Vapor-Solid Growth of Molybdenum Disulfide Nanosheets

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Summary

The goal of this thesis is growth of high-quality molybdenum disulfide (MoS₂) nanosheets composed of a couple of monolayers. These materials are promising for nanoelectronic, optoelectronic, valleytronic, and energy harvesting devices. Its sizable bandgap in visible-light region and many other extraordinary electronic and optoelectronic properties make it a promising potential substitute of Si in conventional electronic application. In this thesis growth of single-crystalline MoS₂ nanosheets composed of a few monolayers using chemical vapor deposition is presented. The characterization of as-grown MoS₂ nanosheets are discussed thereafter, including optical microscopy imaging, Raman spectroscopy, and scanning electron microscopy imaging. Finally a summary chapter is presented.

CHAPTER 1

CRYSTAL STRUCTURE OF TRANSITION-METAL DICHALCOGENIDEs (TMDs)

In this chapter, the crystal structure of transition-metal dichalcogenides (TMDs) are discussed, mainly using molybdenum disulfide (MoS₂) as an example. The fundamental concepts of lattice systems and Bravais Lattices are reviewed before the unit cell and crystal structure of MoS₂ are discussed in detail.

1.1. Basic concepts of crystal structure (lattice system and Bravais lattices)

In crystallography, there are seven types of three-dimensional crystal lattice systems: cubic, tetragonal, orthorhombic, monoclinic, triclinic, trigonal and hexagonal as shown in Figure1.



Figure.1 Seven crystal lattice systems

In triclinic, trigonal, and hexagonal crystal systems, there is only one type of Bravais lattice. Meanwhile, there are two types of Bravais lattices in monoclinic crystal system: simple and base-centered; two types of Bravais lattices in tetragonal crystal system: simple and body-centered; three types of Bravais lattices in cubic crystal system: simple cubic, face-center cubic (FCC) and body center cubic (BCC); four different types of Bravais lattices in orthorhombic crystal system: simple, basecentered, body-centered and face-centered. Therefore, there are 14 different kinds of Bravais lattices, which describe the geometric arrangement and symmetry of lattice.

Cubic: The three nonequivalent Bravais lattices are simple cubic, body-centered cubic and face-centered cubic. The simple cubic lattice has one lattice point at each corner of cube. The atom is shared by the adjacent eight cubes so in each unit cell there is one atom; The body-centered cubic has one more lattice point in the center of cube therefore in each unit cell there are two atoms; The face-centered cubic has 6 more atoms at each center of 6 faces. These atoms are shared between 2 adjacent cubes so there are 4 atoms in total in each unit cell.

Cubic $\alpha = \beta = \gamma = 90^\circ$, a = b = c



Figure.2 Cubic Bravais lattice: Simple body-centered cubic and face-centered cubic

Tetragonal: Symmetry of a cube can be degenerated by stretching it into a rectangular prism. The height of rectangular prism is not equal to the side length of the square base. Such a symmetry group is the tetragonal group. So the tetragonal Bravais is constructed when the simple cubic Bravais lattice is stretched. But only one kind of centered tetragonal is constructed by stretching the body-centered and face-centered cubic lattice similarly because there is no distinction between the two stretched lattices.

Tetragonal $\alpha = \beta = \gamma = 90^\circ$, $a \neq c$



Figure.3 Tetragonal Bravais lattice: Simple tetragonal and body-centered tetragonal

Orthorhombic: Continuing to reduce the symmetry of the cube, one can degrade the symmetry in tetragonal lattices by stretching the square base into rectangles, obtaining a cuboid with three different lengths. The symmetry group of such a cuboid is the orthorhombic group. Simple orthorhombic Bravais lattice is produced by stretching one side of the square base in tetragonal lattice. One can also stretch the square base in tetragonal lattice along the diagonal, producing the base-centered orthorhombic. In the same way, body-centered orthorhombic and face-centered orthorhombic are constructed by reducing the point symmetry of the centered tetragonal lattice. **Orthorhombic** $\alpha = \beta = \gamma = 90^{\circ}$, $a \neq b \neq c$



Fig.4 Orthorhombic Bravais lattice: Simple orthorhombic, base-centered Orthorhombic, body-centered Orthorhombic and face-centered orthorhombic

Monoclinic: Distorting one rectangle faces in the orthorhombic lattices into a parallelogram, one can continue reducing the orthorhombic symmetry. The reduced symmetry group of is monoclinic group. Simple monoclinic lattice is produced by distorting either simple or base-centered orthorhombic Bravais lattice. In a similar way, centered monoclinic Bravais lattice is produced by distorting either the face-centered or body-centered orthorhombic Bravais lattices.



Figure.5 Monoclinic Bravais lattice: Simple monoclinic, base-centered monoclinic

Triclinic: By tilting the axis perpendicular to the other two faces, the symmetry of cube is completely destructed. Then, the only restriction is three pairs of opposite faces are parallel. The triclinic Bravais lattice is produced by distorting either monoclinic Bravais lattice in such way. The three primitive vectors in the lattice has no more relationships to one another. Thus, , triclinic lattice has minimum symmetry among all the Bravais lattice.





No.12 Simple Triclinic

Trigonal: the trigonal lattice has the symmetry produced by stretching a cube along a body diagonal. It is composed by three primitive vectors with equal length and equal angles with one another.

Figure.6 Triclinic Bravais lattice



No.13 Simple Trigonal



The hexagonal lattice has a right prism with a regular hexagon as the base. The simple hexagonal Bravais lattice is the only Bravais lattice in the hexagonal system.



No.14 Base centered hexagonal

Figure.8 Hexagonal Bravais lattice

1.2. Crystal structure of MX₂

The transition metal dichalcogenides are a group of materials which have the general formula MX₂, where M represents a group IV, V or VI transition metal element such as W and Mo, and X represents one chalcogen such as S and Se. The crystal structure of these materials consists of a sandwiched layer X–M–X by covalence-bond between atoms. Each metal-atom layer is sandwiched within two chalcogen-atom layers and the atoms are packed in hexagonal structure in each layer. The van der Waals interaction force holds the adjacent layers together weakly and forms different polytypes of the bulk crystal. The stacking orders and metal atom coordination are also different in each polytype. This is very similar as multiple graphene monolayers van der Waals bonded to graphite.

1.2.1. Overview of MoS₂ crystal structure

As one of the combination mentioned above, in the layered molybdenum disulfide (MoS₂), the MoS₂ hexagonal structure consists of covalently bonded Mo and S atoms. The Mo atom plane is sandwiched between two planes of S atom and forms a trigonal prismatic structure in three dimension space. Such S-Mo-S layered structure attached to each other through van der Waal forces construct the bulk MoS₂.

Naturally occurring MoS₂ has two polytypes, 2H and 3R. Both of them have the trigonal prismatic coordination. While there are two layers per unit cell stacked in the hexagonal symmetry in 2H-type MoS₂, there are three layers in each cell stacked in the rhombohedra symmetry in 3R-type MoS₂. In nature, the 2H-type shows stability and dominance in existence and 3R-type MoS₂ degrades to 2H-type upon heating.

There is another polytype of 1T- MoS₂ which is a metastable structure of MoS₂ under phase transformation when MoS₂ is produced from chemical Li-intercalation and exfoliation. In 1T MoS₂, the Mo atoms are located in an octahedral coordination. Similar to 3R-type MoS₂, 1T-phase MoS₂ is instable and when it's annealed under moderate-temperature, it transforms back to the 2H phase.

The three types of MoS₂ have different lattice structure, point group and space group, resulting in the different physical and electrical properties they have.

1.2.2. Crystal structure of 1H-MoS₂

In order to better understand the structure of 2H-MoS₂ and 3R-MoS₂, it is the first step to have a clear idea of the structure of 1H-unit cell and 1H-monolayer.

In 1H-MoS₂, the lattice constant a, which refers to the physical dimension between two S atoms in the same plane, is about 3.12Å according to local-density approximation (LDA) .The S-Mo bond length is 2.378 Å and the S-Mo-S angle is θ =81.68°. Based on these lattice constant value, one can calculate the 3D coordination positions of each atom in 1H type MoS₂ single cell.



Figure 9. Cell coordination of 1H type MoS₂ single cell

In the calculation, I set the center of 1H type MoS_2 single cell, the Mo atom(yellow ball in Figure 9), in the origin(0,0,0) and distance between two sulfur atoms(white balls in Figure 9) in the same plane is the constant length a according to definition. The distance between two layers of sulfurs, are defined as height h. Because of symmetry, the z position for all three sulfur atoms on the top layer, is h/2 and the z position for all three sulfur atoms at the bottom layer is -h/2. The x position, for three sulfur atoms, from left to right is correspondingly -a/2, 0, a/2. Regarding to the y positions, the sulfur atoms in the front, according to geometric calculation is

$$y = \frac{2}{3} * \sqrt{a^2 - (\frac{a}{2})^2} = \frac{\sqrt{3}}{3}a$$

The y positions of sulfur atoms at the back are calculated in the following way:

$$y = -\frac{1}{3} * \sqrt{a^2 - (\frac{a}{2})^2} = -\frac{\sqrt{3}}{6}a$$



Figure 10. 3D view of 1H unit cell and monolayer in 3Dmax

Structure of 1H-unit cell and 1H-monolayer which are illustrated in the figure 10. The left top structure is the 3D view of 1H-MoS₂ unit cell simulated in 3D max, the yellow balls represent the S atoms and the purple atom represents the Mo atom. The left middle structure is the top view of 1H unit cell where the yellow atoms are located at each corner of a equilateral triangle meanwhile the purple atom is in the center. The left bottom structure is the side view of 1H unit cell.

When the single unit cell is duplicated to form a 1H-monolayer, one obtains the 3D views of 1H-monolayer shown in the right part of Figure 10. The right top

structure is the 3D view of 1H-monolayer where a Mo atom plane is sandwiched between two S atom planes. The right middle structure is the top view of 1H monolayer where one can directly view the hexagonal structure which consists three S atoms and three Mo atoms. The right bottom figure is the side view of 1H monolayer.

1.2.3. Crystal structure of 1T-MoS₂

For 1T type MoS₂, it has tetragonal lattice structure and the point group is P4₂/mnm. Its space group number is 136. The lattice constant a is still 3.12 Å and the lattice constant c is about 5.993 Å, half the value of c in 2H-type MoS₂ and one-third the value of c in 3R-type MoS₂. The single cell in 1T MoS₂ is located in an octahedral coordination and therefore the Mo-S bond distance is $\frac{\sqrt{2}}{2}$ a, the distance between the two sulfur plane is $h = \frac{\sqrt{6}}{3}a = 0.8165a$ and the S-Mo-S angle is 90 °. The Figure 11 shows the cell coordination.



Figure 11. The left figure is the octahedral coordination and the right figure shows cell coordination of 1T type MoS₂ single cell

Similar to the calculation performed for 1H type MoS₂ single cell, the 1T structure MoS₂ coordination can be calculated simple by taking advantage of symmetry. Similarly, I set the Mo atom(yellow ball) in the origin as shown in the right part of

Figure11 and then, the sulfur atoms (white balls) at the top layer have the same coordination positions as those in 1H-MoS₂ unit cell. Then, rotated 180 degrees around axis z, the sulfur atoms coordination value at the bottom plane could be easily obtained.



Figure 12. 3D view of 1T unit cell and monolayer in 3Dmax

In the left middle of Figure12, the top view of 1T-MoS₂ unit cell is in form of a hexagonal structure. Six yellow atoms from two different layers are located at each corner of hexagon and the purple atom is located in the center. In the left bottom of the Figure 14, the side view of 1T-unit cell is in the shape of rhombus. The right part of Figure 14 shows the 3D view of 1T monolayer structure. From top view in right middle, the 4 atoms in red circles form a square, so it is a direct view of understanding the tetragonal lattice structure of 1T-MoS₂.



Figure 13. 3Dmax simulation of 1T-MoS₂ lattice structure

In 1T-MoS₂ structure, there are two layers of 1T-MoS₂ monolayer. According to the definition, one can find the lattice constant c of 1T MoS₂ visually, which is the distance between the two layers of Mo in the left part of Figure 13. The right part of Figure 13 shows the top view of MoS₂.

1.2.4. Crystal structure of 2H-MoS₂

For 2H-MoS₂ which is dominant and the stable structure, it has hexagonal lattice structure and the point group is P6₃/mmc. Its space group number is 194. The lattice constant of 2H t-MoS₂ has been widely calculated and reported. The lattice constant a is about 3.12Å according to local-density approximation (LDA) and the lattice constant c, which is the distance between the top layer and the bottom layer in each unit cell, is about 11.986 Å. The S-Mo bond length is 2.378 Å and the S-Mo-S angle is θ =81.68 °.



Figure 14. The left figure shows the unit cell of $2H-MoS_2$. The middle picture shows the monolayer structure of $2H-MoS_2$. The right figure is the top view of monolayer $2H-MoS_2$

In 2H-MoS₂ structure, there are two layers of 1H-monolayer. The Mo atom in the second layer is located at the projection position of the sulfur atom in the first layer. The bottom layer is the duplication of the first layer to show the repetition of the 2H-MoS₂ structure and better demonstrate the lattice constant c. The lattice constant c of 2H-MoS₂ is the distance between the first layer and the third layer in each unit cell. The value of c is a 11.986 Å. The Figure 14, from left to right, shows the unit cell of 2H-MoS₂, side view of 2H-MoS₂ and top view of 2H-MoS₂ monolayer.

1.2.5. Crystal structure of 3R-MoS₂

For 3R type MoS₂, it has rhombohedral lattice structure and the point group is R3m. Its space group number is 160.The lattice constant a is the same in 3R and 2H type MoS₂, 3.12 Å meanwhile the lattice constant c is about 17.979 Å. The single unit in 3R type MoS₂ is exactly the same as what was illustrated in 2H-MoS₂ case but the arrangement in different layers are different in 2H unit cell. In the 2H unit cell, the middle layer points to the opposite direction of the top and bottom layer. However in 3R MoS₂ unit cell, all the layers point to the same direction as shown in the following figures.



Figure 15. The left figure shows the unit cell of $3R-MoS_2$. The right figure is the monolayer structure of 3R type MoS_2

1.2.6. Crystal structure of other TMDs

The other TMDs have similar crystal structure as MoS_2 . For example, the crystal structure of $MoSe_2$, WS_2 have two types: hexagonal lattice with point group P6₃/mmc and space group 194 and rhombohedral lattice with point group R3m and space group 160 while WSe_2 only has hexagonal lattice structure. These structure are exactly the same as MoS_2 in atom arrangement but the lattice constants are different. Therefore, they share the similar property to MoS_2 .

CHAPTER 2

CHEMICAL VAPOR DEPOSITION GROWTH OF MoS₂ NANOSHEETS

In this chapter, growth of single-crystalline molybdenum disulfide (MoS₂) nanosheets composed of a few monolayers using chemical vapor deposition (CVD) is presented. A home-built chemical vapor deposition system was employed for the synthesis. An introduction section about the growth system is discussed first in this chapter, followed by the discussion on growth of MoS₂.

2.1. Introduction of the home-build CVD growth system

The home-built chemical-vapor deposition growth system is mainly composed of a high-temperature furnace, an integrated temperature control & power supply console, mass flow controllers (MFCs), gas lines, a vacuum pump, and a vacuum gauge. Both ambient-pressure growth and low-pressure growth can be implemented using this system.

The furnace in the home-build CVD system is a single-zone hinged tube furnace as shown in Figure 16. It has an operating temperature up to 1200 °C and allows a fast temperature ramping up rate up to 60 °C/min. The furnace is equipped with a thermocouple for temperature monitoring and feedback to the integrated temperature control & power supply console. The integrated temperature control & power supply console is shown in Figure 17.

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Figure 16. The high-temperature furnace in the home-build chemical vapor deposition system.



Figure 17. The integrated temperature control & power supply console for the high-temperature furnace.

The MFCs are used to control the gas flow.

A wide-range (~0.1 mTorr to atmosphere) vacuum gauge is employed to monitor the pressure of the CVD system. The gauge is equivalent to the integration of a Pirani gauge and a convection gauge.

2.2. Chemical vapor deposition (CVD) growth of MoS₂

MoS₂ composed of a few monolayers were grown with MoO₃ and S powder as sources on SiO₂-on-Si substrates using the home-built CVD system described early. Prior to the growth, the substrates were cleaned using acetone and isopropanol alcohol alternately for multiple times and then rinsed by deionized water. The substrates were inserted into a quartz tube in furnace and placed face-down above a quartz boat near the center of the furnace which contains MoO₃ (99.95% Alfa Aesar) powder while another crucible containing of S (99.5% Alfa Aesar) located upstream of the furnace. The S powder was heated separately either by a heating belt Figure 18 shows the schematics of the growth setup or near the edge of the furnace (which has a lower temperature than the center of the furnace). The base pressure of the CVD growth system was ~10 mTorr. The growth temperature (also MoO₃ source temperature) varies from 700 to 950 °C. The S source temperature is around 150 °C. The Ar gas flow ranges from 50 to 100 sccm. And After the growth, furnace cools down to room temperature.



Figure 18. Setup schematics of chemical vapor deposition growth of MoS₂.

The growth temperature dependent studies reveal that the optimum temperature for the high-quality single-crystalline triangular flakes growth under vacuum is in the range of 800 - 900°C. The S concentration in this process at a given time of the experiment depends on the position of S source relative to the substrates (which are near the center of the furnace), S source temperature, and heating up timing. The experiments demonstrate that, in the case of an insufficient sulfur supply, molybdenum oxysulfide rectangles nucleate and grow instead of MoS₂ triangles.

Chapter 3

Characterizations of as-grown MoS₂ nanosheets

In this chapter, the characterizations of two-dimensional MoS₂ nanosheets are discussed. Optical microscopy images show the morphology of MoS₂ nanosheets. Scanning electron microscopy images show the MoS₂ nanosheets in a high-resolution. Raman spectroscopy is employed for the analysis of the number of monolayers of MoS₂ nanosheets.

3.1. Optical Microscopy

The optical microscopy images of as-grown MoS₂ nanosheets were taken by Olympus microscopes.

Some early reported work on MoS_2 nanosheet growth in 2011-2012 were continuous "thin-film-like" POLYCRYSTALLINE nanosheet with significant amount of grain boundaries. Recently, more and more groups have successfully synthesized monolayer MoS_2 with single crystals in triangle shape. The largest single crystalline MoS_2 monolayer triangle is ~120 µm.

Despite the MoS₂ single crystalline triangles, there are many other intermediate patterns that we observed during characterization. These images offer us clear clues on further growth optimization. For example, some rectangle domains were observed, which were generally nucleated under insufficient sulfur concentration growth condition. With larger sulfur concentration supplied during the growth, the triangle shape gradually appear.

Figure 19 shows optical microscopy image of a representative sample of twodimensional single-crystalline MoS₂ triangle nanosheets. A clear density change of the MoS₂ triangle nanosheets from the region near MoO₃ powder source (left part in the image) to the region far away from the source (right part of the image). The left part of the image shows sparse distribution of MoS₂ triangles while the right part shows dense deposition with superposition of a few layers of MoS₂ triangle monolayers stacking together. The single-crystalline MoS₂ triangle grain has a lateral length 3- 5 μ m. Figure 20 shows optical microscopy image of another representative sample of two-dimensional single-crystalline MoS₂ triangle nanosheets. The single-crystalline MoS₂ triangle nanosheets. The single-crystalline MoS₂ triangle nanosheets.



Figure 19. Optical microscopy image of a representative sample of twodimensional single-crystalline MoS_2 triangle nanosheets. The single-crystalline MoS_2 triangle grain has a lateral length 3-5 μ m.



Figure 20 Optical microscopy image of second representative sample of twodimensional single-crystalline MoS_2 triangle nanosheets. The single-crystalline MoS_2 triangle grain has a lateral length up to ~13 µm.

Figure 21 shows the optical microscopy image of a representative sample under insufficient S growth condition. The nanosheets in the sample show rectangular shapes.



Figure 21 Optical microscopy image of a representative sample under insufficient S growth condition.

3.2. Raman Spectroscopy

Figure 22 shows the Raman spectrum of a representative sample of singlecrystalline MoS₂ triangle nanosheets. The two characteristic peaks E_{2g}^1 and A_{1g} in the Raman spectrum locate at 386.1 cm⁻¹ and 406.3 cm⁻¹, respectively. The strongest peak arise from the Si substrate underneath. The distance between E_{2g}^1 and A_{1g} Raman peaks indicate the MoS₂ nanosheets are composed of monolayers and bilayers.



Figure 22. Raman spectrum of a representative sample of single-crystalline MoS₂ triangle nanosheets composed of 1-2 monolayers. (Accredit to Bo Hsu in YANG Research Group.)

Besides from MoS₂, several intermediate compounds frequently observed during the growth optimization. They show significantly different morphology and Raman spectra comparing to the MoS₂ nanosheets. Figure 23 shows the Raman spectrum of a representative sample with MoO₂ nanoflakes. MoO₂has a characteristic peak at ~750 cm⁻¹



Figure 23. Raman spectrum of a representative sample with MoO₂ nanoflakes. (Accredit to Bo Hsu in YANG Research Group.)

Figure 24 shows the Raman spectrum of a representative sample with MoOS₂

nanoflakes, which shows the characteristic Raman peaks from both MoS₂ and MoO₂.



Figure. 24 Raman spectrum of a representative sample with MoOS₂ nanoflakes. (Accredit to Bo Hsu in YANG Research Group.)

3.3 Scanning electron microscopy

Figure 25 shows the scanning electron microscopy (SEM) image of a

representative sample of two-dimensional single-crystalline MoS₂ triangle

nanosheets. The optical microscopy image of this sample is shown in Figure 19.

WD15.2mm 5.00kV x1.2k IMS SE tem.

Figure 25. SEM image of a representative sample of two-dimensional singlecrystalline MoS₂ triangle nanosheets. The optical microscopy image of this sample is shown in Figure 19. (Accredit to Ketaki Sarkar in YANG Research Group.)

In this chapter, three kinds of characterization of representative samples of twodimensional single-crystalline MoS₂ triangle nanosheets are discussed, including optical microscopy imaging, Raman spectroscopy, scanning electron microscopy. These characterizations are important to analyze the as-grown single-crystalline MoS2 nanosheets.

Chapter 4

SUMMARY

Two-dimensional single-crystalline MoS₂ triangle nanosheets composed of a couple of monolayers were grown using a home-built CVD system. Optical microscopy images and SEM were employed for the morphology study of the asgrown MoS₂ nanosheets. Raman spectroscopy studies confirm the mono- and bilayer nature of the as-grown MoS₂ nanosheets. The synthesized two-dimensional single-crystalline MoS₂ nanosheets are promising for various device applications.

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