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In-plane optical anisotropy in ReS₂ flakes determined by angle-resolved polarized optical contrast spectroscopy

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Abstract

Various in-plane anisotropic properties are observed for layered semiconducting transition metal dichalcogenide (TMD) rhenium disulfide (ReS_2) due to its reduced symmetry. The understanding of these unique anisotropic behaviors in ReS_2 will promote its applications in optoelectronics. In this work, angle-resolved polarized optical contrast spectroscopy is proved as an efficient, quantitative, and non-destructive method to probe the optical anisotropy in ReS_2 flakes with different layer numbers. It is found that the contrast value of ReS_2 displays the maximum intensity when the polarization of incident light is along the Re-Re chain direction, while the contrast shows minimum value when the polarization is perpendicular. An empirical equation for in-plane anisotropic refractive index calculation is proposed and the angle-resolved polarized optical contrasts of 1-3-layer ReS_2 are calculated which show agreements with experimental observations. This indicates the proposed equation is indeed appropriate for the quantitative understanding of birefringence and dichroism in ReS_2 flakes. Our results not only shed light on the identification of crystal axes in anisotropic materials by using angle-resolved polarized contrast spectroscopy, but also provide quantitative information about anisotropy in anisotropic materials such as ReS_2 .

Introduction

As a member in the family of two-dimensional (2D) layered transition metal dichalcogenide (TMD), rhenium disulfide (ReS_2) has attracted enormous attention recently due to its intriguing in-plane anisotropic electronic, catalytic, optoelectronic and optic properties. ReS_2 exists in the 1T' phase with triclinic symmetry due to the formation of Re-Re chains, where such chains distort the monolayer crystal from the more symmetric 1T structure. Various in-plane anisotropic properties are observed in ReS_2 due to its reduced symmetry. For example, single-layer ReS_2 exhibits anisotropic conduction with an order of magnitude difference in different directions which makes it a promising candidate for the fabrication of integrated digital inverter and nano-electronic circuit.^{1,2} In-plane anisotropic optical properties, such as polarization dependent photo-response, linearly polarized exciton, anisotropic absorption coefficient, and anisotropic transient absorption are also observed in ReS_2 , which open up great avenues for creating waveplates or polarization-dependent photodetectors.³⁻⁹

Recent technological demand requires the development of a feasible and industrially compatible growth technique to synthesize 2D materials. A bottom-up chemical vapor deposition (CVD) approach is therefore developed which offers a potential way of large-scale growth of 2D materials. Recently, continuous polycrystalline ReS_2 flakes have been successfully synthesized by low-temperature CVD onto SiO_2/Si substrate.¹⁰⁻¹² The morphology and grain size in CVD samples can be controlled by growth parameters, e.g., mass flux and growth rate.¹³ In order to fully use the anisotropic properties of ReS_2 in the fabrication of polarized detector, sensor,

and photonic device, a fast, facilitated, and easy way of unambiguous identification of grain orientations in ReS₂ flakes is highly needed.

Scanning transmission electron microscopy is a direct technique of observation of lattice arrangement. However, this method is limited by the complex procedure involved sample preparation and is destructive.¹⁴ Angle-resolved conductance measurement has been proved as a way of identifying crystal axes in ReS₂. However, metal-mask patterning is needed before the measurement which increases the complexity of this approach.¹⁻² Angle-resolved polarized Raman scattering has also been shown to permit a determination of Re-Re chain direction in ReS₂ flakes.¹⁴⁻¹⁷ However, it is found that the Raman response of ReS₂ flakes highly depends on the incoming photon energy. And for thick ReS₂ flakes, both optical anisotropy and phase shift are all needed to be considered in the Raman tensor and those effects make polarized Raman scattering of ReS₂ flakes dependent on the layer number.

The reduced symmetry in ReS₂ induces very rich light-matter interactions in ReS₂, e.g., selectively tunable optical stark effect of excitons and polarization-controlled exciton quantum beats have been observed which provide methodologies for fabricating ultrafast optoelectronic devices using ReS₂ flakes.^{18,19} Light-matter interaction, e.g., the amplitude and phase changes of incident light after interacting with the anisotropic material, is important for many applications in optics.^{20,21} In order to fully utilize the anisotropic properties of ReS₂ in the fabrication of optoelectronic devices, a better understanding of its optical behavior is of particular importance. However, reports involving in-plane anisotropic dielectric properties of ReS₂ flakes in

the visible light range, e.g., wavelength and layer-number dependent complex refractive indices of ReS₂ flakes, are still missing. Here, we show that angle-resolved polarized optical contrast spectroscopy not only provides an explicit method for the determination of crystal orientation, but also provides quantitative information about the in-plane anisotropic optical properties of ReS₂ flakes and this will greatly help the understanding of optical birefringence and dichroism in ReS₂ flakes.

In this work, it is found that the contrast value of a ReS₂ flake displays the maximum intensity when the polarization of incident white light is along the Re-Re chain direction, while it shows the minimum value when the polarization is perpendicular. An empirical equation for in-plane anisotropic complex refractive index calculation is proposed in order to describe the anisotropic nature of ReS₂ flakes with different layer numbers. Our results also fulfill the requirement of quantitatively understanding of how light waves (amplitude and phase) are modulated when passing through the crystal.

Experimental detail

ReS₂ flakes are grown on SiO₂ (285 nm)/Si substrate using the molten-salt-assisted CVD method. Re and S powder are used as metal and chalcogen precursors, respectively. KI is used as the assisted salt which can be used to decrease the melting point of the reactants and increase the overall reaction rate. The growth temperature is 700°~750° with argon as the carrier gas. The growth time is 10~15 min. The Raman scattering measurements are performed by a Witec Raman spectrometer excited with a 532 nm (2.33 eV) laser. A 50× working distance objective lens (NA=0.45) with a spot

size of 1.9 μm is used in the Raman and white light reflection experiments. A tungsten halogen lamp is used as the white light source. The polarization of the incident laser and white light are controlled by the same polarizer with a fixed polarization. For the contrast image, the sample is placed on a x-y piezo stage and scanned under the illumination of polarized incident white light. The unpolarized reflection spectra from every spot of the sample are recorded. Data analysis is done by using a WITec Project software.

Results and discussion

Fig. 1(a) shows the optical image of ReS_2 flakes on SiO_2 (285 nm)/Si substrate with different layer (L) numbers. The orientations of two well-defined crystal edges are highlighted with dashed blue lines in this figure. Fig. 1(b) gives the crystal structure of single-layer ReS_2 . The superlattice structure of Re-Re chains, denoted as the b-axis, distorts ReS_2 from the more symmetric 1T structure to the triclinic 1T' structure. The direction of the Re-Re chains is represented by a blue double dashed arrow in this figure. Fig. 1(c) shows the unpolarized Raman spectra of 1-3-L ReS_2 . Due to the limitation of edge filter used, low-frequency modes I and II are not observed in those spectra. 18 first-order Raman active-vibrational modes are reported and observed for ReS_2 flakes.¹⁴⁻¹⁷ The Raman modes here are labeled with Roman numerals from lowest to highest wavenumber followed other reports. The peak positions for modes III to V are $\sim 152.8\text{ cm}^{-1}$, 162.0 cm^{-1} and 213.4 cm^{-1} , individually.¹⁴ The peak positions of some Raman modes are marked by red dots in this figure. Particular attention is then paid to mode V in this work. It has been reported that the angle-resolved polarized Raman

intensity of mode V can be used to determine crystal orientation in a thin ReS₂ flake under excitation of 532 nm.¹⁴⁻¹⁷ From this figure, it can be seen the Raman intensities of the Raman modes increase with an increase in layer number.

The angle-resolved polarized white light contrast spectra of ReS₂ flakes are taken in a backscattering geometry using a tungsten halogen lamp as a white light source. The polarization of the incident white light is controlled by passing through a polarizer whose polarization is indicated by a double white arrow in Fig. 1(a). Unpolarized detection is used to get the reflection spectra from the ReS₂ flake and those from the SiO₂/Si substrate. The angle-resolved reflection spectra are obtained by rotating the ReS₂ flake about the axis normal by θ in a counterclockwise direction every 10° from 0° to 180°. $\theta=0^\circ$ is taken as along one of crystal edges of the samples which turns out to be the b-axis of as shown in Fig. 1(b). The contrast spectrum $C(\lambda)$ of a ReS₂ flake is obtained by eq. 1.^{22,23}

$$C(\lambda) = \frac{R_{\text{Substrate}} - R_{\text{Sample}}}{R_{\text{Substrate}}} \quad (1)$$

Here, $R_{\text{Substrate}}$ is the reflection spectrum from the SiO₂/Si substrate, R_{Sample} represents the reflection spectrum from the ReS₂ flake, and λ is the wavelength of the incident white light.

Fig. 2(a) gives the polarized optical contrast spectra of 1L ReS₂ with rotation angle $\theta=0^\circ$, $\theta=20^\circ$, $\theta=40^\circ$, $\theta=60^\circ$, and $\theta=90^\circ$. The reflection spectrum of 1L ReS₂ is taken from the area marked by a white dotted circle as shown in Fig. 1(a). From Fig. 2(a), it can be seen, the optical contrast of 1L ReS₂ shows a negative peak around 510.0 nm and a positive peak around 608.0 nm. The intensities of contrast peaks change

periodically with rotation angles, and the peak positions are unshifted. With increasing the rotation angle from 0° to 90° , the contrast intensities decrease.

Fig. 2(b) shows the experimental (black squares) and theoretical (red solid line) contrast intensities of 1L ReS₂ at 608.0 nm at varying rotation angles. The theoretical results reproduce experimental results very well. It can be seen the contrast intensity changes periodically with the rotation angle and the period is 180° . The contrast intensity reaches the maximum intensity at 0° , and exhibits the minimum intensity at 90° . When $\theta=0^\circ$, the polarization of incident white light is parallel to the well-defined crystal edges (highlighted by blue dashed lines in Fig. 1(a)) whose directions are further confirmed in line with the Re-Re chain direction by angle-dependent polarized Raman scattering. And those results will be shown later.

Therefore, from the angle-resolved polarized contrast spectra, it is found that the contrast intensity of 1L ReS₂ reaches the maximum value when the polarization of incident white light is parallel to the Re-Re chain direction, and the minimum intensity is observed when the polarization is perpendicular. Thus, the angle-resolved polarized contrast spectra can be used to identify the crystalline direction in a ReS₂ flake and this method is also applicable to other in-plane anisotropic materials. The polarization-dependent reflection from the ReS₂ flake is stemmed from the in-plane anisotropic refractive index of the ReS₂ flake. An empirical model is thus proposed here in order to quantitatively understand the anisotropic optical behavior in ReS₂ flakes.

Fig. 2(c) shows a schematic configuration of this empirical model. The polarization of incident white light is along X-axis. When the Re-Re chain direction makes an angle

θ with the polarization of incident light as schematically shown in this figure, the in-plane anisotropic complex refractive index $\tilde{n}(\theta)$ can be calculated by eq. 2:

$$\frac{1}{\tilde{n}(\theta)^2} = \frac{\cos^2 \theta}{\tilde{n}_1^2} + \frac{\sin^2 \theta}{\tilde{n}_2^2} \quad (2)$$

Here, $\tilde{n}_1$ is the complex refractive index of a ReS₂ flake along Re-Re chain direction and $\tilde{n}_2$ is the complex refractive index of a ReS₂ flake perpendicular. Using the proposed complex refractive index $\tilde{n}(\theta)$, we further calculate angle-resolved polarized contrast of a ReS₂ flake based on Fresnel's equations and the calculated process can be found in Supporting Information.

Here, values of $\tilde{n}_1$ and $\tilde{n}_2$ of ReS₂ flakes with different layer numbers are obtained by using eq. 3

$$\tilde{n}_{1/2}(\lambda) = a_{1/2} \cdot n_{bk}(\lambda) - b_{1/2} \cdot i \cdot k_{bk}(\lambda) \quad (3)$$

n_{bk} and k_{bk} are the real and imaginary parts of refractive index of bulk ReS₂ crystal which are taken from Ref. 9. 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 $\theta=0^\circ / 90^\circ$. It has been reported that due to the distorted 1T structure, the interlayer overlaps of wavefunctions are minimized and the interaction between neighboring layers in ReS₂ is weaker compared with other TMD^{15,24}. Therefore, we use the unpolarized dispersion curve of bulk ReS₂ as the initial value in our fitting and the best-fitted results of $\tilde{n}_1(\lambda)$ ($\theta=0^\circ$) and $\tilde{n}_2(\lambda)$ ($\theta=90^\circ$) of 1-3-L ReS₂ can be found in Supporting Information.

From the obtained refractive index dispersion, it is found that both the real and imaginary parts of refractive indices of the ReS₂ flakes with different layer numbers

along the Re-Re chain direction ($\theta = 0^\circ$) are higher than those perpendicular ($\theta = 90^\circ$). And those in-plane anisotropic properties of ReS₂ flakes also exhibit layer number dependent whose results can be found in Supporting Information. The much larger absorption along the Re-Re chain direction indicates a stronger photon-matter interaction in this direction. When a linearly polarized light beam normally incidents on the ReS₂ flake with polarization making an angle θ with the Re-Re chain direction, the differences of the complex refractive indices along the Re-Re chain direction and perpendicular will gives rise to a remarkable reflectance difference including both amplitude and phase shift, and this results in elliptically polarized light (difference in phase shift $\neq m\pi$, m is an integer) or polarized light (difference in phase shift $=m\pi$, m is an integer). The obtained in-plane anisotropic complex refractive indices thus provide valuable information about how the amplitude and phase of light are modulated after passing through ReS₂ crystals. Our finding, therefore, will facilitate the fabrication of optoelectronic devices using ReS₂ flakes.

Once $\tilde{n}_1$ and $\tilde{n}_2$ of a ReS₂ flake are obtained, by using eq. 2, the in-plane anisotropic complex refractive index $\tilde{n}(\theta)$ can be calculated and the dichroism in ReS₂ flakes is better understood. From Fig. 2(b), it can be seen, the theoretical results show good agreements with the experimental data. This indicates the proposed eq. 2 is indeed appropriate to describe the in-plane anisotropic optical properties in ReS₂ flakes. This empirical equation also helps to gain a better understanding of optical birefringence and dichroism in other anisotropic 2D materials. Figure 2(d) is a polar plot of contrast intensities of 1L ReS₂ at 608.0 nm at varying rotation angles. The

spectrum yields 2-lobed shapes.

Angle-resolved polarized optical contrast spectroscopy is further used to investigate the anisotropic optical properties of 2L and 3L ReS₂ and the results are summarized in Fig. 3. Figs. 3(a) and (b) show the polarized optical contrasts of 2L and 3L ReS₂ with different rotation angles. The optical contrasts of 2L and 3L ReS₂ behave similarly as that of 1L ReS₂. The contrast of 2L (3L) ReS₂ shows a negative peak around 521.0 nm (524.9 nm) and a positive peak around 612.5 nm (617.5 nm). The intensities of contrast peaks change periodically with rotation angles, and peak positions are unshifted.

Fig. 3(c) shows contrast intensities of 1L ReS₂ (black square), 2L ReS₂ (red dot) and 3L ReS₂ (blue triangle) at 612.5 nm at different rotation angles. It can be seen the contrast intensities change periodically with rotation angles and the period is 180°. Those polarization-dependent behaviors are the same for ReS₂ flakes with different layer numbers, with the maximum intensities locating at 0°, and with the minimum intensities appearing at 90°. The solid lines are our theoretical results which are calculated based on the proposed in-plane anisotropic complex refractive index $\tilde{n}(\theta)$. The theoretical results show good agreements with the experimental observations. Therefore, the empirical equation introduced here is also applicable to the multi-layer ReS₂. Figs. 3(d) to (f) are polar plots of contrast intensities at 612.5 nm for 1-3-L ReS₂ at varying rotation angles.

We further confirm the well-defined crystal edges as shown 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. 4(d). Fig. 4(a) gives Raman spectra of single-layer ReS₂ at different rotation angles which are taken from the area marked by a white dotted circle as shown in Fig. 1(a). It can be seen, with an increase in the rotation angle, the Raman intensity of Mode V first decreases and then increases.

The Raman mode intensity in ReS₂ flakes is proportional to $|e_s \cdot R \cdot e_i|^2$, 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, $e_i = e_s = [\cos \theta \quad \sin \theta]$. The Raman tensor of mode V in ReS₂ 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 ReS₂. The angular dependence of the Raman intensity of ReS₂ under parallel-polarized configuration can be expressed as

$$I = (u \cos^2 \theta + 2v \cos \theta \sin \theta + w \sin^2 \theta)^2 \quad (4)$$

Fig. 4(b) shows the experimental data of angular dependence of Raman intensity of Mode V (black squares). Fig. 4(c) is a polar plot of Raman intensity of mode V which yields 2-lobed shapes. The solid curves in Figs. 4(b) and (c) are fitting results using eq. 4. 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.¹⁴ Therefore, those well-defined

crystal edges are parallel to the Re-Re chain direction.

Recently, synthesis of 2D planar ReS₂ flakes has been demonstrated using low-temperature CVD onto SiO₂/Si substrate which has enabled ReS₂ synthesis in a 2D form. However, the ReS₂ flakes synthesized by this approach are typical polycrystalline with morphology and grain size controlled by growth parameters, e.g., mass flux and growth rate. In order to scale up the application of 2D materials in the fabrication of anisotropic electronic and opto-electronic devices, e.g., optical waveplate, polarization-dependent photodetector, and integrated digital inverter, a fast, facilitated, and easy way of identification grains in polycrystalline ReS₂ flakes is highly needed. The different reflections of polarized light from differently orientated domains make polarized optical contrast image a very fast way of identification grains in CVD ReS₂ samples.

Fig. 5(a) shows an unpolarized optical image of ReS₂ flakes with different thicknesses. From this image, the uniform optical contrast can be seen for 1L ReS₂ flake. The reflection spectra of 1L ReS₂ are then separately taken from two white dotted circle areas as shown in Fig. 5(a). Fig. 5(b) shows experimental (black and red squares) and theoretical (black and red solid lines) polarized contrast intensities of 1L ReS₂ at 608.0 nm at varying rotation angles taken from those two areas. It can be seen, the variations of contrast values with rotation angles are different which indicates those two areas belong to different grains. We name them as grain 1 and grain 2, separately. For grain 1, the contrast intensity reaches the maximum intensity at $\theta=0^\circ$, and exhibits the minimum intensity at $\theta=90^\circ$. For grain 2, the contrast intensity reaches the maximum

intensity at $\theta=120^\circ$, and exhibits the minimum intensity at $\theta=30^\circ$. Therefore, the crystal axis, e.g., b axis (along Re-Re chain direction), in grain 2 rotates 120° relative to grain 1. This rotation is further confirmed by the angle-resolved polarized Raman scattering whose results are given in Fig. 5(c). Fig. 5(c) shows the Raman intensities of mode V as a function of rotation angles under parallel-polarized configuration. The solid lines in this figure are fitting results using eq. 4. Consistent with the polarized white light contrast spectroscopy, the polarized Raman spectra of 1L ReS₂ flake indicate the Re-Re chain directions in those two grains rotate 120° relative to each other.

Figs. 5(d) to (f) give polarized contrast intensity images of ReS₂ flakes at 608.0 nm at rotation angles of 0° , 90° and 140° , respectively. The obtained contrast images are further rotated in order to make the orientations of ReS₂ flakes in the contrast images are the same as that of optical image. For a very thick ReS₂ flake, the much stronger reflection from the sample compared with that from the substrate, makes the contrast a negative value. Thus, a dark color can be seen for a thick ReS₂ flake in the contrast image. When rotation angle θ is 0° , the contrast intensity from grain 1 is much higher than that from grain 2. And this is reverse when rotation angle θ is 90° . Clear grain boundaries can be easily identified in those two images. When rotation angle θ is 140° , the contrast intensities from the two grains are similar. From figure 5(b), it can be seen, when rotation angle θ is 0° or 90° , the difference in contrast intensity (highlighted by blue dashed lines in Fig. 5(b)) from two grains is much higher than that when $\theta=140^\circ$. Polarized optical contrast image therefore provides a very fast, ultra-high sensitive, and non-destructive way of identification grains in ReS₂ flakes and this method is also

applicable for grain identifications in other anisotropic 2D materials.

Conclusions

The present work utilizes the angle-resolved polarized white light contrast to identify crystal axes in ReS₂ flakes as well as to probe optical anisotropy in ReS₂ flakes. Layer-number dependent in-plane anisotropic complex refractive indices of ReS₂ flakes are obtained which fulfills the requirement of quantitatively understanding the optical birefringence and dichroism in ReS₂ flakes. It is found the polarized contrast image can be used as a fast, simple, and non-destructive way of identification grains with different orientations in CVD ReS₂ samples. The finding here will facilitate the application of anisotropic materials in the fabrication of electronic and opto-electronic devices.

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Figures

Fig. 1 (a) Optical image of ReS₂ flakes with different layer (L) numbers. (b) Crystal structure of single-layer ReS₂. The Re-Re chain direction is indicated by the blue double dashed arrow in this figure. (c) Unpolarized Raman spectra of 1-3-L ReS₂. The Raman modes here are labeled with Roman numerals from lowest to highest wavenumber followed other reports. The peak positions of some Raman modes are marked by red dots in this figure.

Fig. 2 (a) Polarized optical contrast spectra of 1L ReS₂ with rotation angle $\theta=0^\circ$, $\theta=20^\circ$, $\theta=40^\circ$, $\theta=60^\circ$ and $\theta=90^\circ$. The contrasts of 1L ReS₂ at 608.0 nm are highlighted by a light blue line in this figure. (b) Experimental (black squares) and theoretical (red line) contrast intensities of 1L ReS₂ at 608.0 nm at varying rotation angles. (c) Schematic image of the configuration in the empirical model. The ReS₂ flake is rotated about the surface normal (Z-axis) in an anticlockwise direction. θ is the angle between polarization of incident light and the direction of the Re-Re chains. (d) Polar plot of contrast intensity of 1L ReS₂ at 608.0 nm at varying rotation angles.

Fig. 3 (a) and (b) Polarized optical contrasts of 2L and 3L ReS₂ with different rotation angles. The contrasts of 2L and 3L ReS₂ at 612.5 nm are highlighted by light blue lines in this figure. (c) Contrast intensities of 1L ReS₂ (black squares), 2L ReS₂ (red dots) and 3L ReS₂ (blue triangles) at 612.5 nm at different rotation angles. The solid lines are our theoretical results. (d) to (f) Polar plots of contrast intensities at 612.5 nm for 1-3-L ReS₂ at varying rotation angles.

Fig. 4 (a) Raman spectra of single-layer ReS₂ at different rotation angles which are obtained under the parallel-polarized configuration. (b) Raman intensity of Mode V of ReS₂ as a function of rotation angles. Mode V exhibits the maximum intensity with $\theta=0^\circ$. (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. 4. (d) Optical image of ReS₂ flakes. When $\theta=0^\circ$, 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).

Fig. 5 (a) Unpolarized optical image of ReS₂ flakes with different thicknesses. From this image, the uniform optical contrast can be seen for 1L ReS₂ flake. The reflection spectra of 1L ReS₂ are separately taken from two white dotted circle areas as shown in figure 5(a). (b) Polarized contrast intensities of 1L ReS₂ at 608.0 nm at varying rotation angles taken from two areas. It can be seen, the contrast intensities from those two areas behave very differently. (c) Raman intensities of mode V as a function of rotation angles under parallel-polarized configuration taken from two areas. (d) to (f) Polarized contrast intensity images of ReS₂ flakes at 608.0 nm when rotation angle θ is 0°, 90° and 140°. Those images are rotated correspondingly in order to make the orientations of ReS₂ flakes are the same as that of the optical image.

Fig.1

680x205mm (150 x 150 DPI)

Fig.2

541x393mm (150 x 150 DPI)

Fig.3

731x384mm (150 x 150 DPI)

Fig.4

511x392mm (150 x 150 DPI)

Fig.5

760x517mm (150 x 150 DPI)

Supporting Information

In-plane optical anisotropy in ReS₂ flakes determined by angle-resolved polarized optical contrast spectroscopy

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1. Optical contrast of a ReS₂ 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 ReS₂ flake on the SiO₂/Si substrate.

When a beam of light is incident on an interface with incident angle θ_1 , for example, air/SiO₂ 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/SiO₂/Si system for example, the total reflected amplitude r_0 is governed by eq. (1),

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

Similarly, for air/ReS₂/SiO₂/Si system, the total reflected amplitude r_1 can be calculated by eq. (2),

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

Here, r_{ij} ($i, j=0-3$ and $i \neq j$) is the interface reflection coefficient for the

interfaces involving air (0), ReS₂ (1), SiO₂ (2), and Si (3). At normal incident, r_{ij} can be calculated by $r_{ij} = \frac{\tilde{n}_i - \tilde{n}_j}{\tilde{n}_i + \tilde{n}_j}$. $\tilde{n}_i$ ($\tilde{n}_j$) 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 $\tilde{n}_i / \cos \theta_i \cdot \varphi_i = \frac{2\pi \cdot \tilde{n}_i \cdot d_i \cdot \cos \theta_i}{\lambda}$ 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/(SiO₂ on Si), $R_0(\lambda)$ can be calculated by

$$R_0(\lambda) = |r_0|^2 \quad (3)$$

The reflection spectrum from air/ReS₂/SiO₂/Si system, $R_1(\lambda)$ can be calculated by

$$R_1(\lambda) = |r_1|^2 \quad (4)$$

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

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

Where $\theta_m = \arcsin(NA)$ and Gaussian distribution $W(\theta) = e^{-\frac{2 \sin^2 \theta}{\sin^2 \theta_m}}$ 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 ReS₂ flake is proposed here in order to calculate the angle-resolved polarized optical contrast whose value 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 ReS₂ flake along the Re-Re chain direction and $\tilde{n}_2$ is the complex

refractive index of a ReS₂ flake perpendicular.

2. Complex refractive indices of ReS₂ 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 ReS₂ flakes with different layer number along the Re-Re chain direction $\tilde{n}_1(\lambda)$ ($\theta = 0^\circ$) and perpendicular $\tilde{n}_2(\lambda)$ ($\theta = 90^\circ$) are obtained by using eq. (6)

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

n_{bk} and k_{bk} are the real and imaginary parts of refractive index of bulk ReS₂ 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 $\theta=0^\circ/90^\circ$ as given in Fig.S2(a) to Fig.S4(a). The best-fitted results of $\tilde{n}_1$ ($\theta=0^\circ$) and $\tilde{n}_2$ ($\theta=90^\circ$) of 1-3-L ReS₂ 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 ReS₂ flakes along the Re-Re chain direction are higher than those perpendicular. It can be seen the in-plane anisotropic optical properties of ReS₂ flakes also exhibit a layer-number dependence.

Fig.S2 (a) Polarized white light contrast spectra of 1L ReS₂ with $\theta = 0^\circ$ and $\theta = 90^\circ$.

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 ReS₂ with $\theta = 0^\circ$ and $\theta = 90^\circ$.

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 ReS₂ with $\theta = 0^\circ$ and $\theta = 90^\circ$.

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).

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The quantitatively understanding of birefringence and dichroism in ReS₂ flakes can be obtained from angle-resolved polarized optical contrast spectroscopy.

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