Supporting Information

In-plane optical anisotropy in ReS_2 flakes determined by angle-resolved polarized optical contrast spectroscopy

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1. Optical contrast of a ReS_2 flake is calculated by Fresnel's equations

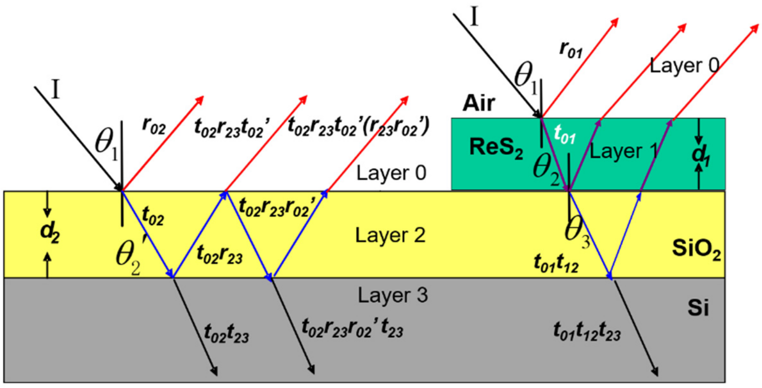

Fig.S1 Multiple reflection and transmission of incident light in a multi-layer thin film system, i.e., a ReS_2 flake on the SiO_2/Si substrate.

When a beam of light is incident on an interface with incident angle θ_1, for example, air/SiO_2 interface, a portion of the beam is reflected from the interface and the rest is transmitted, thus, an infinite number of optical paths are possible as schematically shown in Fig. S1. Take air/SiO_2/Si system for example, the total reflected amplitude r_0 is governed by eq. (1),

$$r_0 = \frac{r_{02} + r_{23} \cdot e^{-2i\phi_2}}{1 + r_{02} \cdot r_{23} \cdot e^{-2i\phi_2}} \tag{1}$$

Similarly, for air/ReS_2/SiO_2/Si system, the total reflected amplitude r_1 can be calculated by eq. (2),

$$r_1 = \frac{r_{01} + r_{01}r_{12}r_{23}e^{-2i\phi_2} + r_{12}e^{-2i\phi_1} + r_{23}e^{-2i(\phi_1+\phi_2)}}{1 + r_{12}r_{23}e^{-2i\phi_2} + r_{01}r_{12}e^{-2i\phi_1} + r_{01}r_{23}e^{-2i(\phi_1+\phi_2)}} \tag{2}$$

Here, r_{ij} (i, j=0-3 and $i \neq j$) is the interface reflection coefficient for the interfaces involving air (0), ReS_2 (1), SiO_2 (2), and Si (3). At normal incident, r_{ij} can be calculated by $r_{ij}=\frac{\tilde{n}_i-\tilde{n}_j}{\tilde{n}_i+\hat{n}_j}$. $\tilde{n}_i$ ($\tilde{n}_j$) is the complex refractive index of layer i (layer j). In this work, the incident white light is treated as a combination of s-polarized and p-polarized light with an equal contribution. In the calculation of reflected amplitude, under oblique incident, for s-polarized light, $\tilde{n}_i$ should be replaced by $\tilde{n}_i\cos\theta_i$. While for p-polarized light, $\tilde{n}_i$ should be replaced by $\tilde{n}_i/\cos\theta_i$. $\varphi_i=\frac{2\pi\cdot\tilde{n}_i\cdot d_i\cdot\cos\theta_i}{\lambda}$ represents the phase difference when light passes through layer i. θ_i is the refraction angle in layer i. d_i is the thickness of layer i. λ is wavelength of incident light. The reflection spectrum from air/(SiO_2 on Si), $R_0(\lambda)$ can be calculated by

$$R_0(\lambda)=|r_0|^2 \tag{3}$$

The reflection spectrum from air/ReS_2/SiO_2/Si system, $R_1(\lambda)$ can be calculated by

$$R_1(\lambda)=|r_1|^2 \tag{4}$$

Furthermore, we include the effect of numerical aperture (NA) of the microscope objective in the calculation of optical contrast, the reflection spectrum $R_{0,1}(\lambda)$ should be modified by numerical integration of the reflectance values (computed for various angles of incidence) over the solid angle determined by NA

$$R_{0,1}=2\pi\int_0^{\theta_m}R_{0,1}(\theta)W(\theta)\sin\theta d\theta \tag{5}$$

Where $\theta_m=\arcsin(NA)$ and Gaussian distribution W(θ)=$e^{-\frac{2\sin^2\theta}{\sin^2\theta_m}}$ is taken in the calculation. When the polarization of incident light making an angle θ with the Re-Re chain direction, the in-plane anisotropic complex refractive index $\tilde{n}(\theta)$ of a ReS_2 flake is proposed here and the angle-resolved polarized optical contrast can be calculated. The proposed in-plane anisotropic complex refractive index $\tilde{n}(\theta)$ is calculated by: $\frac{1}{\tilde{n}(\theta)^2}=\frac{\cos^2\theta}{\tilde{n}_1^2}+\frac{\sin^2\theta}{\tilde{n}_2^2}$. Here, $\tilde{n}_1$ is the complex refractive index of a ReS_2 flake along the Re-Re chain direction and $\tilde{n}_2$ is the complex refractive index of a ReS_2 flake perpendicular.

2. Complex refractive indices of ReS_2 flakes with 1-3 layers along the Re-Re chain direction and perpendicular are obtained from polarized white light contrast spectra

The complex refractive indices of ReS_2 flakes with different thicknesses along the Re-Re chain direction $\tilde{n}_1(\lambda)$ ($\theta=0^o$) and perpendicular $\tilde{n}_2(\lambda)$ ($\theta=90^o$) are obtained by using eq. (6)

$$\tilde{n}_{1/2}(\lambda)=a_{1/2}\cdot n_{bk}(\lambda)-b_{1/2}\cdot i\cdot k_{bk}(\lambda) \quad (6)$$

n_{bk} and k_{bk} are the real and imaginary parts of refractive index of bulk ReS_2 crystal which are taken from Ref. [1]. Here, a_i (i=1, or 2) and b_i (i=1, or 2) act as fitting parameters whose values are determined from least squares fitting by comparing theoretical contrast spectrum with experimental contrast spectrum at θ=0° / 90^o as given in Fig.S2(a) to Fig.S4(a). The best-fitted results of $\tilde{n}_1$ ($\theta=0^o$) and $\tilde{n}_2$ ($\theta=90^o$) of 1-3-L ReS_2 are further given in Fig.S2(b) to Fig.S4(b). From those figures, it can be seen, the real and imaginary parts of refractive indices of ReS_2 flakes along the Re-Re chain direction are larger than those along perpendicular direction. It also can be seen the in-plane anisotropic optical properties of ReS_2 flakes exhibit a layer-number dependence.

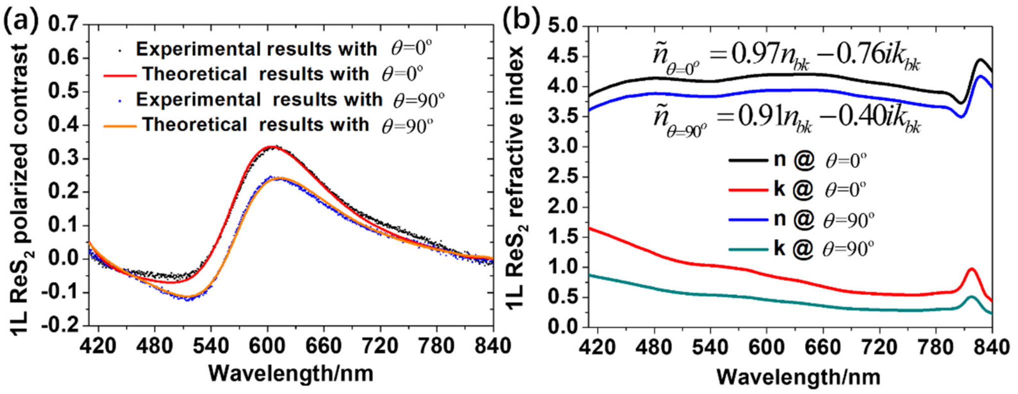

Fig.S2 (a) Polarized white light contrast spectra of 1L ReS_2 with $\theta = 0^o$ and $\theta = 90^o$.

Black and blue dots are experimental results and solid lines with red and orange colors are theoretical results calculated by using complex refractive indices given in Fig.S2(b).

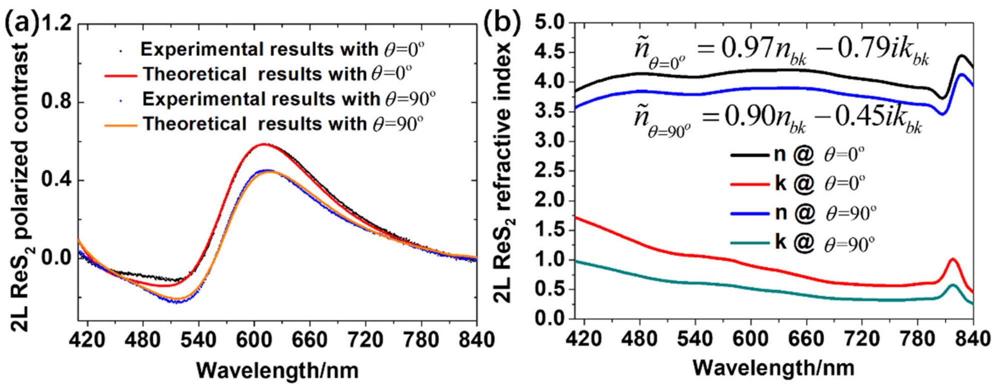

Fig.S3 (a) Polarized white light contrast spectra of 2L ReS_2 with $\theta = 0^o$ and $\theta = 90^o$.

Black and blue dots are experimental results and solid lines with red and orange colors are theoretical results calculated by using complex refractive indices given in Fig.S3(b).

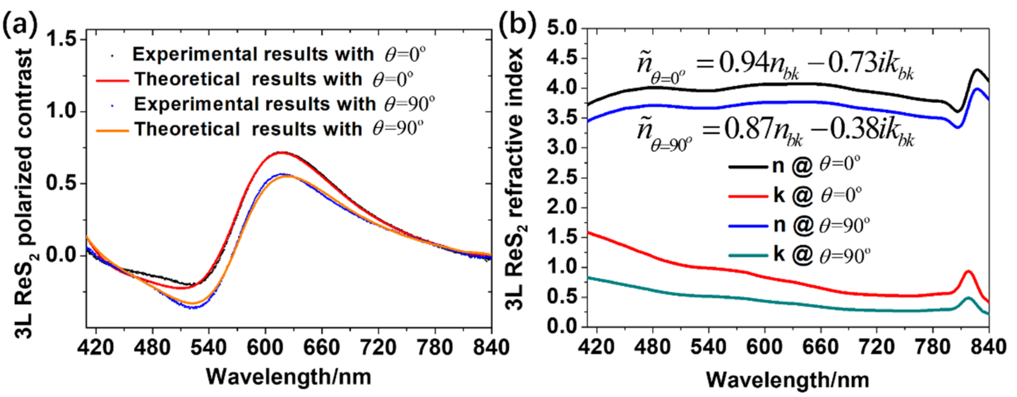

Fig.S4 (a) Polarized white light contrast spectra of 3L ReS_2 with $\theta = 0^o$ and $\theta = 90^o$.

Black and blue dots are experimental results and solid lines with red and orange colors are theoretical results calculated by using complex refractive indices given in Fig.S4(b).

3. **The Re-Re chain direction in a ReS_2 flake can be determined by the angle-resolved polarized Raman scattering**

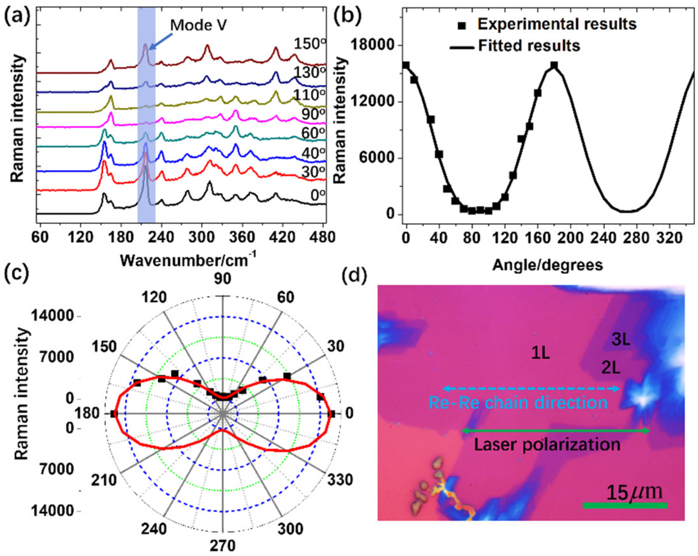

Fig. S5 (a) Raman spectra of single-layer ReS_2 at different rotation angles which are obtained under the parallel-polarized configuration. (b) Raman intensity of Mode V of ReS_2 as a function of rotation angles. Mode V exhibits the maximum intensity with θ=0°. (c) Polar plot of Raman intensity of mode V which yields 2-lobed shapes. The solid curves in (b) and (c) are fitting results using eq. (7). (d) Optical image of ReS_2 flakes. When θ=0°, it is found the polarization of incident laser (green line with a double arrow) is parallel to the Re-Re chain direction (blue dashed line with a double arrow).

We confirm the well-defined crystal edges as shown in paper in Fig. 1(a) are in line with the Re-Re chain direction by angle-resolved polarized Raman scattering. The Raman spectra are taken in a backscattering geometry using a 532 nm laser under the parallel-polarized configuration. The polarization of the laser is controlled by the same polarizer as that of the white light whose polarization is indicated by a double green arrow in Fig. S5(d). Fig. S5(a) gives Raman spectra of single-layer ReS_2 at different rotation angles which are taken from the area marked by a white dotted circle as shown in paper in Fig. 1(a). As can be seen from this figure, with an increase in the rotation angle, the Raman intensity of Mode V first decreases and then increases.

The Raman mode intensity in ReS_2 flakes is proportional to $\left|e_s \cdot R \cdot e_i\right|^2$, where e_i and e_s represent the unit vectors of the incident and scattered lights, individually. R is the Raman tensor. Under parallel-polarized configuration, $e_i = e_s = \left[\cos\theta \quad \sin\theta\right]$. The Raman tensor of mode V in ReS_2 can be expressed as R=$\begin{bmatrix} u & v \\ v & w \end{bmatrix}$, there is an off-diagonal element v due to the anisotropic property of ReS_2. The angular dependence of the Raman intensity of ReS_2 under parallel-polarized configuration can be expressed as[2]

$$I = (\mathrm{u}\cos^2\theta + 2v\cos\theta\sin\theta + w\sin^2\theta)^2 \tag{7}$$

Fig. S5(b) shows the experimental data of angular dependence of Raman intensity of Mode V (black squares). Fig. S5(c) is a polar plot of Raman intensity of mode V which yields 2-lobed shapes. The solid curves in Figs. S5(b) and (c) are fitting results using eq. (7). It can be seen mode V exhibits the maximum intensity when $\theta = 0^\circ$. It has been reported mode V displays the maximum Raman intensity when the polarization of incident laser is parallel to the Re-Re chain direction since this mode contains in-plane vibrations of the rhenium atoms along this direction. Therefore, those well-defined crystal edges as shown in paper in Fig.1(a) are parallel to the Re-Re chain direction.

References:

[1].Cui, Q. N.; He, J. Q.; Bellus, M. Z.; Mirzokarimov, M.; Hofmann, T.; Chiu, H. Y.; Antonik, M.; He, D. W.; Wang, Y. S.; Zhao, H., Transient Absorption Measurements on Anisotropic Monolayer ReS_2. *Small* **2015,** *11* (41), 5565-5571.

[2]. Zhang, S. S.; Mao, N. N.; Zhang, N.; Wu, J. X.; Tong, L. M.; Zhang, J., Anomalous Polarized Raman Scattering and Large Circular Intensity Differential in Layered Triclinic ReS_2. *Acs Nano* **2017,** *11* (10), 10366-10372.