Understanding the Emergence of Negative Photoconductivity in CVD grown ReS_2 thin Film

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Growth of ReS_2 thin film over mica substrate

To have the space confined growth mica micro reactor was used as substrate. A micro-reactor was created by stacking two (or more) freshly cleaved fluor phlogopite mica pieces. The two mica substrates adhered to one another firmly due to the electrostatic force between them and formed a space confined reaction space. The micro-reactor reduced the concentration of precursors, resulting in lower nucleation density and growth rate for ReS_2. We define the bottom face of mica substrate as face 1, inside faces as face 2 and face 3 respectively, topmost face as face 4 as depicted in Figure S1b. Layer-by-layer growth of ReS_2 is facilitated by weak interlayer coupling. As seen in Figure S 1a, the layer number of 2D ReS_2 thin films can be controlled by varying the distances between the ReO_3 powder and the mica substrate. Initially, ReO_3 powder was placed at the center of a 5 cm long quartz boat and mica substrate was placed directly above the ReO_3 powder. Under this growth condition bilayer film deposition was achieved. To promote monolayer growth, we displace the substrate 0.5 cm right to the ReO_3 powder. The 0.5 cm shift reduced the ReO_3 flux to the substrate, resulting in the formation of a thinner film.

The enlarged view of mica micro reactor is depicted in Figure S1b. Face 1 exhibits consistent large-area monolayer ReS_2 growth, while face 2 shows scattered flake growth attributed to confined nucleation.

Raman Spectral analysis. There are three Raman active modes in ReS_2 A_g-like, E_g-like and C_p modes due to in-plane vibration, out-of-plane vibrations and mixed vibration respectively.[1,2] Raman spectrum of ReS_2 exhibits two distinct segments, due to the significant difference in atomic masses between Re and S atoms. Raman spectra of ReS_2 film consisting of 13 first-order Raman active modes is depicted in Figure 1d of main paper. Raman mode below 250 cm^{-1}, correspond to the motion of Re atoms, whereas vibrational modes above 250 cm^{-1} indicate the vibrational behaviour of S atoms.[3] For Re atom in-plane vibration E_g modes are observed at 150.0, 160.4, 212.0 and 233.8 cm^{-1}.[1] The out-of-plane vibration A_g modes of Re atoms were observed at 136.6 cm^{-1}. For sulphur, E_g modes appear at 305.5 cm^{-1} and A_g modes centered at 417.0 and 435.7 cm^{-1}. The contracted vibration of the Re-S atom is located at 279.6 cm^{-1}. Apart from these the mixed in-plane and out-of-plane vibrations of S atoms are centred at 320.2, 345.4, and 372.0 cm^{-1}. All these findings are consistent with the literature and tabulated in table S1, therefore support the synthesis of the 1T′-phase of ReS_2.[4]

Supporting note 5

Supplementary results

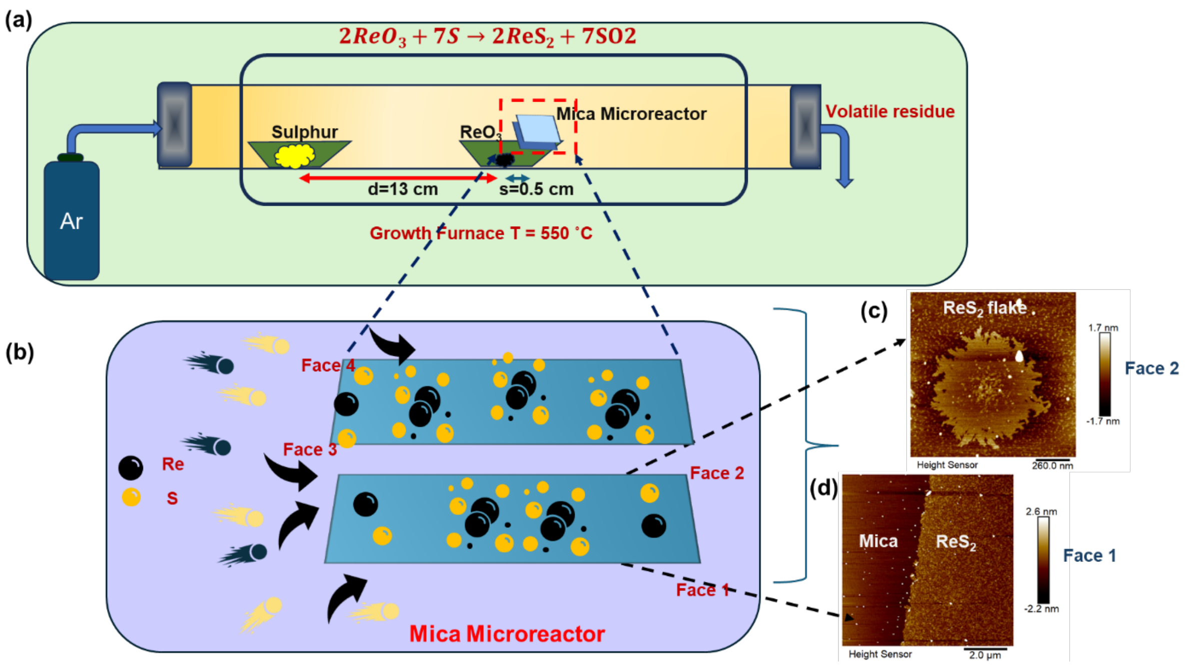

Figure S1. Schematic of CVD grown ReS_2 using mica microreactor as substrate. (b) Enlarged view of the confined space reaction on the mica surface. (c) Monolayer flake growth on face 2. (d) Large area monolayer growth on face 1

Symmetry	Vibrations	Literature Raman shift (cm^{-1})	Experimental (cm^{-1})	FWHM (cm^{-1})
A_g- like	Out-of-plane vibration of Re atoms	140.3	**136.6**	**10.8**
A_g- like	Out-of-plane vibration of Re atoms	145.9		
E_g - like	In-plane vibration of Re atoms	153.1	**150**	**6.4**
E_g - like	In-plane vibration of Re atoms	163.6	**160.4**	**4.9**
E_g - like	In-plane vibration of Re atoms	217.2	**212**	**6.4**
E_g - like	In-plane vibration of Re atoms	237.1	**233.8**	**6.6**
C_p	In-plane and out-of-plane vibration of Re and S atoms	278.3	**277.4**	**13.4**
C_p	In-plane and out-of-plane vibration of Re and S atoms	282.6		
E_g - like	In-plane vibration of S atoms	307.8	**305.5**	**10.4**
E_g - like	In-plane vibration of S atoms	311.0		
C_p	In-plane and out-of-plane vibration of S atoms	320.6	**320.2**	**9.0**
C_p	In-plane and out-of-plane vibration of S atoms	324.9		
C_p	In-plane and out-of-plane vibration of S atoms	348.8	**345.4**	**7.0**
C_p	In-plane and out-of-plane vibration of S atoms	368.9	**372**	**12**
C_p	In-plane and out-of-plane vibration of S atoms	377.9		
C_p	In-plane and out-of-plane vibration of S atoms	407.3	**405.5**	**8.4**
A_g- like	Out-of-plane vibration of S atoms	418.7	**417**	**5.9**
A_g- like	Out-of-plane vibration of S atoms	438.0	**435.7**	**8.5**

Table S1. Comparison of experimental findings of Raman modes with reported literature.

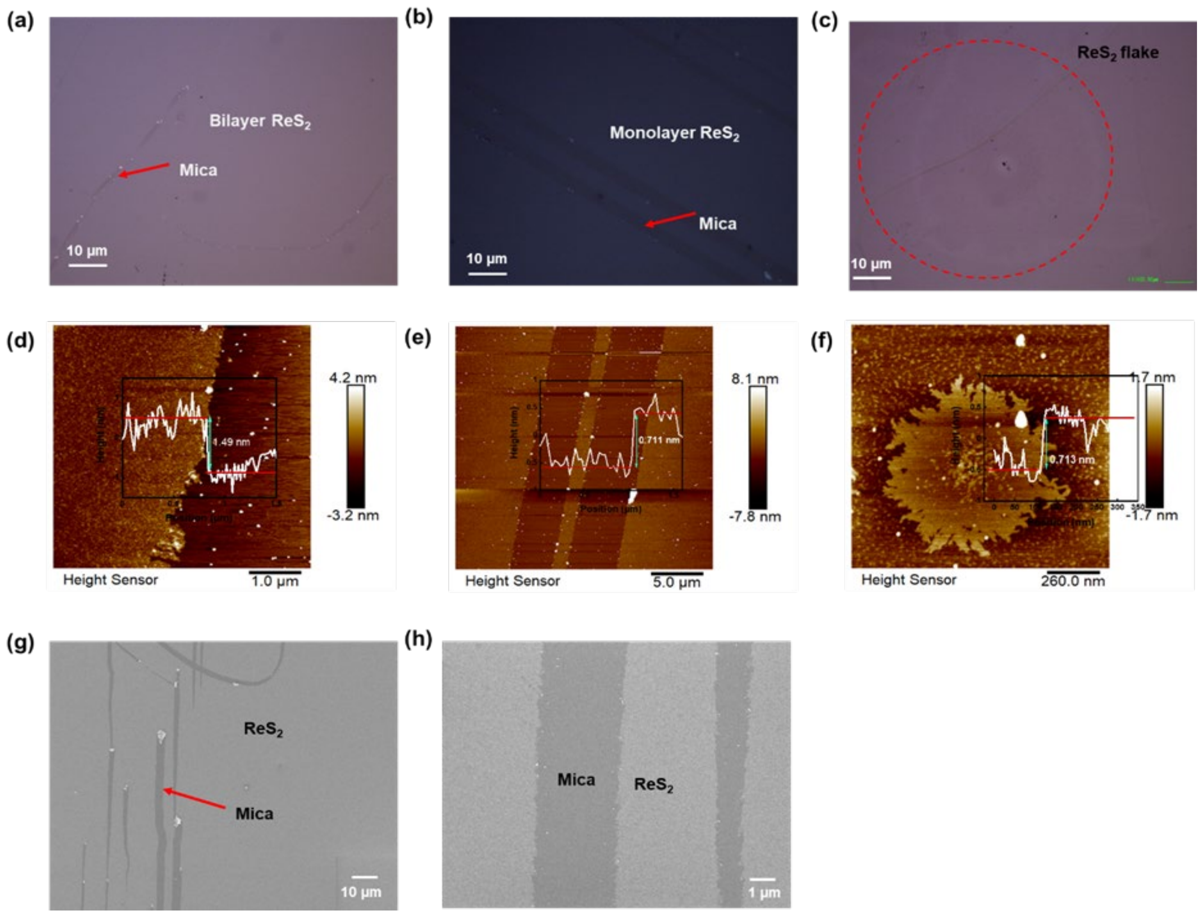

Figure S2. Optical microscopy (OM) images of (a) continuous ReS_2 film (b) Film grown on face1 and (c) Flake growth on face2 over mica substrate. Mica substrate can be easily distinguished through color contrast shown via red arrow. (d-f) AFM images with height profile intact over the step indicate the growth of bilayer and monolayer film (g), (h) FESEM image of as grown ReS_2 indicates the smooth and larger area growth.

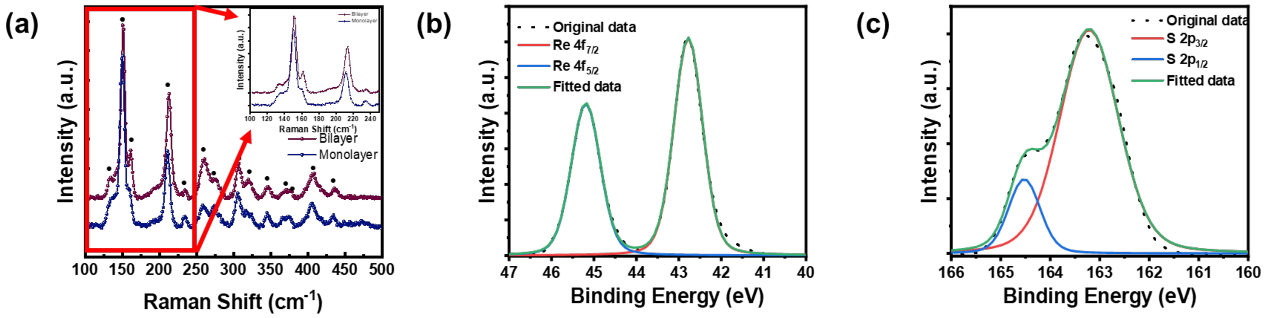

Figure S3. (a) Raman spectra of monolayer and bilayer ReS_2 film grown over mica substrate. Inset shows the magnified Raman spectra of characteristics modes of ReS_2. (b) and (c) Core level spectra of Re and S atoms.

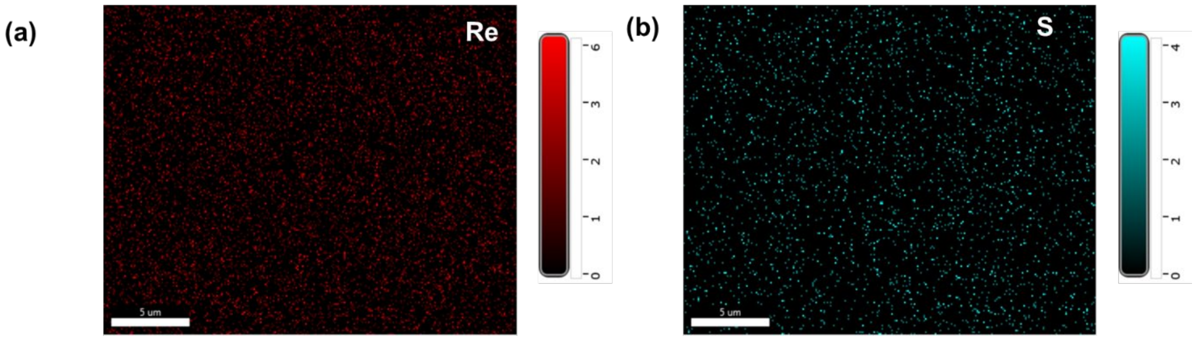

Figure S4. EDX map of as grown ReS_2 film with the scale bar (5µm). Indicates the uniform film formation over large area.

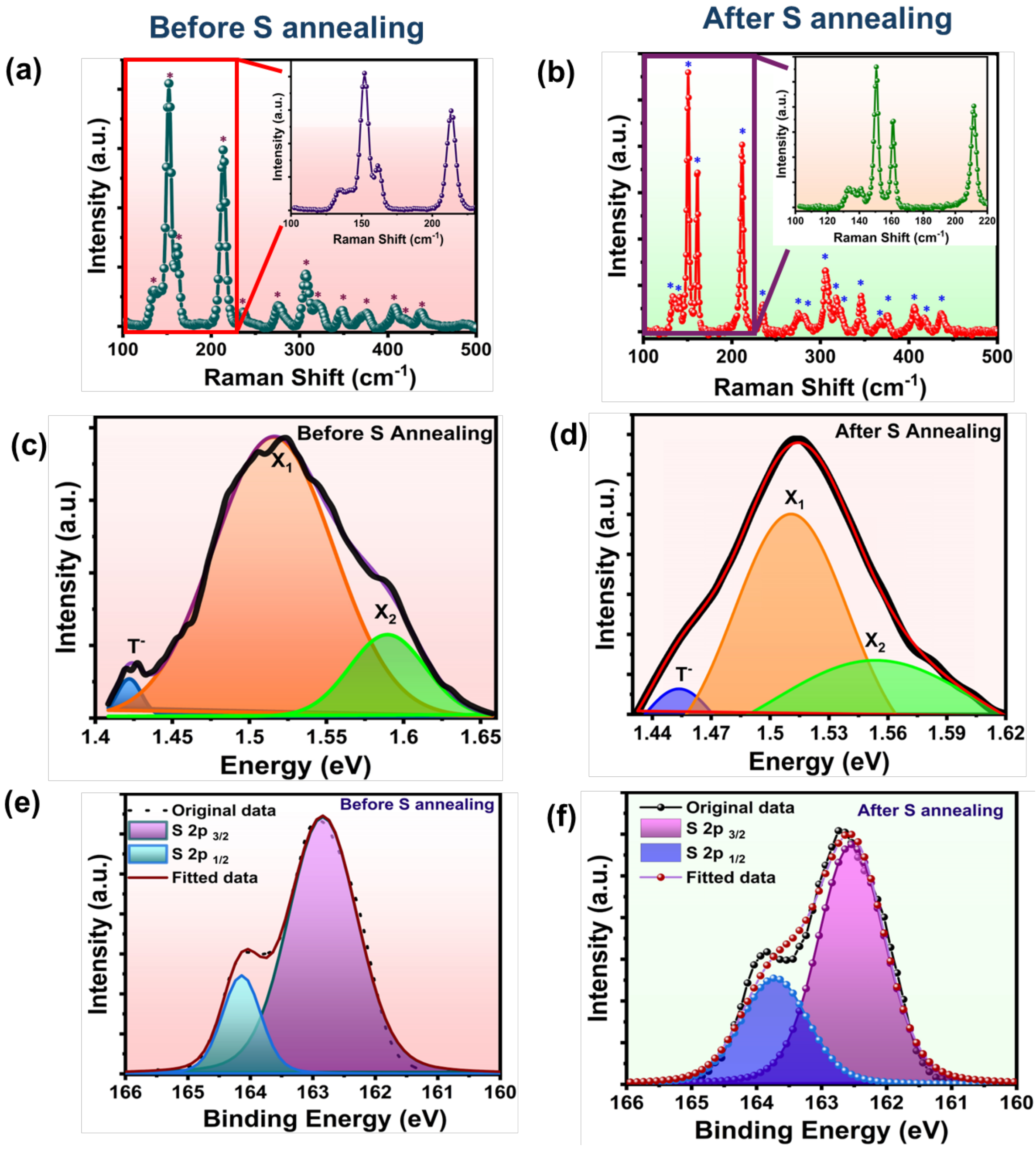

Figure S5. Comparison Raman, PL and XPS spectra before and after S annealing

References

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