Controllable Growth of Monolayer MoS$_2$ and MoSe$_2$ Crystals Using Three-temperature-zone Furnace

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Abstract. Monolayer molybdenum disulfide (MoS$_2$) and molybdenum diselenide (MoSe$_2$) have attracted great attention for their exceptional electronic and optoelectronic properties among the two dimensional family. However, controllable synthesis of monolayer crystals with high quality needs to be improved urgently. Here we demonstrate a chemical vapor deposition (CVD) growth of monolayer MoS$_2$ and MoSe$_2$ crystals using three-temperature-zone furnace. Systematical study of the effects of growth pressure, temperature and time on the thickness, morphology and grain size of crystals shows the good controllability. The photoluminescence (PL) characterizations indicate that the as-grown monolayer MoS$_2$ and MoSe$_2$ crystals possess excellent optical qualities with very small full-width-half-maximum (FWHM) of 96 me V and 57 me V, respectively. It is comparable to that of exfoliated monolayers and reveals their high crystal quality. It is promising that our strategy should be applicable for the growth of other transition metal dichalcogenides (TMDs) monolayer crystals.

1. Introduction
The two-dimensional (2D) atomic crystals of transition metal dichalcogenides (TMDs) have attracted tremendous recent interest due to their unique properties and potential applications [1-3]. For instance, at monolayer thickness, the band structures of some TMDs, like MoS$_2$ and MoSe$_2$, transit from indirect to direct band gap, resulting in dramatic enhancement of photoluminescence [4]. These properties prompt researchers to obtain high-quality monolayer crystals using various approaches, including micromechanical cleavage [5], liquid-phase exfoliation [6], chemical exfoliation [7] and chemical vapor deposition (CVD) [8]. Among them, CVD method is the most promising one to realize high-quality crystals and wafer-scale films. However, most CVD systems used for growing TMD monolayers only include one or two temperature zones. Temperatures of transition metal source, chalcogen source and substrate cannot be controlled independently if their positions are fixed. Moreover, transition metal source, for example moo$_3$ powder, is always put together with substrate in high temperature zone. This brings up an unintended process, MoO$_3$ powder will react with chalcogen source first and partially be reduced to MoO$_2$ powder.

To address the issues mentioned above, in this study, we demonstrate a chemical vapor deposition (CVD) growth of monolayer MoS$_2$ and MoSe$_2$ crystals using three-temperature-zone furnace. The thickness, morphology and grain size of crystals are tunable through control of growth pressure,
temperature and time. Raman and photoluminescence (PL) characterizations are used to confirm the monolayer thickness and high crystal quality. The MoSe$_2$ and MoS$_2$ monolayer crystals possess an excellent optical quality with very small full-width-half-maximum (FWHM) of 57 meV and 96 meV, which are comparable to that of exfoliated single-crystal monolayers [9]. Most importantly, the principles demonstrated on MoS$_2$ and MoSe$_2$ can be extended to growth of other TMD crystals or films.

2. Experimental section

2.1. Materials
Molybdenum (VI) oxide (MoO$_3$, 99.95%), sulfur pieces (S, 99.999%) and selenium powder (Se, 99.999%) were purchased from Alfa Aesar. All materials were used without further purification.

![Figure 1](image). (a) Schematic illustration of growth of monolayer MoS$_2$ or MoSe$_2$ crystals with 3-zones furnace. XRD patterns of MoO$_3$ powders after growth in (b) 2-zones and (c) 3-zones furnaces.

2.2. Growth of monolayer MoS$_2$ crystals
Typically, single crystal silicon substrates with a thermally deposited 300 nm thick silicon oxide (SiO$_2$/Si) were ultrasonically cleaned with acetone, ethyl alcohol and deionized water for 5 min, respectively. After that, the SiO$_2$/Si substrates were dried with compressed argon gas immediately, and placed at zone 3 as shown in Figure 1a. Two small quartz tubes respectively loaded with 500 mg of S and 10 mg of MoO$_3$ powder were put inside the chamber. The MoO$_3$ powder was located at zone 2 and S located at zone 1. Before heating, the chamber was pumped to 0.5 Pa and refilled with ultrapure argon gas three times to reduce oxygen contamination. Followed the last filling process, argon gas was reduced to 50 sccm as a carrier gas. Then, zone 1, zone 2 and zone 3 were respectively heated to 180 °C, 850 °C and 850 °C at the same time. After growing for 15 min under the atmospheric pressure (1 atm), the heating was stopped, and the furnace was opened immediately to rapidly cool down.

2.3. Growth of monolayer MoSe$_2$ crystals
Typically, like growth of MoS$_2$ mentioned above, SiO$_2$/Si substrate, 10 mg of MoO$_3$ and 500 mg of Se powders were placed at zone 3, zone2 and zone1, respectively. After pumping and refilling process, 50 sccm of argon and 5 sccm of hydrogen gases were introduced as carrier and reaction gases. During the growth, the temperatures of zone 1, zone2 and zone 3 were 340 °C, 850 °C and 750 °C, respectively. When growth was finished, the furnace was cool down rapidly.
2.4. Characterizations
The X-ray diffraction (XRD) patterns were recorded on Rigaku D/MAX-rA diffractometer with Cu Kα radiation. The room temperature Raman and photoluminescence (PL) spectra were recorded by using Horiba LabRAM HR spectrometer with laser wavelength of 532 nm. The optical microscope (OM) photographs were obtained by Olympus BX53 optical microscope.

![Figure 2. (a) OM images of growth resulted from different growth pressures: (a) 15 Pa, (b) 0.5 atm and (c) 1 ATM; different growth temperatures: (d) 850 °C, (e) 800 °C and (f) 750 °C and different growth time: (g) 10 min, (h) 15 min and (i) 20 min.](image)

3. Results and discussion
As shown in Figure 1a, in 3-zones CVD system with separate small quartz tubes, two kinds of sources evaporate independently without disturbing each other. The XRD patterns in Figure 1b and c demonstrate that the MoO₃ powder is not been reduced by S vapor using 3-zones CVD system compared with 2-zones furnace in which MoO₃ becomes MoO₂. It indicates that 3-zones furnace avoids unintended reaction and the growth process can be more controllable than 2-zones furnace.

Systematically study of the effects of growth pressure, temperature and time on the thickness, shapes and grain size of MoS₂ crystals is shown in Figure 2. Lots of square MoO₂ crystals appear if the growth pressure is ultralow due to the large evaporation of MoO₃. With pressure rising, triangle MoS₂ crystals begin to form, and the thickness decreases [10]. At atmospheric pressure, we get monolayer MoS₂ crystals with size of 50 µm. The morphology of monolayer MoS₂ crystals can be controlled by temperature of growth zone (zone 3). With temperature decreasing, the shape of monolayer MoS₂ crystals change from triangle to hexagram and hexagon due to the temperature dependent migration coefficient of adatoms on substrate [11]. With increasing growth time, the MoS₂ nucleation density decreases and the grain size increases. After 15 min growth, the surface of substrate is covered mainly by large monolayer MoS₂ crystals. Further growth leads to a continuous MoS₂ film resulted from linking together of many nearest-neighbour MoS₂, and MoS₂ crystals start to grown on the film.

To investigate the thickness of MoS₂, we select the sample which is in an intermediate state between crystals and film. Figure 3a clearly shows some connected triangle MoS₂ crystals. Point A is the first layer, AA’ stacking with the second layer (point B), and point C is AB stacked with point B [12]. Point D is thick MoS₂ crystals with yellow color. Figure 3b is the optical contrast profile in the
red channel of a color charge-coupled-device (CCD) camera, to estimate the sample thickness [13]. It is noticed that with each additional atomic layer, the contrast decreases by around 10% in few-layer MoS\(_2\) on silicon substrate with a 300-nm oxide layer. The preliminary estimation of the MoS\(_2\) layer number is further verified through Raman spectra shown in Figure 3c and d. The two most dominant peaks located around 382 and 404 cm\(^{-1}\) correspond to the in-plane vibration mode (E\(_{12g}\)) and put-of-plane vibration mode (A\(_{1g}\)). As reported earlier [10], the E\(_{12g}\) peak position has a red shift, while the A\(_{1g}\) peak position has a blue-shift with increasing layer thickness, resulting from the growing influence of interlayer coupling on the electron-phonon processes. Figure 3d shows the thickness-dependent E\(_{12g}\) and A\(_{1g}\) peak frequencies. The differences between E\(_{12g}\) and A\(_{1g}\) for point A, B, C and D are 19.5, 12.8, 24.6 and 25.4 cm\(^{-1}\), which is in good agreement with the CVD-grown 1L-, 2L-, 3L- and bulk MoS\(_2\) respectively [14].

![Figure 3](image)

**Figure 3.** (a) OM photograph of MoS\(_2\) crystals. (b) Optical contrast profile in the red channel of the CCD images along the line cuts marked in the inset. (c) Raman spectra from regions marked in (a). (d) The Raman peak frequency of A\(_{1g}\) and E\(_{12g}\) of MoS\(_2\) in (c).

To grow monolayer MoSe\(_2\) crystals, the temperature of zone 1 was set to 340°C to make sure that the saturated vapor pressure of selenium is same as sulfur. By optimizing the parameters slightly, monolayer MoSe\(_2\) crystals were successfully synthesized. Figure 4a shows the hexagon MoSe\(_2\) with

![Figure 4](image)

**Figure 4.** (a) OM photograph and (b) Raman spectrum of monolayer MoSe\(_2\) crystals.
average size of 10 µm. Figure 4b shows three characteristic peaks of MoSe\(_2\) monolayer: a sharp one at 239.3 cm\(^{-1}\) assigned to A\(_{1g}\) mode and two broads peaks at 248.9 and 285.6 cm\(^{-1}\) assigned to E\(_{2g}\) shear and E\(_{1g}\) modes, no B\(_{1g}\) peak exists [15].

It is well known that monolayer MoS\(_2\) and MoSe\(_2\) are direct band gap semiconductors and the quality and thickness of the crystal can be clearly assessed using PL measurements [4]. The blue line in Figure 5 shows one sharp PL peak at 640 and one broad peak at 684 nm, which respectively match the A (1.94 eV) and B (1.81 eV) direct-gap optical transitions of MoS\(_2\) [16]. The red line has a strong peak at 818 nm, corresponding to the direct gap of MoSe\(_2\) (1.52 eV) [15]. The FWHM of MoSe\(_2\) and MoS\(_2\) are found to be as small as 57 and 96 meV, which is comparable to that of exfoliated monolayers. The excellent optical quality confirms the monolayer thickness of as-grown MoS\(_2\) and MoSe\(_2\) and indicates their high crystal quality.

![Figure 5. PL spectra of monolayer MoS2 and MoSe2.](image)

4. Conclusion

We demonstrate a CVD growth of monolayer MoS\(_2\) and MoSe\(_2\) crystals using three-temperature-zone furnace. The thickness, morphology and grain size of crystals are tunable through control of growth pressure, temperature and time. Raman and PL characterizations confirm the monolayer thickness and high crystal quality. The PL characterizations indicate that the as-grown monolayer MoS\(_2\) and MoSe\(_2\) crystals possess excellent optical qualities with very small FWHM of 96 meV and 57 meV, respectively, which are comparable to that of exfoliated monolayers. It is easy to visualize our route might be extended to the growth of other TMDs monolayer crystals.

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