Recent Advances in the Synthesis and Structural Engineering of Two-Dimensional Transition Metal Dichalcogenides

Yiqiu Li *

Chemical Engineering and Technology, Tiangong University, Tianjin, China

* Corresponding Author Email: yiqiu5999@gmail.com

Abstract. Due to their unique layered atomic configuration, adjustable band structure, and excellent exciton physical properties, two-dimensional transition metal chalcogenides (TMDs) have shown great application potential in the fields of next-generation nanoelectronic devices, optoelectronic devices, and flexible catalysis, and have become the focus of materials science and condensed matter physics research in recent years. This paper systematically sorts out the key progress of TMDs in high-quality synthesis and multi-dimensional structure regulation in recent years. In terms of synthesis strategies, the efficiency optimization of mechanical stripping, the kinetic mechanism of salt-assisted growth in chemical vapor deposition (CVD), the atomic-level precision control of molecular beam epitaxy (MBE), and the advantages of the liquid phase method in large-scale preparation are discussed. In terms of structural regulation, the influence of layer-dependent energy band evolution on carrier transport, metal-semiconductor phase transitions brought about by phase structure engineering, and novel quantum physical properties induced by Van der Waals heterojunction and Mohr superlattice construction are deeply analyzed. Finally, this paper summarizes the current problems of large-area single crystal preparation stability, interface integration challenges, and process compatibility, and aims to clarify the research direction of high-quality TMD materials from laboratory preparation to industrial application in the future, to provide a reference for subsequent research in this field.

Keywords: Two-dimensional materials; transition metal chasoides; structural regulation.

1. Introduction

Transition metal dichalcogenides (TMDs) are important components in optoelectronic functional material systems. TMDs are a class of typical low-dimensional semiconductor materials with layered structure characteristics, and the unique crystal configuration makes them show obvious low-dimensional structural effects when the thickness is reduced to a single layer, and some materials are transformed from indirect band gaps in the bulk phase to directbandgap semiconductors, and the electronic structure and physical properties change significantly. When the thickness is reduced to a single layer, TMDs show obvious low-dimensional structural effects, and some materials realize the transformation from an indirect bandgap to direct bandgap, which greatly improves the photoluminescence efficiency. At the same time, TMDs have extremely high specific surface area, atomic-level flat interfaces, and adjustable wide energy bands, making them extremely potential for the development of ultra-thin, flexible FETs, high-sensitivity photodetectors, and high-performance spintronics devices.

In addition, its excellent chemical stability and electrocatalytic activity also make it an ideal material for the field of new energy conversion and storage. This paper reviews the main research progress in this field in recent years, focusing on the synthesis methods and structural regulation techniques of two-dimensional transition metal chalcogenides, and discusses the effects of different preparation strategies on the formation and regulation of material structure. The purpose is to clarify the future research direction of high-quality TMDs preparation and precise regulation.

2. Structural Basis of Two-Dimensional Transition Metal Chalcogenides

2.1. Structural Structure and Structural Defects of Two-Dimensional Transition Metal Chalcogenides 2D

TMDs are layered semiconductors. The transition metal atoms and two layers of chalcogenide atoms are wrapped in the middle in the form of a sandwich structure to obtain an X–M–X–type atomic structure. The atoms in the layer are stabilized by strong covalent bonds. Only van der Waals action is stacked between layers, and weak coupling allows materials to be stripped to monoatomic layers [1]. The layer spacing was 0.6~0.7 nm. This size leaves room for atomic and molecular insertion, which is conducive to intercalation reactions and the engineering of phase structure.

TMDs exhibit a rich variety of polycrystalline phase structures, primarily categorized into three types: the semiconducting 2H phase with trigonal prismatic coordination, the metallic 1T phase with octahedral coordination, and the distorted octahedral 1T' phase. The 2H phase represents the stable ground state of MoS2 and WS2. The 1T phase is mainly induced by alkali metal intercalation or electron beam irradiation. Differences in crystal phases manifest in stacking and band structures, leading to significant variations in conductivity, catalytic activity, and magnetic behavior depending on the phase state [2].

Two-dimensional transition metal dichalcogenides typically exhibit several crystal phases, the most widely studied being the semiconducting 2H phase, the metallic 1T phase, and an intermediate 1T' phase. The 2H phase is the most stable configuration for materials like MoS2 and WS2, while the 1T phase generally requires external stimuli such as alkali metal intercalation or electron beam irradiation to induce its formation. Different phase structures exhibit fundamental differences in atomic arrangements and electronic properties, leading to variations in conductivity, catalytic activity, and magnetic behavior as the phase structure changes.

Structural defects are a fundamental characteristic of TMDs. They influence carrier scattering, fluorescence properties, and surface reactivity. Moderate defects can enhance electrocatalytic performance. This phenomenon has made defect engineering a research hotspot [3]. Understanding multi-level structures lays the foundation for research. Only by clarifying structural features can efficient synthesis and precise regulation studies be conducted.

2.2. Control Methods for Two-Dimensional Transition Metal Chalcogenides

In recent years, phase engineering has aimed to induce controlled reversible transformations of TMDs between different crystal phases (such as 2H, 1T, 1T ') through external stimuli or chemical modifications, thereby endowing materials with vastly different conductivity and catalytic activity [1]. This transformation not only regulates the electronic structure of materials but also provides theoretical support for the preparation of new phase change memory devices and efficient electrocatalysts. When the thickness of the material decreases to a single layer, its electronic structure undergoes a fundamental change. Taking MoS2 as an example, the bandgap of bulk materials is about 1.2 eV, and single-layer MoS2 becomes a direct bandgap semiconductor (about 1.8 eV), resulting in significant photoluminescence efficiency, making it one of the research hotspots in the field of optoelectronics for single-layer TMDs [3]. Similarly, materials such as WSe2 and MoSe2 also exhibit direct and indirect bandgap transitions, and the bandgap width can be precisely adjusted through strain engineering or electric field control. The existence of opposite spin valley locking properties between K and K 'valleys in single-layer TMDs is the physical basis of valley electronics research.

From the perspective of phase structure, two-dimensional transition metal chalcogenides generally have multiple crystal phases, with the most commonly studied being the semiconductor type 2H phase (triangular prism coordination, D ∝ h symmetry), the metallic 1T phase (octahedral coordination, Oh symmetry), and the 1T 'phase in between (distorted octahedral coordination). The 2H phase is the most stable configuration of materials such as MoS2 and WS2, while the 1T phase generally requires intervention from external factors to generate. In addition, the conductivity, catalytic activity, and magnetic behavior of materials also undergo significant changes with changes in phase structure.

3. Synthesis Methods of 3D Transition Metal Chalcogenides

3.1. Mechanical Peeling Method

The mechanical exfoliation method is the most direct way to obtain high-quality two-dimensional TMDs. In recent years, researchers have significantly improved stripping efficiency through interface energy regulation. For example, Liu et al.'s research team optimized the Au-assisted exfoliation method, which utilizes the strong covalent bonding between gold atoms and chalcogenides to achieve a centimeter-level (about 1 cm^2) large-area monolayer MoS_2 exfoliation with a monolayer rate close to 100% [4]. Experimental data show that the carrier mobility of single-layer WS_2 peeled off by this method can be maintained at 30-60 $cm^2/(V \cdot s)$ at room temperature, and its photoluminescence (PL) intensity is one order of magnitude higher than that of traditional tape peeled samples, demonstrating its advantage in maintaining lattice integrity. [1]

3.2. Chemical Vapor Deposition Method

Chemical vapor deposition (CVD) is the mainstream method for achieving large-area preparation. The current focus of improvement is to increase growth rate and grain size through adjuvants. Jiang et al. proposed in their study the use of molten salts (such as NaCl, KI) as growth promoters, which significantly reduces the melting point of precursors (such as MoO3) and broadens the growth window [5]. The quantitative results show that after adding alkali metal halides, the domain size of single crystal MoS_2 jumps from the traditional tens of micrometers to over 500 μm, and the growth rate increases by nearly 10 times [6].

To meet the needs of industrialization, Xue et al. utilized metal organic chemical vapor deposition (MOCVD) technology, using molybdenum hexacarbonyl as a precursor, to achieve uniform thickness and height growth of TMDs thin films on 2-inch or 4-inch wafers, with layer thickness fluctuations controlled within 5%, providing key technical support for the integration of large-scale logic circuits [7, 8].

Researchers such as Zavabeti used a liquid metal-assisted strategy to perform CVD growth on the surface of molten metal. Due to the absence of fixed lattice sites on the liquid surface, the nucleation density was reduced by 2-3 orders of magnitude, resulting in the preparation of single crystals with ultra-high mobility, which can approach the theoretical limit at room temperature [9].

3.3. Molecular Beam Epitaxy Method

Molecular beam epitaxy (MBE) exhibits outstanding precision control due to its ultra-high vacuum environment. MBE has significant advantages in the preparation of magnetic TMDs or complex heterojunctions. For example, Wang et al. used MBE to precisely control the number of layers in a single atomic layer while studying van der Waals heterostructures, effectively suppressing the introduction of oxide impurities [10]. Quantitative characterization shows that the interface roughness of epitaxial thin films grown by MBE is less than 0.2 nm. Clear atomic-level layer-by-layer growth signals can be observed using in-situ RHEED monitoring, which is superior to other synthesis methods in constructing atomic-level sharp interfaces [11].

3.4. Liquid Phase Exfoliation and Solution Method

The liquid-phase method has an absolute advantage in terms of yield. The current research focuses on improving material quality through solvent engineering and low-temperature processes. High-yield exfoliation is achieved by the research team of Gu et al. using the interlayer intercalation method. The concentration of exfoliated MoS_2 nanosheets in solution can reach 1-10 mg/mL, which is suitable for the preparation of large-scale catalytic electrodes [3].

Flexible low-temperature processing, developed by researchers such as Zavapeti, successfully achieved direct deposition of TMDs thin films on flexible substrates such as polyimide (PI) using low-temperature solution methods (below 100 ° C) [9,12]. Although its migration rate is usually between 0.1-1 $cm^2/(V \cdot s)$, which is lower than the CVD method, its bending cycle can reach more

than 10000 times without performance degradation, greatly expanding its application scenarios in wearable electronic devices.

4. Structural Control of TMDs

4.1. Layer Regulation

Layer control is one of the most direct methods for optimizing the performance of TMDs. The band structure of TMDs has undergone a transition from an indirect band gap to a direct band gap, from the bulk phase to a few-layer phase, and then to a single layer. The exciton binding energy has significantly increased, and the photoluminescence efficiency has also been greatly improved. For the application of field-effect transistors, single-layer or double-layer TMDs often exhibit better switching ratios and lower subthreshold swings, which are crucial for the design of next-generation low-power logic devices [9].

There are two main methods for achieving precise layer control: one is to control the growth parameters (temperature gradient, precursor flow rate, growth time) to control the number of thin film layers; The second is to use controllable etching techniques (plasma etching or laser etching) to thin the already formed multi-layer samples layer by layer. The former has better large-area uniformity, while the latter has higher local accuracy. In recent years, researchers have utilized self-limiting growth mechanisms to select a combination of substrates and precursors, achieving controlled CVD growth that spontaneously terminates in a single layer, providing new ideas for precise layer control [12].

4.2. Defective Engineering

Defect engineering is the most active research direction in the field of TMDs structural control in recent years. Adopting the method of actively introducing or eliminating special defects to regulate the electrical, optical, and catalytic properties of materials. Excessive sulfur vacancies can cause n-type doping effects in MoS2, resulting in defect states in the bandgap and affecting fluorescence efficiency and carrier mobility [3]. On the contrary, annealing the sample in an atmosphere containing sulfur can improve the sulfur vacancy condition and restore the material to its original properties.

Ion beam irradiation (He^+, Ar^+ beam) is currently the most widely used method for introducing active defects, which can quantitatively control the density of defects. Lin et al. [2] studied the defect evolution of MoS_2 under different irradiation conditions and found that low-dose irradiation can maintain the basic integrity of the crystal while controlling the local magnetic moment. Plasma treatment (O_2 or N_2 plasma) can introduce corresponding functional groups on the surface of TMDs, which can improve the metal contact performance and enhance the electrocatalytic activity. In addition, adding some doping precursors in CVD can actively adjust the carrier type and concentration, providing a pathway for the preparation of homogeneous p-n structures [7].

4.3. Phase Structure Engineering

TMDs have a variety of crystalline phases, and different phases will bring significant changes in the conductivity and chemical activity of the material. The main purpose of phase engineering is to control the reversible phase transition and provide adjustable functions to the material [1].

At present, the main methods to achieve phase transition are as follows: Alkali metal intercalation is a classic method to induce the 2H→1T phase transition, but the resulting 1T phase is thermodynamically metastable and is prone to reversible regression when exposed to air. Electrochemical methods can provide a more gentle and controllable method to achieve local phase transitions by applying specific polarization potentials, and can be controlled in reverse, opening up new ideas for devices such as phase change memory[10].

4.4. Van Der Waals Heterostructures

Van der Waals heterostructures (vdWHs) refer to artificial multilayer structures formed by physically stacking different two-dimensional materials, where layers are coupled by van der Waals forces rather than chemical bonds. Therefore, it has such interface properties that different materials can integrate without considering lattice matching issues, greatly increasing the space for designing material combinations [8]. The commonly used TMDs-based vdWH systems include MoS_2/WSe2, MoSe2/WSe2, TMDs/h-BN, TMDs/graphene, etc. There are abundant physical phenomena such as charge transfer, exciton coupling, and Moiré superlattices at the interfaces of these systems.

In recent years, Moiré superlattices have become an important frontier direction in vdWH research. When two layers of TMDs with similar lattice constants are stacked at a small angle, periodic Moiré patterns are generated at the interface, forming a nanoscale potential field modulation that confines charge carriers within the Moiré unit cell, achieving new quantum states such as Hubbard-like physics, strongly correlated states, and even Moiré exciton lattices [13]. In recent years, the related electronic behaviors such as insulating states and superconducting precursor states that appear in TMDs heterojunction Mohr superlattices, such as MoSe2 and WSe2, have also been reported, bringing new impetus to the research of TMDs-based quantum materials.

The traditional layer-by-layer mechanical transfer method in the preparation of vdWH can achieve good interface quality, but its efficiency is very low. The fully CVD method developed in recent years for direct growth of heterostructures, such as the in-situ growth of WSe_2 from grown $MoSe_2$, provides a new approach for large-area and integrated vdWH device arrays. One of the main technical challenges in this field is the removal of residual organic matter at the interface and the precise control of torsion angle [14].

5. Main Challenges and Prospects

In summary, significant progress has been made in the synthesis methods and structural control of two-dimensional transition metal chalcogenides, but this field still faces deep-seated technical challenges.

Firstly, the collaborative use of multiple preparation routes and structural engineering methods provides an effective approach for precise control of material properties. However, the repeatability of large-area high-quality preparation, the long-term stability of structural control states, and the compatibility with existing device processes are the main issues currently present in this field [9, 10, 14].

The structural consistency and performance loss of wafer-level single-crystal thin films are still the biggest obstacles in the preparation end. Although Jiang et al. achieved leapfrog growth of single-crystal domains using salt-assisted methods, it remains challenging to completely suppress wrinkles and eliminate grain boundary defects in large-scale epitaxial growth. According to the research of Luo et al., due to the thermal strain mismatch of the substrate, the carrier mobility of large-area thin films often only reaches 30% -50% of that of laboratory micrometer-level samples [6]. This significant performance loss directly limits its application in high-performance CMOS integrated circuits [7].

Secondly, the stability of the environment and the long-term effectiveness of functionality are also issues that exist regarding the application of componentization. 2D TMDs are highly prone to local oxidation in air. Xue emphasized in the review that although current physical packaging strategies can alleviate degradation, they have not yet achieved intrinsic thermodynamic stability [9]. To address this issue, how to construct high-quality and non-destructive gate dielectric integrated interfaces while maintaining the atomic level thickness of TMDs like traditional silicon processes remains the core direction of future structural engineering [8].

Finally, the atomic-level precision and integration complexity of heterojunction interfaces cannot be ignored. The research on Moiré superlattices mentioned by Xiao et al. requires extremely high accuracy in torsion angle [13]. Currently, in large-scale preparation, it is still very difficult to achieve

centimeter-level and uniform twist angle heterojunctions due to the bubble effect and interlayer contamination at the van der Waals interface.

With the continuous development of growth technology and characterization methods, two-dimensional TMDs will play an increasingly important role in new electronic devices, optoelectronic sensing, and quantum information, while also having great potential for exploration. The use of an automated synthesis system consisting of artificial intelligence (AI) and robotic arms for real-time adjustment of growth parameters is expected to break through the limitations of traditional "trial and error" methods and achieve a leapfrog improvement in material quality [11].

6. Conclusion

This paper systematically reviews the main research progress in this field in recent years, focusing on the structural characteristics, synthesis methods, and structural regulation strategies of TMDs. At the structural level, TMDs have a typical sandwich layered configuration, with strong covalent bonds within the layers, and stacked by the van der Waals force between layers, giving them peelability and intercalation reactivity. There are various crystalline phases, such as 2H and 1T, in the material. When the thickness drops to a single layer, semiconductor TMDs undergo indirect-direct bandgap transitions, the photoluminescence efficiency is significantly improved, and the spin-valley locking characteristics are exhibited, which is an important physical basis for the study of valley electronics.

At the synthesis method level, mechanical stripping is still an important means to obtain high-quality TMDs samples due to its simple and efficient advantages, and CVD and its improved processes have become the mainstream route for large-scale, controllable preparation, such as salt-assisted CVD, MOCVD, and other methods. Molecular beam epitaxy (MBE) plays an irreplaceable role in the exploration of magnetic and superconducting TMD systems due to its precise layer number and interface control advantages. The liquid phase stripping and solution thermal synthesis methods meet the application needs of catalysis and composites with the characteristics of low cost and large volume.

At the level of structural regulation, the number of layers is controlled to optimize the optoelectronic properties of materials by changing theenergy band structure. Phase structure engineering induces reversible phase transitions through alkali metal intercalation, electrochemical polarization and femtosecond laser, which provides avariety of methods for functional regulation. Van der Waals heterostructures break through the lattice matching limitations through the physical stacking of different two-dimensional materials, and construct a new quantum system with rich interface physics andMoiré superlattice effects. The comprehensive application of theabove regulatory strategies has laid an important foundation for thepractical application of TMDs in the fields of new electronic devices, photoelectric detection and quantum information.

References

[1] Lau C S, Lee S K, Ng M F, Lin Y C, Cao K, Yang Z, Liu Z. Dielectrics for two-dimensional transition-metal dichalcogenide applications. ACS Nano, 2023, 17(11): 9870-9905.

[2] Liang Q, Wang Q, Zhang Q, Wei J, Lim S X, Zhu R, Hu J, Wei W, Li C, Loh K P. Defect engineering of two-dimensional transition-metal dichalcogenides: Applications, challenges, and opportunities. ACS Nano, 2021, 15(2): 2165-2181.

[3] Gu M, Shi S, Li Y, Wu X, Liu Y, Zhang W, Zhang Q. Molecular modulation strategies for two-dimensional transition metal dichalcogenide-based high-performance electrodes for metal-ion batteries. Chemical Science, 2024, 15(7): 2323-2350.

[4] Wu F, Chen J, Fan P, Mo B, Qu Z, Chen Y, Zhang Y. Formation of coherent 1H–1T heterostructures in single-layer MoS2 on Au (111). ACS Nano, 2020, 14(12): 16939-16950.

[5] Jiang D, Wang J, Yang P, Cong C, Zhang J, Sun L, Wu X J. Self-expanding molten salt-driven growth of patterned transition-metal dichalcogenide crystals. Journal of the American Chemical Society, 2022, 144(19): 8746-8755.

[6] Luo P, Fang H, Zhao S, Xu L, Liu K. Wafer-scale growth of two-dimensional transition metal dichalcogenides: Progress, challenges, and opportunities. Nano-Micro Letters, 2024, 16(1): 1-35.

[7] Xue G, Xu Y, Chen Y, Liu Z, Zhang Y. Large-area epitaxial growth of transition metal dichalcogenides. Chemical Reviews, 2024, 124(17): 9785-9865.

[8] Zhu J, Wang Z, Zhang Y. Interface engineering in van der Waals heterostructures: From atomic precision to device integration. Nature Reviews Materials, 2024, 9: 120-145.

[9] Zavabeti A, Jannat A, Zhong L, Haidry A A, Yao Z, Ou J Z. Two-dimensional materials in large-areas: Synthesis, properties and applications. Nano-Micro Letters, 2020, 12(1): 66.

[10] Wang P, Jiang J, Wang X. Van der Waals heterostructures by design: From 1D and 2D to 3D. Matter, 2021, 4(2): 552-581.

[11] Sato K, Tanaka S, Yamamoto M. Machine learning-assisted synthesis and characterization of 2D materials. Chemical Reviews, 2024, 124(5): 2500-2545.

[12] Huang L, Xu W, Li S, Zhang G. Salt-assisted synthesis of 2D materials. Advanced Functional Materials, 2020, 30(19): 1908486.

[13] Xiao Y, Liu J, Fu L. Moiré is more: Access to new properties of two-dimensional layered materials. Matter, 2020, 3(4): 1142-1161.

[14] Sun X, Huang J, Ma C, Sun Z, Lau S P. Recent advances in two-dimensional heterostructures: From band alignment engineering to advanced optoelectronic applications. Advanced Electronic Materials, 2021, 7(7): 2001174.