Supplementary Information for

Polytypism and Unexpected Strong Interlayer Coupling of two-Dimensional Layered ReS_2

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1. The optical image and AFM image of monolayer ReS_2

The optical image and AFM image of monolayer ReS_2 are displayed in Fig. S1. The different interactions of AFM tip with the flake and with the SiO_2/Si substrate will lead to discrepancies in layer thickness.[1] The AFM image shows the thickness of monolayer ReS_2 is 1.4 nm. Because the thickness of the monolayer ReS2 is about 0.7 nm, the offset of AFM is 0.7 nm.

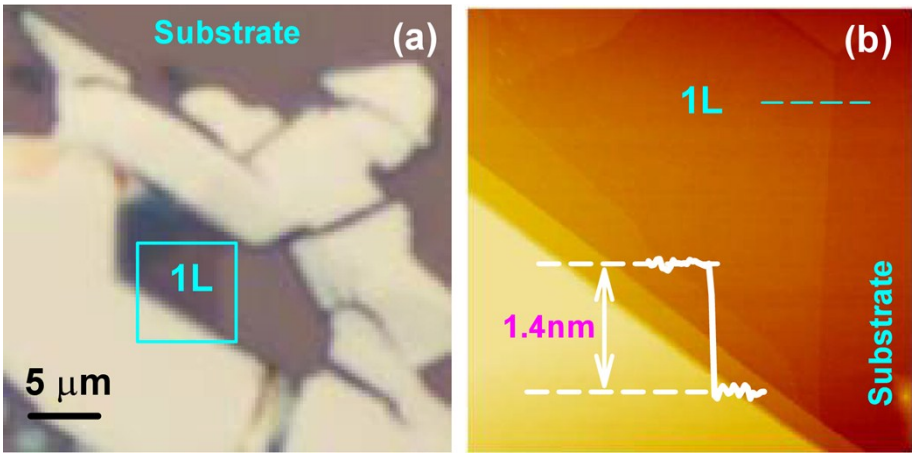

Figure S1 Optical image (a) and AFM image (b) of monolayer ReS_2

2. The polarization dependent Raman spectra of the SA and SB flake in the range of 100-450 cm^{-1}

Due to the reduced in-plane symmetry, the intensities of the intra-layer Raman modes in ReS_2 exhibit pronounced anisotropy. The strong in-plane anisotropy of the high frequency Raman modes is studied by rotating incident polarization angle. Fig. S2 (a) and Fig. S2 (c) displays a series of Raman spectra of the SA and SB flake in the range of 100-450 cm^{-1} at different excitation polarization angles. In the high frequency region of Raman spectrum, more than eighteen peaks are observed, for the SA and SB flake, which are consistent with the report.[2,3] The positions of all Raman modes are

independent of the incident polarization directions, whereas the relative intensities change significantly with the varying incident polarization directions. The intensities of these modes show strong dependence on the polarization direction of the incident laser. Three typical peaks in the SA flake, ma, mb and mc, are located at 134.8 cm^{-1}, 153.8 cm^{-1} and 214.4 cm^{-1}, respectively, while the frequencies of the three typical peaks in the SB flake are 138.0 cm^{-1}, 152.7 cm^{-1} and 213.4 cm^{-1}, respectively. Polar plots of the Raman peak intensities of three typical peaks as a function of the polarization angle are shown in Fig. S2(b) and Fig. S2(d), respectively, for the SA and SB flake. The intensity maximum of different Raman modes is at different polarization of the incident laser, due to different Raman tensor of each Raman peak.

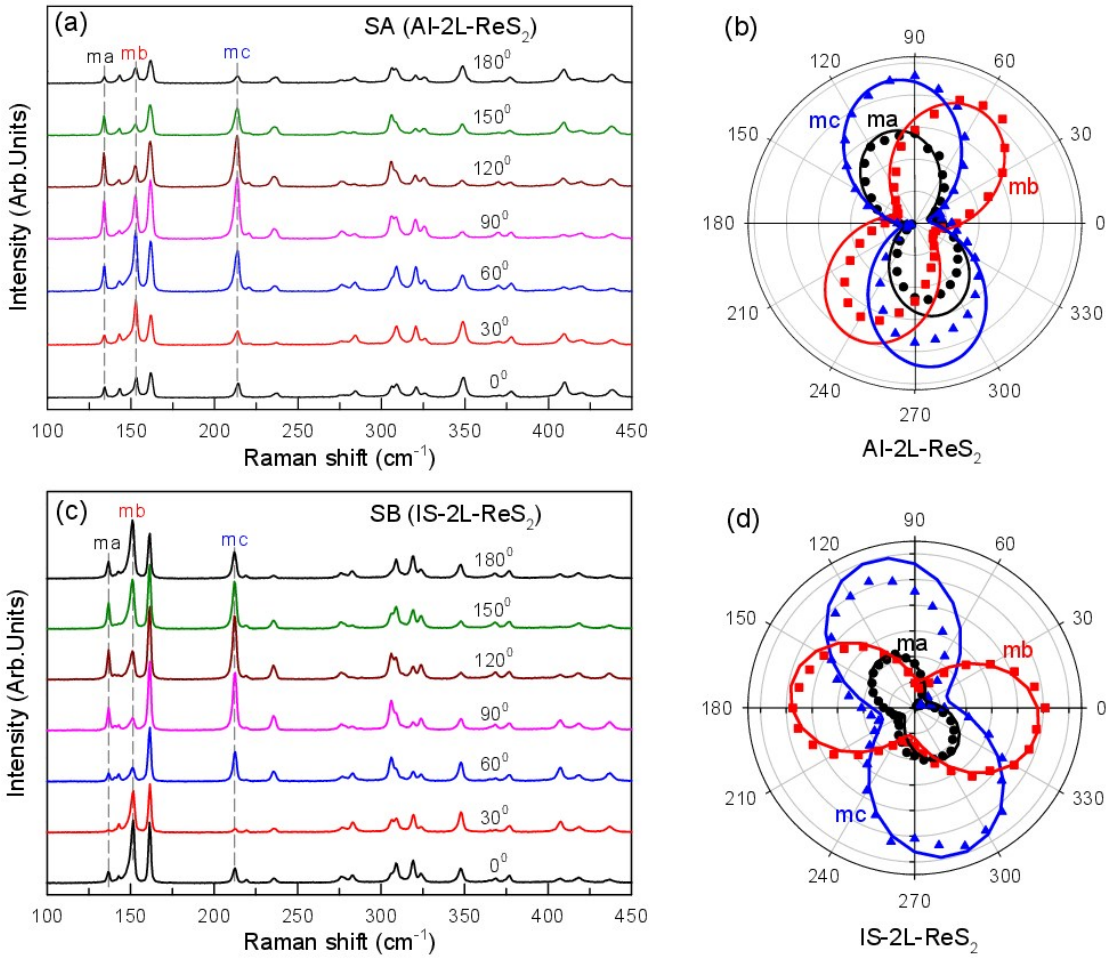

Figure S2 (a,c) Polarized Raman spectra of the SA and SB flake with different polarization angle in 30^0 steps in the 100-450 cm^{-1} range. (b,d) Polar plots of the Raman peak intensities of three typical peaks in the SA and SB flake as a function of the polarization angle.

3. Possible stacking orders for 2L ReS_2

In a bilayer ReS_2 (Fig. S3(**a**) and (**b**)), when stacking two monolayer together, there are two free degrees, orientation of the shortened lattice (black rectangle in Fig. S3(**a**)) and stacking sites around the Re-Re bond (red circle in Fig. S3(**a**)), Which gives 12 possible bilayer configurations. The stacking orientation of the shortened lattice

vectors leads to two different categories of bilayers. Bilayer ReS_2 remains anisotropic if the two shortened lattice directions are parallel or oriented by 60°, see the cartoon in Fig. S3(**c-f**) and (**g-j**). However, if the two directions are stacked with a rotation angle of 120°, both shortened directions, in other words the Re-Re bond, are along the lattice vectors of a bilayer, thus leading to a transformation from the anisotropic bilayer to a nearly isotropic one, as illustrated in Fig. S3(**k-n**). The most stable structures in the same direction are marked by red dashed rectangle and the energy of this structure (set the energy of AI-2L-ReS_2 (**g**) as 0.00 eV) is also shown in Fig. S3. Figures S3(**j**) and (**k**) are the origin structures of the anisotropic-like AI-2L-ReS_2 and isotropic-like IS-2L-ReS_2 mentioned in manuscript.

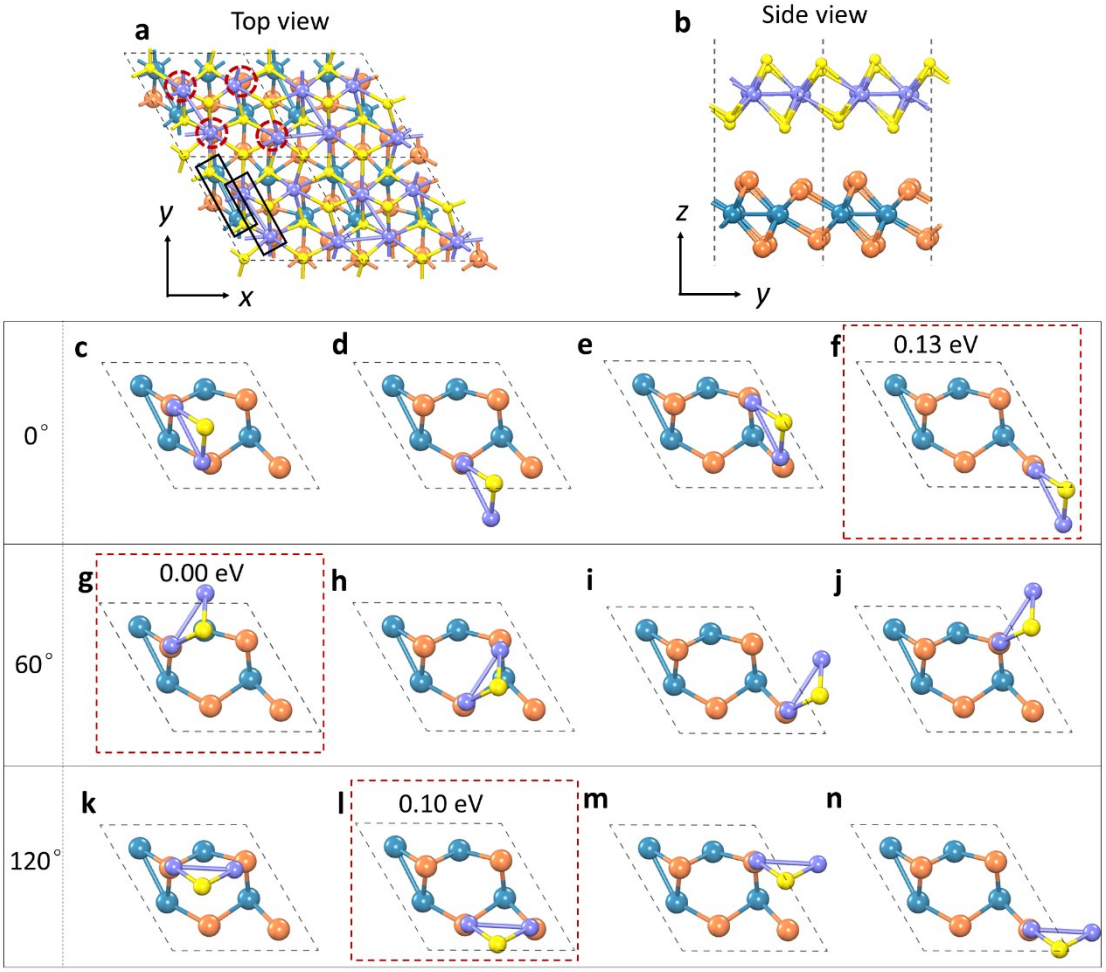

Figure S3 Top (**a**) and side (**b**) views of the atomic structure for one of the considered stacking orders of 2L ReS_2. The shortest Re-Re bond and four Re sites are marked in the red rectangle and green circles in (**a**), respectively. Schematic illustration for all considered stacking orders of 2L ReS_2 are shown in (**c-n**) with the second layer Re-Re bond being oriented to 0° (**c-f**), 60° (**g-j**) and 120° (**k-n**), respectively. Four stacking sites are considered for each stacking orientation and the most stable site for each orientation is marked with a red dashed rectangle.

4. The low frequency Raman spectrum of AI-3L-ReS_2 and AI-4L-ReS_2

Raman spectrum measurement of AI-3L-ReS_2 and AI-4L-ReS_2 was also carried out

(shown in Fig. S4). AI-3L-ReS_2 exhibits a broad and asymmetrical peak, in addition to the two peaks at 10.0 cm^{-1} and 12.6 cm^{-1}. According to its asymmetrical peak profile, the broad peak can be fitted by three peaks at 16.3 cm^{-1}, 19.8 cm^{-1} and 21.0 cm^{-1}, denoted as C_{31}^{y}, LB_{32} and C_{31}^{x}, respectively, as shown in Fig. S4(a). We observed five peaks in the low frequency (<50 cm^{-1}) range of ReS_2 Raman spectrum. Similar to the case of AI-3L-ReS_2, the sub-peak fitting results are shown in Fig. S4(b), for the Raman spectrum of AI-4L-ReS_2. $C_{N,N-j}^{x}$ and $C_{N,N-j}^{y}$ mean shear modes along x and y direction, respectively, while $LB_{N,N-j}$ means layer breathing modes.

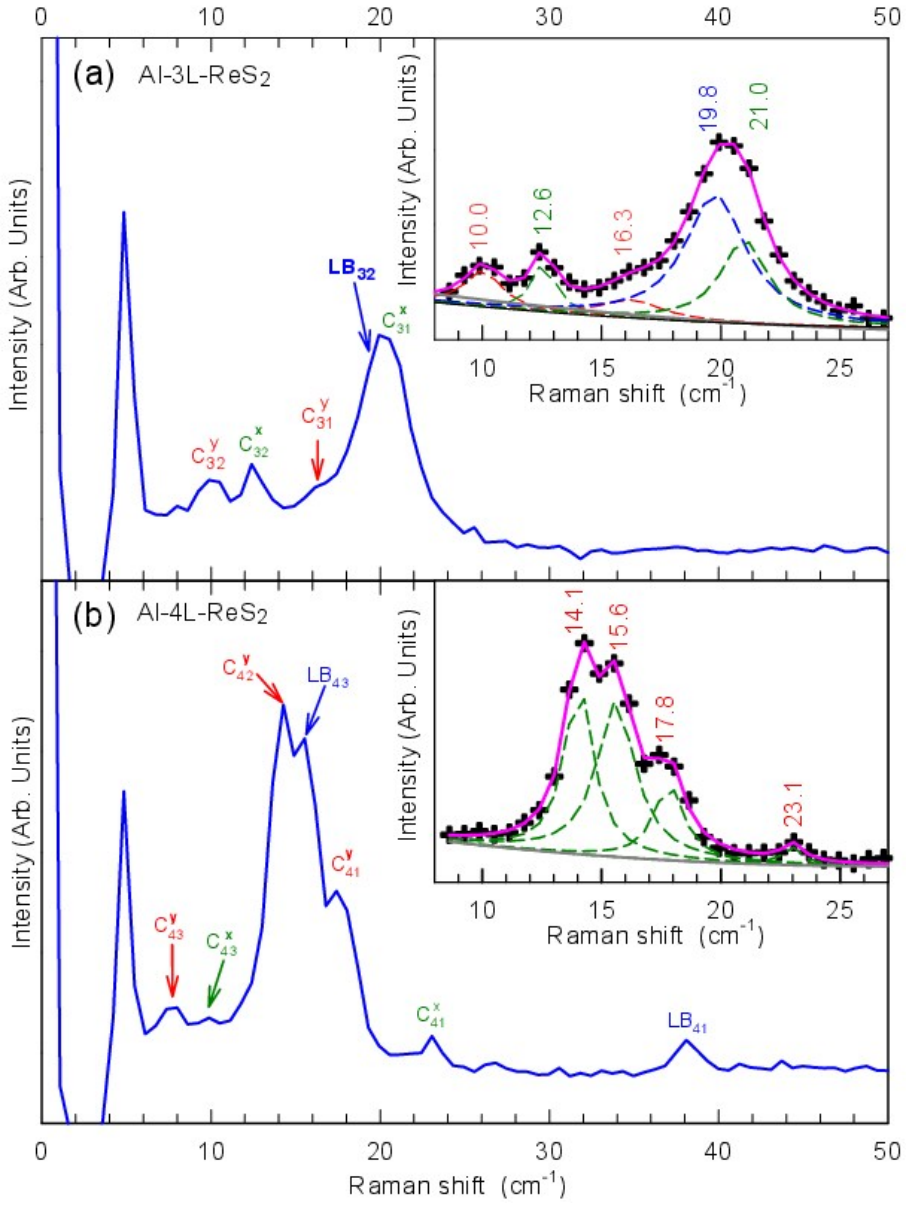

Figure S4 (a) Stokes Raman spectra of AI-3L-ReS_2 in the low frequency region. (b) Stokes Raman spectra of AI-4L-ReS_2 in the low frequency region. The insets show the sub-peak fitting results.

Table S1: The experimental frequencies and the DFPT calculated frequencies of *a* and *b* modes for 1L, the AI- and IS-2L ReS_2

	Mode a (cm^{-1})		Mode b (cm^{-1})		Frequency difference (cm^{-1})	
	Exp.	DFPT	Exp.	DFPT	Exp.	DFPT
1L ReS_2	135.7	132.20	152.4	150.66	16.70	18.46
AI-2L-ReS_2	134.80	130.64	153.80	149.74	19.00	19.10
IS-2L-ReS_2	138.00	135.47	152.70	148.86	14.70	13.39

References:

1. Nemes-Incze, P.; Osvath, Z.; Kamaras, K.; Biro, L. P. Anomalies in thickness measurements of graphene and few layer graphite crystals by tapping mode atomic force microscopy. Carbon, **2008**, *46*, 1435-1442.
2. Feng, Y. Q.; Zhou, W.; Wang, Y. J.; Zhou, J.; Liu, E. F.; Fu, Y. J.; Ni, Z. H.; Wu, X. L.; Yuan, H. T.; Miao, F. et al. Raman Vibrational Spectra of Bulk to Monolayer ReS_2 with Lower Symmetry. *Phys. Rev. B* **2015**, *92*, 054110
3. Chenet, D. A.; Aslan, O. B.; Huang, P. Y.; Fan, C.; van der Zande, A. M.; Heinz, T. F.; Hone, J. C. In-Plane Anisotropy in Mono- and Few-Layer ReS_2 Probed by Raman Spectroscopy and Scanning Transmission Electron Microscopy. *Nano Lett.* **2015**, *15*, 5667–5672.