Advanced 2D Materials
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Advanced 2D Materials

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Masses of strongly bonded layers with very weak interlayer attraction exist in two-dimensional (2D) materials, which permit exfoliation into separate, atomically thick layers. Such super-thin surface percolates free electronic movements in the 2D planes and regulates motion in the third plane with a nanometer thickness. Graphene, transition metal dichalcogenides (TMDs), diatomic hexagonal boron nitride (h-BN), and emerging monoatomic buckled crystals collectively termed Xenes, which include silicene, germanene and phosphorene, are all covered in this book. The integrated unique properties of these different 2D materials therefore provide numerous possibilities to shape the future of advanced technology.

One of the possibilities is to create 2D materials by separating layered structures which are held together by weak van der Waals forces. Chapter 1 describes the various approaches used to fabricate and characterize gallium selenide and demonstrates device characteristics. The challenges associated with high growth rates to obtain atomically thin layers instead of multilayers are balanced by the possibility of controlling the shape of the gallium selenide or even exploring the stacking of 2D materials by growth on graphene. The tunable bandgap and change with number of layers create challenges in the characterization of nonlinear optical properties. The chapter ends with an overview of studies on field effect transistor and photodetector using gallium selenide. In Chapter 2, the stronger interlayer interaction in boron nitride and the difficulties in fabrication compared with graphene are described, and a range of growth approaches are also detailed. The difficulty in growth arises due to the partial ionic B-N bonds caused by the difference in electronegativity between nitrogen and boron. Ultimately this creates chemical bonds between the layers and has a strong impact on the control of the number of layers in boron nitride nanosheets.

The influence of the substrate on graphene and molybdenum disulfide is presented in Chapter 3. Defects and dangling bonds appear due to growth conditions and surface preparation. These are mostly undesired, but in some cases they may be used for internal engineering of the 2D material with the substrate. The uncertainty in the conductivity, for example,
as either n- or p-type character, possibly caused by vacancies or interface properties, is an unclear issue in molybdenum disulfide. In particular, the interface has a strong impact since the 2D materials are only atomically thick. In perspective, the functionalization of the substrate with the 2D materials opens up ways to design devices once the properties are understood. Insights into the properties of 2D materials can be guided by modeling, as presented in Chapter 4 in which the Hubbard model is introduced. The results from the calculation of conductivity in one dimension are used to explore the conductivity in two dimensions. The chapter overviews previous work and in some instances extends the results of the calculations.

In Chapter 5, polymer-matrix nanocomposites for graphene derivatives are reviewed. The fabrication methods of the composites are presented. Their effect on electrical and thermal conductivity, as well as barrier properties, is shown to depend on characteristics like flake size, aspect ratio, loading, dispersion state, and alignment of nanoplatelets within the polymer matrix. As a potential field for further synergetic effects of polymers, the combination of carbon nanofillers with one or two dimensions has been raised. A nanoscale multifunctional platform using polymers and graphene oxide is given in Chapter 6. The nucleation and growth mechanisms of metallic nanoparticles depend on the degree of oxygen functionalization at the surface of graphene oxide. In addition, the graphene oxide can be given additional functionality by surface modification using a variety of polymers. The number of oxygen groups can mediate the type of binding interaction between the surfaces of graphene and graphene oxide and biomolecules to be used, for example, in tissue engineering. Graphene oxide for cleansing water or as mechanical reinforcement in structural applications is also discussed.

Chapter 7 highlights composites of graphene and zinc oxide as photocatalysts which are combined with the manufacturing capability of zinc oxide and the oxygen functionality of graphene oxide. This slows down the charge carrier recombination and improves the photooxidation since the charge transfer is more effective via the graphene. The reduced oxygen activity may also have an enhanced positive effect on the photostability given by the interaction between the graphene and zinc oxide. In addition, some ternary hybrid structures are discussed. Polymer grafting as a means of reducing the agglomeration of graphene oxide which may occur during use is presented in Chapter 8. Both covalent and noncovalent approaches are described. The range of polymers for grafting is increased by using initiators on the surface of graphene for subsequent polymer generation, or by preformed polymers which are attached to the oxygen groups on the surface of graphene oxide. The nanocomposites may also be fabricated
using electrostatic interaction between modified graphene and a polymer, or by hydrogen bonding on the surface of graphene oxide.

In Chapter 9, hybrid structures of graphene and semiconductors are reviewed for use as photocatalysts. Graphene has the effect of increasing the mobility of electrons on the surface as well as enhancing the visible light absorption range of the semiconductor. These properties are reviewed with respect to water splitting and carbon dioxide conversion to liquid fuel. The bandgap of graphene oxide provides a way of making p-n junctions for separation of carriers as well as increasing the range of absorption of the solar spectrum. Further on, sensor design from graphene is described in Chapter 10. Fabrication, properties and applications of three graphene types are considered: pristine, nanocomposite and functionalized forms.

A review of graphene composites for biomedical applications is given in Chapter 11. Optical- and non-optical-based imaging is introduced and drug delivery and tissue engineering are described. Finally, bioceramic nanocomposites for orthopedic applications are presented in Chapter 12. The use of hard tissue rehabilitation materials creates a need for having a bone graft material with good mechanical and biological responses. Hydroxyapatite provides a suitable surface for bone growth and integration but has poor fracture toughness and wear resistance. Therefore, the chapter presents graphene as a secondary material in hydroxyapatite to improve the physical and biological properties.

In summation, this book brings together innovative methodologies and strategies adopted in the research and development of advanced 2D materials. Well-known worldwide researchers deliberate subjects on (1) synthesis, characterizations, modeling and properties, (2) state-of-the-art design and (3) innovative uses of 2D materials. The book is written for readers from diverse backgrounds across the fields of chemistry, physics, materials science and engineering, nanoscience and nanotechnology, biotechnology, and biomedical engineering. It offers a comprehensive overview of cutting-edge research on 2D materials and technologies.

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Part 1
SYNTHESIS, CHARACTERIZATIONS, MODELING AND PROPERTIES
Two-Dimensional Layered Gallium Selenide: Preparation, Properties, and Applications

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Abstract

Gallium selenide (GaSe) is a layered III–VI semiconductor. It consists of covalently bonded stacks of four atomic layers in the sequence of Se–Ga–Ga–Se to form the tetra layers that are held together by a weak interaction of the van der Waals (vdW) force. The layered structure suggests the possibility of existence of two-dimensional (2D) GaSe like its pioneer graphene. Besides micro-mechanical exfoliation, 2D GaSe sheets can be obtained by various methods of vapor-phase mass transport, vdW epitaxy, molecular beam epitaxy, and pulse laser deposition. The fabricated 2D GaSe flakes have a tunable indirect band gap which is little lower than their direct counterpart. For monolayer, the experimental value of mobility is about 0.6 cm\(^2\) V\(^{-1}\) s\(^{-1}\) according to the transport properties of field-effect transistors (FETs). As expected, the 2D GaSe flakes exhibit layer-dependent nonlinear optical properties. The fabricated GaSe layers can enable the design of electronic and optoelectronic devices to realize functional applications of FETs and photodetectors. In this chapter, we focus on the scientific progress of 2D layered GaSe crystals to date, including various synthesis methods, characterization techniques, and electrical and optical properties as well as electronic and optoelectronic applications.

Keywords: Gallium selenide, two-dimensional materials, optoelectronic, field-effect transistors, photodetectors
1.1 Introduction

Two-dimensional (2D) layered materials have drawn extensive attention since the discovery of graphene through the method of mechanical exfoliation by Geim’s group in 2004 [1]. Graphene, with its unique 2D layered structure, exhibits outstanding and fascinating electronic, thermal, optical, and mechanical properties [2, 3]. Single-layer graphene has an ultra-high intrinsic mobility (200 000 cm$^2$ V$^{-1}$ s$^{-1}$) [4] and electrical conductivity [5, 6], excellent thermal conductivity (~5000 W$^{-1}$K$^{-1}$) [7], transparency with very low absorption in white light spectrum (~2.3%) [8], and high Young’s modulus (~1.0 TPa) [9]. Accordingly, graphene has been explored in a wide range of applications such as optoelectronics, spintronics, sensors, supercapacitors, solar cells, and so on [10, 11]. And now, graphene is considered to be one of the most promising materials for future applications in nanoelectronics [12, 13]. The use of simple micro-mechanical cleavage technique has been expanded from graphene to other layered materials [14]. Besides graphene, a large variety of 2D materials can be exfoliated from their bulk materials with the stacked structure like graphite. A big category in 2D family is transition metal dichalcogenides (TMDCs), consisting of hexagonal layers of transition metal atoms and sandwiched between two layers of chalcogen atoms such as MoS$_2$ and WS$_2$ [15, 16]. The TMDCs exhibit exotic properties, especially a tunable band gap, which is absent in graphene. Among them, MoS$_2$ is one of the most widely studied 2D materials with a tunable band gap shifting from the indirect gap of 1.29 eV to the direct gap of about 1.90 eV when decreasing the thickness from bulk to single layer [16]. MoS$_2$ has been widely employed to integrate with many functional materials [17, 18] and 2D material of graphene [19], suggesting potential applications in future electronic and optoelectronic devices.

Gallium selenide (GaSe) is a layered III–VI semiconductor, which consists of covalently bonded stacks of four atomic layers that are held together by a weak van der Waals (vdW)–type interaction. The stack is a sandwich with top and bottom layers of Se and two layers of Ga ions in the middle, i.e., in the sequence of Se–Ga–Ga–Se, with a lattice constant of 0.374 nm and a basic layer thickness of about 0.9 nm. Initially, monolayer GaSe flakes were obtained by mechanical cleavage methods [20]. The exfoliated ultrathin layers have been transferred onto SiO$_2$/Si substrates for the fabrication of p-type field-effect transistors (FETs) and high-performance photodetectors [21, 22]. Following the roadmap of graphene, 2D GaSe crystals show potential in future applications of electronic and optoelectronic devices. In this chapter, various synthesis methods such as vapor-phase mass transport (VMT), vdW epitaxy, molecular beam epitaxy (MBE), and pulse laser
deposition (PLD) are overviewed. The electrical and optical properties, especially the nonlinear optical properties of 2D layered GaSe, are summarized. The characteristics of fabricated nano- or micro-devices based on 2D GaSe flakes such as FETs and photodetectors are discussed.

1.2 Preparation of 2D Layered GaSe Crystals

1.2.1 Mechanical Exfoliation

Monolayer GaSe was firstly experimentally obtained in 2012 by Late et al. via the mechanical exfoliation method [20], similar to that employed for the production of graphene. Actually, after the discovery of graphene, the growth method has been expanded to other 2D layered materials. It is a convenient way to obtain micro-scale nanosheets with high quality from their bulk crystals in laboratory. This is also a widely used method to obtain high-quality 2D GaSe flakes. The 2D layered GaSe sheets, including mono-, bi-, and multilayer ones, are prepared by using Scotch tape from a piece of layered GaSe crystal. Then the nanosheets on the adhesive tape are transferred onto a target substrate, typically, 300-nm SiO$_2$-coated Si substrate. Thus, the GaSe nanosheets can be prepared by using a two-step process, involving synthesis of bulk GaSe crystals and then the subsequent exfoliation of the bulk flakes onto target substrate.

1.2.1.1 Synthesis of Bulk GaSe Crystals

GaSe crystals are typically fabricated by a modified Bridgman method [23]. This process can be divided into two steps: synthesis of polycrystalline powder and single-crystal bulk GaSe. Firstly, the polycrystalline powder can be obtained by heating (typically to a temperature of above the melting point of GaSe of 960 °C for about 1 h) the mixture of gallium and selenium or Ga$_2$Se$_3$ and gallium at the molar ratio of 1:1, which is sealed in an evacuated quartz tube at low pressure. Then the tube is cooled to a lower temperature for a period of time followed by natural cooling to synthesize polycrystalline GaSe powder. Secondly, the synthesized GaSe powder is sealed in high-vacuum quartz ampoule, which is put in a suitable temperature gradient furnace. There are three temperature zones from top to bottom in the furnace, i.e., the high-temperature zone, the gradient zone, and the low-temperature zone. The ampoule is allowed to move from top to bottom along the axis of the gradient furnace at a very low speed and is also rotated during the downward movement to keep a uniform temperature distribution. Through the two-step process, single-crystal GaSe
crystals can be well prepared for synthesis of 2D GaSe by mechanical exfoliation method.

1.2.1.2 Synthesis of 2D Nanosheets

The fabricated GaSe crystal has a layered structure with a weak interlayer coupling of vdW force, which is easy to be cleaved to synthesize 2D flakes. A small piece of GaSe crystal is put on a clean adhesive tape. Then, the tape is refolded and pressed firmly. After that, the tape is gently unfolded, leaving two mirrored areas of GaSe crystals on the tape. This process should be repeated for several times until a large dark grey portion appears. After performing these processes, some micro-scale GaSe flakes can be obtained on the adhesive tape. Then, the tape with 2D GaSe flakes is put onto a SiO₂ wafer and pressed firmly, followed by gently removing the tape. Then some GaSe sheets with different layer numbers can be obtained on top surface of the SiO₂ wafer.

These GaSe layers can be observed by using an optical microscope. A 300-nm-thick SiO₂ is an ideal substrate because it allows GaSe nanosheets to be visible under white light, and more importantly, contrast between these nanosheets with different thicknesses is relatively high. The GaSe nanosheets prepared by the mechanical exfoliation method are in-plane micro-scale and out-of-plane atomically thin, and typically single-crystal with high quality.

1.2.2 Vapor-Phase Mass Transport

After the exfoliation of monolayer GaSe, many methods have been employed to grow these ultrathin crystals. The VMT method was firstly reported to prepare large-area atomically thin GaSe layers on insulating substrates in 2013 by Lei et al. [24]. In this method, grounded GaSe powder were used as source and small GaSe flakes as seeds for 2D crystal growth. The GaSe source and seeds were prepared with high-purity Ga₂Se₃ and gallium at a molar ratio of 1:1. The mixed powder was sealed in an evacuated quartz tube with argon of 10⁻³ Torr as protecting gas. The mixture was heated to a high temperature of 950 °C for 2 h and was maintained at this temperature for a period of time, and then the mixture was cooled to fabricate GaSe crystals with layered structure. The seeds for VMT growth were prepared by sonicating a small amount of GaSe crystals in isopropanol. Then the seeds were transferred onto a wafer-scale SiO₂ substrate. Another part of GaSe crystals was ground into powder to serve as evaporation source. Then, the wafer with seeds on top and GaSe powder as source
were sealed in a quartz tube as illustrated in Figure 1.1a. In a vacuum environment, the mean free path of the precursor was large enough for mass transfer. The source powder and substrate were heated, followed by a rapid cooling to room temperature. After that, the 2D GaSe flakes could be grown on the substrate.

Through the VMT method, thin GaSe layers can be obtained in triangle, truncated triangle, and hexagonal shapes on the SiO₂ substrate. The shape of the fabricated 2D flakes can be tuned by the distance from nucleation sites to the source. However, it is difficult to control the growth process because it is very fast. The as-grown 2D crystal becomes multilayer quickly after the nucleation. The shape of GaSe flakes could also be controlled by the concentration of the source. Similar to the growth of MoS₂ atomic layers, the shape of the MoS₂ flakes could be tuned to transform from triangles to hexagons by decreasing the concentration of sulfur [25, 26]. In the VMT process, two decomposed species of Se₂ and Ga₂Se from the source

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**Figure 1.1** (a) Schematic of the synthesis of GaSe flakes by the VMT method. (b) RHEED oscillations for synthesis eight-layer GaSe flakes, suggesting the layer-by-layer growth. The inset is a RHEED streaky pattern of the GaSe atomically thin film, indicating a well-ordered and atomically flat surface. (c) Schematic of experimental setup for the PLD method.
GaSe crystals could individually diffuse to the target substrate with different velocities and mean free paths. Then, the two species recombined to form GaSe nanosheets at the nucleation sites on the target substrate.

However, only few-layer GaSe sheets with thickness down to 2 nm could be achieved by this method. The controllable method to synthesize monolayer GaSe crystals is still needed.

1.2.3 Van der Waals’ Epitaxy

Zhou et al. proposed the controlled synthesis of high-quality single- and multi-layer GaSe crystals on flexible transparent mica substrates via the vdW epitaxy method [27]. Very recently, Li et al. also used this method to grow GaSe layers with preferred orientation on graphene to fabricate vdW heterostructures [28]. The proposed vdW epitaxy method is based on a vapor transport and deposition process. Thus, source materials are needed to form GaSe vapor transport. Different from aforementioned VMT methods, vdW epitaxy process does not need additional seeds of GaSe flakes. For GaSe grown on mica substrate, the source material was polycrystalline GaSe powder prepared with gallium and selenium by a modified Bridgman method, while for GaSe on graphene, the source material was the mixture of GaSe crystals and Ga$_2$Se$_3$ powder at a molar ratio of 50:1. The reaction was conducted in a tube furnace system, where the source was placed right at the center region of the furnace, while the substrate (graphene/SiO$_2$ or mica) was located downstream at the expected location. Through heating, the produced GaSe vapor was carried downstream by argon and deposited on the target substrate. Thus, the argon used in this process actually served as carrier gas, which is different from argon in VMT deposition serving as protective gas. The substrate of graphene/SiO$_2$ was obtained by transferring chemical vapor deposition (CVD)-grown monolayer graphene onto SiO$_2$/Si via a standard transfer process. Transparent and flexible mica was achieved by cleaving fluorophlogopite mica with pseudohexagonal Z$_2$O$_5$ (Z = Si, Al) layered structure. Both transferred monolayer graphene and cleaved transparent mica with (pseudo)hexagonal structures were well suited for the efficient vdW epitaxial growth of GaSe atomic layers, including single-, bi-, and multilayer crystals.

The GaSe epilayers grown layer by layer had identical orientations and terrace structures on pseudohexagonal mica substrates with a lattice mismatch of about 35% between them. Initially, nucleation of 2D GaSe nanosheets took place on the mica surface, followed by lateral covalent bonding of incoming atoms at the edge of the nucleation site. In vertical
orientation, the top surface remained passivated by chemically saturated Se atoms. As a consequence, the crystal grew very fast in the lateral dimension compared to that in vertical dimension. Thus, it is feasible to grow single-layer GaSe, which is not achieved by the VMT method. Besides, the 2D GaSe flakes grown on flexible transparent insulating mica substrates can serve as a good platform for the measurements of their optical and optoelectronic properties.

On the other hand, GaSe epilayers on graphene started to nucleate and grow from random wrinkles or grain boundaries of the underlying graphene. The GaSe epilayers with irregular shapes had different lattice orientation from the graphene layers, which could be determined by the competition between the growth rate and the diffusion rate of the grown GaSe layers on the graphene. Generally, the formed rotation angle of 10.5 ± 0.3 was observed in the prepared GaSe epilayers. Besides, the as-prepared GaSe monolayers possessed sharp edges. Each edge was well aligned with 60° angles of neighboring contiguous islands. The vdW epitaxial single-layer GaSe flakes on graphene were large (tens of microns) irregularly shaped with single-crystalline domains and preferential nucleation on random wrinkles or grain boundaries of graphene.

1.2.4 Molecular Beam Epitaxy

Besides the aforementioned chemical deposition methods, some physical methods have been employed to grow 2D layered GaSe, such as MBE and PLD methods. MBE is well established to prepare high-quality and uniform epitaxial layers. This method has also been used for the preparation of 2D materials. Combined with in situ reflection high-energy electron diffraction (RHEED), the thickness of the prepared epitaxial layer can be precisely controlled. Very recently, Yuan et al. reported layer-by-layer growth of 2D GaSe on n-type Si substrates by the MBE method [29]. High-purity Ga and Se were evaporated and deposited on well-cleaned Si substrate with the Se/Ga flux ratio of 10:1 and the growth temperature of 580 °C. The as-prepared GaSe layers grew along [0001] direction. Periodic RHEED oscillations suggested layer-by-layer growth mode with a growth rate of about 2.8 min/layer, as shown in Figure 1.1b. The streaky RHEED pattern also indicated a well-ordered and atomically flat surface. Besides, there was a clear interfacial phase between epitaxial GaSe layers and Si substrates. GaSe layers with thickness from three layer to multilayer can be well prepared on Si substrates owning to the vdW interaction between layers. This not only provides approach to grow wafer scale 2D GaSe layers but also provides opportunity to form vdW heterostructure of p-type
GaSe and n-type Si for fabrication of optoelectronic device. Furthermore, epitaxial GaSe layers can be well grown on freshly sliced mica substrates by the MBE method, suggesting an approach of substrate-independent epitaxial growth of GaSe.

### 1.2.5 Pulse Laser Deposition

Besides the aforementioned physical deposition method of MBE, PLD technique was also been employed to grow 2D GaSe nanosheets [30]. The GaSe target was prepared by highly pure Ga and Se via high-temperature process in a high-vacuum system. The target was irradiated by excimer laser with a wavelength of 248 nm and a pulse duration of 20 ns, as schematically shown in Figure 1.1c. The optimal growth temperature for GaSe nanosheets was 600 °C on the SiO2/Si substrate. If the deposition temperature was below 500 °C, the prepared GaSe thin films would be amorphous GaSe, and no deposition could be observed if the deposition temperature was higher than 750 °C. Both out-of-plane and in-plane growths of GaSe nanosheets were controllably synthesized by adjusting the deposition rate (via laser repetition rate) and surface diffusion rate (via substrate temperature). Besides, the stoichiometric growth of 2D GaSe nanosheets required high Ar background with a background gas pressure of about 1 Torr. Individual 1–3 layer GaSe triangular nanosheets with a domain size of about 200 nm were formed within 30 laser pulses. When the pulse number was in excess of 100, individual nanosheets could grow to form nanosheet networks. The thickness of the deposited networks increased linearly with pulse number. This growth behavior at the beginning can be described by the classic Volmer–Weber mode. A large number of small nuclei grow, forming planar, triangular, crystalline GaSe nanosheets, which then coalesce into a thin film. Similar to the aforementioned MBE method, layer-by-layer-like growth within each GaSe nanosheets is due to the weak vdW force between each unit layer of Se–Ga–Ga–Se. Through controlling the deposition temperature and rate, GaSe single layer and nanosheets network could be prepared.

### 1.3 Structure, Characterization, and Properties

#### 1.3.1 Crystal Structure

GaSe is a layered III–VI semiconductor that consists of covalently bonded stacks with top and bottom layers of Se and two layers of Ga ions in the
Two-Dimensional Layered Gallium Selenide

middle, i.e., in the sequence of Se–Ga–Ga–Se, with a lattice constant of $a = b = 0.374$ nm. The covalently bonded layers, named tetra-layers (TLs), are held together by a weak interaction of the vdW force, implying possibility of existence of 2D GaSe layers. The stacking sequence of the TLs determines the polytypes of GaSe crystals. There are several different modifications that differ in the stacking sequence for GaSe crystals, and the three most important classifications are so-called $\beta$-GaSe, $\varepsilon$-GaSe, and $\gamma$-GaSe [31], as schematically shown in Figure 1.2a. Among them, $\gamma$-GaSe has a 3R stacking sequence, belonging to non-centrosymmetric space group of $C_{6v}^4$ with the lattice constant of $c = 2.392$ nm. Both $\beta$-GaSe and $\varepsilon$-GaSe are hexagonally symmetric with a 2H stacking and the lattice constant of $c = 1.595$ nm. There are two TLs in one unit cell of 2H-stacking GaSe. For $\beta$-GaSe, belonging to space group of $D_{4h}^4$, the second layer is formed by the rotation of the first layer. On the other hand, $\varepsilon$-modification is generated from one basic layer by translations. Thus, the $\varepsilon$-GaSe belongs to space group of $D_{3h}^1$.

**Figure 1.2** (a) Crystal structure. (b) Optical image of mechanically exfoliated GaSe flakes on SiO$_2$ substrate. (c) AFM image of monolayer triangular GaSe flake. Inset is the line profile in the direction of the dashed arrows. (d) SEM image of monolayer triangular GaSe flakes.
1.3.2 Characterization

Various techniques are employed to characterize 2D materials such as optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy. These techniques have also been used to analyze 2D GaSe crystals. Among them, optical microscopy is a good method for identifying the atomically thin films by using the interference effect. Similar to graphene, this requires such 2D layers located on silicon oxide substrates for good contrast. Figure 1.2b shows optical image of exfoliated GaSe flakes [22]. A single-layer sheet located at the center part exhibits clear optical contrast and can be visible. Besides, optical microscopy is convenient, non-destructive, and also the cheapest in laboratories. However, it could not independently determine the layer number of 2D GaSe. A combination of optical microscope and other techniques could provide conclusive evidence of the crystal thickness.

AFM is an imaging technique that can completely identify the layer number of the atomically thin GaSe. By using tapping mode, the height profile can clearly determine whether a given nanosheet is single, double, or multilayered. Figure 1.2c shows the AFM image of a triangular GaSe flake [32]. The height profile clearly indicated that the GaSe triangle is single layer. Besides, AFM is also non-destructive for the 2D layers. On the other hand, SEM also could provide top morphology image of 2D GaSe, especially fabricated layers by chemical and physical deposition methods [30, 32]. Figure 1.2d shows the fabricated monolayer GaSe flakes by a controlled vapor deposition method [32]. Compared to AFM, SEM can provide relatively large-scale image of such 2D layers.

Besides optical microscopy, AFM, and SEM, HRTEM and Raman spectroscopy are frequently used to characterize 2D GaSe layers.

1.3.2.1 Transmission Electron Microscopy

In general, TEM is widely used to characterize nanoscale materials with high resolution. The operation of TEM relies on a transmitted electron beam passing through ultrathin samples and reaching to the imaging lenses and detector. After the discovery of graphene, TEM has been frequently employed to detect 2D materials. Xiao’s group has been conducting a series of research about 2D GaSe flakes by using TEM to study their grain structures and stacking orders [32, 33]. In their studies, triangular GaSe flakes were prepared by a controlled vapor deposition method, which is similar to the aforementioned vdW epitaxial growth technique. The 2D samples for TEM characterizations were grown directly on 5-nm-thick amorphous