Epitaxial Growth of Monolayer MoS₂ on SrTiO₃ Single Crystal Substrates for Applications in Nanoelectronics

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ABSTRACT: Monolayer molybdenum disulfide (MoS₂) crystals grown on amorphous substrates such as SiO₂ are randomly oriented. However, when MoS₂ 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 MoS₂ on three different terminations of single crystal strontium titanate (SrTiO₃) substrates. On SrTiO₃(111), the monolayer MoS₂ crystals form equilateral triangles with two main orientations, in which they align their (2110)-type directions (i.e., the sulfur-terminated edge directions) with the (110)-type directions on SrTiO₃. This arrangement allows near-perfect coincidence epitaxy between seven MoS₂ unit cells and four SrTiO₃ unit cells. On SrTiO₃(110), the MoS₂ crystals tend to align their edges with both the (110) and (112) directions on SrTiO₃ because these both provide favorable coincidence lattice registry. This distorts the crystal shapes and introduces an additional strain detectable by photoluminescence. When triangular MoS₂ crystals are grown on SrTiO₃(001), they again show a preference to align their edges with the (110) directions on SrTiO₃. Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS₂ monolayers and SrTiO₃ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this paper is that the vdw interaction between MoS₂ and SrTiO₃ substrates determines the supported crystal shapes and orientations by epitaxial relations. Controlled crystal orientations make the growth of large sheets of MoS₂ 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 MoS₂ in next-generation nanoelectronic devices.

KEYWORDS: MoS₂, SrTiO₃, van der Waals epitaxy, scanning tunneling microscopy, chemical vapor deposition, Raman spectroscopy, photoluminescence, 2D materials

1. INTRODUCTION

Monolayer MoS₂ has been extensively studied as the prototypical material of the family of transition-metal dichalcogenides (TMDCs). It was discovered that the electronic properties of TMDCs are drastically affected by dimensionality: MoS₂ 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. These band-gap energies span the visible and near-infrared range of the electromagnetic spectrum, and therefore MoS₂ is a promising candidate for optoelectronic applications. Monolayer MoS₂ is also viewed as a two-dimensional (2D) semiconductor with great potential because of its high charge mobility of more than 200 cm² V⁻¹ s⁻¹ and an on/off current ratio of up to ~10⁸. These properties make it competitive with graphene for use in novel low-power digital electronics.

For a 2D material like MoS₂, 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 MoS₂ monolayers. This is important from a technological point of view because the properties of a 2D material can be highly sensitive to its interfaces. CVD growth on a well-prepared substrate results in a collection of large MoS₂ domains that have controllable morphology. In particular, epitaxy has been shown to effectively control MoS₂ crystal orientations, which is required to minimize the concentration of grain boundaries in the MoS₂ layer. This is especially important in the large-area synthesis of MoS₂ because grain boundaries are detrimental to the electrical properties (e.g., charge mobility) of polycrystalline films. By its nature, epitaxial growth cannot occur on amorphous substrates like SiO₂. 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, e.g., c-plane sapphire and Au(111). 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 MoS₂ bilayers, where the AA and AB stacking configurations (0° and 60° relative layer rotation) are overwhelmingly favored.
compared to others.\textsuperscript{16} Furthermore, the indirect-to-direct transition of the MoS\textsubscript{2} 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\textsubscript{2} and its substrate. Nevertheless, other possible interfacial bonding mechanisms have also been reported, including electrostatic attraction between MoS\textsubscript{2} and sapphire\textsuperscript{7} and chemical bonding between sulfur and various metals.\textsuperscript{17−20} The nature of the Au−S bond is particularly controversial; it is claimed to perturb the electronic structure very little in some studies\textsuperscript{15,18} and have a covalent nature in others.\textsuperscript{17} Finding suitable substrate materials is an important step toward epitaxy or orientation control in the synthesis of MoS\textsubscript{2} films. The substrates used in our work are electrically conducting niobium (Nb)-doped (0.5 wt %) SrTiO\textsubscript{3} crystals. SrTiO\textsubscript{3} has attracted substantial interest since the 1970s mostly because of its versatile crystal surfaces.\textsuperscript{23−25} It was chosen for our study because several surface terminations with different symmetries can be readily prepared. MoS\textsubscript{2} was grown on the three well-studied SrTiO\textsubscript{3} terminations, (111), (110), and (001). The crystallinity of SrTiO\textsubscript{3} encourages MoS\textsubscript{2} monolayer crystals to grow epitaxially, and the different symmetries of the three terminations lead to distinct epitaxial behavior. Overall, the interaction between MoS\textsubscript{2} and SrTiO\textsubscript{3} is found to influence the orientations, shapes, and optical properties of MoS\textsubscript{2} monolayers. The ability to regulate these properties of monolayer MoS\textsubscript{2} 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\textsubscript{2} in its application to nanoelectronics and optoelectronics.

2. EXPERIMENTAL SECTION

2.1. Preparation of Substrates. SrTiO\textsubscript{3} single crystals (7 × 2 × 0.5 mm\textsuperscript{3}) doped with Nb at 0.5% by weight were supplied by PI-KEM, U.K., with epi-polished (111), (110), and (001) surfaces. SrTiO\textsubscript{3} is an insulator with a band gap of 3.2 eV at 25 °C.\textsuperscript{22} 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\textsubscript{3} surfaces were carried out in an ultrahigh vacuum (UHV) scanning tunneling microscope, which is a custom-built JEOL JSTM 4500s model (base pressure 10\textsuperscript{−9} Pa). SrTiO\textsubscript{3} surfaces were prepared to terminate with previously well-characterized reconstructions, requiring different Ar\textsuperscript{+} ion sputtering conditions, annealing temperatures, durations, and O\textsubscript{2} partial pressures.\textsuperscript{23−25}
2.2. CVD Growth and Transfer of MoS2. Molybdenum trioxide (MoO3 powder, ≥99.5%, Sigma-Aldrich) and sulfur (S powder, ≥99.5%, Sigma-Aldrich) were used to synthesize MoS2 monolayers on SrTiO3 using the atmospheric-pressure CVD method. A schematic diagram of the CVD setup is shown in Figure 1c. SrTiO3 substrates were placed face-up and downstream with respect to the precursors, which were 20 mg of MoO3 and 300 mg of S, loaded into two tubes with 12 mm and 22 mm diameters, respectively. The system was first flushed with 500 scm 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 MoS2 crystals were triangles with S-edge terminations. Then the MoO3 precursor and SrTiO3 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.

MoS2 monolayers grown on a SiO2/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 SiO2 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 MoS2 monolayer was released. The isolated film of PMMA/MoS2 was then rinsed in deionized (DI) water three times for 1 h each time. Following this, a precleaned SrTiO3 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 MoS2–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 MoS2 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,27,28 Gwyddion,14 and WSxM.29 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 MoS2 and SrTiO3 for the purpose of epitaxial analysis. Figure 1a.i is the side view of the 3D structure of 2H-MoS2, the thermodynamically stable polytype of MoS2.30 Two other common polytypes are called 1T- and 3R-MoS2, but they are not discussed here. The 2H-MoS2 crystal consists of covalently bonded S–Mo–S sandwich layers held together by vdW forces.29,30 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 α = β = 90°, γ = 120°; the space group is P63/mmc (No. 194).30 Figure 1a.ii is the top view of MoS2. In common with other hexagonal systems, it is useful to employ a four-index notation to emphasize the equivalence between crystallographically equivalent directions.31 For example, the a1, a2, and a3 directions in Figure 1a.ii are all of the (2110) type,31,32 which highlights the symmetry of the structure. Many studies term the basal plane of MoS2 as (001),15,33 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 MoS2 monolayers, which are 60° (or 180°) rotated with respect to each other. Their S-terminated edges are aligned along the (2110)-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 [01̅0] and [01̅1̅0], and they are inequivalent. Note that these directions are equivalent in a bulk MoS2 crystal, which has in-plane hexagonal symmetry, which is reduced to 3-fold symmetry in a monolayer.

SrTiO3 adopts a perovskite structure with a cubic lattice above 105 K (α = 3.905 Å),25 and its unit cell is shown in Figure 1b.i. The Ti4+ ions are octahedrally coordinated with respect to the O2− ions, and the Sr2+ ions are in a site that is 12-fold-coordinated by O2− 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 SrTiO3(111), [11̅2] and [1̅1̅2], a pair of inequivalent directions. Next, the (110) surface of SrTiO3 has 2-fold symmetry, and the unit cell is a rectangle (Figure 1b.ii). Finally, SrTiO3(001) has 4-fold symmetry with a square surface unit cell (Figure 1b.ii).

Although the as-supplied SrTiO3 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+-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 MoS2 crystals and SrTiO3 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 MoO3 and S precursors were loaded into two quartz tubes in two separate furnaces for independent control of their temperatures. The SrTiO3 substrate was supported on a larger SiO2/Si wafer acting as a holder. The precursor vapors were transported by argon flow under atmospheric pressure downstream onto the substrate surface to grow MoS2.

For the purposes of comparison, we first present data from an amorphous substrate. Figure 2 is an SEM image of MoS2 crystals grown on SiO2/Si. As one would expect from S-rich growth conditions, the MoS2 monolayers preferentially adopt triangular geometries.14 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
demonstrates that the vdW interaction between the amorphous substrate and MoS_{2} monolayers induces no orientation preferences for the crystal growth.

3.1. MoS_{2} on SrTiO_{3}(111). Figure 3a is an STM image of the SrTiO_{3}(111) surface composed of domains of (3 × 3) and (4 × 4) reconstructions, with the average terrace step height being measured as 0.23 ± 0.03 nm (d_{111} lattice spacing = 0.225 nm). This surface is generated by Ar+ ion sputtering at 500 eV for 8 min and subsequent annealing at 1140 °C for 3 h in 4.5 × 10^{-4} Pa O_{2}. 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_{3} surfaces reported. In previous epitaxial studies of MoS_{2} on crystalline substrates, e.g., c-plane sapphire, 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_{2} crystals on SrTiO_{3}(111). The larger crystals (those with lateral sizes of over 5 μm) with S-terminated edges 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_{3}(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_{3}(111), resulting in two main orientations, as represented by the two blue schematic triangles. Another observation is that one of the two preferred orientations of the MoS_{2} crystals: "(0001)_{MoS_{2}} [\{11\overline{2}\}SrTiO_{3} \{01\overline{1}\}]_{MoS_{2}}[\{1\overline{1}\}SrTiO_{3} \{010\}]_{MoS_{2}}[\{1\overline{1}\}SrTiO_{3}" demonstrates that the vdW interaction between the substrate. Another interesting possibility is that the smaller MoS_{2} 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 XSS 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_{2} crystals sit in the same way as those in Figure 1a.iii. We illustrate in Figure 1a.iii and b.ii that on both monolayer MoS_{2} and SrTiO_{3}(111), the crystallographic directions pointing up and down are distinct. Hence, the two orientations of MoS_{2} crystals on SrTiO_{3}(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_{2} on SrTiO_{3}(110). The SrTiO_{3}(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. Figure 4b is a typical SEM image of MoS_{2} on SrTiO_{3}(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
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, [11̅2] is at 55° anticlockwise relative to [1̅10], which is also shown in Figure 4c. If we refer to Figure 4c, we can see that such triangles with their edges parallel to [1̅10], [1̅12], and [112] have three internal angles of 70°, 55°, and 55°.

The [1̅10] direction is favored because of the 7:4 coincidence epitaxy, similar to the case on SrTiO₃(111). However, on SrTiO₃(110), only one edge of any MoS₂ triangle can align with such a direction. Nevertheless, among those low-index (i.e., relatively close-packed) lattice directions which are at ∼60° to ⟨11̅0⟩, the ⟨112⟩ directions are favored for two reasons. The first one is again lattice commensuration: the unit length along ⟨112⟩ is 0.9564 nm, which is 3 times the in-plane S–S distance in MoS₂ (0.316 nm), with a 0.9% difference. Second, [1̅10], [1̅12], and [112] on SrTiO₃(110) form a set of

Figure 3. Models and images of SrTiO₃(111) and MoS₂ on SrTiO₃(111). (a) STM image of reconstructed SrTiO₃(111), showing terraces with (3 × 3) and (4 × 4) reconstructed domains. Two example domains are labeled. Each step height is 0.23 ± 0.03 nm and corresponds to the d₁₁₁ lattice spacing (Vₛ = 2.0 V; Iₜ = 0.38 nA). (b) SEM image showing MoS₂ crystals with a large range of sizes (laterally 0.5–30 μm). (c) SEM image of small crystals (1–3 μm). The preferred crystal orientations are drawn as schematics, where the darker blue triangle is preferred. (d) STM image showing very small MoS₂ crystals (200–400 nm), with a line profile showing the monolayer thickness (Vₛ = 1.5 V; Iₜ = 0.09 nA). An atomic model of monolayer MoS₂ is superimposed, assuming that S atoms are imaged by the STM. (f) Atomic models showing the two preferred orientations of MoS₂ crystals on SrTiO₃(111). The interface crystallography is written next to each orientation. Also, seven MoS₂ unit cell lengths (S–S spacings) = four SrTiO₃ ⟨110⟩ unit lengths (Sr–Sr spacings). The substrate lattice directions in panel a also apply to panels b–f. (g) Orientation histograms for MoS₂ crystals of different sizes, measured according to the standard on the far right.
directions arranged in a nearly regular-hexagonal way (Figure 4c), with included angles of 70°, 55°, and 55°. In practice, an equilateral triangle of MoS2 cannot be distorted to a 70°/55°/55° 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°/55°/55° triangle. Some internal angles are still 60°, which point to a perfect MoS2 lattice, while some angles are closer to 55°, meaning the lattice may have been partially rotated and/or distorted to align one edge with $\langle 11\bar{2}\rangle$. Figure 4f presents an atomic model of MoS2 that follows the shape in Figure 4e, including the zigzags and notches along the edges with an S termination. The substrate lattice directions in part a also apply to panels b, c, e, and f.

3.3. MoS2 on SrTiO3(001). On the final surface in our study, SrTiO3(001), we generated the c(4×2) reconstruction, as shown in Figure 5a. It was produced by Ar+-ion sputtering at 500 eV for 10 min, followed by annealing at 1100 °C for 30 min in UHV.

MoS2 crystals grown on SrTiO3(001) clearly show a distinct morphology compared with the other SrTiO3 terminations (Figure 5b). The dendritic growth of MoS2 on SrTiO3(001) has been studied by Zhang et al. 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 SrTiO3 sample, the MoS2 crystals are perfectly sharp and triangular (Figure 2). Therefore, the dendritic growth can be safely attributed to the substrate effect of SrTiO3(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. The
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$_2$ structures, as indicated by the red arrows. A close-up SEM image of these structures is shown in Figure 5d. The monolayer MoS$_2$ 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$_3$(001). The interfacial crystallographic relationship can be described as “(0001)$_{\text{MoS}_2}$∥(001)$_{\text{SrTiO}_3}$, [210]$_{\text{MoS}_2}$∥[110]$_{\text{SrTiO}_3}$.”

Again, in these orientations, one edge of the triangular MoS$_2$ crystal aligns with the ⟨110⟩ directions on SrTiO$_3$(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$_2$ structures have many of their edges aligned with the ⟨110⟩ directions on SrTiO$_3$(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$_2$ on different substrates (Figures 6 and 7). The Raman and PL spectra are known to be influenced by the layer thickness, lattice strain, doping level, and lattice defects of MoS$_2$. These depend on the substrate surface (Figure 6a,b), the MoS$_2$ crystal morphology (Figure 6c,d), and the MoS$_2$ layer number (Figure 6e,f).

Detailed information can be extracted through Lorentzian fitting for the PL spectra of monolayer MoS$_2$ on different substrates (Figure 7). In addition to the samples mentioned previously, we also studied MoS$_2$ monolayer crystals transferred onto a SrTiO$_3$ 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$_2$−SrTiO$_3$ interface adhesion. Therefore, its doping level can be considered nearly the same as that in MoS$_2$ directly grown on SrTiO$_3$.

Parts a, c, and e of Figure 6 show the two characteristic Raman modes of MoS$_2$, E$_{2g}^1$ (382.0−384.3 cm$^{-1}$) and A$_{1g}$ (403.0−407.5 cm$^{-1}$). The E$_{2g}^1$ and A$_{1g}$ modes are...
preferentially excited for terrace and edge terminations, respectively. Therefore, the relative integrated intensities of $A_{1g}$ and $E_{2g}$ can provide information on the texture of MoS$_2$. Regardless of the substrate, all of the MoS$_2$ monolayers predominant with terrace sites exhibit similar integrated intensity ratios of $A_{1g}/E_{2g} \sim 1.05$, whereas the few-layer MoS$_2$ terminated more by edges shows an increased ratio of $A_{1g}/E_{2g} \sim 1.82$ (Figure 6a,c,e), conforming well to those reported previously. Also, the frequency difference between the $A_{1g}$ and $E_{2g}$ modes can be used to precisely determine the layer number of MoS$_2$. Our values are $\leq 19.5$ cm$^{-1}$ for all of the monolayer MoS$_2$ and $\geq 23.1$ cm$^{-1}$ for the few-layer MoS$_2$ (Figure 6a,c,e), in good agreement with the literature. An example of the few-layer structures is shown in Figure 5d. Figure 6f presents the PL of the monolayer and few-layer MoS$_2$ on the same substrate termination, SrTiO$_3$(001).

In addition to the direct transitions ($K \rightarrow K$) involving two split valence bands for the emissions of A and B excitons, few-layer MoS$_2$ shows an additional peak (I) originating from the indirect transition ($\Lambda \rightarrow \Gamma$). Compared to the monolayer MoS$_2$, the few-layer MoS$_2$ 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$_2$ develops via two processes. The first is epitaxial growth associated with the lattice mismatch between MoS$_2$ and the substrate. The second is fast cooling where the strain develops due to different thermal expansion coefficients (TECs) of MoS$_2$ and the substrate. The TEC of the as-prepared 2H-phase MoS$_2$ ($\alpha_{MoS_2} = 1.9 \times 10^{-6}$ K$^{-1}$ and $\alpha_{MoS_2c} = 8.65 \times 10^{-6}$ K$^{-1}$, 293–1073 K) is approximately an
order of magnitude larger than that of SiO$_2$ (typical value $\alpha_{\text{SiO}_2} = 5.6 \times 10^{-7}$ K$^{-1}$),\textsuperscript{61} while it is about an order of magnitude smaller than that of SrTiO$_3$ ($\alpha_{\text{SrTiO}_3} = 3.23 \times 10^{-5}$ K$^{-1}$, 300–1800 K).\textsuperscript{62} As a result, in the fast-cooling stage following MoS$_2$ growth, tensile strain develops in the SiO$_2$-supported MoS$_2$, whereas compressive strain is introduced in MoS$_2$ on SrTiO$_3$.\textsuperscript{59} The tensile and compressive strains respectively lead to red and blue shifts of the E$_{2g}^1$ and A$_1g$ Raman peaks and the A-exciton PL peak, relative to the transferred sample (Figure 6a,b).\textsuperscript{47–52} However, these three peaks are all red-shifted for the monolayer MoS$_2$ crystals grown on SrTiO$_3$(110) and (001), which is attributed to epitaxial growth. As manifested in Figures 4 and 5, the MoS$_2$ monolayer crystals show a large lattice mismatch with the SrTiO$_3$(110) and (001) terminations, leading to tensile strain. To estimate the growth-induced tensile strains in the MoS$_2$ monolayers grown on SrTiO$_3$(110) and (001), we use their peak shifts of the E$_{2g}^1$ Raman mode with respect to that on SrTiO$_3$(111).\textsuperscript{63} As stated in section 3.1, the small difference of $<0.2\%$ in the lattice parameters between MoS$_2$ and SrTiO$_3$(111) should give rise to a compressive strain of $\sim0.18\%$ in the MoS$_2$ adlayer. Taking this into account, the growth-induced tensile strain is $\sim0.58\%$ on SrTiO$_3$(110), caused by the attempt of the MoS$_2$ crystal edges to align with both $\langle 110 \rangle$ and $\langle 1\bar{1}2 \rangle$ crystallographic directions. It is $\sim0.34\%$ on SrTiO$_3$(001), ascribed to the lattice mismatch along the two nonpseudotaxial edges of the monolayer MoS$_2$ crystal. Finally, the growth-induced strain can be considered negligible in the monolayer MoS$_2$ grown on SiO$_2$/Si because of the amorphous substrate surface, which leads to random orientations of the MoS$_2$ crystals in Figure 2. \textsuperscript{63}

Figure 6b also shows that the tensile strains in the monolayer MoS$_2$ supported on SrTiO$_3$(110) and (001) and SiO$_2$/Si substrates commonly lead to decreased PL intensities compared to the transferred sample.\textsuperscript{50} In particular, significant PL quenching is observed on SrTiO$_3$(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$_3$(111), the PL intensity is enhanced by $58\%$ with a slightly narrower peak width (decrease in the full-width at half-maximum $\Delta$FWHM = 7.05 meV) compared to the transferred sample because of compressive strain,\textsuperscript{49} which agrees with the Raman results.

Moreover, the crystal morphology also impacts the strain level in MoS$_2$. As shown in Figure 6c,d, the dendritic MoS$_2$ crystals on SrTiO$_3$(001) display small blue shifts of Raman peaks and the A-exciton PL peak relative to the compact triangular crystals. (Note that the E$_{2g}^1$ Raman mode corresponding to the in-plane Mo$-$S phonon is more sensitive to strain than the A$_{1g}$ mode corresponding to the out-of-plane Mo$-$S phonon.\textsuperscript{48–52}) 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$_2$ 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$^-$ peaks for A-exciton emission, the B peak for B-exciton emission, and localized states (LSs) correlated with the structural disorder of MoS$_2$ (Figure 7).\textsuperscript{55} The LS peaks indicate the defect level in the as-grown MoS$_2$ crystals: SrTiO$_3$(110) $>$ SrTiO$_3$(001) $>$ SrTiO$_3$(111). This depends on the degree of lattice mismatch between MoS$_2$ and the SrTiO$_3$ 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 MoS2 on all substrates. The intensity ratio of exciton-to-trion peaks (A/A−) can be used to indicate the doping level.64 The larger A/A− ratio on the SiO2/Si substrate proves that the charge impurities induce heavier n-doping into the supported MoS2 than the Nb in SrTiO3 substrates. Nonetheless, the doping level of MoS2 on all SrTiO3 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 MoS2 on different terminations of SrTiO3.

4. DISCUSSION

We have shown that on three different crystal terminations of SrTiO3, MoS2 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 MoS2 nucleus is free to rotate in the initial stage, it gets “locked” into the lowest-energy orientation,6 i.e., in the epitaxial configurations that we observed. Other bonding types, e.g., electrostatic attraction7 and chemical bonds,8 are less likely to exist between MoS2 and SrTiO3. This is because they are stronger than vdW bonding by orders of magnitude and would lock the MoS2 monolayers exclusively into certain orientations, e.g., as observed on Au(111).8 Gold, an electronegative metal, is a very different substrate from SrTiO3, an oxide ceramic, and can interact with MoS2 via a stronger bonding type. Nb doping (0.5 wt %), which makes SrTiO3 conductive, may also have played a role in its bonding with MoS2 monolayers, but we expect any effects to be minimal.

On SrTiO3(111), it is advantageous to align the ⟨2110⟩ directions of MoS2 with ⟨110⟩ on SrTiO3 with a favorable coincidence lattice registry. In previous studies of MoS2 grown on ceramic substrates, SiO2 does not induce epitaxy because it is amorphous9 c-plane sapphire, another 3-fold-symmetric substrate, reveals preferred orientations similar to those of MoS2 on SrTiO3(111) (0° and 60°).10 In these orientations, either interfacial electrostatic attraction (as a result of charge transfer)7 or greatly enhanced vdW bonding 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 MoS2 and sapphire. Their in-plane periodicities, 0.316 nm for MoS2 and 0.476 nm for sapphire, have a 2:3 ratio with a 0.4% difference.7 Therefore, we speculate that both SrTiO3(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 SrTiO3(111) is more strongly preferred, and a similar situation is found in the MoS2-on-Au(111) system. A single 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 “MoS2-on-hcp” and “MoS2-on-fcc” configurations,14 but the crystals turn out to exclusively orient in only one way.15 The termination of Au(111) alternates between hcp and fcc across a ridge of the herringbone structure, so that the MoS2 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).35 On the other hand, SrTiO3(111) shows a uniform termination with surface step heights always equivalent to the d11 lattice parameter.23,66 Hence, the 0° and 60° orientations of MoS2 are indeed distinct, possibly with a very small but noticeable energy difference like that on Au(111).

On SrTiO3(110), the strong tendency to maximize coincidence epitaxial directions (i.e., ⟨110⟩ and ⟨112⟩) competes with the equilibrium shape of the MoS2 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 MoS2 but must have been overcome by the reduction in the interfacial energy because of the improved bonding. Even on SrTiO3(001), where it is only possible to satisfy one direction of good coincidence epitaxy along ⟨110⟩, the MoS2 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 MoS2. It cannot be the bulk termination of SrTiO3 because the surface bonds tend to rearrange themselves to stabilize the surface polarity. However, we do know that there are certain ways in which SrTiO3 reconstructs. For example, SrTiO3(111)-(4×4) is one of the lowest-energy reconstructions of the (111) termination, which forms most easily in partial pressures of oxygen.23,34 If MoS2 grows on SrTiO3(111)-(4×4), the substrate periodicity (i.e., the unit length along ⟨110⟩) becomes 4 times that of the bulk. The coincidence epitaxy then turns into a 7:1 ratio, which is an attractive epitaxial relationship. On SrTiO3(110), (1×4), (3×4), (6×4), and (6×4) reconstructions have been reported previously,23,67 which make the periodicity along ⟨110⟩ 4 times that in the bulk as well. Similarly on SrTiO3(001), there is a ⟨4×4⟩ reconstruction that does the same;68 there is also a ⟨4×4⟩ reconstruction, which makes the periodicity along ⟨110⟩ 2√2 times that of the bulk, and this turns the coincidence epitaxy into a 5:1 ratio with a mismatch of 1.2%.58,69

Based on the above, our understanding of what drives the epitaxy is the interfacial lattice commensuration between ⟨2110⟩ (i.e., the S edge directions) of MoS2 and ⟨110⟩ on SrTiO3. We stress the strength of this vdW interaction, which can powerfully control the growth of MoS2 crystals. Developing a deeper understanding of MoS2 epitaxy is an important step toward integrating MoS2 in future novel electronic devices. This is because when MoS2 is grown in perfect lattice registry with its crystalline substrate, grain boundaries are eliminated. This allows large-area monolayers of MoS2 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 MoS2 on a ceramic substrate, and a high-resolution image like Figure 3e is rare. If such images could be obtained on all terminations of SrTiO3 substrates, they would provide useful information about the strain or lattice distortion in monolayer MoS2. Many good atomic images of MoS2 monolayers on Au(111) have been reported,15,37,55,56,59 but it was difficult for the same group of researchers to obtain high-resolution images of MoS2 on
TiO₂. It is not yet clear to us why it is a lot harder to image MoS₂ 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 MoS₂ crystals are strongly influenced by substrate interactions with SrTiO₃. 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 if 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 MoS₂ (to maintain its equilateral triangular shape) and the interfacial energy associated with the MoS₂-substrate interactions. The results also confirm that the vdW interaction is sufficiently strong to regulate epitaxy in a powerful way. The strain levels in MoS₂ are found to be adjusted by the different epitaxial relationships with the substrate. This allows us a more rigorous control in the synthesis of large-scale uniform MoS₂ layers for optimal electronic properties and enables the manipulation of inbuilt strains to fine-tune the band gap, which improve the applicability of monolayer MoS₂ in next-generation nanoelectronic devices.

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Notes

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Acknowledgments

The authors thank Chris Spencer (JEOL UK) for technical support and Dr. Krishnan Murugappan and Jiawei Jiang for taking TEM images on the Zeiss Merlin. We are also grateful to the EPSRC for funding (Grant EP/K032518/1). J.H.W. is supported by the Royal Society and the European Research Council (Grant 725258 LATO CoG 2016).

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