Linearly Polarized Excitons in Single- and Few-Layer ReS₂ Crystals

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Ⓢ Supporting Information

ABSTRACT: Rhenium disulfide (ReS₂), a layered group VII transition metal dichalcogenide, has been studied by optical spectroscopy. We demonstrate that the reduced crystal symmetry, as compared to the molybdenum and tungsten dichalcogenides, leads to anisotropic optical properties that persist from the bulk down to the monolayer limit. We find that the direct optical gap blueshifts from 1.47 eV in the bulk to 1.61 eV in the monolayer limit. In the ultrathin limit, we observe polarization-dependent absorption and polarized emission from the band-edge optical transitions. We thus establish ultrathin ReS₂ as a birefringent material with strongly polarized direct optical transitions that vary in energy and orientation with sample thickness.

KEYWORDS: *layered 2D materials, rhenium disulfide, optical anisotropy, excitons, birefringence, optical absorption spectrum, photoluminescence*
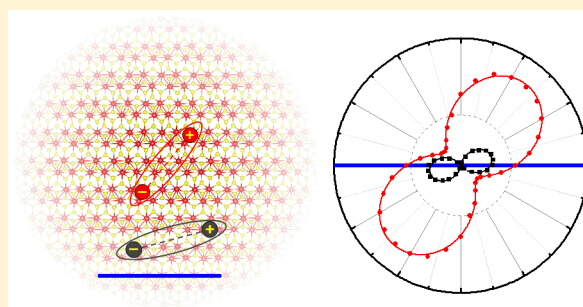
Anisotropic optical properties are present in bulk crystals of sufficiently low symmetry. In layered materials, in-plane anisotropy can be significant, as in the case of black phosphorus.[1−4] The group VI transition metal dichalcogenides such as MoS₂, MoSe₂, WS₂, and WSe₂ are also layered materials with distinctive optical properties.[5,6] Their monolayers provide, for example, valley selective excitation of band-edge excitons[7−9] using circularly polarized light as a consequence of their broken inversion symmetry.[10] However, because of the high symmetry of the crystal structure, their linear optical properties of absorption and emission are isotropic in the plane of the layer.

ReS₂, a layered group VII transition metal dichalcogenide, possesses reduced crystal symmetry compared to the molybdenum and tungsten dichalcogenides. This reduced symmetry gives rise to anisotropic in-plane optical properties. ReS₂, thus, merits special attention. While the anisotropic optical and electric properties of bulk ReS₂ crystals and the basic optical properties of ultrathin layers have been previously studied,[11−17] anisotropic optical effects in ultrathin layers of ReS₂ remain unexplored.

In this Letter, we demonstrate the anisotropic optical properties of single- and few-layer ReS₂ crystals through polarization-resolved reflectance and photoluminescence spectroscopy. We find that the near band-edge excitons in ultrathin crystals absorb and emit light with preferred linear polarizations. We also observe that the transition energies of the excitons can be tuned with layer thickness. We thus establish that ultrathin ReS₂ has optical transitions with strengths and transition energies that depend on thickness and polarization of the optical radiation.

Figure 1a is a schematic of the crystal structure of single layer (1L) ReS₂ from the top and a side view along the *b*-axis.[18,19] Each layer consists of Re atoms sandwiched between two S sheets, with distorted trigonal antiprismatic coordination and strong covalent bonding between the Re and S atoms;[17,19,20] bulk ReS₂ is composed of stacks of such layers held together by weak van der Waals forces. The dashed arrow in Figure 1a depicts the location of the center of inversion[12] present in monolayers. Rhenium atoms (red) form a chain due to the Re—Re bonds, which is parallel to the *b*-axis (blue line), as denoted in the literature.[15] Due to that strong metal—metal bond, ReS₂ is expected to break preferentially along the *b*-axis.[21,22] When an ultrathin flake is found to be attached to a thick flake, its *b*-axis can often be identified by its cleavage axis. Figure 1b shows a few-layer sample attached to a bulk-like region (indicated by the white arrow) with just such a well-defined cleaved edge. This sample was mechanically exfoliated onto a polydimethylsiloxane (PDMS) substrate. The inset in Figure 1b presents a profile of the green-channel signal (*G*) of an optical image of the sample. Such data provide a simple means of determining the layer thickness,[23] since each layer increases *G* by 12−13%. This result was confirmed with the aid of Raman spectroscopy measurements.[22]
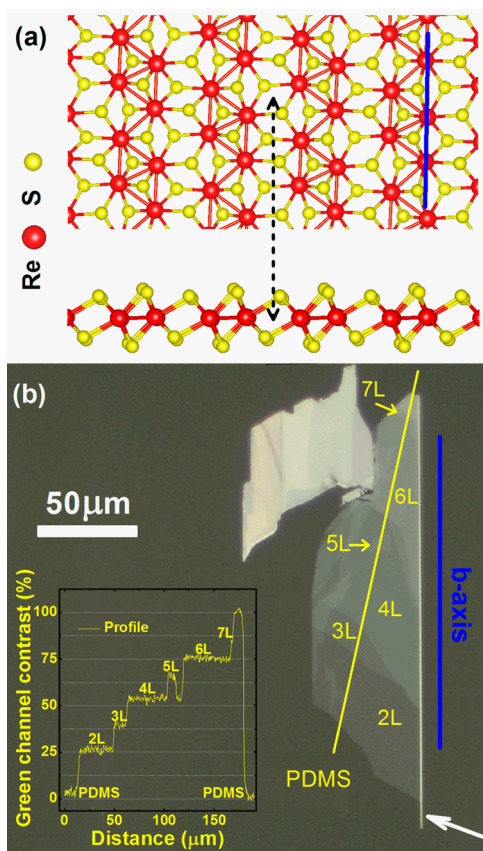
Figure 1. (a) Representation of the crystal structure of single-layer (1L) ReS_2, shown from the top (upper figure) and from the side (lower figure), as viewed along the *b*-axis (blue line). The end points of the dashed arrow identify a point of inversion symmetry for the structure. (b) Optical microscopy image of a few-layer ReS_2 flake. The sample includes a sharp edge of bulk material (indicated by the white arrow), which reveals the *b*-axis (blue line). The inset shows the green-channel contrast profile (relative to the substrate) along the yellow line shown in the image. The labels 2L, 3L, 4L, ... refer to the layer thickness of the corresponding region.

We have probed the anisotropic optical response of ReS_2 layers using a combination of unpolarized and polarization-resolved reflection, reflection contrast, and photoluminescence (PL) measurements. In reflection contrast measurements, we record the differential reflectance of the sample normalized by the reflectance of the substrate, that is, $\Delta R/R = (R_{ReS_2+PDMS} - R_{PDMS})/R_{PDMS}$, where R_{ReS_2+PDMS} and R_{PDMS} represent, respectively, the reflectance of the thin ReS_2 sample on the PDMS substrate and of the bare PDMS substrate. In the polarization-resolved measurements, a strain-free objective was used to ensure that we illuminated the sample with linearly polarized light and detected the reflected light of the same polarization. Furthermore, normalization by R_{PDMS} eliminates any anisotropy in the collection efficiency. For sufficiently small values of the reflection contrast for a sample on a thick transparent substrate, as in our case, we can determine the absorbance $\mathcal{A}$ of the unsupported thin ReS_2 from $\Delta R/R$ as $\mathcal{A} = \frac{1}{4}(n_{PDMS}^2 - 1)\left(\frac{\Delta R}{R}\right)$,[24−26] where n_{PDMS} denotes the refractive index of PDMS.[27,28] We can thus probe the absorption spectra of sufficiently thin samples through measurements of the reflection contrast. In this fashion, we study the energies and strengths of the direct optical transitions. Indirect transitions are not expected to be observable, since they give rise to a very weak contribution to the absorbance. The lowest-lying transition can generally be identified in the photoluminescence spectra, even when it is indirect in character. In polarization-resolved PL measurements, only emitted photons with polarization parallel or perpendicular to the incident laser were collected, and spectra were recorded as the sample was rotated about its surface normal while keeping the collection geometry fixed (see Methods for details).

We first give an overview of the optical response of the monolayer and bulk material using measurements with unpolarized radiation. Figure 2 displays the unpolarized photoluminescence and reflectance spectra for a bulk sample (Figure 2a) and for a monolayer (Figure 2b). In this figure, the reflectance spectrum of the bulk (differentiated with respect to photon energy) is plotted to emphasize the optical transitions. For the monolayer, we show the reflection contrast spectrum, which, as discussed above, is proportional to the absorption spectrum of the sample. In these spectra (plotted in red in Figure 2), we identify three optical transitions. These transitions were previously observed in bulk ReS_2 and exhibited
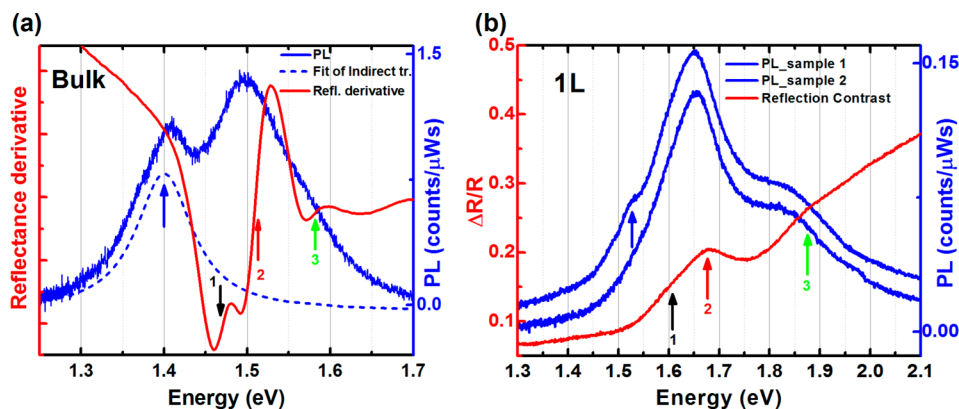

Figure 2. (a) Optical spectra of a bulk ReS_2 crystal: photoluminescence (PL, blue) and reflectance spectra (red), the latter differentiated with respect to photon energy. The dashed blue curve is the contribution to the PL from a transition at 1.40 eV. (b) Optical spectra for 1L ReS_2 crystals: PL (blue, upper spectrum offset) and reflection contrast spectrum (red). The arrows indicate the peak positions of the optical transitions. The PL of the bulk crystal shows a transition indicated by a blue arrow, which is not observed in the reflectance measurements, and corresponds to an indirect optical gap of 1.40 eV. All of these measurements were performed without polarization analysis.
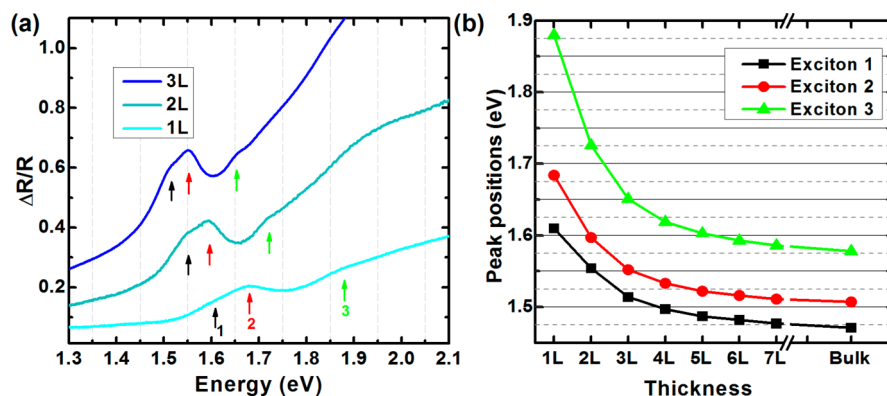
Figure 3. (a) Reflection contrast spectra of 1L, 2L, 3L ReS$_2$ crystals based on measurements with unpolarized light. The arrows indicate the peak positions of the optical transitions. (b) Energies of different excitonic transitions extracted from reflection contrast measurements. The energies shift significantly with thickness up to approximately 5L.

excitonic line shapes.[21,29] We correspondingly refer to them as excitons 1, 2, and 3 and also fit the spectra using Lorentzian contributions. Because exciton 3 is weak, we cannot directly exclude the possibility that this feature arises, for thin layers, from the onset of a band-edge free-carrier transition. However, the increasing strength of excitonic interactions with decreasing layer thickness renders this possibility unlikely, since oscillator strength would be transferred from free-carrier to excitonic transitions. A more probable scenario would be that exciton 3 is an excited (Rydberg) excitonic state of the lower-lying excitons. This result would be compatible with the increasing separation in energy of exciton 3 from excitons 1 and 2 with decreasing layer thickness. The thinner samples would exhibit increased exciton binding energy and, hence, increased energy separation between the transitions.

In the bulk crystal, these transitions appear at photon energies of 1.47, 1.51, and 1.58 eV, respectively, as identified in the reflectance derivative spectrum by points of inflection. These inferred transition energies agree well with an earlier report[30] of values of 1.48 and 1.52 eV for excitons 1 and 2. In the monolayer sample, the features in the reflectance contrast spectra shift to energies of 1.61, 1.68, and 1.88 eV. (Polarization-resolved measurements discussed below will further clarify these assignments.) Figure 2 also presents photoluminescence data for the bulk sample and the monolayer. For the bulk crystal, the photoluminescence spectrum exhibits an additional lower-energy peak at 1.40 eV that is not observed in reflectivity spectrum. We highlight this transition, plotted as a dashed blue line, by subtracting the contributions of the optical transitions observed in the reflectivity spectra.

In agreement with previous studies[13,31] and in contrast to a recent report,[17] these data thus suggest that bulk ReS$_2$ possesses an indirect optical gap at 1.40 eV, lying slightly below the direct optical gap at 1.47 eV identified in the reflectance spectrum. The energy for the indirect-gap transition in this study agrees well with earlier literature values of 1.37 ± 0.02[13] and 1.40 eV[31] for the indirect optical transition. In the monolayer, we also observe a similar feature in the PL spectrum (blue arrow in Figure 2b) at a lower energy than the direct transitions identified in the reflection contrast spectrum. We have not, however, seen this feature consistently in other monolayer samples, for example, in the second PL spectrum in Figure 2b or spectra for few-layer samples. We are consequently

currently unable to identify definitively whether this weak feature arises from an indirect transition or from defect states.

Figure 2 also shows higher-energy (hot) PL for both bulk and monolayer ReS$_2$ samples. Similar behavior (not shown) is observed in the few-layer samples. Interestingly, PL from exciton 2 (red arrow) is stronger than the PL from lower-energy exciton 1 (black arrow) for all sample thicknesses. This indicates that the emission time from exciton 1 is very short and comparable to the relaxation time of the higher-lying exciton. This behavior, we note, differs from the more typical case seen in the Mo and W dichalcogenide monolayers where emission from the lower-energy peak is much stronger than from the higher-energy peak.[32−34] For the case of ReS$_2$, the short emission time for exciton 1 presumably reflects the presence either of a still lower-lying indirect transition or of rapid nonradiative relaxation associated with defects. The relative weakness of emission from exciton 1 is also expected based on the lower oscillator strength compared with exciton 2 revealed in the reflection contrast spectrum. In contrast to the situation for the Mo and W dichalcogenides,[17] we do not observe increased photoluminescence efficiency for monolayer samples. There is, thus, no signature of a transition from an indirect-gap bulk material to a direct-gap semiconductor at monolayer thickness. Unfortunately, we do not see a well-defined emission peak below the direct transition identified in the absorption spectra of the single- and few-layer samples, which would allow us to identify the indirect gap energy. This situation would be expected for a difference between the direct and the indirect transition energies that does not greatly exceed the thermal energy, in which case the modestly higher equilibrium population associated with the indirect transition would not compensate for its lower radiative rate. The role of defects in reducing exciton lifetimes may further impede identification of emission from the indirect gap.

In order to determine the positions of the optical transitions for few-layer ReS$_2$ crystals, we extend these measurements to thicker samples. Figure 3a presents unpolarized reflection contrast spectra for 1L, 2L, and 3L crystals, with transition energies of the excitons 1, 2, and 3 indicated by arrows. Figure 3b displays the transition energies for 1L−7L samples and for the bulk crystal. To extract the peak positions for 1L−5L samples, each spectrum was fit by one Lorentzian line per peak in the region of interest and one additional Lorentzian feature to represent the contributions of the higher-energy transitions. Because of distortions arising from substrate interference
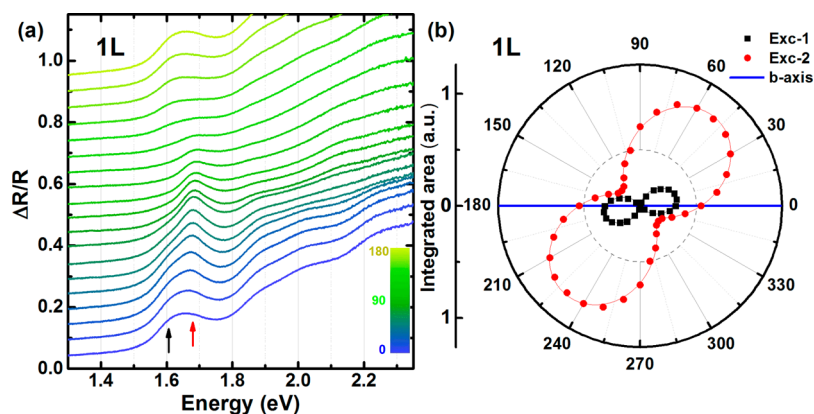
Figure 4. Anisotropic optical response of 1L ReS$_2$. (a) Polarization-resolved reflection contrast spectra, measured at 10° intervals from 0° to 180° and offset for clarity. The arrows indicate the peak positions of the optical transitions. (b) Integrated areas (arbitrary units) of the Lorentzian fits to the transitions for excitons 1 and 2. The solid lines are fits to the data, as discussed in the text. The data are presented in a polar plot over a 360° range for clarity.
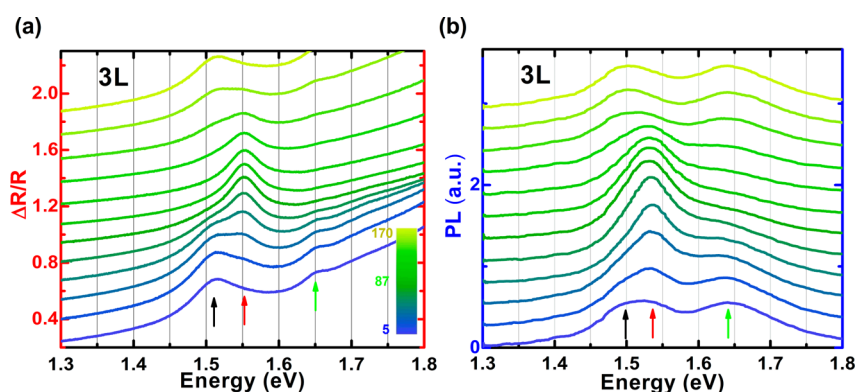

Figure 5. Anisotropic optical response of 3L ReS$_2$. (a) Polarization-resolved reflection contrast spectra measured at 15° intervals from 5° to 170° and offset for clarity. (b) Corresponding photoluminescence spectra, normalized, smoothed, and offset for clarity. The PL is normalized by the maximum intensity in all of the spectra and is smoothed by averaging the data spectrally over a window of ~10 meV. The peaks of the absorption and emission spectra are indicated by black, red, and green arrows.

effects, the 6L and 7L samples were analyzed using the energy derivative of the reflection contrast spectra. The data show blue shifts of these three transitions of 140, 160, 300 meV for excitons 1, 2, and 3, respectively, from the bulk to the monolayer limit.

The blue shifts in the ReS$_2$ transition energies with decreasing layer thickness are much greater than those observed for the *direct* transitions (A exciton) in MoS$_2$,[35] MoSe$_2$,[35] MoTe$_2$,[36] WS$_2$,[37] and WSe$_2$,[35] which are, respectively, approximately 30, 15, 20, 50, 60 meV; the blue shifts are, however, smaller than those seen for the *indirect* transitions in the same material systems. The larger shift observed in ReS$_2$ compared with direct transition in the group VI transition metal dichalcogenides might be influenced by two factors. The first is stronger electronic coupling in the former than is found at the K-point of the Brillouin zone of the latter, where the direct optical transitions occur. This is consistent with the recent DFT calculations,[17] indicating that the direct gap of ReS$_2$ occurs at the Γ-point of the Brillouin zone. A second possible factor would be the influence of a smaller exciton binding energy in ReS$_2$. The reduced screening of the electron–hole interaction and concomitant increase in binding energy for thinner layers would thus provide less compensation for the expected increase in transition energy from quantum confinement in ReS$_2$ than

for the reference case of the group VI transition metal dichalcogenides.[37]

We now examine the role of anisotropy in the optical response of the ReS$_2$ layers by measurement of polarization-resolved spectra. Figures 4 and 5 present such spectra for 1L and 3L samples, respectively. In Figure 4a we see the dependence of the polarized reflection contrast spectra on polarization (or, equivalently, sample) rotation. The data can be described in terms of a variation of the spectral weights of the near-gap excitons with angle, without any change in their position or width. Figure 4b quantifies this effect by the spectral weight of the first two excitons as a function of light polarization. Both transitions show a double-lobed structure. However, the two excitons do not exhibit the same polarization. The exciton orientation is determined by fitting the weight of the relevant exciton in the polarized reflection contrast data to the form $I_0 + I_1 \cos^2(\theta - \theta_{max})$, where I_0 and I_1 are constants, θ is the angle of measurement relative to angle at which b-axis is parallel to the incident electric field, and θ_{max} is the angle at which the weight is maximized. In the monolayer, the absorption from excitons 1 and 2 exhibits a maximum for light polarized, respectively, at ~15 and ~50° from the orientation of the cleaved edge. These measurements have been repeated on other mono- and few-layer ReS$_2$ crystals. For the few-layer samples, similar results (not shown) have been

obtained, but with the polarization of excitons 1 and 2 shifted compared to the monolayer. For the bulk crystal at a temperature of 110 K, a previous study[14] has shown that excitons 1 and 2 are polarized, respectively, at ~17° and ~86° from the b-axis (see Supporting Information (SI) for a graphical representation).

The observed polarization dependence of the optical spectra provides a purely noncontact method of determining the crystallographic orientation of the sample. This is of considerable importance given the strong anisotropy in the transport properties of the material, with the b-axis exhibiting the highest dc conductivity both in bulk[16] and in monolayer samples.[22] We note that the optical anisotropy near the excitonic resonances implies that the absorption of these layers varies strongly as a function of the light polarization. This provides a possible means for near-field control of radiation. (See the SI for a plot of absorption anisotropy of a 1L crystal near the resonance of exciton 1.)

The general behavior for a sample of 3L thickness is similar to that seen for the monolayer. Figure 5a shows reflection contrast spectra of 3L samples, which are quite analogous to the spectra for the 1L case in Figure 4a. For the 3L sample, we have also measured polarization-resolved photoluminescence spectra (Figure 5b). The emission spectra further confirm the strongly anisotropic character of the excitonic transitions. A Stokes shift of ~15 meV between the absorption and the emission peak energies is inferred from fitting the spectra. The existence of two distinct absorption and emission features with different strengths depending on sample orientation and polarization gives rise to variable optical properties. This might explain the different interpretation of interlayer interactions extracted from the PL peak positions for few-layer and bulk ReS_2 in ref 17.

In conclusion, we have characterized the optical properties and anisotropy of single-, few-layer, and bulk ReS_2 crystals. Through photoluminescence and reflectance spectroscopy, we confirm the earlier studies on the indirect nature of the bulk material. The direct excitonic transitions are found to shift significantly with decreasing thickness from the bulk to the monolayer, unlike those of Mo and W dichalcogenides. Furthermore, the excitons exhibit linearly polarized absorption and emission features, which can be correlated to the sample's crystallographic orientation. From the point of view of optical materials, the strong and highly anisotropic response of ReS_2 could be used for the control of optical fields on the nanoscale. ReS_2 thus provides a new building block in the family of atomically thin 2D semiconductors, stable down to monolayer thickness, with strongly anisotropic optical properties.

METHODS

Sample Preparation. Large flakes of ReS_2 were deposited from bulk ReS_2 crystals (>99.998% purity from HQgraphene) by mechanical exfoliation. The substrate was a thick polydimethylsiloxane (PDMS) film (base:curing agent ratios of 10:1). The PDMS substrate has negligible optical absorption over the spectral range of interest.[27] The layer thicknesses of the ultrathin ReS_2 crystals were determined by Raman spectroscopy[22] and optical contrast measurements, as discussed above.

Reflection Contrast and Photoluminescence Measurements. The reflection contrast spectra were obtained with radiation from a tungsten halogen source, in conjunction with a beam splitter and a 50× objective (NA = 0.42). A

monochromator dispersed the reflected light from the sample onto a liquid-nitrogen cooled Si CCD array.

The equation used for extracting the absorption spectra remains valid while the reflection contrast is less than unity, which is the case even for three layers of ReS_2 because of the comparatively weak optical transitions. The peak positions of those optical transitions are less affected than their magnitude as the absorption spectra slightly deviates from the equation used. Therefore, reflection contrast measurements provide an appropriate approach to finding the peak positions of the optical transitions of few-layer ReS_2 without the need for determining the full complex dielectric function.

The photoluminescence (PL) measurements were performed using a commercial micro-Raman instrument (Renishaw In-Via) in a backscattering geometry. Excitation was provided by a linearly polarized laser at a wavelength of 532 nm, which was focused by a 100× objective (NA = 0.85) onto the sample. The emitted photons were analyzed in a spectrometer equipped with a grating with 600 lines/mm. The laser power for the PL measurements was approximately 25 μW for the bulk crystal and 300 μW for the ultrathin films. For polarization-resolved PL measurements, we collected emitted photons with a polarization perpendicular to that of the incident laser radiation.

We note that for nominally *unpolarized* measurements, the optical setup might lead to slightly different weightings of the response, but not to a degree to change any conclusions of this Article.

All experiments were performed at room temperature.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.5b00486.

> Sample preparation, image of the sample in Figure 1, results analogous to Figure 5 for 1L ReS_2, absorption contrast of 1L at a photon energy of 1.61 eV, comparison of absorption and PL peaks for 3L ReS_2 along with Figures S1−S6 (PDF).

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Notes
The authors declare no competing financial interest.

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