Layer-dependent electrical and optoelectronic responses of ReSe$_2$ nanosheet transistors†

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The ability to control the appropriate layer thickness of transition metal dichalcogenides (TMDs) affords the opportunity to engineer many properties for a variety of applications in possible technological fields. Here we demonstrate that bandgap and mobility of ReSe$_2$ nanosheet, a new member of the TMDs, increase when the layer number decreases, thus influencing the performances of ReSe$_2$ transistors with different layers. A single-layer ReSe$_2$ transistor shows much higher device mobility of 9.78 cm$^2$ V$^{-1}$ s$^{-1}$ than few-layer transistors (0.10 cm$^2$ V$^{-1}$ s$^{-1}$). Moreover, a single-layer device shows high sensitivity to red light (633 nm) and has a light-improved mobility of 14.1 cm$^2$ V$^{-1}$ s$^{-1}$. Molecular physisorption is used as “gating” to modulate the carrier density of our single-layer transistors, resulting in a high photoresponsivity (R$_p$) of 95 A W$^{-1}$ and external quantum efficiency (EQE) of 18 645% in O$_2$ environment. This work highlights the fact that the properties of ReSe$_2$ can be tuned in terms of the number of layers and gas molecule gating, and single-layer ReSe$_2$ with appropriate bandgap is a promising material for future functional device applications.

1. Introduction

Many transition metal dichalcogenides (TMDs) are two-dimensional (2D) layered materials, which possess a wide range of excellent physical and chemical properties, allowing them to have various potential applications.$^{1–6}$ Some remarkable changes in material properties of TMDs have been discovered as the layer number varies.$^{7,8}$ When the thickness of 2D layered materials is reduced down to a single layer or a few layers, due to quantum effects, electronic properties of these layered materials will start to change.$^9$ Therefore, control of appropriate thickness is particularly important and useful to tune the properties of 2D layered materials. For example, the breakdown voltage of h-BN sheets is affected by the layer number.$^{9,10}$ Lee et al.$^{11}$ showed through conductive atomic force microscopy (C-AFM) that, for h-BN sheets, low-bias direct tunneling could be observed in mono-, bi-, and tri-layer h-BN samples, whereas thicker samples were insulating at low bias. The tunneling current of thicker samples showed sharp increases at breakdown voltages that increased with thickness. Another example is the bandgap change of MoS$_2$ with thickness by theoretical prediction.$^{12,13}$ Lee et al.$^{14}$ fabricated MoS$_2$ phototransistors with different layer thickness. They found that single- and double-layer samples were useful for green light detection, whereas triple-layer MoS$_2$ exhibited red light detection capability, which could be attributed to different energy band-gaps of MoS$_2$ modulated by the number of layers. Field-effect transistors (FETs) based on single- and multilayer MoS$_2$ sheets have also been fabricated for sensing NO gas.$^{15}$ For single-layer MoS$_2$ FET, a rapid and dramatic response to NO was observed, but the current was found to be unstable. On the contrary, two-, three-, and four-layer MoS$_2$ FET devices showed both stable and sensitive responses with detection limits of around 0.8 ppm NO. Moreover, in few-layer MoSe$_2$, indirect and direct band-gaps are nearly degenerate, so temperature rise can effectively drive the crossover from the indirect band-gap in the bulk limit to the direct band-gap in the quantum (2D) limit, resulting in huge photoluminescence intensity enhancement as seen from a few layers to a single layer.$^{16}$

ReSe$_2$ is a recently discovered new member of the layered transition metal dichalcogenides (LTMDs), possessing extremely anisotropic electrical, optical and mechanical properties.$^{7,17}$ Fig. 1a shows the structure of ReSe$_2$ nanosheet in the
distorted 1-T phase, which is unlike most hexagonal LTMDs. Density functional theory (DFT) calculations show that the undistorted 1-T phase of ReSe$_2$ is unstable and has higher total energy (−17.395 eV per molecule) than the distorted 1T-ReSe$_2$ phase (−18.473 eV per molecule), proving the stability of distorted 1T-ReSe$_2$ phase (ESI, Fig. S1†). ReSe$_2$ crystals with triclinic symmetry are optically biaxial with a clustering of “diamond chains” composed of Re ions forming along the b-axis. However other hexagonal LTMDs (such as 2H-MoS$_2$ and MoSe$_2$) are optically uniaxial and the optical axis in these LTMDs is perpendicular to the van der Waals plane. The structural distortion of 1T-ReSe$_2$ makes it exhibit anisotropic responses in many properties, with the expectation of linearly polarized light perpendicular to the basal plane. DFT calculations find that the binding energy of bilayer ReSe$_2$ is 0.109 eV per molecule, similar to that of bilayer MoS$_2$ (0.112 eV per molecule), but lower than that of four-layer ReSe$_2$ (0.165 eV per molecule), indicating the existence of relatively long-range interlayer interactions.

Here we report that the band-gap and mobility of ReSe$_2$ can be modulated by the layer thickness in ReSe$_2$ nanosheet transistors. The related electrical properties are enhanced dramatically from a few layers to a single layer, similar to that reported for MoS$_2$ phototransistors with thickness-modulated optical energy gap. An increase of layer thickness causes a reduction of band-gap energy and the loss of electric properties of thick ReSe$_2$. The properties of the single-layer transistors can be further improved by light assistance, resulting in a higher light-induced mobility of 14.1 cm$^2$ V$^{-1}$ s$^{-1}$ under red light illumination, which is ~100-fold higher than that of the first MoS$_2$ single-layer device. With the aid of “O$_2$ molecular gating”, a single-layer ReSe$_2$ transistor also exhibits a fast and high photoresponsivity reaching 95 A W$^{-1}$ with external quantum efficiency (EQE) rising to ~18 645%, which is almost 30 000-fold higher than that of the first graphene photodetector.

2. Results and discussion

Mono- and few-layer (four-layer as shown in ESI, S2†) ReSe$_2$ nanosheets were mechanically exfoliated from bulk crystals onto thermally oxidized (300 nm thick SiO$_2$) Si substrates. The exfoliation process is more difficult than that for other LTMDs, due to the increased interaction between layers with layer numbers. ReSe$_2$ displays complex Raman spectra due to the reduced crystal symmetry, as shown in ESI, Fig. S3.† SEM image of single-layer ReSe$_2$ is shown in Fig. 1c. The ReSe$_2$ nanosheets were then vacuum-annealed to remove remaining residue, which could influence some physical properties of the ReSe$_2$ sheets. Electrical contacts were fabricated using electron-beam lithography followed by electron-beam evaporation of 5 nm thick Cr and 50 nm thick gold (Fig. 1d). After that, the devices were wire-bonded; a schematic diagram of the resulting structure of FET based on single-layer ReSe$_2$ is shown in Fig. 1b. The AFM image of the device in Fig. 1e shows that the ReSe$_2$ nanosheet is a monolayer with a thickness of 0.66 nm. The width (W) and length (L) of the channel in the device are both ~2 μm.

The characterization of the FETs was performed using a semiconductor parameter analyzer and shielded probe station. We first measured the linear output characteristics (gate-dependent drain-source current ($I_{ds}$) versus voltage ($V_{ds}$) curves) of single-layer FETs by applying different back-gate voltages $V_{bg}$ (−40 V → 40 V) to the silicon substrate. The source–drain contacts of our FETs are almost Ohmic with respect to gold electrodes. With increasing back-gate voltage ($V_{bg}$: −40 V → 40 V), the conductance of the single-layer ReSe$_2$ decreases, revealing a p-type conductivity of the FETs (Fig. 2a). For high negative $V_{bg}$ of −40 V, no saturation of $I_{ds}$ is obtained, which indicates high-performance operation of our FETs. To determine the efficiency of the gating behavior, the transfer characteristic curve ($I_{ds}$–$V_{bg}$) under a fixed $V_{ds}$ of −1 V is shown in Fig. 2b. From the data presented in Fig. 2b, we calculate the field effect mobility of single-layer ReSe$_2$ using the equation $\mu = \frac{[dI_{ds}/dV_{bg}] 	imes [L/(WC_1V_{ds})]}{[C_i\times \varepsilon_0 fr/d]}$, where $C_i = 1.15 \times 10^{-4}$ F m$^{-2}$ is the capacitance per unit area between the conducting channel and the back gate ($C_i = \varepsilon_0 fr/d$); the relative dielectric constant $\varepsilon_r$ of insulating layer SiO$_2$ is 3.9 with 300 nm thickness, $d$). The calculated mobility of the single-layer ReSe$_2$ is ca. 9.78 cm$^2$ V$^{-1}$ s$^{-1}$, similar to that of other back-gated FETs without dielectric, but lower than that of top-gate FETs with deposited high-k gate dielectric. This is because, for the Ohmic contact, deposition of a high-k gate dielectric can improve the mobility of our single-layer FETs.

Light can also play a role as an additional terminal to tune the characteristics of FETs in comparison to the conventional three-terminal devices (source, drain, and gate electrodes). For example, Lee et al. fabricated few-layer MoS$_2$-based phototransistors and explored their photo-detection capabilities for different thicknesses. Yin et al. fabricated single-layer MoS$_2$ phototransistors and investigated the light-induced electric properties of the devices. Therefore, we compare the characteristics of FETs measured in the dark to those measured under
Fig. 2 Characterization of transistors based on ReSe$_2$ nanosheets. (a) Output characteristics of single-layer ReSe$_2$ in the dark recorded for different back-gate voltages $V_{bg}$ (–40 to 40 V). The inset curves are the linear region of the current at small bias voltages. (b) Room-temperature transfer characteristics measured in the dark for the single-layer transistors with –1 V bias drain–source voltage $V_{ds}$ on a linear scale (left-hand axis) and on a log scale (right-hand axis). (c) Output characteristics of single-layer ReSe$_2$ measured in the dark or under red light (633 nm, 10 mW cm$^{-2}$) illumination at different $V_{bg}$ (–30 to 30 V). (d) Room-temperature transfer characteristics of single-layer ReSe$_2$ in the dark or under red light (633 nm, 10 mW cm$^{-2}$) illumination with –1 V applied bias voltage $V_{bg}$. (e) Output characteristics of few-layer transistors in the dark recorded at different $V_{bg}$ (–40 to 40 V). (f) Room-temperature transfer characteristics measured in the dark for few-layer transistors with –1 V bias drain–source voltage $V_{ds}$ on a linear scale (left-hand axis) and on a log scale (right-hand axis).

Fig. 3 The band-gaps of ReSe$_2$ nanosheets. (a) The density of states (DOS) of ReSe$_2$ nanosheets with different thickness (1L, 2L, 4L, bulk). (b) A schematic diagram of band-gap as a function of layer thickness.

red light illumination (633 nm, 10 mW cm$^{-2}$), as shown in Fig. 2c and d. We find that the FET properties are improved after the illumination, with increased mobility of 14.1 cm$^2$ V$^{-1}$ s$^{-1}$. Remarkably, after the red light illumination, $I_{ds}$ increases to a much higher value than $I_{ds}$ under dark conditions at the same $V_{bg}$, which can be attributed to the photo-generation of electrons and holes in the system. Fig. 2e and f show the output and transfer characteristics of few-layer ReSe$_2$ transistors. They show diminished properties with lower mobility of 0.10 cm$^2$ V$^{-1}$ s$^{-1}$. $I_{ds}$ of the few-layer FETs also exhibits poor switching properties as a function of $V_{bg}$ even at high $V_{ds}$. This indicates that the mobility and on/off ratio of the transistors can be modulated by layer thickness, as observed in MoS$_2$ phototransistors.

To understand the band-gap variation of these ReSe$_2$ layered structures as a function of layer thickness, the density of states (DOS) of bulk and layered 2D systems with different layer numbers is calculated and shown in Fig. 3a. It is found that the band-gap varies significantly when the dimension decreases from a three-dimensional structure to its 2D counterpart. More specifically, the calculated band-gaps of bulk, monolayer, bilayer and four-layer (bulk, 1L, 2L, 4L) ReSe$_2$ are 0.995, 1.239, 1.165 and 1.092 eV, respectively, indicating that the band-gap decreases with an increase of the number of ReSe$_2$ layers in 2D systems (Fig. 3b). As it is generally known that DFT within generalized gradient approximation and local density approximation usually underestimates the band-gap to a large degree, we predict that the genuine band-gaps of bulk and 2D systems should be much larger. The increasing layer thickness can be the origin of the reduced band-gap, and can also cause the loss of low-dimensional electric properties of few-layer ReSe$_2$, as a result of thickness-direction scattering and dielectric screening.

TMDs with high surface-to-volume ratio have the possibility for use as sensors, because their electronic, optoelectronic and chemical properties can change when their surrounding environment changes. The charge transfer or doping from the environment can change the carrier density or resistivity of the intrinsically n/p-doped TMDs. For example, changes of electrical property of TMDs resulting from the physisorption of gas molecules can be effectively detected by measuring the related current curves as a function of voltage or time. Our group previously reported the different photoresponses of a few-layer GaS nanosheet photodetector in various gas environments, which was owing to different charge transfer direction and quantity between the GaS nanosheet and adsorbed gas molecules. For the single-layer ReSe$_2$ transistors, we probed their time-dependent photoresponses using a focused laser beam ($\lambda = 633$ nm) with optical power of 100 mW cm$^{-2}$ in various gas environments (Fig. 4a). The applied bias voltage $V_{ds}$ was 0.5 V, and no $V_{bg}$ was imposed. The current exhibits stable and repeatable responses with light switching on and off in the three gas environments, O$_2$, air or NH$_3$, and the best photoresponse is obtained in O$_2$ environment. Photoresponse ($R_i = I_{ph}/I_{ds}$) and external quantum efficiency (EQE = $hcR_i/(\lambda\epsilon)$) are calculated for these three gas environments, where $I_{ph}$ is the photocurrent, $P$ is incident optical power (100 mW cm$^{-2}$), $S$ is the effective illumination area (~$4 \mu$m$^2$), and $\lambda$ is the excitation wavelength of 633 nm. The related parameters are listed in ESI (Table S1†). $I_{ds}$–$V_{ds}$ curves measured in the dark and under light illumination are both linear and symmetric for O$_2$ and air environments, shown in Fig. 4b, indicating that our gold contacts are Ohmic. $I_{ds}$ can also be modulated by the red light, and the current rapidly increases under light illumination compared with under dark condition. For O$_2$ environment, the
photocurrent shows an increase by several orders of magnitude compared to that obtained in air. The photocurrent increase with $V_{ds}$ is predicted to be because of the increase in carrier drift velocity and reduction of the carrier transit time. We also recorded the photocurrent generation as a function of $V_{ds}$ with various incident optical densities in O$_2$ gas (from 20 to 100 mW cm$^{-2}$), as shown in Fig. 4c. The photocurrent in such a single-layer ReSe$_2$ transistor under constant $V_{ds}$ increases linearly as a function of the optical density, confirming that the photocurrent is solely determined by the amount of photo-generated carriers under illumination. This proportional relation is expressed by $I_{ph} = (\text{e}\alpha p E) WD = A P^\alpha$, where $p$ is the charge carrier concentration, $E$ is the electrical field in the channel, $D$ is the depth of the absorption region, $A$ is the fitting parameter, and $\alpha$ is an exponent. To study the photo-switching rate of a single-layer ReSe$_2$ transistor, the change of photocurrent in a short time was measured in O$_2$ environment (Fig. 4d). The photocurrent rise and decay stage times are ~68 ms and 34 ms, respectively, similar to those of the first monolayer MoS$_2$ phototransistor.

First-principles calculations are used to investigate the charge transfer process between adsorbed gas molecules and a single-layer ReSe$_2$ nanosheet. A 4 x 4 ReSe$_2$ monolayer supercell with a single gas molecule adsorbed to it is chosen as the system for computational investigation. The calculated adsorption energy for O$_2$ is $-162$ meV, which indicates that the interaction between the O$_2$ molecule and ReSe$_2$ monolayer can be characterized as physisorption due to the small adsorption energy. The O$_2$ molecule serves as a charge acceptor and gets approximately 0.048 electrons from the ReSe$_2$ monolayer, increasing the carrier density of p-type ReSe$_2$ nanosheet (Fig. 5a). In previous reported work, point defects in 2D materials could enhance the charge transfer. As vacancy defects exist in monolayer ReSe$_2$ nanosheet caused by annealing, about 1.071 electrons are transferred from ReSe$_2$ monolayer to O$_2$ molecule, as shown in Fig. 5b and c, which enhances the hole carrier density of p-type single-layer ReSe$_2$. On the contrary, an NH$_3$ molecule physisorbed on the monolayer ReSe$_2$ acts as a charge donor to the ReSe$_2$ nanosheet, reducing the hole carrier density of the p-type monolayer (ESI, Fig. S4†). Counting the amount of the (opposite) charge transfer and the resulting carrier density, single-layer ReSe$_2$ transistors show superior photoresponse in O$_2$ environment than in NH$_3$.

3. Conclusions

In conclusion, FETs based on single- and few-layer ReSe$_2$ as conductive channel have been fabricated. The single-layer ReSe$_2$ FETs exhibit p-type conductivity at room temperature with a mobility of 9.78 cm$^2$ V$^{-1}$ s$^{-1}$, which is higher than that of few-layer transistors (0.1 cm$^2$ V$^{-1}$ s$^{-1}$). The increased thickness and reduction of band-gap affect the low-dimensional electric properties of few-layer ReSe$_2$. The single-layer devices show superior properties to the few-layer devices. Under red light illumination, the performance of single-layer ReSe$_2$ transistors is enhanced and they show high mobility of 14.1 cm$^2$ V$^{-1}$ s$^{-1}$. After the physisorption of O$_2$ molecules on ReSe$_2$ that served as “gating”, a single-layer ReSe$_2$ FET exhibits a fast and high photoresponsivity, reaching 95 A W$^{-1}$, which is much higher than that of the first MoS$_2$ monolayer and graphene photodevices. This is because the adsorbed O$_2$ molecules as electron acceptors increase the hole carrier density of the p-type ReSe$_2$ monolayer, thus improving its photoresponsivity. Our findings show that the new TMD, ReSe$_2$, whose band-gap and mobility

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**Fig. 4** Photoreponsivity of the single-layer FETs in different gas environments. (a) Time-dependent photoresponse with bias voltage $V_{ds} = 0.5$ V in O$_2$, air or NH$_3$ environment with light (633 nm, 100 mW cm$^{-2}$) switching on/off ($V_{bg} = 0$ V). (b) Drain–source $I_{ds}$–$V_{ds}$ curves of single-layer transistors measured in O$_2$ or air in the dark or under red light (633 nm, 100 mW cm$^{-2}$) illumination. (c) $I_{ds}$–$V_{ds}$ characteristics of single-layer transistors in the dark and under different incident optical power (633 nm) for O$_2$ environment ($V_{gs} = 0.5$ V). (d) Photoresponse rate of single-layer FETs at $V_{ds} = 0.5$ V in O$_2$ environment (633 nm, 100 mW cm$^{-2}$).

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**Fig. 5** O$_2$ molecule adsorbed on ReSe$_2$ monolayer. Charge density difference plots for (a) without defects and (b) with defects (side view), and (c) with defects for top view on ReSe$_2$ monolayer. The iso-surface value without defects is set to be 5 × 10$^{-3}$ e Å$^{-3}$ and that with defects is 1 × 10$^{-3}$ e Å$^{-3}$. Yellow and blue distributions correspond to charge accumulation and depletion, respectively.
change with layer number, has excellent electrical, optoelectronic and sensing properties for applications in many possible technological fields.

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Notes and references


