Supporting Information

GeSe/WSe_2 mixed dimensional p-n junction photoelectric properties

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1. Supporting information for growing WSe_2 two-dimensional (2D) materials

The Chemical Vapor Deposition (CVD) preparation process for WSe_2 2D materials in this work is as follows:

① SiO_2/Si Substrate Cleaning Steps: Initially, utilize 50 mL of acetone for a 10-minute ultrasonic cleaning to eliminate organic impurities on the substrate. Subsequently, employ 50 mL of anhydrous ethanol for another 10-minute ultrasonic cleaning to remove the acetone. Lastly, perform an ultrasonic cleaning with deionized water, followed by drying the substrate with high-purity N_2 for subsequent use.

② Weighing of Raw Materials: Measure 120 mg of selenium powder and 65 mg of WO_3. Weigh a certain amount of NaCl as a growth promoter and thoroughly mix it with the WO_3. Subsequently, evenly distribute the mixture into two quartz boats. Place the SiO_2/Si substrate with its polished side facing downwards over the quartz boat containing WO_3.

③ Material Growth Pretreatment: Place the quartz boat into the tubular furnace with Se powder in the first temperature zone and WO_3, NaCl, and SiO_2/Si substrate in the second temperature zone, as shown in Figure S1(a), which depicts the arrangement of materials within the furnace. After sealing, set the temperature-raising program according to Figure S1(b). Pump to create a vacuum of <5Pa, then purge with Ar gas at 300 sccm to reach atmospheric pressure. Repeat this purge process twice to remove impurity gases.

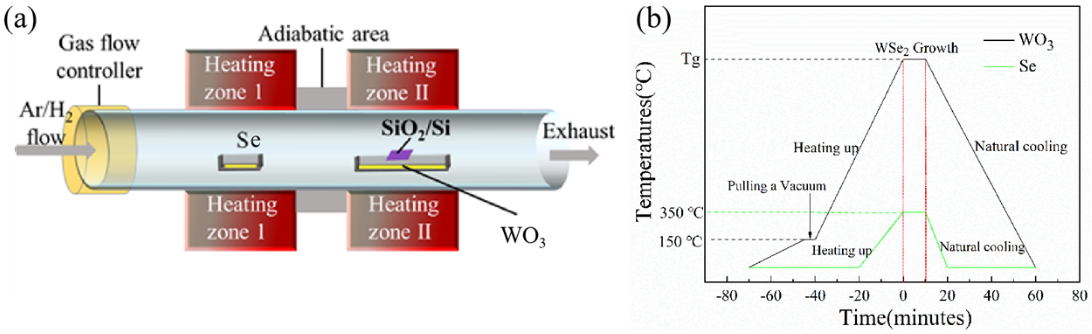

Figure S1 (a) Schematic diagrams of the CVD system, (b) Growth process temperature curve of WSe_2 material.

④ Material Growth: After the gas purging process is completed, initiate the temperature rise in both temperature zones of the tubular furnace while simultaneously opening the inlet and outlet valves to introduce Ar gas at a flow rate of 65 sccm. When the temperature in the second temperature zone reaches 350 °C, close the inlet and outlet valves and repeat the gas purging process to remove impurities such as water vapor generated within the quartz tube due to heating. Continue introducing Ar gas at a flow rate of 65 sccm after the purging process is finished. As the growth temperature (maximum temperature) is approached, switch to an Ar/H_2 mixture while maintaining the same flow rate. After the growth process is completed, allow natural cooling down to 600 °C before switching back to Ar gas. Cool to room temperature before removing the samples for further use.

The mixed H_2 in the Ar/H_2 atmosphere acts as a reducing agent during the reaction process. The chemical reactions that occur during the synthesis process are as follows:

$$2WO_3 + 2NaCl \rightarrow WO_2Cl_2 + Na_2WO_4 \tag{1}$$

$$WO_2Cl_2 + 4H_2 + 3S \rightarrow WS_2 + 2HCl + 2H_2O + H_2S \tag{2}$$

2. Supporting information for an effective approach to ensure simultaneous optimization of both size and quality of WSe_2 material

The methods and control strategies we employed to simultaneously optimize the size and quality of WSe_2 through the CVD process are as follows:

Firstly, in terms of substrate selection, we chose SiO_2/Si with high crystallinity and low defect density. We then employed rigorous cleaning and pretreatment steps to remove surface contaminants, ensuring a clean and smooth substrate surface, which is crucial for the formation of high-quality, large-sized WSe_2 crystals. To simultaneously optimize the size and quality of the WSe_2 crystals, we fine-tuned the critical growth parameters, including reaction temperature, reaction time, carrier gas flow rate, and the ratio of selenium-to-tungsten precursors.

During the investigation of the controllable synthesis of WSe_2, we first explored the suitable temperature for Se powder (the first temperature zone). In order to determine the optimal temperature for the first temperature zone for the preparation of WSe_2, while keeping other conditions constant, we conducted multiple experiments with the temperature of the first temperature zone set at 250 ℃, 280 ℃, 300 ℃, 330 ℃, 350 ℃, and 380 ℃, respectively, considering the melting point of Se powder to be 221 ℃. Figure S2(a-f) presents optical microscope images of the WSe_2 samples prepared at these temperatures of the first temperature zone: 250 ℃, 280 ℃, 300 ℃, 330 ℃, 350 ℃, and 380 ℃, respectively.

As observed from the optical images, when Se powder is heated to a relatively low temperature (<280 ℃), the grown WSe_2 samples are mostly polygons or truncated triangles with sizes below 100 μm, as shown in Figure S2 (a-b). This is because at lower temperatures, the concentration of evaporated Se vapor is too low to provide sufficient Se source for the growth of WSe_2. As the temperature in the first heating zone rises, the WSe_2 samples exhibit increasingly well-defined triangular shapes, with their sizes gradually increasing. When the temperature reaches 330 °C, the WSe_2 samples mostly have sizes around 500 μm, as shown in Figure S2 (d). By further increasing the temperature in the first heating zone to 350 °C, the WSe_2 samples are large-area monolayer films, as shown in Figure S2 (e). Upon further temperature elevation, the WSe_2 exhibit distinct grain boundaries and multilayer stacking phenomena , as shown in Figure S2 (f). The following conclusions can be drawn from the experimental results: The size of WSe_2 prepared by CVD is basically proportional to the heating temperature of Se powder, but multilayer formation occurs when the temperature exceeds 350 °C. Based on the results of multiple experiments, 350 °C is identified as the optimal temperature in the first heating zone for preparing large-size, high-quality 2D WSe_2 materials.

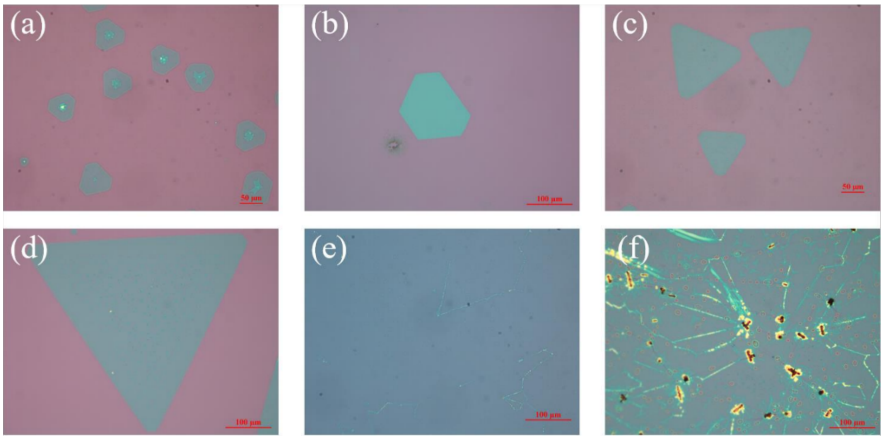

Figure S2 Optical microscope images of WSe_2 samples synthesized at different temperatures in the first temperature zone: 250 °C(a), 280 °C(b), 300 °C(c), 330 °C(d), 350 °C(e) and 380 °C(f).

Similarly, parameters such as reaction time, carrier gas flow rate, and the ratio of selenium-to-tungsten precursors during the growth process of WSe_2 can also be optimized through similar methodologies.

3. Supporting information for additional characterization results of the grown WSe_2 materials

(a) The test results of Scanning Electron Microscope (SEM)

We characterized the surface roughness of the prepared WSe_2 samples using SEM, as depicted in Figure S3. The SEM images indicate that the surface of the WSe_2 samples is smooth and free from delamination.

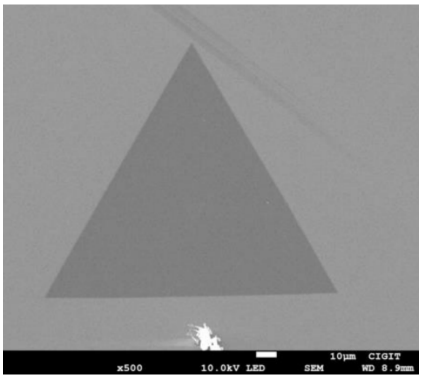

Figure S3 SEM image of the WSe_2 sample.

(b) The test results of Energy Dispersive Spectrometer (SEM)

To determine the elemental composition of the WSe_2 samples prepared by CVD, we conducted EDS analysis to identify the sample's constituents. Figure S4 presents the EDS spectrum of the WSe_2 sample, which reveals that, apart from the abundant O and Si elements from the SiO_2/Si substrate, the atomic ratio of W:Se is 1:2, confirming that the prepared samples are WSe_2.

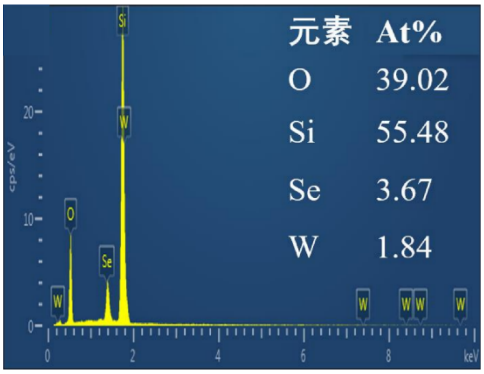

Figure S4 EDS spectrum of the WSe_2 sample.

4. Supporting information for the preparation process of GeSe/WSe_2 p-n heterojunction preparation

(a) The specific operational steps for the preparation of Au electrodes are as follows:

①The first layer of LOR photoresist is spin-coated using a spin coater, with the spin coating speed and time divided into two stages. The parameters are: 500 rpm for 5 seconds, followed by 3500 rpm for 35 seconds.

②Bake on a drying platform set to 170°C for 10 minutes.

③Spin-coat the second layer of S1805 photoresist using a spin coater, with the spin coating speed and time divided into three stages. The parameters are: 500 rpm for 5 seconds, 2000 rpm for 25 seconds, and 3000 rpm for 3 seconds.

④Bake on a drying platform set to 100°C for 10 minutes.

⑤Perform laser direct writing on the selected area of the sample using the designed electrode pattern.

⑥Develop in AZ300 developer for 60 seconds to remove the exposed and degraded photoresist. Rinse off the developer with deionized water and dry with nitrogen gas.

⑦Deposit gold electrodes using a sputtering coater with magnetron sputtering technology.

⑧Soak the sample in acetone for 20 to 30 minutes to perform stripping, until successful electrode stripping is confirmed under a microscope. Dissolve the remaining LOR photoresist with AZ400 developer for 30 seconds. Subsequently, gently clean the material with alcohol and deionized water, respectively. Finally, blow off the water on the sample surface with nitrogen gas.

The prepared Au electrodes are constructed with one end on the WSe_2 material and the other end on the SiO_2/Si substrate, as shown in Figure 2(d) of the manuscript.

(b) Using polydimethylsiloxane (PDMS) as the transfer medium, the exfoliated GeSe thin film is transferred onto the WSe_2 material through a micro-area spot transfer technique, ensuring that GeSe is in contact with both the WSe_2 and the Au electrodes on the SiO_2/Si substrate. The specific operational steps for the transfer process of GeSe are as follows:

①An appropriate amount of GeSe is adhered from a GeSe bulk material using adhesive tape and folded over 5 to 7 times to thin the GeSe material. Then, the GeSe on the tape is bonded with the prepared PDMS on a slide glass and gently pressed. After removing the tape, part of the GeSe will remain on the PDMS. The PDMS with GeSe is set aside for later use. In this process, PDMS serves as the transfer medium to ensure the cleanliness of the sample surface.

②Under an optical microscope, locate the target WSe_2 sample on the substrate and fix the slide glass with GeSe/PDMS onto a slide glass holder. Under the microscope, use a three-axis micrometer to adjust the positions of WSe_2 on the substrate and GeSe on the PDMS, in order to achieve precise alignment of the GeSe on the PDMS with the WSe_2 on the substrate.

③Gradually lower the height of the slide glass until contact between the GeSe and WSe_2 is observed under the microscope. Properly heat the sample (approximately 70°C) to facilitate the separation of GeSe from the PDMS.

④Slowly lift the slide glass, and the GeSe will detach from the PDMS and remain on the WSe_2 due to the van der Waals interaction between the GeSe and the WSe_2 material/substrate, as shown in Figure S5.

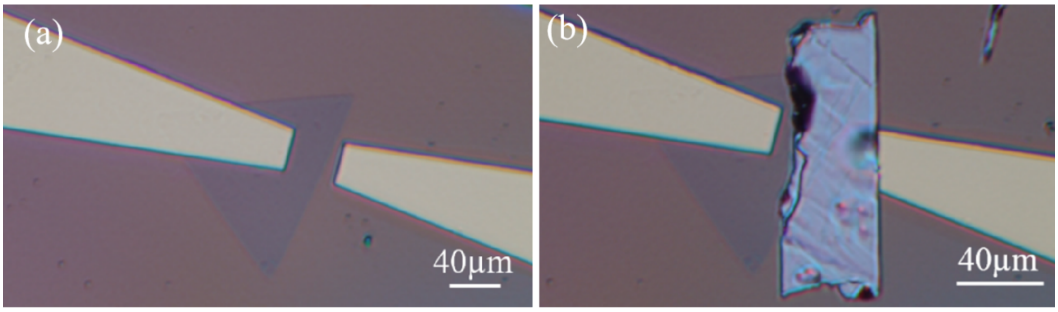

Figure S5 Optical microscope images of the sample(a)before and (b)after GeSe transfer.