Electronic Supporting Information

Controlled Growth of Large-area Anisotropic ReS$_2$ Atomic Layer and its Photodetector Application

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1) Thermogravimetric analysis of ReO$_3$.

![Thermogravimetric analysis of ReO$_3$ measured under N$_2$ atmosphere. The temperature increment is 10 ºC/min.](image)

**Fig. S1.** Thermogravimetric analysis of ReO$_3$ measured under N$_2$ atmosphere. The temperature increment is 10 ºC/min.

For reasonable controlling the growth of ReS$_2$ film with ReO$_3$ as Re precursor, we studied the pyrolysis process of ReO$_3$ by using thermogravimetric (TG) analysis. As show in Fig. S1, the weight of ReO$_3$ decrease sharply in the temperature range from 400 to 550 ºC, attributing to the fast decomposition of ReO$_3$ into volatile Re$_2$O$_7$ and nonvolatile ReO$_2$ through a disproportionation reaction. For CVD growth of high quality 2D materials, the growth temperature usually need above 500 ºC with the temperature increment up to 25 ºC/min. In this case, the volatile Re$_2$O$_7$ (melting point: 220 ºC and boiling point: 360 ºC) would sublimes quickly into vapor at the growth temperature, leading to supersaturated Re source in the CVD system, and thus large amount of flower-like ReS$_2$ thick flakes preferably obtained when grow with conventional CVD approach.
2) Role of space-confinement in the CVD growth of ReS$_2$.

![Schematic diagram of various regions on the growth substrate](image)

**Fig. S2.** Schematic diagram of various regions on the growth substrate which is covered by another mica substrate forms a micro-reactor. According to the cover region on the substrate, it was divided into three regions: outside, inside and interface. Corresponding optical images of the ReS$_2$ film grow at different regions of substrate. Scale bars for all these images are 50 $\mu$m.

For more clearly revealing the role of space-confinement in the CVD growth of ReS$_2$, we performed an in-situ contrast experiment by covering half of the mica surface with another mica layer. The covered part forms a micro-reactor for ReS$_2$ growth. In this case, the growth substrate can be divided into three regions (Fig. S2), one region at the outside of micro-reactor, another region at the inside of micro-reactor, and the third region at their interface. Clearly, the results of ReS$_2$ grow at these three regions show obvious difference. Flower-like ReS$_2$ thick flake with irregular morphology are densely grown on the outside region, while uniform monolayer film can be obtained on the inside region with a transition from thick layer to monolayer at the interface region. The stark contrast of the grown results between outside and inside regions highlights the importance of the constructed micro-reactor, which plays a space-confinement role in the controlled growth of ReS$_2$ film.
3) Layer number dependent Raman and fluorescence spectrum of grown ReS$_2$.

Fig. S3. (a) Raman and (b) fluorescence spectra of CVD grown ReS$_2$ film with thickness vary from monolayer to few-layer. The energy position of PL increases with decreasing layer numbers, ranging from 1.48 eV of few-layer to 1.61 eV of monolayer, while the PL intensity decreases with layer number decreasing.
4) Substrate dependent growth behavior of ReS$_2$ atomic layer.

**Fig. S4.** Morphology characterizations of ReS$_2$ film grow on mica and SiO$_2$ substrates.
(a) OM and (b,c) SEM images of ReS$_2$ transferred from mica onto SiO$_2$ substrate. (d) OM, (e) SEM and (f) 3D AFM images of ReS$_2$ grown on SiO$_2$ substrate.

To confirm the difference of the growth behavior of ReS$_2$ on mica and SiO$_2$ substrate, we compared the results of ReS$_2$ grown on these two substrates. Clearly, only thick flake or flower-like structure ReS$_2$ with small domain size (~5 µm) were grown on SiO$_2$ substrate. The flower-like structure grown on SiO$_2$ substrate, indicates an out-of-plane growth, arises much easier in most of our experiment and recent reported work. In contrast, large area, hexagon ReS$_2$ films with uniform monolayer thickness and large domain (~60 µm) size were grown on the mica substrate, indicating a well controlled epitaxial growth.
5) Temperature dependent crystal quality of CVD-grown ReS$_2$ atomic layer.

Fig. S5. Raman spectra of monolayer ReS$_2$ film grow at different temperatures.
6) Photoelectric property of the CVD-grown monolayer ReS$_2$ phototransistor.

**Fig. S6.** (a) Photocurrent (PC) as a function of drain–source voltage ($V_{ds}$) under various light irradiation power at $V_g = 0$ V. (b) Time-dependence $I_{ds}$ of the device with and without the laser illumination measured at $V_{ds} = 1$ V and $V_g = 30$ V.

The dynamic response of our device during the on-and-off switching of an incident light exhibits a fast rising (60-80 ms) while a slow falling (30-50 s), which is compared with the results obtained from exfoliated thick layers ReS$_2$ and InSe photodetectors,\textsuperscript{1, 2} indicates the existence of trap states. Such trap states exacerbated further due to the high surface-to-volume ratio of monolayer ReS$_2$ film.

**REFERENCES**