Thermal Degradation of Monolayer MoS₂ on SrTiO₃ Supports

Peiyu Chen^{†}, Wenshuo Xu[†], Yakun Gao, Philip Holdway, Jamie H. Warner, Martin R. Castell^{*}*

Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, United Kingdom

Abstract

Monolayer MoS₂ is a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. We report the results of a study on thermal degradation of MoS₂ monolayers supported on SrTiO₃ substrates in ultra-high vacuum (UHV). Our studies were carried out on the (111), (110), and (001) terminations of SrTiO₃ substrates but MoS₂ was found to degrade on all these surfaces in a similar way. By using scanning tunneling microscopy, we show that MoS₂ monolayer crystals maintain their structure up to 700 °C in UHV, at which point triangular etch trenches appear along the $\langle 2\bar{1}\bar{1}0 \rangle$ lattice directions (i.e., sulfur-terminated edge directions) of the MoS₂ crystals. The trenches are due to the preferential loss of sulfur, allowing molybdenum to be oxidized by oxygen originating from the SrTiO₃ substrate. The A-exciton photoluminescence (PL) peak and the E_{2g}¹ and A_{1g} Raman signals are significantly reduced in intensity following treatment at this temperature. The crystals continue to degrade at higher annealing temperatures in UHV until they transform into MoO_x (x = 2–3) particles at 900 °C, and the optical properties characteristic of MoS₂ are lost entirely in PL and Raman spectra. The initial sulfur loss and the formation of MoO_x are confirmed by X-ray photoelectron spectroscopy. The macroscopic triangular shapes of the MoS₂ crystals are retained until the residual particles evaporate at above 1000 °C. The optical properties of the 700 °C- and 800 °C-UHV annealed samples can be partially recovered upon sulfur annealing. This work establishes a pathway of the thermal degradation of

SrTiO₃-supported monolayer MoS₂ in vacuum, from smooth MoS₂ crystals to crystals with sulfur vacancies (etch trenches), followed by MoO₂ and finally MoO₃ particles. We also demonstrate how sulfur annealing can be used to heal the defects.

1. Introduction

Many transistors, circuits, and sensors require electronic materials that can operate at high temperatures.¹ Wide-bandgap semiconductors have been found to function effectively at elevated temperatures,² and increasing attention is being directed towards the use of monolayer molybdenum disulfide (MoS₂) in high-temperature applications.¹ Atomically thin MoS₂ has a direct bandgap of 1.8–1.9 eV.³ The intense interest in this material is due to its relatively high charge mobility,⁴ optical transparency, and extreme mechanical flexibility.⁵ It is therefore important to understand the effects of high-temperature processing on the structure and optical properties of monolayer MoS₂.

Previous studies in this area were mostly carried out as part of the synthesis of MoS₂ or immediately after its growth. They were used to enhance the crystallinity,^{6–10} optical properties,^{6–8,10} or electronic properties of the MoS₂ crystals.^{11,12} A few studies also explored the thermally-accelerated oxidation of MoS₂ into MoO₃ under ambient conditions, starting from 100 °C until complete transformation into MoO₃ at up to 550 °C.^{13–18} In these studies, the MoS₂ samples were either monolayer (ML) / few-layered (FL) (supported on SiO₂) or powdered. In the absence of oxygen, MoS₂ is much more stable: the atomic structure of monolayer MoS₂ crystals on Au(111) was seen to be unperturbed up to 630 °C.¹⁹ On FL MoS₂ crystals on oxide / nitride substrates, thermal decomposition did not occur until 850 °C in the absence of oxygen.⁶ In a bulk MoS₂ crystal, S is not completely removed until above 1203 °C in vacuum.²⁰ Atomic force microscopy (AFM) was used to determine that the oxidation of MoS₂

monolayers started with triangular pits in air.^{16,17} Nevertheless, to date there has not been a systematic report of the morphology of thermally-degraded MoS₂ monolayers in vacuum. Additionally, any methods to recover the properties of degraded MoS₂ are also of significant interest.¹⁰

In this paper we examine the thermal decomposition in vacuum of monolayer MoS₂ supported on single crystal substrates of strontium titanate (SrTiO₃) terminated with (111), (110), and (001) surfaces. In contrast to most of the studies mentioned above, we exclusively study monolayer MoS₂ islands, which are of greater technological interest compared with thicker MoS₂ crystals. In vacuum, we exclude the effects of oxygen in the atmosphere, so that all changes upon annealing can be attributed to the MoS₂ itself and its oxide substrate. This set-up allows us to assess how MoS₂ crystals would behave in devices which require high-temperature processing. We used chemical vapor deposition (CVD) to grow MoS₂ crystals, which is a scalable method that produces large-area transition metal dichalcogenides (TMDCs) of high quality. Such a growth technique is ideal for high-turnover industrial manufacturing of 2D materials.

In our study, the step-by-step changes in MoS₂ monolayers were tracked from its initial degradation at 700 °C to the complete evaporation of MoO_x ($x = 2-3$) residues at temperatures above 1000 °C. The changes were monitored by optical microscopy (OM), scanning electron microscopy (SEM), scanning tunneling microscopy (STM), X-ray photoemission spectroscopy (XPS), photoluminescence (PL), and Raman spectroscopy. Although the optical properties of MoS₂ crystals deteriorated to a large extent after annealing in vacuum, it was found that they can be partially recovered via a follow-up annealing treatment in a sulfur atmosphere. This raises the possibility of healing any non-substantial defects via a sulfur annealing step during the fabrication of MoS₂-based devices.

2. Experimental Methods

2.1 SrTiO₃ substrate preparation. SrTiO₃ single crystals ($7 \times 2 \times 0.5$ mm³) doped with niobium (Nb) at 0.5% by weight were supplied by PI-KEM, U.K, with epi-polished (111), (110), and (001) surfaces. SrTiO₃ is an insulator with a band gap of 3.2 eV at 25 °C.²¹ The Nb dopant was included to generate sufficient electrical conductivity at room temperature for STM imaging. The substrate surfaces were studied in an ultra-high vacuum (UHV)-STM, which is a custom-built JEOL JSTM 4500s model (base pressure 10^{-8} Pa). SrTiO₃ surfaces were prepared to terminate with previously well-characterized reconstructions, requiring different Ar⁺ ion sputtering conditions, annealing temperatures and durations, and O₂ partial pressures.^{22–24} The observation of surface reconstructions ensure that crystalline, atomically flat, and contaminant-free terminations have been achieved.

2.2 Growth of monolayer MoS₂. The atmospheric pressure CVD method was used to grow monolayer MoS₂ crystals on the reconstructed SrTiO₃ substrates, using the precursors molybdenum trioxide (MoO₃, powder, $\geq 99.5\%$, Sigma-Aldrich) and sulfur (S, powder, $\geq 99.5\%$, Sigma-Aldrich). The CVD setup is shown in Figure 1d. SrTiO₃ substrates were placed at a fixed position downstream for consistent results. The MoO₃ (20 mg) and S (450 mg) powders were loaded in a set of double-walled quartz tubes with different diameters so that the reaction region was strictly defined around the substrate surface, and their temperatures were independently controlled by two separate furnaces. After oxygen in the system was driven off by 500 sccm argon (Ar) flow for 30 min, S vapor at 180 °C was pre-introduced by 150 sccm Ar for 15 min. This created a sulfur-rich environment, which was maintained by increasing the temperature of S at a rate of 0.7 °C s⁻¹ during the synthesis. The substrates were heated up to 210 °C at the same time to avoid S condensation. The MoO₃ and S precursors and the substrate were then heated to 300, 180, and 800 °C, respectively. There were three stages in the

MoS₂ synthesis – nucleation (20 min with 150 sccm Ar), main growth (25 min with 50 sccm Ar), and atom migration (15 min with 5 sccm Ar), completed by a rapid cooling process.

2.3 Thermal annealing of monolayer MoS₂. Following growth, the MoS₂ samples were introduced into the UHV-STM chamber for annealing. The samples were heated by resistively passing a direct current through the substrates (Figure 1c). The temperature was measured through a viewpoint with an optical pyrometer. The temperature was ramped up and down at a rate of 2.5–5.5 °C min⁻¹, and each anneal lasted 0.5–5.5 hrs.

2.4 Characterization of monolayer MoS₂. Optical microscope images of the MoS₂ crystals were taken using an Axioskop 2 MAT by Carl Zeiss Co., Ltd. SEM was performed using a Zeiss Merlin and a Hitachi-4300, both at an accelerating voltage of 3 kV. STM images were processed by Smart Align,^{25,26} Gwyddion, and WSxM.²⁷ PL and Raman spectroscopy 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 5 s for PL and 35 s for Raman. XPS measurements were performed on a Thermo Scientific K-Alpha XPS instrument equipped with a microfocused monochromated Al X-ray source (1486.6 eV). The source was operated at 12 keV and a 400 μm spot size was used. The analyzer operated at a constant analyzer energy (CAE) of 50 eV. Charge neutralization was applied using a combined low energy / ion flood source.

2.5 Sulfur annealing of defective monolayer MoS₂. The defective vacuum-annealed MoS₂ samples and sulfur powder were loaded in two quartz tubes (2-inch diameter) at the centers of two furnaces, so that their temperatures could be controlled independently. After the system was flushed with 500 sccm Ar flow for 30 min, MoS₂ and S were heated to 300 °C and 200 °C. The S vapor was carried by 500 sccm Ar flow downstream to the MoS₂ sample. The S atmosphere was maintained for

1 h, after which both the MoS₂ samples and S were cooled down.

3. Results

Figure 1a shows a cubic unit cell of the substrate material SrTiO₃ with a Sr²⁺ ion (green) in the middle, Ti⁴⁺ ions (blue) at the corners, and the O²⁻ ions (red) along the cube edges. Previously, we reported the distinct epitaxial behavior of MoS₂ crystals on the (111), (110), and (001) substrate terminations of SrTiO₃,²⁸ but here no distinct differences were noticed between their thermal stability on the different SrTiO₃ terminations. The terminations used in each case are specified in the figure captions in the remaining images of this paper. Figure 1b is the top view of a monolayer MoS₂ crystal. Figure 1c shows the UHV sample holder. This setup is used for both the high-temperature substrate preparation and the thermal annealing of MoS₂ crystals in UHV. Figure 1d shows the CVD system used to synthesize MoS₂. The sulfur annealing of defective MoS₂ crystals was carried out using the same setup without MoO₃ in the inner quartz tube.

Figure 1. Crystal structures of MoS₂ and SrTiO₃, the UHV annealing setup, and the CVD system. (a) Cubit unit cell of SrTiO₃. (b) Top view of a monolayer triangular crystal of MoS₂. (c) UHV sample holder for direct resistive heating, for both SrTiO₃ substrate preparation and the thermal annealing of MoS₂ crystals on SrTiO₃. (d) Schematic diagram of the CVD setup for the synthesis of MoS₂ crystals. The Si chip serves as a substrate holder.

3.1 SEM and STM experiments

MoS₂ crystals on a SrTiO₃(111) substrate were annealed in UHV for 2 hrs with a temperature gradient across the sample. The temperature was 700 °C at the cooler end and 800 °C at the hotter end. SEM images were taken after the sample was cooled down (Figure 2a.i, ii). The crystals at the cool end (Figure 2a.i) are clear and black; they look no different from the as-grown crystals. Towards the hotter end, the crystals appear fainter (Figure 2a.ii). Figure 2a.ii was acquired soon after Figure 2a.i with the same brightness and contrast settings, which means that the contrast between the MoS₂ crystals and the substrate has changed. Although the more detailed internal structure cannot be resolved by SEM, we expect that the MoS₂ crystals have degraded through desulfuration. Figure 2b.i and b.ii are another pair of images demonstrating the effect of a UHV anneal at 1150 °C for 3 hrs. This treatment further lowers the visibility of the crystals, where they have clearly decomposed with some residues remaining in triangular shapes. Similar survivor traces have been observed after a lift-off process of WS₂.²⁹

Figure 2. SEM images of MoS₂ crystals on SrTiO₃ substrates: after UHV annealing at (a.i) 700 °C and (a.ii) 800 °C for 2 hrs on SrTiO₃(111), and (b.i) before and (b.ii) after UHV annealing at 1150 °C for 3 hrs on SrTiO₃(001). The contrast of (b.ii) is enhanced to show the residues.

STM studies can elucidate the structural transformations at higher resolution than SEM. Under 700 °C, the samples are only degassed, i.e., adsorbates and contaminants are removed. Not much difference is seen after these gentle UHV anneals in STM. The MoS₂ layer is uniform and conforms well to the substrate terraces with a thickness of 0.63 ± 0.06 nm (Figure 3a), which is typical of a monolayer.^{1,30} The atomic model of MoS₂ overlaid shows the orientation of the triangular crystal, and it also applies to the other panels in Figure 3. The SrTiO₃(111) substrate was processed to generate a (4×4) reconstruction in UHV before the CVD growth of MoS₂,^{22,31} although the reconstruction

would not have survived in an ambient environment, the terraces still remain. Figure 3a.i and a.ii are two high-magnification images illustrating the typical morphologies outside of and on top of the MoS₂ monolayer, respectively. There are clusters of small triangles aligned on the substrate with a periodicity of 2.20 ± 0.05 nm (Figure 3a.i), and these islands are seen to raise the height of the MoS₂ monolayer (Figure 3a.ii). These clusters are believed to be due to an intermediate step during the high-temperature formation of the SrTiO₃(111)-(4 × 4) reconstruction and will not be discussed further.

After being UHV annealed to 700 °C, the MoS₂ crystals start to degrade and triangular etch trenches appear, as shown in Figure 3b. The trenches are typically measured to be less than 0.1 nm deep. The etch lines run in three directions along the $\langle 2\bar{1}10 \rangle$ -type crystallographic directions of MoS₂, which are the sulfur-terminated edge directions of the triangular MoS₂ crystal (c.f. the atomic model of MoS₂ in Figure 3a). The high-magnification image in Figure 3b.ii shows that there are etch dots as well as etch lines. Figure 3b.i is an area similar to that in Figure 3a.ii, but annealed to 700 °C. It has a complex morphology in which the clusters protruding from the substrate are still visible and the triangular etch trenches coexist with them. The etch dots and lines are likely to be due to the preferential evaporation of sulfur from the MoS₂ monolayers.

At UHV annealing temperatures above 800 °C, the MoS₂ crystals decompose into particles. Figure 3c shows a MoS₂ monolayer (on top of SrTiO₃(001)-c(4 × 2) substrate terraces) that has partially degraded into particles.^{24,32,33} When the annealing temperature exceeds 900 °C, the MoS₂ crystals degrade entirely and only particle residues are observed in place of the original triangular crystals (Figure 3d). Below the particles is the reconstructed SrTiO₃(110)-(4 × 1) substrate.^{23,34,35} The residual particles are typically 2–5 nm high and 5–10 nm in diameter.

Figure 3. STM images of various stages of the thermal degradation of monolayer MoS₂ crystals. (a) The MoS₂ monolayer with a smooth surface up to 600 °C, conforming well to the substrate terraces ($V_s = 2.0$ V, $I_t =$

0.05 nA). The monolayer has a typical thickness of 0.63 ± 0.06 nm. The MoS₂ atomic model overlaid illustrates the lattice orientation, and it also applies to the other panels. (a.i, a.ii) Zoomed-in images of the morphologies of the SrTiO₃(111) substrate and the MoS₂ monolayer, respectively (a.i: $V_s = 2.0$ V, $I_t = 0.10$ nA; a.ii: $V_s = 2.0$ V, $I_t = 0.03$ nA). (b) Triangular etch trenches on the MoS₂ monolayer on SrTiO₃(111) formed during a UHV anneal at 700 °C ($V_s = 2.0$ V, $I_t = 0.11$ nA). (b.ii) Details of the etch trenches ($V_s = 2.0$ V, $I_t = 0.11$ nA). (b.i) An area similar to that in (a.ii), for comparison, except for a higher annealing temperature. A line profile across a trench shows a dip of 0.09 nm ($V_s = 2.0$ V, $I_t = 0.03$ nA). (c) Degradation of the MoS₂ monolayer into particles while partially retaining the film upon UHV anneals at 800 °C. The substrate is SrTiO₃(001)-*c*(4 × 2) with straight terraces ($V_s = 2.0$ V, $I_t = 0.05$ nA). The inset is a high-magnification image ($V_s = 2.0$ V, $I_t = 0.05$ nA). (d) Residual particles left at 900 °C, which remain in the original triangular shape of the MoS₂ crystal, on a SrTiO₃(110)-(4 × 1) substrate ($V_s = 2.0$ V, $I_t = 0.05$ nA). The inset shows the details of the residues ($V_s = 1.5$ V, $I_t = 0.20$ nA). All images are single scans except (a.ii) and (b.i), which are averaged over 16 and 22 frames by Smart Align,²⁶ respectively.

3.2 XPS analysis

The pristine and thermally-decomposed products of MoS₂ crystals were investigated by XPS. Figure 4 shows the core level spectra from the Mo 3*d* and S 2*p* regions of the samples. In each column from top to bottom, the spectra compare the compositions of differently treated samples, as labelled in the top-right corner of each figure: as-grown FL MoS₂ crystals, as-grown ML MoS₂ crystals, and monolayer MoS₂ crystals UHV annealed to 700 °C, 800 °C, 900 °C, and 1000 °C.

In the molybdenum spectra (Figure 4a), it can be seen that Mo exists in both the Mo⁶⁺ and Mo⁴⁺ ionization states. Both these ionization states have a doublet peak in their 3*d* spectra: 235.2 eV and

232.3 eV correspond to $\text{Mo}^{6+} 3d_{3/2}$ and $\text{Mo}^{6+} 3d_{5/2}$, typical of MoO_3 ;³⁶ 232.1 eV and 229.2 eV correspond to $\text{Mo}^{4+} 3d_{3/2}$ and $\text{Mo}^{4+} 3d_{5/2}$, typical of MoS_2 and MoO_2 .^{37–40} It should be noted that the $\text{Mo}^{6+} 3d_{5/2}$ and $\text{Mo}^{4+} 3d_{3/2}$ peaks are almost coincident, giving rise to the characteristic three-peak shape of Mo^{6+} and Mo^{4+} .⁴⁰ Along with the Mo peaks, another peak observed at 226.3 eV belongs to S 2s.³⁸ In the sulfur spectra (Figure 4b), the S 2p peaks are observed at 163.2 eV and 162.0 eV, representing S $2p_{1/2}$ and S $2p_{3/2}$ orbital splitting.⁴¹

Interpreting the XPS observations, we can infer that the as-grown samples (marked as ‘FL’ and ‘ML’) are MoS_2 crystals mixed with a small amount of unreacted MoO_3 precursor and the intermediate product MoO_2 .⁴² Sulfur completely leaves the structure at a temperature between 700 °C and 800 °C, when the MoS_2 is fully oxidized. At increasingly higher temperatures, the amount of Mo^{6+} increases because more MoO_3 is formed as MoS_2 is oxidized by the SrTiO_3 substrate. Afterwards, the molybdenum oxides all evaporate at $T > 1000$ °C.

Figure 4. XPS spectra of the (a) Mo 3d and (b) S 2p core-level peaks of the MoS_2 crystals grown on SrTiO_3 substrates. From top to bottom: as-grown few-layer (FL) MoS_2 crystals, as-grown monolayer (ML) MoS_2 crystals, and monolayer MoS_2 crystals UHV annealed to 700 °C, 800 °C, 900 °C, and 1000 °C.

The relative amounts of MoO_3 , MoO_2 , and MoS_2 in various samples are estimated from the areas of the Gaussian curves of Mo^{6+} , Mo^{4+} , and S^{2-} and by using the relative sensitivity values of the different elements reported in the literature.⁴³ The results are plotted in Figure 5, with the errors estimated from the uncertainties during peak fitting. The FL, ML, and 700 °C-UHV annealed samples have similar amounts of MoO_3 , MoO_2 , and MoS_2 , where the oxides are the unreacted / incompletely reacted precursor.⁴² The FL sample has slightly more MoO_3 than the ML sample, because it had a larger amount of precursors deposited. At 700 °C there is a slightly increased amount of MoO_2 and a virtually unchanged amount of MoO_3 when compared with the ML pristine sample. This means that at 700 °C a small but noticeable amount of MoS_2 has been converted into MoO_2 (but not MoO_3 yet). At 800 °C the % MoS_2 value rapidly decreases to a negligibly small percentage, and similar amounts of MoO_2 and MoO_3 are present. At 900 °C, over 75% of the residue is MoO_3 . Therefore the compositional change is likely to follow the route $\text{MoS}_2 \rightarrow \text{MoO}_2 \rightarrow \text{MoO}_3$. At $T \geq 1000$ °C, the atomic percentages of all substances are zero as the molybdenum oxides have evaporated.

Figure 5. Atomic percentage of substances in the as-grown MoS_2 crystals (few-layer and monolayer) and MoS_2 monolayers UHV annealed to 700 °C, 800 °C, 900 °C, and 1000 °C.

3.3 PL and Raman spectroscopy

In order to gain further insight into the thermal degradation of MoS₂ crystals, PL and Raman spectroscopy were carried out (Figure 6). Upon laser excitation, the as-grown sample exhibits a strong PL peak at the photon energy of 1.88 eV (black curve in Figure 6a), characteristic of monolayer MoS₂.^{3,44-47} In the Raman spectrum (black curve in Figure 6b) there are two peaks at 382.2 cm⁻¹ and 403.0 cm⁻¹, corresponding to the in-plane E_{2g}¹ and out-of-plane A_{1g} vibrational modes of MoS₂, respectively.^{48,49} The frequency difference of ~20 cm⁻¹ between the peaks is the signature of MoS₂ monolayers, while the difference for thicker and bulk MoS₂ is ~25 cm⁻¹.⁴⁷⁻⁵² UHV annealing at 700 °C results in significantly decreased intensities of the PL and Raman peaks (red curves in Figure 6), demonstrating the deteriorated crystallinity of the MoS₂ monolayers. When the UHV annealing temperature reaches 800 °C, no PL or Raman signals can be observed (green curves in Figure 6).

Both the PL and Raman peaks have shifted after the samples were UHV annealed at 700 °C. Before the peak shifts are discussed it should be mentioned that strains form in the MoS₂ crystals during the fast cooling process in the CVD reactor. This is due to the different thermal expansion coefficients (TEC) of MoS₂ and the SrTiO₃ substrate.⁵³ The TEC of the as-prepared 2H-phase MoS₂ ($\alpha_{\text{MoS}_2,a} = 1.9 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{\text{MoS}_2,c} = 8.65 \times 10^{-6} \text{ K}^{-1}$, 293–1073 K) is approximately one order of magnitude smaller than that of SrTiO₃ ($\alpha_{\text{SrTiO}_3} = 3.23 \times 10^{-5} \text{ K}^{-1}$, 300–1800 K).^{54,55} This difference introduces compressive strain in the MoS₂ layers on SrTiO₃. In addition, there are strains induced by the epitaxial relationship on different terminations of SrTiO₃ substrates, which are compressive on SrTiO₃(111) and tensile on SrTiO₃(001).²⁸ Overall, MoS₂ crystals on SrTiO₃(111) are in compression and those on SrTiO₃(001) are in tension.²⁸

The post-annealing PL peak position of MoS₂ on SrTiO₃(111) is shifted to a lower photon energy

(red shift), as shown in Figure 6a. This is because the compressive strain in the MoS₂ crystals is partially released: the TEC-induced strain is released by the low heating / cooling rates (2–5 °C min⁻¹) before and after the 700 °C UHV annealing, and the epitaxy-induced strain is released by the degradation of the MoS₂ crystal structure. The red shift could be additionally attributed to more localized states,¹⁰ which in turn are associated with structural defects.⁵⁶

After being UHV annealed at 700 °C, the Raman peaks of MoS₂ on SrTiO₃(001) are both shifted to higher wavenumbers (‘stiffening’ or blue shifts), accompanied by peak broadening. This is again due to a release of strain, though the strain was initially tensile in the case of a (001)-terminated SrTiO₃ substrate.

Figure 6. (a) PL spectra of monolayer MoS₂ crystals on SrTiO₃(111) and (b) Raman spectra of monolayer MoS₂ crystals on SrTiO₃(001): as-grown (black), UHV annealed to 700 °C (red), and UHV annealed to 800 °C (green).

3.4 Optical microscopy (OM)

UHV annealing up to 1000 °C does not appear to affect the MoS₂ crystal shapes when investigated using only OM. Above 1000 °C the crystals evaporate and can no longer be seen by OM. Figure 7 shows some MoS₂ crystals on SrTiO₃(110) imaged by OM (a) before and (b) after UHV annealing at

1000 °C for 5.5 hrs. As previously shown, substantial changes have occurred in the internal structure: the triangles in Figure 7a are pristine MoS₂ crystals while those in Figure 7b are residual MoO₃ nanoparticles retaining the original triangular footprint. However, OM does not show any apparent differences, and care should therefore be taken when using OM on its own to describe the quality of MoS₂ crystals.

Figure 7. Optical microscope images of MoS₂ crystals on SrTiO₃(110) (a) before and (b) after UHV annealing at 1000 °C for 5.5 hrs.

3.5 Sulfur annealing

To study whether we could heal the defects formed in the MoS₂ monolayers, we created a sulfur atmosphere in the CVD reactor at an elevated temperature and transported the sulfur vapor to the MoS₂ surface by argon flow. As indicated by SEM, the 700 °C-UHV annealed MoS₂ crystals look similar before (Figure 2a.i) and after (Figure 8a) sulfur annealing. On the other hand, the 800 °C-UHV annealed crystals largely recovered their morphology (Figure 8b): they become clear and black, with enhanced contrast when compared with the faint triangles in Figure 2a.ii. This indicates partial recovery of the structural degradation. The crystals look similar to the as-grown crystals, though a few more holes are observed in the larger crystals (indicated by red arrows).

Figure 8. SEM images of (a) 700 °C- and (b) 800 °C-UHV annealed MoS₂ crystals on SrTiO₃(111) substrates after sulfur annealing.

The optical properties of the sulfur-annealed samples have also partially recovered: Figure 9a shows that the PL intensity of the 700 °C-UHV annealed MoS₂ crystal is enhanced and the peak position is blue-shifted back to a higher photon energy, close to that of the newly grown MoS₂ crystals. The Raman signals are also largely restored in terms of the peak intensities and positions (Figure 9c). The peak position restoration is due to the epitaxy-induced strains being re-introduced as the MoS₂ crystallinity is improved. The strains are compressive on SrTiO₃(111) and tensile on SrTiO₃(001),²⁸ leading to the blue shift of the PL peak in Figure 9a and the red shifts of the Raman peaks in Figure 9c.

On the other hand, after sulfur treatment of the 800 °C-UHV annealed MoS₂ crystals, the recovery of the PL and Raman signals are weak (Figure 9b,d). Also, the frequency difference of 21.4 cm⁻¹ between them indicates that the healed MoS₂ is a mixture of ML and FL crystals.⁴⁸ Note that the presence of FL MoS₂ crystals is not obvious from the PL peak position at 1.87 eV (Figure 9b), which corresponds to direct excitonic transitions from ML MoS₂ only.⁴⁶ This is because the PL signal strength of FL MoS₂ is negligible compared with that of ML MoS₂.³

Figure 9. (a,b) PL and (c,d) Raman spectra of the sulfur-annealed MoS₂ crystals compared with those before (i.e., as-grown) and after the UHV annealing at (a,c) 700 °C and (b,d) 800 °C. (a,b) PL spectra are measured on MoS₂ crystals supported on SrTiO₃(111); (c,d) Raman spectra are measured on MoS₂ crystals supported on SrTiO₃(001).

4. Discussion

We now have a deeper understanding of the UHV degradation and healing mechanisms of SrTiO₃-supported monolayer MoS₂ crystals, as summarized in Table 1. The structural changes start at 700 °C, which is reflected by the compositional change of the sample at 700 °C compared with the pristine ML

sample in XPS, where slightly less MoS₂ is present (Figure 5). The desulfurization is not visible in SEM (Figure 2a.i) but the sulfur vacancies appear as etch dots and lines in STM images (Figure 3b). The structural defects are also observed in the decreased PL and Raman intensities (Figure 6). For comparison, previous studies show that when MoS₂ is etched in air at lower temperatures of 300–340 °C,^{16,17} triangular surface pits rather than etch lines are the first sign of degradation, suggesting the oxidation of Mo into MoO₃ and the removal of S in a volatile state.^{15,18}

After the 800 °C UHV anneal, XPS results (Figures 4 and 5) demonstrate that no sulfur remains and MoO₂ and MoO₃ are formed as the oxidation products of the remaining Mo. The structural change is visualized via the deteriorated contrast in the SEM image (Figure 2a.ii). No PL and Raman signals of MoS₂ are observed any more (Figure 6). The particles in the STM images (Figure 3c) are therefore MoO_x ($x = 2-3$) particles. At 900 °C, further oxidation occurs, and a larger proportion of MoO₃ (> 75%) is detected by XPS (Figure 5).

In the thermally-assisted oxidation of monolayer MoS₂ crystals in air, it has been previously reported that sulfur escapes as SO₂,^{15,18} leaving oxidized Mo on the surface.^{13–18} The thermal degradation of MoS₂ in UHV is likely to follow a different route from that in an O₂-rich environment. We postulate that at 700 °C, the thermal energy breaks the Mo-S covalent bonds and releases the S atoms into the vacuum. This bond-breaking process requires a higher activation temperature compared with the oxidation of S in an ambient environment.^{13–18} Upon higher-temperature UHV annealing (> 800 °C), the SrTiO₃ substrate can supply increasing amounts of oxygen, which oxidizes the remaining Mo, converting it into MoO₂ and then MoO₃.

The high temperatures applied to MoS₂ breaks the Mo-S covalent bonds, which are stronger than the van der Waals (vdW) interaction between the MoS₂ sheet and the substrate by orders of magnitude.

This explains the observation that the thermal degradation behavior of MoS₂ on different terminations of SrTiO₃ substrates is similar, as only their interfacial vdW interaction with the substrate differs.

Finally, the sulfur annealing process partially heals the MoS₂ crystals, as confirmed by SEM observations (Figure 8) and PL and Raman spectroscopy (Figure 9). This recovery is due to the sulfur vacancies in the MoS₂ crystals being restored in the hot sulfur atmosphere.¹⁰ However, the recovery is not full for the 700 °C- / 800 °C-treated samples, and the crystals that were UHV annealed at 900 °C or above could not be healed by sulfur annealing at all. This is because once any Mo has been oxidized, it can no longer be sulfurized under the sulfur annealing conditions, or specifically, at a substrate temperature of 300 °C. The reason for this is that the conversion of MoO₃ / MoO₂ into MoS₂ requires a higher reaction temperature of 650–800 °C, as in the CVD growth of MoS₂.^{10,42} Also MoO₃ / MoO₂ has to be in the gaseous phase for the sulfurization reaction to occur.^{10,42} Although there may be a low vapor pressure of MoO₃ / MoO₂ at 300 °C, the high Ar flow rate of 500 sccm would quickly remove any vaporized Mo oxides downstream in the furnace. Therefore, no sulfurization of the Mo oxides occurred during the sulfur annealing, and any recovered MoS₂ is due to the filling of sulfur vacancies only. In order for this process to be possible, the Mo atoms need to have largely remained in their original lattice positions of MoS₂ so that the sulfur can easily fill the vacancies. This is true for the crystals that were UHV annealed at 700 °C and 800 °C: the former only lost a small amount of sulfur (Figures 4 and 5) and remained as a film with some etch trenches (Figure 3b); the latter lost all sulfur (Figures 4 and 5) but survived partly as film (Figure 3c). The more film-structure that survived, the stronger the recovery of the optical properties (Figure 9). Also, after the 800 °C-UHV anneal, because the film has partially turned into granules, the recovered MoS₂ has some FL crystals mixed with it, as mentioned at the end of section 3.5. The partial recovery of the 700 °C- / 800 °C-UHV annealed

samples also tells us that in these samples there is a certain amount of MoS₂ that has lost S but has not been oxidized after UHV annealing. However, in the XPS calculations that produced Figure 5, any Mo⁴⁺ without S was attributed to MoO₂. The calculations are hence not perfect but remain a good estimate of the relative amounts of MoO₃, MoO₂, and MoS₂ given the XPS data available. A further issue is that a proportion of Mo that may be present in the metallic state in UHV will become oxidized during the ambient transfer to the XPS chamber.

Table 1. UHV Thermal Degradation and Sulfur Annealing Results of MoS₂ Crystals on SrTiO₃

Substrates.

Sample	UHV annealing time / hr	Morphology	Substances (excluding unreacted MoO ₃ / MoO ₂)	Recovery of optical properties upon sulfur annealing
FL	-	Smooth crystal	MoS ₂	-
ML	-	Smooth crystal	MoS ₂	-
700 °C	0.5–2.0	Crystal + etch trenches	MoS ₂ (mainly) + MoO ₂	Near full recovery
800 °C	0.5–2.0	Crystal + particles	MoO ₂ + MoO ₃ (similar amounts)	Weak recovery
900 °C	0.5–1.0	Particles	MoO ₂ + MoO ₃ (mainly)	No recovery
1000 °C	2.0–5.5	Particles / evaporated	-	No recovery

5. Conclusion

This study uncovers the thermal degradation behavior of monolayer MoS₂ in UHV due to sulfur loss, which begins at 700 °C. The sulfur vacancies can be filled by annealing the crystals in a hot sulfur atmosphere, and the optical properties of monolayer MoS₂ can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the SrTiO₃ substrates into MoO₂ and MoO₃. The sulfur annealing no longer takes effect when all the Mo has been oxidized, which happens at a temperature between 800 °C and 900 °C in UHV. The MoS₂ crystal shapes are stable upon

annealing until the residual MoO₃ particles evaporate at above 1000 °C. This infers that any triangular crystals that look intact under low-magnification OM and SEM may not mean pristine MoS₂ and OM should be used with care. We conclude that for retaining the properties of MoS₂ it is important to avoid desulfuration and its exposure to oxygen, including the use of oxide substrates. The sulfur vacancies can be restored in a vaporous sulfur environment while the oxidation cannot be reversed. This study provides helpful insights for expanding the high-temperature applications of monolayer MoS₂ crystals in electronics and sensors.

Author Information

Corresponding Authors

*Email: martin.castell@materials.ox.ac.uk (M.R.C.).

*Email: peiyu.chen@materials.ox.ac.uk (P.C.).

Author Contributions

[†]P.C. and W.X. contributed equally.

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors would like to thank Chris Spencer (JEOL UK) for technical support and Dr. Krishnan Murugappan and Jiawei Jiang for taking SEM images on the Zeiss Merlin. J.H.W. thanks the support of the Royal Society.

References

- (1) Jiang, C.; Rumyantsev, S. L.; Samnakay, R.; Shur, M. S.; Balandin, A. A. High-Temperature Performance of MoS₂ Thin-Film Transistors: Direct Current and Pulse Current-Voltage Characteristics. *J. Appl. Phys.* **2015**, *117*, 064301.
- (2) Neudeck, P. G.; Okojie, R. S.; Chen, L.-Y. High-Temperature Electronics—A Role for Wide Bandgap Semiconductors? *Proc. IEEE* **2002**, *90*, 1065–1076.
- (3) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105*, 136805.
- (4) Fivaz, R.; Mooser, E. Mobility of Charge Carriers in Semiconducting Layer Structures. *Phys. Rev.* **1967**, *163*, 743–755.
- (5) Lee, G.-H.; Yu, Y.-J.; Cui, X.; Petrone, N.; Lee, C.-H.; Choi, M. S.; Lee, D.-Y.; Lee, C.; Yoo, W. J.; Watanabe, K.; **et al.** Flexible and Transparent MoS₂ Field-Effect Transistors on Hexagonal Boron Nitride-Graphene Heterostructures. *ACS Nano* **2013**, *7*, 7931–7936.
- (6) Marx, M.; Nordmann, S.; Knoch, J.; Franzen, C.; Stampfer, C.; Andrzejewski, D.; Kümmell, T.; Bacher, G.; Heuken, M.; Kalisch, H.; **et al.** Large-Area MoS₂ Deposition via MOVPE. *J. Cryst. Growth* **2017**, *464*, 100–104.
- (7) Lamouchi, A.; Assaker, I. B.; Chtourou, R. Effect of Annealing Temperature on the Structural, Optical, and Electrical Properties of MoS₂ Electrodeposited onto Stainless Steel Mesh. *J. Mater. Sci.* **2017**, *52*, 4635–4646.
- (8) Barvat, A.; Prakash, N.; Satpati, B.; Singha, S. S.; Kumar, G.; Singh, D. K.; Dogra, A.; Khanna, S. P.; Singha, A.; Pal, P. Emerging Photoluminescence from Bilayer Large-Area 2D MoS₂ Films Grown by Pulsed Laser Deposition on Different Substrates. *J. Appl. Phys.* **2017**, *122*, 015304.
- (9) Kaindl, R.; Bayer, B. C.; Resel, R.; Müller, T.; Skakalova, V.; Habler, G.; Abart, R.; Cherevan, A. S.; Eder, D.; Blatter, M.; **et al.** Growth, Structure and Stability of Sputter-Deposited MoS₂ Thin Films. *Beilstein J. Nanotechnol.* **2017**, *8*, 1115–1126.
- (10) Xu, W.; Li, S.; Zhou, S.; Lee, J. K.; Wang, S.; Sarwat, S. G.; Wang, X.; Bhaskaran, H.; Pasta,

- M.; Warner, J. H. Large Dendritic Monolayer MoS₂ Grown by Atmospheric Pressure Chemical Vapor Deposition for Electrocatalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4630–4639.
- (11) Heo, S.; Hayakawa, R.; Wakayama, Y. Carrier Transport Properties of MoS₂ Field-Effect Transistors Produced by Multi-Step Chemical Vapor Deposition Method. *J. Appl. Phys.* **2017**, *121*, 024301.
 - (12) Ahn, J.-H.; Parkin, W. M.; Naylor, C. H.; Johnson, A. T. C.; Drndić, M. Ambient Effects on Electrical Characteristics of CVD-Grown Monolayer MoS₂ Field-Effect Transistors. *Sci. Rep.* **2017**, *7*, 4075.
 - (13) Budania, P.; Baine, P. T.; Montgomery, J. H.; McNeill, D. W.; Mitchell, S. J. N.; Modreanu, M.; Hurley, P. K. Effect of Post-Exfoliation Treatments on Mechanically Exfoliated MoS₂. *Mater. Res. Express* **2017**, *4*, 025022.
 - (14) Ponomarev, E. A.; Neumann-Spallart, M.; Hodes, G.; Lévy-Clément, C. Electrochemical Deposition of MoS₂ Thin Films by Reduction of Tetrathiomolybdate. *Thin Solid Films* **1996**, *280*, 86–89.
 - (15) Windom, B. C.; Sawyer, W. G.; Hahn, D. W. A Raman Spectroscopic Study of MoS₂ and MoO₃: Applications to Tribological Systems. *Tribol. Lett.* **2011**, *42*, 301–310.
 - (16) Wu, J.; Li, H.; Yin, Z.; Li, H.; Liu, J.; Cao, X.; Zhang, Q.; Zhang, H. Layer Thinning and Etching of Mechanically Exfoliated MoS₂ Nanosheets by Thermal Annealing in Air. *Small* **2013**, *9*, 3314–3319.
 - (17) Yamamoto, M.; Einstein, T. L.; Fuhrer, M. S.; Cullen, W. G. Anisotropic Etching of Atomically Thin MoS₂. *J. Phys. Chem. C* **2013**, *117*, 25643–25649.
 - (18) Bandaru, N.; Kumar, R. S.; Sneed, D.; Tschauner, O.; Baker, J.; Antonio, D.; Luo, S.-N.; Hartmann, T.; Zhao, Y.; Venkat, R. Effect of Pressure and Temperature on Structural Stability of MoS₂. *J. Phys. Chem. C* **2014**, *118*, 3230–3235.
 - (19) Grønborg, S. S.; Ulstrup, S.; Bianchi, M.; Dendzik, M.; Sanders, C. E.; Lauritsen, J. V.; Hofmann, P.; Miwa, J. A. Synthesis of Epitaxial Single-Layer MoS₂ on Au(111). *Langmuir* **2015**, *31*, 9700–9706.
 - (20) Liu, D.; Chen, X.; Li, D.; Wang, F.; Luo, X.; Yang, B. Simulation of MoS₂ Crystal Structure and the Experimental Study of Thermal Decomposition. *J. Mol. Struct.* **2010**, *980*, 66–71.
 - (21) Noland, J. A. Optical Absorption of Single-Crystal Strontium Titanate. *Phys. Rev.* **1954**, *94*, 724.
 - (22) Russell, B. C.; Castell, M. R. Surface of Sputtered and Annealed Polar SrTiO₃(111): TiO_x-Rich (n × n) Reconstructions. *J. Phys. Chem. C* **2008**, *112*, 6538–6545.
 - (23) Russell, B. C.; Castell, M. R. Reconstructions on the Polar SrTiO₃(110) Surface: Analysis Using STM, LEED, and AES. *Phys. Rev. B* **2008**, *77*, 245414.
 - (24) Castell, M. R. Scanning Tunneling Microscopy of Reconstructions on the SrTiO₃(001) Surface. *Surf. Sci.* **2002**, *505*, 1–13.

- (25) Jones, L.; Yang, H.; Pennycook, T. J.; Marshall, M. S. J.; Van Aert, S.; Browning, N. D.; Castell, M. R.; Nellist, P. D. Smart Align—A New Tool for Robust Non-Rigid Registration of Scanning Microscope Data. *Adv. Struct. Chem. Imaging* **2015**, *1*, 8.
- (26) Jones, L.; Wang, S.; Hu, X.; ur Rahman, S.; Castell, M. R. Maximising the Resolving Power of the Scanning Tunneling Microscope. *Adv. Struct. Chem. Imaging* **2018**, *4*, 7.
- (27) Horcas, I.; Fernández, R.; Gómez-Rodríguez, J. M.; Colchero, J.; Gómez-Herrero, J.; Baro, A. M. WSXM: A Software for Scanning Probe Microscopy and a Tool for Nanotechnology. *Rev. Sci. Instrum.* **2007**, *78*, 013705.
- (28) Chen, P.; Xu, W.; Gao, Y.; Warner, J. H.; Castell, M. R. Epitaxial Growth of Monolayer MoS₂ on SrTiO₃ Single Crystal Substrates. *ACS Appl. Nano Mater.* **2018**, *1*, 6976–6988.
- (29) Sheng, Y.; Xu, W.; Wang, X.; He, Z.; Rong, Y.; Warner, J. H. Mixed Multilayered Vertical Heterostructures Utilizing Strained Monolayer WS₂. *Nanoscale* **2016**, *8*, 2639–2647.
- (30) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- (31) Marks, L. D.; Chiaramonti, A. N.; ur Rahman, S.; Castell, M. R. Transition from Order to Configurational Disorder for Surface Reconstructions on SrTiO₃(111). *Phys. Rev. Lett.* **2015**, *114*, 226101.
- (32) Becerra-Toledo, A. E.; Marshall, M. S. J.; Castell, M. R.; Marks, L. D. $c(4 \times 2)$ and Related Structural Units on the SrTiO₃(001) Surface: Scanning Tunneling Microscopy, Density Functional Theory, and Atomic Structure. *J. Chem. Phys.* **2012**, *136*, 214701.
- (33) Erdman, N.; Warschkow, O.; Asta, M.; Poeppelmeier, K. R.; Ellis, D. E.; Marks, L. D. Surface Structures of SrTiO₃ (001): A TiO₂-Rich Reconstruction with a $c(4 \times 2)$ Unit Cell. *J. Am. Chem. Soc.* **2003**, *125*, 10050–10056.
- (34) Enterkin, J. A.; Subramanian, A. K.; Russell, B. C.; Castell, M. R.; Poeppelmeier, K. R.; Marks, L. D. A Homologous Series of Structures on the Surface of SrTiO₃(110). *Nat. Mater.* **2010**, *9*, 245–248.
- (35) Wang, Z.; Loon, A.; Subramanian, A.; Gerhold, S.; McDermott, E.; Enterkin, J. A.; Hieckel, M.; Russell, B. C.; Green, R. J.; Moewes, A.; **et al.** Transition from Reconstruction toward Thin Film on the (110) Surface of Strontium Titanate. *Nano Lett.* **2016**, *16*, 2407–2412.
- (36) Qin, P.; Fang, G.; Ke, W.; Cheng, F.; Zheng, Q.; Wan, J.; Lei, H.; Zhao, X. In Situ Growth of Double-Layer MoO₃/MoS₂ Film from MoS₂ for Hole-Transport Layers in Organic Solar Cell. *J. Mater. Chem. A* **2014**, *2*, 2742–2756.
- (37) Jiang, L.; Zhang, S.; Kulinich, S. A.; Song, X.; Zhu, J.; Wang, X.; Zeng, H. Optimizing Hybridization of 1T and 2H Phases in MoS₂ Monolayers to Improve Capacitances of Supercapacitors. *Mater. Res. Lett.* **2015**, *3*, 177–183.
- (38) Kumar, P.; Singh, M.; Sharma, R. K.; Reddy, G. B. A Study on Role of Partial Pressure in Controlled Synthesis of Core-Shell MoO₃/MoS₂ Nanoflakes. *Mater. Chem. Phys.* **2016**, *178*, 6–11.

- (39) Sun, Y.; Hu, X.; Luo, W.; Huang, Y. Ultrafine MoO₂ Nanoparticles Embedded in a Carbon Matrix as a High-Capacity and Long-Life Anode for Lithium-Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 425–431.
- (40) Jin, Y.; Shen, P. K. Nanoflower-Like Metallic Conductive MoO₂ as a High-Performance Non-Precious Metal Electrocatalyst for the Hydrogen Evolution Reaction. *J. Mater. Chem. A* **2015**, *3*, 20080–20085.
- (41) Shi, Y.; Huang, J.-K.; Jin, L.; Hsu, Y.-T.; Yu, S. F.; Li, L.-J.; Yang, H. Y. Selective Decoration of Au Nanoparticles on Monolayer MoS₂ Single Crystals. *Sci. Rep.* **2013**, *3*, 1839.
- (42) Pondick, J. V.; Woods, J. M.; Xing, J.; Zhou, Y.; Cha, J. J. Stepwise Sulfurization from MoO₃ to MoS₂ via Chemical Vapor Deposition. *ACS Appl. Nano Mater.* **2018**, *1*, 5655–5661.
- (43) Briggs, D.; Seah, M. P. *Practical Surface Analysis: Auger and X-ray Photoelectron Spectroscopy*; John Wiley & Sons: New York, 1990.
- (44) Dhakal, K. P.; Duong, D. L.; Lee, J.; Nam, H.; Kim, M.; Kan, M.; Lee, Y. H.; Kim, J. Confocal Absorption Spectral Imaging of MoS₂: Optical Transitions Depending on the Atomic Thickness of Intrinsic and Chemically Doped MoS₂. *Nanoscale* **2014**, *6*, 13028–13035.
- (45) Zhou, X.; Kang, K.; Xie, S.; Dadgar, A.; Monahan, N. R.; Zhu, X.-Y.; Park, J.; Pasupathy, A. N. Atomic-Scale Spectroscopy of Gated Monolayer MoS₂. *Nano Lett.* **2016**, *16*, 3148–3154.
- (46) Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F. Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10*, 1271–1275.
- (47) Ling, X.; Lee, Y.-H.; Lin, Y.; Fang, W.; Yu, L.; Dresselhaus, M. S.; Kong, J. Role of the Seeding Promoter in MoS₂ Growth by Chemical Vapor Deposition. *Nano Lett.* **2014**, *14*, 464–472.
- (48) Lee, C.; Yan, H.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS₂. *ACS Nano* **2010**, *4*, 2695–2700.
- (49) Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Edwin, T. H. T.; Olivier, A.; Baillargeat, D. From Bulk to Monolayer MoS₂: Evolution of Raman Scattering. *Adv. Funct. Mater.* **2012**, *22*, 1385–1390.
- (50) Eda, G.; Yamaguchi, H.; Voiry, D.; Fujita, T.; Chen, M.; Chhowalla, M. Photoluminescence from Chemically Exfoliated MoS₂. *Nano Lett.* **2011**, *11*, 5111–5116.
- (51) Wang, S.; Rong, Y.; Fan, Y.; Pacios, M.; Bhaskaran, H.; He, K.; Warner, J. H. Shape Evolution of Monolayer MoS₂ Crystals Grown by Chemical Vapor Deposition. *Chem. Mater.* **2014**, *26*, 6371–6379.
- (52) Yu, Y.; Li, C.; Liu, Y.; Su, L.; Zhang, Y.; Cao, L. Controlled Scalable Synthesis of Uniform, High-Quality Monolayer and Few-Layer MoS₂ Films. *Sci. Rep.* **2013**, *3*, 1866.
- (53) Liu, Z.; Amani, M.; Najmaei, S.; Xu, Q.; Zou, X.; Zhou, W.; Yu, T.; Qiu, C.; Birdwell, A. G.; Crowne, F. J.; **et al.** Strain and Structure Heterogeneity in MoS₂ Atomic Layers Grown by Chemical Vapour Deposition. *Nat. Commun.* **2014**, *5*, 5246.
- (54) El-Mahalawy, S. H.; Evans, B. L. The Thermal Expansion of 2H-MoS₂, 2H-MoSe₂ and 2H-

WSe₂ between 20 and 800 °C. *J. Appl. Crystallogr.* **1976**, 9, 403–406.

(55) de Ligny, D.; Richet, P. High-Temperature Heat Capacity and Thermal Expansion of SrTiO₃ and SrZrO₃ Perovskites. *Phys. Rev. B* **1996**, 53, 3013–3022.

(56) Qiu, H.; Xu, T.; Wang, Z.; Ren, W.; Nan, H.; Ni, Z.; Chen, Q.; Yuan, S.; Miao, F.; Song, F.; et al. Hopping Transport Through Defect-Induced Localized States in Molybdenum Disulphide. *Nat. Commun.* **2013**, 4, 2642.

TOC Graphic