

Supplementary Information for
**Defect-assisted reversible phase transition in mono- and
few-layer ReS₂**

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STEM experiments and simulations of ML and BL ReS₂

Details of the experimental procedure

The ADF STEM collection angle range of 65-146 mrad produces Z-contrast images [S1; S2; S3] where primarily the Re atom positions are visible while the S positions are invisible. Other collection angles more suitable for light-element imaging, such as annular bright field STEM imaging [S4], yielded poor results due to the signal from the SiN support.

The accelerating voltage of 200 keV was selected because lower voltages made it more difficult to achieve sufficient atomic contrast of the Re atoms above the SiN support background intensity. The accelerating voltage of 200 keV is above the known knock-on threshold energy for sulfur vacancy generation in TMD materials [S5]. However, the 44 picoampere (pA) probe current and 4-32 $\mu\text{s}/\text{pixel}$ dwell times were sufficient to image ReS₂ before significant structural damage occurred. These beam conditions enabled the observation of both the initial undamaged atomic structure and the dynamic evolution of the atomic structure as sulfur vacancies were generated.

For PACBED experiments, an accelerating voltage of 80 keV was beneficial for two primary reasons. First, it minimized damage to the sample and enabled long PACBED exposure times, which were required to reveal the weak ML and BL diffraction signals above the noise level. 80 keV is slightly above the knock-on damage threshold for most TMD materials [S5], but subsequent PACBED acquisitions of the same area showed no signs of a changing structure and damage. Second, lowering the accelerating voltage increases the Bragg scattering angles of the ReS₂ diffraction signals. This effectively separates the diffraction discs, causes less disc overlap, and makes it easier to identify PACBED patterns from different phases. PACBED patterns were acquired by scanning the STEM beam over a 10-20 nm² area for 300 s while continuously acquiring the diffraction pattern. This acquisition technique enables a sufficient sampling and position-averaging of probe positions over the structure to produce high-quality PACBED patterns, as well as distributes the electron dose over a larger area to minimize sample damage. To see the ML and BL ReS₂ PACBED patterns more clearly, careful corrections of the dark signal and SiN support signal were manually performed. The dark-signal was corrected by subtracting a reference dark pattern that was acquired directly after the ReS₂ PACBED pattern. The SiN support adds a diffuse amorphous signal to the PACBED pattern. This SiN support signal was removed by subtracting a reference pattern that was acquired from only the SiN support near the flake. The dark and SiN reference patterns were acquired with the same acquisition parameters as the ReS₂ patterns. The resulting PACBED patterns were binned by 4 $\times$ 4 pixels to enhance the signal-to-noise ratio and gain more clarity in the diffraction signals.

The ADF STEM image shown in Figure 2a (main text) is a single-pass STEM image acquired with a size of 1024 $\times$ 1024 pixels, a dwell time of 32 $\mu\text{s}/\text{pixel}$, a pixel size of 0.039 nm/pixel, a flyback time of 500 μs , and a total electron dose of $6\times 10^4 \text{ e}^{-1}\text{\AA}^{-2}$. All of the doses reported in this publication include the dose associated with the line flyback time. The template-matched average image shown in the lower left inset image of Figure 2a (main text) is the average of 3195 template images from within Figure 2a. The template images that were selected for the averaging were determined using an in-house written IGOR Pro script that locates the maxima in the normalized cross-correlation between a user-selected input template image and all other possible template images (see Figure S1 for more details).

The ADF STEM images shown in Figure 2c (main text) are sub-regions extracted from a single-pass STEM image that was acquired directly after a higher magnification image series which damaged the ML. The single-pass image is shown in Figure S2 and was acquired with a size of 1024 $\times$ 1024 pixels, a dwell time of 64 $\mu\text{s}/\text{pixel}$, a pixel size of

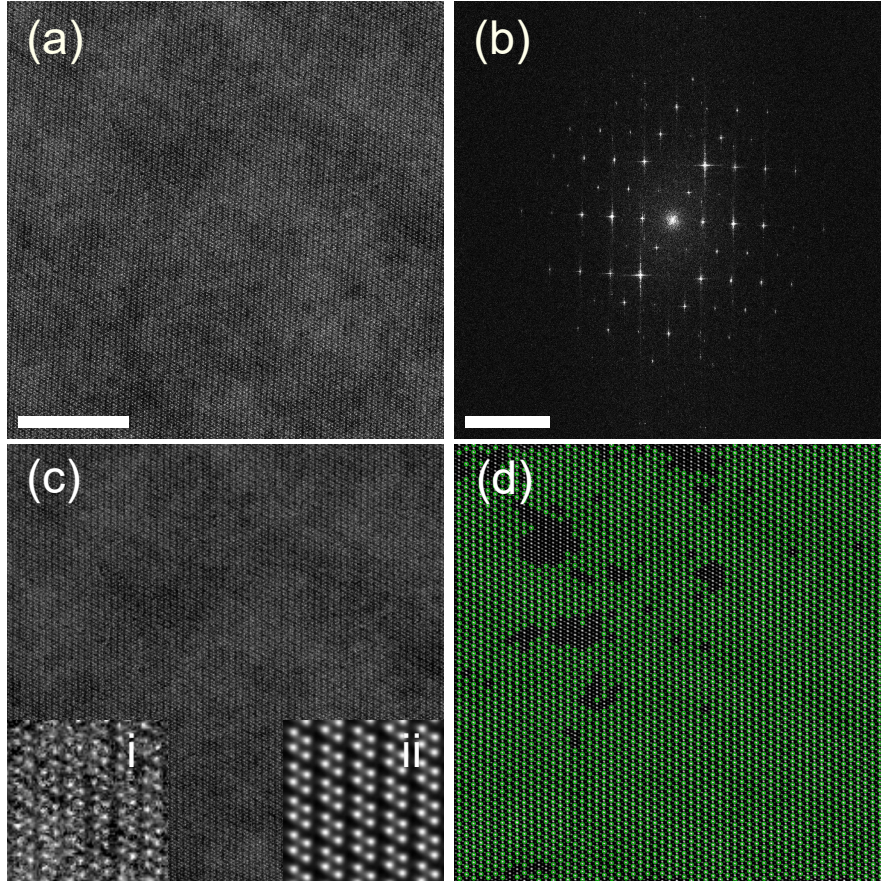


Figure S1: Experimental ADF STEM of undamaged ML ReS₂. (a) Raw experimental ADF STEM image of ML ReS₂. (b) Fast Fourier transform (FFT) of (a). The scale bars in (a) and (b) are 10 nm and 5 nm⁻¹, respectively. (c) The same image as (a) that has been rotated and cropped to align one crystallographic axis to the y -image axis. (c) is shown in Figure 2a and was used as the input image for template matching averaging. (c.i) The user-selected input template image is a cropped sub-region of (c). The green circles in (d) mark the 3195 normalized cross-correlation peaks that were selected as the set of maximum peaks used for producing the final averaged template image. The maximum peaks were identified using an in-house written IGOR Pro script that utilizes thresholding of the normalized cross-correlation image. (d) Normalized cross-correlation image between (c.i) the user-selected input template image and all possible template images of the same size in (c). (c.ii) The final averaged template image that was produced by averaging the set of selected template images identified in (d).

0.048 nm/pixel, a flyback time of 500 μ s, and a total electron dose of 7.6×10^4 e⁻¹Å⁻². Figure S2 also shows the locations of the cropped images displayed in Figure 2c (main text) and their associated FFTs, which further show the changes in atomic structure and orientation. The higher magnification image series that damaged the ML is shown SI Movie 2 and was acquired at the center of the single-pass image shown in Figure S2. The image series was acquired with 100 frames, a size of 512×512 pixels, a dwell time of 16 μ s/pixel, a pixel size of 0.02 nm/pixel, a flyback time of 500 μ s, and a total electron dose of 1.2×10^7 e⁻¹Å⁻². An additional ADF STEM image series that reveals the dynamics of the structural changes caused by electron irradiation is shown in SI Movie 1. It was acquired with 100 frames, a size of 1024×1024 pixels, a dwell time of 4 μ s/pixel, a pixel size of 0.016 nm/pixel, a flyback time of 500 μ s, and a total electron dose of 4.8×10^6 e⁻¹Å⁻². The series displayed in SI Movie 1 was spatially binned by 4×4 pixels and smoothed with a 3×3 pixel Gaussian to improve the signal-to-noise ratio and enhance

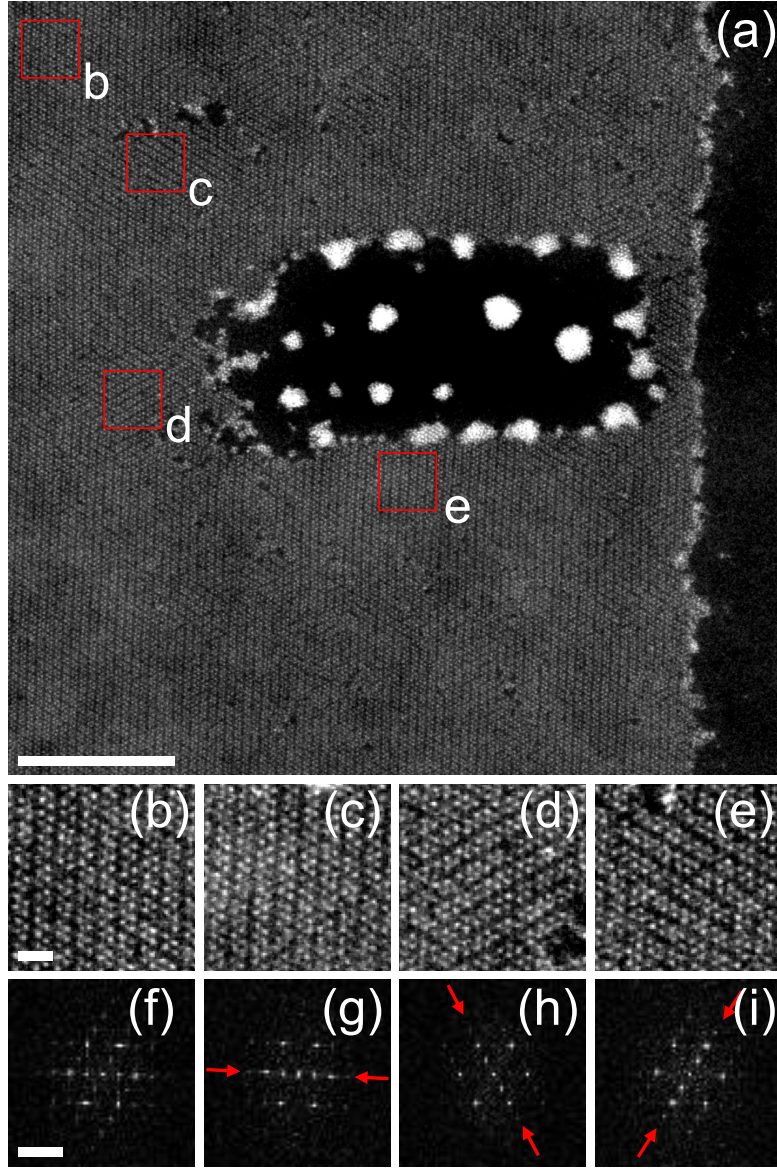


Figure S2: STEM imaging of electron irradiated ML ReS₂. (a) A single-pass ADF STEM image of damaged ML ReS₂ that was used to produce the cropped images displayed in Figure 2c. This image was acquired directly after a higher magnification STEM image series (SI Movie 2) was acquired at the center of (a) that damaged the ML ReS₂. (b-e) Cropped regions from (a) marked by the indicated red squares. (f-i) Fast Fourier transform (FFT) of (b-e), respectively. The ADF STEM image in (b) is of undamaged ML ReS₂ and is consistent with the expected atomic structure of the 1T'' phase (see Figure 2a and Figure S3). The associated FFT in (f) is also consistent with the FFT from undamaged 1T'' ReS₂ (see Figure S1b). The damaged ML ReS₂ shown in (c-e) appears to have only one distortion axis and therefore has lost one distortion axis compared to the the undamaged double distorted 1T'' phase. Furthermore, the single distortion axis appears to have three possible orientations, each of which is rotated by 60° about the c-axis. The FFTs in (g-i) are different than the undamaged 1T'' FFT in (f), and also reveal the 60° rotation between the orientations, as indicated by the red arrows. The scale bars in (a), (b), and (f) are 10 nm, 1 nm and 5 nm⁻¹, respectively.

the visibility of the atomic structure.

The ADF STEM image shown in Figure 2d (main text) is an average of an image time series that was non-rigidly registered [S6] to correct the effects of the microscope, sample, and environmental instabilities. The image series was acquired with 50 frames, a size of 512×512 pixels, a dwell time of $8 \mu\text{s}/\text{pixel}$, a pixel size of $0.04 \text{ nm}/\text{pixel}$, a flyback time of $500 \mu\text{s}$, and a total electron dose of $7.9 \times 10^5 \text{ e}^{-1} \text{ \AA}^{-2}$. The non-rigidly registered and a temporally binned version are shown in SI Movies 3 and 4, respectively. These movies, in combination with Figure S4, show that negligible structural damage was caused by the electron irradiation. The template-matched average image shown in the lower left inset image of Figure 2d is the average of 843 template images from within Figure 2d that were determined using the same process discussed above for Figure 2a (see Figure S5 for more details).

The ADF STEM images shown in Figure 2f are sub-regions extracted from frames of an image time series that damaged the bilayer. The total image series is composed of two separate consecutively acquired image series of the same sample area, each of which were acquired with 50 frames, a size of 512×512 pixels, a dwell time of $16 \mu\text{s}/\text{pixel}$, a pixel size of $0.0395 \text{ nm}/\text{pixel}$, a flyback time of $500 \mu\text{s}$, and a total electron dose of $1.5 \times 10^6 \text{ e}^{-1} \text{ \AA}^{-2}$. Each image series was non-rigidly registered [S6] to correct the effects of the microscope, sample, and environmental instabilities. Both series were temporally binned by 5 frames to improve the signal-to-noise ratio and the visibility of the structural changes, producing image series with 10 frames. The images shown in Figure 2f (main text) are extracted regions from (i) frame 1 of 10 in series 1, (ii) frame 10 of 10 in series 1, (iii) frame 4 of 10 in series 2, and (iv) frame 10 of 10 in series 2. These 4 images have been smoothed with a 3×3 pixel Gaussian to improve the signal-to-noise ratio and enhance the visibility of the atomic structure. The non-rigidly registered image series are provided in SI Movie 5-6 and the temporally binned image series are provided in SI Movie 7-8.

ADF STEM and PACBED simulations were calculated using the frozen phonon multislice algorithm implemented in the GPU-accelerated software Prismatic 2.0 [S7]. DFT relaxed atomic models of the different ML and BL phases were used as input structures for the calculations. All calculations utilized root-mean-square displacements of $0.045 \text{ \AA}$ and $0.077 \text{ \AA}$ for the Re and S atoms, respectively. ML ADF STEM image simulations were performed with an accelerating voltage of 200 keV , a STEM probe convergence half-angle of 26.69 mrad , 10 phonon configurations, atomic models with a size of around $150 \text{ \AA} \times 150 \text{ \AA}$, a potential space sampling of $0.04 \text{ \AA}$, an ADF detector range of $50\text{-}155 \text{ mrad}$, and a probe step size of $0.1 \text{ \AA}$. ML PACBED simulations were performed with an accelerating voltage of 80 keV , a STEM probe convergence half-angle of 6.35 mrad , 10 phonon configurations, atomic models with a size of around $150 \text{ \AA} \times 150 \text{ \AA}$, a potential space sampling of $0.05 \text{ \AA}$, and a probe step size of around $1.6 \text{ \AA}$, which is sufficient for Nyquist sampling. Bilayer ADF STEM image simulations were performed with an accelerating voltage of 200 keV , a STEM probe convergence half-angle of 26.69 mrad , 10 phonon configurations, atomic models with a size of around $50 \text{ \AA} \times 50 \text{ \AA}$, a potential space sampling of $0.03 \text{ \AA}$, an ADF detector range of $50\text{-}155 \text{ mrad}$, and a probe step size of $0.05 \text{ \AA}$. Bilayer PACBED simulations were performed with an accelerating voltage of 80 keV , a STEM probe convergence half-angle of 6.35 mrad , 30 phonon configurations, atomic models with a size of around $100 \text{ \AA} \times 100 \text{ \AA}$, a potential space sampling of $0.1 \text{ \AA}$, and a probe step size of around $1.6 \text{ \AA}$, which is sufficient for Nyquist sampling.

Description of electron microscopy supplementary figures

Figure S1 shows ADF STEM data from unperturbed ML ReS_2 that provides evidence the starting phase is $1\text{T}''$. Figure S1a is a single-shot ADF STEM image and is the

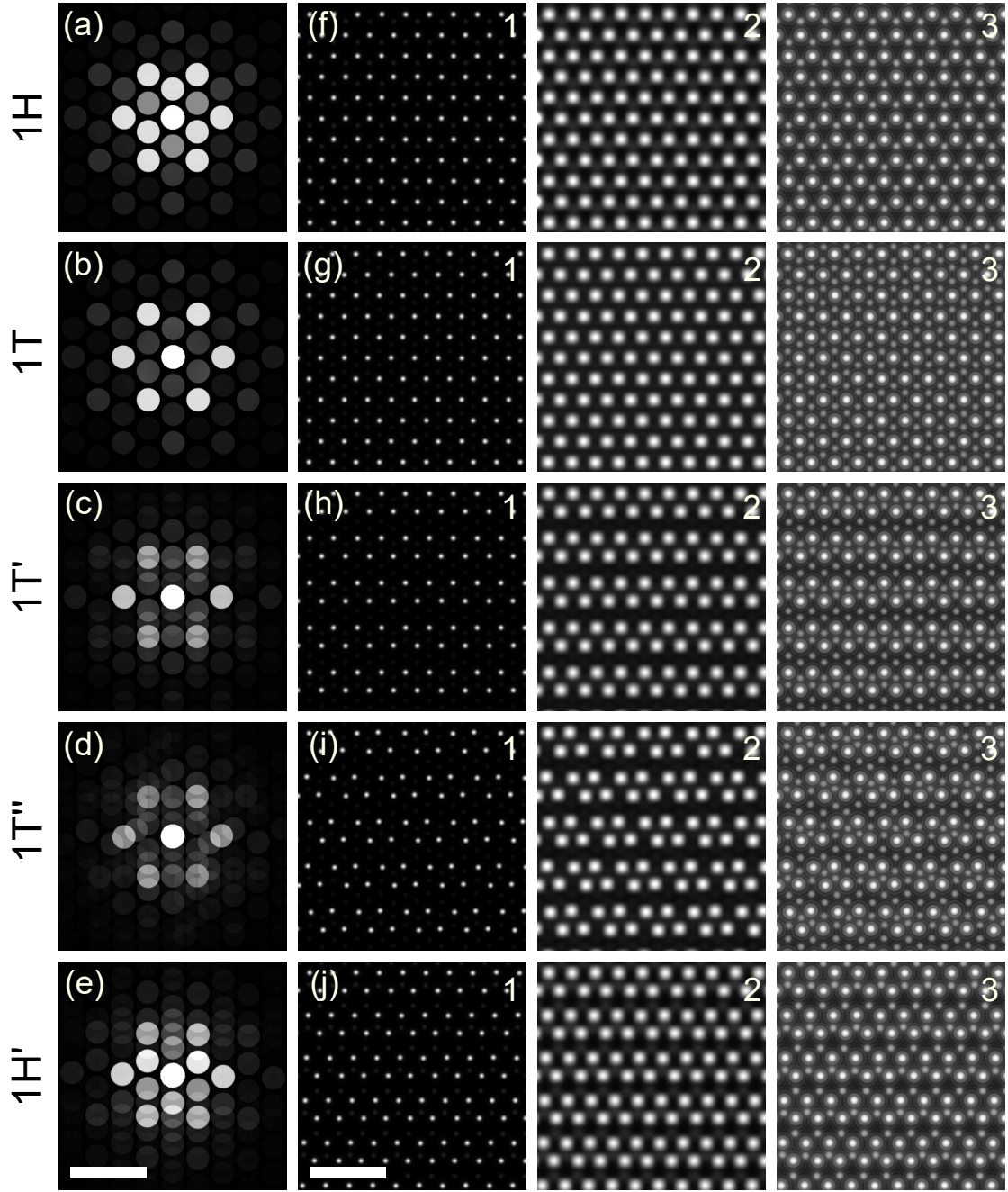


Figure S3: Simulated ADF STEM and PACBED of ML ReS_2 phases. (a-e) Simulated PACBED patterns using 80 keV electrons for 5 different monolayer ReS_2 phases. The scale bar in (e) is $1 \text{ \AA}^{-1}$ and is true for (a)-(e). (f1-j1) Simulated ADF STEM images using 200 keV electrons for 5 different monolayer ReS_2 phases. (f2-j2) The same simulated ADF STEM images in (f1-j1) that have been convolved with a 19 pixel wide Gaussian function in order to more closely match the experimental spatial resolution. (f3-j3) The same simulated ADF STEM images in (f1-j1) on a log intensity scale in order to clearly see the weak intensity from the S atoms. The S atoms are not resolvable in experiments, but if they were resolved they could be used to directly distinguish phases that are not distinguishable from only the Re positions in the ADF STEM images. The scale bar in (j1) is 1 nm and is true for all ADF STEM images. Rows 1 – 5 are for the 1H, 1T, 1T', 1T'', and 1H' phases, respectively.

first exposure of electrons to this area of the sample. No obvious electron irradiation damage is present in the image. However, subsequent images would show evidence of electron beam-induced damage. Figure S1b is a Fast Fourier transform of (a), which is later used in combination with Figure S2 to help identify a phase transition in ML ReS₂ using ADF STEM images. Figure S1c is a rotated and cropped version of (a) which was used for the template matching analysis discussed below and in the methods section. Figure S1(c.i) and (c.ii) are the input template image and final average template image, respectively. The final average template image in Figure S1(c.ii) was produced by averaging 3195 unique template images within Figure S1c. The positions of these 3195 template images are marked by the green circles in the normalized cross-correlation image shown in Figure S1d. These positions were identified by thresholding the normalized cross-correlation image. It is important to note that it was crucial to threshold the normalized cross-correlation image so that only the largest intensity peaks were identified. If lower intensity peaks were included, the template matching analysis produces erroneous results that lead to the wrong phase identification. By comparing the averaged template matched image in Figure S1(c.ii) and Figure 2a to the simulated ADF STEM images of the five possible ML ReS₂ phases in Figure S3(f-j), it is clear the starting phase is 1T''.

Figure S2 shows ADF STEM data of ML ReS₂ after it has been irradiated with the electron beam during an image series (SI Movie 2) that was acquired at higher magnification near the center of (a). The area that was imaged during SI Movie 2 is identifiable at the center of Figure S2a from the loss of 2D crystallinity and the presence of Re nanoparticles. Outside but in the vicinity of this heavily damaged area, there is evidence of additional electron irradiation damage, such as vacancy clusters and a change in the 1T'' starting phase. To highlight this change in phase, Figure S2(b-e) show cropped and magnified regions of (a), as indicated by the labels in (a). Panel (b) is from a region far away from the electron irradiated area, and still exhibits the 1T'' initial phase. Panels (c-e) are from regions closer to the electron irradiated region, and they each exhibit a change from the 1T'' phase to a single distorted phase. The distortion axis in (c), (d), and (e) are each oriented 60° from the others, displaying the three possible in-plane orientations of the single distorted phase. To provide more evidence for this phase change, a Fast Fourier transform (FFT) analysis was conducted on these cropped regions. (f-i) are the FFT of images (b-e) respectively. The FFT shown in (f) is consistent with the FFT of the 1T'' starting phase in Figure S1b, despite the reduced quality of (f) caused by the limited image size and number of pixels in (b). The FFTs in (g-i) show differences compared to (f) (and Figure S1b), indicating a structural change. (g-i) also reveal the 60° in-plane rotation of the single distorted phase orientation, as marked by the red arrows.

Figure S3 shows simulated PACBED and ADF STEM data of ML ReS₂. Five possible ML ReS₂ phases are included in our analyses: 1H, 1T, 1T', 1T'', and 1H'. Details about the simulations are included earlier in the SI. Each of the 5 PACBED patterns from the 5 considered phases in Figure S3(a-e) are unique and distinguishable from one another, enabling the unique classification of phase from a PACBED pattern. This allowed the identification of the 1T'' phase of ML ReS₂ from the experimental PACBED pattern (Figure 2b). The identification of ML phase from ADF STEM images is more nuanced. Because the ADF STEM images are dominated by Z-contrast and only the Re atom positions are visible in experimental images, some of the phases are indistinguishable from ADF STEM images while others are uniquely distinguishable. For example, the 1H and 1T ADF images, and the 1T' and 1H' images are almost indistinguishable when looking at the contrast from only the Re atom positions (columns 1 and 2). Fortunately, the 1T'' phase is uniquely distinguishable from the other four phases under normal ADF STEM image contrast. This fact allowed the 1T'' phase identification from an

experimental ADF STEM image (Figure 2a). If the ADF STEM images are visualized using a log intensity scale (column 3), one can clearly see the very weak intensity coming from the S atom positions, making each phase distinguishable from the images. The S is not visible in our experimental ADF STEM images, making the unique identification of all phases from ADF STEM images not possible. However, if S visibility was possible, unique identification of all 5 phases would be possible.

Figure S4 shows ADF STEM data extracted from an image series from BL ReS₂ in an area that had not previously been exposed to the electron beam. The 50 frame image series was non-rigidly registered to correct any effects from environmental, instrumental, and sample instabilities and this registered series is shown in SI Movie 3. The first and last (50th) registered images are shown in Figure S4(a and b) respectively. Their similarity confirms very little structural damage occurred during the electron irradiation of this image series. In order to more clearly show this, the registered image series was temporally binned by 5 frames to increase the signal-to-noise and enhance the visibility of the Re atoms. The binned image series is shown in SI Movie 4 and the first and last frame from this series is shown in Figure S4(c and d) respectively. These frames also confirm negligible damage occurred in the BL ReS₂ during this image series. Therefore, we could use this ADF STEM data to analyze the initial starting phase of BL ReS₂, as shown in Figure 2d.

Figure S5 shows ADF STEM data from unperturbed BL ReS₂ that provides evidence the starting phase is 2T''. Figure S5a is the non-rigidly registered and averaged ADF STEM image of the image series shown in SI Movie 3 and Figure S4. This image series was the first exposure of electrons to this area of the sample and no obvious electron irradiation damage is observed, as discussed above and shown in Figure S4. Figure S5b is a rotated version of (a) which was used for the template matching analysis discussed below and in the methods section. Figure S5(d and e) are the input template image and final average template image, respectively. The final average template image in Figure S5e was produced by averaging 843 unique template images within Figure S5b. The positions of these 843 template images are marked by the green circles in the normalized cross-correlation image shown in Figure S5c. These positions were identified by thresholding the normalized cross-correlation image. It is important to note that it was crucial to threshold the normalized cross-correlation image so that only the largest intensity peaks were identified. If lower intensity peaks were included, the template matching analysis produces erroneous results that could lead to the wrong phase identification. By comparing the averaged template matched image in Figure S5e and Figure 2d (main text) to the simulated ADF STEM images of the 15 possible BL ReS₂ phases in Figure S7 and Figure S8, it is clear the starting phase is one of the 2T'' variants, and most likely the 2T''_e variant.

Figure S6 shows experimental and simulated PACBED data from unperturbed BL ReS₂ that provides evidence the starting phase is 2T''_e. The experimental PACBED pattern (a and c) and simulated PACBED pattern of 2T''_e (b and d) exhibit an extraordinary agreement, especially when viewed on a log intensity scale (c and d) which reveals the very weak PACBED signals. This agreement provides additional strong evidence that unperturbed BL ReS₂ has the 2T''_e phase.

Figure S7 shows simulated ADF STEM images of the 15 possible phases of BL ReS₂. These images were used to help provide evidence of the phase of BL ReS₂, as shown in Figure 2d (main text).

Figure S8 shows simulated ADF STEM images of the 15 possible phases of BL ReS₂. These are the same images that are shown in Figure S7 except on a log intensity scale in order to show the weak image intensity from the S atoms. These images demonstrate that if the S atoms could be experimentally resolved, they would provide further evidence of the BL phase.

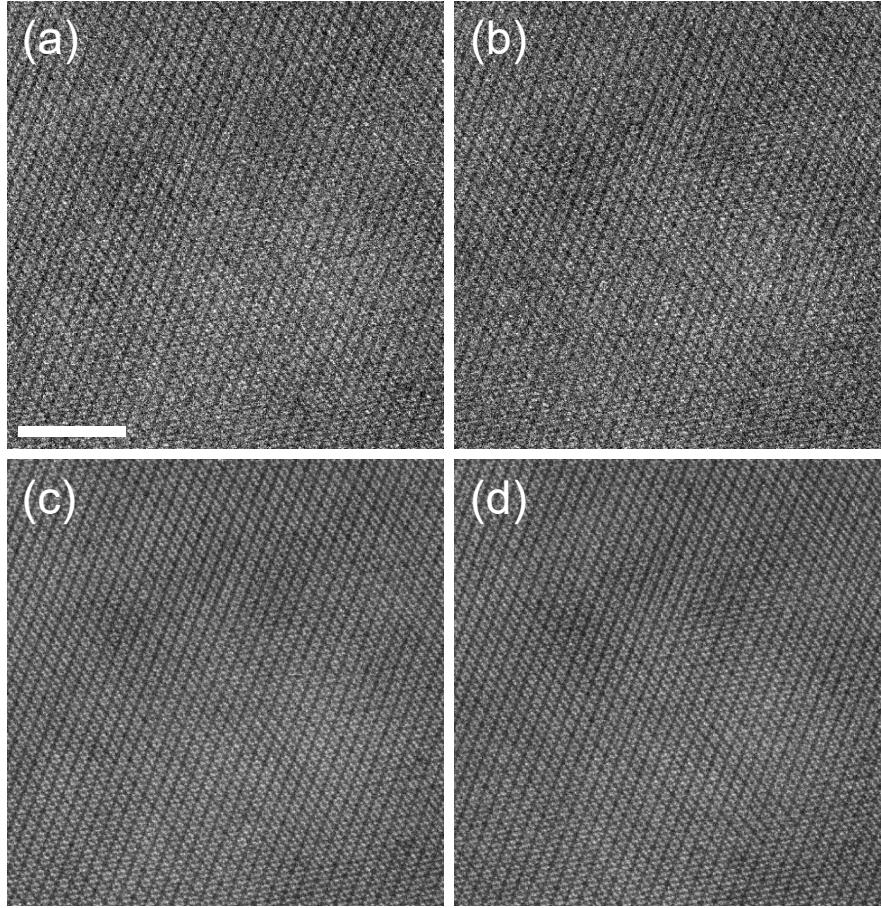


Figure S4: Experimental ADF STEM of undamaged BL ReS₂. (a) The first frame of SI Movie 3. SI Movie 3 is a non-rigidly registered experimental ADF STEM image series of BL ReS₂ that was used to produce the image in Figure 2(d). The scale bar in (a) is 10 nm. (b) The last (50th) frame of SI Movie 3. The similarity of (a) and (b) provides evidence there was negligible structural damage caused by the electron irradiation during the acquisition of this image series. (c) The first frame of SI Movie 4. SI Movie 4 is an image series that was produced by temporally binning by 5 frames the image series in SI Movie 3. The temporal binning increases the signal-to-noise ratio of the image and enables a more careful comparison of the initial and final atomic structures during the image series acquisition. (d) The last (10th) frame of SI Movie 4. The similarity of (c) and (d) provides further evidence there was negligible structural damage caused by the electron irradiation during the acquisition of this image series.

Figure S9 shows simulated PACBED patterns of the 15 possible phases of BL ReS₂. Each PACBED pattern from the 15 considered phases are unique and distinguishable from one another, enabling the unique classification of BL phase from a PACBED pattern. This allowed the identification of the 2T''e phase of BL ReS₂ from the experimental PACBED pattern (Figure 2e).

Supplementary movies

SI Movie 1: An ADF STEM image series of ML ReS₂ revealing electron-beam induced damage. The movie is created with 15 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 16.5 nm.

SI Movie 2: An ADF STEM image series of ML ReS₂ revealing electron-beam induced damage. The movie is created with 15 frames per second. The acquisition details are

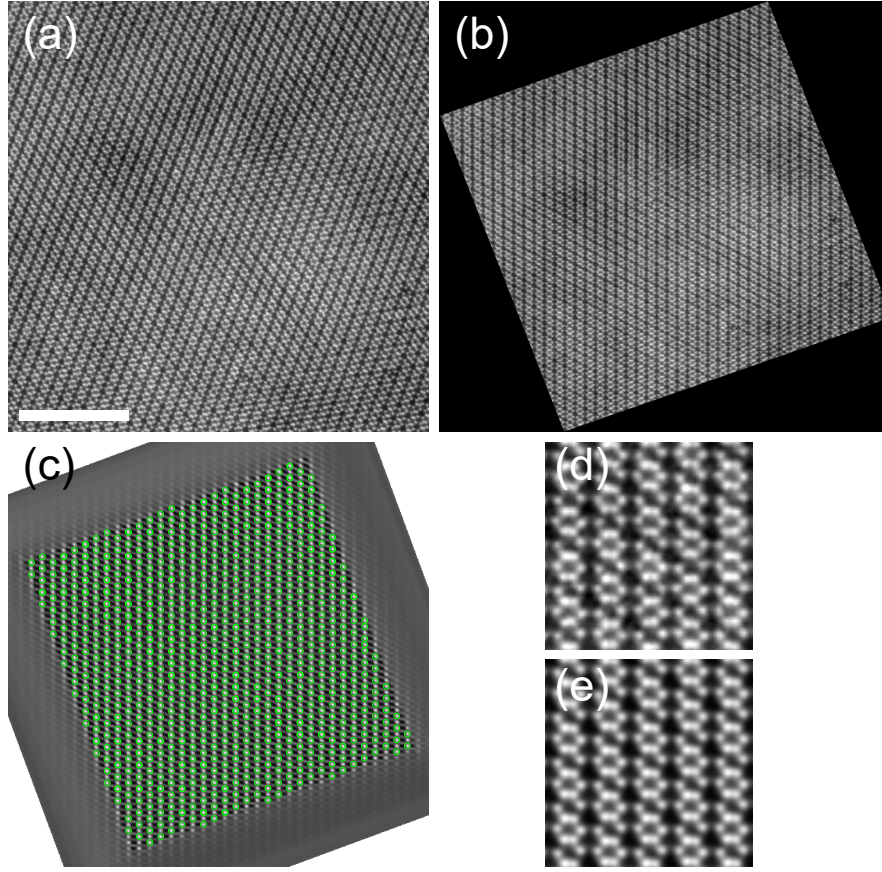


Figure S5: STEM template matching of undamaged BL ReS₂. (a) Non-rigidly registered and averaged experimental ADF STEM image of BL ReS₂. The image series shown in SI Movie 3 was averaged to create (a). The scale bar in (a) is 5 nm. (b) The same image as (a) that has been rotated to align one crystallographic axis to the y -image axis. A cropped version of (b) was used for Figure 2d, while the entire image was used as an input for the template matching routine. (c) Normalized cross-correlation image between (d) the user-selected input template image and all possible template images of the same size in (b). (d) The user-selected input template image is a cropped sub-region of (b). The green circles in (c) mark the 843 normalized cross-correlation peaks that were selected as the set of maximum peaks used for producing the final averaged template image. The maximum peaks were identified using an in-house written IGOR Pro script that utilizes a thresholding of the normalized cross-correlation image. (e) The final averaged template image that was produced by averaging the set of selected template images identified in (c).

discussed in the Methods and SI. The horizontal image length is 10.1 nm.

SI Movie 3: A registered ADF STEM image series of BL ReS₂. The movie is created with 20 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 19.1 nm.

SI Movie 4: The ADF STEM image series of BL ReS₂ shown in SI Movie 3 that has been temporally binned by 5 frames. The movie is created with 5 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 19.1 nm.

SI Movie 5: A registered ADF STEM image series of BL ReS₂. The movie is created with 10 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 17.5 nm.

SI Movie 6: A registered ADF STEM image series of BL ReS₂ that was acquired

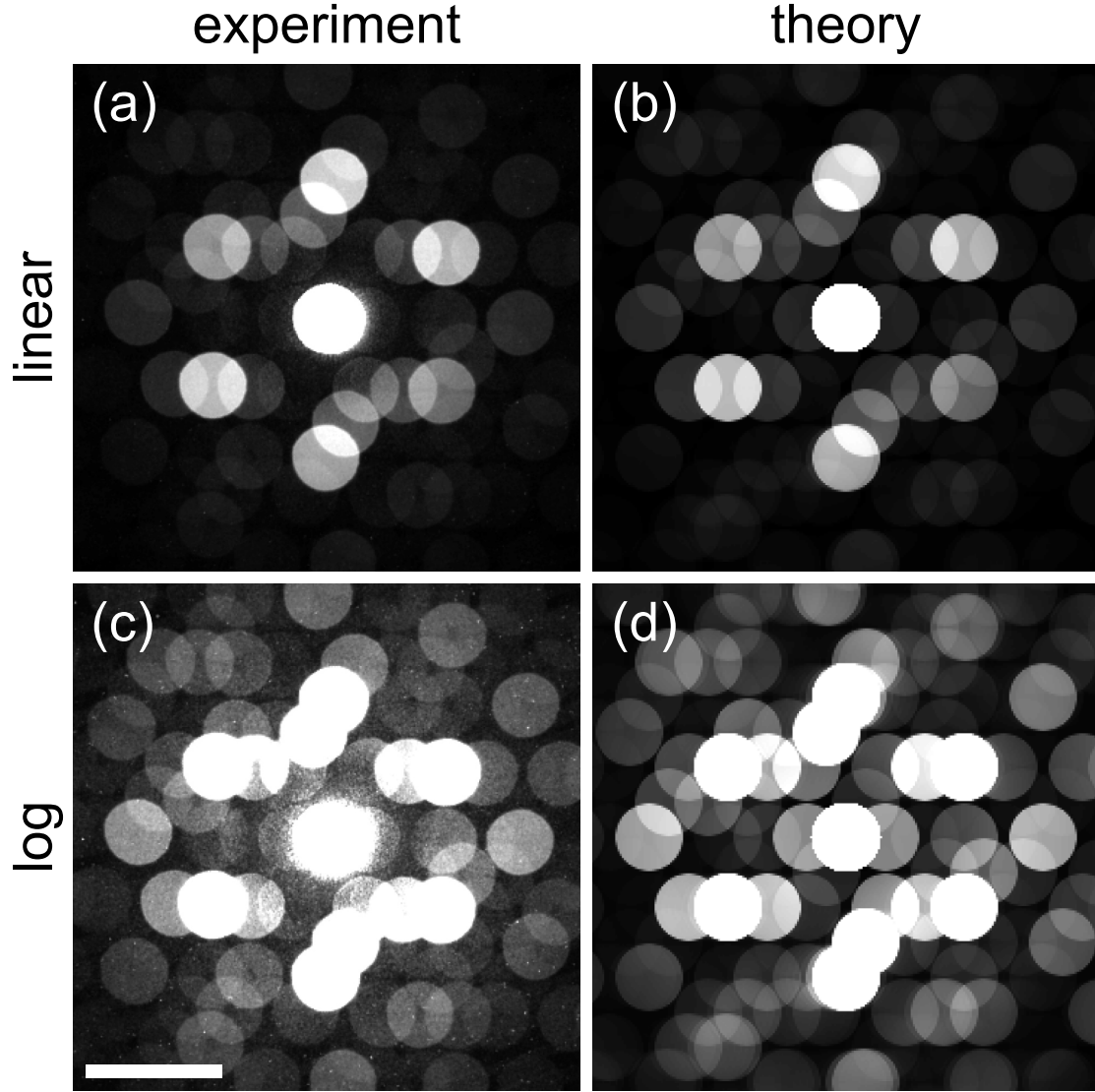


Figure S6: PACBED of undamaged BL ReS₂. (a) Experimental PACBED pattern of BL ReS₂ on a linear intensity scale acquired at 80 keV. (b) Simulated PACBED pattern of 2T''e BL ReS₂ on a linear intensity scale calculated at 80 keV. (c) and (d) The same PACBED patterns shown in (a) and (b), respectively, but on a log intensity scale to reveal low intensity features. The extraordinary similarity between (a) and (b), and (c) and (d) provides evidence that undamaged ReS₂ has the 2T''e phase. The scale bar in (c) is $0.6 \text{ \AA}^{-1}$.

directly after SI Movie 5 of the same area. The movie is created with 10 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 19 nm.

SI Movie 7: The ADF STEM image series of BL ReS₂ shown in SI Movie 5 that has been temporally binned by 5 frames. The movie is created with 2 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 17.5 nm.

SI Movie 8: The ADF STEM image series of BL ReS₂ shown in SI Movie 6 that has been temporally binned by 5 frames. The movie is created with 2 frames per second. The acquisition details are discussed in the Methods and SI. The horizontal image length is 19 nm.

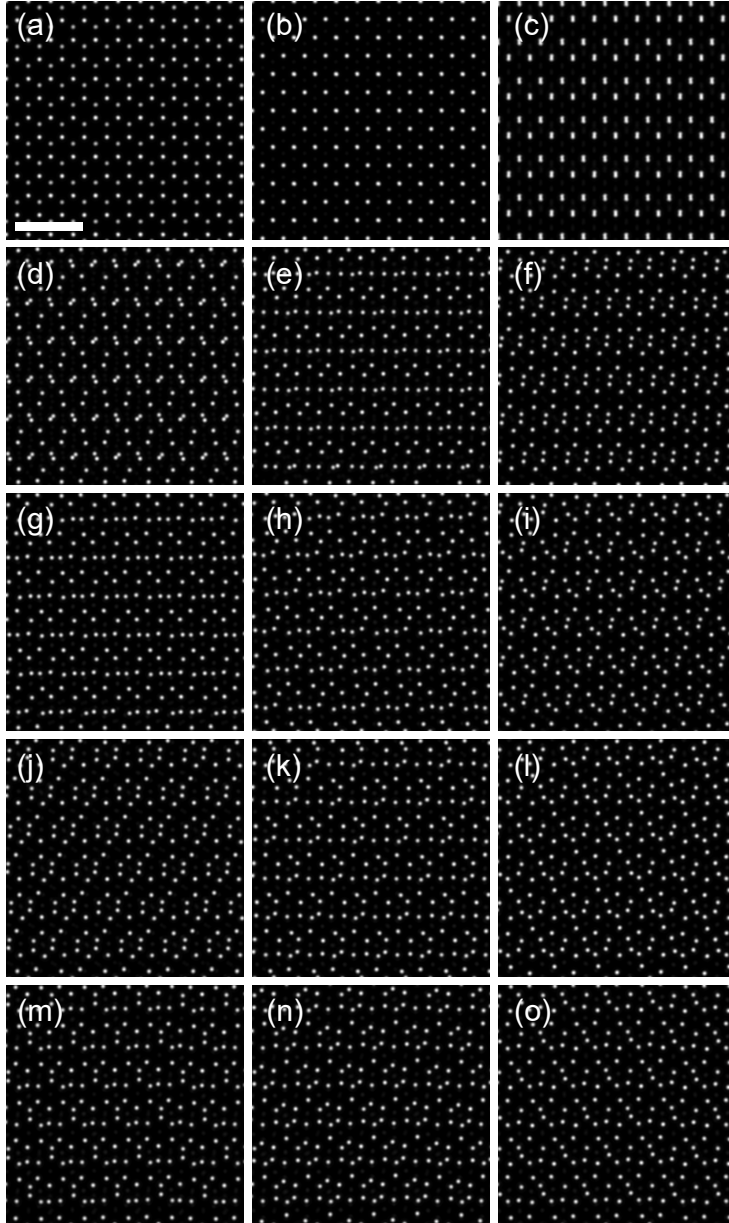


Figure S7: Simulated ADF STEM images of BL ReS₂ phases. Simulated ADF STEM images on a linear intensity scale of different phases of BL ReS₂: (a) 2H, (b) 2T, (c) 2T', (d) 2T''c, (e) 2T''d, (f) 2T''e, (g) 2T''f, (h) 2T''g, (i) 2T''h, (j) 2T''i, (k) 2T''j, (l) 2T''k, (m) 2T''l, (n) 2T''m, (o) 2T''n. The scale bar in (a) is 1 nm.

AFM of monolayer ReS₂ flakes

To confirm the thickness of the ReS₂ flake in Figure 3 of the main text, we performed high-resolution AFM studies. Because of possible charge accumulation on the studied flakes, we compared AFM scans of a direct bandgap semiconductor, monolayer WS₂ flake, with ReS₂ flake. The WS₂ flakes possess a direct bandgap transition only in a monolayer form, while multilayer WS₂ is an indirect gap semiconductor thereby lacking PL emission. Such an approach towards optical confirmation of the thickness is used in Fig. S10a, where an optical image is overlapped with PL emission microscopy image to highlight the areas that emit PL.

After identifying the emissive areas, we carefully analyzed them with AFM. Fig. S10b demonstrates AFM of the WS₂ flakes. The particular area of interest is marked with

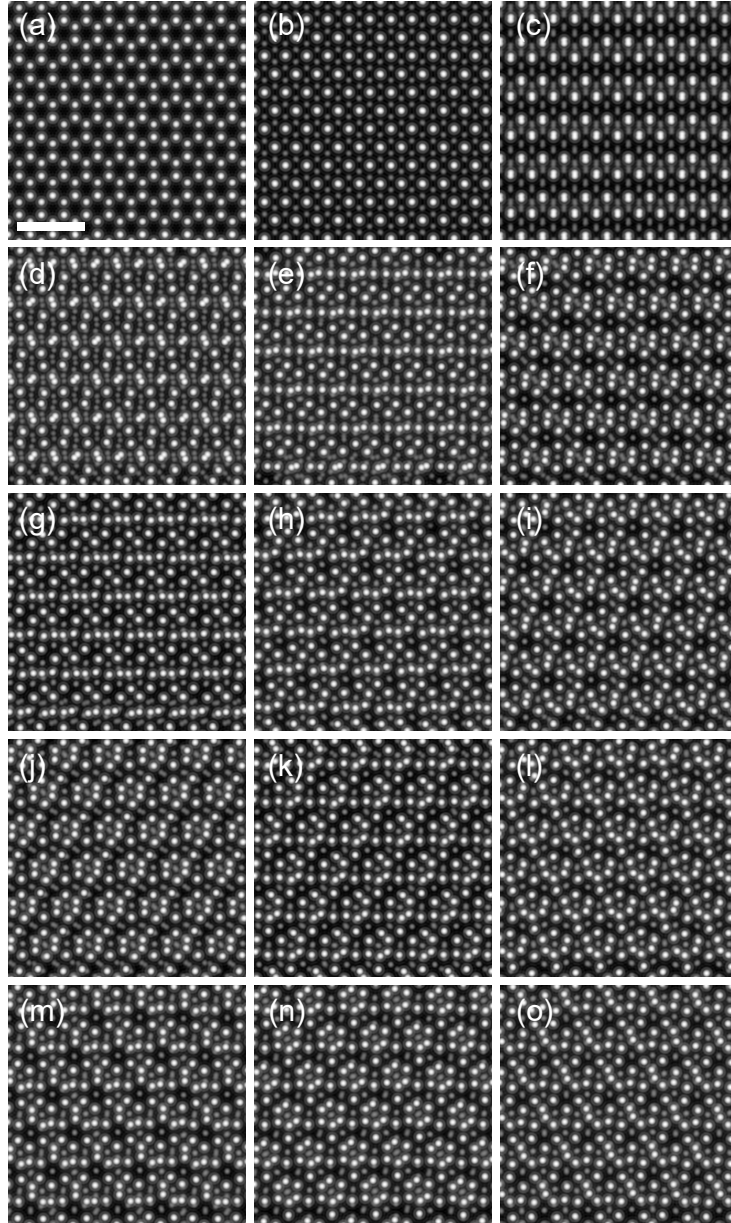


Figure S8: Simulated ADF STEM images of BL ReS₂ phases on a log intensity scale. Simulated ADF STEM images on a log intensity scale of different phases of BL ReS₂: (a) 2H, (b) 2T, (c) 2T', (d) 2T''c, (e) 2T''d, (f) 2T''e, (g) 2T''f, (h) 2T''g, (i) 2T''h, (j) 2T''i, (k) 2T''j, (l) 2T''k, (m) 2T''l, (n) 2T''m, (o) 2T''n. The scale bar in (a) is 1 nm.

a blue line. A direct head-to-head comparison of the PL-confirmed monolayer of WS₂ (blue line) and ReS₂ monolayer from Figure 3 of the main text (red line) is shown in Fig. S10c. The height we extract from the AFM scans is much greater than the anticipated sub-1 nm thicknesses for monolayer, however, this does not take into account electrostatic forces and substrate roughness. Therefore the $\sim 3-4$ nm estimation of the thickness by AFM can be used as the reference for a monolayer ReS₂ structure in our case. We, therefore, conclude that the ReS₂ flake presented in Figure 3 of the main text is a monolayer, in accordance with the referenced against monolayer WS₂ AFM data presented in Fig. S10d.

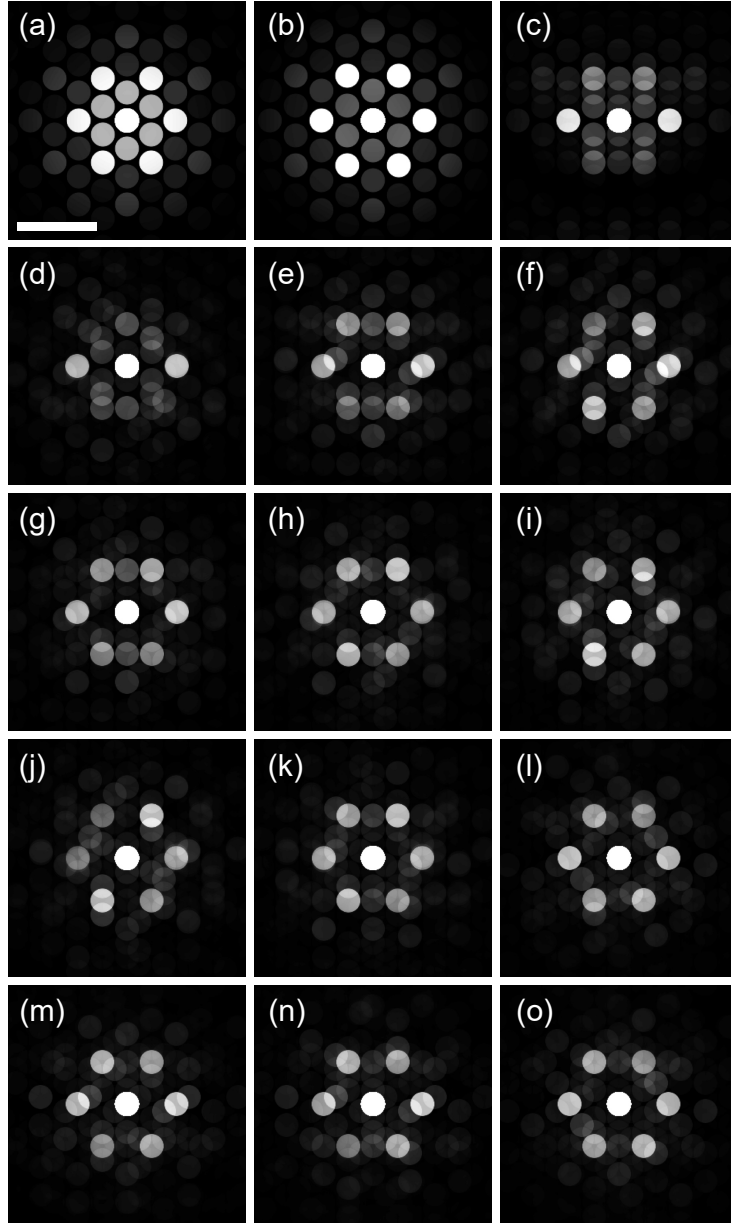


Figure S9: Simulated PACBED of BL ReS₂ phases. Simulated PACBED of different phases of BL ReS₂: (a) 2H, (b) 2T, (c) 2T', (d) 2T''c, (e) 2T''d, (f) 2T''e, (g) 2T''f, (h) 2T''g, (i) 2T''h, (j) 2T''i, (k) 2T''j, (l) 2T''k, (m) 2T''l, (n) 2T''m, (o) 2T''n. The scale bar in (a) is $1 \text{ \AA}^{-1}$.

Monitoring phase transition in trilayer ReS₂ by SHG and PL

Figure S11 shows the progression of the optical properties of a trilayer ReS₂ flake on a glass substrate before laser exposure (pristine), immediately after (patterned), and 48 hours later (partially recovered). Patterning refers to the process of exposing the material to intense fs-laser exposure with specific exposure times (1040 nm central wavelength and average power of 2 mW) to create structural changes, as described in [S8]. The trilayer flake area was patterned as depicted with white dashed lines in the optical image (Figure S11).

The selection of trilayer as a structure for optical property analysis was made to ensure sufficient PL signal could be acquired from both pristine and patterned phases under ambient conditions. However, PL measurements are technically challenging, and

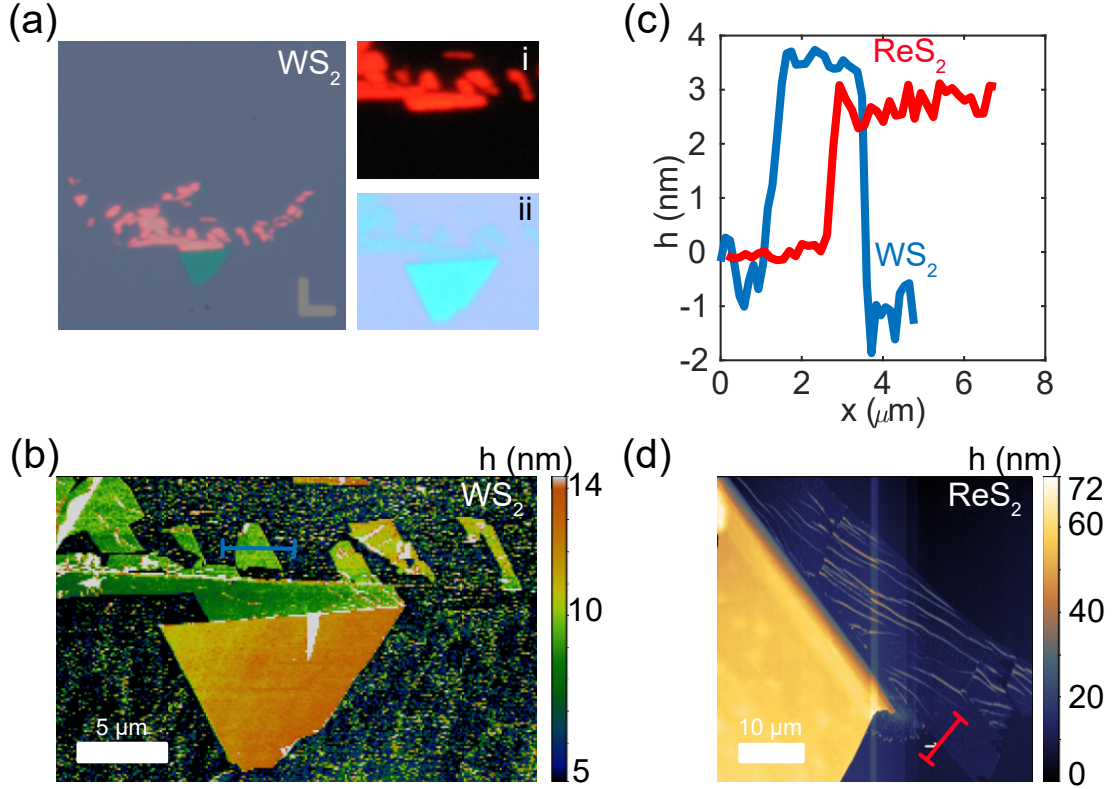


Figure S10: AFM of the ML WS₂ and ReS₂. (a) Optical image of WS₂ flakes overlapped with the PL microscopy image. Inset (i) depicts the PL image and inset (ii) shows an optical image of the WS₂ flakes. (b) AFM mapping of the area from (a). (c) Comparison of the AFM cross-sections for WS₂ from (b) (blue line) and ReS₂ from (d) (red line). (d) AFM microscopy of the ReS₂ flake for the sample from Figure 3 of the main text.

only by using a 60 $\times$ NA=1.49 oil immersion objective with a 60 s collection time for each analyzer angle was it possible to resolve the PL of the patterned trilayer (as seen in the acid green curve in Figure S11h).

The pristine SHG intensity mapping is shown in Figure S11, while Figure S11b displays a dramatic increase in SHG counts after patterning. The sample partially recovers toward its initial SHG intensity counts after 48 hours at room temperature (Figure S11c). The residual signal of the SHG (black in Figure S11d) can be compared to unpatterned (red) and freshly patterned (acid green). The residual signal is still pronounced, which indicates incomplete recovery (trilayers and bilayers may have different recovery rates; see for example Figure 5).

The polarization-resolved SHG spectroscopy shows a pronounced evolution of $\chi^{(2)}$ tensor after patterning, demonstrating that the SHG signal arises from structural or phase changes, and not from damaging the area of interest. The initial SHG signal is weak and barely shows any polarization dependence, consistent with the 1T'' phase of the ReS₂ flakes in their ground state. After patterning, the SHG counts increase dramatically and show a pronounced 4-fold symmetry, indicating a phase transition from a centrosymmetric to a non-centrosymmetric state.

Further analysis of the trilayer material was performed using polarization-resolved photoluminescence (PL) measurements. Unpolarized 447 nm light was directed at both patterned and unpatterned areas, as depicted in Figure S11e. To ensure that the sample was not thermally heated through light absorption, the pump power (see Methods section for more details) was carefully chosen to be high enough to detect PL signals but low

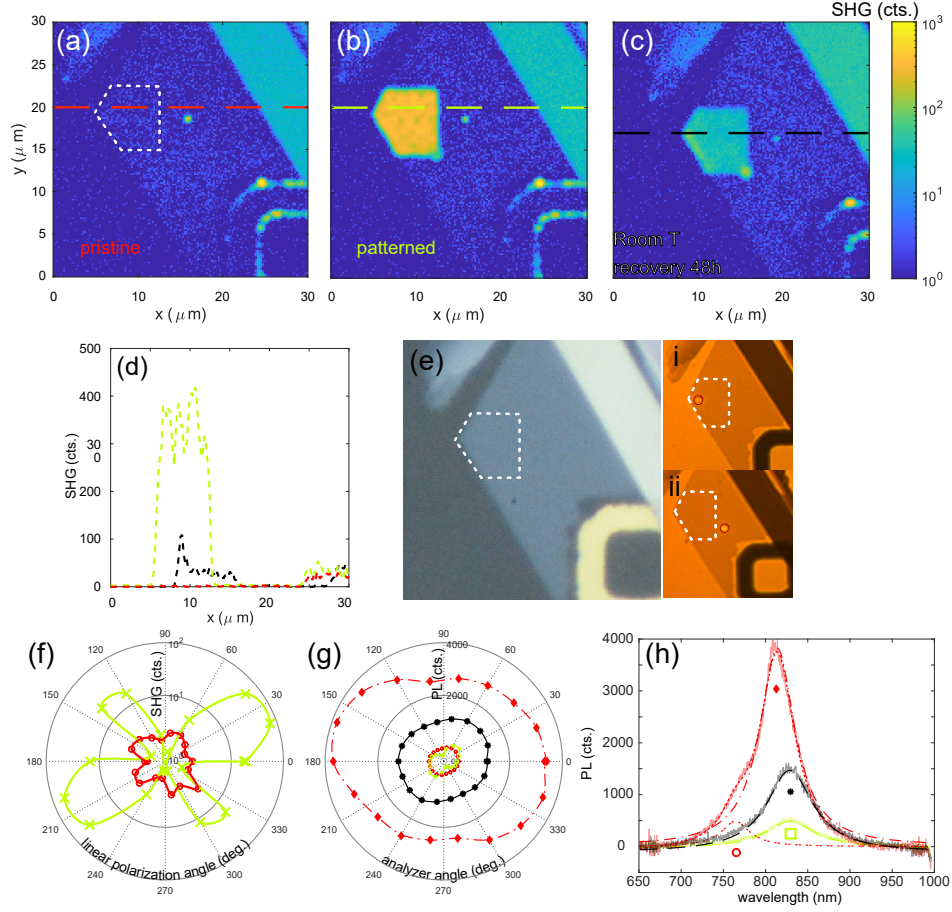


Figure S11: Fs-induced phase transition in ReS₂ trilayer. SHG intensity 2D colormaps in log-scale of a ReS₂ trilayer flake on a glass substrate in (a) pristine conditions; (b) after fs-laser exposure; (c) after 48 hours at room temperature ambient conditions. (d) depicts an explicit comparison of SHG intensity counts of the (a-c) cross-sections, where red – pristine, acid green – patterned, and black – after 48 hours of recovery. (e) is the optical microscopy image of the sample and insets (i, ii) represent that no visible damage was done before and after fs-laser exposure. Red circles represent the areas of PL signal collection for patterned and unpatterned areas for (g). (f) linear polarization-resolved SHG intensity polar plots in logscale of unpatterned (red) and patterned (acid green) trilayer area shown in (a, e) with dashed lines. (g) polarization-resolved PL intensity of unpatterned (red, two peaks), freshly patterned (acid green), and after 48 hours at ambient conditions (black). (h) explicit PL spectra comparison between unpatterned (red, two peaks), freshly patterned (acid green), and after 48 hours at ambient conditions (black) at selected analyzer angle position.

enough to prevent sample damage. A comparison of PL signals in the unpatterned (red), freshly patterned (acid green), and partially recovered (black) samples is shown in Figure S11h, revealing a suppression of PL signal intensity by a factor of ~ 10 in the patterned phase, which is consistent with the predictions that the patterned phase should be semimetallic H' (see main text) and therefore inactive in PL.

In addition to variations in PL intensity, the shape of the PL spectrum also changed dramatically. The pristine sample had two prominent spectral shoulders, representing two excitons, each with its own polarization dependence, as shown in Figure S11g (red dashed-dotted, red double-dashed). To conclude, the results of fs-laser light exposure of the trilayer ReS₂ sample in the near-infrared region indicate a reversible phase transition from the ground state to a transient state and partially back at room temperature

(after 48 hours), as concluded from SHG and PL measurements and the absence of visible surface damage on the sample. These changes are consistent with a T''-H' phase transition discussed in the main text.

The impact of laser-induced phase transition on electronic transport properties of ReS₂

Finally, we performed electrical transport measurements using a field-effect transistor (FET) to prove and understand the effect of laser-induced phase transition from the semiconducting T'' phase to the semimetallic H' phase. Figure S12 summarizes the SHG signal and their respective electronic measurements. We would like to mention that the electrical measurements were performed just after the laser patterning. Figure S12a is the intensity mapping of the generated SHG signal from the area of interest under different conditions. The thickness of the ReS₂ flakes here corresponds to monolayer ReS₂. The contact location is schematically depicted by the white dashed lines. The transfer characteristics of the respective device under different conditions are shown in Figure S12b at a drain-source voltage (V_{DS}) of 1 V. The corresponding optical image is also shown in the inset of Figure S12b. We systematically performed the optical and electrical measurements over 3 months at the same device. The laser-induced phase transition leads to a change in the electronic properties. Therefore, we focus on the two primary observables: the change in the current (I_{on}) and the shift in the threshold voltage (V_{th}). The first two SHG intensity maps are taken for the pristine monolayer ReS₂ flake between the contacts and aged for two months at room temperature to exclude any aging-related effects (the background signal is different due to different background conditions). The transfer characteristics also displayed a similar behavior with the same threshold voltage over 2 months. Next, we performed the first fs-laser-induced patterning (6 mW, 200 ms, 50 nm step) of the channel (the ReS₂ film between the contacts). It was observed that areas closer to contacts showed higher SHG counts (SHG hot spots) than the rest of the area. The gold contacts locally increase the intensity of the electromagnetic field during the fs-laser exposure, therefore the areas near contacts showed SHG hot spots in SHG mapping. We would like to point out that initially, our V_{th} is around -0.5 V for the pristine sample and that after two months of aging, V_{th} shifted to the negative side with a value of -2.65 V after the first fs-laser patterning. The negative shift indicates the increase in electron density concentration after the first laser patterning. The effect of the first laser patterning is partially recovered in electrical measurements by heating the flake for 25 min at 80°C. We waited for enough time to avoid any discrepancy due to the heating of the flakes. Unlike the electrical properties, the SHG counts of ReS₂ monolayer do not recover entirely through heating, as one can see from the fourth SHG map in Figure S12a around the area of the contacts. Finally, we performed an intense fs-laser patterning (8 mW, 200 ms, 50 nm step) of the channel area, which resulted in an expected increase in SHG counts. Associated with that, we observed a strong shift in threshold voltage to the negative side with a value of -5 V whereas the on-current dropped by an order of magnitude compared to the pristine case. The drop in current may be attributed to the formation of defects. The first laser exposure strongly patterned the area near the contact, which did not fully recover after the annealing. Thus, the area near the contacts has a higher number of defects than the rest of the channel before the second, more intense, laser patterning with annealing at 80°C, and can possibly contain the products of the chemical reaction between the adhesion contact Cr layer and MoS₂ [S9; S10; S11]. Interestingly, we observed significantly degraded transport characteristics after 100°C annealing for 35 min, which, following Figure 5 of the main text, implies the occurrence of thermal damage or another unrelated to T''-H' phase transition process.

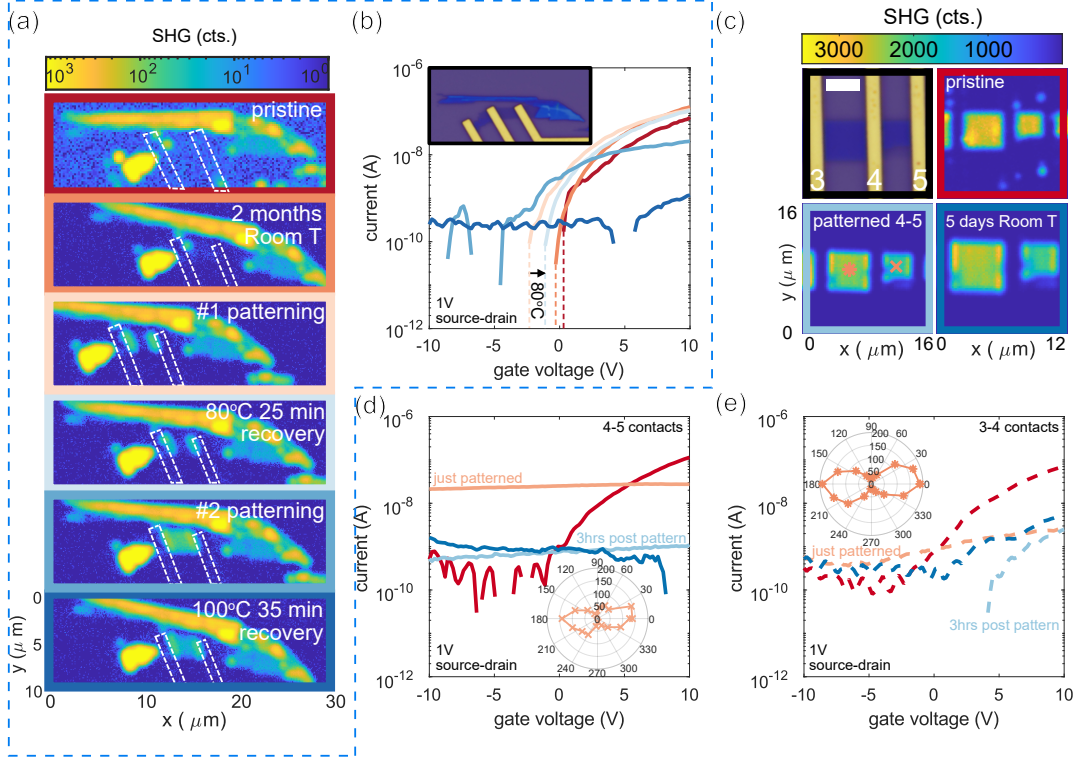


Figure S12: Transport properties in ML (a-b) and BL (c-e) ReS_2 upon phase transition. (a) SHG intensity maps of a flake with attached gold contacts - dashed white lines. The area between two contacts is a monolayer of ReS_2 , which is proved by AFM. The conditions from red to blue are the following: pristine sample, 2 months-aged, fs-laser patterning between two contacts, 25 min on an 80°C plate, second patterning, 35 min on a 100°C plate. (b) FET current versus gate voltage of the monolayer from (a) for 1V source-drain voltage. Respective color corresponds to specific conditions from (a). The inset is an optical image of the sample. (c) Optical image and the SHG intensity maps of a bilayer ReS_2 flake with gold contacts. FET current versus gate voltage of the bilayer (d) between contacts 4-5 and (e) between contacts 3-4. Insets in (d), and (e) are polarization-resolved SHG intensities depicting phase switching at respective color conditions.

To reveal more details on how the defects and the number of layers of the flake affect the phase transition from the electronic point of view, we are studying a free-standing bilayer ReS_2 flake separated with two pairs of contacts, where one area is kept pristine as a reference (between contacts 3-4 in the top left image of Figure S12c) and the other undergoes fs-laser exposure (4-5 contacts) as shown in Figure S12c. In pristine conditions, the performance of 3-4 and 4-5 ReS_2 bilayer areas in the FET scheme is roughly the same in the threshold voltage and the maximum current point of view as seen in Figures S12(d, e), where solid lines correspond to 4-5 contacts and 3-4 are dashed lines. The colors of respective plots from blue to red correspond to different conditions. The same color between both plots corresponds to the same conditions. After the fs-laser exposure of the area between contacts 4-5, the I-V curve flattens in a conductor-like behavior (purple line in Figure S12d) – that one can not even estimate the threshold voltage, however, from the respective measurement of the unpatterned 3-4 contacts one can also clearly observe a significant change but in another manner – the threshold voltage is shifted to around -10 V and the maximum current dropped by two orders of magnitude. The flattening of the I-V curve in 4-5 contacts we link to the T'' - H' phase transition in ReS_2 bilayer flake occurring in the specific area, which is also

manifested by a drop of the SHG intensity counts. Moreover, the inset in Figure S12d proves the drop of the counts and the appearance of the sub-lobe in polarization-resolved SHG intensity as compared to the pristine case in Figure S12e reflecting perfect 8-shape response. However, the area that was never exposed to severe fs-laser light, namely 3-4 contacts, switches its electronic behavior due to the possible electron enrichment and defect diffusion in the bilayer, since the flake is homogeneous and contacts are fabricated on top of the same flake. After approximately 3 hours, the maximum current in the patterned sample dropped by 2 orders of magnitude, keeping the same flat feature. This indicates deteriorating dynamics occurring on the few-hour time scale, which could be attributed to the interaction of the freshly patterned sample (and newly generated defects in it) with the environmental oxygen [S12; S13]. However, after residing for 5 days at room temperature, the sample became electrically non-conductive with a significant dip at 8 V gate voltage, as seen in Figure S12d (thus, the sample does not recover to its original condition from the electronic transport point of view). Notably, the pristine (from the SHG standpoint) part of the flake between contacts 3-4, which was kept in the $1T''$ phase, drops its performance in the maximum current by approximately two orders of magnitude 5 days after patterning. However, it recovers its V_{th} value, as seen in Figure S12e – dark blue dashed line. This indicates modulation of the transport properties of the part of the flake that was not directly patterned by the laser, suggesting that the defects generated during the patterned process in the contact 4-5 area are mobile and deteriorate the performance of the 3-4 area.

In conclusion, the FET data supports the hypothesis of defect-assisted phase transition in mono- and bilayer ReS_2 ; however, the impact of defects on the transport properties is dominant. Furthermore, since the formation of defects is an irreversible process (as opposed to the T'' - H' phase transition), the deterioration of transport properties is also irreversible.

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