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**Pressure-induced structural and electronic transitions,
metallization and enhanced visible-light responsiveness in layered
rhenium disulphide**

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[†] Supplemental Materials available: Detailed sample characterizations (including crystal structure and pressure-dependence of lattice parameters of layered ReS₂, enthalpy curve of ReS₂ as a function of pressure, schematics of electrical resistance measurements in DAC, and electrical resistance results using large volume press).

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ABSTRACT: Triclinic rhenium disulphide (ReS₂) is a promising candidate for post-silicon electronics because of its unique optic-electronic properties. The electrical and optical properties of ReS₂ under high pressure, however, remain unclear. Here we present a joint experimental and theoretical study on the structure, electronic and vibrational properties, and visible-light responses of ReS₂ up to 50 GPa. There is a direct to indirect band gap transition in 1T-ReS₂ under low pressure regime up to 5 GPa. Upon further compression, 1T-ReS₂ undergoes a structural transition to distorted-1T' phase at 7.7 GPa, followed by the isostructural metallization at 38.5 GPa. Both *in situ* Raman spectrum and electronic structure analysis reveal that interlayer sulphur–sulphur interaction is greatly enhanced during compression, leading to the remarkable modifications on the electronic properties observed in our subsequent experimental measurements, such as band gap closure and enhanced photo-responsiveness. This study demonstrates the critical role of pressure in tuning materials properties and the potential usage of layered ReS₂ for pressure-responsive optoelectronic applications.

Keywords: high-pressure, layered ReS₂, phase transition, visible-light response, first principles calculation

I. INTRODUCTION

In recent years, the layered transition-metal dichalcogenides (TMDs) (MX_2 , where M denotes metal atoms Mo, W, Re, etc., and X denotes S, Se and Te), as a new class of quasi two-dimensional (2D) materials beyond graphene, have attracted tremendous interests [1-7]. Atomically thin monolayer TMDs, prepared by mechanical exfoliation or chemical vapor transports, have been found to exhibit a variety of exotic transport properties such as quantum spin Hall effect (QSH) [8], charge density waves (CDW) [9-11] and superconductivity [12-14], thus enabling many potentials applications.

In the crystal structures of TMDs, metal atoms (M) are sandwiched between graphene-like layers of chalcogen atoms (X), forming a layered structure with MX_2 stoichiometry. The metal atoms can either occupy the original prismatic holes between chalcogen layers as H phase, or the octahedral holes as T phase. The most common form in TMDs is the H-phase, whereas T-phases are reported to be metastable. However, ReS_2 is an exception, in which the most stable form under ambient condition is a distorted 1T-phase with triclinic symmetry, due to the pronounced Peierls distortion [15-20]. Unlike in other TMDs, Peierls distortion of the 1T structure of ReS_2 weakens the coupling interaction, which in turn hinders S-Re-S layers from stacking orderly and minimizes the interlayer overlap of wave-functions to open a band gap (~ 1.4 eV) [15] in the bulk ReS_2 . Moreover, it has been proposed that ReS_2 holds a direct band gap in both bulk and monolayer forms, whereas most TMDs undergo a transition from indirect to direct band gap semiconductor when reduced from bulk to monolayer. This robust direct band gap feature makes ReS_2 very promising for practical applications [15, 17, 21, 22].

High-pressure has been proved an effective mean to tune the physical properties of materials *via* modifying the atomic and electronic structures [23-28]. For example, the pressure-response of MoS₂ (the most common one in TMD family) has been widely investigated. Nayak *et al.* reported an electronic transition from a semiconducting to metallic state at ~19 GPa in MoS₂ due to pressure induced lattice distortion [25]. In addition to the bulk form, pressure is also able to control the band structure and optoelectronic properties of monolayered MoS₂. Bandaru *et al.* showed a pressure-induced isostructural hexagonal distortion to a 2H_a-hexagonal *P*6₃/mmc phase in MoS₂ around 26 GPa [28]. Going to higher pressure, Chi *et al.* observed the metallization (60 GPa) [23], and eventually the emergence of superconductivity (90 GPa) in pristine 2H-MoS₂ [14]. Remarkably, the superconductivity transition temperature T_c reached up to 12 K under substantial compression [14]. The similar pressure-induced semiconductor-to-metal transition has also been found in MoSe₂ [24], WS₂ [26, 27], and VS₂ [29].

Despite the growing studies on *MX*₂, the high-pressure behavior of ReS₂ remains largely unexplored until recently [20, 30]. Hou *et al.* reported that ReS₂ undergoes a phase transition at about 10.5 GPa based on x-ray diffraction (XRD) patterns analysis [30]. Unfortunately, the crystal structure of high pressure phase could not be determined due to insufficient quality of XRD data. This puzzling high-pressure phase was further studied in a theoretical work, which revealed that multilayered ReS₂ would undergo a structural transition to another *P*-1 phase (denoted as distorted-1T' hereafter), followed by a sluggish semiconducting to metallic (S–M) transition upon continuous compression [20]. However, the inadequate quality of the experimental diffraction data prevented convincing agreement between experiment and theory.

More interestingly, there have been growing disputes regarding the claimed direct band gap in bulk ReS₂ in previous studies [15-22]. Recent photoluminescence (PL) and reflectance spectrum experiments at ambient conditions indicated that multilayer ReS₂ possesses an indirect optical gap at 1.40 eV [31]. If ReS₂ is indeed the indirect band gap semiconductor, how will its electronic structure respond to pressure? Yan *et al.* made the first step in a recent study, in which they reported an intriguing indirect-indirect band gap transition at 2.7 GPa by both high-pressure PL and *ab initio* calculations [32]. However, systematic study in a wider pressure range and detailed opto-electronic properties characterization upon compression are still lacking. This motivated us to perform a comprehensive study to address these challenges.

In this paper, combining *in situ* synchrotron XRD, Raman scattering, electrical transport study, visible-light-response measurements and *ab initio* calculations, we have systematically investigated crystal structures, metallization, vibrational response and photocurrents of ReS₂ at pressures up to 50 GPa. The new high-pressure ReS₂ phase has been predicted from *ab initio* calculation and further confirmed by the experimental XRD data. Both experiment and calculation suggest that ReS₂ undergoes a distorted-1T to distorted-1T' phase transition at ~7.7 GPa and a further S-M transition at ~38.5 GPa. The photo-responsiveness of ReS₂ polycrystalline samples continuously increases due to the structural modification under high pressure.

□. EXPERIMENTAL AND COMPUTATIONAL DETAILS

A. *In situ* high-pressure characterizations

Powder and single-crystal ReS₂ samples were purchased from Alfa Aesar and 2D Semiconductors, respectively. High-pressure *in situ* powder XRD experiments were carried out by use of a symmetric diamond anvil cell (DAC) with a culet size of 300 □ μm at 16-IDB of the High Pressure Collaborative

Access Team (HPCAT), Advanced Photon Source (APS), Argonne National Laboratory (ANL) using a monochromatic X-ray beam with a wavelength of 0.4066 Å and 5 μm in diameter in size. Powder ReS₂ samples were loaded into a pre-indented rhenium gasket hole of 170 μm in diameter for XRD and Raman spectroscopy experiments, while the pressure was determined using ruby-fluorescence method and neon was used as the pressure-transmitting medium [33]. XRD patterns were collected by a PILATUS area detector and integrated into one-dimensional profile with the Fit2D program [34]. Structure refinements were performed using Pawley method [35]. High-pressure electrical resistance (ER) was measured using a quasi-four-probe resistance measurement system consisting of a Keithley 6221 current source, a 2182A nanovoltmeter and 7001 voltage/current switch system in a DAC and a cubic large-volume press (LVP) [36-38]. Photocurrent measurements of powder and single-crystal samples were performed using an Autolab PGSTAT128N workstation to keep track of the current-time (I-t) data [38]. A 20 W incandescent lamp was chosen as the illumination source (~2 W/cm² on the sample). Dark current at μA level was produced by applying a constant voltage, which varies from 0.002 to 0.3 V at a given pressure point (for example, 0.3 V at 4.7 GPa and 0.002 V at 39.3 GPa, respectively) owing to the changing of ER along the loading pressure [38].

B. First principles calculations

The search for high-pressure structures was carried out with variable-cell structure prediction simulations using the evolutionary algorithm USPEX [39-41]. All structures were locally optimized using the DFT method within the generalized gradient approximation (GGA) combining with VASP package [42]. The all-electron projector augmented wave (PAW) method was adopted with a plane-wave kinetic energy cutoff of 500 eV for all calculations [43]. For the band structure calculations of bulk ReS₂, a set of 16×16×16 *k*-mesh samplings was employed for Brillouin zone integration. The convergence criterion of self-consistent field calculations for ionic relaxations was set for 10⁻⁵ eV for the totally energy. All unit cells and atomic positions were optimized until the atomic forces were less than ~0.01 eV/Å. Pressures on the lattice unit cell for the convergence criterion of relaxation were reduced to values less than 0.02 GPa and the Hellman-Feynman forces on the ions were less than 0.001 eV/Å.

□. RESULTS AND DISCUSSIONS

A. *In situ* synchrotron XRD patterns and structural transition

At ambient condition, ReS₂ adopts a distorted CdCl₂-type layered structure with triclinic symmetry (space group *P*-1) [44, 45]. As shown in Fig. 1a, in each layer sulfur atoms form an octahedral coordination around rhenium atoms. Figure 1b shows the *in situ* high-pressure synchrotron XRD experimental set-up in DAC. By sharing the edges, [ReS₆] octahedra are packed together in the *bc*-plane, forming the ReS₂ monolayer perpendicular to *a*-axis. In the unit cell there is only one S-Re-S sandwich. This stacking mode is known as distorted-1T ReS₂. Due to the Peierls distortion, Re atoms dimerize each other to form the zigzag line of parallelogram-shaped Re₄ clusters (Figure S1 and S2) [46], which gives the composition of Re₄S₈ in the unit cell.

Figure 1d shows the selected XRD patterns of ReS₂ under high-pressure. Upon compression, while all peaks shifted to larger two theta (smaller *d*-spacing), the (200) peak representing the interlayer spacing along the *a*-axis moved faster to smaller *d*-spacing and merged with (1 $\bar{2}$ 0) peak into a single broad feature between 7.7 and 18.3 GPa. The more rapid shift of (200) peak suggests that the *a*-axis is more compressible than the *b* and *c* axes owing to the interlayer decoupling interactions (Figure S3) [46]. There appeared a new peak (marked with red-star) at the left shoulder of the (12 $\bar{2}$) peak at 7.7 GPa, whose intensity increased with increasing pressure during subsequent compression to 42.4 GPa. A phase transition is hence inferred to have occurred at 7.7 GPa or a lower value due to the sluggish kinetics of the phase transformation.

From the XRD profile, the new phase looks similar to the new high-pressure phase

previously reported by Hou *et al* [30]. The new phase, i.e., the distorted-1T' phase, was resolved to have a triclinic structure with the same space group of $P-1$ and 12 atoms in the unit cell in a recent theoretical study (see Fig. 1c) [20]. Indeed, our *ab initio* structure search also yielded the same structure. More importantly, the high-quality synchrotron XRD data with more intensive peaks in the current study allowed us to perform a better comparison with theoretical prediction (see Fig. 1d and Fig. S4) [46]. We therefore conclude that the distorted-1T' phase is the high-pressure phase observed in our experiment. In distorted-1T', all Re atoms sharing the same (x, y) coordinates form different S-Re-S triple layer packing (Fig. 1c). To minimize the interlayer S...S repulsion, the angles between each sandwich of distorted-1T' phase are more contorted than in 1T-ReS₂. According to our calculation, the phase transition between 1T and distorted-1T' is expected to take place at or near 3.1 GPa (Fig. S5) [46], which is in qualitative agreement with the experimental observations.

The crystal structure of distorted-1T' ReS₂ from prediction was then used for further Pawley refinement (see Table S1) [46]. By fitting the P - V data to a third-order Birch-Murnaghan equation of state (BM-EoS) as shown in Fig. 1e [47]:

$$P = \frac{3}{2}B_0 \left[\left(\frac{V}{V_0} \right)^{-\frac{7}{3}} - \left(\frac{V}{V_0} \right)^{-\frac{5}{3}} \right] \left\{ 1 + \frac{3}{4}(B'_0 - 4) \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \right\} \quad (1)$$

where B_0 is the bulk modulus at ambient condition, and B'_0 the pressure derivative of B_0 . We obtained bulk modulus $B_0 = 35.6 \pm 5.2$ GPa with $B'_0 = 10.8 \pm 2.4$ and $V_0 = 219.49 \pm 0.81$ Å³ for distorted-1T phase, and $B_0 = 49 \pm 10$ GPa with $B'_0 = 5.4 \pm 0.7$ and $V_0 = 218.83 \pm 3.65$ Å³ for distorted-1T' phase, respectively. Values of bulk modulus and its pressure derivative for distorted-1T ReS₂ are substantially different from those in previous study [30]. To verify the quality of the BM-EoS fits, we

converted P - V data to the Eulerian strain f and the corresponding normalized pressure F using V_0 's from BM-EoS analyses for each respective phase according to the following formula [48-51]:

$$F = P[3f(1 + 2f)^{5/2}]^{-1} \quad (2)$$

$$f = \frac{1}{2} \left[\left(\frac{V}{V_0} \right)^{-\frac{2}{3}} - 1 \right] \quad (3)$$

The linear relationship between F and f is described as:

$$F = B_0 + [3B_0(B'_0 - 4)f]/2 \quad (4)$$

where B_0 is the bulk modulus at ambient pressure, and B'_0 the pressure derivative. Unlike in simple P - V plot, F - f data show a clear change in slope (Fig. 2a), indicating a change in mechanical performances likely associated with a polymorphic phase transformation [50]. The maximum change in slope is between Eulerian strain values of $\square 0.030 - 0.050$ corresponding to pressure values of 4.7 - 10.6 GPa. Linear regressions based on Equation (4) to two sets of F - f data yield $B_0 = 35.6 \pm 1$ GPa with $B'_0 = 10.7 \pm 0.8$ for the 1T phase and $B_0 = 49.8 \pm 1.1$ GPa with $B'_0 = 5.4 \pm 0.2$ for the 1T' phase, all in good agreement with the result from BM-EoS fitting. It should be noted that the B_0 and B'_0 obtained for the 1T' phase in the present study are for a hypothetical state of the unquenchable 1T' phase. From the linear fit to F - f data between 8.9 to 42.4 GPa (i.e., pure 1T' phase) calculated by using the measured unit-cell volume at 8.9 GPa as reference [51], we obtained a bulk modulus of 90.1 ± 2.2 GPa and a pressure derivative of 5.1 ± 0.3 for 1T' phase at 8.9 GPa (Fig. 2b). The structural changes in both phases upon compression are highly anisotropic, as evidenced by the relationship between the lattice parameters and pressure (Fig. S3) [46]. The a -axis along layering direction is more compressible than b -axis and c -axis

owing to weaker interlayer coupling forces.

B. Raman spectra and evolution of S-S interaction under pressure

The phase transition from 1T to 1T' is also supported by the *in situ* Raman data (Fig. 3a). The Raman spectroscopy revealed a large number (18) of vibrational modes for 1T-ReS₂ due to its low lattice symmetry [18]. Most Raman active modes undergo subtle changes under compression, except the discontinuous changes in A_g -like (438 cm⁻¹) and C_p (377.9 cm⁻¹) at 9.4 GPa (Fig 3a). Figure 3b shows the pressure-induced evolution for the most prominent Raman peaks in bulk ReS₂. The low frequency Raman peaks (153.1, 163.6, 217.2, and 237.2 cm⁻¹) due to Re vibration are less sensitive to hydrostatic pressure when compared to other TMDs owing to decoupled vibration in ReS₂. The pressure dependence of the low vibrational frequencies follows almost linear behavior, which indicates nearly identical Re vibration in both 1T and 1T' phases. However, the slopes of C_p (377.9 cm⁻¹) and A_g -like (438 cm⁻¹) are significantly greater than those of the E_g -like modes. According to Ref 18, A_g -like mode is assigned to the out-of-plane S vibrations located at 438 cm⁻¹ (a surface mode), while C_p mode simply represents the in-plane and out-of-plane coupled mode of Re and S atoms. The distinct features above 250 cm⁻¹ are mainly contributed by intensive S atoms motions, which account for the layer sliding and continuously increasing interlayer S··S interaction [18, 23-27]. Indeed, the enhanced S··S interaction is also evident from the evolution of S-S interlayer distances, which dropped significantly from 4.036 Å at ambient pressure to 2.365 Å at 65 GPa (Fig. 3c and 3f). For reference, the vdW radii for sulfur are typically 1.80 Å, while the covalent radii are 1.05 Å. This monotonic decrease suggests that S-S interaction undergoes a transition from vdW-like to covalent-like bonding. Compared to the S-S

interactions in pyrite FeS₂, in which the S-S covalent bonds are less compressible than Fe-S bonds, the S-S distance in ReS₂ decreases much faster than Re-S bond length with increasing pressure due to the weak inter-layer interaction. After formation of covalent-like bonding of S-S at high pressure, the contraction of S-S distance starts to slow down and the coupled librational and stretching motions of S-S dimer could be split into A_g -like mode and C_p [52, 53]. To further understand the chemical bonding, we also performed the calculations on Electron localization function (ELF) [54]. Clearly shown in Fig. 3 (d-f), the significant ELF accumulation between S-S already appeared at 14.5 GPa, confirming the formation of S-S bonds as well.

C. *In situ* resistance measurements.

To better understand the electronic properties of ReS₂ at high pressure, we performed *in situ* resistance (R) measurements using quasi-four-probe method in DAC and LVP (Fig. S6 and S7) [46]. Figure 4a-4d shows the electrical resistance as a function of pressure and temperature (T). Upon compression, the resistance value dropped dramatically with increasing pressure, at least by four orders of magnitude, to a stable value of less than $\sim 1 \Omega$ at about 45.7 GPa, suggesting a semiconductor to metal transition. *In situ* temperature-dependent resistance measurements (see Fig. 4b-4d) further confirmed the metallic behavior above 38.5 GPa. Bulk ReS₂ displays the classical semiconducting behavior at low pressures as the temperature coefficient of resistance (dR/dT) is negative at 12.3 GPa (Fig. 4b). At 17.6 GPa, temperature-resistance curve reflects a semiconducting behavior at low temperature region and a metallic one above 200 K with a positive dR/dT [20, 23-27]. A full metallization of ReS₂ was realized at 38.5 GPa as a positive dR/dT remained throughout all temperatures. The theoretical calculation predicts the band gap closure of ReS₂ at ~ 40

GPa (Fig. 4e), in excellent agreement with the experimental results.

D. Band structure evolution

It has been claimed that ReS₂ has a robust direct band gap regardless the thickness of materials (from single-layer, a few-layers to bulk forms), making ReS₂ advantageous over other TMDs for device applications [20, 23-27]. However, this was challenged by recent experiments on PL spectra and electrical transport properties that indicated the characteristics of indirect behavior. This controversy was further discussed by several groups recently [55, 56]. It has been found that an appreciable interplane interaction results in an experimentally measured difference of 100–200 meV between the valence band maxima at the Z point (0, 0, 0.5) and the Γ point (0, 0, 0) of the three-dimensional (3D) Brillouin zone [54]. This leads to a direct gap at Z and a close-lying but larger gap at Γ . These studies indicated that the band structure of 1T-ReS₂ might have a strong dispersion in the 3D reciprocal space, though most of the previous calculations only considered the *K*-points path based on the hexagonal MoS₂, and predicted the gap to be direct at Γ point. To gain a complete understanding of pressure effects on 1T-ReS₂, we performed the band structure calculations on 1T-ReS₂ at both 0 and 5 GPa. Figure 5a, b shows that the valence band (VB) and conduction band (CB) maxima are ($k_x, k_y, 0$) and ($k_x, k_y, 0.5$) planes of 1T-ReS₂ at 0 GPa. Clearly, it has an indirect band gap at ($k_x, k_y, 0$), but the global valence band maxima (VBM) and conduction band maxima (CBM) are actually located at (0, 0, 0.5), resulting in a direct band gap of 1.288 eV at GGA level. This is in quantitative agreement with the previous studies [55]. Furthermore, the pressure tends to complicate the band distribution. At 5 GPa, we observed a substantial change of CBM and VBM positions at ($k_x, k_y, 0$) plane (Fig. 5c), while the changes at ($k_x, k_y, 0.5$)

plane (Fig. 5d) seems barely minimal, making 1T-ReS₂ a direct semiconductor with a slightly smaller band gap (1.178 eV). However, the global VBM at 5 GPa shifts from (0, 0, 0.5) to the vicinity of (0, -0.25, 0.25), by lowering the energy of ~70 meV. Our results are different from a recent study by Yan *et al* [32], which studied only a few k -points paths and found 1T-ReS₂ has an indirect band gap at both ambient and high pressure. This example highlights the complex 3D dispersion features in 1T-ReS₂, hence a full sampling in the full Brillouin Zone is necessary.

In order to obtain more insights, we also computed the angular momentum resolved density of states (LDOS) of distorted-1T phase at 0 GPa and distorted-1T' phase at 42 GPa (Fig. 6(a-d)). Under compression, the band dispersions of conduction band and valence band have more crossovers due to the broadening of CBM and VBM. Clearly, main contributions to the VBM and the CBM are from hybridized Re- d and S- p states. The Re d_z^2 orbital's contribution to CBM increases, while the contribution from Re- p orbitals decreases (see Fig. 6b and 6d). Likewise, the contribution from S- p_x and S- p_y to CBM decreases with the increase of pressure, while the contribution from S- p_z increases (see Fig. 6a and 6c). This is similar to what have been found in MoS₂ in the previous study [25].

E. Visible-light responsiveness measurements

Visible-light harvesting ability for solar energy conversion applications is an important consideration for photovoltaic materials [15, 17, 19, 21, 22, 36, 38]. *In-situ* photocurrent measurements of single-crystal and powder semiconducting ReS₂ samples were carried out under high pressure in DAC (Fig. S6) [46]. Both single-crystal and powder ReS₂ samples exhibit typical response to visible-light with on-off

switch throughout all pressures, as shown in Fig. 7a and 7b. Upon the increase of pressure, the photo responsiveness of ReS₂ gradually rises, owing to the continuous decreases in the resistance value and band-gap (Fig. 6c). Therefore, the valence electrons are much easier to be excited by visible-light and overcome the band gap into CB. Subsequently, photocurrent increases greatly because photoelectron carriers start to migrate quickly and form closed-circuit (Fig. 7c). Bulk ReS₂ can still be excited up to 39.3 GPa, indicating that either the sample is semi-metal or the semiconducting samples were present due to incomplete electronic transition. More interestingly, the photocurrent signals in single-crystal ReS₂ disappear at 27.8 GPa, which is much lower than that found in bulk ReS₂, presumably attributed to the anisotropic conductivity of single-crystal ReS₂ due to its low lattice symmetry. The successive modulation of the electronic structure and band gap under visible-light irradiation indicates possible pressure-controlled optoelectronics applications of ReS₂.

□. CONCLUSIONS

In summary, we systematically investigated the structure evolution, electrical transport, vibrational properties and visible-light responsiveness of ReS₂ under high-pressure up to 50 GPa combined with *ab initio* calculations. Both *in situ* XRD and theoretical calculations suggest that ReS₂ undergoes the structural transition at ~7.7 GPa or a lower pressure followed by another semiconductor-metal transition at ~38.5 GPa. Raman spectrum, low temperature resistivity measurements and ELF calculation reveal that semiconductor-metal transition of ReS₂ originates from the overlap of the valence and conduction bands due to sulphur–sulphur interlayer sliding as the interlayer spacing decreases upon compression. Lastly, photocurrent measurements

indicate a substantial enhancement in visible-light responsiveness of the layered ReS₂ under high pressure.

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Figure captions

Figure 1. (Color online) Structure details, synchrotron XRD patterns and pressure dependence of the unit-cell volume of ReS₂. (a) The cross-section illustration of layered distorted-1T ReS₂. (b) Schematic diagram of the high-pressure diamond anvil cell (DAC) set-up. (c) The cross-section illustration of layered distorted-1T' ReS₂. (d) Selected XRD patterns of ReS₂ under high pressure. Red stars marking the new diffraction peak from distorted 1T'. (e) The volume data of both phases of ReS₂ as function of pressure fitted by 3rd order Birch-Murnaghan equation of state.

Figure 2. (Color online) Normalized pressure F vs Eulerian strain f . (a) F and f derived with reference volumes at ambient pressure (V_0) from BM-EoS for both phases. (b) F and f calculated using the reference pressure of 8.9 GPa for 1T' phase. Solid lines in both plots are linear fits using Equation (4).

Figure 3. (Color online) Raman spectra results of ReS₂ under high-pressure. (a) At room temperature and various pressures up to 50 GPa. The prominent modes E_g , E_g -like, C_p and A_g -like were indicated by arrows. (b) The evolution of the most prominent Raman peaks of ReS₂ as a function of pressure. (c) The calculated bond lengths in 1T-phase and 1T'-phase ReS₂ as a function of pressure. Insert shows the shortest S-S bond between layers. (d-f) The key out-of-plane phonon mode A_g -like is shown in ELF profiles.

Figure 4. (Color online) Electric property measurements and the evolution of band gaps of ReS₂ under high-pressure. (a) Electrical resistance of ReS₂ as a function of pressure at room temperature. (b-d) The temperature dependence of the resistance of ReS₂ at 12.3, 17.6 and 38.5 GPa, respectively. (e) The calculated pressure-dependent band gap of layered ReS₂. The first two data points calculated from distorted 1T phase, others from distorted 1T' phase. The band gap closure is observed at 40 GPa.

The band gap dependence on pressure was fitted using a quadratic function, $E_g = E_0 + aP + bP^2$, where $a = -51 \text{ meV GPa}^{-1}$ and $b = 0.47 \text{ meV GPa}^{-2}$.

Figure 5. (Color online) The calculated valence band and conduction band for various models of 1T-ReS₂. (a) ($k_x, k_y, 0$) at 0 GPa; (b) ($k_x, k_y, 0.5$) at 0 GPa; (c) ($k_x, k_y, 0$) at 5 GPa; (d) ($k_x, k_y, 0.5$) at 5 GPa.

Figure 6. (Color online) The calculated density of states for (a, b) distorted-1T-ReS₂ at 0 GPa; (c, d) distorted-1T'-ReS₂ at 65 GPa

Figure 7. (Color online) Photocurrent of (a) bulk ReS₂ sample and (b) single-crystal ReS₂ sample as a function of pressure. The sign of “on” and “off” represent visible-light source switch on and switch off, respectively. (c) Photocurrent—pressure dependence of bulk and single-crystal ReS₂ samples.

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