Electronic Supplementary Material (ESI) for Nanoscale Horizons.

Supporting Information

Orientation-polarization dependence of pressure-induced Raman anomalies in anisotropic 2D ReS_2

Ting Wen[1], Maodi Zhang[1], Jing Li[1], Chenyin Jiao[1], Shenghai Pei[1], Zenghui Wang[1], Juan Xia[1]

[1]*Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054 China.*

Email: zenghui.wang@uestc.edu.cn, juanxia@uestc.edu.cn

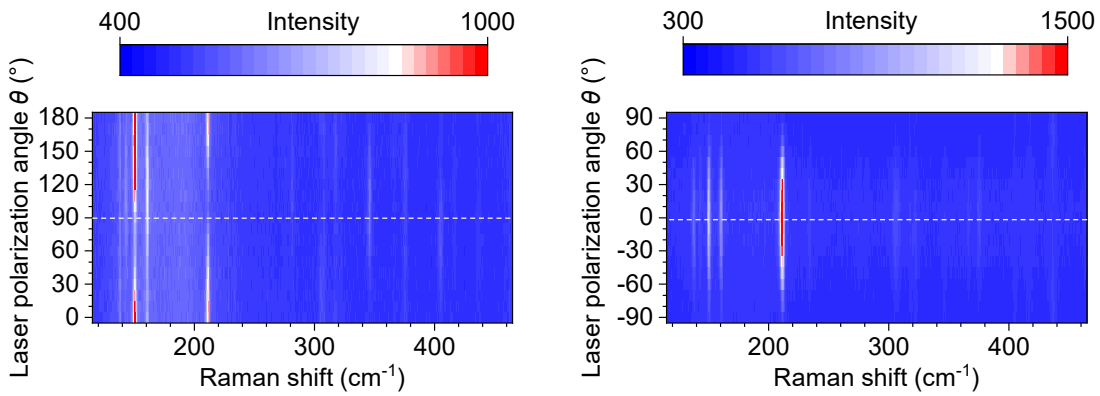

Figure S1. 2D color plots of the angle-resolved Raman spectra of ReS_2 crystals with laser polarization rotated from 0° to 180° under H (a) and V (b) configurations.

Peak	*f*(cm^{-1})	Mode	Peak	*f*(cm^{-1})	Mode
1	137	A_g_like	10	305	E_g_like
2	142	E_g_like	11	316	A_g_like
3	150	E_g_like	12	320	A_g_like
4	160	E_g_like	13	344	E_g_like
5	210	A_g_like	14	365	A_g_like
6	232	A_g_like	15	374	E_g_like
7	273	A_g_like	16	403	A_g_like
8	279	E_g_like	17	415	A_g_like
9	303	A_g_like	18	435	A_g

Table S1. Summary and mode assignment of measured Raman intensity of all the 18 Raman active modes in ReS_2 crystal.

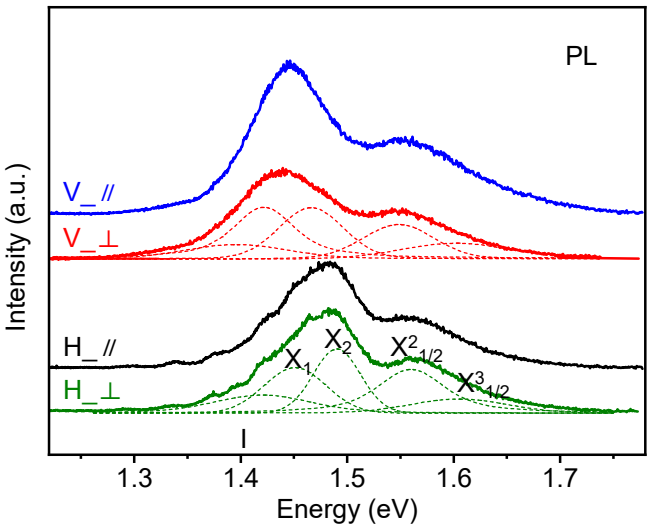

Figure S2 PL spectra of ReS_2 crystal with four representative orientation-polarization configurations at ambient pressure: sample H with laser polarization parallel (H_//) and perpendicular (H_⊥) to the ReS_2 crystal *b* axis; and sample V with laser polarization parallel (V_//) and perpendicular (V_⊥) to the *b* axis. The dotted curves are fitted by Voigt functions.

the PL peaks are fitted by Voigt functions, consisting of five prominent peaks at 1.42, 1.45, 1.49, 1.56 and 1.60 eV. The peak I corresponds to the lowest-energy indirect transition. The other four peaks are found to originate from two direct excitons (X_1, X_2): peak X_1 and X_2 are the ground state of the two direct excitons corresponding to the recombination emission of excitons along and perpendicular to the Re-Re chain in ReS_2 crystal; peak $X^2_{1/2}$ and peak $X^3_{1/2}$ are attributed to a nonthermalized hot PL process from direct hydrogenic Rydberg exciton series. The slight difference in PL spectra under H and V configurations could be attributed to the thickness difference in samples and absorption deference among different configurations.

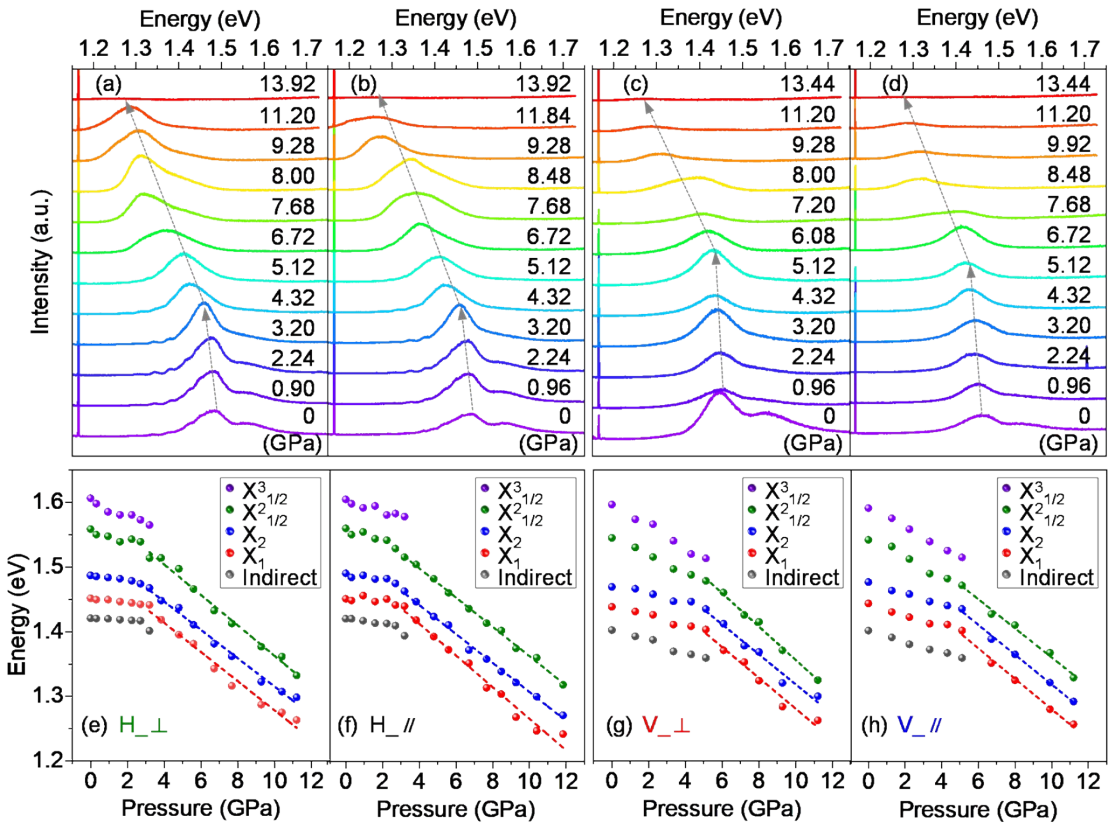

Figure S3 (a)-(d) The evolution of PL spectrum of ReS_2 crystal with pressures (0-14 GPa), for H_//, H_⊥, V_// and V_⊥ configurations. (e)-(h) The exciton energy of the five PL peaks (see fittings in Figure S2) from data in (a)-(d) as a function of pressure. The gray dotted arrows guide the shift of the peaks. All measurements are conducted at room temperature.

Figure S3 shows the evolution of PL spectrum of ReS_2 crystal with applied pressure (0-14 GPa) for different configurations, where the PL peak intensities change with pressure, and are quenched above 14 GPa. In addition, we also observe distinctive changes of peak width and peak position with pressure for H and V configurations, offering important clues for analyzing the electronic structure of ReS_2 crystals. Specifically, in the H configurations (Figures S3a & S3b), all five excitonic peaks show red shift with pressure, with a change of pressure coefficients ($\partial E/\partial P$) at 3.20 GPa. This corresponds to the different response of 1T' phase (< 3.20 GPa) and distorted 1T' (> 3.20 GPa) to applied pressure. Further, the indirect excitonic peak and the high-energy excitonic peak $X^3_{1/2}$ disappear at 3.20 GPa (Figures S3e & S3f), suggesting a transition from the indirect bandgap to direct bandgap in the ReS_2 crystal. Interestingly, such

transition takes place at 5.12 GPa in the V configurations (Figures S3c & S3d and Figures S3g & S3h), which is in excellent agreement with the phase transition processes observed in previous Raman results.

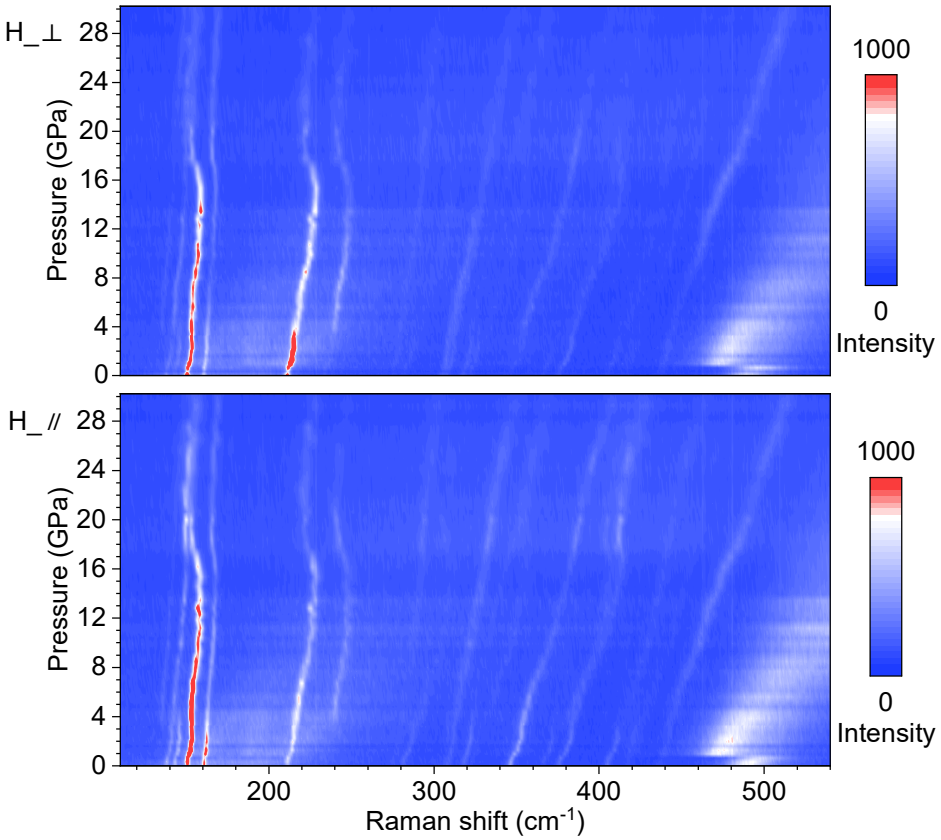

Figure S4. Evolution of Raman spectrum of ReS_2 crystal in the frequency range 110-540 cm^{-1} from ambient to 30.24 GPa for H configuration.

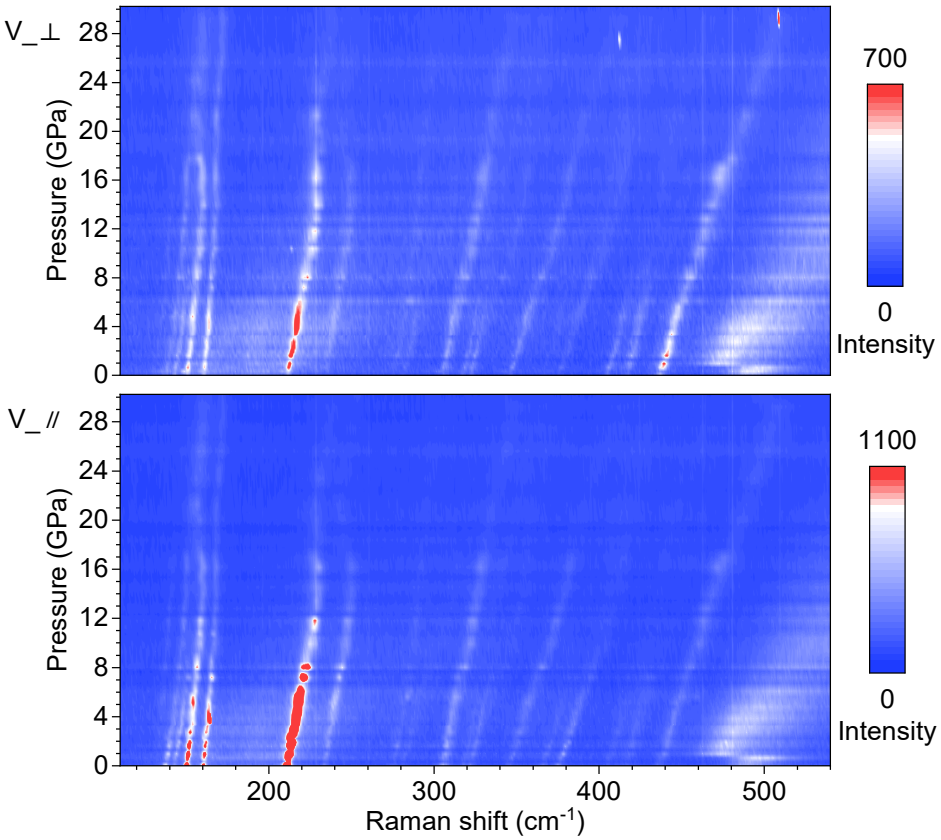

Figure S5. Evolution of Raman spectrum of ReS_2 crystal in the frequency range 110-540 cm^{-1} from ambient to 30.24 GPa for V configuration.

Peak	*f*(cm^{-1})	Mode	H_// (GPa)	H_⊥ (GPa)	V_// (GPa)	V_⊥ (GPa)
α	~137	-	3.20 - 25.60	3.20 - 25.60	5.12 - 17.76	5.12 - 17.76
1	137	A_g-like	0 - 20.00	0 - 20.00	0 - 17.76	0 - 17.76
2	142	E_g-like	0 - 3.20	0 - 3.20	0 - 9.92	0 - 9.92
10	305	E_g-like	0 -	0 -	0 - 5.12	0 - 5.12
11	316	A_g-like	0 -	0 -	0 - 5.12	0 - 5.12
12	320	A_g-like	0 - 20.00	0 - 20.00	0 - 17.76	0 - 17.76
13	344	E_g-like	0 -	0 -	0 - 17.76	0 -
14	365	A_g-like	0 - 3.20	0 - 3.20	0 - 5.12	0 - 5.12
15	374	E_g-like	0 - 11.84<	0 - 11.84<	0 - 17.76	0 - 17.76
16	403	A_g-like	0 -	0 - 25.60	0 - 5.12	0 - 9.92
17	415	A_g-like	0 - 20.00	0 - 25.60	0 - 5.12	0 - 9.92

Table S2. The emerging (red), splitting (green) and vanishing (black) behaviors of Raman peaks for H_//, H_⊥, V_// and V_⊥ configurations at different pressure values. "<" represents the splitting behavior of the peak after this pressure. The hyphens indicate the blue-shift Raman peaks without splitting or vanishing behavior in the measured pressure range.