Stacking-Order-Driven Optical Properties and Carrier Dynamics in ReS$_2$

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Electronic screening of external field,[1] Raman vibrations,[2] and electron transport,[3] in transition metal dichalcogenides (TMDs), a rich family of 2D semiconductors, however, the effect of stacking order was rarely explored,[4,5] even though first principles calculations suggested stacking-order-driven valence band splitting and exciton binding energy change.[6] TMDs possess many intriguing quantum phenomena for novel electronic devices.[7–9] ReS$_2$, a rising star among TMDs, has drawn much attention in recent years. ReS$_2$ possesses a distorted 1T triclinic crystal structure where the additional $d$ valence electrons of Re atoms form zigzag Re chains parallel to the $b$ axis, drastically reducing its symmetry. Even though properties of bulk ReS$_2$ have been studied since 1997,[10–21] research on the 2D form of ReS$_2$ only began to surge around 2014.[22] Comparing with other TMDs, interlayer coupling of ReS$_2$ is much weaker.[22] The uniqueness of ReS$_2$ lies in its in-plane anisotropic properties, which have been demonstrated as early as 2001 in bulk.[15] In 2D ReS$_2$, properties observed are polarization-dependent excitons,[23,24] nonlinear absorption,[25] electron transport and SHG emission,[26,27] etc. Comparing

Two distinct stacking orders in ReS$_2$ are identified without ambiguity and their influence on vibrational, optical properties and carrier dynamics are investigated. With atomic resolution scanning transmission electron microscopy (STEM), two stacking orders are determined as AA stacking with negligible displacement across layers, and AB stacking with about a one-unit cell displacement along the $a$ axis. First-principles calculations confirm that these two stacking orders correspond to two local energy minima. Raman spectra inform a consistent difference of modes I & III, about 13 cm$^{-1}$ for AA stacking, and 20 cm$^{-1}$ for AB stacking, making a simple tool for determining the stacking orders in ReS$_2$. Polarized photoluminescence (PL) reveals that AB stacking possesses blueshifted PL peak positions, and broader peak widths, compared with AA stacking, indicating stronger interlayer interaction. Transient transmission measured with femtosecond pump–probe spectroscopy suggests exciton dynamics being more anisotropic in AB stacking, where excited state absorption related to Exc. III mode disappears when probe polarization aligns perpendicular to $b$ axis. The findings underscore the stacking-order driven optical properties and carrier dynamics of ReS$_2$, mediate many seemingly contradictory results in the literature, and open up an opportunity to engineer electronic devices with new functionalities by manipulating the stacking order.

In trilayer graphene, stacking order provides an important degree of freedom to manipulate its properties, where ABC and ABA stackings display dramatically different behavior in electronic screening of external field,[1] Raman vibrations,[2] and electron transport.[3] In transition metal dichalcogenides (TMDs), a rich family of 2D semiconductors, however, the effect of stacking order was rarely explored,[4,5] even though first principles calculations suggested stacking-order-driven valence band splitting and exciton binding energy change.[6] TMDs possess many intriguing quantum phenomena for novel electronic devices.[7–9] ReS$_2$, a rising star among TMDs, has drawn much attention in recent years. ReS$_2$ possesses a distorted 1T triclinic crystal structure where the additional $d$ valence electrons of Re atoms form zigzag Re chains parallel to the $b$ axis, drastically reducing its symmetry. Even though properties of bulk ReS$_2$ have been studied since 1997,[10–21] research on the 2D form of ReS$_2$ only began to surge around 2014.[22] Comparing with other TMDs, interlayer coupling of ReS$_2$ is much weaker.[22] The uniqueness of ReS$_2$ lies in its in-plane anisotropic properties, which have been demonstrated as early as 2001 in bulk.[15] In 2D ReS$_2$, properties observed are polarization-dependent excitons,[23,24] nonlinear absorption,[25] electron transport and SHG emission,[26,27] etc. Comparing
with black phosphorus (BP), which also shows in-plane anisotropic properties, ReS₂ is more stable in ambient environment, which makes it more suitable for optoelectronic devices. Among the studies of ReS₂, many contradictory findings have been reported.[24,28–33] For example, Tongay et al. suggested that the monolayer behavior of ReS₂ still persists in bulk,[24] which, however, was challenged by several later studies.[28,30,31] Also, scanning transmission electron microscope (STEM) images of multilayer ReS₂ reported by different groups show drastically different features.[31,32] Similar inconsistencies also exist in the determination of indirect-direct bandgap transition.[28] Raman vibrational modes and second harmonic generation (SHG) spectra.[26–30,34] These results suggest that some other intrinsic parameter that governs the electronic and optical properties of spectra.[26–30,34] These results suggest that some other intrinsic vibrational modes and second harmonic generation (SHG) predictions can be reproduced if the top layer moves relative to the bottom layer about one unit cell along a axis.

To confirm our proposed structure of stackings AA and AB, we also performed first principles calculations for bilayer ReS₂. As shown in Figure 1c, after scanning through the displacement space along a axis, two local energy minima appear. Figure 1d,e depict the relaxed lattice structures at these two minima. At first energy minima, the two layers have minimal displacement. At the second energy minima, there is about a one-unit cell (=2.5 Å) displacement along a axis. This is consistent with the STEM images and confirms our proposed structures for both stacking AA and AB. Qiao et al. proposed two possible stacking orders in ReS₂ based on the vibrational states measured with Raman and DFT calculations, where the second layer has a rotational displacement of 60° and 120° with respect to the first layer.[28] However, the problem with this proposed structure is that the universal b axis (Re-Re chain) should no longer exist, which contradicts the previously published findings of a clearly defined b axis for ReS₂.[13] With similar approaches, He et al. proposed three possible stacking orders with translational displacements along the direction perpendicular to b axis.[90] Compared with these obscure results, our STEM images and first principles calculations show without ambiguity that there are two possible stacking orders existing in ReS₂, AA stacking (with negligible displacement among layers), and AB stacking (with translational displacement along a axis).

In order to reveal the impact of stacking order on vibrational properties, Raman measurements were conducted on multiple exfoliated samples, with thicknesses ranging from 55 to 580 nm (Figures S5 & S6, Supporting Information). Figure 2a,b shows mode I and mode III of all samples, which correspond to the A₁g (cross-plane) and E₁g-like (in-plane) modes. Among the 9 samples studied, the peak of mode III lies consistently slightly above 150 cm⁻¹, while that of mode I shows up either close to 130 or 140 cm⁻¹. When plotting the difference between these two modes, Δ = mode III − mode I, the samples may be clearly categorized into two groups (A & B) (Figure 2c). Group B has a Δ of about 20 cm⁻¹, and group A has a Δ of about 13 cm⁻¹. We also calculated the Raman spectra of stacking AA and AB, as plotted in Figure 2d. What we observed is that mode III peak positions are the same in both stackings, but the mode I peak in stacking AA is about 4.7 cm⁻¹ higher than that in stacking AB. These calculations confirm that group A samples in Figure 2c possess stacking order AA and group B samples possess stacking order AB. Even more astonishing, the stacking order of ReS₂ is robust enough to persist even in bulk samples. The difference between Raman peaks of mode I and mode III can be used as an indicator of stacking order in ReS₂, similar to what was proposed by Qiao et al. in multilayer ReS₂.[38] It is not surprising that mode III does not vary much among different samples since it corresponds to in-plane lattice vibrations. Mode I originates from out-of-plane vibrations within a single
layer, and is more prone to the stacking order. Higher mode I frequency in stacking AA samples indicates stronger interatomic bonding within a single layer along cross-plane direction, which may be further understood as weaker interlayer interaction. We also calculated the Raman spectra of interlayer breathing ($B$) and shear modes ($S_\parallel$, $S_\perp$), as shown in Figure 2e. $S_\parallel$ represents the shear mode along Re chain ($b$ axis) and $S_\perp$ represents the shear mode perpendicular to the Re chain. For all three low-frequency modes, the values in stacking AB are higher than those in stacking AA, with $\Delta S_\parallel = 3.1 \text{ cm}^{-1}$, $\Delta S_\perp = 0.61 \text{ cm}^{-1}$, $\Delta B = 0.66 \text{ cm}^{-1}$. Higher-frequency breathing and shear modes in stacking AB indicate stronger interlayer interaction.\cite{35}

In the relaxed crystal structure, the interlayer distance of stacking AB is 2.59 Å, smaller than that of stacking AA, 2.71 Å, which also supports the stronger interlayer interaction in stacking AB.

To investigate how the stacking order of ReS$_2$ affects its optical properties, we conducted polarized PL measurements. The results of two representative samples, AA* (sample 2 in Figure 2a) and AB* (sample 7 in Figure 2b), are plotted in Figure 3. We found that while the PL spectra do not show obvious effect from the polarization of incident beam, they are very sensitive to that of collection beam. As a result, we fixed the polarization of incident beam along $b$ axis (0°), but, aligned the polarization of collection beam both along (0°) and perpendicular (90°) to $b$ axis. Voigt function was used to fit the PL spectra to determine the peak positions and widths (full width at half maximum, FWHM), also plotted in Figure 3. Four peaks are identified, with the peak around 1.4 eV being the optical transition at the indirect bandgap, and the other three peaks assigned to exciton I, II and III, respectively.\cite{24}

For both samples, Exc. I is more prominent when collection polarization is along 0°, and Exc. II is more prominent along 90°. This is consistent with previous studies suggesting that Exc. I and Exc. II are polarized along different directions.\cite{15,24} For Exc. III, in both stackings it is more prominent along 0° than 90°. However, the PL peak of Exc. III is much more prominent in sample AA* than that in sample AB* (Figures S17 and S18, Supporting Information). For AB*, Exc. III almost vanishes at 90°. In ReS$_2$, the Rydberg series was observed and the behavior can be well-explained by Wannier excitons.\cite{23} Exc. III was assigned as an excited Rydberg exciton state of lower-lying excitons.\cite{23,24} Since the excited states of Exc. I & II lie very close to each other and both close to the Exc. III energy, even

Figure 1. a,b) STEM images of AA and AB stacking orders, with proposed relative replacement between two layers. Green color represents the bottom layer, blue the top layer. The red dashed circles mark the bright dots in STEM images, which come from the almost overlapping atoms of two layers. c) First-principles calculations of total energy of a bilayer ReS$_2$ structure against displacement along $a$ axis. d,e) Snapshots of crystal structures predicted with ab initio calculations at two local energy minima, as they correspond to AA and AB stacking orders. Note the relative shift in AB stacking along $a$ axis, which is negligible in AA stacking.
though they have different preferable polarization, we can view Exc. III as a superposition of two excited states from Exc. I & II. The higher PL intensity of Exc. III along 0° collection polarization suggests that the excited state of Exc. I contributes a larger portion to Exc. III. High lying excited states such as Exc. III are very sensitive to the environment. The greatly reduced PL intensity of Exc. III in AB* indicates that the excited excitons are weakened substantially, especially along 90° collection polarization.

For all three excitons, AB* has blueshifted PL peak positions (20–25 meV) and broader widths than stacking AA*. Even though only two samples are presented in Figure 3, this general trend is seen in other samples sharing the same stacking order (Figures S8–S16, Supporting Information). The position of the PL exciton peak, \( E_{\text{exc}} \), is determined by both the optical transition of electronic bandgap (\( E_{\text{BG}} \)) and exciton binding energy (\( \Delta_{\text{binding}} \)).

\[ E_{\text{exc}} = E_{\text{BG}} - \Delta_{\text{binding}} \]

Broader exciton peak width in AB* suggests a shorter radiative lifetime, which further implies stronger exciton oscillation strength. Our first principles calculations predicted an interlayer distances of 2.71 Å for AA stacking and 2.59 Å for AB stacking. A shorter interlayer distance allows the wave functions of carriers in different layers to have a higher probability to interact, which results in a larger dielectric constant and stronger interlayer interaction. It is known that a larger dielectric constant environment screens the Coulomb force of intralayer excitons, which usually results in a blueshift of the exciton. Stronger interlayer interaction means stronger carrier scattering, and a shorter radiative lifetime.

To study how the stacking order affects the exciton dynamics, we performed ultrafast pump–probe spectroscopy with degenerate pump/probe pulses. We mainly focus on the dynamics of Exc. III since its energy level almost resonates with our laser photon energy (790 nm, 1.57 eV). From PL spectra (Figure 3), the Exc. III energy level shifts slightly in different stacking orders. To probe Exc. III resonantly, which usually delivers largest signal, we performed spectrally resolved measurement to determine the optimum pump/probe wavelength. Moreover, PL spectra also reveals that Exc. II has a very broad peak that overlaps with that of Exc. III significantly. To separate the dynamics of Exc. II and Exc. III, we narrow the laser spectrum width down to 7 nm (FWHM), much smaller than the PL peak difference between Exc. II and Exc. III (25–30 nm). We also conducted a set of spectrally resolved measurements in sample AA* that cover both Exc. II and Exc. III, to make sure the dynamics of Exc. II and Exc. III do not interfere with each other under our experimental conditions (Figure S22, Supporting Information). Figure 4 shows the transient transmission signals for AA* and AB*. Because the signals do not have obvious dependence on pump polarization, but are very sensitive to probe polarization (Figure S21, Supporting Information), only four polarization combinations are presented. We chose cross-polarized pump and probe beams for ease of data acquisition. For AA*, the transmission signals show negative peaks for both 0° and 90° probe polarizations. For AB*, the signal displays a negative peak when the probe is along 0°, while a positive peak when the probe is along 90°.

Under resonant probe conditions, the transmission signal is usually related to the imaginary part of the refractive index and hence reflects the absorption change in the material. A decrease of transmission (negative peaks) at time zero indicates increasing absorption of probe photons, while positive peaks indicate decreasing absorption. Since pump pulse excites carriers to the Exc. III level, the negative peak means these excited carriers can further absorb probe photons and experience intraband transition to even higher energy levels (Figure 4a–c). This phenomenon is called excited state absorption (ESA). To observe ESA experimentally, the laser pulse width has to be shorter than the relaxation time of Exc. III. The pulse width of our femtosecond laser is about 400 fs (FWHM) at the sample position, much shorter than the reported exciton recombination time in ReS2. The positive ΔT/T peak (Figure 4d) is usually explained as a result of phase-filling. Due to fermion nature of electrons (or holes), each quantum state on the same energy level only allows for two electrons with opposite spins. When all the states are occupied, the Pauli-blocking effect prevents...
further excitation of carriers and hence absorption decreases. In light of this understanding, we propose that for AA*, ESA dominates near time zero for both probe polarizations: for AB*, ESA only dominates when the probe is along 0°, while the phase-filling effect dominates for 90° probe. The phenomena observed in transient transmission experiments are

Figure 3. a) PL spectra of sample AA* with 0° polarization for both incident and collection beams; b) PL spectra of sample AA* with 0° polarization for incident beam and 90° for collection beam; c) PL spectra of sample AB* with 0° polarization for both incident and collection beams; d) PL spectra of sample AB* with 0° polarization for incident beam and 90° for collection beam.

Figure 4. Transient transmission signal measured with femtosecond pump–probe spectroscopy: a,b) in sample AA*, with pump polarized at 90° and probe at 0° (a), with pump polarized at 0° and probe at 90° (b), c,d) in sample AB*, with pump polarized at 90° and probe at 0° (c), and with pump polarized at 0° and probe at 90° (d).
consistent with the nonlinear absorption results measured in ReS₂ (Figure S23, Supporting Information). In stacking AA, strong ESA exists with light polarization along both 0° and 90°. In stacking AB, ESA dominates when light polarization is 0°, and saturable absorption (SA, where absorption decreases with light intensity by the phase filling effect) dominates when polarization is near 100°.[43] Our nonlinear absorption data of AB stacking was published in 2018, before which time the existence of stacking order in ReS₂ had not yet been recognized in the scientific community.

ESL requires a large number of excitons to exist at level Exc. III, which in turn requires available states at Exc. III. For stacking AA, since the relative shift between layers is negligible, it is reasonable to expect that these higher exciton levels are preserved along all directions, similar to those in monolayer. In stacking AB, however, the one unit-cell relative shift along the a-axis causes disorder to be introduced along the perpendicular direction and, as a result, the high lying exciton levels may be disrupted and fewer states available at Exc. III. This explanation is also consistent with the PL spectra presented in Figure 3 for both collection polarizations of AA° and for the 0° collection in AB°, where the PL peaks of Exc. III are quite prominent. At the 90° collection in AB°, the PL peak of Exc. III almost disappears. This weak PL peak indicates less available states, and therefore we expect to observe stronger phase-filling effects in transient absorption and SA in nonlinear absorption.

For all the four cases, after the negative/positive peaks, the signals decay monotonically, which corresponds to several factors, including the relaxation from high-lying to lower exciton levels, indirect band edge, and exciton recombination.

Identifying the stacking order of ReS₂ mediates many seemingly “controversial” results published in the literature. For example, the STEM images of multilayer ReS₂ reported by different groups are inconsistent, some having very clean and well-arranged Re atoms,[24] and others not.[31] These different images must come from samples with different stacking orders. Second, even though most studies in the literature show that bulk ReS₂ is an indirect semiconductor, there is lack of agreement on the bandgap in few-layer samples. From our first-principle calculations with GaN approximation (Figure S4, Supporting Information), we found that the bilayer AA stacking ReS₂ has a direct bandgap while bilayer AB stacking has an indirect bandgap. This suggests that the bilayer sample studied by Gehlmann et al.[44] has AA stacking. Wang et al. studied a 3L ReS₂ with Raman and PL.[43] From the Raman spectra, their sample also has AA stacking. From their PL spectra at 10 K, a clear indirect band transition was observed. Comparing with our calculation results, we may conclude that stacking AA transits from direct bandgap to indirect bandgap at three layers. In Table S4, we summarized all the previously reported results and identified the stacking order for most samples based on available information. A third example is the SHG spectra, as reported by Song et al. where SHG signals of ReS₂ can only be observed in even number layers,[26] while Dhakal et al. showed that the SHG signal increases with thickness of ReS₂ starting from monolayer, regardless of the number of layers.[27] These discrepancies can be explained with ease if the factor of stacking order is considered. SHG is determined by the symmetry of crystal. With AA stacking, where there is negligible displacement among layers, the symmetry is expected to be the same as the monolayer, which explains the observation by Song et al. With AB stacking, symmetry is defined by two-layers, rather than one, hence the SHG signal only appears in even numbers of layers.

While surveying 11 exfoliated ReS₂ samples, we did observe two samples showing mixed stacking orders, as shown in Figure S24 in the Supporting Information, which might come from lattice rotation during sample growth process. For the samples with definite stacking order identified (either AA or AB), the stacking order is robust and does not depend on the number of layers. Lastly, from the temperature dependent Raman measurements (Figure. S25, Supporting Information), we found that both stacking orders are stable when temperature increases up to 573 K. Our results underscore the stacking-order-driven optical properties and carrier dynamics in ReS₂, which opens opportunities to pursue new functionalities and engineer new electronic devices by manipulating stacking order.

Experimental Section

Sample Preparation: Samples were prepared by mechanical exfoliation, with single crystals purchased from HQ Graphene. For STEM measurements, the samples were firstly exfoliated onto SiO₂/Si (Addison Engineering). Then, after being characterized by Raman and PL, the few-layer samples were transferred onto the Quantifoil TEM grid (TED PELLA, INC). For Ultrafast carrier dynamics measurements, the samples were exfoliated onto glass substrate (TED PELLA, INC).

Raman and PL Measurements: Both Polarized Raman and PL measurements were conducted by inVia confocal Raman microscope (Renishaw) with 532 nm excitation. For Raman, 2400 lines mm⁻¹ grating were used. In order to control the polarization, the samples were mounted on a rotational stage. For PL, 1200 lines mm⁻¹ grating were used.

STEM Measurements: Experiments were conducted by JEOL JEM-ARM 200F at 80 kV.

Ultrafast Carrier Dynamics Measurements: The ultrafast carrier dynamics measurements were made by degenerate pump–probe method at room temperature. Both pulses (pump and probe) were generated from a femtosecond Ti: Sapphire Oscillator (spectra physics, Tsunami), with 7 nm spectral linewidth (FWHM) and 400 fs pulse width at the sample position. The spot size (1/e² diameter of Gaussian beam) for pump and probe were about 13.3 and 6.7 μm, respectively.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, carrier dynamics first-principles calculations, optical properties, pump–probe, ReS$_2$

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