

Supplementary information for:
Rapidly resolving bilayer stacking orientation in industrially compatible
MOCVD-grown MoS₂ films through second harmonic generation imaging

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LIST OF FIGURES

Figure S1	Bright-field, white-light microscopy image of a MoS ₂ film	5
Figure S2	Histograms of bilayer island sizes	6
Figure S3	Wide-field image of the area shown in Figure 3	7
Figure S4	Additional AFM traces of bilayers	8
Figure S5	Microscopy of trilayers	9
Figure S6	Fitting of PL spectra	10
Figure S7	Additional SHG maps of exfoliated MoS ₂ 2H bilayers	11
Figure S8	Additional PL maps	12

EXPERIMENTAL

1. *Second harmonic microscopy*

Second harmonic generation (SHG) microscopy was conducted on a commercial multi-photon inverted microscope (Nikon A1R-MP). Laser excitation was provided by a tunable Ti:Sapphire laser (MaiTai DeepSee) with an output of up to 8 mW at the sample at $\lambda = 900$ nm with a repetition rate of 80 MHz. The pulse duration as measured with FROG was 87 fs. Laser excitation was focused onto the sample through a 0.75 NA, 20 $\times$ objective lens (Nikon) and signal from the sample was collected confocally. The laser excitation spot, as measured by two-photon fluorescence from 40 nm polystyrene beads, was (650 ± 70) nm. The second harmonic at $\lambda = 450$ nm was sent to a photomultiplier tube detector (Hamamatsu) with a quantum efficiency of $\sim 20\%$ at 450 nm, filtering off the fundamental and background light with a series of filters. To generate SHG images, the laser was scanned over an area of 80×80 μm , while a motorized stage was used to scan the sample over larger areas up to several mm^2 , stitching frames together. Each frame was scanned 32 times and the signals averaged to increase the signal to noise ratio.

Images were processed in ImageJ, converted to txt images, and plotted in python to generate color scales. Intensity linescans were taken with ImageJ, averaged over lines 10 pixels wide, and plotted in python. For bilayer island sizing, a brightness threshold was applied to isolate either 2H or 3R islands, followed by an edge-detection algorithm to find the islands. Thereafter the particle sizing function in ImageJ was used to measure the size of

each island, from which histograms were produced (Figure S2).

2. *Bright-field, white-light microscopy*

Bright-field, white-light imaging was conducted in a customized, modular microscope (WiTec AlphaR). Samples were illuminated with a broadband LED in confocal geometry, with images collected on a CCD camera. Wide-field images were taken with a $5\times$ objective (Olympus) with frames stitched together by moving the sample with a motorized stage. High-resolution images were taken with a 0.9 NA, $100\times$ objective lens (Olympus). To take contrast linescans, images were analyzed in ImageJ in a similar manner to the SHG maps.

3. *Photoluminescence spectroscopy and mapping*

Photoluminescence (PL) spectra and maps were taken on the same WiTec microscope used for bright-field, white-light microscopy images. Samples were excited with a diode laser with a wavelength of 532 nm at a power of 100 μ W focused through a NA=0.9, $100\times$ magnification objective lens (Olympus) in a confocal geometry. The excitation laser was filtered off, and the PL signal was collected with a fiber and sent to a grating spectrometer and dispersed with a 150 gr/mm 500 nm blaze grating onto a CCD camera (WiTec Oxford Instruments). For mapping, spectra were collected with an integration time of 0.2 seconds, with a scan area of 100×100 pixels and $7 \times 7 \mu\text{m}$.

PL spectra were fitted with pseudo-voigt lineshapes for components from the A exciton, B exciton, and indirect gap emission, labeled X_A , X_B , I , respectively. Intensity maps were generated by integrating over the fitted peak for each component, other hyperspectral maps were generated by plotting the corresponding fit parameter. Spectra shown in Figures 4b and S6 are averaged over a 2×2 pixel square to improve the signal to noise ratio.

4. *Atomic force microscopy*

Atomic force microscopy (AFM) was conducted on a Bruker Dimension Icon, operated in tapping mode with 150 kHz Si tips (Bruker) with a scan rate of less than 0.5 Hz and a resolution of 1024×1024 (points x lines). AFM images were processed in Gwyddion,

with background subtraction by binomial fits to the background, aligning rows, and plane leveling. Linescans over individual bilayers was done by averaging over three adjacent lines.

5. *Sample preparation*

MoS₂ films were synthesized by metal-organic chemical vapor deposition (MOCVD) according to previously reported procedures.¹ Briefly, MoS₂ was deposited on 2 inch 1° off-A-axis cut sapphire wafers in a modified cross-flow reactor (Polygon8200) using 200 mm Silicon platform at IMEC. H₂S and Mo(CO)₆ were used as S and Mo precursors with N₂ carrier gas. The deposition was conducted at 1000 °C at a pressure of 75 Torr for 25 mins, followed by cooling in sulfur-rich atmosphere.

MOCVD-synthesized films were transferred to a freshly cleaned sapphire substrate for subsequent imaging and spectroscopy experiments using a previously reported technique.² Briefly, the coupon transfer uses a thermally responsive polymer adhesive tape to delaminate the MoS₂ film coated with PMMA from its growth substrate with the aid of intercalated water, followed by stamping on a target substrate and heating to remove the polymer stamp.

Samples exfoliated from bulk crystals were prepared using the gold-assisted exfoliation (GAE) technique.³ Bulk 2H-phase MoS₂ single crystals were used to exfoliate large-area monolayers on sapphire substrates, with some small additional layers from the parent crystal resulting in 2H-stacked bi- or multi-layers, with layer number identified by correlation between AFM, Raman spectroscopy, and optical imaging.

SUPPLEMENTAL DATA

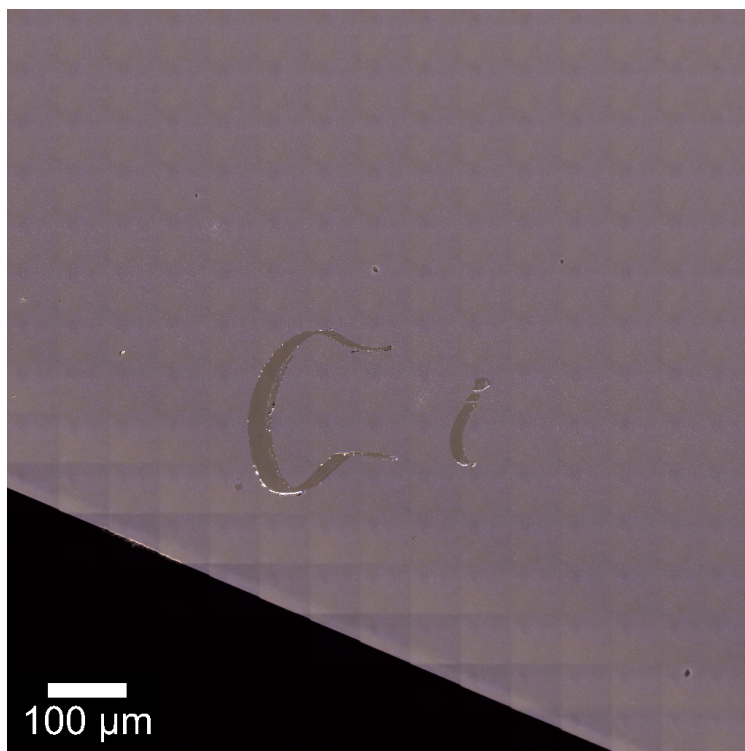


Figure S1: Low-magnification, bright-field, white-light microscopy image of one of the MOCVD-grown MoS₂ films studied. The image is composed of several images taken with a 5× magnification objective and stitched together while scanning with a motorized stage.

Alt text: Low-magnification, bright-field, white-light microscopy image of one of the MOCVD-grown MoS₂ films studied

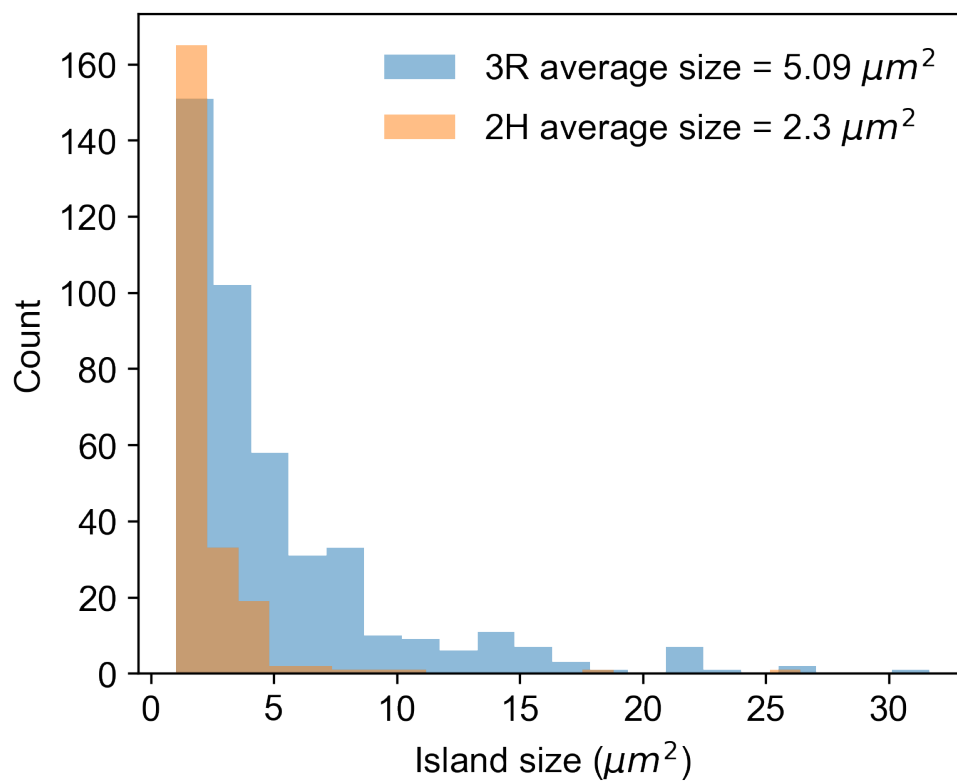


Figure S2: Histogram of 2H (orange) and 3R (blue) bilayer island sizes as measured from SHG maps.

Alt text: Histogram of 2H and 3R bilayer island sizes as measured from SHG maps

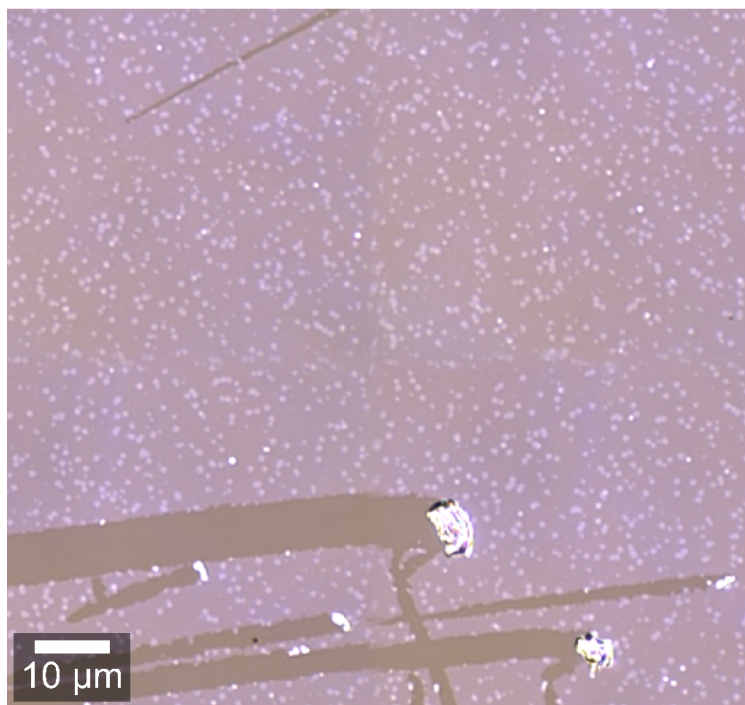


Figure S3: Wide-field, bright-field, white-light microscopy image of the area imaged with SHG, AFM, and PL shown in Figure 3 of the main text.

Alt text: Wide-field, bright-field, white-light microscopy image of the area imaged with SHG, AFM, and PL shown in Figure 3 of the main text

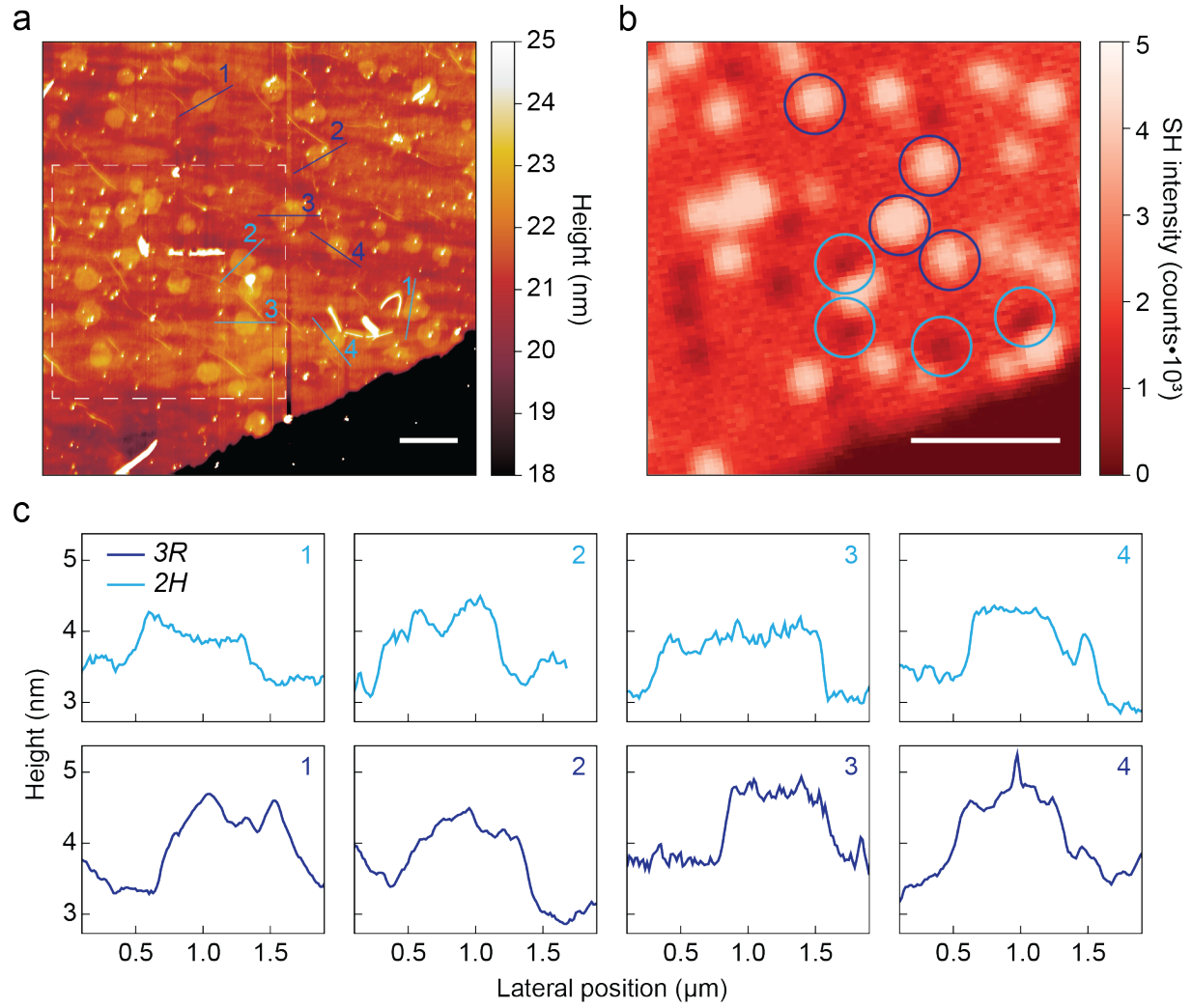


Figure S4: **a)** AFM image from which traces for additional bilayers were taken. Traces of 3R bilayers are indicated by dark blue lines; 2H, light blue. White dashed box indicates the region shown in Figures 3 and 4 of the main text. Scalebar: $2\mu\text{m}$. **b)** SHG image of the corresponding area in (a), with dark blue (light blue) circles indicating 3R (2H) bilayers traced in (a). Scalebar: $5\mu\text{m}$. **c)** Plotted height scans from corresponding numbered bilayers in (a).

Alt text: Further AFM images and linescans of bilayers

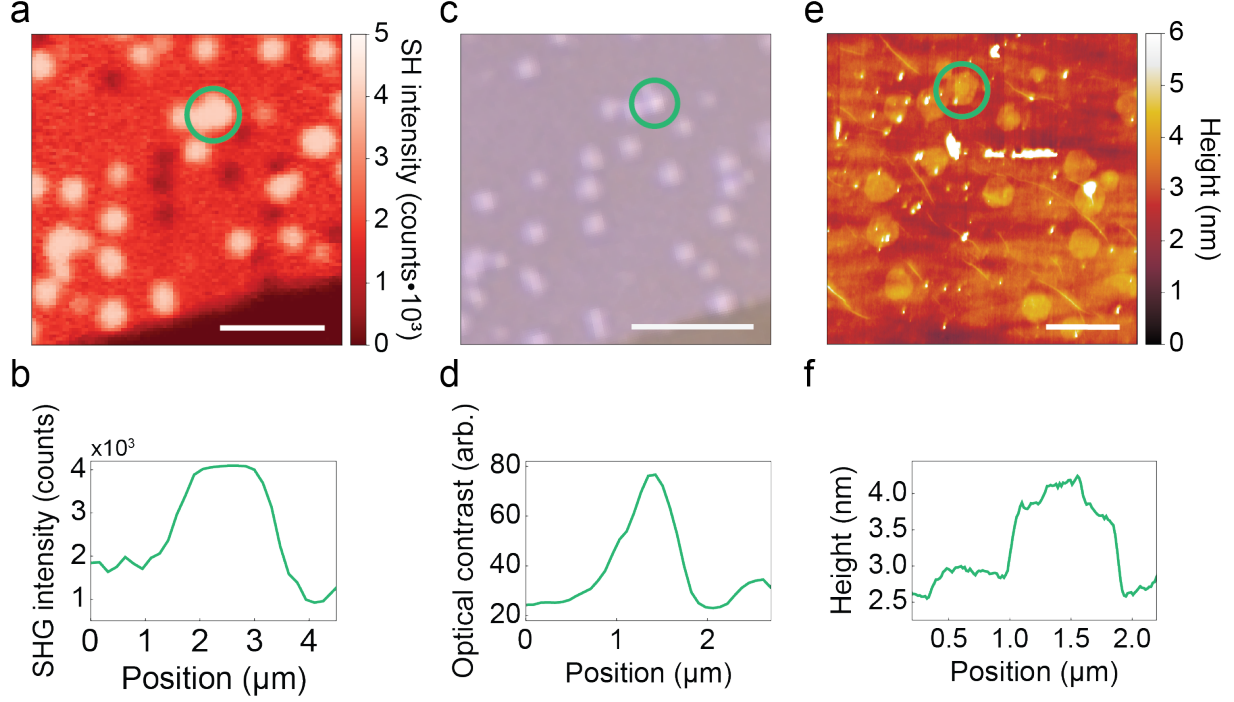


Figure S5: **a)** SHG map of a MoS₂ monolayer film and multilayer islands as shown in Figure 3 of the main text. Green circle indicated a trilayer island. Scalebar: 5 μm . **b)** SH intensity trace of the trilayer circled in (a). **c)** bright-field, white-light microscopy image of the same region as (a). Scalebar: 5 μm . **d)** Optical contrast trace of the trilayer circled in (c). **e)** AFM image of the same area as (a). Scalebar: 2 μm . **f)** AFM linescan from circled areas in (e) showing the clear formation of a third layer on top of a bilayer island.

Alt text: Optical, SHG, and AFM imaging of a trilayer

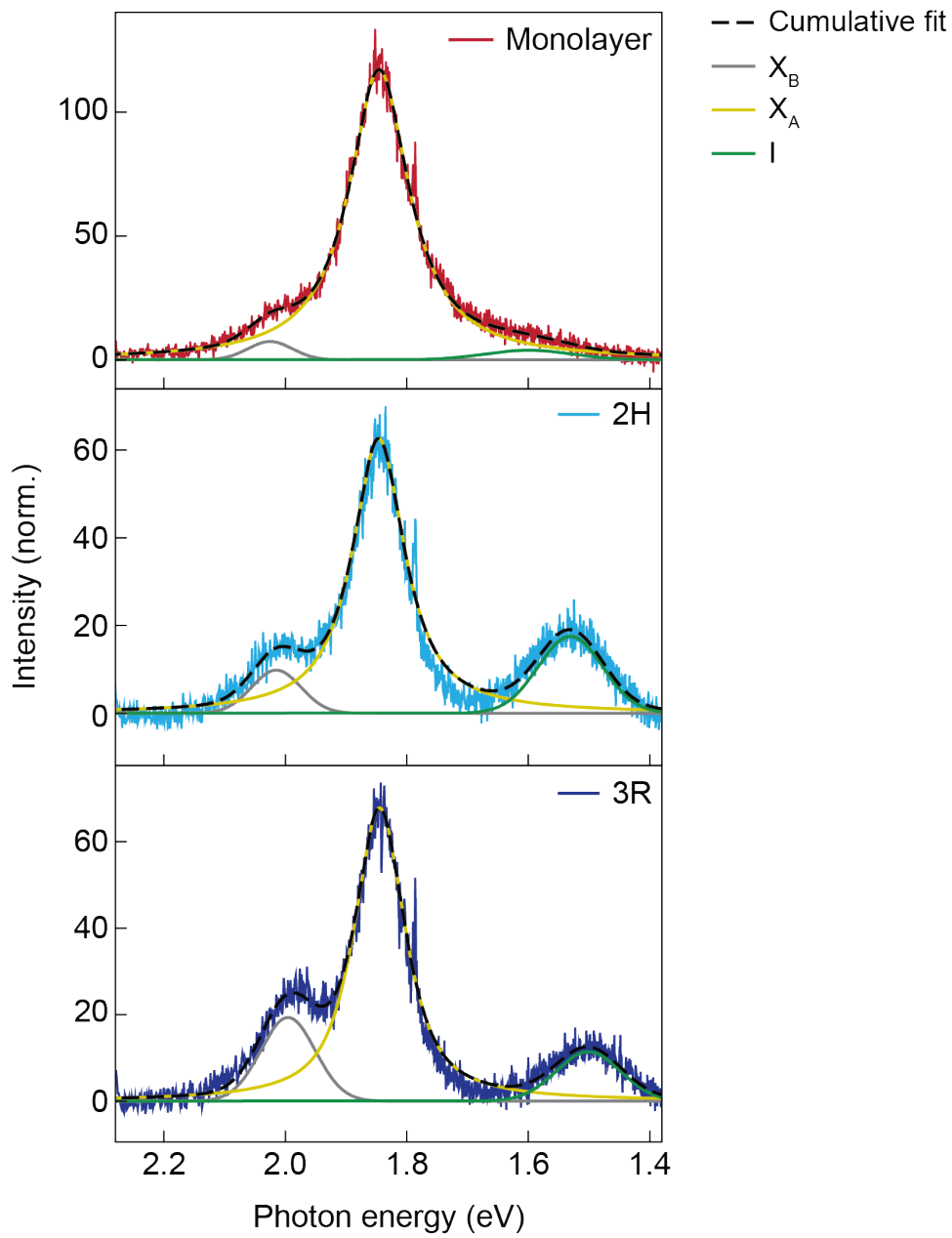


Figure S6: Fits to the spectra shown in figure 4b in the main text showing contributions from X_A (yellow), X_B (purple), I (green).

Alt text: PL spectra with fits for B exciton, A exciton, and indirect emission

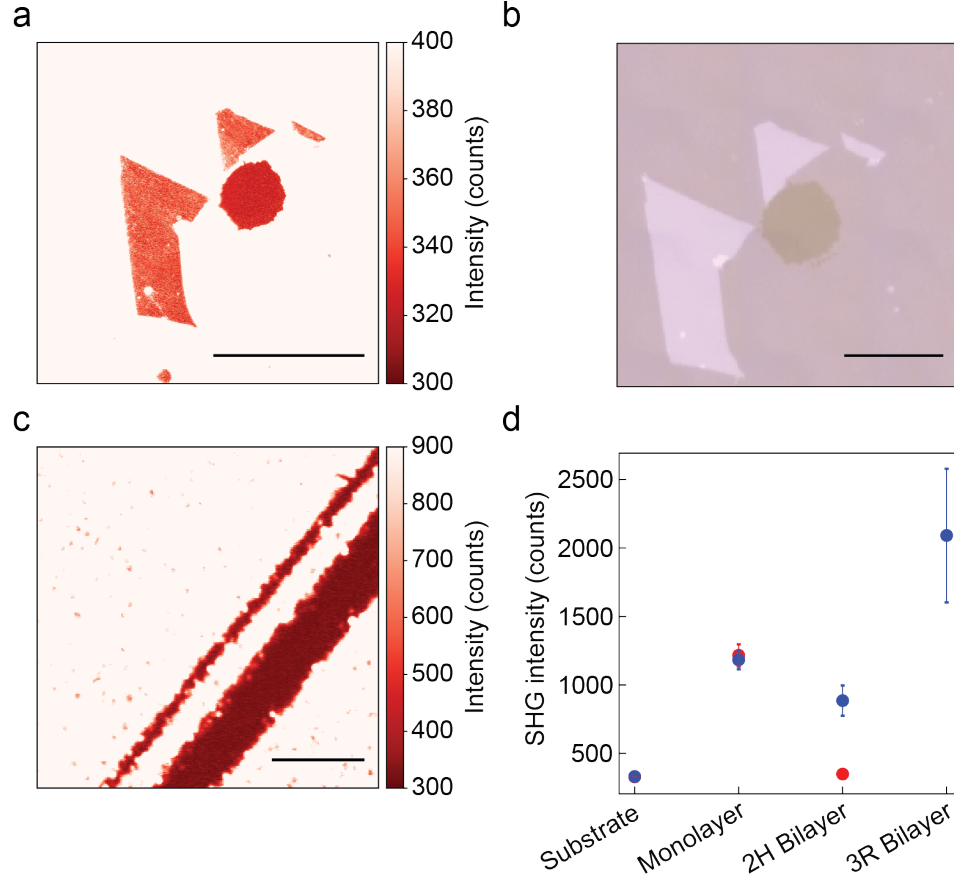


Figure S7: Additional SHG maps of exfoliated and MOCVD-grown MoS₂ highlighting bilayers and substrate signal. **a)** SHG map of a MoS₂ flake exfoliated from a bulk 2H-phase crystal onto a sapphire substrate, with the intensity scale highlighting the response of the substrate and bilayers within the crystal. Scalebar: 100 μ m. **b)** White-light, bright-field microscopy image of the same exfoliated crystal as in **(a)** showing that the circular region is a void in the crystal with only the SHG response of sapphire and the straight-edged domains corresponding to 2H bilayer MoS₂. Scalebar: 50 μ m. **c)** SHG image of an MOCVD-grown MoS₂ film on sapphire with the intensity range similarly narrowed to highlight the difference between the SHG signal from the substrate and 2H bilayer islands. Scalebar: 20 μ m. **d)** Scatter plot of average intensities from SHG maps **(a)** and **(b)** from regions with bare sapphire substrate, monolayer, 2H bilayer, and 3R bilayer which is only observed in the case of MOCVD-grown films.

Alt text: Additional SHG maps of exfoliated and MOCVD-grown MoS₂ highlighting bilayers and substrate signal

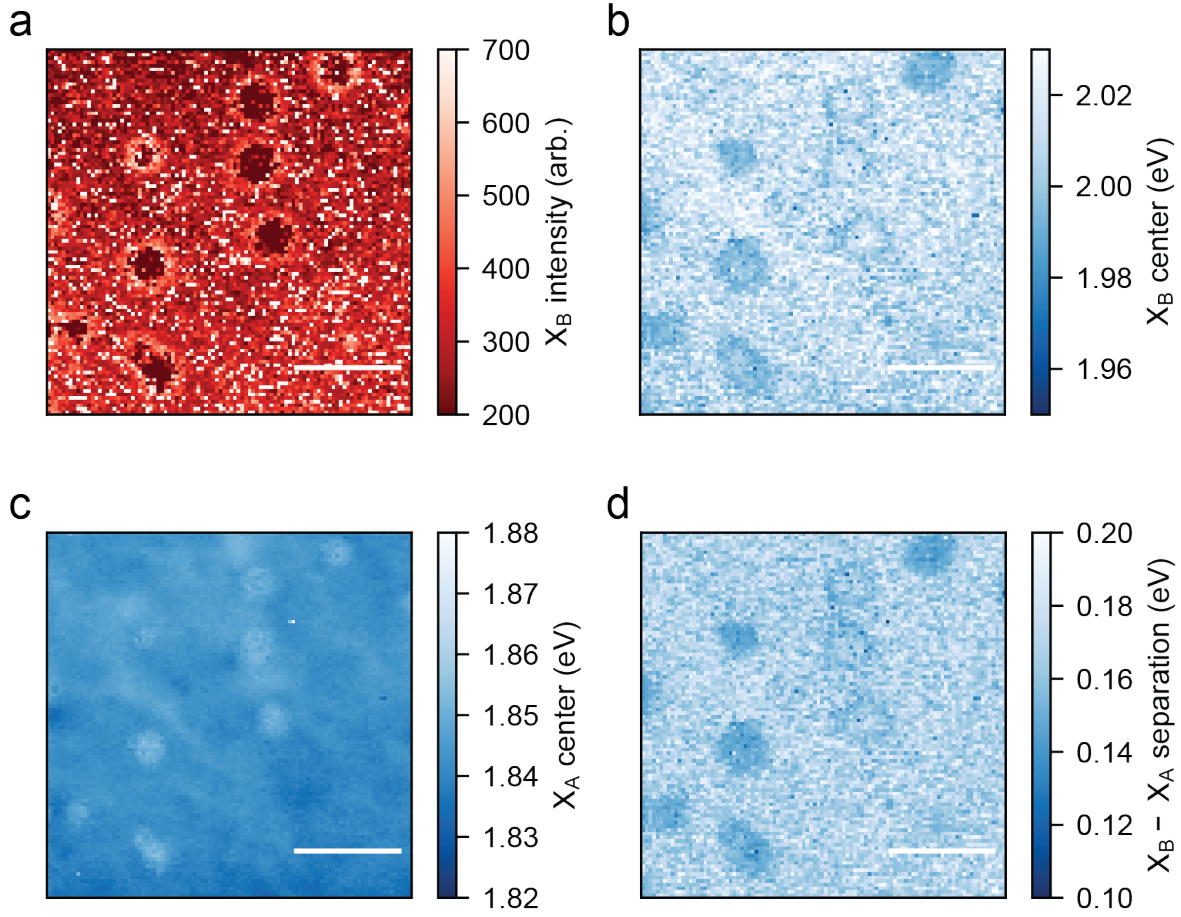


Figure S8: Additional hyperspectral PL maps from the same map as shown in figure 4 of the main text. **a)** Map of fitted X_B peak intensity. **b)** Map of fitted X_B peak position. **c)** Map of fitted X_A peak position. **d)** Map of difference in fitted peak position between X_B and X_A . Scalebars: 2 μm

Alt text: Additional hyperspectral PL maps from the same map as shown in figure 4 of the main text

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