Controlled growth of large-area anisotropic ReS$_2$ atomic layer and its photodetector application†

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As an anisotropic 2D layered material, rhenium disulfide (ReS$_2$) has attracted much attention because of its unusual properties and promising applications in electronic and optoelectronic devices. However, the low lattice symmetry and interlayer decoupling of ReS$_2$ make asymmetric growth and out-of-plane growth occur quite easily; therefore, thick flake, dendritic and flower-like structures of ReS$_2$ have mostly been obtained previously. Here, we report on an approach based on space-confined epitaxial growth for the controlled synthesis of ReS$_2$ films. Using this approach, large-area and high-quality ReS$_2$ films with uniform monolayer thickness can grow on a mica substrate. Furthermore, the weak van der Waals interaction between the surface of mica and ReS$_2$ clusters, which favors surface-confined growth while avoiding out-of-plane growth, is critical for growing ReS$_2$ with uniform monolayer thickness. The morphological evolution of ReS$_2$ with the growth temperature reveals that asymmetric growth can be suppressed at relatively low temperatures. A ReS$_2$ field-effect transistor displayed a current on/off ratio of $10^6$ and an electron mobility of up to 40 cm$^2$ V$^{-1}$ s$^{-1}$, with outstanding photoresponsivity of 12 A W$^{-1}$. This work not only promotes the large-scale employment of ReS$_2$ in high-performance optoelectronic devices, but also provides a means of controlling the unusual growth behavior of low-lattice-symmetry 2D layered materials.

1. Introduction

Two-dimensional (2D) layered materials with strong in-plane anisotropic properties such as rhenium disulfide (ReS$_2$), rhenium diselenide (ReSe$_2$) and black phosphorus have been proposed for developing new devices with promising applications in electronics, optoelectronics and thermoelectrics.$^1$–$^5$ Unlike most 2D layered materials that have been investigated such as graphene and MoS$_2$, which have high lattice symmetry, the lattice symmetry of ReS$_2$ is quite low.$^6$ Usually, ReS$_2$ crystallizes in a distorted octahedral (1T) crystal structure,$^7$ which gives rise to strong anisotropy in its optical and electrical properties.$^8$–$^9$ Furthermore, in contrast to other TMDs, ReS$_2$ exhibits an unusual interlayer decoupling feature owing to a Peierls distortion in the 1T structure.$^3$ In addition, ReS$_2$ is a direct-band-gap semiconductor (1.5 to 1.6 eV) from monolayers to bulk materials.$^{10}$ Recently, few-layer Re$_2$S$_2$ sheets, which exhibit quite distinct properties from those of group VI TMDs, have been used in high-performance field-effect transistors, digital inverters, and photodetectors.$^{10}$–$^{14}$

Although anisotropic ReS$_2$ has many promising applications, most studies of ReS$_2$ have been based on mechanically exfoliated samples.$^{12,13}$ Until recently, 2D ReS$_2$ flakes and monolayer films have been successfully synthesized using chemical vapor deposition (CVD) growth with Re powder and NH$_4$ReO$_4$ molecules as the Re precursors, respectively.$^{15,16}$ Many efforts have been made in the preparation of 2D Re$_2$S$_2$, but control of the crystal quality, domain size, thickness and morphology of Re$_2$S$_2$ still poses a great challenge owing to several outstanding problems. For example, the high volatility and versatile valence states of Re oxides make the controlled synthesis of high-quality Re$_2$S$_2$ films difficult. In particular, the distorted 1T structure and weaker interlayer coupling of Re$_2$S$_2$ could make asymmetric growth and out-of-plane growth occur quite easily; therefore, thick flake, dendritic and flower-like structures have mostly been observed previously for Re$_2$S$_2$ synthesized by CVD.$^{10,16}$–$^{18}$ These specific features of Re$_2$S$_2$ pose
more difficulties and challenges to its controllable preparation in comparison to that of traditional TMDs such as MoS$_2$ and WS$_2$.\textsuperscript{3,4} Furthermore, much less is known about the growth behavior of low-lattice-symmetry 2D materials, which should be different from that of high-lattice-symmetry 2D TMDs.

In this work, a large-area, high-quality uniform monolayer ReS$_2$ film was synthesized using an approach based on space-confined CVD growth (Fig. 1a). Experimentally, volatile rhenium trioxide (ReO$_3$) was used as the Re precursor to ensure the efficiency of the growth, and mica with a low surface energy was used as a substrate to achieve epitaxial growth. To achieve controllable growth, an approach based on space-confined growth was adopted by constructing a micro-reactor between two mica substrates in the CVD system. This procedure efficiently reduced the nucleation density and growth rate of ReS$_2$ and thus favored large-area epitaxial growth. Moreover, to gain insight into the unusual growth mechanism of the low-lattice-symmetry 2D material ReS$_2$, the growth behavior of ReS$_2$ on mica and SiO$_2$ substrates was studied in detail. The results indicate that two different growth processes (out-of-plane/surface-confined) are responsible for the morphological differences in ReS$_2$ obtained on SiO$_2$ and mica substrates. These are determined by three key factors, which include anisotropic growth induced by the distorted 1T structure, the weak interlayer coupling in ReS$_2$, and the barrier energy to surface migration of the substrate. Besides, the asymmetric growth of ReS$_2$, which leads to its growth into a dendritic morphology, can be suppressed at relatively low temperatures (<700 °C). FETs based on the grown ReS$_2$ exhibited superior electrical (mobility of up to 40 cm$^2$ V$^{-1}$ s$^{-1}$) and photoelectrical properties. The high crystal quality and superior anisotropy of ReS$_2$, together with its controllable growth, endow it with great potential for future applications in high-performance electronic devices.

2. Experimental section

Epitaxial growth and transfer of ReS$_2$ film

CVD growth was carried out in a single-temperature-zone tubular furnace under atmospheric pressure. Before growth, ReO$_3$ powder (purity 99.9%) and sulfur powder (purity 99.5%) were placed at the center and the outside edge (∼200 °C) of the hot zone, respectively. Two (or several) pieces of freshly cleaved fluorophlogopite mica substrate (1 cubic centimeter in size) were stacked together to form a microreactor by simply putting one piece onto another piece. The electrostatic force between two mica substrates made them adhere together tightly. Then, they were put onto a ceramic boat containing ReO$_3$ powder. Argon was used as a carrier gas with a flow rate of 80 sccm during the whole growth process. The furnace temperature was ramped to the growth temperature (500–800 °C) at 25 °C min$^{-1}$ and then maintained for 3 min for the growth of ReS$_2$. The as-grown ReS$_2$ sample was then transferred onto a SiO$_2$/Si (300 nm) substrate via a poly(methyl methacrylate)-mediated transfer process. Hydrofluoric acid (20 wt%) was used as an etchant to delaminate ReS$_2$ film from the mica substrate.

Characterization of grown ReS$_2$ film

The surface morphologies of ReS$_2$ samples were characterized by optical microscopy (Olympus BX51), SEM (Nova NanoSEM 450) and AFM (Bruker Dimension ICON). Raman and fluorescence spectra of different ReS$_2$ layers were recorded in a confocal Raman microscopy system (Renishaw). Absorption spectra were recorded using a UV/vis/near infrared spectrometer (Lambda 950). TEM images were obtained with an HRTEM (Tecnai G2 F20; accelerating voltage, 200 kV). The TEM samples were prepared by transferring ReS$_2$ film onto lacy carbon film-supported copper grids in a similar method to that described in the last paragraph.

Device fabrication and electrical measurements

A ReS$_2$ sample was transferred onto a SiO$_2$/Si (300 nm) substrate. Electrical contacts with the ReS$_2$ sample were achieved using standard electron beam lithography and thermal evaporation of 5 nm Cr and 50 nm Au. Electrical transport and photoelectric properties were measured in ambient air conditions using an Agilent B2912A source meter unit with a 532 nm laser as a light source. The laser power was adjusted from 430 to 0.73 µW mm$^{-2}$ using an optical attenuator (Thorlabs NDC-50C-4M) and was measured using a laser power meter (Thorlabs PM 100D).

3. Results and discussion

To synthesize a monolayer ReS$_2$ film, a CVD system equipped with a single-zone furnace was employed (Fig. 1a). Rhenium

Fig. 1 (a) Schematic diagram of the space-confined CVD growth of ReS$_2$ and the surface reaction during the epitaxial growth process of a ReS$_2$ atomic layer on mica. Optical images of ReS$_2$ grown on the (b) B face and (c) A face of a mica substrate. (d and e) Optical images of ReS$_2$ grown on the A face after being transferred onto a SiO$_2$/Si (300 nm) substrate. (f) AFM image of as-grown ReS$_2$ on a mica substrate.
trioxide (ReO₃) and sulphur (S) were used as the Re and S precursors, respectively, and argon (Ar) was used as a carrier gas during the growth process. The typical growth temperature and growth time were set at 600 °C and 3 min, respectively. As can be imagined, ReO₃ should be a much better Re precursor for growing ReS₂ in comparison to Re metal (melting point 3180 °C) and NH₄ReO₄ molecules (which bring about low crystal quality), which were used in previous work,¹⁵,¹⁶,¹⁸ and can ensure high growth efficiency and high crystal quality at low growth temperatures. However, it also faces serious problems: unstable ReO₃ quickly decomposes into Re₂O₇ (which sublimes easily) and ReO₂ (which is less volatile) via a disproportionation reaction (reaction (1)) when the temperature rises to 400 °C (see its thermogravimetric analysis in Fig. S1†).

\[
3\text{ReO}_3 \rightarrow \text{Re}_2\text{O}_7 + \text{ReO}_2 \quad (1)
\]

The very high volatility of Re₂O₇ (melting point: 220 °C and boiling point: 360 °C) results in abundant vapor and nucleation sites, which lead to the growth of a large amount of thick 3D flower-like ReS₂ flakes on the substrate (Fig. 1b). To solve this problem, two pieces of freshly exfoliated mica were stacked together to form an envelope-like structure and placed above the ceramic boat (Fig. 1a). Here, the inner mica surface and the outer mica surface are defined as the A face and B face, respectively. It can be seen that ReS₂ grown on the B face (Fig. 1b) and A face (Fig. 1c) of each mica substrate exhibits great differences.

As shown in Fig. 1a, when two pieces of the mica substrate were tightly stacked together, the small crevice between them formed a microreactor for the growth of ReS₂. The micro-reactor exerted a space-confining effect in decreasing the concentration of precursors and thus decreased the nucleation density and growth rate of ReS₂. As a result, a large-scale ReS₂ film with hexagonal morphology and a domain size of up to 60 μm could grow on the A faces (Fig. 1c and d), and a continuous uniform ReS₂ monolayer film could even be obtained (Fig. 1e) when the growth time was prolonged to 8 min. The important role of space confinement in the controlled growth of ReS₂ was further confirmed by performing in situ contrast experiments (Fig. S2†). An AFM image (Fig. 1f) reveals that the grown ReS₂ has a smooth surface with a thickness of ~0.73 nm, which indicates monolayer thickness.²⁰ Moreover, when several pieces of mica were stacked together to form a multilayer sandwich structure to serve as a growth substrate, a uniform monolayer ReS₂ film could grow on the A face of each piece of mica, which indicated the high-yield synthesis of ReS₂ film using this approach. Furthermore, we also synthesized ReS₂ on a SiO₂ substrate using a similar growth approach, but only thick flakes and flower-like ReS₂ were obtained, which were similar to the results obtained in most recent research works.¹⁰,¹⁷ The different growth behavior could be understood from an analysis of the surface properties of the growth substrate and the special structure of ReS₂ itself, as is discussed below.

The Raman spectra of as-grown ReS₂ films with different thicknesses are shown in Fig. 2a. The primary Raman shifts of the III, IV, V, and VI peaks are located at 152, 161, 212, and 235 cm⁻¹, respectively, which match well with those of mechanically exfoliated ReS₂ samples.²¹,²² In a similar way to previous findings,²¹ only the low Raman shifts of the I and II peaks at 134 and 141 cm⁻¹ display slight sensitivity to the layer number (Fig. S3af). Photoluminescence (PL) and absorption measurements were performed to determine the band gap of the as-grown ReS₂ film (Fig. 2b). The energy positions of the PL and absorption peaks match well at about 1.61 eV, which is consistent with the band gap value of monolayer ReS₂. In addition, the measured band gap became narrower with an increase in the layer number, ranging from 1.61 eV for a monolayer to 1.48 eV for few layers (Fig. S3bf), which demonstrated the dependence on the layer number of the band gap. All these spectral features of CVD-grown ReS₂ exhibit a stark contrast to the typical behavior seen in Mo- and W-based TMDs,²³ which is attributed to the interlayer decoupling properties of ReS₂.

X-ray photoelectron spectroscopy (XPS) was utilized to confirm the elemental composition and bonding types of the grown ReS₂ film. Five elements are present in the spectrum that was acquired (Fig. 2c). The signals of Re and S arise from the ReS₂ sample, those of Si and O originate from the SiO₂ substrate and that of C arises from residues of PMMA used
during transfer. The primary peaks at 164.30 and 40.41 eV correspond to S 2p and Re 4f states, respectively. The two characteristic peaks at 38.80 and 41.20 eV are attributed to the Re 4f7/2 and 4f5/2 binding energies of Re4+ (Fig. 2d). The core-level peaks (Fig. 2e) that correspond to the 2p3/2 and 2p1/2 binding energies of divalent sulfide ions (S2−) are located at 161.20 and 160.00 eV, respectively. In addition, the atomic ratio between Re and S elements is 1:1.97, which indicates that the grown ReS2 is reasonably stoichiometric.

To further analyze the crystallographic structure of the grown ReS2, we performed high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) by transferring ReS2 onto a TEM grid. Fig. 2f shows a low-magnification TEM image of ReS2 film, in which a clean uniform membrane can be seen. The distorted 1T structural characteristics of ReS2 with visible DS-chain lattice fringes of Re are distinctly observed in the HRTEM image (Fig. 2g). The interplanar distances along the b-axis and a-axis, which correspond to the (010) and (100) lattice planes of ReS2, were measured to be 0.34 and 0.31 nm, respectively. The SAED pattern and fast Fourier transform (FFT) image clearly confirm the a[100] and b[010] orientation of the distorted 1T crystal with an angle of ∼59.9° (Fig. 2h), which suggests that our ReS2 has high crystal quality.

To reveal the unusual growth mechanism of low-lattice-symmetry ReS2, we studied its growth behavior on different substrates and at different temperatures. Fig. 3 shows the morphology of ReS2 obtained on SiO2 and mica substrates in the same growth conditions and a corresponding schematic diagram of the growth behavior on these two substrates. Obviously, thick flakes and flower-like shapes of ReS2 tended to grow on the SiO2 substrate (Fig. 3 and S4†), which occur much more easily in the growth of ReS2 in comparison to that of traditional TMDs. This unusual growth feature could be understood from the surface properties of the growth substrate and the distorted 1T structure of ReS2 itself. The rough surface of the SiO2 substrate with abundant dangling bonds and defects brings about a high energy barrier to the surface migration of adatoms on the substrate during growth (Fig. 3a). In contrast, the weak interlayer coupling of ReS2 allows the free migration of adatoms on its own surface. Thus, thick ReS2 flakes with small domain sizes are easily grown on a SiO2 substrate. Besides, flower-like morphology of ReS2 indicates out-of-plane growth, which is another typical feature of the growth of low-lattice-symmetry 2D materials. As is known, out-of-plane growth occurs occasionally in the growth of traditional TMDs at an extremely high precursor concentration but occurs quite easily for ReS2 even at a low precursor concentration (Fig. 3b and c). We suspect that the anisotropic growth of low-lattice-symmetry ReS2 induces strain or defects during its initial nucleation period, which makes out-of-plane growth occur much more easily. In addition, the interlayer decoupling of ReS2 could make the growth of ReS2 free from the influence of other layers. Thus, the unusual structure and interlayer decoupling of ReS2 should be the root cause of the out-of-plane growth on the SiO2 substrate.

In contrast, the flat and inert surface of the mica substrate makes the energy barrier to the surface migration of adatoms on it much lower than that on the SiO2 substrate. Hence, the atomically flat surface of mica facilitates the migration of adatoms on it during CVD growth (Fig. 3d), in which atoms have a fast diffusion rate and longer diffusion length. This renders the growth of ReS2 on mica surface-dominated, which is responsible for the nucleation and growth of a ReS2 film that lies flat on the mica surface. In addition, the weak van der Waals interaction between the surface of mica and adatoms exerts a surface-confining (induction) role during the epitaxial growth process of ReS2, which could efficiently suppress out-of-plane growth. As a result, a ReS2 film with large domains, hexagonal morphology and uniform monolayer thickness could be obtained on the mica substrate (Fig. 3e and f). In this regard, we could control the growth model (in-plane/out-of-plane) to obtain flat 2D ReS2 films or vertical 3D ReS2 nanoflowers by choosing appropriate growth substrates. These two types of ReS2 structure have promising applications in electronic devices and catalysis (and lithium batteries), respectively. Interestingly, the morphology of ReS2 grown at different temperatures exhibits obvious variations (Fig. 4), changing from regular round and hexagonal shapes to irregular serrated and dendritic shapes with an increase in temperature. Dendritic morphology of ReS2 indicates an asymmetric growth model, which is a typical growth feature of low-lattice-symmetry 2D materials. This unusual growth model is attributed to the anisotropic interfacial energy induced by the distorted 1T structure. The temperature-modulated evolution of morphology can be understood from the temperature-dependent migration coefficient (D) of adatoms on a substrate (see eqn (2)):

\[ D \propto e^{-E_m/kT} \]  

where \( E_m \) is the energy barrier to migration, \( k \) is Boltzmann’s constant and \( T \) is the substrate temperature. At low growth temperatures, atomic diffusion is relatively slow and the attachment and detachment of adatoms at the edges of ReS2 are limited, which makes epitaxial growth occur in the
directions of the two crystal axes at nearly the same rate. Thus, symmetric growth is dominant, which allows ReS₂ to grow into regular hexagonal shapes. On the basis of recent studies, we know that hexagonal ReS₂ domains should be composed of six subdomains, in which the direction of Re chains changes by 60° from one subdomain to another. However, at high growth temperatures, atomic diffusion becomes fast and adatoms are enabled to migrate and attach in the highly activated growth direction along the crystal axis where this is energetically favorable. As a consequence, asymmetric growth becomes apparent, which makes ReS₂ grow into an irregular dendritic shape. Our results indicate that the asymmetric growth of this type of material, which brings about irregular morphology of ReS₂, is reduced markedly when growth occurs at a low temperature (<700 °C), and thus materials with regular morphology can be obtained. Of course, the temperature cannot be excessively low (<500 °C), otherwise amorphous domains would grow on the monolayer surface owing to the reduction in the migration energy of adatoms. Furthermore, the quality of ReS₂ decreases when the growth temperature is below 500 °C (Fig. S5†). Therefore, the morphology and crystal quality of ReS₂ can be effectively controlled by tuning its growth temperature.

Fig. 4 Temperature-modulated growth behavior of ReS₂ film. OM images of ReS₂ grown at (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C on a mica substrate (the scale bar represents 30 μm). (e–h) Corresponding OM images of ReS₂ film transferred onto a SiO₂/Si substrate (the scale bar represents 30 μm). (i–l) Corresponding AFM images of as-grown ReS₂ on mica (the scale bar represents 10 μm).

Fig. 5 Electrical and photoelectrical properties of devices made from CVD-grown monolayer ReS₂ film. (a) Schematic diagram of a back-gated ReS₂ phototransistor. The inset shows an OM image of a typical ReS₂ device on 300 nm SiO₂/Si (the scale bar represents 10 μm). (b) Source–drain current (Iₛd) versus voltage (Vₛd) characteristics of the device at various values of the gate voltage (V₉). (c) Transfer curve (Iₛd versus V₉) curve for the same device at various values of Vₛd. (d) Transfer curve of a ReS₂ FET (another device) measured under various light irradiation powers at Vₛd = 0.5 V. (e) Photocurrent (PC) and responsivity (R) as a function of light irradiation power measured at Vₛd = 0.5 V and V₉ = 0 V. The dotted lines for PC (R) are the best fits to the data using the functions PC = Pβ (R = Pβ−1), where P is the effective power of the irradiating light on the device and β is a constant. (f) 3D photocurrent map of the ReS₂ phototransistor with varying values of V₉ and power of light determined at Vₛd = 0.5 V. The effective power of light is obtained with a device area of 189 μm².
where $L$, $W$, and $C_g$ are the channel length, width, and gate capacitance per unit area, respectively.\(^\text{31}\) Notably, this is the highest value of electron mobility recently reported for CVD-grown ReS$_2$, and is even comparable with that of mechanically exfoliated ReS$_2$ flakes (1–50 cm$^2$ V$^{-1}$ s$^{-1}$).\(^{11,12}\) which highlights the high crystal quality of the grown ReS$_2$ samples.

As shown in Fig. 5d, the measured values of $I_{ds}$ as a function of $V_g$ at various light irradiation powers ($P$) reveal the obvious gate tunability of the photocurrent response of the ReS$_2$ phototransistor. The photoresponsivity, which is defined as the photocurrent generated per unit power of incident light, is critical for the controlled growth of ReS$_2$ from a volatile ReO$_3$ precursor. In addition, the out-of-plane growth and carrier recombination. The photoresponse of the ReS$_2$ device is determined by a photoconductive mechanism. In addition, the photocurrent depends linearly on the value of $V_{ds}$ and increases gradually with an increase in the power of the incident light (Fig. S6a†). An increase in $V_{ds}$ reduces the carrier transit time by providing a stronger electric field in the conduction channel, which thus reduces the possibility of carrier recombination. The photoresponse of the ReS$_2$ device to the switching on and off of light exhibits better temporal resolution (Fig. S6b†). A 3D photocurrent map of the ReS$_2$ device clearly shows that the photocurrent can be modulated by tuning the value of $V_g$ (Fig. 5f), where $V_g$ can modulate the energy barriers between the Fermi level of Au and the conduction band of ReS$_2$. Such gate-tunable photoresponse by adjusting the Schottky barriers is important for pixelated imaging applications.

### 4. Conclusions

In summary, we present an approach based on space-confined CVD growth for the controlled synthesis of a large-area highly crystalline uniform monolayer ReS$_2$ film. The microreaction chamber that was constructed, which exerts a space-confining effect to reduce the nucleation density and growth rate of ReS$_2$, is critical for the controlled growth of ReS$_2$ from a volatile ReO$_3$ precursor. In addition, the out-of-plane growth and asymmetric growth of low-lattice-symmetry ReS$_2$ can be suppressed by growing it on a substrate with low surface energy at a relatively low temperature. The high crystal quality, in combination with the superior electrical and photoelectric properties of the CVD-grown ReS$_2$, endows it with great potential for use in electronic and optoelectronic devices. Furthermore, our results are beneficial for understanding and controlling the unusual growth behavior of low-lattice-symmetry 2D layered materials.

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### Notes and references

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