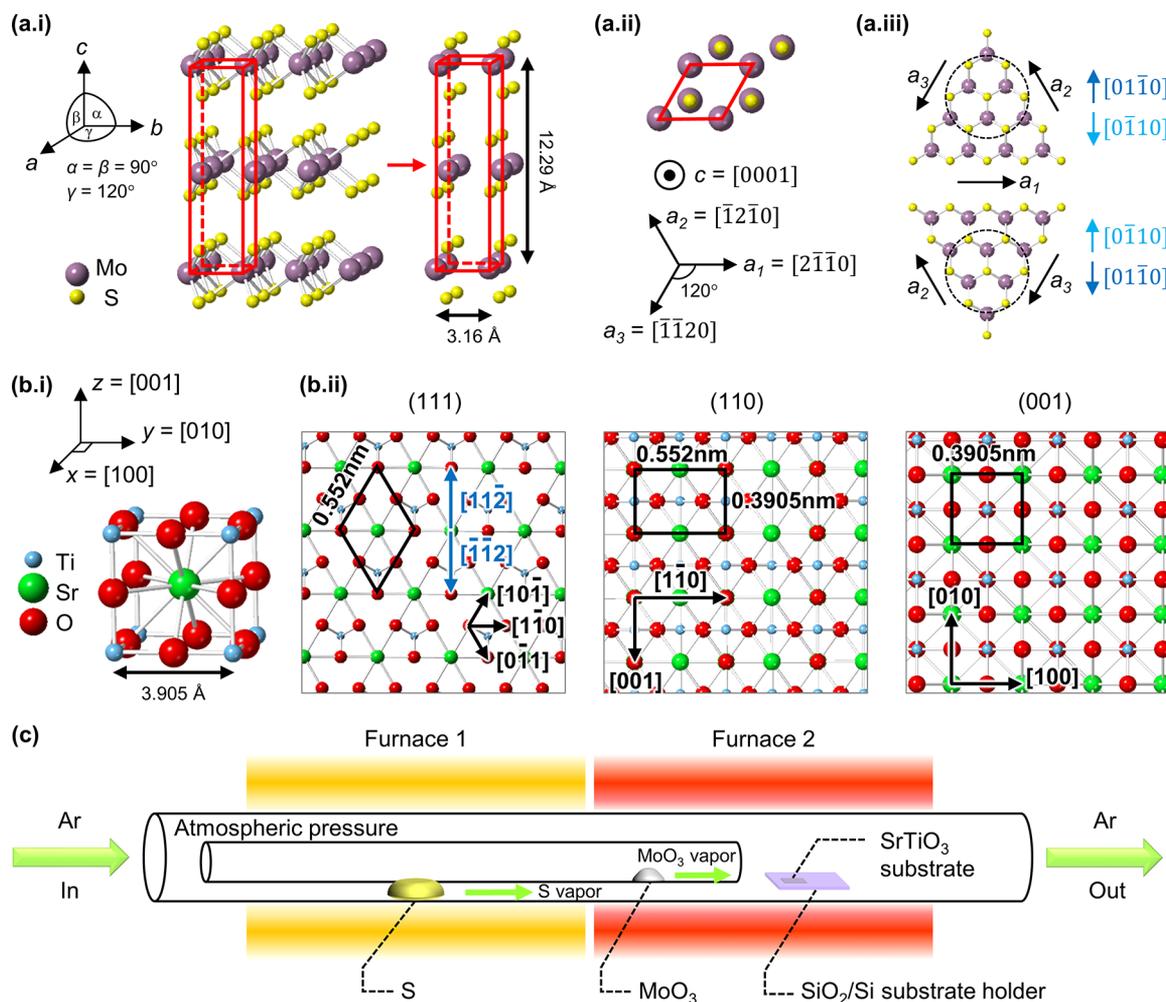
For a 2D material like MoS<sub>2</sub>, the growth technique of chemical vapor deposition (CVD) has the advantage over exfoliation in that it allows the substrate to influence the chemistry and properties of the MoS<sub>2</sub> monolayers. This is important from a technological point of view because the properties of a 2D material can be highly sensitive to its

interfaces.<sup>1</sup> CVD growth on a well-prepared substrate results in a collection of large MoS<sub>2</sub> domains that have controllable morphology.<sup>6,7</sup> In particular, epitaxy has been shown to effectively control MoS<sub>2</sub> crystal orientations, which is required to minimize the concentration of grain boundaries in the MoS<sub>2</sub> layer.<sup>7,8</sup> This is especially important in the large-area synthesis of MoS<sub>2</sub> because grain boundaries are detrimental to the electrical properties (e.g., charge mobility) of polycrystalline films.<sup>9–11</sup> By its nature, epitaxial growth cannot occur on amorphous substrates like SiO<sub>2</sub>.<sup>12</sup> On crystalline substrates, the main mechanism that allows epitaxy to occur is generally believed to be due to van der Waals (vdW) forces for both metallic and nonmetallic substrates,<sup>7,8,13–15</sup> e.g., *c*-plane sapphire<sup>7,8</sup> and Au(111).<sup>15</sup> Although the vdW interaction is relatively weak compared to the in-plane covalent bonding, it still provides a significant force between two 2D sheets. It has been confirmed to powerfully control the interlayer epitaxy of MoS<sub>2</sub> bilayers, where the AA and AB stacking configurations (0° and 60° relative layer rotation) are overwhelmingly favored

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**Figure 1.** Crystal structures of MoS<sub>2</sub> and SrTiO<sub>3</sub> and the CVD system. (a.i) Bulk MoS<sub>2</sub> with a red rhombic prismatic unit cell. (a.ii) Top view of MoS<sub>2</sub>, with the crystallography defined by the four-index notation. (a.iii) Top view of monolayer triangular crystals of MoS<sub>2</sub>. (b.i) Unit cell of SrTiO<sub>3</sub>. (b.ii) Atomic top view of bulk-terminated SrTiO<sub>3</sub>(111), (110), and (001) planes, with unit cells and lattice directions labeled. In (111), only two layers of atoms are shown for clarity. (c) CVD setup for the synthesis of MoS<sub>2</sub> crystals.

compared to others.<sup>16</sup> Furthermore, the indirect-to-direct transition of the MoS<sub>2</sub> band gap in the monolayer limit is a direct consequence of the absence of neighboring layers, which only interact via vdW forces. This means that the interlayer forces perturb each other's electronic band structures. Therefore, the importance of vdW bonding should not be overlooked with respect to interfacial bonding between MoS<sub>2</sub> and its substrate. Nevertheless, other possible interfacial bonding mechanisms have also been reported, including electrostatic attraction between MoS<sub>2</sub> and sapphire<sup>7</sup> and chemical bonding between sulfur and various metals.<sup>17–20</sup> The nature of the Au–S bond is particularly controversial; it is claimed to perturb the electronic structure very little in some studies<sup>15,18</sup> and have a covalent nature in others.<sup>17</sup>

Finding suitable substrate materials is an important step toward epitaxy or orientation control in the synthesis of MoS<sub>2</sub> films. The substrates used in our work are electrically conducting niobium (Nb)-doped (0.5 wt %) SrTiO<sub>3</sub> crystals. SrTiO<sub>3</sub> has attracted substantial interest since the 1970s mostly because of its versatile crystal surfaces.<sup>21</sup> It was chosen for our study because several surface terminations with different symmetries can be readily prepared. MoS<sub>2</sub> was grown on the three well-studied SrTiO<sub>3</sub> terminations, (111), (110), and (001). The crystallinity of SrTiO<sub>3</sub> encourages MoS<sub>2</sub> monolayer

crystals to grow epitaxially, and the different symmetries of the three terminations lead to distinct epitaxial behavior. Overall, the interaction between MoS<sub>2</sub> and SrTiO<sub>3</sub> is found to influence the orientations, shapes, and optical properties of MoS<sub>2</sub> monolayers. The ability to regulate these properties of monolayer MoS<sub>2</sub> is important in the synthesis of large-scale layers of the material with minimal grain boundaries and controlled band gaps. This will improve the potential of monolayer MoS<sub>2</sub> in its application to nanoelectronics and optoelectronics.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of Substrates.** SrTiO<sub>3</sub> single crystals (7 × 2 × 0.5 mm<sup>3</sup>) doped with Nb at 0.5% by weight were supplied by PI-KEM, U.K., with epi-polished (111), (110), and (001) surfaces. SrTiO<sub>3</sub> is an insulator with a band gap of 3.2 eV at 25 °C.<sup>22</sup> The Nb dopant was included to generate sufficient electrical conductivity at room temperature for scanning tunneling microscopy (STM) imaging. The preparation and imaging of the SrTiO<sub>3</sub> surfaces were carried out in an ultrahigh vacuum (UHV) scanning tunneling microscope, which is a custom-built JEOL JSTM 4500s model (base pressure 10<sup>−8</sup> Pa). SrTiO<sub>3</sub> surfaces were prepared to terminate with previously well-characterized reconstructions, requiring different Ar<sup>+</sup> ion sputtering conditions, annealing temperatures, durations, and O<sub>2</sub> partial pressures.<sup>23–25</sup>

**2.2. CVD Growth and Transfer of MoS<sub>2</sub>.** Molybdenum trioxide (MoO<sub>3</sub> powder, ≥99.5%, Sigma-Aldrich) and sulfur (S powder, ≥99.5%, Sigma-Aldrich) were used to synthesize MoS<sub>2</sub> monolayers on SrTiO<sub>3</sub> using the atmospheric-pressure CVD method. A schematic diagram of the CVD setup is shown in Figure 1c. SrTiO<sub>3</sub> substrates were placed face-up and downstream with respect to the precursors, which were 20 mg of MoO<sub>3</sub> and 300 mg of S, loaded into two tubes with 12 mm and 22 mm diameters, respectively. The system was first flushed with 500 sccm argon to drive off oxygen. Subsequently, S vapor was preintroduced at 190 °C for 15 min with a decreased argon flow rate of 150 sccm, which ensured that the system was S-rich so that the as-grown MoS<sub>2</sub> crystals were triangles with S-edge terminations. Then the MoO<sub>3</sub> precursor and SrTiO<sub>3</sub> substrate were heated to 300 and 782 °C, respectively. The reaction lasted 30 min with 100 sccm argon carrier gas and finished with a fast cooling process.

MoS<sub>2</sub> monolayers grown on a SiO<sub>2</sub>/silicon (Si) substrate were first spin-coated with a thin film of poly(methyl methacrylate) (PMMA, 8 wt % in anisole, 495k molecular weight) at 4500 rpm for 60 s, followed by a 90 s curing process at 180 °C. The SiO<sub>2</sub> layer was etched off by floating the samples on a 1 M potassium hydroxide (KOH, Sigma-Aldrich) aqueous solution at room temperature, whereby the planar strain in the MoS<sub>2</sub> monolayer was released. The isolated film of PMMA/MoS<sub>2</sub> was then rinsed in deionized (DI) water three times for 1 h each time. Following this, a precleaned SrTiO<sub>3</sub> substrate was submerged in DI water to support the film. The as-transferred sample was dried overnight in a ventilation environment, after which it was baked at 150 °C for 20 min to enhance the MoS<sub>2</sub>-substrate adhesion. The PMMA coating was removed by soaking the sample in a 55 °C acetone bath for 6 h. Finally, to remove the trapped contaminants for a cleaner interface, the sample was annealed at 200 °C for 1 h with 150 sccm argon as the carrier gas.

**2.3. Characterization.** The MoS<sub>2</sub> crystals were imaged by scanning electron microscopy (SEM) and STM. SEM was performed using Zeiss Merlin and Hitachi-4300 microscopes, both at an accelerating voltage of 3 kV. STM images were processed by *Smart Align*,<sup>27,28</sup> *Gwyddion*, and *WSxM*.<sup>29</sup> Raman spectroscopy and photoluminescence (PL) were conducted using a JY Horiba LabRAM ARAMIS imaging confocal Raman microscope with a 532 nm excitation wavelength and 12.5 mW laser power. The laser spot size was ~1 μm, and the acquisition times were 35 s for Raman spectra and 5 s for PL spectra.

### 3. RESULTS

Prior to the presentation of our experimental results, it is helpful to unambiguously define the crystallography of both MoS<sub>2</sub> and SrTiO<sub>3</sub> for the purpose of epitaxial analysis. Figure 1a.i is the side view of the 3D structure of 2H-MoS<sub>2</sub>, the thermodynamically stable polytype of MoS<sub>2</sub>.<sup>30</sup> Two other common polytypes are called 1T- and 3R-MoS<sub>2</sub>, but they are not discussed here. The 2H-MoS<sub>2</sub> crystal consists of covalently bonded S–Mo–S sandwich layers held together by vdW forces.<sup>2,3,30</sup> The unit cell is labeled in red, and a single unit cell of the lattice is shown to the right of the red arrow. It is a hexagonal structure with lattice parameters of  $a = b = 3.1602$  Å,  $c = 12.294$  Å and angles of  $\alpha = \beta = 90^\circ$ ,  $\gamma = 120^\circ$ ; the space group is  $P6_3/mmc$  (No. 194).<sup>30</sup> Figure 1a.ii is the top view of MoS<sub>2</sub>. In common with other hexagonal systems, it is useful to employ a four-index notation to emphasize the equivalence between crystallographically equivalent directions.<sup>31</sup> For example, the  $a_1$ ,  $a_2$ , and  $a_3$  directions in Figure 1a.ii are all of the  $\langle 2\bar{1}10 \rangle$  type,<sup>31,32</sup> which highlights the symmetry of the structure. Many studies term the basal plane of MoS<sub>2</sub> as (0001),<sup>15,33</sup> implying the use of the four-index notation, although the in-plane crystallography tends not to be discussed. Figure 1a.iii shows the top view of triangular MoS<sub>2</sub> monolayers, which are 60° (or 180°) rotated with

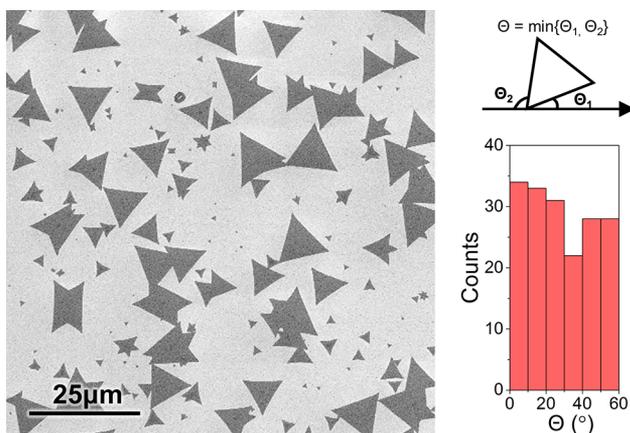
respect to each other. Their S-terminated edges are aligned along the  $\langle 2\bar{1}10 \rangle$ -type directions. It should be noted that the orientations of the two crystals are not equivalent. For example, in the dashed circles, the two structures have the same skeleton of S atoms, but the Mo atoms are located differently. In other words, if the bottom layer of S atoms chooses to orient in a specific way on the substrate, it can result in two different overall configurations due to the Mo atoms. For convenient subsequent analysis, it is useful to define the upward and downward crystallographic directions, which are  $[01\bar{1}0]$  and  $[0\bar{1}10]$ , and they are inequivalent. Note that these directions are equivalent in a bulk MoS<sub>2</sub> crystal, which has in-plane hexagonal symmetry, which is reduced to 3-fold symmetry in a monolayer.

SrTiO<sub>3</sub> adopts a perovskite structure with a cubic lattice above 105 K ( $a = 3.905$  Å),<sup>23</sup> and its unit cell is shown in Figure 1b.i. The Ti<sup>4+</sup> ions are octahedrally coordinated with respect to the O<sup>2-</sup> ions, and the Sr<sup>2+</sup> ions are in a site that is 12-fold-coordinated by O<sup>2-</sup> ions. The three surface terminations of interest in our study are presented in Figure 1b.ii. The (111) termination is a 3-fold-symmetric surface with a rhombic unit cell drawn in black. Upon close inspection of the unit cell, it can be seen that the upper and lower halves are not equivalent because there is an additional Ti atom in the lower half, one atomic layer down from the topmost Sr and O atoms. The Ti layer reduces the symmetry of the topmost layer from 6-fold to 3-fold. Again, it is helpful to define the upward and downward crystallographic directions on SrTiO<sub>3</sub>(111),  $[11\bar{2}]$  and  $[\bar{1}12]$ , a pair of inequivalent directions. Next, the (110) surface of SrTiO<sub>3</sub> has 2-fold symmetry, and the unit cell is a rectangle (Figure 1b.ii). Finally, SrTiO<sub>3</sub>(001) has 4-fold symmetry with a square surface unit cell (Figure 1b.ii).

Although the as-supplied SrTiO<sub>3</sub> samples used in this work were epi-polished on the top surface by the manufacturer to a mirror finish, a small depth of disordered polishing damage will remain. Therefore, in order to ensure that the crystallinity of the sample extends to the top atomic surface layer, we processed all of our samples through UHV annealing and/or Ar<sup>+</sup>-ion sputtering. This preparation process eliminates the polishing damage and allows the surface to become crystalline, atomically flat, and relatively free of contaminants. The surface reconstructions we observe following UHV annealing cannot survive in an ambient environment. Therefore, the interface between the MoS<sub>2</sub> crystals and SrTiO<sub>3</sub> substrates will differ from that of the UHV-prepared samples, but with our procedure, we ensure that the maximum degree of substrate crystallinity is created prior to CVD growth.

A schematic diagram of the CVD system is shown in Figure 1c. The MoO<sub>3</sub> and S precursors were loaded into two quartz tubes in two separate furnaces for independent control of their temperatures. The SrTiO<sub>3</sub> substrate was supported on a larger SiO<sub>2</sub>/Si wafer acting as a holder. The precursor vapors were transported by argon flow under atmospheric pressure downstream onto the substrate surface to grow MoS<sub>2</sub>.

For the purposes of comparison, we first present data from an amorphous substrate. Figure 2 is an SEM image of MoS<sub>2</sub> crystals grown on SiO<sub>2</sub>/Si. As one would expect from S-rich growth conditions, the MoS<sub>2</sub> monolayers preferentially adopt triangular geometries.<sup>12</sup> The orientation of any crystal was measured as the angle that it makes with the horizontal line below it, whichever side is smaller (Figure 2, top right). Their orientations are randomly distributed, as shown in the histogram in the right-hand panel. The random distribution



**Figure 2.** SEM image of monolayer MoS<sub>2</sub> crystals on SiO<sub>2</sub>/Si and the orientation histogram of the MoS<sub>2</sub> crystals, measured according to the standard in the top right part of the figure.

demonstrates that the vdW interaction between the amorphous substrate and MoS<sub>2</sub> monolayers induces no orientation preferences for the crystal growth.

**3.1. MoS<sub>2</sub> on SrTiO<sub>3</sub>(111).** Figure 3a is an STM image of the SrTiO<sub>3</sub>(111) surface composed of domains of (3 × 3) and (4 × 4) reconstructions,<sup>23,34</sup> with the average terrace step height being measured as 0.23 ± 0.03 nm (*d*<sub>111</sub> lattice spacing = 0.225 nm). This surface is generated by Ar<sup>+</sup>-ion sputtering at 500 eV for 8 min and subsequent annealing at 1140 °C for 3 h in 4.5 × 10<sup>-4</sup> Pa O<sub>2</sub>. This demonstrates that the outermost surface of our substrate is crystalline. Note that the white dots in Figure 3a may be contaminants or regions that are not well reconstructed, which cannot be completely avoided even by careful UHV treatment. They exist in the best STM images of the SrTiO<sub>3</sub> surfaces reported.<sup>23–25</sup> In previous epitaxial studies of MoS<sub>2</sub> on crystalline substrates, e.g., *c*-plane sapphire,<sup>7,8</sup> as-received/epi-polished substrates were used. These substrates contain polishing damage and contaminants that are orders of magnitude greater than UHV-treated samples, but epitaxy was still found and studied.

Figure 3b shows a typical SEM image of MoS<sub>2</sub> crystals on SrTiO<sub>3</sub>(111). The larger crystals (those with lateral sizes of over 5 μm) with S-terminated edges<sup>12,35,36</sup> appear to be randomly oriented, but in the close-up image of the smaller crystals (Figure 3c), the crystals show more regular alignment. The lattice directions of the SrTiO<sub>3</sub>(111) substrate are also drawn at the top-left corner for reference: one can see that the small triangles mostly have their three sides parallel to the three <110>-type directions on SrTiO<sub>3</sub>(111), resulting in two main orientations, as represented by the two blue schematic triangles. Another observation is that one of the two preferred orientations is more abundant (the darker blue triangle pointing up). Even smaller crystals were examined by STM, as shown in Figure 3d. This figure also shows that the STM images show the height of the MoS<sub>2</sub> monolayers to be 0.63 ± 0.06 nm. This agrees with the previously reported value of 0.65 nm.<sup>5,37</sup> An atomically resolved STM image in Figure 3e shows a triangular pattern of bright dots with a periodicity of 3.16 ± 0.09 Å, which agrees with the literature value of 3.16 Å.<sup>30</sup> Because monolayer MoS<sub>2</sub> terminates with an outer plane of S atoms, from the topographical point of view, the bright protrusions in STM images are generally thought to be S atoms.<sup>38,39</sup>

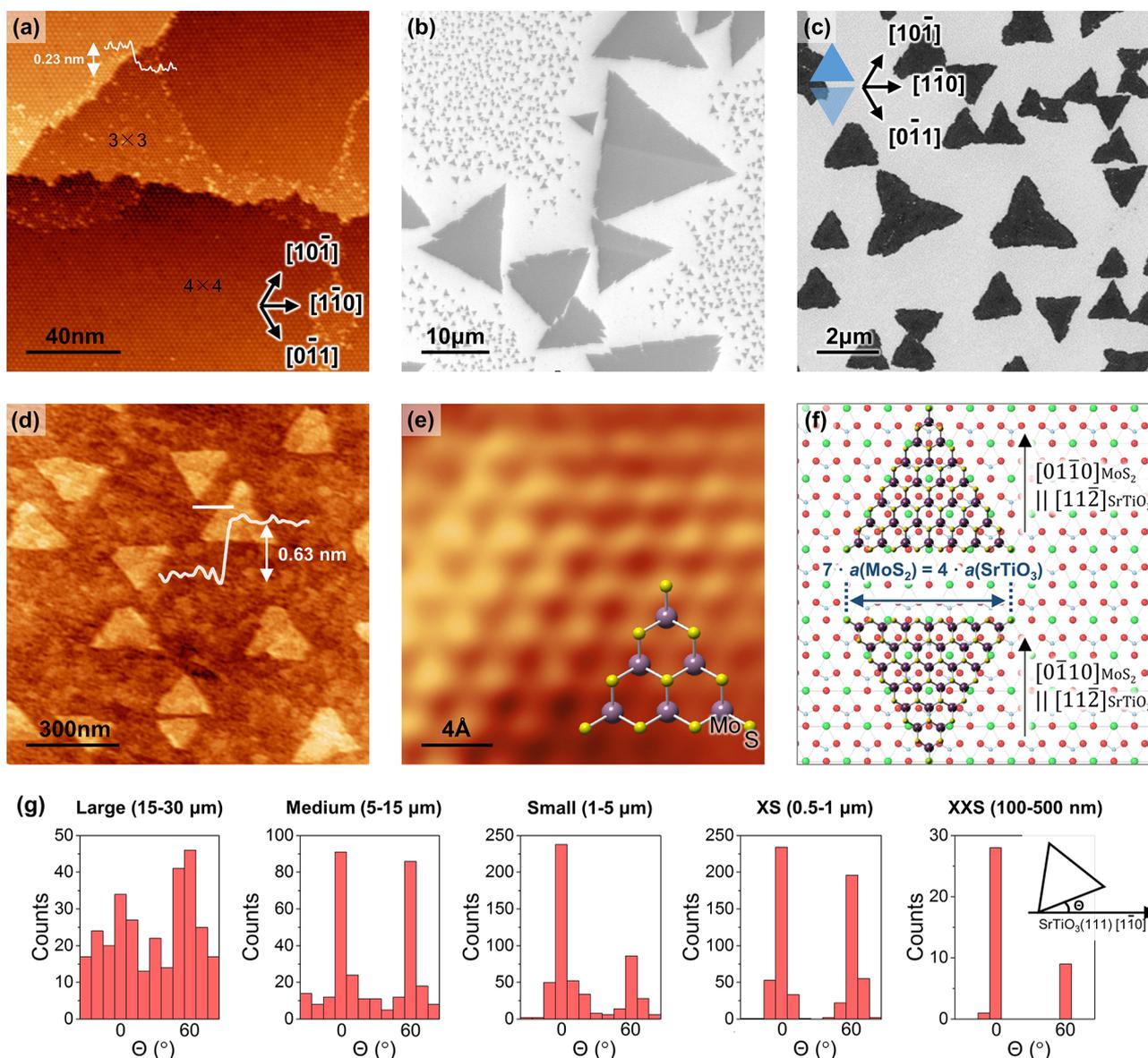
The observations regarding epitaxy were statistically visualized by orientation histograms and are shown in Figure 3g. Note that in the SEM images (Figure 3b,c) some triangles have zigzag or concave edges, which are S-terminated because the MoS<sub>2</sub> crystals were grown in a S-rich environment.<sup>12</sup> When an edge is not completely flat, its direction is measured as that of the straight line connecting its two ends, which is a good estimate of the S-termination direction.<sup>12</sup> The MoS<sub>2</sub> crystals were grouped into large (15–30 μm), medium (5–15 μm), small (1–5 μm), XS (0.5–1 μm), and XXS (100–500 nm), according to their lateral sizes. In all cases, the two highest peaks are at 0° and 60°, indicating the two dominant orientations of the MoS<sub>2</sub> crystals: “(0001)<sub>MoS<sub>2</sub></sub>||[(111)<sub>SrTiO<sub>3</sub></sub>, [011̄0]<sub>MoS<sub>2</sub></sub>||[(112̄)<sub>SrTiO<sub>3</sub></sub>” and “(0001)<sub>MoS<sub>2</sub></sub>||[(111)<sub>SrTiO<sub>3</sub></sub>, [011̄0]<sub>MoS<sub>2</sub></sub>||[(112̄)<sub>SrTiO<sub>3</sub></sub>”.

In the preferred orientations, MoS<sub>2</sub> and SrTiO<sub>3</sub>(111) are both symmetry-coincident and lattice-commensurate: the length of seven MoS<sub>2</sub> unit cells (7 × 0.316 nm = 2.212 nm) equals the length of four SrTiO<sub>3</sub> unit cells (4 × 0.552 nm = 2.208 nm) with a small difference of <0.2%, as illustrated in Figure 3f. In the histograms in Figure 3g, the preferred angular orientations are better defined for smaller crystals, and this can be explained by kinetics. The large crystals undergo a rapid growth process with little time to optimize their orientations relative to the substrate. However, the smaller crystals grow slowly and are able to rotate into orientations that optimize the vdW interaction with the substrate. Another interesting possibility is that the smaller MoS<sub>2</sub> islands are constrained by the lattice commensuration so that they cannot grow to larger sizes. If so, the crystals would have grown rapidly to a certain size, beyond which it is difficult to expand further because of the lattice constraints. In this case, we should observe a disproportionately large number of crystals at that size. However, such an uneven size distribution is not seen.

It is likely that one of the two preferred orientations is thermodynamically more stable. Particularly in the histograms for small and XXS crystals, there is a statistically significant difference between the heights of the two peaks. In Figure 3f are the atomic models of the two preferred orientations, in which the MoS<sub>2</sub> crystals sit in the same way as those in Figure 1a.iii. We illustrated in Figure 1a.iii and b.ii that on both monolayer MoS<sub>2</sub> and SrTiO<sub>3</sub>(111), the crystallographic directions pointing up and down are distinct. Hence, the two orientations of MoS<sub>2</sub> crystals on SrTiO<sub>3</sub>(111) shown in Figure 3f are physically distinct, and their respective interface crystallography is labeled next to them. We conclude that one of the two orientations is favored, but they are not distinguishable from our results.

**3.2. MoS<sub>2</sub> on SrTiO<sub>3</sub>(110).** The SrTiO<sub>3</sub>(110) substrates are treated in UHV to create a well-defined crystalline top surface. An STM image of the terraces is presented in Figure 4a, produced by annealing at 890 °C for 2 h, followed by another anneal at 910 °C for 3 h, both in UHV. This mainly consists of (6 × 1) reconstruction.<sup>24,40,41</sup>

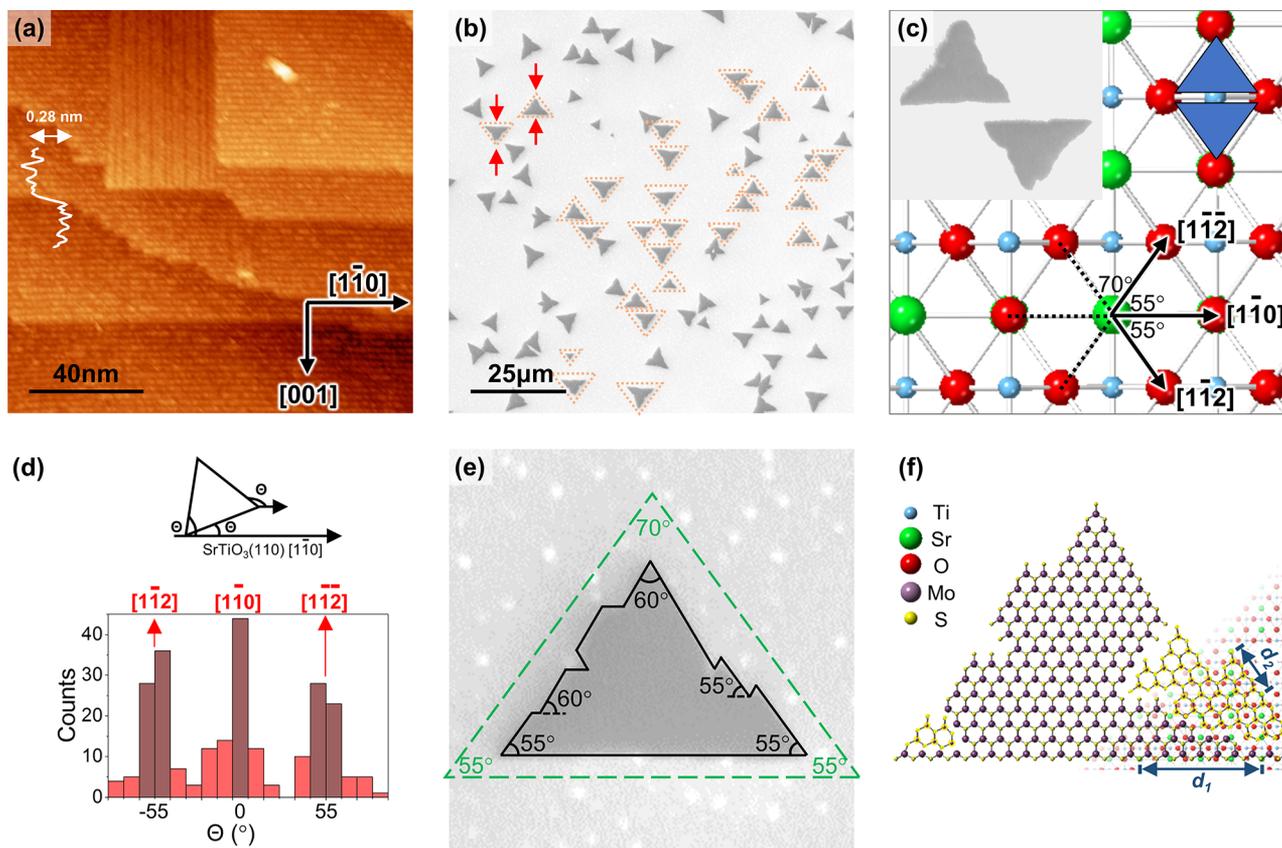
Figure 4b is a typical SEM image of MoS<sub>2</sub> on SrTiO<sub>3</sub>(110), from which it is noticeable that some triangles appear to be vertically distorted compared to the shape of equilateral triangles. This is illustrated on two of them by the red arrows at the top left of the image. There are two most commonly observed orientations, which are shown in the SEM image in Figure 4c and also drawn as blue schematic triangles on the atomic model of the substrate. Compared with the substrate



**Figure 3.** Models and images of  $\text{SrTiO}_3(111)$  and  $\text{MoS}_2$  on  $\text{SrTiO}_3(111)$ . (a) STM image of reconstructed  $\text{SrTiO}_3(111)$ , showing terraces with  $(3 \times 3)$  and  $(4 \times 4)$  reconstructed domains. Two example domains are labeled. Each step height is  $0.23 \pm 0.03$  nm and corresponds to the  $d_{111}$  lattice spacing ( $V_s = 2.0$  V;  $I_t = 0.38$  nA). (b) SEM image showing  $\text{MoS}_2$  crystals with a large range of sizes (laterally  $0.5\text{--}30$   $\mu\text{m}$ ). (c) SEM image of small crystals ( $1\text{--}3$   $\mu\text{m}$ ). The preferred crystal orientations are drawn as schematics, where the darker blue triangle is preferred. (d) STM image showing very small  $\text{MoS}_2$  crystals ( $200\text{--}400$  nm), with a line profile showing the monolayer thickness ( $V_s = 1.5$  V;  $I_t = 0.09$  nA). (e) Atomically resolved STM image of a  $\text{MoS}_2$  monolayer showing a triangular atomic lattice with a periodicity of  $3.16 \pm 0.09$  Å, corresponding to the in-plane S–S distance ( $V_s = 1.1$  V;  $I_t = 0.14$  nA). An atomic model of monolayer  $\text{MoS}_2$  is superimposed, assuming that S atoms are imaged by the STM. (f) Atomic models showing the two preferred orientations of  $\text{MoS}_2$  crystals on  $\text{SrTiO}_3(111)$ . The interface crystallography is written next to each orientation. Also, seven  $\text{MoS}_2$  unit cell lengths (S–S spacings) = four  $\text{SrTiO}_3$  ( $1\bar{1}0$ ) unit lengths (Sr–Sr spacings). The substrate lattice directions in part a also apply to panels b–f. (g) Orientation histograms for  $\text{MoS}_2$  crystals of different sizes, measured according to the standard on the far right.

lattice, they each have their three sides parallel to  $[1\bar{1}0]$ ,  $[1\bar{1}2]$ , and  $[1\bar{1}\bar{2}]$  of the  $\text{SrTiO}_3(110)$  substrate. In this case, the direction of each crystal edge was measured according to the standard in Figure 4d. In the resulting histogram, the brown peaks correspond to the three directions identified above, as expected. For example,  $[1\bar{1}\bar{2}]$  is at  $55^\circ$  anticlockwise relative to  $[1\bar{1}0]$ , which is also shown in Figure 4c. If we refer to Figure 4c, we can see that such triangles with their edges parallel to  $[1\bar{1}0]$ ,  $[1\bar{1}2]$ , and  $[1\bar{1}\bar{2}]$  have three internal angles of  $70^\circ$ ,  $55^\circ$ , and  $55^\circ$ .

The  $[1\bar{1}0]$  direction is favored because of the 7:4 coincidence epitaxy, similar to the case on  $\text{SrTiO}_3(111)$ . However, on  $\text{SrTiO}_3(110)$ , only one edge of any  $\text{MoS}_2$  triangle can align with such a direction. Nevertheless, among those low-index (i.e., relatively close-packed) lattice directions which are at  $\sim 60^\circ$  to  $\langle 1\bar{1}0 \rangle$ , the  $\langle 1\bar{1}\bar{2} \rangle$  directions are favored for two reasons. The first one is again lattice commensuration: the unit length along  $\langle 1\bar{1}\bar{2} \rangle$  is  $0.9564$  nm, which is 3 times the in-plane S–S distance in  $\text{MoS}_2$  ( $0.316$  nm), with a 0.9% difference. Second,  $[1\bar{1}0]$ ,  $[1\bar{1}2]$ , and  $[1\bar{1}\bar{2}]$  on  $\text{SrTiO}_3(110)$  form a set of



**Figure 4.** Models and images of  $\text{SrTiO}_3(110)$  and  $\text{MoS}_2$  on  $\text{SrTiO}_3(110)$ . (a) STM image of  $\text{SrTiO}_3(110)$  showing terraces mainly made of the  $(6 \times 1)$  reconstruction. Each step height is  $0.28 \pm 0.04$  nm, corresponding to the  $d_{110}$  lattice spacing ( $V_s = 1.0$  V;  $I_t = 0.40$  nA). (b) SEM image of  $\text{MoS}_2$  on  $\text{SrTiO}_3(110)$ . Some crystal shapes are “compressed” along the  $[001]$  direction compared to equilateral triangles (outlined by orange dashed lines and red arrows at the top left). (c) Blue schematic triangles on the atomic model of  $\text{SrTiO}_3(110)$  representing the most commonly observed crystal orientations of  $\text{MoS}_2$ . The inset is an SEM image of  $\text{MoS}_2$  crystals with the preferred orientations. (d) Edge orientation histogram of  $\text{MoS}_2$  crystals on  $\text{SrTiO}_3(110)$ , measured according to the standard above. (e) SEM image of a typically shaped  $\text{MoS}_2$  crystal, with its rough edges highlighted in black. (f) Atomic model of a  $\text{MoS}_2$  crystal on  $\text{SrTiO}_3(110)$ , with the same shape as that in panel e. The rotated lattice parts are highlighted in yellow.  $d_1 =$  seven  $\text{MoS}_2$  unit cell lengths (S–S spacings) = four  $\text{SrTiO}_3[1\bar{1}0]$  unit lengths (Sr–Sr spacings).  $d_2 =$  three  $\text{MoS}_2$  unit cell lengths (S–S spacings) = one  $\text{SrTiO}_3[1\bar{1}2]$  unit length (Sr–Sr spacing). The substrate lattice directions in part a also apply to panels b, c, e, and f.

directions arranged in a nearly regular-hexagonal way (Figure 4c), with included angles of  $70^\circ$ ,  $55^\circ$ , and  $55^\circ$ .

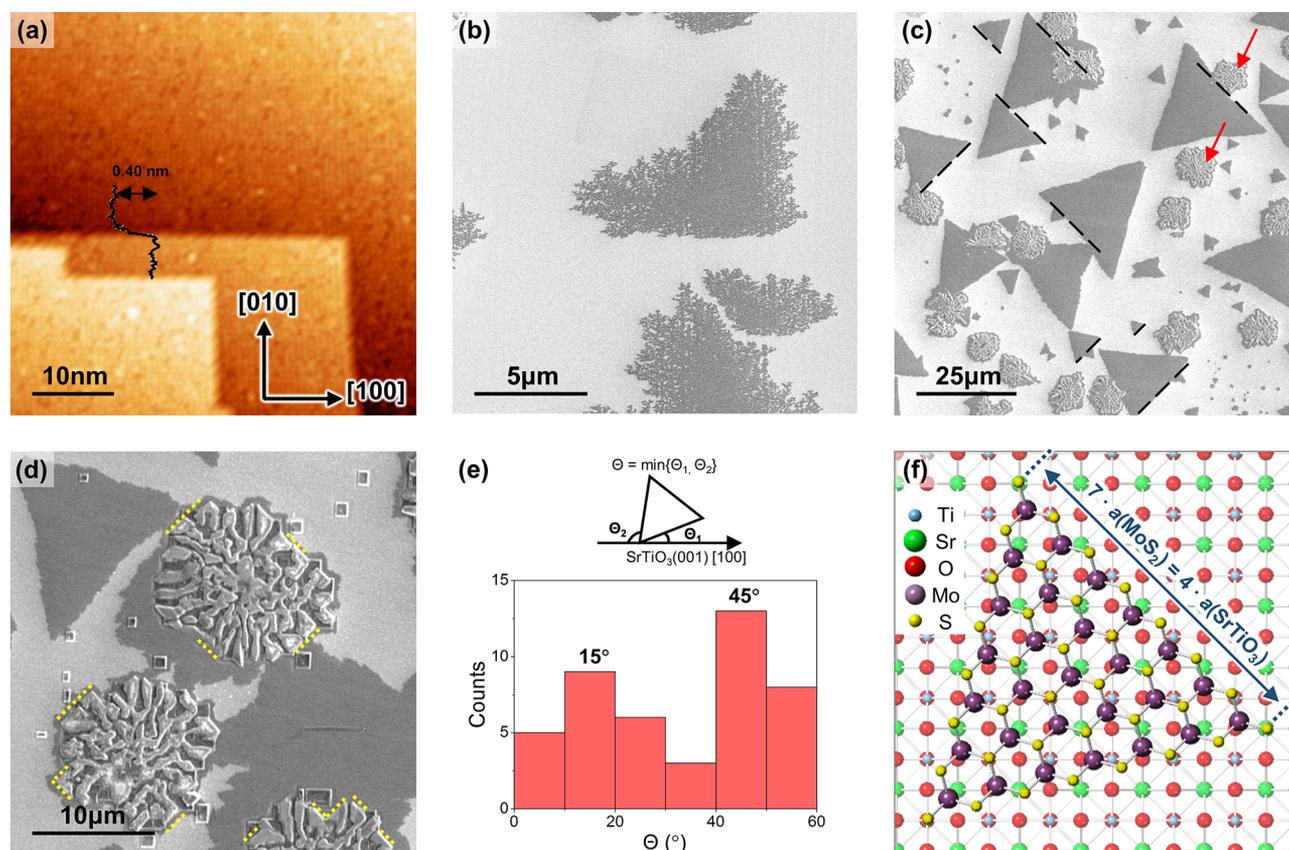
In practice, an equilateral triangle of  $\text{MoS}_2$  cannot be distorted to a  $70^\circ/55^\circ/55^\circ$  triangle while maintaining a perfect crystal structure; this would require an unphysical compressive strain of 18%. Figure 4e is a close-up SEM image of a crystal with its edges outlined in black, with an overall shape of a  $70^\circ/55^\circ/55^\circ$  triangle. Some internal angles are still  $60^\circ$ , which point to a perfect  $\text{MoS}_2$  lattice, while some angles are closer to  $55^\circ$ , meaning the lattice may have been partially rotated and/or distorted to align one edge with  $\langle 1\bar{1}2 \rangle$ . Figure 4f presents an atomic model of  $\text{MoS}_2$  that follows the shape in Figure 4e, including the zigzags and notches along the edges with an S termination. The bottom edge of the crystal is parallel to  $[1\bar{1}0]$  on the substrate, along the labeled  $d_1$ , which is a distance corresponding to seven unit lengths in  $\text{MoS}_2$  and four unit lengths along  $\text{SrTiO}_3[1\bar{1}0]$ . The  $\text{MoS}_2$  crystal also has some parts of its lattice rotated to align one edge with  $\langle 1\bar{1}2 \rangle$  of  $\text{SrTiO}_3$ , highlighted in yellow.  $d_2$  is labeled along the  $[1\bar{1}2]$  direction, and its length represents one unit length along  $[1\bar{1}2]$  and three unit lengths in  $\text{MoS}_2$ . The fact that this  $\text{MoS}_2$  crystal tries to align with both  $\langle 1\bar{1}0 \rangle$  and  $\langle 1\bar{1}2 \rangle$  inevitably induces lattice defects (e.g., around the rotated areas) plus a small

degree of lattice distortion. The associated strain is confirmed by PL (see later). On  $\text{SrTiO}_3(110)$ , the interfacial crystallographic relationship is “ $(0001)_{\text{MoS}_2} \parallel (110)_{\text{SrTiO}_3}$ ,  $[2\bar{1}\bar{1}0]_{\text{MoS}_2} \parallel [1\bar{1}0]_{\text{SrTiO}_3}$ ” and partially “ $(0001)_{\text{MoS}_2} \parallel (110)_{\text{SrTiO}_3}$ ,  $[2\bar{1}\bar{1}0]_{\text{MoS}_2} \parallel [1\bar{1}2]_{\text{SrTiO}_3}$ ”.

**3.3.  $\text{MoS}_2$  on  $\text{SrTiO}_3(001)$ .** On the final surface in our study,  $\text{SrTiO}_3(001)$ , we generated the  $c(4 \times 2)$  reconstruction, as shown in Figure 5a.<sup>25,42,43</sup> It was produced by  $\text{Ar}^+$ -ion sputtering at 500 eV for 10 min, followed by annealing at  $1100^\circ\text{C}$  for 30 min in UHV.

$\text{MoS}_2$  crystals grown on  $\text{SrTiO}_3(001)$  clearly show a distinct morphology compared with the other  $\text{SrTiO}_3$  terminations (Figure 5b). The dendritic growth of  $\text{MoS}_2$  on  $\text{SrTiO}_3(001)$  has been studied by Zhang et al.<sup>44,45</sup> and will not be discussed further here. For comparison, during the same CVD growth on an amorphous silica substrate, placed side by side with the  $\text{SrTiO}_3$  sample, the  $\text{MoS}_2$  crystals are perfectly sharp and triangular (Figure 2). Therefore, the dendritic growth can be safely attributed to the substrate effect of  $\text{SrTiO}_3(001)$ .

To consistently study the epitaxy of compact crystals, we obtained compact triangular crystals when the precursors were placed closer to the substrate in the CVD furnace.<sup>44</sup> The



**Figure 5.** Models and images of SrTiO<sub>3</sub>(001) and MoS<sub>2</sub> on SrTiO<sub>3</sub>(001). (a) STM image of SrTiO<sub>3</sub>(001) showing terraces consisting of the  $c(4 \times 2)$  reconstruction. The step height is  $0.40 \pm 0.04$  nm, corresponding to the  $d_{001}$  lattice spacing ( $V_s = 2.0$  V;  $I_t = 0.15$  nA). (b) SEM image of MoS<sub>2</sub> crystals on SrTiO<sub>3</sub>(001) with a dendritic morphology. (c) SEM image of MoS<sub>2</sub> crystals on SrTiO<sub>3</sub>(001) grown with a shorter source–substrate distance in the CVD furnace. The monolayer crystals are compact and much larger than the dendrites (dark triangles), with few-layer (to bulk) MoS<sub>2</sub> also formed (indicated by red arrows). (d) SEM images of few-layer (to bulk) MoS<sub>2</sub> structures. (e) Orientation histogram of monolayer MoS<sub>2</sub> crystals, measured according to the standard above. (f) Atomic model of MoS<sub>2</sub> on SrTiO<sub>3</sub>(001). Seven MoS<sub>2</sub> unit cell lengths (S–S spacings) = four SrTiO<sub>3</sub>[110] unit lengths (Sr–Sr spacings). The substrate lattice directions in part a also apply to panels b–d and f.

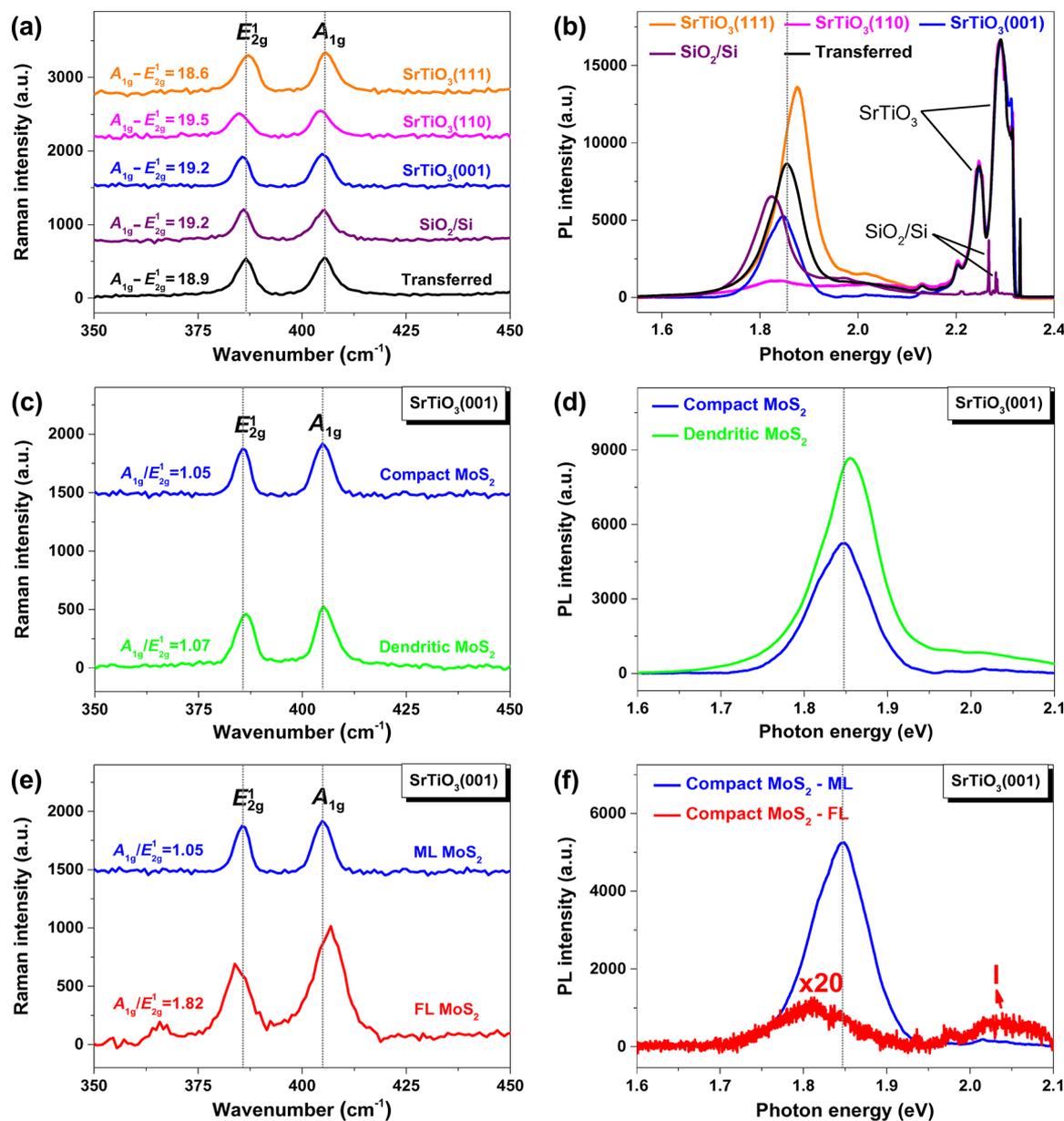
resulting crystals are shown in Figure 5c, which are compact and much larger than the dendrites (note the very different scale bars in Figure 5b and c), and no dendrites are observed. Using these growth conditions, it was difficult to completely avoid building up few-layer (to bulk) MoS<sub>2</sub> structures, as indicated by the red arrows. A close-up SEM image of these structures is shown in Figure 5d. The monolayer MoS<sub>2</sub> crystals in Figure 5c (dark triangles) are measured in terms of their crystal orientations, and the resulting histogram is shown in Figure 5e. Two peaks are identified at 15° and 45°, relative to the substrate [100] direction. They are two crystallographically equivalent orientations because of the 4-fold symmetry of SrTiO<sub>3</sub>(001). The interfacial crystallographic relationship can be described as “(0001)<sub>MoS<sub>2</sub></sub> || (001)<sub>SrTiO<sub>3</sub></sub>, [2110]<sub>MoS<sub>2</sub></sub> || [110]<sub>SrTiO<sub>3</sub></sub>”.

Again, in these orientations, one edge of the triangular MoS<sub>2</sub> crystal aligns with the  $\langle 1\bar{1}0 \rangle$  directions on SrTiO<sub>3</sub>(001) because of the 7:4 coincidence epitaxy. A selection of such edges are highlighted by black dashed lines in Figure 5c. It is also interesting to note that even the few-layer (to bulk) MoS<sub>2</sub> structures have many of their edges aligned with the  $\langle 1\bar{1}0 \rangle$  directions on SrTiO<sub>3</sub>(001), as highlighted in yellow in Figure 5d. An atomic model is drawn in Figure 5f to show an example monolayer crystal and the lattice commensuration. It should be noted that the histogram peaks at 15° and 45° are not sharp

because the crystals measured are mostly large (15–30 μm), and their growth is more kinetically controlled than for the smaller ones, as discussed in section 3.1.

**3.4. Raman Spectroscopy and PL.** Raman spectroscopy and PL were performed to investigate some of the structural properties of the CVD-grown MoS<sub>2</sub> on different substrates (Figures 6 and 7). The Raman and PL spectra are known to be influenced by the layer thickness,<sup>46</sup> lattice strain,<sup>47–52</sup> doping level,<sup>53,54</sup> and lattice defects<sup>55</sup> of MoS<sub>2</sub>. These depend on the substrate surface (Figure 6a,b), the MoS<sub>2</sub> crystal morphology (Figure 6c,d), and the MoS<sub>2</sub> layer number (Figure 6e,f). Detailed information can be extracted through Lorentzian fitting for the PL spectra of monolayer MoS<sub>2</sub> on different substrates (Figure 7). In addition to the samples mentioned previously, we also studied MoS<sub>2</sub> monolayer crystals transferred onto a SrTiO<sub>3</sub> substrate. This sample serves as a reference for strain calculations because the crystals have released their strain during the transfer process. Note that the transferred sample is also Nb-doped (0.5 wt %) and was annealed after the transfer to remove the trapped contaminants and improve the MoS<sub>2</sub>–SrTiO<sub>3</sub> interface adhesion. Therefore, its doping level can be considered nearly the same as that in MoS<sub>2</sub> directly grown on SrTiO<sub>3</sub>.

Parts a, c, and e of Figure 6 show the two characteristic Raman modes of MoS<sub>2</sub>, E<sub>2g</sub><sup>1</sup> (382.0–384.3 cm<sup>-1</sup>) and A<sub>1g</sub><sup>1</sup> (403.0–407.5 cm<sup>-1</sup>).<sup>46</sup> The E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub><sup>1</sup> modes are

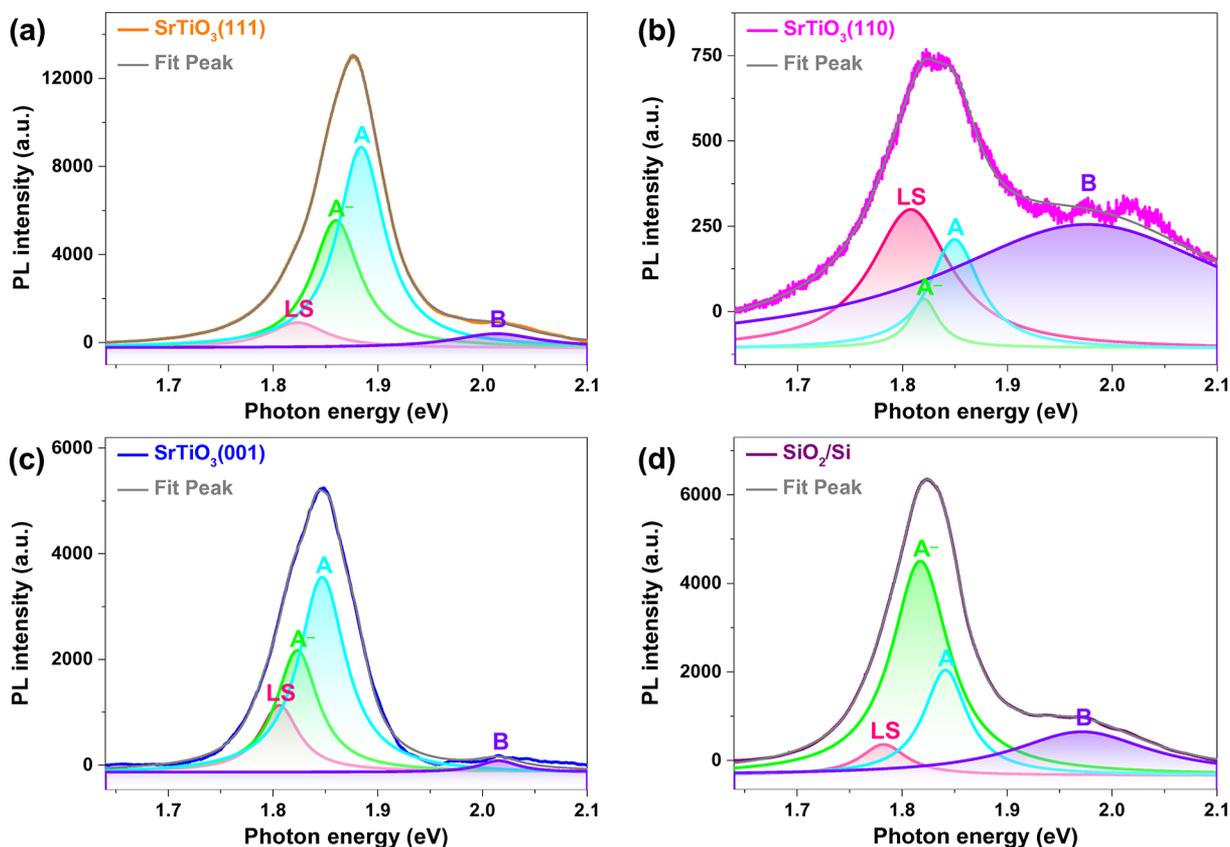


**Figure 6.** Raman and PL measurements. (a, c, and e) Raman and (b, d, and f) PL spectra of the MoS<sub>2</sub> single crystals (a and b) on different substrate surfaces, i.e., SrTiO<sub>3</sub>(111), (110), (001), SiO<sub>2</sub>/Si, and MoS<sub>2</sub> transferred onto SrTiO<sub>3</sub>, (c and d) with different morphologies, i.e., compact- and dendritic-shaped MoS<sub>2</sub>, and (e and f) with different layer numbers, i.e., monolayer (ML) and few-layer (FL) MoS<sub>2</sub>. “I” indicates the indirect optical transition.

preferentially excited for terrace and edge terminations, respectively.<sup>56</sup> Therefore, the relative integrated intensities of A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> can provide information on the texture of MoS<sub>2</sub>.<sup>26,56,57</sup> Regardless of the substrate, all of the MoS<sub>2</sub> monolayers predominant with terrace sites exhibit similar integrated intensity ratios of A<sub>1g</sub>/E<sub>2g</sub><sup>1</sup> ~ 1.05, whereas the few-layer MoS<sub>2</sub> terminated more by edges shows an increased ratio of A<sub>1g</sub>/E<sub>2g</sub><sup>1</sup> ~ 1.82 (Figure 6a,c,e), conforming well to those reported previously.<sup>26,46</sup> Also, the frequency difference between the A<sub>1g</sub> and E<sub>2g</sub><sup>1</sup> modes can be used to precisely determine the layer number of MoS<sub>2</sub>. Our values are ≤19.5 cm<sup>-1</sup> for all of the monolayer MoS<sub>2</sub> and ≥23.1 cm<sup>-1</sup> for the few-layer MoS<sub>2</sub> (Figure 6a,c,e), in good agreement with the literature.<sup>46</sup> An example of the few-layer structures is shown in Figure 5d. Figure 6f presents the PL of the monolayer and few-layer MoS<sub>2</sub> on the same substrate termination, SrTiO<sub>3</sub>(001).

In addition to the direct transitions (K → K) involving two split valence bands for the emissions of A and B excitons, few-layer MoS<sub>2</sub> shows an additional peak (I) originating from the indirect transition (Λ → Γ).<sup>2,3,58</sup> Compared to the monolayer MoS<sub>2</sub>, the few-layer MoS<sub>2</sub> exhibits much weaker PL with lower emission energies (monolayer, 1.85 eV for A excitons and 2.02 eV for B excitons; few-layer, 1.81 eV for A excitons, 1.98 eV for B excitons, and 2.04 eV for indirect excitons).

The lattice strain in MoS<sub>2</sub> develops via two processes. The first is epitaxial growth associated with the lattice mismatch between MoS<sub>2</sub> and the substrate. The second is fast cooling where the strain develops due to different thermal expansion coefficients (TECs) of MoS<sub>2</sub> and the substrate.<sup>59</sup> The TEC of the as-prepared 2H-phase MoS<sub>2</sub> (α<sub>MoS<sub>2</sub>a</sub> = 1.9 × 10<sup>-6</sup> K<sup>-1</sup> and α<sub>MoS<sub>2</sub>c</sub> = 8.65 × 10<sup>-6</sup> K<sup>-1</sup>, 293–1073 K)<sup>60</sup> is approximately an



**Figure 7.** Lorentzian-fitted PL spectra of the monolayer MoS<sub>2</sub> grown on (a) SrTiO<sub>3</sub>(111), (b) SrTiO<sub>3</sub>(110), (c) SrTiO<sub>3</sub>(001), and (d) SiO<sub>2</sub>/Si substrates, revealing the presence of A excitons (A), B excitons (B), negatively charged A excitons (trions, A<sup>-</sup>), and localized states (LS).

order of magnitude larger than that of SiO<sub>2</sub> (typical value  $\alpha_{\text{SiO}_2} = 5.6 \times 10^{-7} \text{ K}^{-1}$ ),<sup>61</sup> while it is about an order of magnitude smaller than that of SrTiO<sub>3</sub> ( $\alpha_{\text{SrTiO}_3} = 3.23 \times 10^{-5} \text{ K}^{-1}$ , 300–1800 K).<sup>62</sup> As a result, in the fast-cooling stage following MoS<sub>2</sub> growth, tensile strain develops in the SiO<sub>2</sub>-supported MoS<sub>2</sub>, whereas compressive strain is introduced in MoS<sub>2</sub> on SrTiO<sub>3</sub>.<sup>59</sup> The tensile and compressive strains respectively lead to red and blue shifts of the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> Raman peaks and the A-exciton PL peak, relative to the transferred sample (Figure 6a,b).<sup>47–52</sup> However, these three peaks are all red-shifted for the monolayer MoS<sub>2</sub> crystals grown on SrTiO<sub>3</sub>(110) and (001), which is attributed to epitaxial growth. As manifested in Figures 4 and 5, the MoS<sub>2</sub> monolayer crystals show a large lattice mismatch with the SrTiO<sub>3</sub>(110) and (001) terminations, leading to tensile strain. To estimate the growth-induced tensile strains in the MoS<sub>2</sub> monolayers grown on SrTiO<sub>3</sub>(110) and (001), we use their peak shifts of the E<sub>2g</sub><sup>1</sup> Raman mode with respect to that on SrTiO<sub>3</sub>(111).<sup>63</sup> As stated in section 3.1, the small difference of <0.2% in the lattice parameters between MoS<sub>2</sub> and SrTiO<sub>3</sub>(111) should give rise to a compressive strain of  $\sim 0.18\%$  in the MoS<sub>2</sub> adlayer. Taking this into account, the growth-induced tensile strain is  $\sim 0.58\%$  on SrTiO<sub>3</sub>(110), caused by the attempt of the MoS<sub>2</sub> crystal edges to align with both  $\langle 110 \rangle$  and  $\langle 11\bar{2} \rangle$  crystallographic directions. It is  $\sim 0.34\%$  on SrTiO<sub>3</sub>(001), ascribed to the lattice mismatch along the two nonepitaxial edges of the monolayer MoS<sub>2</sub> crystal. Finally, the growth-induced strain can be considered negligible in the monolayer MoS<sub>2</sub> grown on SiO<sub>2</sub>/Si because of the amorphous substrate surface, which leads to random orientations of the MoS<sub>2</sub> crystals in Figure 2.

Figure 6b also shows that the tensile strains in the monolayer MoS<sub>2</sub> supported on SrTiO<sub>3</sub>(110) and (001) and SiO<sub>2</sub>/Si substrates commonly lead to decreased PL intensities compared to the transferred sample.<sup>50</sup> In particular, significant PL quenching is observed on SrTiO<sub>3</sub>(110), which stems from the epitaxy-induced lattice defects in the crystals previously shown in Figure 4f, which will be discussed later. However, on SrTiO<sub>3</sub>(111), the PL intensity is enhanced by 58% with a slightly narrower peak width (decrease in the full-width at half-maximum  $\Delta\text{fwhm} = 7.05 \text{ meV}$ ) compared to the transferred sample because of compressive strain,<sup>49</sup> which agrees with the Raman results.

Moreover, the crystal morphology also impacts the strain level in MoS<sub>2</sub>. As shown in Figure 6c,d, the dendritic MoS<sub>2</sub> crystals on SrTiO<sub>3</sub>(001) display small blue shifts of Raman peaks and the A-exciton PL peak relative to the compact triangular crystals. (Note that the E<sub>2g</sub><sup>1</sup> Raman mode corresponding to the in-plane Mo–S phonon is more sensitive to strain than the A<sub>1g</sub> mode corresponding to the out-of-plane Mo–S phonon.<sup>48–52</sup>) This is because the dendrites could have partially released the growth-induced tensile strain by generating numerous fragmental edges. This suppresses the deterioration of the MoS<sub>2</sub> lattice and its optical properties, which also results in the stronger PL intensity for the dendrites.

The PL spectra are also fitted with the A and A<sup>-</sup> peaks for A-exciton emission, the B peak for B-exciton emission, and localized states (LSs) correlated with the structural disorder of MoS<sub>2</sub> (Figure 7).<sup>55</sup> The LS peaks indicate the defect level in the as-grown MoS<sub>2</sub> crystals: SrTiO<sub>3</sub>(110) > SrTiO<sub>3</sub>(001) > SrTiO<sub>3</sub>(111). This depends on the degree of lattice mismatch between MoS<sub>2</sub> and the SrTiO<sub>3</sub> surface termination. In addition

to the neutral A exciton, the negatively charged exciton (trion,  $A^-$ ) in Figure 7 suggests n-type doping in the monolayer  $\text{MoS}_2$  on all substrates. The intensity ratio of exciton-to-trion peaks ( $A/A^-$ ) can be used to indicate the doping level.<sup>64</sup> The larger  $A/A^-$  ratio on the  $\text{SiO}_2/\text{Si}$  substrate proves that the charge impurities induce heavier n-doping into the supported  $\text{MoS}_2$  than the Nb in  $\text{SrTiO}_3$  substrates. Nonetheless, the doping level of  $\text{MoS}_2$  on all  $\text{SrTiO}_3$  substrates (all Nb-doped at 0.5 wt %) is the same. Therefore, the growth-induced strains can be safely deduced from the Raman and the A-exciton PL peak positions of  $\text{MoS}_2$  on different terminations of  $\text{SrTiO}_3$ .

#### 4. DISCUSSION

We have shown that on three different crystal terminations of  $\text{SrTiO}_3$ ,  $\text{MoS}_2$  crystals tend to adopt the orientations that allow its lattice to match that of the substrate via coincidence epitaxy. The equilibrium orientations and crystal shapes maximize the number of directions along which this is achieved. The interfacial vdW bonding is strengthened in the epitaxial orientations via lattice registry, giving rise to a greater number of bonding sites and closer proximity between the two layers. Therefore, when a  $\text{MoS}_2$  nucleus is free to rotate in the initial stage, it gets “locked” into the lowest-energy orientation,<sup>8</sup> i.e., in the epitaxial configurations that we observed. Other bonding types, e.g., electrostatic attraction<sup>7</sup> and chemical bonds,<sup>65</sup> are less likely to exist between  $\text{MoS}_2$  and  $\text{SrTiO}_3$ . This is because they are stronger than vdW bonding by orders of magnitude and would lock the  $\text{MoS}_2$  monolayers exclusively into certain orientations, e.g., as observed on  $\text{Au}(111)$ .<sup>35</sup> Gold, an electronegative metal, is a very different substrate from  $\text{SrTiO}_3$ , an oxide ceramic, and can interact with  $\text{MoS}_2$  via a stronger bonding type. Nb doping (0.5 wt %), which makes  $\text{SrTiO}_3$  conductive, may also have played a role in its bonding with  $\text{MoS}_2$  monolayers, but we expect any effects to be minimal.

On  $\text{SrTiO}_3(111)$ , it is advantageous to align the  $\langle 2\bar{1}\bar{1}0 \rangle$  directions of  $\text{MoS}_2$  with  $\langle 1\bar{1}0 \rangle$  on  $\text{SrTiO}_3$  with a favorable coincidence lattice registry. In previous studies of  $\text{MoS}_2$  grown on ceramic substrates,  $\text{SiO}_2$  does not induce epitaxy because it is amorphous;<sup>12</sup> *c*-plane sapphire, another 3-fold-symmetric substrate, reveals preferred orientations similar to those of  $\text{MoS}_2$  on  $\text{SrTiO}_3(111)$  ( $0^\circ$  and  $60^\circ$ ).<sup>7,8</sup> In these orientations, either interfacial electrostatic attraction (as a result of charge transfer)<sup>7</sup> or greatly enhanced vdW bonding<sup>8</sup> was proposed. It was not explicitly mentioned why the interfacial bonding prefers particular orientations, but this is likely to be the good lattice registry between  $\text{MoS}_2$  and sapphire. Their in-plane periodicities, 0.316 nm for  $\text{MoS}_2$  and 0.476 nm for sapphire, have a 2:3 ratio with a 0.4% difference.<sup>7</sup> Therefore, we speculate that both  $\text{SrTiO}_3(111)$  and *c*-plane sapphire show similar low-energy coincidence epitaxial relationships because of lattice commensuration with negligible strain.

Also, one of the two lattice-coincident orientations on  $\text{SrTiO}_3(111)$  is more strongly preferred, and a similar situation is found in the  $\text{MoS}_2$ -on- $\text{Au}(111)$  system. A single  $\text{Au}(111)$  layer is 6-fold-symmetric, while a second layer reduces it to 3-fold because of the differentiated face-centered-cubic (fcc) and hexagonal-close-packed (hcp) sites. Theoretical studies by Bruix et al. reveal a very slim energy difference (16 meV per unit cell) between the “ $\text{MoS}_2$ -on-hcp” and “ $\text{MoS}_2$ -on-fcc” configurations,<sup>17</sup> but the crystals turn out to exclusively orient in only one way.<sup>35</sup> The termination of  $\text{Au}(111)$  alternates between hcp and fcc across a ridge of the herringbone

structure, so that the  $\text{MoS}_2$  triangles “flipping” their directions across each ridge means the same stacking. This exclusivity is also assisted by a much slower growth method adopted than CVD, which results in nanometer-sized crystals (all  $<8$  nm).<sup>35</sup> On the other hand,  $\text{SrTiO}_3(111)$  shows a uniform termination with surface step heights always equivalent to the  $d_{111}$  lattice parameter.<sup>23,66</sup> Hence, the  $0^\circ$  and  $60^\circ$  orientations of  $\text{MoS}_2$  are indeed distinct, possibly with a very small but noticeable energy difference like that on  $\text{Au}(111)$ .

On  $\text{SrTiO}_3(110)$ , the strong tendency to maximize coincidence epitaxial directions (i.e.,  $\langle 1\bar{1}0 \rangle$  and  $\langle 1\bar{1}\bar{2} \rangle$ ) competes with the equilibrium shape of the  $\text{MoS}_2$  crystals. To accommodate the shape distortions, there is an increased defect density and an additional element of strain energy. These both increase the lattice energy of  $\text{MoS}_2$  but must have been overcome by the reduction in the interfacial energy because of the improved bonding. Even on  $\text{SrTiO}_3(001)$ , where it is only possible to satisfy one direction of good coincidence epitaxy along  $\langle 1\bar{1}0 \rangle$ , the  $\text{MoS}_2$  crystals still show a preference to orient in such a way.

It is worth noting that, because the substrate surface reconstructions prepared in vacuum do not usually survive in the atmosphere, we do not know what the exact interface is at the time of CVD growth of  $\text{MoS}_2$ . It cannot be the bulk termination of  $\text{SrTiO}_3$  because the surface bonds tend to rearrange themselves to stabilize the surface polarity. However, we do know that there are certain ways in which  $\text{SrTiO}_3$  reconstructs. For example,  $\text{SrTiO}_3(111)-(4 \times 4)$  is one of the lowest-energy reconstructions of the (111) termination, which forms most easily in partial pressures of oxygen.<sup>23,34</sup> If  $\text{MoS}_2$  grows on  $\text{SrTiO}_3(111)-(4 \times 4)$ , the substrate periodicity (i.e., the unit length along  $\langle 1\bar{1}0 \rangle$ ) becomes 4 times that of the bulk. The coincidence epitaxy then turns into a 7:1 ratio, which is an attractive epitaxial relationship. On  $\text{SrTiO}_3(110)$ ,  $(1 \times 4)$ ,  $(3 \times 4)$ ,  $(4 \times 4)$ , and  $(6 \times 4)$  reconstructions have been reported previously,<sup>24,67</sup> which make the periodicity along  $\langle 1\bar{1}0 \rangle$  4 times that in the bulk as well. Similarly on  $\text{SrTiO}_3(001)$ , there is a  $(4 \times 4)$  reconstruction that does the same thing;<sup>68</sup> there is also a  $c(4 \times 4)$  reconstruction, which makes the periodicity along  $\langle 1\bar{1}0 \rangle$   $2\sqrt{2}$  times that of the bulk, and this turns the coincidence epitaxy into a 5:1 ratio with a mismatch of 1.2%.<sup>68,69</sup>

Based on the above, our understanding of what drives the epitaxy is the interfacial lattice commensuration between  $\langle 2\bar{1}\bar{1}0 \rangle$  (i.e., the S edge directions) of  $\text{MoS}_2$  and  $\langle 1\bar{1}0 \rangle$  on  $\text{SrTiO}_3$ . We stress the strength of this vdW interaction, which can powerfully control the growth of  $\text{MoS}_2$  crystals. Developing a deeper understanding of  $\text{MoS}_2$  epitaxy is an important step toward integrating  $\text{MoS}_2$  in future novel electronic devices. This is because when  $\text{MoS}_2$  is grown in perfect lattice registry with its crystalline substrate, grain boundaries are eliminated. This allows large-area monolayers of  $\text{MoS}_2$  to be grown even when there are multiple nucleation sites.

Finally, we mention that it is very difficult to obtain atomically resolved STM images of  $\text{MoS}_2$  on a ceramic substrate, and a high-resolution image like Figure 3e is rare. If such images could be obtained on all terminations of  $\text{SrTiO}_3$  substrates, they would provide useful information about the strain or lattice distortion in monolayer  $\text{MoS}_2$ . Many good atomic images of  $\text{MoS}_2$  monolayers on  $\text{Au}(111)$  have been reported,<sup>15,17,35,36,39</sup> but it was difficult for the same group of researchers to obtain high-resolution images of  $\text{MoS}_2$  on

TiO<sub>2</sub>.<sup>65</sup> It is not yet clear to us why it is a lot harder to image MoS<sub>2</sub> on ceramic substrates than on metal substrates. This is no doubt an interesting area for future study.

## 5. CONCLUSIONS

In summary, the orientations and shapes of MoS<sub>2</sub> crystals are strongly influenced by substrate interactions with SrTiO<sub>3</sub>. The equilibrium orientations maximize the interfacial vdW bonding via coincidence epitaxy and hence enhanced bonding, which is assisted by lattice defects and crystal shape distortions when possible. This offers a broader interpretation of epitaxy, which involves minimization of the total energy of the system in a more complex way. It is the sum of the lattice energy of MoS<sub>2</sub> (to maintain its equilateral triangular shape) and the interfacial energy associated with the MoS<sub>2</sub>–substrate interactions. The results also confirm that the vdW interaction is sufficiently strong to regulate epitaxy in a powerful way. The strain levels in MoS<sub>2</sub> are found to be adjusted by the different epitaxial relationships with the substrate. This allows us more rigorous control in the synthesis of large-scale uniform MoS<sub>2</sub> layers for optimal electronic properties and enables the manipulation of inbuilt strains to fine-tune the band gap, which improve the applicability of monolayer MoS<sub>2</sub> in next-generation nano-electronic devices.

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### Notes

The authors declare no competing financial interest.

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