Nanoscale Research Letters

NANO EXPRESS Open Access

The Polarization Properties of the Reflection Spectra of Single-Layer MoS_2 and ReS_2 on SiO_2/Si and Quartz Substrates

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Abstract

MoS_2 and ReS_2 are typical transition metal chalcogenides with many excellent electrical and optical properties. Due to different lattice symmetries, ReS_2 offers one more dimension than MoS_2 to tune its physical properties. In this paper, we studied the polarized reflection spectra in single-layer MoS_2 and ReS_2. The explicit difference identifies strong angle-dependent properties in single-layer ReS_2 distinct from single-layer MoS_2. The results of samples on both SiO_2/Si substrate and quartz substrate show single-layer ReS_2 is in-plane anisotropic and the change period of reflection intensity is estimated with the polarization angles.

Keywords: MoS_2, ReS_2, Reflection spectra, Polarization angle, Anisotropic material, Isotropic material

Introduction

The rapid progress of graphene research has stimulated interest in other several types of two-dimensional layered materials. Recently, transition metal dichalcogenides (TMDs) have attracted considerable attention since the observation of remarkable electronic and optical properties [1–3]. These TMD crystals can be grown or mechanically exfoliated to monolayer thickness, similar to the exfoliation of graphene. However, in contrast to graphene, monolayer TMDs consist of more than one element, which makes their physical properties more complex than graphene. Among the TMDs, MoS_2 is the most extensively studied, where one Mo plane is sandwiched between two S planes usually with a 2H-structure [4]. In contrast to these high-symmetry hexagonal structures such as MoS_2, another kind of TMDs such as ReS_2 is attracting much interest, which exhibits a distorted 1T'-structure [5]. The upper and lower S atoms sandwich the middle layer of Re atoms with a hexagonal structure having an additional Peierls twist [5]. This is because the rhenium atom possesses one extra valence electron, leading to the formation of additional Re–Re bonds in ReS_2 (atomic structure diagram of a single-layer MoS_2 and ReS_2 is shown in Additional file 1: Figure S1.) The reduced symmetry in ReS_2 induces significant in-plane anisotropy and therefore adds an additional degree of freedom, which makes ReS_2 an interesting material for the fabrication of FETs and polarization-sensitive photodetectors [5, 6]. In this paper, we probed the polarization properties of single-layer (abbreviated as the notation SL) MoS_2 and ReS_2 flakes by angular-dependent reflection spectra measurements on SiO_2/Si and quartz substrates. Our results will shed light on the new effects in those strongly anisotropic layered materials and can empirically be used to identify the crystal orientation.

Materials and Methods

The MoS_2 and ReS_2 flakes with different numbers of layers in this paper were exfoliated from bulk MoS_2 and ReS_2 crystals by micromechanical cleavage method and were prepared on substrates. The interaction between samples and substrates was different and the influence of substrates on experimental results should be considered. Thus, we selected two kinds of substrates: one is the Si {100} substrate covered with an 89 nm SiO_2 and the other is the quartz crystal with a thickness of 1 mm, to support MoS_2 and ReS_2 flakes (the optical microscopic images of SL MoS_2 and SL ReS_2 flakes supported

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on SiO_2/Si substrate and supported on quartz substrate are shown in Additional file 1: Figure S2.) The SL dichalcogenides have a thickness between 0.6 and 0.7 nm which are extremely sensitive to measurement accuracy of measuring instruments. We used ultra-low frequency Raman spectroscopy [7, 8] (the ultra-low frequency Raman spectra of SL MoS_2 and SL ReS_2 flakes supported on SiO_2/Si substrate and supported on quartz substrate are shown in Additional file 1: Figure S3.) and photoluminescence (PL) spectroscopy [8, 9] (the PL spectra of SL MoS_2 and SL ReS_2 flakes supported on SiO_2/Si substrate and supported on quartz substrate are shown in Additional file 1: Figure S4.) to accurately determine the SL MoS_2 and ReS_2 flakes.

Reflection spectrum measurements were performed in a backscattering geometry using a Jobin-Yvon HR800 micro-Raman system. The tungsten halogen lamp was used as a light source with the spot size below 2 μm. The objective of × 100 (NA = 0.9) was used to ensure the accuracy of tests with the size of samples above 5 μm. The best reflected light signal was achieved by focusing the microscope to get maximum peak intensity. The reflection spectra were measured from the samples and bare substrates in the broad wavelength range of 400–800 nm. The 600 lines per millimeter grating was used, which enables one to have each CCD pixel to cover 1 nm. A polarizer was placed on the light path in front of the sample. By continuously rotating the polarizer from 0 to 360°, polarization directions of incident and reflected light were simultaneously varied with polarization angles from 0 to 360°. When the polarizer was rotated to an angle, the reflection spectra of the sample (SL MoS_2 or SL ReS_2) and the substrate (SiO_2/Si or quartz) were measured once. All of the polarization reflection spectra were measured under the condition of keeping the lamp intensity unchanged. We used R (sam + sub) and R (sub) to respectively indicate the reflection intensities of samples and bare substrates and used the optical contrast method to normalize the data by the formula of $R_{OC} = 1 - R$ (sam + sub)/R (sub) (the substrate is SiO_2/Si) or $R_{OC} = R$ (sam + sub)/R (sub) − 1 (the substrate is quartz). In the following studies, the angular-dependent optical contrasts of SL MoS_2 and ReS_2 on different substrates were demonstrated respectively.

Results and Discussion

SL MoS_2 on SiO_2/Si Substrate

We firstly measured the polarization reflection spectra of SL MoS_2 supported on SiO_2/Si substrate by continuously rotating the polarizer from 0 to 360°. The polarizer was rotated once every 30°. Figure 1 a shows the variation of optical contrasts with polarization angles from 0 to 180°. The original curves were overlapping each other and the processed curves were offset for clarity. There are two peaks at ~ 611 nm and ~ 658 nm due to A and B

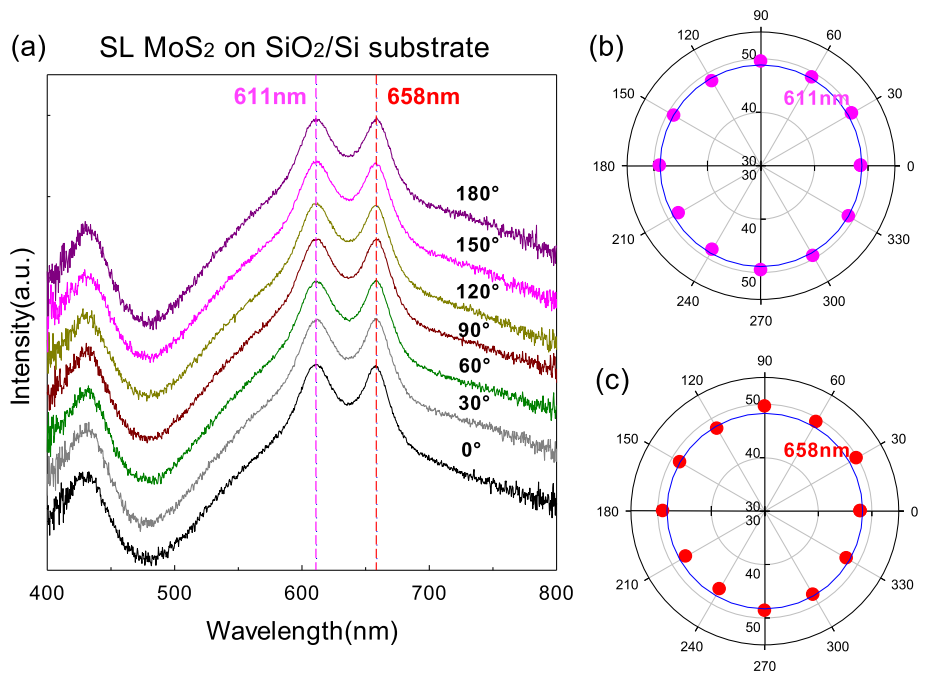

Fig. 1 **a** The polarization optical contrast curves of SL MoS_2 flakes supported on SiO_2/Si substrate. **b** The intensity variation at ~ 611 nm from 0 to 360°. **c** The intensity variation at ~ 658 nm from 0 to 360°

exciton emission [10, 11]. We selected them as references and showed their intensities with the polarization angles from 0 to 360° in Fig. 1 b and c by pink and red circles, respectively. The intensities of two peaks are basically unchanged, which is we should predict since the SL MoS_2 is hexagonally symmetrical.

SL ReS_2 on SiO_2/Si Substrate

The polarization reflection spectra of SL ReS_2 supported on SiO_2/Si substrate were measured as followed. The optical contrast curves of SL ReS_2 flake with varying polarization angles from 0 to 180° are shown in Fig. 2 a and are offset for clarity. There is a valley at ~ 457 nm and a peak at ~ 629 nm [12] suggesting that SL ReS_2 crystallizes in a different crystal structure from SL MoS_2. The intensities at ~ 457 nm and ~ 629 nm changed as the polarization angle changed. Taking them as references, we showed their intensities with the polarization angles from 0 to 360° in Fig. 2 b and c by pink and red circles, respectively. Both of the intensities at two positions show polarization dependence on the polarization angles, which is directly resulted from the low crystal symmetry in SL ReS_2. The in-plane distortion of SL ReS_2 lattice is expected to affect profoundly the interlayer coupling in multilayer ReS_2 crystals because the similar polarization dependence has been found in the optical contrast curves of anisotropic-like-stacked 2 L ReS_2 flakes supported on SiO_2/Si substrate [12] and even in the ultra-low frequency Raman spectra and PL spectra of isotropic-like-stacked 2 L ReS_2 flakes [8].

We fitted the function of the intensities at ~ 457 nm and ~ 629 nm as the polarization angles by a first-order Fourier formula: $f(\theta) = a0 + a1 \times \cos(\theta \times w) + b1 \times \sin(\theta \times w)$, where θ is the polarization angle; a0, a1, and b1 are the amplitudes; and w is the frequency. The positions of minimum and maximum intensities were read as 20° and 110°, respectively, at both of ~ 457 nm and ~ 629 nm. The fitted curves were also plotted in Fig. 2 b and c with blue lines. At ~ 457 nm, a0 = 8.269, a1 = − 4.878, b1 = − 4.585, and w = 0.0348, and at ~ 629 nm, a0 = 34.27, a1 = − 5.99, b1 = − 4.747, and w = 0.03525. They have the basically identical change period with the polarization angles due to the nearly equal w. It should be derived from the distorted structure in the SL ReS_2.

SL MoS_2 on Quartz Substrate

Because SiO_2/Si substrate is opaque, the incident light passed through interfaces of air/sample and sample/substrate and finally was absorbed by the substrate. Meanwhile, the reflected light was collected from each interface and finally transmitted into the air. The optical interference occurred in the multilayered structures and physical properties of the substrate were included in the outgoing-reflected signals in addition to the sample [12]. The SiO_2/Si substrate was a polarized substrate although we used the optical contrast method to normalize the

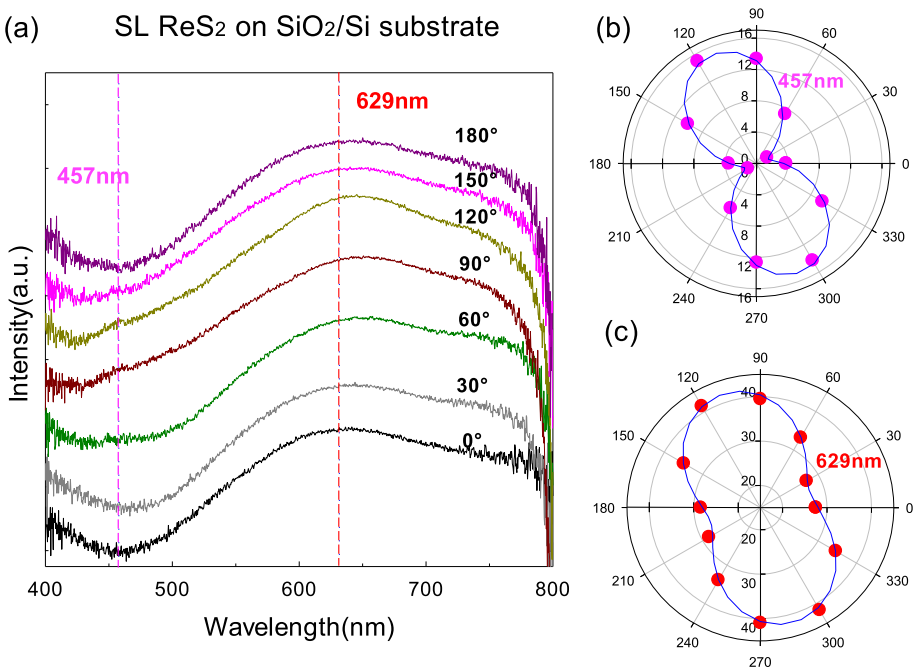

Fig. 2 **a** The polarization optical contrast curves of SL ReS_2 flakes supported on SiO_2/Si substrate. **b** The intensity variation at ~ 457 nm from 0 to 360°. **c** The intensity variation at ~ 629 nm from 0 to 360°

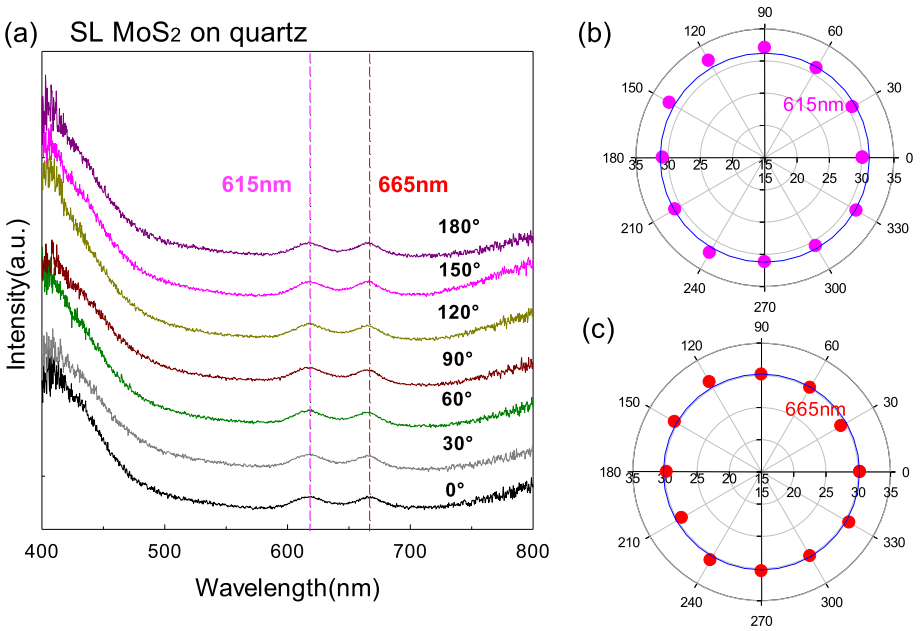

Fig. 3 a The polarization optical contrast curves of SL MoS_2 flakes supported on quartz substrate. **b** The intensity variation at ~ 615 nm from 0 to 360°. **c** The intensity variation at ~ 665 nm from 0 to 360°

data by the formula of $R_{OC} = 1 - R\ (\text{sam} + \text{sub})/R\ (\text{sub})$. In order to eliminate the disturbance of polarized properties from the substrate, we then measured the polarization reflection spectra of SL MoS_2 and ReS_2 on the quartz substrate due to the transparency and isotropy of the quartz substrate.

Since the quartz substrate is transparent, the sample stage should be placed suspended to ensure transparency during measuring. The incident light passed through interfaces of air/sample, sample/substrate, and substrate/air and finally was absorbed by the air to avoid disturbing the collecting of reflected light. We used the formula

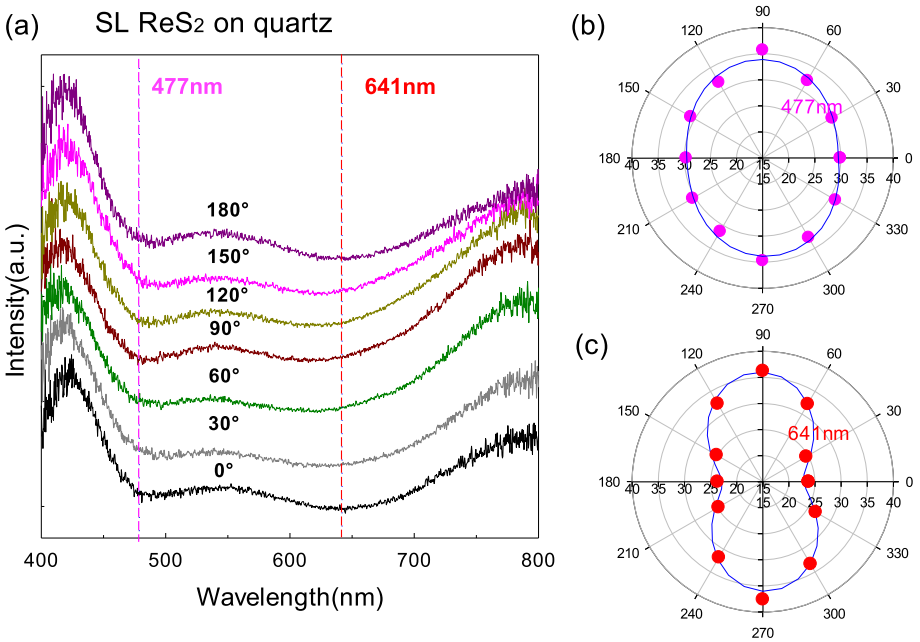

Fig. 4 a The polarization optical contrast curves of SL ReS_2 flakes supported on quartz substrate. **b** The intensity variation at ~ 477 nm from 0 to 360°. **c** The intensity variation at ~ 641 nm from 0 to 360°

of $R_{OC} = R$ (sam + sub)/R (sub) − 1 to normalize the data. Figure 3 a shows the polarized optical contrast curves of SL MoS_2 flake on the quartz substrate with varying polarization angles from 0 to 180°. As can be seen, there are also two peaks related to A and B exciton at ~ 615 nm and ~ 665 nm, respectively. Their position has some shift towards long wavelength than that supported on SiO_2/Si substrate due to interference effects on different substrates [11]. We plotted their intensities with the polarization angles in Fig. 3 b and c. The intensities of two peaks are almost no change as the polarization angle changes, which indicates that in-plane isotropic properties of SL MoS_2 are unchangeable when they are attached to whatever substrates.

SL ReS_2 on Quartz Substrate

Figure 4 a shows the polarized optical contrast curves of SL ReS_2 flake on the quartz substrate, in which there are two valleys at ~ 477 nm and ~ 641 nm, respectively. The difference of features between supported on the quartz substrate and supported on SiO_2/Si substrate is also due to interference effects on different substrates [11]. Figure 4 b and c show the intensities of two valleys with the polarization angles. Both of them show polarization dependence on the polarization angles, which indicates that SL ReS_2 is in-plane anisotropic regardless of substrates. We fitted the relation of the intensities at ~ 477 nm and ~ 641 nm with the polarization angles by a first-order Fourier formula: $f(\theta) = a0 + a1 \times \cos(\theta \times w) + b1 \times \sin(\theta \times w)$, where a0 = 0.3168, a1 = − 0.02215, b1 = − 0.0004139, and $w = 0.03422$ at ~ 477 nm and a0 = 0.2941, a1 = − 0.06608, b1 = − 0.005685, and $w = 0.0349$ at ~ 641 nm. The positions of minimum and maximum intensities were read as 0° and 90°, respectively, at both of ~ 477 nm and ~ 641 nm. The fitted curves were also plotted in Fig. 4 b and c with blue lines. The w is basically identical at both ~ 477 nm and ~ 641 nm and nearly equal to that at ~ 457 nm and ~ 629 nm of SL ReS_2 flakes supported on SiO_2/Si substrate, which means that the polarized properties in SL ReS_2 flakes exhibit a change tendency in the sin or cos function as the polarization angle changes from 0 to 360° and the period is uniform when they are attached to whatever substrates.

Conclusions

In conclusion, SL MoS_2 and ReS_2 on SiO_2/Si substrate and on quartz substrate have been studied by polarization reflection spectra, which identify a significant in-plane isotropy in SL MoS_2 due to a hexagonal structure and in-plane anisotropy in SL ReS_2 due to an additional distorted structure with a hexagonal structure. According to the polarized optical contrast curves with the polarization angles, there are some wavelength-dependent peaks or valleys in SL MoS_2 and ReS_2 predicted by different crystal structures. The variation of intensities at peaks or valleys with the polarization angles confirms the existence of different angle-dependent properties in SL MoS_2 and ReS_2. The same properties exist in some SL 2D materials having a similar structure with MoS_2 such as WS_2, $MoSe_2$, and WSe_2, and having a similar structure with ReS_2 such as $ReSe_2$ and WTe_2. There are many other SL 2D materials that have other types of asymmetric lattice structures, such as BP and SnSe, which have strongly buckled honeycomb sheets with "troughs" running along the y-axis. These samples might also show anisotropic features. It implies that some new polarization-dependent electronic devices may soon be realized and promoted considering the wide variety of samples.

Supplementary information

Supplementary information accompanies this paper at https://doi.org/10.1186/s11671-020-3280-8.

Additional file 1: Figure S1 Atomic structure diagram of SL MoS2 and SL ReS2. **Figure S2** The optical microscopic images of SL MoS2 and SL ReS2 flakes supported on SiO2/Si substrate and supported on quartz substrate. **Figure S3** The ultralow-frequency Raman spectra of SL MoS2 and SL ReS2 flakes supported on SiO2/Si substrate and supported on quartz substrate. **Figure S4** The PL spectra of SL MoS2 and SL ReS2 flakes supported on SiO2/Si substrate and supported on quartz substrate.

Abbreviations

PL: Photoluminescence; SL: Single-layer; TMDs: Transition metal dichalcogenides

Acknowledgements

The authors are grateful to Professor Pingheng Tan for the Raman spectra measurements.

Authors' Contributions

YS and LW contributed equally to this work. Data curation was done by YS, XQ, and SL. Formal analysis was done by LW and YL. Project administration was done by XL and XZ. All authors participated in the discussions and read and approved the final manuscript.

Funding

This work is supported by the Youth Project of Hebei Province Natural Science Foundation (A2017201012), the Postgraduate Innovation Project of Hebei University (hbu2019ss033).

Availability of Data and Materials

The SL MoS_2 and SL ReS_2 flakes were exfoliated from bulk MoS_2 and ReS_2 crystals by micromechanical cleavage method, prepared on two kinds of substrates: the Si {100} substrate covered with a 89-nm SiO_2 and the quartz crystal with a thickness of 1 mm, and identified by ultra-low frequency Raman spectroscopy and PL spectroscopy. Reflection spectra measurements were performed in a backscattering geometry using a Jobin-Yvon HR800 micro-Raman system. The tungsten halogen lamp was used as a light source. A polarizer was placed on the light path in front of the sample. By continuously rotating the polarizer from 0 to 360°, the polarization reflection spectra of samples and substrates were measured and the optical contrast method was used to normalize the data.

Competing Interests

The authors declare that they have no competing interests.

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Received: 25 July 2019 Accepted: 4 February 2020
Published online: 17 February 2020

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