In-Situ High Temperature Atomic Level Dynamics of Large Inversion Domain Formations in Monolayer MoS₂

*Jun Chen[†], Si Zhou[†], Yi Wen[†], Gyeong Hee Ryu[†], Christopher Allen^{†‡}, Yang Lu[†], Angus I. Kirkland^{†‡},
Jamie H. Warner^{†*}*

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

[‡] Electron Physical Sciences Imaging Center, Diamond Light Source Ltd., Didcot, Oxfordshire, OX11 0DE, United Kingdom

Abstract:

Here, we study the high-temperature formation and dynamics of large inversion domains (IDs) that form in monolayer MoS₂ using atomic-resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) with an in-situ heating stage. We use temperatures above 700°C to thermally activate rapid S vacancy migration and this leads to a formation mechanism of IDs that differs from the one at room temperature, where S vacancy migration is limited. We show that at high temperatures the formation of IDs occurs from intersected networks of long S vacancy line defects, whose strain fields are non-orthogonal and trigger large scale atomic reconstructions. Once formed, the IDs are influenced by the dynamic behaviour of nearby line defects and voids. With Mo and S atoms undergoing movement, the two types of ID grain boundaries can shift to allow further expansion of the ID area along the adjoining line defects. We reveal that IDs serve as metastable configurations between line defect rearrangements and eventual void formation under electron beam irradiation during heating. The formation of voids near to the IDs causes them to revert back to pristine lattice, which has the effect of restricting the ID domain size to a certain range (eg. 3–5 nm in our observation) instead of continuously

enlarging. This study provides insights into how the MoS₂ IDs form and evolve at high temperature and can benefit the tailoring of electronic properties of two dimensional materials by structural manipulation.

KEYWORDS: Inversion domain, Defects, Grain Boundaries, MoS₂, STEM

Introduction

Two-dimensional transition metal dichalcogenides (TMDs) are a family of layered materials with unique electronic and optical properties that have opened up new 2D device applications. Among them, monolayer hexagonal molybdenum disulphide (2H-MoS₂) is a direct-band-gap semiconductor which has been synthesized with large crystal sizes by chemical vapour deposition (CVD) and has shown immense potential in thin electronic and opto-electronic devices.¹⁻⁵ Lattice imperfections that are always present in chemically grown MoS₂ and other TMD members, can significantly influence their electronic, optical, magnetic, and chemical properties. Through manipulating structural defects, we can further extend the applications of TMDs in a wide range of fields. The studies on TMDs defects have been focused on ranging from zero-dimensional (point defects),⁶⁻⁹ to one-dimensional (1D) defects like vacancy lines,¹⁰⁻¹² edges,¹³⁻¹⁶ and grain boundaries (GBs).^{8, 17-18} The GBs formed when two 60° oriented monolayer grains merge together, comprises 4-member rings and dislocations, which are calculated to be metallic conducting nanowires embedded in the semiconducting monolayer TMDs.^{8, 19-20} Experimental results have also demonstrated a slightly increased in-plane electrical conductivity and photoluminescence quenching caused by 60° GB.¹⁷ Such distinct transporting properties add useful functionality for engineered GBs rather than a negative role that is more often reported.

Coupled by linear 60° GBs in three zigzag directions due to the three-fold symmetry of the TMD monolayers, inversion domains (IDs) with 60° lattice rotation can form at a local region. The antiphase GBs with similar structure to 60° GBs can be artificially produced within 2H/1T phase by the combination of electron irradiation and thermal stimulation at the temperature of 600°C , which induced the phase transformation of Re-doped MoS_2 from 2H to 1T locally.²¹ The IDs with 60° GBs can be created by heating or electron-irradiating as well. It was shown that the MoSe_2 IDs could emerge in the monolayer sample grown by molecular beam epitaxy with the Se-deficient environment and heating condition.²² In the MoTe_2 system, a large concentration of IDs were found after vacuum annealing at high temperature which provided thermal energies and Te vacancies as the driving forces.²³ In these studies, the formation of IDs is usually considered to be associated with two factors, the chalcogen atoms vacancies resulted from chalcogen deficiency and thermal energy. However, the mechanism of the ID formation at high temperature still needs to be understood, especially the large-scale transformations that occur when long line defects are present.

Chalcogen vacancies are commonly seen in TMDs monolayers due to their comparatively low displacement threshold energy (the minimum initial kinetic energy of the recoil atom, beyond which the atoms displacement can occur, eg. ~ 6.5 eV for S in the MoS_2 lattice),²⁴⁻²⁵ and the S vacancies tend to agglomerate to construct line defects when the energy barrier of migration is overcome. Prior work using ADF-STEM imaging at room temperature showed the electron beam driven formation of small IDs in MoSe_2 ,²⁶ which was explained to be triggered by Se point vacancies that assemble to form line vacancies. These IDs were relatively small (1–2nm) and are surrounded by many other point S vacancies, holes, and line vacancies due to the low mobility of S vacancies at room temperature resulting from the high-energy barrier of S vacancy migration.^{10, 27} This makes it difficult to elucidate the strain dynamics in

the system due to the heavily distorted lattice on the larger scale from so many defects in the vicinity.

Recent work has shown that at high temperature ($>700^{\circ}\text{C}$), thermal energy activates the rapid migration of S point vacancies and they assemble into ultralong line defects.²⁸ The total number of line vacancies at high temperature is much less than at room temperature because newly created S point vacancies tend to migrate to join an existing vacancy line rather than start a new one.²⁸ Therefore the formation process and strain fields of IDs at these higher temperatures should be much easier to understand because of the more uniform defect structures. Ex-situ high temperature annealing in vacuum has shown that IDs with larger area can be produced.^{23, 26} Thermal treatments are usually involved in fabricating and processing monolayer TMDs for opto-electronic devices, it is crucial to understand the structural transformations that occur at high temperatures and whether IDs can be stable and controllably formed.

Here, we use aberration corrected annular dark field STEM (ADF-STEM) with an *in-situ* heating stage to investigate the mechanism of ID formation and evolution in monolayer MoS_2 at the atomic level under the high temperature of 800°C . We track the details of the ID evolution after formation, including further expansion by GB migration, interplay with the formed void in the vicinity, as well as the final disappearance. The high temperature in this study also ensures a highly clean MoS_2 lattice surface for revealing unambiguous dynamics of the ID without interference from attached contamination.

Results and discussion

MoS_2 monolayers grown by the CVD method are transferred to an *in-situ* heating holder TEM chip covered by a Si_3N_4 membrane with numerous pre-cut slits, and then heated up to a high temperature of 800°C in-situ when doing annular dark field scanning transmission

electron microscopy (ADF-STEM) at a low accelerating voltage of 60 kV. Figure 1a exhibits the ADF-STEM image of a typical inversion domain (ID) formed at 800 °C after electron beam induced vacancies are introduced into the system. The IDs formed at high temperature are generally much larger than those formed at room temperature, with a triangular side length of around 20 Mo atoms, compared to 7-10 at room temperature.^{22,23} The lattices of Mo and S atoms inside (Figure 1b) and outside (Figure 1c) the domain have a rotation of 60°, namely show the inverted orientations. Two different grain boundaries (GBs) structures are observed at this ID, as presented in Figure 1d-i. One is composed of a 4|4 edge (4|4E) sharing structure with two rows of single sulphur atoms bridging at the boundary (Figure 1d,e), and the other is a 4|4 point (4|4P) sharing mirror twin boundary (Figure 1g,h), which are similar to the previously reported boundary structures.⁸ These two types of 60° GBs possess the same local stoichiometry, and both were calculated to be energetically favourable (only 0.04 eV/Å difference in energy).⁸ Their simulated images in Figure 1f,i also show a good accordance with the experimental images.

Figure 1 (a) ADF-STEM image of large-area inversion domain (ID) formed at 800 °C by electron beam induced S vacancies embedded in monolayer MoS₂. The domain size is around 7 nm of the edge length. Cyan dots indicate the edge of the ID. (b, c) Magnified views of the boxed regions in (a), showing the inverted lattice orientation within the ID. (d, g) Magnified views of the boxed regions in (a), indicating two types of boundary structures of the ID. (e) Atomic model and (f) Multislice simulated ADF-STEM image corresponding to (d). (h) Atomic model and (i) Multislice simulated ADF-STEM image corresponding to (g).

Figure 2a-d shows a series of ADF-STEM images obtained at 800 °C that reveal how the ID forms from the S vacancy line defects. At this high temperature, the MoS₂ film is clean without surface contamination which has been evaporated. Under the electron beam irradiation,

several long sulphur-vacancy lines (SVLs) are produced in the MoS₂ monolayer and grow fast both in number and length (Figure 2a-c). The sulphur vacancies are rapidly generated and quickly migrate at high temperature, consequently forming an area with a large density of line vacancies crossing each other (Figure 2c). Noticeably, in the region where several line defects are intersecting and interacting, a large ID with the size of ~4 nm suddenly forms, along with the readjustment of the direction of one of the two SVLs (iv and v). The enlarged views of the lattice involved in the ID before and after formation are presented in Figure 2e and 2f respectively, which show a compact SVL (marked by blue arrow) migrates and turns 120°, to the side of the ID triangle, and another 2SVL (SVL losing two sulphur rows, marked by white dashed rectangular) forms the boundary of the domain. This 2SVL structure is highlighted in Figure 2g with a schematic atom model in Figure 2h, as previously reported.¹² The ID in Figure 2f also consists of a 4|4E GB and a 4|4P GB (Figure S1), which are similar to the previously reported boundary structures.⁸ These two GBs are connected in the corner of the ID (Figure 2i, j), with the 2SVL being the extending line of the 4|4E GB.

It is common to see SVLs in the vicinity of IDs, and the SVLs form one GB side of the IDs, as demonstrated in Figure S2. Creating an atomic model of an ID without utilizing a SVL (Figure S3), requires significant lattice shrinkage in the pristine MoS₂. In the experimental data, the SVLs have provided the required lattice contraction, for example, the 2SVL in Figure 2f. Notably, it can be clearly seen from Figure 2a-d that the appearance of the ID is not a simple result of certain point defects or one individual SVL alone, but is related to the whole network of the interlacing line defects.

Figure 2. ID formation process at high temperature of 800°C. (a-d) Time series of ADF-STEM images at the heating temperature of 800 °C, where i-iv with red arrows represent line defects around this region, and the formed ID is marked by dashed yellow triangle in (d). (e,f) Magnified views of the boxed regions highlighted in (c) and (d), shown in false colour with atomic smoothness, where the atoms in the ID are overlaid by a blue colour mask, and the line defect across this region is marked by white dashed lines. (g, i) Magnified views of the blue-line-boxed regions in (e, f), with schematic atomic models of Mo (blue), 2S (yellow), and single S (pink) atoms overlaid. (h) and (j) The atomic model corresponding to (g) and (i), respectively.

We then examine the strain field of the MoS₂ lattice containing line defects, before ID formation (Figure 3). The strain distributions for the ADF-STEM image (Figure 3a) are evaluated using geometric phase analysis (GPA).²⁹⁻³⁰ The detailed parameters for using GPA analysis is shown in Figure S4. Figure 3b and 3c are the obtained strain maps of the normal

strain field component along x direction (ϵ_{xx}) and y directions (ϵ_{yy}), respectively. Each SVL in this network gives compressive strain to the adjacent lattice (with colour black, red, and green in the map) in the perpendicular direction, in agreement with the previous report on line defects,^{12,15} as well as according with the GPA analysis on another ADF-STEM image with line defects, which likewise shows compressive stain for each vacancy line (Figure S5). As reported previously, the obvious lattice compression occurring in perpendicular direction of line defects is mainly from the out-of-plane distortions of the lattice with missing S atom rows.¹² The intersecting line defects yield non-orthogonal strains, making the strain fields in this whole lattice complicated. The strain fields in the marked region in Figure 2b are particularly strong and complex with several SVL close to each other with the angle of 60°. Interestingly, within this region, a distinct strain field is narrowly localized at the small end area of SVLs (ii) and (iii), as highlighted in the large view in Figure 3d. The corresponding strain transition points are shown in Figure 3e,f. Along the long SVL, the contraction increases from 50% to 150%, then suddenly decays to 0, followed by tension strain varying from 150% to 50% when another SVL is nearly reaching from the right side, and the strain finally becomes compression strain at the SVL tip. It is at this region indicated by figure 3e, where the ID forms, as marked by red arrows in Figure S6 showing the strain fields before and after the generation of an ID. At the same time, the strain has been reduced at the ID boundary (Figure S6e) compared to the original line defect in Figure S6b.

Figure 3 Strain field analysis of line vacancies from figure 2c, i.e before forming an ID. (a) ADF-STEM image prior to the ID formation. Same image as in frame 2c, but in false colour (b,c) Strain components ϵ_{xx} and ϵ_{yy} , respectively, based on geometric phase analysis of (a). (d) Enlarged view of the boxed region in (b), showing complex strain variation at the region where the tip of SVL (ii) nearly reach SVL (iii). (e, f) Magnified image of the boxed regions in (d) with scales of the strain intensity.

The lattice change and atomic displacements at this region, required for generating the ID, are displayed in Figure 4a-d. The overlaid atoms mark the original positions of Mo and S atoms in Figure 4a, and the arrows in Figure 4b-d show the atomic displacements needed for creating the ID. The results show that the atoms in the pristine area have moved towards the two compact SVLs in a 120° angle with intense strain fields, and Mo are the main shifting atoms driven by the need to reduce the strain fields. The Mo atomic displacement value is around 1.6 Å. The transformations from a MoS_2 lattice with a 2SVL to an ID is illustrated in the schematic models in Figure S7, indicating that the migration of Mo atoms by half a lattice on one side of the 2SVL can create the $4|4\text{E}$ GB and $4|4\text{P}$ GB simultaneously, thus forming the ID. For the 2SVL lattice transforming to the $4|4\text{E}$ GB, only tiny displacements of atoms are needed (Figure

4d), suggesting that the presence of 2SVL makes the structural change more feasible. Another example of an ID formation process with similar behaviour of Mo atoms shifting during lattice inversion is presented in Figure S8.

Figure 4 (a, b) ADF-STEM images of (a) pristine and (b) ID region, taken from Figure 2 (e,f). (c,d) Expanded view of the boxed region in (b). The schematic atomic models in (a-c) overlaid represent the original position of Mo (green) and 2S (navy) atoms in the pristine structure, showing the structural reconstruction of MoS₂ lattice to form ID, and the displacement direction of these atoms are indicated by arrows. The sulphur vacancies (1S) of line defects are shown by yellow atoms. (e-g) Schematic illustration of the ID formation process corresponding to the transformation from (a) to (b), with atoms moving triggered by strains, the green lines represent the line defects, the dashed arrows show their compressive strain, and the blue arrows in (f) signify the shift direction of Mo atoms within ID, corresponding to (b). The roman numerals marked near each line defect correspond to those in Figure 2 (c,d).

Based on the above analysis of strain fields and the relevant atomic displacements, the schematic illustration in Figure 4e-h shows how this ID (Figure 2-4) forms influenced by the network of line defects. Under high temperature, extended line defects are easily formed and

grow along zig-zag lattice directions at 60° until they intersect one another while each of them has a compressive strain field (Figure 4e). At the corner when two line defects are approaching, the strain fields become intense and complex, driving the vacancies and atoms to migrate (Figure 4e to 4f). In this crossing region of a line defect network (Figure 4f), the strain fields coming from each line defect are non-orthogonal and thus are competing. As a result, the composited strain triggers the displacement of atoms and reconstruction of lattice, finally generating an ID (Figure 4g). The high mobility of vacancies at high temperature can also facilitate the reconstruction.

Figure 5 displays the ADF-STEM image sequence captured at 800°C , which shows strong interplay between IDs and the nearby defect network including line defects as well as the formed void. From Figure 5a to 5b, a hole opens up at one corner of ID. That corner is the junction of two compact multi-SVLs in an angle of 120° (Figure 5a), (Figure S9). This causes it to form a void under beam irradiation. During that time, the ID remains steady by retaining all of its boundaries at the original position (Figure 5b, c). Under continuous electron beam irradiation, the ID expands along the direction of the 2SVL, as highlighted by white dashed rectangular in Figure 5c,d, and the expanding direction is marked by the arrow in Figure 5d. This expansion is achieved by the migration of its $4|4\text{P}$ GB toward the outer region as well as the elongation of the $4|4\text{E}$ GB along the 2SVL. During that time, the adjoining void is increasing as well. The ID further enlarges until its top vertex reaches another line defect (Figure 5e), and at that time the void grows to be a 60° triangular shape along zig-zag direction. The tendency of the void developing to be triangular shape is attributed to the three-fold symmetry of the hexagonal MoS_2 lattice. With the further growth of the void under continuous electron beam irradiation, the ID finally disappears, as shown from Figure 5f to h. It can be seen from this dynamic process that the ID growth is always along the line defect direction, while the line defect network together with the formed void restrict the size of IDs to typically

less than 5nm. This shows that the ID serves as a metastable state between the line defect rearrangement and void formation under continual vacancy production.

Figure 5 Sequence of ADF-STEM images showing the dynamics of an ID at a high temperature of 800 °C after formation. The ID is highlighted by colour, and the overlaid shapes in different colours indicate the expansion and evolution of the ID. Scale bar: 3 nm.

Figure 6 presents the expansion mechanism of ID by migrating its 4|4P GB. The process of growing the ID area from Figure 5c to 5d is analysed in Figure 6a,b. MoS₂ lattice at the outer side region of the 4|4P GB undergoes atomic displacement and bond reconstruction, making the 4|4P GB migrate outward. As highlighted in Figure 6c, Mo atoms outside the 4|4P GB including half of the Mo atoms in the GB itself shift to the centre point of two shoulder Mo atoms and re-bond with the adjacent S atoms, causing the lattice to be inverted. It can be observed from Figure 6b that the shifting direction of the Mo atoms is towards the void formed at the left corner of the ID. This void is increasing by sputtering S atoms and absorbing Mo

atoms to transport to its edge with excessive agglomerated Mo atoms, which influences the Mo movement required for 4|4P GB migration. The 4|4P GB migrating process from Figure 6a to 6b is illustrated in Figure 6d-f, through the shifting of Mo atoms at one side of 4|4P GB to the shoulder positions (Figure 6d), tiny adjustment of S atoms positions (Figure 6e), and reconstruction of Mo—S bonding (Figure 6f). We also present another example of the ID increase by migrating the 4|4P GB (Figure 6g,h), which is realized by moving Mo atoms outside the 4|4P GB as well. The involved Mo atoms shift to the geometric centre of the hexagon, as demonstrated in the ADF-STEM image region overlaid with atoms (Figure 6h) and the corresponding atomic model (Figure 6i). This moving pathway slightly differs from that in the former example (Figure 6c) as they are surrounded by a different environment, where their Mo atomic displacement directions are both affected by the adjoining void.

Figure 6 ID expansion through the migration of its 4|4P grain boundary (GB). (a,b) ADF-STEM images showing (a) the original ID and (b) expanded ID cropped from Figure 5(c,d). The outlines of the IDs are marked by white dashed triangles. The large green arrow presents the migrating direction of the 4|4P GB. The circled lattices in (b) show the removed atoms in the void. (c) Magnified view of the boxed region highlighted in (b). The schematic atomic models of Mo (green, larger balls) and 2S (royal, smaller balls) overlaid mark the original position of the atoms before expansion, and the circles drawn by dashed yellow lines represent the shifted Mo atomic positions with the yellow arrows showing the displacement pathways. (d-f) Schematic illustration depicting the corresponding atomic movement during 4|4P GB migration in (a-b). (g,h) Another example of ID expansion with 4|4P (GB) migration. (g) Original ID highlighted by a colour mask. The large green arrow shows the expanding direction. (h) Partial view of the enlarged ID in the boxed region in (g), with the solid schematic atomic models overlaid marking the original atoms positions before domain expansion, and the transparent models representing the shifted atoms positions. (i) Schematic atomic model showing Mo atoms movement corresponding to (h).

The other mode of ID expansion is through the migration of 4|4E GB, shown in the ADF-STEM sequence in Figure 7. This ID is also embedded within a network of line defects and is influenced by the behaviour of the adjacent line defects. The boundary structures of the increased ID (Figure 7b) and the original one (Figure 7a) are interpreted in Figure S10, which comprise a 4|4P GB (i) and two 4|4E GBs (ii and iii) with one 4|4E GB adjoining an extended 2SVL. For growing the ID from Figure 7a to 7b, the 4|4E GB (ii) migrates outward when the other two GBs extend. The 4|4E GB (iii) elongates along its 2SVL, and the 4|4P GB (i) lengthens together with the migration of multi-SVL (marked by the light blue arrow) crossing the vertex of the GBs (i) and (ii). The typical structural change of this process is highlighted by two representative junction regions, displayed in Figure 7c-e and 7f-h, respectively. As shown in Figure 7c-e with its overlaid atoms in Figure 7c'-e', the 4|4E GB (iii) adjusts by sliding one single S row near the extended 2SVL with slight Mo atomic displacement, Figure S11. At the same time, the 4|4E GB (ii) migrates by shifting the S atoms outside the ID. This migration process is illustrated by atomic models in Figure 7i-k based on the atomic displacement analysis in Figure 7d'. The two rows of single S atoms at the contracted 4|4E GB merge to be the pristine 2S configuration with one single S row sliding toward the ID direction (Figure 7i to j). The next 2S rows then split to be the 4|4E GB as one S row shifts by half lattice and re-bonds to the Mo atoms (Figure 7j to k). For the vertex in Figure 7f-h, the migration of the crossing SVL as marked in Figure 7a,b leads to atomic movement and lattice reconstruction. The Mo and S atoms shift along opposite directions during the SVL migration, which makes the 4|4P GB (i) extend accompanied by associated lattice inversion in the domain. The overall dynamics of the connected line defects and the 4|4E GB result in the further growth of the ID.

Figure 7 ID expansion via the migration of its 4|4E GB. (a,b) ADF-STEM images of (a) original ID and (b) expanded domain. Three GBs of the ID in (a) are labelled (i-iii). The blue arrows in (a,b) show the movement of the related line defect. The green arrow in (b) presents the migration direction of the 4|4E GB. (c, e) Magnified views of boxed region in (a,b) of the corner crossed by two 4|4E GB with one leaning a 2SVL as a extending line, with (c', e') overlaid by atomic models of Mo (green), 2S (royal) and single S (orange or light blue in different S rows). (d, d') Schematic atomic models illustrating the atomic displacement during the transformation from (c) to (e). (f, h) Magnified views of boxed region in (a,b) of the other corner crossed by 4|4E GB, 4|4P GB and a line defect in another direction. (g) Atoms shift and lattice change from (f) to (h). (i-k) Schematic illustration showing the atomic movement during 4|4E GB migration.

The boundaries of ID are not always atomically sharp, but can exhibit staggered structure as well, as shown in Figure 8. This ID is also embedded in the intersected line defects (i) and (ii), which serve as the extending lines of the domain boundaries. Similar to other aforementioned IDs, it grows along the two extended line defects from Figure 8a to 8c, by

shifting the 4|4P GB outward. At the stage in Figure 8b, the 4|4P GB evolved to be a stepped structure with three steps of 4|4P GBs. As highlighted in Figure 8d and e, this structure is connected by several 4-member rings with single S atom conjunctions. It can be seen that the growth of this ID is initiated from the cross-point (marked by blue arrow in Figure 8a) of the 4|4P GB and the broad multi-S vacancy line (i), then propagates to the other boundary tip step by step. At a certain stage the 2S atoms at the boundary step junctions split and one S slides to form these metastable 4-member rings, making the staggered boundary. It finally evolves to be the atomically flat boundary with prolonged electron beam irradiation (Figure 8c).

For the ID, we can observe quick interconversion between two kinds of GBs, 4|4E GB and 4|4P GB, as shown in Figure 9. The upright 4|4E GB of the ID in Figure 9a transforms to be the 4|4P GB structure in Figure 9b while the other side of the domain with a 4|4P GB structure converts to form the 4|4E type GB. By overlapping these two ADF-STEM frames (Figure 9c), we find an entire slide of the lattice outside the two GBs of the ID toward the directions as indicated by the green arrows, and the displacement is the lattice spacing of two neighbour armchair rows of MoS₂, namely, the (110) inter-planar distance (~0.16 nm). This transformation is illustrated in Figure 9d, when translating the lattice in one side of the 4|4P GB by 0.16 nm along the zig-zag direction together with sliding one single row of S atoms, it can change to the 4|4E GB structure, and vice versa. The overall lattice outside the two GBs of ID is involved in this transition, manifesting a wider range of the interplay between the pristine lattice with the embedded large ID.

Figure 8 Staggered boundary of an ID. (a-c) ADF-STEM image sequence during ID growth, where (b) presents a staggered boundary as highlighted by the white dashed box. The roman numerals indicate the adjoin line defects. (d) Magnified view of the boxed region in (b), with schematic atoms showing the step boundary structure. (e) Atomic model corresponding to (d).

Figure 9 Conversion between two kinds of GBs in IDs, 4|4E GB and 4|4P GB. (a,b) Two successive frames of ADF-STEM images, with the 4|4E GB and 4|4P GB of the ID transforming to be 4|4P GB and 4|4E GB structure, respectively. (c) Lattice shifts revealed by overlaying the two frames in (a,b) during that change. (d) Schematic illustration of the lattice conversion between 4|4E GB and 4|4P GB.

The ID can finally disappear after continuously irradiating the sample with the electron beam to further increase the number of S vacancies. Figure 10 shows a vanishing process as

the last stage of high-temperature evolution of the ID taken from Figure 5. As the triangular void beside the ID further enlarges, the ID appears to be consumed by the void (Figure 10a to c). According to the overlapped image of the two frames in Figure 10b, the Mo atoms inside the ID have all migrated toward the void. The void growth is due to an increasing concentration of S vacancies produced by extended electron beam irradiation, and Mo atoms that are difficult to be sputtered agglomerate at the void edge and form the MoS nanowire structure.³¹ The strain near the void edge drives Mo atoms to migrate toward it, and the inverted lattices reconstruct to be the pristine structure to balance the strain. This mechanism reveals an initiating effect on the faceted void formation given by the dynamics and collapse of vacancy line defects and IDs. It may also exist in the faceted void formation under synthetic process in S-deficient conditions and thermal heating, like in the scalable faceted voids during the CVD growth.³² Figure 10d highlights the displacement of the Mo atoms near the 4|4P GB, which shows that the Mo atoms at the inverted side of the GB have shifted by half lattice while the outer MoS₂ stays unchanged. The corresponding lattice transformation process for ID disappearing near the 4|4P GB is illustrated by schematic atomic models in Figure 10e-g.

Figure 10 ID vanishing into the void. ADF-STEM images of an ID (a) before and (c) after vanishing. The ID area is highlighted by colour mask in (a). (b) Atomic movement and lattice changes are revealed by overlaying (a) and (c). (d) Magnified view in the boxed region in (d), showing the Mo atoms shifting near the 4|4P GB. (e-g) Schematic atomic models showing the corresponding vanishing process.

Conclusion

We show the formation, enlargement and vanishing evolution mechanisms of large IDs ($\sim 4\text{nm}$) at high temperatures using an *in-situ* high-temperature holder in an ADF-STEM with atomic resolution. Thermal energy provides the sulphur vacancies with high mobility which makes defects evolve fast, as well as eliminates the effect derived from surface contamination on the defect behaviour. The IDs formed at high temperature are much larger than those at room temperature (e.g. a triangular side length of 20 Mo atoms, in contrast to those of 7–10 at room temperature). We find the formation of large IDs is not simply caused by single point vacancies or individual line defects, but rather as a result of a network of non-orthogonal line vacancies with competing strain fields that trigger ID formation. The maximum size of IDs formed are $\sim 3\text{--}5\text{nm}$, after which void formation takes over. When interplaying with the surrounding defect

network, IDs can further expand through the migration of any of its two types of grain boundaries, 4|4E GB and 4|4P GB, by S or Mo atoms displacement, respectively. As the adjoining void grows under prolonged electron irradiation, the ID will eventually be consumed by the void. This study gives insights into the high-temperature dynamics of large ID, and also highlights the important interplay between line defects, grain boundaries, voids, and the ID in a large scale, which is promising to underpin the defects engineering of 2D materials in atomic level targeting at electronic properties tailoring.

Methods

Synthesis of Monolayer MoS₂: MoS₂ monolayers were prepared through chemical vapour deposition (CVD) growth method with argon (Ar) as carrier at atmosphere pressure, similar to previously reported strategies with some modifications.³³⁻³⁴ Molybdenum trioxide (MoO₃, ≥ 99.5%, Sigma-Aldrich) of 20 mg and sulphur (S, ≥ 99.5%, Sigma-Aldrich) powder of 300 mg were utilized as the precursors to growth MoS₂ on a Si substrate with 300 nm-thick SiO₂ on the surface. We use two furnaces to control temperature separately on the precursors and substrate, and two different-diameter quart tubes with one inside the other. The substrate is cleaned with acetone and isopropanol, followed by O₂ plasma for 5 min, then placed horizontally into the outer quart tube and located at the centre of Furnace-2. S powder was loaded in the outer quart tube at the Furnace-1 midpoint, while MoO₃ was in the inner tube with a distance of ~11 cm to the tube flow exit. After flushing with 500 sccm Ar for 30 min, Furnace-1 was heated to 200 °C to pre-introduce S vapour, and Furnace-2 was heated up to 800 °C, maintaining for 15 min under 150 sccm argon flow, and then another 25 min under decreased flow of 10 sccm before the growth stopped. After a fast cooling process, monolayer MoS₂ grown on the SiO₂/Si substrate was collected.

Transfer of Monolayer MoS₂: To transfer the MoS₂, a thin film of poly(methyl methacrylate) (PMMA) was firstly spin-coated on the surface of MoS₂/SiO₂/Si substrate, which was then floating on the liquid surface of 1 mol L⁻¹ potassium hydroxide (KOH) solution, etching for several hours until it peeled off. Subsequently, PMMA/MoS₂ film was scooped up and placed on the deionized ion (DI) water which was renewed repeatedly. The rinsed PMMA/MoS₂ film was transferred onto a prefabricated in situ TEM heating chip, dried at room temperature overnight. After baked at 150 °C for 40 min, the heating chip was rinsed in acetone for over 24 h to remove PMMA.

Scanning Transmission Electron Microscopy and Image Processing: Annular dark field scanning transmission electron microscopy (ADF-STEM) was conducted with an in situ heating holder, using an aberration corrected JEOL ARM300CF STEM equipped with a JEOL ETA corrector,³⁵ located in the electron Physical Sciences Imaging Centre (ePSIC) at Diamond Light Source, and the operation accelerating voltage was 60 kV. Imaging process was carried out with dwell times of 5–20 μs and a pixel size of 0.006 nm px⁻¹. The convergence semi-angle was 39.1 mrad with a beam current of 48.5 pA, and the applied inner-outer acquisition angles were 56.4–207.1 mrad. The ADF-STEM im aging temperature was increased to 800 °C by utilizing a commercial in situ heating holder (DENS Solutions, SH30-4M-FS), and TEM heating chips (DENS Solutions, DENS-C-30) imbedded with a platinum resistive coil. Slits were cut into the thin Si₃N₄ membranes on the heating chips by using focused ion beam milling. Sample was heated by controlling a current through the platinum coil, whose resistance was detected in a four-point contact device, and the temperature was calculated according to the Callendar-Van Dusen equation with the calibration coefficients from the manufacturer. The obtained ADF-STEM images were processed using Image J software. The Gaussian blur of 2–3 was applied to highlight the positions of atoms in the images, and a fire false colour was

performed on the original greyscale images to increase the visual contrast. The atomic models were constructed using Accelrys Discovery Studio Visualizer software.

Acknowledgement

J. H. W. thanks the support from the Royal Society and the ERC Consolidator grant (LATO 725258). J. C. thanks the support from China Scholarship Council (CSC). We thank Diamond Light Source for access and support in use of the electron Physical Science Imaging Centre.

Reference

- (1) Wang, X.; Wang, P.; Wang, J.; Hu, W.; Zhou, X.; Guo, N.; Huang, H.; Sun, S.; Shen, H.; Lin, T., Ultrasensitive and Broadband MoS₂ Photodetector Driven by Ferroelectrics. *Adv. Mater.* **2015**, *27*, 6575–6581.
- (2) Kappera, R.; Voiry, D.; Yalcin, S. E.; Branch, B.; Gupta, G.; Mohite, A. D.; Chhowalla, M., Phase-Engineered Low-Resistance Contacts for Ultrathin MoS₂ Transistors. *Nat. Mater.* **2014**, *13*, 1128–1134.
- (3) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, i. V.; Kis, A., Single-Layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.
- (4) 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.
- (5) Chen, J.; Tang, W.; Tian, B.; Liu, B.; Zhao, X.; Liu, Y.; Ren, T.; Liu, W.; Geng, D.; Jeong, H. Y.; Shin, H. S.; Zhou, W.; Loh, K. P., Chemical Vapor Deposition of High-Quality Large-Sized MoS₂ Crystals on Silicon Dioxide Substrates. *Adv. Sci.* **2016**, *3*, 1500033.
- (6) Hong, J.; Hu, Z.; Probert, M.; Li, K.; Lv, D.; Yang, X.; Gu, L.; Mao, N.; Feng, Q.; Xie, L.; Zhang, J.; Wu, D.; Zhang, Z.; Jin, C.; Ji, W.; Zhang, X.; Yuan, J.; Zhang, Z., Exploring Atomic Defects in Molybdenum Disulphide Monolayers. *Nat. Commun.* **2015**, *6*, 6293.
- (7) Lin, Y. C.; Bjorkman, T.; Komsa, H. P.; Teng, P. Y.; Yeh, C. H.; Huang, F. S.; Lin, K. H.; Jadczyk, J.; Huang, Y. S.; Chiu, P. W.; Krashennnikov, A. V.; Suenaga, K., Three-Fold Rotational Defects in Two-Dimensional Transition Metal Dichalcogenides. *Nat. Commun.* **2015**, *6*, 6736.

- (8) Zhou, W.; Zou, X.; Najmaei, S.; Liu, Z.; Shi, Y.; Kong, J.; Lou, J.; Ajayan, P. M.; Yakobson, B. I.; Idrobo, J.-C., Intrinsic Structural Defects in Monolayer Molybdenum Disulfide. *Nano Lett.* **2013**, *13*, 2615–2622.
- (9) Precner, M.; Polaković, T.; Qiao, Q.; Trainer, D. J.; Putilov, A. V.; Di Giorgio, C.; Cone, I.; Zhu, Y.; Xi, X. X.; Iavarone, M.; Karapetrov, G., Evolution of Metastable Defects and Its Effect on the Electronic Properties of MoS₂ Films. *Sci. Rep.* **2018**, *8*, 6724.
- (10) Komsa, H.-P.; Kurasch, S.; Lehtinen, O.; Kaiser, U.; Krasheninnikov, A. V., From Point to Extended Defects in Two-Dimensional MoS₂: Evolution of Atomic Structure under Electron Irradiation. *Phys. Rev. B* **2013**, *88*, 035301.
- (11) Enyashin, A. N.; Bar-Sadan, M.; Houben, L.; Seifert, G., Line Defects in Molybdenum Disulfide Layers. *J. Phys. Chem. C* **2013**, *117*, 10842–10848.
- (12) Wang, S.; Lee, G. D.; Lee, S.; Yoon, E.; Warner, J. H., Detailed Atomic Reconstruction of Extended Line Defects in Monolayer MoS₂. *ACS Nano* **2016**, *10*, 5419–5430.
- (13) Bollinger, M.; Jacobsen, K. W.; Nørskov, J. K., Atomic and Electronic Structure of MoS₂ Nanoparticles. *Phys. Rev. B* **2003**, *67*, 085410.
- (14) Li, Y.; Zhou, Z.; Zhang, S.; Chen, Z., MoS₂ Nanoribbons: High Stability and Unusual Electronic and Magnetic Properties. *J. Am. Chem. Soc.* **2008**, *130*, 16739–16744.
- (15) Chen, Q.; Li, H.; Xu, W.; Wang, S.; Sawada, H.; Allen, C. S.; Kirkland, A. I.; Grossman, J. C.; Warner, J. H., Atomically Flat Zigzag Edges in Monolayer MoS₂ by Thermal Annealing. *Nano Lett.* **2017**, *17*, 5502–5507.
- (16) Zhao, X.; Fu, D.; Ding, Z.; Zhang, Y. Y.; Wan, D.; Tan, S. J. R.; Chen, Z.; Leng, K.; Dan, J.; Fu, W.; Geng, D.; Song, P.; Du, Y.; Venkatesan, T.; Pantelides, S. T.; Pennycook, S. J.; Zhou, W.; Loh, K. P., Mo-Terminated Edge Reconstructions in Nanoporous Molybdenum Disulfide Film. *Nano Lett.* **2018**, *18*, 482–490.
- (17) van der Zande, A. M.; Huang, P. Y.; Chenet, D. A.; Berkelbach, T. C.; You, Y.; Lee, G. H.; Heinz, T. F.; Reichman, D. R.; Muller, D. A.; Hone, J. C., Grains and Grain Boundaries in Highly Crystalline Monolayer Molybdenum Disulphide. *Nat. Mater.* **2013**, *12*, 554–561.

- (18) Zhao, X.; Ding, Z.; Chen, J.; Dan, J.; Poh, S. M.; Fu, W.; Pennycook, S. J.; Zhou, W.; Loh, K. P., Strain Modulation by van der Waals Coupling in Bilayer Transition Metal Dichalcogenide. *ACS Nano* **2018**, *12*, 1940–1948.
- (19) Najmaei, S.; Liu, Z.; Zhou, W.; Zou, X.; Shi, G.; Lei, S.; Yakobson, B. I.; Idrobo, J. C.; Ajayan, P. M.; Lou, J., Vapour Phase Growth and Grain Boundary Structure of Molybdenum Disulphide Atomic Layers. *Nat. Mater.* **2013**, *12*, 754–759.
- (20) Zou, X.; Liu, Y.; Yakobson, B. I., Predicting Dislocations and Grain Boundaries in Two-Dimensional Metal-Disulfides from the First Principles. *Nano Lett.* **2012**, *13*, 253–258.
- (21) Lin, Y.-C.; Dumcenco, D. O.; Huang, Y.-S.; Suenaga, K., Atomic Mechanism of the Semiconducting-to-Metallic Phase Transition in Single-Layered MoS₂. *Nat. Nanotechnol.* **2014**, *9*, 391–396.
- (22) Lehtinen, O.; Komsa, H.-P.; Pulkin, A.; Whitwick, M. B.; Chen, M.-W.; Lehnert, T.; Mohn, M. J.; Yazyev, O. V.; Kis, A.; Kaiser, U., Atomic Scale Microstructure and Properties of Se-Deficient Two-Dimensional MoSe₂. *ACS Nano* **2015**, *9*, 3274–3283.
- (23) Zhu, H.; Wang, Q.; Cheng, L.; Addou, R.; Kim, J.; Kim, M. J.; Wallace, R. M., Defects and Surface Structural Stability of MoTe₂ under Vacuum Annealing. *ACS Nano* **2017**, *11*, 11005–11014.
- (24) Komsa, H.-P.; Kotakoski, J.; Kurasch, S.; Lehtinen, O.; Kaiser, U.; Krasheninnikov, A. V., Two-Dimensional Transition Metal Dichalcogenides under Electron Irradiation: Defect Production and Doping. *Phys. Rev. Lett.* **2012**, *109*, 035503.
- (25) Zan, R.; Ramasse, Q. M.; Jalil, R.; Georgiou, T.; Bangert, U.; Novoselov, K. S., Control of Radiation Damage in MoS₂ by Graphene Encapsulation. *ACS Nano* **2013**, *7*, 10167–10174.
- (26) Lin, J.; Pantelides, S. T.; Zhou, W., Vacancy-Induced Formation and Growth of Inversion Domains in Transition-Metal Dichalcogenide Monolayer. *ACS Nano* **2015**, *9*, 5189–5197.
- (27) Sensoy, M. G.; Vinichenko, D.; Chen, W.; Friend, C. M.; Kaxiras, E., Strain Effects on the Behavior of Isolated and Paired Sulfur Vacancy Defects in Monolayer MoS₂. *Phys. Rev. B* **2017**, *95*, 014106.

- (28) Chen, Q.; Li, H.; Zhou, S.; Xu, W.; Chen, J.; Sawada, H.; Allen, C. S.; Kirkland, A. I.; Grossman, J. C.; Warner, J. H., Ultralong 1D Vacancy Channels for Rapid Atomic Migration during 2D Void Formation in Monolayer MoS₂. *ACS Nano* **2018**, Articles ASAP, DOI: 10.1021/acsnano.8b01610.
- (29) Hýtch, M.; Snoeck, E.; Kilaas, R., Quantitative Measurement of Displacement and Strain Fields from HREM Micrographs. *Ultramicroscopy* **1998**, *74*, 131–146.
- (30) Hýtch, M. J.; Putaux, J.-L.; Pénisson, J.-M., Measurement of the Displacement Field of Dislocations to 0.03 Å by Electron Microscopy. *Nature* **2003**, *423*, 270–273.
- (31) Koh, A. L.; Wang, S.; Ataca, C.; Grossman, J. C.; Sinclair, R.; Warner, J. H., Torsional Deformations in Subnanometer MoS Interconnecting Wires. *Nano Lett.* **2016**, *16*, 1210–1217.
- (32) Kumar, P.; Chatterjee, D.; Maeda, T.; Roy, A.; Kaneko, K.; Balakrishnan, V., Scalable Faceted Voids with Luminescent Enhanced Edges in WS₂ Monolayers. *Nanoscale* **2018**, *10*, 16321–16331.
- (33) Wang, S.; Wang, X.; Warner, J. H., All Chemical Vapor Deposition Growth of MoS₂: h-BN Vertical van der Waals Heterostructures. *ACS Nano* **2015**, *9*, 5246–5254.
- (34) Wang, S.; Pacios, M.; Bhaskaran, H.; Warner, J. H., Substrate Control for Large Area Continuous Films of Monolayer MoS₂ by Atmospheric Pressure Chemical Vapor Deposition. *Nanotechnology* **2016**, *27*, 085604.
- (35) Hosokawa, F.; Sawada, H.; Kondo, Y.; Takayanagi, K.; Suenaga, K., Development of Cs and Cc Correctors for Transmission Electron Microscopy. *Microscopy* **2013**, *62*, 23–41.

TOC graphic