Sulfur vacancy activated field effect transistors based on ReS$_2$ nanosheets†

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Rhenium disulphide (ReS$_2$) is a recently discovered new member of the transition metal dichalcogenides. Most impressively, it exhibits a direct bandgap from bulk to monolayer. However, the growth of ReS$_2$ nanosheets (NSs) still remains a challenge and in turn their applications are unexplored. In this study, we successfully synthesized high-quality ReS$_2$ NSs via chemical vapor deposition. A high-performance field effect transistor of ReS$_2$ NSs with an on/off ratio of $\sim 10^5$ was demonstrated. Through both electrical transport measurements at varying temperatures (80 K–360 K) and first-principles calculations, we find sulfur vacancies, which exist intrinsically in ReS$_2$ NSs and significantly affect the performance of the ReS$_2$ FET device. Furthermore, we demonstrated that sulfur vacancies can efficiently adsorb and recognize oxidizing (O$_2$) and reducing (NH$_3$) gases, which electronically interact with ReS$_2$ only at defect sites. Our findings provide experimental groundwork for the synthesis of new transition metal dichalcogenides, supply guidelines for understanding the physical nature of ReS$_2$ FETs, and offer a new route toward tailoring their electrical properties by defect engineering in the future.

Introduction

Graphene has shown many fascinating properties such as high carrier mobility, outstanding mechanical properties, excellent thermal conductivity, and surprising molecular barrier properties. However, the high leakage current, caused by its zero bandgap, limits its wide applications in electronics and optoelectronics. In contrast, as another 2D material, transition metal dichalcogenides (TMDs) possess sizable bandgaps of around 1–2 eV, which make them highly promising building blocks for high-performance electronic and optoelectronic applications. One of the prominent properties of TMDs is that they undergo a crossover from indirect bandgap in the bulk to direct bandgap in a monolayer, and as a result monolayer TMDs absorb and emit light efficiently. Furthermore, layered TMDs display high electron mobility, possess a relatively large spin–orbit interaction and possess valley polarization, thus opening up new prospects for electronic, spintronic and valleytron devices. As a representative, MoS$_2$ FETs have shown relatively high channel mobility of 200–500 cm$^2$ V$^{-1}$ s$^{-1}$ and high on/off ratio of $\sim 10^{11}$. Single layer and few-layer TMDs structure and heterostructures have been studied recently. The heterostructure based on monolayer MoS$_2$/WSe$_2$ realizes a p–n junction at the ultimate thick limit and constitutes the ultimate functional unit for nanoscale electronic and optoelectronic devices.

Motivated by the achievements in MoS$_2$, many other 2D materials, such as WS$_2$, WSe$_2$, GaS, Bi$_2$Se$_3$, and SnS$_2$, have been studied extensively. Rhenium disulphide (ReS$_2$) is another important member of TMDs family. Moreover, from bulk to monolayer, ReS$_2$ remains a direct bandgap semiconductor, which may enable it to be a promising candidate for building atomically layered optical and photovoltaic devices. To date, monolayer and few-layer ReS$_2$ have been mainly synthesized via micromechanical exfoliation. However, this method fails to realize large-scale and uniform samples with high yield and controllability. An effective synthesis method is highly desired, and chemical vapor deposition (CVD) has proven to be a successful method to synthesize graphene and TMDs materials such as MoS$_2$ and WSe$_2$. The great challenge in synthesizing large size and high quality ReS$_2$ is most likely due to its complicated crystal structure. Fig. 1a and b show the crystal structure of ReS$_2$ with triclinic symmetry, which is unlike most hexagonal TMDs.

It is noteworthy that point defects and grain boundaries are unavoidable when layered crystals are synthesized. These structural defects in layered materials play a critical role on

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driving force comes from Peierls distortion, which results in a reduction of symmetry from \( \text{P}_{6}_{3}/\text{mmc} \) of hexagonal TMDs to \( \text{P}_{1} \).\textsuperscript{16,24} To synthesize atomic layered ReS\textsubscript{2}, sulfur powder was ground as the chalcogen precursor, while rhenium oxide powder was used as the Re precursor. Fig. S1a (ESI) schematically illustrates horizontal two-zone tube furnace prepared by us, which was used for synthesizing thin ReS\textsubscript{2} layers. ReO\textsubscript{3} powder (99.9% Alfa Aesar) was placed in a quartz boat and SiO\textsubscript{2}/Si substrate was faced downward and mounted on the top of the boat. A separate quartz boat with S powder was placed in the front zone. During the synthesis process, the temperature of the back zone was increased to \( \sim 500 \) °C in an argon environment. The relatively mild reaction conditions enable the high-density deposition of ReS\textsubscript{2} NSs on a variety of substrates, including rigid SiO\textsubscript{2}/Si and flexible carbon fibers, as displayed in Fig. S1b and c. More details of the experiments are shown in the experimental section in the ESL.\textsuperscript{†} The corresponding X-ray energy dispersive spectroscopy characterization confirms that the atomic percent ratio of Re and S is exactly 1:2. Typically, the thicknesses of ReS\textsubscript{2} NSs are found to be in the range of 4–15 nm by atomic force microscopic (AFM) measurements (Fig. S2†). Fig. 1c and d present cross-sectional view and AFM image of an ReS\textsubscript{2} NSs device with the thickness of \( \sim 4.8 \) nm, respectively.

A Raman spectrum of ReS\textsubscript{2} NSs excited by a 532 nm laser in the backscattering geometry is shown in Fig. 2a. Due to the reduced crystal symmetry, ReS\textsubscript{2} manifests a more complex Raman spectrum than conventional TMDs with higher crystal symmetries. The Raman spectrum for ReS\textsubscript{2} NSs includes two very prominent modes: 160 and 210 cm\textsuperscript{-1}, which are attributed to the in-plane and mostly out-of-plane modes and are consist-

**Results and discussion**

ReS\textsubscript{2} with triclinic crystal symmetry can be considered as a distortion of the metal ions away from their ideal sites. The mechanical, thermal, electrical and optical properties. For example, the high mobility of \( >80 \text{cm}^{2} \text{V}^{-1} \text{s}^{-1} \) for monolayer MoS\textsubscript{2} FET was achieved by developing a low-temperature thiol chemistry route to repair the sulfur vacancies.\textsuperscript{19} By suppressing thermally activated Gallium vacancies, multilayer GaTe FET with an on/off ratio of \( \sim 10^5 \) was obtained.\textsuperscript{20} On the other hand, the existing point defects may break the intrinsic surface states, which are free of dangling bonds, to make TMDs adsorb gases effectively.\textsuperscript{21–23} This not only can be applied to gas detection and recognition, but also facilitates the modulation of the electrical property of TMDs by charge doping. Therefore, understanding the defect physics in TMDs is crucial to explore various applications and design high performance devices.

Herein, we design the controlled growth of large-scale ReS\textsubscript{2} NSs via the CVD method. All characterizations clearly illustrate that the as-synthesized ReS\textsubscript{2} NSs possess high crystal quality, uniform surface and large-scale crystals with high yield and controllability. The FET based on ReS\textsubscript{2} NSs, with an on/off ratio of \( \sim 10^5 \), is demonstrated successfully. Combining electrical transport measurements at varying temperatures (80 K – 360 K) with first-principles calculations, we find that sulfur vacancies unintentionally exist in the synthesized ReS\textsubscript{2} NSs and significantly affect the performance of devices. Furthermore, the electrical properties of the ReS\textsubscript{2} NSs are measured in an atmosphere with oxidizing gas (O\textsubscript{2}) and reducing gas (NH\textsubscript{3}), and we find that sulfur vacancies can not only efficiently adsorb and recognize both oxidizing gases and reducing gases, but also modulate the electrical property of ReS\textsubscript{2} NSs. Our findings are of scientific importance to understand the physics of intrinsic ReS\textsubscript{2} transistors and open up new exciting opportunities for tailoring their electrical properties by defect engineering in the future.
ent with previous ReS₂ Raman results. The complex Raman peaks result from the low crystal symmetry and fundamental Raman modes coupled to each other and to acoustic phonons. In addition, the resistance to oxidation, which indicates the stability of ReS₂ materials, is suitably used for photoelectronic applications and laser thinning for manufacturing single layers. X-ray photoemission spectroscopy (XPS) was used to measure the binding energies of Re and S in the ReS₂ NSs, as shown in Fig. 2b. The two peaks at 42.7 and 45.1 eV correspond to the Re 4f7/2 and Re 4f5/2 binding energies, and the peaks at 162.8 and 164.1 eV are attributed to the S 2p₁/₂ and S 2p₃/₂ states, respectively. In addition, more accurate compositional analyses from XPS analysis indicate that the ReS₂ NSs contain ~33 at% Re and ~67 at% S. Fig. 2c shows the TEM images of a typical thin ReS₂ NS deposited directly on a TEM carbon membrane. The lattice fringe with the distance of 0.284 nm is obtained in Fig. 2d, which corresponds to the (−201) plane of triclinic ReS₂. The corresponding selected area electron diffraction (SAED) pattern shown in the inset of Fig. 2d shows that ReS₂ NS is highly crystalline. All the characteristics mentioned above clearly illustrate that the ReS₂ NSs, which were prepared by CVD synthesis, possess oxidation resistance, high crystal quality, uniform surface, large-scale crystals and great application prospects for nanoscale electronic and optoelectronic devices.

To evaluate the quality of the synthesized ReS₂ NSs, a backgate multilayer ReS₂ FET was fabricated on a 300 nm-thick p-doped silicon substrate. Electrical contacts were made using electron beam lithography followed by thermal deposition of Cr/Au (8 nm/60 nm) electrodes. The device was annealed at 300 °C for 3 hours to remove the resist residue and decrease contact resistance. We first measured the electrical properties of ReS₂ NSs in ambient conditions. The linearity of I–V curves indicates the ohmic contacts between ReS₂ NSs and Cr/Au electrodes, as shown in Fig. S3a. Then, we characterized our ReS₂ NS FET by applying a drain source bias V_ds (3 V) to the pair of electrodes and backgate voltage V_bg (−50 V–50 V) to the p-doped silicon substrate. Fig. 3a shows the typical behavior of ReS₂ FET devices with n-type channels and an on/off ratio of ~10⁶. The AFM image presented in Fig. 1d indicates that the ReS₂ NS has a uniform thickness of ~4 nm, as well as the channel length and width of approximately 1.9 and 0.9 μm, respectively. From the data in Fig. 3a, we extract the electron field-effect mobility of ~1.5 cm² V⁻¹ s⁻¹ using the standard method: μ = Lgs/W(dIdV/dVgs), which is comparable to ~0.1–10 cm² V⁻¹ s⁻¹ for the single-layered MoS₂ FET exfoliated onto SiO₂. In addition, compared with tens of nanometers high-k dielectrics (such as HfO₂, ZrO₂), the thicker and low-k dielectric (SiO₂) usually results in the loss of electrostatic control by the gate and thus relatively poor SS. The output characteristics of ReS₂ FET in ambient conditions did not tend to saturate when the source drain voltage was scanned from 0 to 0.5 V (Fig. S3b).

Generally, the electrical properties of TMDs are strongly influenced by environmental conditions, which include temperature and vacuum. Therefore, the temperature dependence of electrical measurements using theoretical simulation were conducted first. We measured the transfer characteristics of ReS₂ FET from 80 K to 360 K, as shown in Fig. 3b. With the increase in temperature, V_th moved to the negative direction, which indicates that more electrons are generated. For a typical semiconductor, the thermally excited carrier concentration decreases at low temperatures. Then, we extracted the 2D charge concentration using the parallel-plate capacitor model, with

$$n_{2D} = C_{ox} \Delta V_{bg}/\varepsilon$$

where $C_{ox} = \varepsilon_{r} \varepsilon_0/d_{ox}$, $\varepsilon_0 = 8.85 \times 10^{-12}$ F m⁻¹, $\varepsilon_r = 3.9$, $d_{ox} = 300$ nm, $\varepsilon = 1.6 \times 10^{-10}$ C and $\Delta V_{bg} = V_{bg} - V_{bg,th}$. The $V_{bg,th}$ is estimated from the transfer curve in the back-gate voltage, $V_{bg}$ range of 45–50 V. The relationship between $n_{2D}$ and temperature is plotted in Fig. 3c. In the high-temperature regime (180 K < T < 360 K), the electron concentration increases sharply, while in the low-temperature regime (80 K < T < 180 K), it changes very little. The relationship between resistance and temperature is also shown in the inset of Fig. 3c. Here, the activated behavior can be well fitted by the Arrhenius equation:

$$R = R_0 e^{E_a/k_B T}.$$  

We obtained an extracted activation energy of $E_a = 175$ meV, which can be explained by the presence of impurity energy levels close to the conduction band. A similar activation energy of ~167 meV is also obtained for another ReS₂ FET device with a thickness of 15 nm, which is presented in Fig. S6. Subsequently, we discuss the possibilities of the observed electron doping. One possibility is the impurity atoms inside the crystal. During the process of the CVD synthesis of ReS₂, the tube is pumped and flushed with Ar gas to remove impurity materials, and ReO₃ (99.9%) and S powder.
(99.5%) precursor have high purity. Therefore, we exclude this possibility. Another possibility is formative point defects in the synthesis process. To illuminate this possibility persuasively, first-principle total energy and electronic structure calculations were performed in the framework of the density functional theory (see Methods). The calculated defects, including Re vacancies, S vacancies and anti-sites, are displayed in Fig. 3d. Because of inversion symmetry in the ReS2 structure, $S_1$ ($S_3$) and $S_6$ ($S_8$), as shown in Fig. 3d, are equivalent. Thus, lines $S_1$ ($S_3$) overlaps line $S_6$ ($S_8$), as presented in Fig. 3e. In addition, the formation energy of defect is possibly thickness dependent, especially when the thickness is only a few atomic layers. As the thickness would increase, the influence of the sample surface on the inside defect states would be gradually weakened considerably, and thus the formation energy on the inside should converge with that in the bulk system. Fig. 3e shows that the formation energy of the $S_4$ vacancies is lower than that of the other defects, which indicates that S vacancies exist most possibly in our CVD synthesized samples. Based on the abovementioned experiments and discussions, the thermal activated n-type defects above 180 K in Fig. 3c largely correspond to the S vacancies. The theoretical simulations are in agreement with the experimental results, which show that S vacancies exist in the synthesized ReS2 NSs intrinsically and they significantly affect the performance of devices.

To further study the impact of S vacancies on the electrical property of ReS2 NS in different environmental conditions, the electrical measurements were carried out in vacuum, oxidizing gas (O2) and reducing gas (NH3) atmospheres. The device was held for 2 hours in vacuum ($6 \times 10^{-5}$ torr) to detach surface adsorbates. A relatively large increase of the drain currents in Fig. 3a suggests that the formation energy of the $S_4$ vacancies is lower than that of the other defects, which indicates that S vacancies exist most possibly in our CVD synthesized samples. Based on the abovementioned experiments and discussions, the thermal activated n-type defects above 180 K in Fig. 3c largely correspond to the S vacancies. The theoretical simulations are in agreement with the experimental results, which show that S vacancies exist in the synthesized ReS2 NSs intrinsically and they significantly affect the performance of devices.

Fig. 4 (a) Transfer curves of ReS2 FET in oxidizing gas (O2) and reducing gas (NH3) atmosphere. (b) Output curves of ReS2 FET. Inset: $I_{ds}$ vs. $V_{ds}$ with the time of O2 injection fitted by the Langmuir isotherm. (c) O2 molecule adsorbed on the ReS2 surface and just above the vacancy site: (d) NH3 molecule adsorbed on the ReS2 surface and just above the vacancy. The isosurface value is $2.0 \times 10^{-3}$ e Å$^{-3}$ for the O2 adsorption and $2.0 \times 10^{-3}$ e Å$^{-3}$ for the NH3 adsorption. Yellow and blue distributions correspond to charge accumulation and depletion, respectively.

For O2 molecule, a prominent decrease in $I_{ds}$ occurs, which indicates that O2 molecule serves as a charge acceptor. The experimental results manifest that ReS2 NSs can efficiently recognize oxidizing gases and reducing gases. Moreover, the electrical property of ReS2 NSs can be modulated by charge doping, which is a vital stepping-stone in the process of integrating TMDs into future electronic devices. The current of O2 adsorption versus time is fitted to the Langmuir isotherm in the inset of Fig. 4b via

$$I(t) = I_{initial} + \varphi/(1 + \varphi)(1 - e^{-t/\tau})$$

where $I_{initial}$ is the initial current, $\varphi$ is a dimensionless parameter characterizing surface coverage, and $\tau$ is the adsorption time constant. The adsorption time $\tau$ is determined to be $\sim 15$ min, which is comparable to other physisorption FET gas sensors.22

To understand the charge transfer processes for the O2 and NH3 molecules adsorbed on the monolayer ReS2 NSs near the vacancy sites, we performed the first-principles calculations of these systems based on the density functional theory (DFT)32,33 within generalized-gradient approximations (GGA)34 as implemented in the Vienna ab initio simulation package (VASP).35-37 In the first-principles calculations, the electron and core interaction are included based on the frozen-core projected-augmented wave (PAW)38 approach. A $3 \times 3$ supercell containing a single gas molecule adsorption on the monolayer ReS2 surface was constructed as the computational system. Out of the monolayer plane, a 20 Å vacuum spacing was added to prevent the interaction with its image. In the simulation of adsorption process, all the atoms were allowed to relax until the quantum mechanical forces acting on them were less than 0.02 eV Å$^{-1}$. To analyze the charge transfer process, the charge density difference is a very useful quantity; it is defined as $\rho(A, \alpha)$, $\rho(\text{ReS}_2, \alpha)$ and $\rho(A)$, which are the charge densities of the whole absorption system containing an adsorbate $A$ (O2 or NH3 molecule), a defect $\alpha$ and monolayer ReS2, and monolayer ReS2 containing a defect $\alpha$ and a molecule alone, respectively. The calculated adsorption energy for O2 molecule adsorption on the ReS2 surface is $-0.037$ eV, which indicates a weak interaction between the O2 molecules and ReS2 monolayer and it is physisorption. Because the electronegativity of O atom is larger than that of Re and S atoms, the O2 molecule is expected...
to behave as the charge accumulator in the system of O$_2$ adsorption on the ReS$_2$ surface. In terms of Bader analysis, it is indeed found that the O$_2$ molecule approximately receives 0.01 electrons from Re$_2$S$_2$. Therefore, it can also be expected that if O$_2$ molecule is placed near n-type S vacancies, electron carrier density of the n-type doping will probably be further reduced by the transfer of electrons around the O$_2$ molecule because the O$_2$ molecule functions as an electron accumulator in the interaction between the O$_2$ molecules and defects. Fig. 4c shows the charge density difference of the whole system for the adsorption of O$_2$ molecules on the surface of monolayer ReS$_2$, which possesses an S vacancy defect. It is apparent that the electrons are accumulated around the O$_2$ molecule and are depleted near the defect. In this case, the Bader analysis predicts that about 0.834 electrons are transferred from the S vacancy to the O$_2$ molecule, which is remarkably larger than that in the case of O$_2$ adsorbed on pure Re$_2$S$_2$ without any defect. Thus, with respect to the interaction between the O$_2$ molecule and S vacancy in Re$_2$S$_2$, the interaction between the O$_2$ molecule and pure Re$_2$S$_2$ is negligible. O$_2$ molecules electronically interact with Re$_2$S$_2$ only at the defect sites. In the case of the adsorption of NH$_3$ molecule, the calculated adsorption energy between NH$_3$ molecule and monolayer Re$_2$S$_2$ is $-0.031$ eV, which is also attributed to physiosorption, similar to the O$_2$ adsorption on the Re$_2$S$_2$ surface. However, we predict that Re$_2$S$_2$ approximately receives 0.011 electrons from the NH$_3$ molecule, which indicates that the NH$_3$ molecule serves as a charge donor and enhances the electron carrier density of n-type Re$_2$S$_2$. Fig. 4d shows that in the case of Re$_2$S$_2$ possessing an S vacancy, the electrons are depleted rather than accumulated around the NH$_3$ molecule. The first-principles DFT calculated adsorption energy of the adsorption of NH$_3$ molecule on Re$_2$S$_2$ with an S vacancy is $-0.046$ eV, which is larger than that observed by the NH$_3$ molecule on pure Re$_2$S$_2$. This implies that having S vacancy defects in the Re$_2$S$_2$ monolayer, the NH$_3$ molecule adsorbate could significantly enhance the n-type doping. Therefore, by combining electrical measurements in O$_2$ or NH$_3$ gas atmosphere and theoretical simulations, we demonstrate that S vacancies in Re$_2$S$_2$ can recognize oxidizing gas (O$_2$) and reducing gas (NH$_3$) with large electronic interactions. Such unintended defects are expected to play a significant role in device performance.

Conclusions

In summary, we have synthesized large-scale Re$_2$S$_2$ NSs on a variety of substrates, including rigid SiO$_2$/Si and flexible carbon fibers, via CVD. These NSs were synthesized at 500 °C using ReO$_3$ and S powder as precursors. By combining SEM, TEM and AFM measurements, the Re$_2$S$_2$ NSs synthesized by CVD are shown to possess high crystal quality, uniform surface and large-scale crystals. The more accurate compositional analyses from XPS measurements manifest that the Re$_2$S$_2$ NSs contain $\sim$33 at% Re and $\sim$67 at% S. The high performance FET of Re$_2$S$_2$ NSs with an on/off ratio of $\sim$10$^5$ was demonstrated. Using electrical transport measurements at varying temperatures [80 K–360 K] and first-principles calculations, we found that sulfur vacancies intrinsically exist in the Re$_2$S$_2$ NSs. Furthermore, the electrical properties of the Re$_2$S$_2$ FET were determined under vacuum, O$_2$ and NH$_3$ atmospheres. We demonstrate that S vacancies can efficiently adsorb and recognize oxidizing gases and reducing gases. Together with calculation simulations, we find that O$_2$ and NH$_3$ molecules electronically interact with Re$_2$S$_2$ only at defect sites. Our research study may provide a new scope for the synthesis of new TMDs, which are important to understand the physical nature of FETs, and will open up new exciting opportunities for enhancing and expanding their applications in electronics and photoelectronics in future.

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Notes and references


