Correlating 3D atomic defects and electronic properties of 2D materials with picometer precision

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Two-dimensional (2D) materials and heterostructures exhibit exceptional electronic, optical and chemical properties, promising to find applications ranging from electronics and photovoltaics to quantum information science¹⁻³. However, the exceptional properties of these materials strongly depend on their 3D atomic structure especially crystal defects⁴⁻¹¹. Using Re-doped MoS₂ as a model, we develop scanning atomic electron tomography (sAET) to determine the atomic positions and crystal defects such as dopants, vacancies and ripples with a 3D
precision down to 4 picometers. We measure the full 3D strain tensor and quantify local strains induced by single dopants. By directly providing experimental 3D atomic coordinates to density functional theory (DFT), we obtain more truthful electronic band structures than those derived from conventional DFT calculations relying on relaxed 3D atomic models, which is confirmed by photoluminescence spectra measurements. Furthermore, we observe that the local strain induced by atomic defects along the z-axis is larger than that along the x- and y-axis and thus more strongly affects the electronic property of the 2D material. We anticipate that sAET is not only generally applicable to the determination of the 3D atomic coordinates of 2D materials, heterostructures and thin films, but also could transform \textit{ab initio} calculations by using experimental atomic coordinates as direct input to reveal more realistic physical, material, chemical and electronic properties.

To understand the structure-property relationship of 2D layered materials at the fundamental level, we must precisely know their 3D atomic arrangement\textsuperscript{1-3}. Although x-ray diffraction can determine the 3D crystal structure of these materials at atomic resolution, it is blind to crystal defects such as dopants, vacancies, dislocations, grain boundaries, strains, ripples and interfaces, which strongly influence material properties and functionality\textsuperscript{4-11}. Aberration-corrected electron microscopy and scanning probe microscopy allow us to see individual atoms without the constraint of crystal averaging\textsuperscript{1,7-13}. But, seeing atoms is not the same as knowing their 3D coordinates with high precision, which is required for an accurate prediction of properties using quantum mechanics. No \textit{ab initio} calculations can take a 2D image of atoms as direct input to determine material properties\textsuperscript{14-16}. 
Here, we developed sAET to localize the 3D atomic coordinates in 2D materials and heterostructures with picometer precision. AET allows the determination of 3D atomic structure of crystal defects and disorder systems\textsuperscript{17-23}, and has recently been advanced to capture nucleation at 4D atomic resolution\textsuperscript{24}. However, AET has thus far been limited to metallic nanoparticles and needle-shaped samples. Application of AET to 2D materials and heterostructures would open a new frontier in 3D atomic structure characterization, but requires overcoming three obstacles. First, these materials are electron beam sensitive and the experiments must be performed with low electron doses\textsuperscript{1,2}. Second, the 3D precision of experimental atomic coordinates must be on the picometer scale so that they can be used as direct input to quantum mechanical calculations to determine physical, material and electronic properties\textsuperscript{14-16}. Third, due to the geometric constraint of 2D materials and heterostructures, the tilt range of data acquisition is limited by the reduced depth of focus of aberration-corrected electron microscopy\textsuperscript{25}. Using a Re-doped MoS\textsubscript{2} monolayer, we demonstrated a general sAET method to overcome these limitations and determined the 3D coordinates of individual atoms with high precision. We identified 3D crystal defects such as dopants, vacancies and atomic-scale ripples and measured the 3D atomic displacement and the full strain tensor of the 2D material. Furthermore, the experimental 3D atomic coordinates were used as direct input to DFT to correlate crystal defects with the electronic band structure at the single-atom level. We observed stark differences between the band structures obtained from the experimental and relaxed atomic models.

The experiment was performed using an aberration-corrected scanning transmission electron microscope (STEM), operated at 60 kV in annular dark-field mode (ADF). Two data sets were collected from the Re-doped MoS\textsubscript{2} monolayer, each
consisting of 13 projections with small double tilt ranges (Extended Data Fig. 1 and Table 1). A low-dose data acquisition scheme was implemented with a total dose of 4.1×10^5 e/Å² for each data set, which is comparable to that of a single high-resolution ADF-STEM image. Comparison of the first and last images of each data set indicates the consistency of the atomic structure during data acquisition (Extended Data Fig. 2). After applying denoising, drift, vibration and angular correction to each data set (Extended Data Figs. 3 and 4), we performed sAET reconstruction of the aligned projections (Fig. 1a). sAET takes advantage of the relationship, $d \propto \frac{D}{N}$, where $d$ is the 3D resolution, $D$ is the size of the object to be reconstructed and $N$ is the number of projections. For a small $N$ limited by the electron dose, we can improve $d$ by reducing $D$. To implement sAET, we first chose a 3D window of 60×60×60 voxels and located the corresponding region in each of the 13 projections (Fig. 1a). We then scanned the window along the x and y axis with a step size of 30 voxels. At each step, we identified the corresponding regions in the projections for each window. After all the projections were partitioned into small image stacks, each 3D window was reconstructed by a generalized Fourier iterative reconstruction algorithm. All the 3D windows were then stitched together to form a full reconstruction, where the overlap volume between neighboring windows containing artifacts due to boundary effects was discarded.

Figure 2a, Supplementary Video 1 and Extended Data Fig. 5a show the reconstructions of data sets 1 and 2, where all the Re dopants are direct replacements of Mo atoms. The side view images in Fig. 2a (inset) illustrate the intensities of Mo, S, and Re atoms with S vacancies indicated by arrows. From each reconstruction, the 3D atomic coordinates and chemical species were traced, refined and corroborated. Data set 1 consists of 1381 S, 686 Mo, 21 Re atoms and 15 S vacancies (Fig. 2b and Supplementary Video 2),
while data set 2 comprises 1083 S, 531Mo, 16 Re atoms and 4 S vacancies (Extended Data Fig. 5b).

To estimate the 3D precision of the atomic positions, we implemented two independent methods for cross validation. First, we identified the x and y coordinates of the Re and Mo atoms in the aligned projections of each data set (Extended Data Fig. 6a), whereas the S atom positions could not be accurately localized from the 2D projections. From these 2D coordinates, we used least square fitting to calibrate the tilt angles (Extended Data Table 2) and determine the 3D coordinates of the Re and Mo atoms (Extended Data Fig. 6b). The Re and Mo atomic coordinates are consistent with those obtained by sAET with a root mean square deviation (RMSD) of 13 pm and 2 pm, respectively (Extended Data Figs. 6c and d). Second, we performed multislice simulations to calculate 13 projections from the experimental 3D atomic model. The multislice projections are in good agreement with the corresponding experimental ones (Extended Data Fig. 7). By applying the same reconstruction, atom tracing, and refinement procedures, we obtained a new 3D atomic model from the 13 multislice projections with all atoms and defects correctly identified. The RMSD between the experimental and new atomic models is 15 pm, 12 pm and 4 pm for S, Re and Mo atoms, respectively (Fig. 1b). The 3D precision of the Re and Mo atoms is consistent with those obtained by the least square fitting method. Due to the dynamic scattering effect, the Re atom precision is lower than that of the Mo atoms as confirmed by multislice simulations.

From the experimental 3D atomic coordinates, we determined the Mo-Mo, Mo-Re, S-S, Mo-S and Re-S bond lengths in two data sets to be 3.16±0.04 Å, 3.11±0.09 Å, 3.17±0.06 Å, 2.39±0.17 Å and 2.20±0.29 Å, respectively (Fig. 2c). By plotting the 3D
positions of the Mo and Re atoms, we observed atomic-scale ripples in the 2D material (Fig. 2d and Extended Data Fig. 5c). The standard deviation of the Mo and Re atoms along the z-axis was estimated to be 0.19 Å and 0.16 Å for data sets 1 and 2, respectively (Fig. 2e and Extended Data Fig. 5d). Next, we measured the 3D atomic displacements and full strain tensors of the 2D material. Figure 3a-c shows the displacements of the Mo and Re atoms in data set 1 along the x-, y- and z-axis, respectively. We observed a shear along the x-axis and compression along the y-axis, while the z direction shows non-uniform displacements. From the atomic displacements, we determined the full 3D strain tensor of both data sets. Figure 3d-i and Extended Data Fig. 8 show the six components of the strain tensor in three atomic layers, where the $\varepsilon_{zz}$ map is larger in magnitude and more heterogeneous than other components. To quantify the local strains induced by single Re dopants, we chose spheres with a radius of 3.16 Å centered at Re and Mo atoms in the two data sets. We measured the local strain distribution within the spheres and observed that due to the Re dopants, the average local strains of $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$ changed by 0.42%, 0.33% and 1.1%, respectively (Extended Data Fig. 9). This result is consistent with the shortened Re-S bond lengths compared to the Mo-S bond lengths (Fig. 2d).

To correlate 3D crystal defects with the electronic structure of the Re-doped MoS$_2$ monolayer, we selected four supercells in different regions of data set 1, each consisting of 6×6×1 unit cells (Fig. 4a-e). The supercells include a dopant-free MoS$_2$ structure, a single Re dopant, double Re dopants, and mixture of a Re dopant and a S vacancy (Fig. 4a-e). The experimental 3D atomic coordinates of each supercell were used as direct input to DFT to reveal the electronic band structure via band unfolding techniques (Fig. 4a-d left), which determine the effective band structure of each
supercell and reveals the underlying electronic symmetries\textsuperscript{26}. For comparison, the same experimental atomic coordinates were theoretically relaxed and directly provided to DFT to obtain the band structures (Fig. 4a-d middle). The band structures obtained directly from the experimental coordinates show indirect band gaps of the 2D material with a large number of shadow bands. In contrast, the band structures of the relaxed experimental coordinates exhibit direct band gaps with significantly reduced shadow bands\textsuperscript{30}. To study the effects of local strains on the band structures, we calculated the principal strains by solving for the eigenvalues and eigenvectors of the strain tensor within each supercell. The principal strains of Fig. 4a-d are [0.4\%, -0.23\%, -1.15\%], [0.5\% -1.00\%, -0.60\%], [0.14\%, -0.71\%, -1.58\%] and [-0.04\%, -1.84\%, 1.35\%], respectively\textsuperscript{26} (Extended Data Fig. 10), indicating that the increase of local strains generates more shadow bands. In addition to shadow bands, we also observed defect states in the band structure of the supercell containing one Re dopant (Fig. 4b left and middle). With the supercell including two Re dopants, more defect states appear between the band gaps (Fig. 4c left and middle). The striking differences between the band structures of the experimental and relaxed atomic coordinates suggest that the experimental structure is in a metastable state due to the complex strain distribution induced by 3D crystal defects, while the relaxed structure is in the equilibrium state. The metastable and equilibrium states exhibit different electronic properties as shown in Fig. 4a-d. To experimentally study the differences, we measured photoluminescence spectra of pristine MoS\textsubscript{2} and Re-doped MoS\textsubscript{2} monolayers synthesized under the same conditions\textsuperscript{26} (see Fig. 4f). Compared to the pristine MoS\textsubscript{2} spectrum, the Re-doped MoS\textsubscript{2} data exhibit much lower peak intensity with slightly shifted peak position (Fig. 4f). This result confirms that the Re-doped MoS\textsubscript{2} material is an indirect band gap semiconductor,
which is consistent with the band structures directly obtained from the experimental 3D atomic coordinates (Fig. 4a-d left).

In conclusion, using Re-doped MoS$_2$ as a model, we developed sAET to determine the 3D atomic coordinates of 2D materials with picometer precision. We identified 3D crystal defects such as dopants, vacancies and ripples, measured the 3D atomic displacements and full strain tensor, and quantified the local strains induced by single dopants. Furthermore, the experimental 3D atomic coordinates were used as direct input to DFT to reveal the electronic band structures of the 2D material, which were corroborated by photoluminescence measurements. The importance of this work is fourfold. First, compared to other approaches that can image the 3D structure of graphene from only one or two images$^{31,32}$, sAET is a more general method to determine the 3D atomic coordinates of 2D materials, heterostructures and thin films with high precision, while keeping the total electron dose comparable to that of a single high-resolution ADF-STEM image. Furthermore, the combination of sAET and ptychography is expected to further improve the 3D precision of localizing individual atoms and reduce the electron dose$^{33,34}$. Second, our study demonstrates the necessity and importance of directly providing experimental 3D atomic coordinates to DFT to reveal electronic properties in metastable states, whereas $ab$ $initio$ calculations relying on relaxed 3D atomic models can only predict material properties in the equilibrium state. Third, our traditional understanding of 2D materials suggests that their 2D atomic arrangement is important in determining the physical, chemical and electronic properties, which explains how the name of this class of materials came from. However, our experimental results show that the local strain induced by atomic defects along the z-axis is larger than that along the x- and y-axis and more strongly affects the electronic
band structures (Figs. 3 and 4, Extended Data Figs. 8-10). Thus, to engineer the physical, chemical and electronic properties of 2D materials at the fundamental level, it is more important to characterize and control the atomic structure in 3D than in 2D. Finally, with the increase of computational power in the future, the complete set of experimental 3D atomic coordinates determined by sAET and deposited in the Materials Data Bank can be used as direct input to DFT to correlate crystal defects with the electronic, optical, transport and chemical properties of 2D materials and heterostructures. We anticipate that sAET, coupled with DFT and the Materials Data Bank, will not only represent an important advance of \textit{ab initio} calculations to better understand the structure-property relationship, but also provide feedback to materials engineering at the single-atom level.

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Data availability The raw and processed experimental data and all the Matlab source codes for the image reconstruction and data analysis will be freely available at www.physics.ucla.edu/research/imaging/sAET immediately after this work is published. The experimental 3D atomic coordinates of the two data sets will be deposited in the Materials Data Bank (www.materialsdatabank.org).
Figures and figure legends

Figure 2 | Scanning atomic electron tomography (sAET). a. A limited number of projections are acquired from a 2D material or heterostructure with a low electron dose. A small 3D window is chosen and scanned along the x- and y-axis with overlap between two neighboring windows. At each scanning position, the corresponding regions in the projections are identified for each window. After all the projections are partitioned into a series of image stacks, the 3D windows are reconstructed from the image stacks and stitched together to form a full reconstruction. b. Using multislice simulations, we validated the 3D precision of the S, Re and Mo atoms determined by sAET to be 15 pm, 12 pm and 4 pm, respectively.
Figure 2 | 3D atomic coordinates and crystal defects in Re-doped MoS₂. 

a, Top view of the 3D reconstruction of data set 1. The inset shows the side view of MoS₂ (panel 1), MoS₂ with a Re dopant and a S vacancy (panel 2), and MoS₂ with 3 S vacancies (panel 3), where arrows indicate the vacancies. Scale bar, 1 nm and scale bar (inset), 2 Å. 

b, 3D atomic model of the bounded region in (a), consisting of 1381 S, 686 Mo and 21 Re atoms with 15 S vacancies. 

c, The distribution of the Mo-Mo, Mo-Re, S-S, Mo-S and Re-S bond lengths measured from two data sets. 

d, 3D plot of the Mo/Re layer showing atomics-scale ripples in data set 1, where the dots represent the Mo/Re atoms. 

e, Histogram of the distribution of the z coordinates of the Mo/Re atoms in data set 1 with a standard deviation (σ) of 0.19 Å.
Figure 3 | Measurements of 3D atomic displacements and the full strain tensor in Re-doped MoS$_2$. a-c, 3D atomic displacements of Mo (dots) and Re (circled dots) atoms along the x-, y- and z-axis, respectively. d-i, Six components of the strain tensor in the Mo/Re layer, where the Re dopants (circles) induced local strains in the $\varepsilon_{xx}$, $\varepsilon_{yy}$, and $\varepsilon_{zz}$ maps. The x-, y- and z-axis are along the [1,0,0], [0,1,0] and [0,0,1] directions, respectively. The strain tensor of the two S layers is shown in Extended Data Fig. 8. Scale bar, 2 nm.
Figure 4 | Electronic band structures obtained from experimental 3D atomic coordinates and photoluminescence measurements. a-d, Four supercells selected from different regions of Re-doped MoS$_2$ (e), including a dopant-free MoS$_2$ structure, a single Re dopant, double Re dopants, and mixture of a Re dopant and a S vacancy. The experimental coordinates of the supercells were used as direct input to DFT to reveal the electronic band structures (a-d, left). For comparison, the experimental atomic coordinates were theoretically relaxed and then fed to DFT to obtain the electronic band structures (a-d, middle). f, Photoluminescence (PL) spectra of as synthesized pristine MoS$_2$ (blue) and Re-doped MoS$_2$ monolayers (black). Scale bar, 2 nm.
**METHODS**

**2D materials synthesis.** Molybdenum oxide powder (99%, Sigma Aldrich), sulfur powder (99.5%, Sigma Aldrich) and ammonium perrhenate (99%, Sigma Aldrich) were used as precursors for chemical vapor deposition growth. A selected ratio of molybdenum oxide and ammonium perrhenate was added to an alumina boat with a Si/SiO₂ (285 nm) wafer cover. The furnace temperature was ramped to 550 °C in 15 min and then kept at 550 °C for another 15 min for the growth of the Re-doped MoS₂ alloy materials. We found the films to show a doping concentration of roughly $x = 0.04$. Sulfur powder in another alumina boat was placed upstream where the temperature was roughly 200 °C. After growth, the furnace was cooled to room temperature using natural convection. The growth process was carried out under 50 SCCM argon at atmospheric pressure. The Re-doped MoS₂ flakes were transferred to 3 mm Quantifoil TEM grids by spin coating the samples with PMMA to support the flakes, and then were etched with KOH to release the flakes from the substrates. The sample was dipped into Acetone for 2 hours to wash away PMMA and then baked in vacuum at 10⁻³ Pa and 160 °C.

**Low-dose data acquisition of 2D materials.** Two data sets, each consisting of 13 projections, were acquired from different regions of a Re-doped MoS₂ monolayer using a Nion UltraSTEM 100™ aberration-corrected scanning transmission electron microscope (STEM) (Extended Data Table 1). Images were collected at 60 kV in annular dark-field (ADF)-STEM mode. The beam convergence semi-angle was 30 mrad and the detector collection angle was in the range of 30-300 mrad, where a small detector inner angle was chosen to reduce the electron dose. The energy spread of the electron beam was 0.3 eV. A double tilt sample holder was used to collect the data sets (Extended Data Table 2). To reduce the total electron dose, 10 images per angle were measured with a beam current of 15 pA and a dwell time of 4 μs per image. To monitor any potential structural changes induced by the electron beam, the first and last projections of each data set were compared to ensure that no noticeable structural changes were observed during data acquisition (Extended Data Fig. 2). The total electron dose of each data set was estimated to be $4.1 \times 10^5 \, \text{e}^-/\text{Å}^2$ (Extended Data Table 1).

**Image processing and denoising.** The ten images at each tilt angle were registered using normalized cross correlation and summed. Linear stage drift was estimated during the image registration and corrected for each image. The raw ADF-STEM images contain mixed Poisson and Gaussian noise, and a sparse 3D transform-domain collaborative filtering (BM3D) was applied to denoise the average image of each tilt angle. Two different sets of denoising parameters were applied for the BM3D: one is the exact noise level estimated from the experimental images (termed BM3D 100%), and the other is by doubling the estimated noise level (termed BM3D 200%). There are two reasons for the use of BM3D 100% and 200%. First, this would allow us to cross-validate the reconstructions with different denoising parameters. Second, the BM3D 100% reconstruction provided better contrast between the Re, Mo and S atoms, while BM3D 200% produced better reconstruction for the S atoms. All these post-processing and denoising methods have been previously demonstrated to be robust for dealing with ADF-STEM images.

**Angle calibration and 3D coordinate fitting of the Re and Mo atoms.** The nominal angles were measured by the Nion double tilt stage (Extended Data Table 2). After denoising each projection, we
determined the x and y coordinates of each Re and Mo atom by fitting a 2D Gaussian in a 5×5 pixel region. According to a geometric relation, the x and y coordinates of the Re and Mo atoms in each data set change as a function of the tilt angle. To calibrate the tilt angles and determine the 3D coordinates of the Re and Mo atoms, we used the least square method to minimize the following equation,

\[ S = \sum_i \sum_j \left( [P_x(r_i, \alpha_j, \beta_j) - x_i]^2 + [P_y(r_i, \alpha_j, \beta_j) - y_i]^2 \right) \]  

where \( P_x \) and \( P_y \) are the functions of projecting the 3D coordinates of the Re and Mo atoms to the x and y coordinates in the projections, respectively, \( r_i \) is the 3D coordinates of the \( i^{th} \) Re or Mo atom, \( \alpha_j \) and \( \beta_j \) are the tilt angles of the \( j^{th} \) projection, \( x_i^f \) and \( y_i^f \) are the measured x and y coordinates in the \( i^{th} \) atom in the \( j^{th} \) projection, respectively. By minimizing \( S \), we calibrated the tilt angles of the 13 projections (Extended Data Table 2) and obtained the 3D coordinates of all the Re and Mo atoms in each data set (Extended Data Fig. 6). This least square fitting method is robust and produces consistent results regardless of different initial input.

**Deconvolution for vibrational correction.** Due to the high length/thickness ratio and the free-standing structure, we observed the 2D material suffered from vibrational blurring along the perpendicular direction to the TEM grid during data acquisition. The vibrational blurring is equivalent to convolving the images with a kernel and can be removed through deconvolution if the blurring kernel is known. In this experiment, the blurring kernel was estimated based on the fact that all atoms should be spherical. We performed deconvolution using the following procedure. First, we interpolated each experimental image by a factor of 2 with linear interpolation and cropped a region of 100×100 pixels without Re dopants. Second, a MoS\(_2\) model of the same experimental tilt angle was used to create a reference image of the same size as the cropped experimental image but with spherical atoms. The reference image was normalized and aligned with the experimental image. Third, a vibrational kernel was constructed by adjusting the vibrational direction, vibration amplitude and Gaussian blurring. The experimental image was deconvolved with the constructed kernel using the Lucy-Richardson algorithm\(^{39,40}\) and compared with the reference image. A brute-force process was conducted until an optimal kernel was obtained, creating the best match between the experimental and reference images. Finally, the optimal kernel was applied to the whole experimental image using the Lucy-Richardson algorithm. The deconvolved image was binned to be its original scale. A comparison between before and after deconvolution is shown in Extended Data Fig. 3.

**Image partition and reconstruction with sAET.** To implement sAET, we chose a 3D window of 60×60×60 voxels and scanned it along the x and y axis with a step size of 30 voxels. This step size offsets each partition to include a 30 voxel overlap between neighboring partitions on each side. At each step, the corresponding regions from all 13 projections in each data set were cropped and grouped into an image stack. Each image stack consists of 13 images with varied shapes, corresponding to the projection of the 3D window along different tilt angles. After a full 2D scan was completed, all the projections were partitioned into image stacks. All the image stacks were aligned and reconstructed in parallel by the generalized Fourier iterative reconstruction (GENFIRE) algorithm\(^{29}\). Each GENFIRE reconstruction used
a 33-voxel support along the z-axis and ran 1000 iterations. Due to the extended nature of the 2D materials along the x and y axis, the reconstruction of each image stack contained artifacts near the boundary. To remove these artifacts, we stitched together only the central 30x30x33 voxels of the reconstructed windows to produce a full 3D reconstruction. By applying this partition and reconstruction procedure, we obtained the full 3D reconstructions of both the BM3D 100% and 200% projections of each data set.

Initial localization of 3D atomic coordinates and species. The 3D atomic coordinates and species of the 2D material were initially traced from the 3D reconstructions using the following procedure. We first identified all local maxima in the BM3D 200% reconstruction of each data set. Starting from the highest-intensity local maximum peak, we cropped a 1.71x1.71x1.71 Å$^3$ (5x5x5 voxel) volume with the selected local peak as the center. We fitted the volume with a 3D Gaussian function described elsewhere$^{22-24}$. If a fitted peak position satisfied a minimum distance of 1.6 Å away from any previously fitted peak (i.e. a minimum distance constraint), we added it to a list of potential atoms. By applying the 3D Gaussian fitting algorithm to all the identified atoms, we obtained a complete list of potential atom positions. These positions were manually checked to correct for unidentified or misidentified atoms due to fitting failure or areas with connected intensity blobs from multiple atoms. We then assigned the atomic species based on the 3D intensity distribution of the traced potential Re, Mo and S atoms.

Refinement of 3D atomic coordinates and species and identification of S vacancies. The traced 3D atomic coordinates and species were refined by the following procedure. First, each experimental image of BM3D 100% was converted to Fourier slices $F_{obs}^j(q)$ with $j = 1,\ldots,13$, by the fast Fourier transform. Next, 13 Fourier slices were calculated with the atomic model by

$$F_{calc}^j(q) = \sum_{n=1}^{N} H f_e(q) e^{-B'_q r_n^2} \frac{4}{2\pi i} r_n \cdot q,$$

where $N$ is the number of atoms, $H$ is the scaling factor for different atomic species, the $B'$ factor accounts for the electron probe size, the missing wedge and the thermal motion of each atomic species, $f_e(q)$ is a normalized electron scattering factor, $r_n$ is the 3D position of the $n^{th}$ atom. An error function was then calculated by

$$E = \sum_{j=1}^{13} \sum_{q} |F_{obs}^j(q) - F_{calc}^j(q)|^2,$$

which was minimized with respect to the atomic positions ($r_n$) by a gradient descent method$^{22-24}$.

From the refined 3D atomic model, we developed an atom pair flipping method to identify the S vacancies, which consists of the following four steps. First, we randomly chose a pair of S atoms between the top and bottom atomic layers. For each selected S pair, projection images were calculated for all the tilt angles by flipping the pair among four cases: i) both atoms are S, ii) both are vacancies, iii) the top is a S atom and the bottom is a vacancy, and iv) the top is a vacancy and the bottom is a S atom. Four atomic models were generated accordingly to the four cases, with the same $H$ and $B'$ factors. Second, four sets of 13 projections with the experimental tilt angles were calculated from the atomic models. An $R_1$ factor was computed between measured and calculated projections.
\[ R_1^j = \frac{\sum_{x,y} |f_{\text{obs}}^j(x,y) - f_{\text{calc}}^j(x,y)|}{\sum_{x,y} |f_{\text{obs}}^j(x,y)|}, \]  

(4)

\[ R_1 = \frac{\sum_j R_1^j}{13}, \]  

(5)

where \( f_{\text{obs}}^j(x,y) \) and \( f_{\text{calc}}^j(x,y) \) are the \( j \)th measured and calculated projection. As flipping a pair of atoms only affects a small cylindrical volume for each tilt angle, we only calculated a small area of projection along a cylindrical volume containing the atom pair. By comparing the \( R_1 \) factor among the four cases, the one with the smallest error \( R_1 \) was chosen and updated in the atomic model. Third, we repeated the first two steps for all the S atom pairs and obtained an updated 3D atomic model. A global scale factor was calculated for the updated atomic model to minimize the error between the measured and calculated projections. Fourth, we iterated steps one to three for all the S atom pairs until there was no change in the atomic species. The atom pair flipping method was robust and converged after a few iterations for both data sets. After identifying all the S vacancies, we refined the 3D atomic coordinates once more using equations (2) and (3).

**Dynamic refinement of the S atoms near the Re atoms.** Due to the use of a low energy electron beam (60 keV) and a small detector inner angle to reduce the electron dose, we observed the dynamic scattering effect of the Re atoms (see the next section in detail), which influenced some nearby S atoms. We implemented a brute-force approach to perform dynamic refinement of these Re and S atoms. We first identified those S atoms nearby the Re atoms, which either violated a minimum distance of 1.6 Å (caused by the refinement) or deviated from the S atomic layer more than 1 Å. There were 11 and 13 such S atoms in data set 1 and 2, respectively. For each of these S and Re atoms, we performed a 3D scan of its position with a range of ±40 pm along the x and y axis and ±120 pm along the z axis. The step size is 20 pm, 20 pm and 30 pm along the x, y and z axis, respectively. At each scanning step, we used multislice simulations to calculate 13 projection images of 40×40 pixels in size at different tilt angles and computed the \( R_1 \) factor relative to the measured images. The S atom in the atomic model was updated to the position corresponding to the minimum \( R_1 \) factor. We repeated this dynamic refinement procedure for all the S atoms whose positions were influenced by nearby Re atoms.

**Multislice simulations for precision estimation.** We performed multislice simulations to estimate the 3D precision of the atomic coordinates and species\(^{41,42}\). The experimental atomic model was placed in a rectangular super cell. The super cell was divided into multiple 2 Å slices along the z axis, and the x–y plane was discretized into 1,920×1,920 pixels. The same experimental parameters were used for the multislice simulations (E: 60 keV; C3: 0 mm; C5: 5 mm; convergence semi-angle: 30 mrad; detector inner angle: 30 mrad and detector outer angle: 300 mrad). Each STEM image was generated by a raster scan in the x–y plane with a step size of 0.34 Å. For each tilt angle, we averaged 12 phonon configurations to obtain a projection image. The image was convolved with a 5×5 pixel Gaussian kernel (\( \sigma = 1.0 \)) to account for the electron probe size, thermal vibrations, and other incoherent effects. The mixture of Gaussian and Poisson noise determined from the experimental images was added to the multislice images (Extended Data Fig. 7). From the 13 multislice images of data set 1, we used the same imaging processing, sAET reconstruction, atom tracing and refinement procedures to obtain a new 3D atomic
model. By comparing it with the experimental 3D atomic model, we found all the atom species were correctly identified including all S vacancies. The RMSD of the S, Re and Mo atoms is 15 pm, 12 pm and 4 pm, respectively (Fig. 1b).

Next, we performed multislice simulations using the same parameters except changing the detector inner angle to 50 mrad. We added Gaussian and Poisson noise to the multislice projections with the same electron dose and obtained another 3D atomic model. In comparison to the experimental atomic model, all the atom species were correctly identified and the RMSD of the S, Re and Mo atoms is 18 pm, 3 pm and 3 pm, respectively. Compared to the 30 mrad detector inner angle results, the RMSD of the Re atoms is decreased due to the reduced dynamic scattering effect, while the RMSD of the S atoms is increased due to the weaker intensity in the 50 mrad detector inner angle case.

**Measurement of the 3D strain tensor of Re-doped MoS$_2$**. The strain tensor was determined from the experimental 3D atomic coordinates using a procedure described elsewhere. The experimental atomic model of each data set was least-square fitted to an ideal MoS$_2$ model. The displacement vectors, $\Delta \mathbf{u}$, were calculated as the difference in the atomic positions between the experimental and ideal model. Each displacement component ($\Delta x$, $\Delta y$, $\Delta z$) was interpolated to a cubic grid through kernel density estimation. A 3D Gaussian kernel with $\sigma = 3.16$ Å was convolved with the displacement fields, which increases the precision of the strain tensor measurement, but reduces the resolution. The six components of the strain tensor of the two data sets are shown in Extended Data Fig. 8.

To estimate the local strain tensor induced by single Re dopants, we drew spheres of a radius of 3.16 Å centered at the Re atoms. The histograms of the local strain tensor within the spheres for the two data sets are shown in Extended Data Fig. 9. For comparison, we also drew 3.16-Å-radius spheres centered at the Mo atoms without including any Re atom and obtained the histograms of the local strain tensor within the spheres (Extended Data Fig. 9). We observed that, due to the single Re dopants, the average local strains of the $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$ component changed by 0.42%, 0.33% and 1.1%, respectively, while the change of the average $\varepsilon_{xy}$, $\varepsilon_{xz}$ and $\varepsilon_{yz}$ component was very small.

To determine the principal strain of the four supercells in Fig. 4, we calculated the average strain tensor within each supercell and then solved for the eigenvalues and eigenvectors of the average strain tensor. The principal strain and three corresponding directions are [0.4%, -0.23%, -1.15%], [0.86,0.20,0.47], [0.15,0.79,-0.60] and [-0.49,0.58,0.65] for supercell A, [0.5%,-1.00%, -0.60%], [-0.87,-0.37,-0.32], [-0.48,0.75,0.44] and [0.08,0.54,-0.84] for supercell B, [0.14%,-0.71%, -1.58%], [0.93,0.37,0.04], [-0.37,0.92,0.10] and [0.00,-0.11,0.99] for supercell C, and [-0.04%,-1.84%, 1.35%], [-0.92,-0.20,0.34], [-0.26,0.95,-0.15] and [0.30,0.23,0.92] for supercell D.

**DFT calculations of the effective band structure**. To perform DFT calculations of the electronic properties of the Re-doped MoS$_2$ materials from the experimental 3D coordinates, a 20 Hartree plane-wave energy cutoff was applied on a $3\times3\times1$ K-point mesh on $6\times6\times1$ supercells of the MoS$_2$ sub-regions. We employed ultrasoft pseudopotentials and modeled the exchange and correlation interactions with the PBEsol functional. A Fermi smearing of 0.01 Hartrees was used to more accurately account for temperature effects present during experimental measurements at room temperature. In order to
adequately describe the isolated monolayer without neighboring image effects, a Coulomb truncation scheme was used in the out-of-plane direction\textsuperscript{44}. All calculations were performed using JDFTx\textsuperscript{45}.

**Band Unfolding.** Due to the relationship between reciprocal and real space, the Brillouin zone of a supercell is some fraction of the size of a primitive cell Brillouin zone. To recover information about the cell with respect to a reference primitive cell, one must apply band unfolding techniques to the Kohn-Sham wavefunctions\textsuperscript{46,47}, which were used to obtain the effective band structures shown in Fig. 4. The reciprocal spaces of a primitive unit cell and a supercell are geometrically related, with the lattice vectors of one being an integer matrix transformation of the other. We unfolded each cell onto a primitive cell with a hexagonal lattice constant equal to the experimental value. Because we modeled each subsystem as a supercell, periodic boundary conditions were applied to a larger real space lattice than in a traditional primitive cell. As a result, the Brillouin zone of our sub-regions is smaller than that of a primitive cell hexagonal lattice, and the high symmetry k point path differs between the two.

This leads naturally to a description of the supercell Bloch states in terms of the primitive cell \( \mathbf{k} \) states for which \( \mathbf{k} \) in the primitive cell is equivalent to \( \mathbf{K} \) in the super cell by a reciprocal lattice vector translation. In particular, the overlap of the supercell Bloch states (indexed by a supercell wave vector \( \mathbf{K} \) and band index \( m \)) with the Bloch states of a primitive cell is given by the spectral weight:

\[
P_{\mathbf{K}m}(\mathbf{k}_i) = \sum_n |\langle \mathbf{K}m | \mathbf{k}_i n \rangle|^2 . \tag{6}
\]

where the supercell \( \mathbf{K} \)-point is projected (unfolded) to the \( \mathbf{k}_i \)-points in the primitive cell. In practice, the spectral weights can be obtained without reference to the primitive cell Bloch states, provided the matrix is known which transforms the desired primitive cell lattice to that of the supercell. The spectral weights are used to find the spectral function, defined by:

\[
A(\mathbf{k}_i, E) = \sum_n P_{\mathbf{K}m}(\mathbf{k}_i) \delta(E_m - E) . \tag{7}
\]

In the effective band structure, the relative weight of the spectral function is referenced via the color map intensity for each point in the primitive cell Brillouin zone. The formalism for this is principally exact. The spectral function technique directly quantifies the degree to which the primitive cell symmetry is maintained in the supercell. If a state with wave vector \( \mathbf{K} \) at some energy does not possess any of the symmetries of the primitive cell, the spectral weight of these points will be zero, such that they do not appear in the resulting band structure. For the case of a supercell constructed purely from some reference primitive cell, the unfolding procedure will produce the expected band structure exactly because the supercell possesses all of the same higher symmetries as the primitive cell, and the spectral weights will all be unity.

On the other hand, disordered, strained, or otherwise non-perfect supercells will possess shadow bands or broadening: points of the primitive cell Brillouin zone where the spectral weights have intermediate values between 0 and 1. This indicates that some, but not all, of the underlying symmetries are preserved. While these methods should not be expected to exactly reproduce standard results in these situations, these features can be useful in understanding the nature of a given cell.
**Photoluminescence measurements.** The photoluminescence spectroscopy experiment was performed at room temperature using a Renishaw inVia instrument. Both pristine MoS$_2$ and Re-doped MoS$_2$ monolayer samples were synthesized under the same conditions and placed on SiO$_2$ substrates. An excitation laser of 514.5 nm wavelengths was focused onto the samples via a 100X objective lens, producing a spot diameter of ~1 µm. The laser power was kept at 5 mW. The photoluminescence spectra show the MoS$_2$ monolayer is a direct band gap semiconductor and the Re-doped MoS$_2$ monolayer is an indirect band gap semiconductor (Fig. 4f).

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Extended Data Figure 1 | A tilt series of 13 experimental projections of a Re-doped MoS$_2$ monolayer (data set 1). The bright dots are individual Re dopants. Scale bar, 2 nm.
Extended Data Figure 2 | Sample Consistency check. a and b. Comparison of the first and last images for data set 1 and data set 2, respectively, indicating the consistency of the atomic structure during data acquisition. Scale bar, 1 nm.
Extended Data Figure 3 | Image deconvolution for sample vibration correction. a, A representative image of the Re-doped MoS$_2$ monolayer at a high tilt angle, where the atoms are elongated due to vibrational blurring. b, The same image after deconvolution using a harmonic oscillator kernel, where the atoms become spherical. c, The harmonic oscillator deconvolution kernel. Scale bar, 1 nm.
Extended Data Figure 4 | The same tilt series of 13 experimental projections shown in Fig. 1 after denoising and deconvolution. Scale bar, 2 nm.
Extended Data Figure 5 | 3D atomic coordinates and crystal defects in data set 2. a, Top view of the 3D reconstruction. Scale bar, 1 nm. b, 3D atomic model of the bounded region in (a), consisting of 1083 S, 531 Mo and 16 Re atoms with 4 S vacancies. c, 3D plot of the Mo/Re layer showing atomics-scale ripples, where the dots represent the Mo/Re atoms. d, Histogram of the distribution of the z coordinates of the Mo/Re atoms in data set 1 with a standard deviation (σ) of 0.16 Å.
Extended Data Figure 6 | Least square fitting to determine the 3D coordinates of the Re and Mo atoms. 

**a**, The x and y coordinates of the Re and Mo atoms were localized from the aligned projections of each data set. **b**, From these 2D coordinates, the tilt angles were calibrated and the 3D coordinates of the Re and Mo atoms were determined for each data set. The 3D atomic coordinates are consistent with those obtained by sAET with a RMSD of 2 pm and 13 pm for Mo (c) and Re (d) atoms, respectively. Scale bar, 1 nm.
Extended Data Figure 7 | Multislice simulation results. a, The experiment image versus the multislice image of the same region. b and c, The intensity profiles corresponding to labelled regions 1 and 2 in (a), where the high, medium and low intensity peaks represent the Re, Mo and S atoms, respectively.
Extended Data Figure 8 | Full 3D strain tensor of data set 1 (a) and data set 2 (b). The six strain components are shown from left to right columns, and the three atomic layers are displayed from top to bottom. Scale bar, 2 nm.
Extended Data Figure 9 | Histograms of the local strain tensor near the Mo atoms (blue) and the Re atoms (black). The Re dopants induced a mean local strain change of the $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$ components by 0.42%, 0.33% and 1.1%, respectively, while the change of the mean local strain of the $\varepsilon_{xy}$, $\varepsilon_{xz}$ and $\varepsilon_{yz}$ components is very small.

Extended Data Figure 10 | Strain tensor maps of $\varepsilon_{xx}$ (A), $\varepsilon_{yy}$ (B), $\varepsilon_{zz}$ (C) of the Mo/Re layer in data set 1 are highlighted with areas representing four 6×6×1 supercells used in DFT calculations with labels (a), (b), (c) and (d) in Fig. 4. Scale bar, 2nm.
Extended Data Table 1 | sAET data collection, reconstruction, refinement statistics.

| Data collection and processing | Data set 1 | Data set 2 |
|-------------------------------|-----------|-----------|
| Voltage (kV)                  | 60        | 60        |
| Convergence semi-angle (mrad) | 30        | 30        |
| Probe size (Å)                | 1.3       | 1.3       |
| Detector inner angle (mrad)   | 30        | 30        |
| Detector outer angle (mrad)   | 300       | 300       |
| Depth of focus (nm)           | 10        | 10        |
| Pixel size (Å)                | 0.34      | 0.34      |
| # of projections              | 13        | 13        |
| Tilt range                    | See table S2 | See table S2 |
| Electron dose (10^5 e/Å^2)    | 4.1       | 4.1       |

**Reconstruction**

| Algorithm                   | GENFIRE   | GENFIRE   |
|----------------------------|-----------|-----------|
| Interpolation radius (voxel)| 0.3       | 0.3       |
| Oversampling ratio          | 3         | 3         |
| Number of iterations        | 1,000     | 1,000     |

**Refinement**

| R_l (%)                     | 13.4      | 13.0      |
|----------------------------|-----------|-----------|
| R (%)^a                     | 25.5      | 24.2      |
| B’ factors (Å^2)            |           |           |
| Mo atoms                    | 13.4      | 14.6      |
| S atoms                     | 13.0      | 13.0      |
| Re atoms                    | 14.2      | 15.8      |
| # of total atoms            | 2,103     | 1,634     |
| # of Mo atoms               | 686       | 531       |
| # of S atoms                | 1,381     | 1,083     |
| # of Re atoms               | 21        | 16        |
| # of S vacancies            | 15        | 4         |

^aThe R factor was calculated by \( R = \frac{\sum |F_{obs}| - |F_{calc}|}{\sum |F_{obs}|} \), where \(|F_{obs}|\) is the Fourier magnitude obtained from experimental projections and \(|F_{calc}|\) is the Fourier magnitude calculated from a 3D atomic model.
## Extended Data Table 2 | Angle calibration for a double tilt Nion stage.

The nominal angles were read out from the microscope. The angles were calibrated by 3D coordinate fitting of the Re and Mo atoms using least square minimization.

| Tilt axis | Nominal angles (°) | Calibrated angles (°) Data set 1 | Calibrated angles (°) Data set 2 |
|-----------|--------------------|----------------------------------|----------------------------------|
|           | α                  | β                                | α                                | β                                |
| Tilt axis | [0 -1 0]           | [ -1 0 0]                        | [-0.1 1.0 0]                     | [ -1.0 0.2 0.2]                  |
| Projection| 0                  | 0                                | 0                                | 0                                |
| #1        |                    |                                  |                                  |                                  |
| #2        | -14.3              | -22.9                            | -15.1                            | -17.8                            |
| #3        | -14.3              | 17.1                             | -12.6                            | 16.8                             |
| #4        | 20.1               | 17.1                             | 19.1                             | 18.2                             |
| #5        | 20.1               | -20.1                            | 17.7                             | -19.8                            |
| #6        | 12.6               | -12.6                            | 13.1                             | -12.0                            |
| #7        | 12.6               | 12.6                             | 13.0                             | 12.8                             |
| #8        | -12.6              | 12.6                             | -13.1                            | 13.6                             |
| #9        | -12.6              | -12.6                            | -14.4                            | -9.2                             |
| #10       | -6.3               | -6.3                             | -8.2                             | -3.6                             |
| #11       | -6.3               | 6.3                              | -7.6                             | 8.0                              |
| #12       | 6.3                | 6.3                              | 5.2                              | 8.5                              |
| #13       | 6.3                | -6.3                             | 4.9                              | -4.9                             |

**Supplementary Video 1.** 3D sAET reconstruction of the Re-doped MoS$_2$ monolayer (data set 1), showing the different intensity distribution of the Re, Mo and S atoms as well as the S vacancies.

**Supplementary Video 2.** 3D atomic model of the Re-doped MoS$_2$ monolayer (data set 1) determined by sAET, consisting of 1380 S (in yellow), 686 Mo (in blue), 21 Re atoms (in black) and 16 S vacancies (in pink). Compared to an ideal MoS$_2$ atomic model (in lighter colors), the experimental model shows 3D crystal defects, atomic displacements and full strain tensors of the 2D material. The local strains induced by single Re dopants are also visible.