Step-By-Step Atomic Insights into Structural Reordering from 2D to 3D MoS$_2$

Heena Inani,* Dong Hoon Shin, Jacob Madsen, HyunJeong Jeong, Min Hee Kwon, Niall McEvoy, Toma Susi, Clemens Mangler, Sang Wook Lee, Kimmo Mustonen, and Jani Kotakoski*

Vertically stacked low-dimensional heterostructures are outstanding systems both for exploring fundamental physics and creating new devices. Due to nanometer-scale building blocks, atomic scale phenomena become of fundamental importance, including during device operation. These can be accessed in situ in aberration-corrected scanning transmission electron microscopy (STEM) experiments. Here, the dynamics of a graphene-MoS$_2$ heterostructure are studied under Joule heating, where the graphene serves as a high temperature atomically thin and electron transparent “hot plate” for the MoS$_2$. Structural dynamics and evolution of the system are shown at the atomic scale, demonstrating that at the highest temperatures (estimated to exceed 2000 K), the continuous 2D MoS$_2$ transforms into separated 3D nanocrystals, initiated by sulfur vacancy creation and migration followed by formation of voids and clustering at their edges. The resulting nanocrystals exhibit predominantly hexagonal shapes with the 2H and hybrid (2H/3R, 3R/TZ) polytypes. The observed morphology of the crystals is further discussed during and after the transformation, as well as their different edge configurations and stability under electron irradiation. These observations of MoS$_2$ at extreme temperatures provide insights into the operation of devices based on graphene/MoS$_2$ heterostructures and ultimately may help device fabrication techniques to create MoS$_2$-based nanostructures, for example, in hydrogen evolution reaction applications.

1. Introduction

Atomically thin 2D materials are finding their way to a number of applications due to their diverse electronic properties as semiconductors, metals, and superconductors. Many of these structures with strong in-plane covalent bonds can be separated from layered bulk crystals by overcoming the weak interlayer van der Waals (vdW) interaction.[1,2] The thus created 2D systems possess properties that differ from their 3D counterparts, and that can be to some extent controlled by choosing the number of layers, their relative stacking order and rotations.[3] Among 2D materials, graphene, the atomically thin carbon structure with a honeycomb-like lattice,[4] is famous for its many unique properties[5,6] and high charge carrier mobility,[7] which makes it an exciting choice for many electronic applications. However, the lack of an intrinsic electronic energy band gap limits its use in semiconductor devices. Fortunately, some transition metal dichalcogenides (TMDs), for which the monolayer consists of one transition metal (M) layer sandwiched between two chalcogen (X) layers (X–M–X), have tunable band gaps in the range of 1–2 eV, which is relevant for devices operated at room temperature.[8] Molybdenum disulfide (MoS$_2$) is so far probably the most studied of the TMDs and has already found use as a catalyst,[9] in energy storage,[10,11] in optical devices,[12] and in flexible electronics.[13] Stacking different low-dimensional materials[8] utilizing vdW forces allows artificial solids to be created in the form of vdW heterostructures. Despite the low binding energy between the layers (typically in the range of tens of meVs per atom), stacking can lead to a...
measurable change in the material properties that range from charge transfer and proximity effects[18] (as also observed in graphene/MoS2 heterostructures[19]) to the alignment and deformation of suspended heterostructures made of hexagonal boron nitride[16] or carbon nanotubes[17] and graphene. Such systems are promising candidates for many potential applications. For example, 2D MoS2/mesoporous carbon and MoS2/graphene nanosheets superstructures could be used as anode materials and for lithium storage in lithium ion batteries.[18]

The atomically thin nature of 2D materials makes them sensitive to external perturbations, which further allows control over their properties through chemical and physical treatments that thus facilitate their use in applications. Indeed, several studies have reported on the manipulation of structural properties of TMDs by phase and defect engineering,[19] functionalization,[20] and surface engineering.[21] However, to fully understand their response in applications, atomically resolved observations under a wide spectrum of environmental conditions are needed, including at least electronic bias, elevated temperatures, and under particle irradiation. In recent times, in situ techniques combining elevated temperatures and electron irradiation have also been explored for nanopatterning of 2D structures (e.g., refs. [22–28]). While mono- and bilayer TMDs have been among the studied structures up to temperatures of 1200 °C,[29,30] their heterostructures and observations at higher temperatures have received less attention. In contrast, graphene encapsulated in hexagonal boron nitride has been shown to sustain high electric biasing and temperatures up to 2800 K,[31] and to emit visible light in a strong electric field.[32] In a recent study, we observed dynamics of polymer residues on suspended graphene that was heated to temperatures up to ≈2000 K by Joule heating, thus showing that graphene can be used as an electron transparent “hot plate” for high temperature electron microscopy experiments.[33]

Here, we report on the structural transformation of a 2D MoS2 monolayer into 3D nanocrystals on the graphene hot plate. In situ two probe measurements were performed at atomic resolution on a graphene/MoS2 heterostructure using the dedicated scanning transmission electron microscopy (STEM) instrument Nion UltraSTEM 100 in Vienna, operated at 60 kV. Low bias voltages up to 2 V (0.68 mA) were applied to remove residue from sample transfer and environmental contaminants from the surface of the sample. At higher bias voltages, we observed the carbon-based contamination partially turning into graphitic layers. Finally, at 3 V (0.53 mA), the initially 2D MoS2 layer gradually transformed into separated 3D nanocrystals via sulfur vacancy creation and migration, void formation and crystallite growth at the edges of the material and the voids. Although structural changes in MoS2 upon heating have been reported before, the complete 2D to 3D transformation at the highest temperatures allowed by the graphene hot plate is here reported for the first time. The observed nanocrystals exhibit different shapes, thicknesses and polytypes, of which 2H hexagon-shaped structures are the most common ones. However, we also found heterophase crystals containing, for example, mixed 3R/TZ and 2H/TZ polytypes, where TZ stands for transitional zone structure. Of the found structures, the 3R polytype was found to be sensitive to electron irradiation at 60 keV electron energy. Overall, our results improve the understanding of MoS2 structural integrity under extreme conditions and provide insight into nanofabrication techniques that might be beneficial, for example, for catalysis applications.

2. Results and Discussion

2.1. Device Fabrication and In Situ Measurements

The graphene/MoS2 heterostructure was fabricated by two consecutive wet transfer steps from exfoliated graphene and MoS2 grown via chemical vapor deposition (CVD). For in situ electrical measurements, atomic-resolution STEM imaging was conducted on electrified TEM supports from Protochips Inc. The chip consisted of an array of a total of nine 5 μm holes etched through a silicon nitride membrane, and four contact electrodes. The heterostructures were sandwiched between the electrodes by first depositing Au contact pads on the heterostructure and finally placing the entire assembly on top of the existing pads on the chip. A schematic representation of the device fabrication steps is shown in Figure S1 (Supporting Information). The STEM instrument was operated at 60 kV to minimize irradiation-induced damage in the sample. Figure 1a,b show low-magnification bright field images of the device and the heterostructure, respectively. STEM medium angle annular dark field (MAADF) image of the heterostructure is shown in Figure 1c with the corresponding Fourier transform (FT) shown in the inset.

MoS2 exhibits a number of phases and polymorphs, depending on intralayer and interlayer arrangement of Mo and S atoms (see Figure S2 in the Supporting Information), each with their own characteristic properties. The most common phases are semiconducting 1H, metallic 1T and semimetallic 1T'. In 1H and 1T phases, S–Mo–S layers are arranged in ABA and ABC stacking, respectively. 1H, the most stable one under normal conditions, can be transformed into 1T by sliding one of the S layers along the armchair direction. 1T', however, is thermodynamically unstable at room temperature and turns into the distorted 1T' that has a lower symmetry. Upon stacking, MoS2 layers can form different polymorphs, the most common of which are 2H and 3R that are formed from differently stacked 1H layers. Additionally, a transitional zone (TZ) configuration can be formed through sliding of the layers. Apart from the basal plane, edges, line defects and grain boundaries in TMDs are known to give rise to properties that differ from those of the perfect material. For example, grain boundaries in WS2 behave as conducting channels[34] while MoS2 edges are catalytically active toward the hydrogen evolution reaction.[35]

All surfaces exposed to the ambient environment become over time buried under a certain amount of impurities. These typically contain at least water and hydrocarbon molecules adsorbed from the atmosphere but can also contain residues from sample transfer, as is the case here. When two 2D materials are brought in contact to create a van der Waals heterostructure, the weakly bound surface contaminants are squeezed into pockets or bubbles between the atomic layers.[36] For an example, see Figure 1c. Additionally, as-prepared MoS2 invariably contains sulfur vacancies as shown by line profiles in Figure S3 (Supporting Information), and occasionally also antisite defects (not visible in the presented image).

2.2. TMD Edge Evolution and Growth of Graphitic Nanostructures

At first, few cycles of low bias voltage (0–2 V) sweeps were applied across the sample to clean the surface while observing
the interface under simultaneous effect of electron irradiation and Joule heating. Graphene can sustain very high current densities resulting in a significant increase in temperature, that may through defect recombination even improve its structural quality.\[37\] The total of 1.6 mW (3 V, 0.53 mA) of power dissipated at 67.5 mm² of graphene results in a power density of $2.4 \times 10^7$ W m⁻², leading to evaporation and migration of contaminants on its surface. Note that since the MoS₂ does not span the whole distance between the electrodes, we assume that Joule heating takes place mainly in graphene, which then transfers some of the heat to the MoS₂ similar to a hot plate. As shown here, in the MoS₂ layer on top of the graphene, heating results in the creation of sulfur vacancies within the basal plane and restructuring of the edge of the material.\[38\] Upon increasing the maximum bias to 2.3 V (Figure 3), a nanopore is created within the MoS₂ basal plane. After this point, the pore grows while new pores are simultaneously created. Meanwhile, changes at the MoS₂ edges start to become more apparent. While at lower voltages uniform disordering of the edge was the most prominent feature, at higher bias small clusters appear at the edge of the material and the pore. This is in agreement with earlier studies\[39\] reporting vacancy agglomeration and void

---

**Figure 1.** Graphene/MoS₂ heterostructure device. a) Device structure, a hole with graphene and MoS₂ is marked with a white circle. b) Suspended area of the heterostructure. The yellow dashed line shows the edge of the MoS₂ flake. c) Higher magnification image of the edge area, with the inset showing the corresponding FT with graphene (green) and MoS₂ (yellow) peaks marked with hexagons. White arrow points at an example of the contamination bubbles discussed in the text. d) Further magnification of the MoS₂ edge. e) Atomic-resolution image of clean graphene recorded at the position of the red rectangle in panel (d). f) Atomic-resolution image of MoS₂ recorded at the position of the yellow rectangle in panel (d). g) The I–V response of the system at low bias voltages. STEM images in panels (a) and (b) were acquired with the Ronchigram camera and those in panels (c)–(f) using the MAADF detector.
expansion in MoS$_2$ at high temperatures. The MoS$_2$ structure shrinks throughout the experiment through edge atom evaporation and transformation, a process which appears to accelerate upon increasing the maximum voltage. At 2.7 V, the edge configuration transforms from the Mo-ZZ into 1T$'$-like and Klein-like structures. The Mo agglomeration that is observed in the top part of the image is also indicated with the arrows. Finally, at 3 V, the remainder of the MoS$_2$ island breaks apart, which happens much faster than our image acquisition rate, and only individual clusters remain on the graphene support.

The hydrocarbon contamination supported on graphene turned into graphitic structures outside the area covered by the MoS$_2$ layer as can be seen in Figure 4a–d. This is similar to what has been reported earlier by others$^{[40,41]}$ but in contrast to our own earlier experiments.$^{[33]}$ The reason for this discrepancy is not entirely clear, but one possible explanation is the greater extent of amorphous contamination on heterostructure samples as compared to graphene. Moreover, there exists a temperature gradient on the sample that originates from its geometry, which leads to different observed dynamics at different parts of the sample. For example, cleaning effects and structural transformations are predominantly observed at the center and upper part of the suspended area, which thus implies respectively higher temperature. This is apparent, for example, in the overview (composite) image shown in Figure 4e. The overview image was constructed from several 2048 × 2048 nm$^2$ images taken by mapping the entire sample area. The $I$–$V$ characteristics (in Figure 4f) show linear behavior up to $\approx$1.5 V, beyond which the current saturation indicates a significant heating of the graphene support.

2.3. 2D to 3D Transformation

After the sudden disintegration of the 2D MoS$_2$, the remaining nanocrystals show a variety of thicknesses, phases and polymorphs. Based on the structural changes observed before this event, it appears that the crystals form due to the combined effect of edge evaporation and thermal migration of edge atoms onto the basal plane. Importantly, these transformations happen everywhere on the sample, and not just under the electron beam, indicating that the process is thermally
activated and independent of the electron irradiation. Based on numerical simulations, we estimate that the temperature of the graphene support could reach up to 2800 K at around 3 V.

Figure 3. a–h) Pore formation and edge evaporation during I–V sweeps up to 3 V. STEM-MAADF images showing the appearance and growth of nanopores and Mo agglomeration at the edges with the MoS$_2$ layer shrinking as the experiment proceeds. White arrows mark nanopore and edge evaporation. The highest applied bias voltage is marked in the respective panels. Yellow arrow marks an individual crystal in panel (h).

Figure 4. Graphitization of carbon-based contamination. a–d) STEM-MAADF image series down to atomic resolution showing graphitic nanostructures that have formed from the carbon-based contamination. e) STEM-MAADF overview image of the suspended area displaying cleaner and more contaminated areas after a voltage sweep to up to 2.5 V. Composite image of several 2048 × 2048 nm$^2$ images. f) Corresponding I–V characteristics.

Figure 5a–d shows an overview and high-magnification STEM-MAADF images of the crystals formed in the top part of the sample with the highest temperature. The less affected
(lower) part comprises of linearly arranged features that could again be associated with out-of-plane distortion of the structure. At this point, also the native pores along MoS$_2$ grain boundaries\cite{42} have become decorated with nanocrystals (Figure 5g,h), similar to all other edges of the MoS$_2$. Recently\cite{30} in situ formation of heterointerfaces in bilayer MoS$_2$ was reported through sculpting, etching and folding of the material under the combined effect of high temperature and electron irradiation. While we also observed such dynamics, we focus here rather on the morphology and growth of the nanocrystals. To understand the dynamics of the nanocrystal formation, we chose one island with a size of ~30 nm (Figure 6), which comprises mixed edge configurations including Mo-ZZ, Mo-Klein, and 1T$'$-like edges and sulfur vacancies within its 1H basal plane. Figure 6a shows a STEM-MAADF image series during the step-by-step formation of nanocrystals from this island under the combined effect of electron irradiation and heat. Each frame was recorded after a bias sweep up to maximum bias voltages between 2.3 and 2.7 V. Initially, edge distortions form and expand, followed by the appearance of sulfur vacancies, while Mo atoms appear to agglomerate into crystallites near the pore edges. Folding is also apparent at some parts of the edges as is the appearance of line-like features and along grain boundaries (Figure 5).

![Figure 5](image1.png)

**Figure 5.** Nanocrystal formation at MoS$_2$ edges and line-like features. a–d) STEM-MAADF images of nanocrystals at the edges in the high-temperature area of the sample. e–h) STEM-MAADF images of line-like features and along a grain boundary in the lower-temperature area.

![Figure 6](image2.png)

**Figure 6.** Transformation of a 2D MoS$_2$ island into 3D nanocrystals. a) STEM-MAADF image series of the step-by-step transformation due to repeated voltage sweeps to up to 2.3–2.7 V. b) Different configurations of the edge of the island at the location marked with the yellow rectangle in the first frame of panel (a). c) Shape distribution of the individual freely dispersed crystals on graphene. d) Area distribution of freely dispersed hexagonal crystals.
of nanovoids inside the island. During the experiment, one of the observed voids notably expands, apparently facilitated by edge evaporation, while another void starts to form. The process continues until the island completely disappears and only individual crystalline structures remain randomly dispersed on graphene (Videos are available as the Supporting Information). The recurrence of emerging crystal shapes are compared in Figure 6c, revealing the predominance of hexagonal edges. The size distribution with a mean area of ≈16.57 nm² is shown in Figure 6d.

In Figure 7, we present STEM-MAADF/HAADF images of a selection of nanocrystals that have grown at the edges of MoS₂. For interpretation of the experimental data, simulated STEM images of different MoS₂ phases and polymorphs are shown below (Figure 7i–l). Although the actual atomic scale dynamics are too fast to be recorded at our experimental time resolution, the intermediate structures between the initial, continuous 2D and the final dispersed 3D crystals can provide insights into the 2D to 3D transformation. In general, there are three possible ways for the crystals to be created on top of the island: 1) through migration of edge atoms on top of the island where they can become trapped at defect sites on the basal plane and thus nucleate inward growth; 2) through migration along the edge, where crystallites can nucleate outward growth at edge defects; 3) through folding of the edge on top of itself. Of the selected crystals, especially the one shown in Figure 7a could have formed through inward growth, whereas the one in Figure 7b appears as a folded edge. While some of the crystals (e.g., Figure 7c,d) have the appearance of outward growing crystals, we believe that they have also resulted from inward growth, since we never observed crystals that would have formed outside the original perimeter of the initial MoS₂ island. Independent of the actual formation mechanism, which depends sensitively on migration barriers as well as surface and edge energetics,[43,44] it is interesting to note that the crystals exhibit a number of different shapes, edges, phases and polymorphs. For instance, Figure 7a shows a nearly triangular structure that has formed at a Mo-ZZ edge of the 1H lattice, and has itself Mo-ZZ and S-Klein-like edges. In contrast, Figure 7b shows a polygonal crystal with a sulfur terminated edge that has formed at a S-Klein-like edge. Figure 7c,d shows two further examples of triangular crystals that extend outward at 1T'-like edges and exhibit 2H and 3R polymorphs, respectively. Finally, some of the crystals contain more than one polymorph or phase, such as the heterophase 3R/TZ and 2H/TZ crystals seen in Figure 7e,f, respectively. After the crystals become free from the host 2D structure, they become predominantly hexagon-shaped (as discussed earlier), such as the crystal shown in Figure 7g. Since the crystal orientations appear random with respect to graphene (see the composite FT in inset of Figure 7g), we assume that graphene serves merely a supporting role for the crystals with little influence on their structure. The composite FT was constructed by FT of the crystal and FT of monolayer graphene and MoS₂ areas to compare the orientation of crystal with respect to graphene and MoS₂. Note that although the
2H phase crystals are stable when irradiated with 60 keV electrons and graphene remained largely unchanged throughout the previous experimental steps, thus implying that both the contacts and graphene remained largely unchanged throughout the experiment (see Figure 7h). Finally, we also explored the electron beam stability of the formed crystals. While the most common 2H phase crystals are stable when irradiated with 60 keV electrons, the 3R polymorph is not, as can be seen in Figure S5 (Supporting Information). The likeliest explanation is a combination of electronic excitations and knock-on damage\cite{45,46} (Supporting Information). The final crystals predominantly show hexagonal patterns are partially evaporated and partially transformed into the crystal turns into a disordered structure. The different structures created during the process are stable over experimental time scales, which indicates that they will not change due to thermal activation after the voltage swipes. We believe that all structural changes that we observe during imaging are caused by electron irradiation, which is not present in typical applications. Hence, it can be expected that if processing parameters (maximum bias voltage, duration of the sweep) can be optimized for creating specific structures, those structures will also remain stable in applications.

3. Conclusion

In summary, in situ STEM electrical measurements were performed on graphene/MoS2 heterostructures to explore structural dynamics in MoS2 at (estimated) temperatures up to 2800 K. Using a Joule-heated nearly electron transparent graphene “hot plate,” we demonstrate the transformation of a 2D TMD layer into dispersed 3D nanocrystals. Heating leads to the appearance of vacancies, line defects and out-of-plane distortions in the basal plane of MoS2, whereas carbon-based contaminants are partially evaporated and partially transformed into graphitic structures. The defective MoS2 layer further evolves into a structure containing nanovoids and nanocrystallites at its edges before breaking into freely dispersed nanocrystals that have varying shapes, sizes, edge structures, phases and polymorphs. The final crystals predominantly show hexagonal-like structures with most common and stable 2H polytype and mixed edge structures. While most nanocrystals were stable under typical electron irradiation required for imaging, heterophase crystals tend to transform under the electron beam, especially at the 3R areas. This study provides the first insights into in situ 2D to 3D transformation in the electron microscope, paving the way toward new nanofabrication techniques for 2D materials for applications in catalysis and other fields.

4. Experimental Section

Material Synthesis and Device Fabrication: First, graphene/MoS2 heterostructure with two Au electrodes was fabricated on a SiO2/Si substrate by standard e-beam lithography, evaporation, and wet transfer methods. To begin with, monolayer graphene and MoS2 were obtained on SiO2/Si substrate by mechanical exfoliation and chemical vapor deposition,\cite{47} respectively. Graphene substrate was coated with polymethyl methacrylate (PMMA) and left into a KOH solution to etch the oxide layer. Then, PMMA/graphene layer was separated, transferred onto MoS2, and soaked into acetone for 1 h to dissolve the PMMA. To fabricate Au electrodes, a stencil mask was placed on the heterostructure and gold was evaporated using e-beam evaporation.

For device fabrication, an assembly with the as-fabricated heterostructure with Au electrodes was transferred onto a customized electrical chip from Protochips Inc. using the typical PMMA wet transfer method. The PMMA was spun on assembly, heated at 180°C for 2 min and soaked into KOH solution to etch the substrate. Then, PMMA layer/assembly was transferred onto the electric chip so that the fabricated electrodes overlapped with the ones already existing on the chip. Finally, PMMA was dissolved by soaking the chip in acetone and isopropanol for 6 h, leaving the heterostructure sandwiched between electrodes. To prevent the structure from collapsing, a critical point drying process was used.

STEM Imaging and In Situ Measurements: An aberration corrected STEM instrument, Nion UltraSTEM 100 in Vienna, was operated at 60 kV to minimize irradiation-induced damage, with sample in near ultrahigh vacuum conditions (2 × 10−6 Pa). Images were acquired using both medium and high angle annular dark field (MAADF/HAADF) detectors. The MAADF detector (60–200 mrad) provides better signal-to-noise ratio especially with light elements and allows imaging both materials, whereas HAADF (80–300 mrad) was mostly used to image relatively thick nanocrystals. For image acquisition, dwell times of 8–16 μs and 1024 × 1024 pixels were used. The convergence semiangle of the electron probe was 30 mrad.

The in situ two-probe electrical measurements were performed using the Nion electron cartridge with an inset from Protochips inc. The microfabricated chip consists of four electrodes on a SiN window with a 3 × 3 array of 5 μm holes. Additionally, fabricated electrodes were used to enhance the contact with the suspended heterostructure. The current–voltage characteristics were measured by applying the voltage across adjacent electrodes in the range of 0–3 V.

Image Processing and Image Simulation: ImageJ was used for postprocessing of images. A Gaussian blur filter of 1–3 pixels was applied to STEM MAADF/HAADF-images to reduce the noise and to highlight the atomic structure. The mpl-virdis look-up-table was applied to ease the visualization of the images. Unprocessed images are shown in the Supporting Information.

STEM image simulations were carried out using the multislice method with the abTEM library\cite{48} with a spherical aberration coefficient of 1 μm, energy spread of 0.48 mrad and MAADF/HAADF detector angles set to the experimental ranges. The illumination semiangle was set to 30 mrad. Atomic models were created with the atomic simulation environment (ASE) and visualized with VMD.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

J.K., H.I., and K.M. acknowledge the support from Austrian Science Fund (FWF) project 13181-N36, and K.M. further by the Finnish Cultural Foundation through a grant from the Finnish Postdoc Pool. J.M. and T.S. acknowledge funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (Grant Agreement No. 756277-ATMEN). D.H.S., H.J.J., M.H.K., and S.W.L. were supported by the International Collaboration Program - National Research Foundation of Korea (NRF-2016K2A9A1A03-905001), and the Basic Research Program - National Research Foundation of Korea (NRF-2019R1A4A1029052, NRF-2019R1A2C1085647). H.I. further extends the acknowledgement for the support from Vienna Doctoral School in Physics. The supporting information file was updated on March 24, 2021, after initial online publication.
