

Synthetic Two Dimensional Hexagonal Boron Nitride and Gallium Sulfide Crystals Using Chemical Vapor Deposition Growth

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Submitted in conformity with the requirements for the Degree of

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Abstract

Synthetic Two Dimensional Hexagonal Boron Nitride and Gallium Sulfide Crystals
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Two dimensional (2D) materials have promising potential in the next generation electronics and optoelectronics devices. This requires scalable production methods which can provide high quality material. This DPhil project is about using chemical vapor deposition (CVD) method to grow multilayer hexagonal boron nitride (h-BN) and monolayer gallium sulfide (GaS). A range of characterisation methods is used to examine the morphology of these grown materials, as well as their structural, vibrational, and optical properties. In addition, the growth mechanism of h-BN and GaS are discussed based on the observed results.

Multilayer h-BN films are grown on copper substrates using an atmospheric pressure CVD (APCVD) method and the commonly used precursor, ammonia borane (AB). The h-BN films produced from AB precursor are compared to the films produced from two other precursors, such as dimeric diborazane (DAB) and trimeric triborazane (TAB). SEM results indicate that the DAB leads to fully continuous h-BN film in a shorter period of time. Quantitative surface analysis reveals that DAB and TAB precursors increase the coverage of contaminant nanoparticles on the surface of the grown h-BN films. Finally, the growth mechanism of h-BN on copper substrate is discussed.

Gallium sulfide mixture phase ($\text{GaS}/\text{Ga}_2\text{S}_3$) thin film is produced by a one-step thermolysis of single source precursor Ga_2S_3 . It is deposited on both SiO_2/Si and glassy carbon substrates *via* an APCVD method. The as-grown films have flakes and its thickness is between 4.5 nm and 30 nm depending on the growth time. The $\text{GaS}/\text{Ga}_2\text{S}_3$ thin films on glassy carbon substrates are explored as hydrogen evolution reaction (HER) catalysts. One of the samples exhibits a 126 mV/dec Tafel slope with 5.50 A/cm^2 . Its cathodic current behaves almost the same after a 1000-cycle durability test.

At last, the monolayer GaS film with triangular domains is achieved. The diagonal of the monolayer GaS continuous film is about 0.7 cm. The modified APCVD method results the sharp precursor concentration gradient and the change in the kinetic growth dynamics at substrate edge. This project provides important insights of grown 2D GaS material, in term of enlarging the domain size and understanding its growth mechanism.

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In memory of my 4.5 year at Oxford between 2013 and 2018.

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Publications

Here presents a list of research accomplishments during the course of this DPhil. The result chapters (Chapter 4 and Chapter 6) in this thesis are based on 2 published first author publications.

Chapter 4

X. Wang, T. N. Hooper, A. Kumar, I. K. Priest, Y. Sheng, T. O. M. Samuels, S. Wang, A. W. Robertson, M. Pacios, H. Bhaskaran, A. S. Weller, J. H. Warner. Oligomeric Aminoborane Precursors for the Chemical Vapor Deposition Growth of Few-Layer Hexagonal Boron Nitride, *CrystEngComm*. 2017 19, 285–294.

Chapter 6

X. Wang, Y. Sheng, R. Chang, J. K. Lee, Y. Zhou, S. Li, T. Chen, H. Huang, B. F. Porter, H. Bhaskaran, and J. H. Warner. Chemical Vapor Deposition Growth of Two-Dimensional Monolayer Gallium Sulfide Crystals Using Hydrogen Reduction of Ga₂S₃, *ACS Omega*, 2018, 3,7897-7903.

Co-author Publications

1. R. Chang, H. Tan, **X. Wang**, B. Porter, T. Chen, Y. Sheng, Y. Zhou, H. Huang, H. Bhaskaran, J. H. Warner. High Performance All-2D Layered Tin Disulfide:Graphene Photodetecting Transistors with Thickness Controlled Interface Dynamics. *Appl. Mater. Interfaces*, 2018.
2. W. Xu, D. Kozawa, Y. Liu, Y. Sheng, K. Wei, V. B. Koman, S. Wang, **X. Wang**, T. Jiang, M. S. Strano, J. H. Warner. Determining the Optimized Interlayer Separation Distance in Vertical Stacked 2D WS₂:hBN:MoS₂ Heterostructures for Excitation Energy Transfer, *Small*, 2018, 1703727.
3. W. Xu, S. Li, S. Zhou, J. K. Lee, S. Wang, S. G. Sarwat, **X. Wang**, H. Bhasjaraan, M. Pasta, J. H. Warner. Large Dendritic Monolayer MoS₂ Grown by Atmospheric Pressure Chemical Vapor Deposition for Electrocatalysis. *ACS Appl. Mater. Interfaces*, 2018
4. T. Chen, Y. Zhou, Y. Sheng, **X. Wang**, S. Zhou, J. H. Warner. Hydrogen Assisted Growth of Large Area Continuous Films of MoS₂ on Monolayer Graphene, *ACS Appl. Mater. Interfaces*, 2018.

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6. G. Han, K. Tu, F. Niroui, W. Xu, S. Zhou, **X. Wang**, V. Bulovic, C. A. Ross, J. H. Warner, J. Grossman. Photoluminescent Arrays of Nanopatterned Monolayer MoS₂. *Advanced Functional Materials*, 2017, 27, 1703688.
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Chapter 1

Introduction

1.1 Project Aim

The objective of this doctoral project is to systemically establish, understand and optimize chemical vapor deposition (CVD) methods for the growth of multilayer h-BN films and monolayer GaS films, respectively. Subsequently their morphologies, vibrational, and catalytic activity are characterised by a range of techniques.

1.2 Scope of this Thesis

The thesis covers the research that has been implemented over the course of 4.5 years DPhil study in the Department of Materials, University of Oxford. Chapter 2 comprises a literature review outlining the h-BN and the GaS materials, summarizing the studies of the structures, properties, the recent progress about their CVD synthesis methods, and corresponding applications. Chapter 3 describes the experimental setups for the CVD synthesis of multilayer h-BN films, gallium sulfide mixture phase (GaS/Ga₂S₃) thin films and monolayer GaS films, respectively. Characterisation techniques with detailed procedures and corresponding data processing methods are included. This may aid colleagues in carrying out the synthesis and characterisation of these materials.

The first task of my project is to establish a CVD system, which is then used to synthesise h-BN materials. Multilayer h-BN films are produced from three aminoborane based precursors. This project is published and presented in Chapter 4. The developed CVD recipe of multilayer h-BN film is used by colleagues and helps their projects. The next parts of my research focus on the CVD synthesis of gallium sulfide mixture phase (GaS/Ga₂S₃) thin films under atmospheric pressure conditions. In Chapter 5, I summarise

the work about the CVD synthesis of GaS/Ga₂S₃ thin films on both SiO₂/Si and glassy carbon substrates and show its catalytic reactivity in hydrogen evolution reaction (HER). In Chapter 6, I further improve the growth method and eventually achieve monolayer GaS continuous films. The modifications in the CVD method result the sharp precursor concentration gradient and the change in the kinetic growth dynamics at substrate edges. This provides important insights into novel approaches for enlarging the domain size and understanding the growth mechanisms of GaS crystals.

The conclusion summarises above mentioned projects. An outlook is discussed about potential future works.

Chapter 2

Literature Review

A review of current research on hexagonal boron nitride (h-BN) and gallium sulfide (GaS) is presented in this chapter. This review first introduces their crystal structures, electronic, optoelectronic and vibrational properties, respectively. Then, chemical vapor deposition (CVD) synthesis and the characterisation are also reviewed in detail.

2.1.0 Introduction

Since the discovery of graphene in 2004, two-dimensional (2D) materials have been extensively explored.^{1,2} Graphene is a 2D material with one-atom-thickness and made of sp^2 -bonded carbon arranged in a honeycomb structure. Figure 2.1 (a) displays the structure of graphene and how it relates to the fullerene, carbon nanotube, and graphite. Moreover, due to its unique properties, numerous fundamental studies have been carried out. Owing to its zero-bandgap and structure, graphene exhibits remarkable electronic, thermal, optical and mechanical properties. It has ultrahigh mobility of charge carriers, superior thermal conductivity, high optical transmittance, and high specific surface area. Graphene has become a disruptive technology.³⁻⁶ This is particularly true in the semiconductor industry, the large carrier mobility makes graphene a promising material for the next-generation high frequency electronic devices. Its low optical absorbance combined with semi-metallic nature makes graphene an ideal transparent conductor.^{7,8} Significant progress has also been made in other areas such as superconductivity,¹¹ optoelectronics,¹⁰ energy generation and storage devices and so on.⁹

Generally, the discovery of graphene has encouraged researchers to apply this idea to many other materials such as 2D chalcogenides and 2D oxides, as shown in Figure 2.1 (b).^{12,13} Nowadays the study and development of novel 2D materials are prospering in

terms of the structures, fundamental studies, new preparation methods, characterisation methods and potential applications. Research papers about these materials are regularly published. Beyond graphene, other 2D materials have drawn significant attention such as hexagonal boron nitride (h-BN) and gallium sulfide (GaS) which is from layered group III metal chalcogenides. This review introduces h-BN and GaS in separate sections including their crystal structures, properties, preparation methods, and applications. Due to the nature of this thesis, chemical vapor deposition (CVD) synthesis methods are focused on, as well as the characterisation of h-BN and GaS materials.

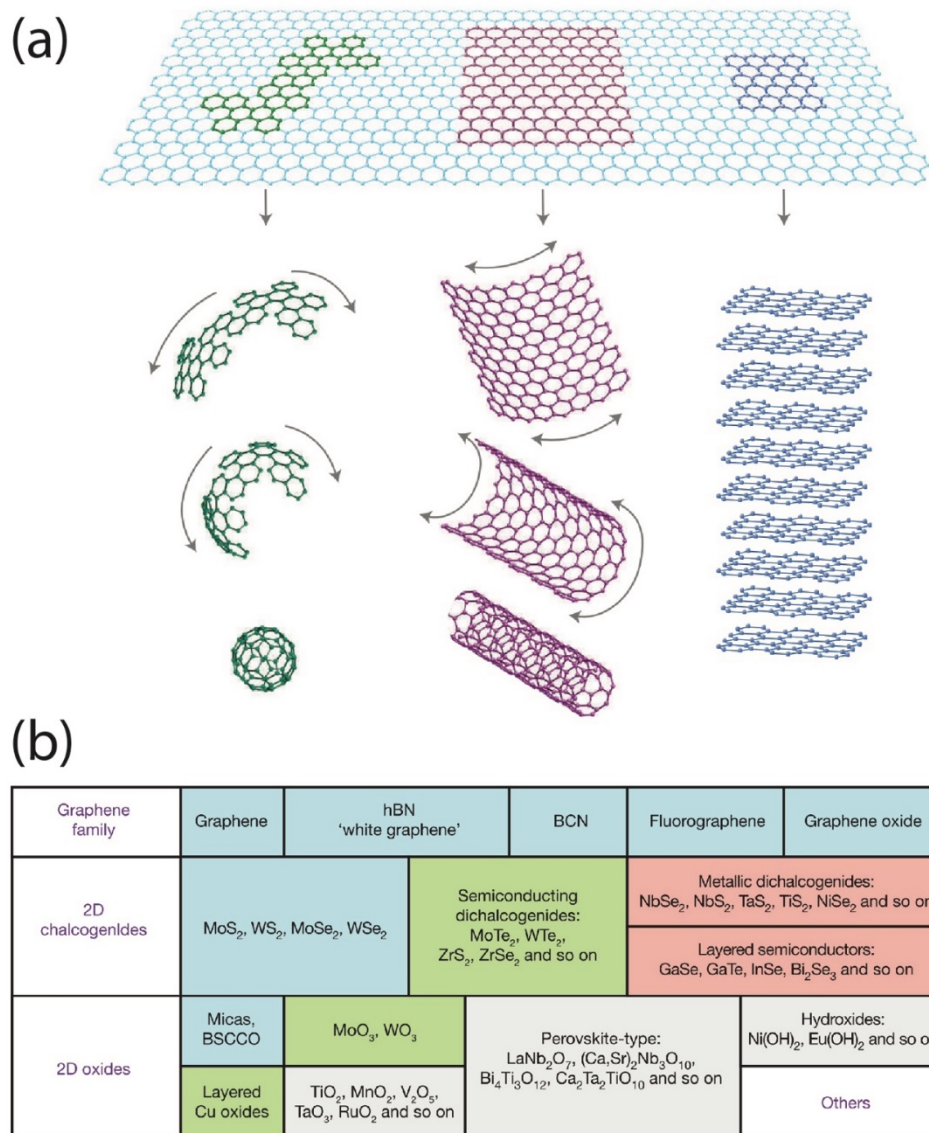


Figure 2.1. (a) Schematic diagram of graphene and its three configurations 0D buckyball, 1D nanotubes and 3D graphite structures. (b) Current 2D crystals library with three classes such as graphene family, 2D chalcogenides and 2D oxides. Reprint (adapted) with permission from (a), ref. (2), © 2007 Nature Publishing Group; (b), ref. (12), © 2013 Macmillan Publisher Limited.

2.2.0 Hexagonal Boron Nitride

Hexagonal boron nitride (h-BN) has a long history, it is originally synthesised by Balmain in 1842 and its structure arrangement is proposed for the first time in 1952 by Pease.^{14,15} h-BN can be vertically stacked in multilayers separated by 0.333 nm *via* Van der Waals forces. The monolayer structure of h-BN is planar and comprised of alternating boron and nitrogen atoms in a honeycomb arrangement with lattice parameters of 0.250 nm. Recently, h-BN is gained a great deal of attention as an exceptional substrate for graphene, because of atomically smooth surface and small lattice mismatch.,^{16,17} Although the crystal structures of h-BN and graphene are similar, h-BN is an insulator with a wide bandgap between 5.76 and 5.96 eV due to the polar nature of the sp^2 B-N bond.^{18,19} The other outstanding properties of h-BN include high thermal conductivity, high temperature stability, high resistance to corrosion and oxidation, low dielectric constant, and nontoxicity.^{20,21} Along with other 2D materials, h-BN has emerged as one of the fundamental building blocks for the Van der Waals heterostructures.¹² In such structures, h-BN serves as a dielectric layer for electronic device applications *e.g.* graphene field effect transistors, and 2D capacitors.²²⁻²⁴

Boron nitride, isoelectronic and isostructural to its carbon counterpart, is an III-V material and exists in four polymorphic forms. They are two dense sp^3 hybridization structures (cubic BN (c-BN) and wurtzite BN (w-BN)) and two graphite-like sp^2 hybridize structures (hexagonal BN (h-BN)) and rhombohedral BN (r-BN)). The synthesis of bulk cubic BN requires the application of high temperature and pressures, similar to the synthesis of diamond.²⁵ h-BN is isostructural with graphite and it is stable at room temperature and ambient pressure. c-BN and w-BN can be directly formed from h-BN under extreme conditions.^{26,27} For multilayer h-BN, B and N atoms sit alternatively on top of each other resulting in ABABAB stacking. This unique stacking configuration is reflected in its vibrational properties; and the phonon modes of monolayer h-BN are weak

due to small elastic constants.²⁸ In addition, two more crystalline polymorphic phases are reported, such as the one-dimensional BN nanotubes and zero-dimensional fullerene-like BN.^{29,30} Regarding the edges of h-BN, theoretical modelling shows all three edges of synthesised triangular domains are dominated by N atoms due to lower energy than B terminated edges.³¹ Hexagonal h-BN domains are also reported with alternating N and B terminated edges on electropolished copper substrates.³² The overview atomic structures of BN are presented in Figure 2.2. Among them, both covalent and ionic character are exhibited, and the nature of ionic B-N bond strongly influences its structure and properties.

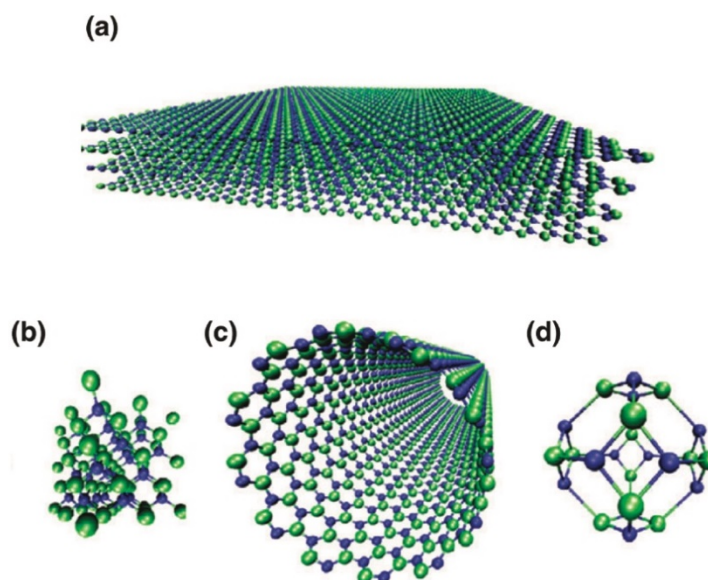


Figure 2.2 Atomic structure schematics of boron nitride materials: (a) stacked h-BN films, (b) c-BN, (c) single-walled BN nanotube and (d) fullerene-like BN, where green ball represents the boron atoms and purple ball represents the nitrogen atoms. Reprint (adapted) with permission from (a-d), ref. (28), © 2015 John Wiley & Sons, Ltd.

Electronic Properties

h-BN is known as a wide bandgap semiconductor, however whether h-BN is a direct or indirect bandgap semiconductor is uncertain. Both direct and indirect properties of its bandgap have been reported and supported by *ab initio* band structure calculations and optical measurements. The bandgap energy of h-BN is between 3.2 and 7.1 eV.^{18,33-35} Since boron and nitrogen sit either side of carbon in the periodic table, each boron and nitrogen atom has three and five valence electrons respectively. The sp^2 hybridization of their atomic orbitals allows both B and N to form a hexagonal lattice as carbon does in graphene. The difference in the electronic occupancy of the p_z -orbital leads to a highly ionic bond between the atoms. This reduced covalent character results in a less electron-delocalization and poor electrical conductivity, in addition to a large band gap. Furthermore, the σ -orbital and π -orbital exhibit a strong mixing and approach including all the 2s and 2p electrons instead of only the P_z electron.²⁸

In 2004, Watanabe *et al.* first measured the exciton-related luminescence and absorption near the edge of their synthesised h-BN sample. The results show a single peak of ultraviolet luminescence at 5.765 eV at room temperature. The intrinsic fundamental absorption spectra has a value from 5.822 to 5.968 eV, and it is related to an s-like direct exciton structure.¹⁸ These results are shown in Figure 2.3 (a) and (b). On the contrary, *ab initio* calculations predict an indirect bandgap of h-BN and its band structure is located around the M and K points in the Brillouin zone.^{34,35} In Figure 2.3 (c), both the local-density approximation (LDA, thin solid lines) and GW (solid lines with open circles) band structures are plotted along the high-symmetry directions. In this plot, a 5.95 eV indirect bandgap is found between the T_1 point at the top valence band and the M point at the lowest unoccupied band. More recently, Cassabois *et al.* demonstrated that h-BN has an indirect bandgap of 5.955 eV by two-photon spectroscopy in 2016. In Figure 2.3 (d), the photoluminescence (PL) spectrum of h-BN shows the peak around 5.76 eV at

low temperature.¹⁹ Two new photon excitation schemes are detected around 5.930 eV and 5.955 eV. The indirect band gap h-BN is a Wannier type and the binding energy is about 130 meV between 1s and 2p exciton states, as shown in Figure 2.3 (e).¹⁹ In addition, research also shows that the monolayer h-BN band structure can be tuned by applied tensile strain and their relationship is bilinear dependence.³⁶

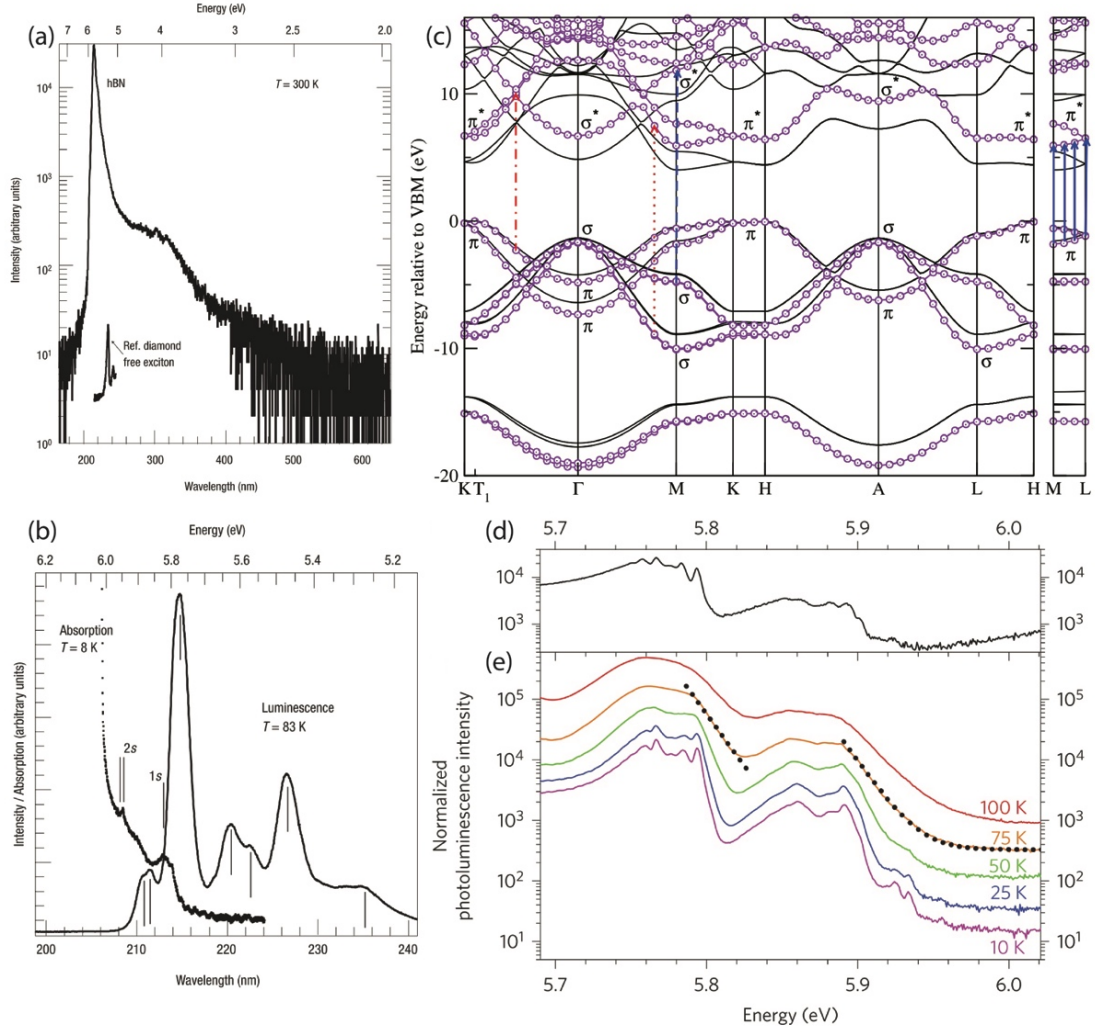


Figure 2.3 (a) Cathodoluminescence spectrum of h-BN at room temperature. Indirect free exciton luminescence of pure diamond is shown as a reference. (b) Fundamental absorption spectrum of h-BN at 8 K and luminescence spectrum of h-BN at 83 K. (c) Calculated electronic band structure along high-symmetry lines for bulk h-BN. The thin solid lines display the LDA results, and the solid lines with open circles represent the GW approximation results. The energy scale is relative to the top of the valence band maximum (VBM) located at the T_1 point near K along the Γ -K high-symmetry direction. (d) Photoluminescence spectrum of h-BN at 10 K with 6.3 eV one-photon excitation. (e) Photoluminescence spectra of h-BN with two-photon excitation at 3.03 eV as a function of temperature. Reprint (adapted) with permission from (a and b), ref(18), © 2004 Nature

Publishing Group; (c), ref (34), © 2006 The American Physical Society; and (d and e), ref (19), © 2016 Macmillan Publishers Limited.

Optical Properties

2D h-BN does not exhibit any optical absorption in the visible region of the electromagnetic spectrum (390-700 nm). Generally, it is transparent as a thin film or appears white when accumulated in bulk quantities. Later explains why BN nanomaterial is sometimes referred to “white graphene” in the literature.³⁷ There have been several optical measurements on h-BN in the deep UV range. Although the results are quite conflicting in nature, the optical band gap values range from 5.2 to 6.07 eV.^{35,38-40} First-principles calculations and Green’s function quasiparticles approach illustrate that the low dimensional BN materials have larger exciton binding energies than bulk h-BN.^{28,41,42} One main reason for this controversial finding is that obtaining high quality single crystal h-BN is crucial. Poor-quality h-BN samples, including polycrystalline BN, pyrolytic BN, or flaky single-crystal BN varies the results, and their flatness makes it difficult for accurate reflectance measurements. The optical band gap of h-BN film can be derived from UV-visible adsorption measurements. The following equation is used:

$$\alpha = C(E-E_g)^{1/2}/E \quad (1)$$

where α is the absorption coefficient, C is a constant, E is the photon energy of incident light, and E_g is the optical band gap of the h-BN film. The absorption coefficient can be obtained by $\alpha=A/l$, where A is the optical absorption of the film measured by UV-vis spectroscopy, and l is the average thickness of the h-BN film. The plot of $(\alpha E)^2$ against E gives a straight line, and therefore, when $(\alpha E)^2 = 0$, the corresponding E value equals to the E_g . Gao *et al.* reported that the optical band gap of h-BN increases as the layer number decreases due to the interlayer interactions enhancing the dispersion of the electronic bands.³⁹ Figure 2.4 shows the UV-visible absorption spectrum and the analysis

of the optical band gap of a monolayer h-BN film. Similarly, Kobayashi *et al.* demonstrated that the linear dependence between photon energy and the squared absorption coefficient and reported the optical band gap is 5.9 eV from a metalorganic vapor phase epitaxy grown h-BN film.⁴³ Furthermore, Kim *et al.* and Tay *et al.* both showed the optical band gap of single layer h-BN is close to 6 eV. These measured h-BN films are prepared by CVD method.^{32,40}

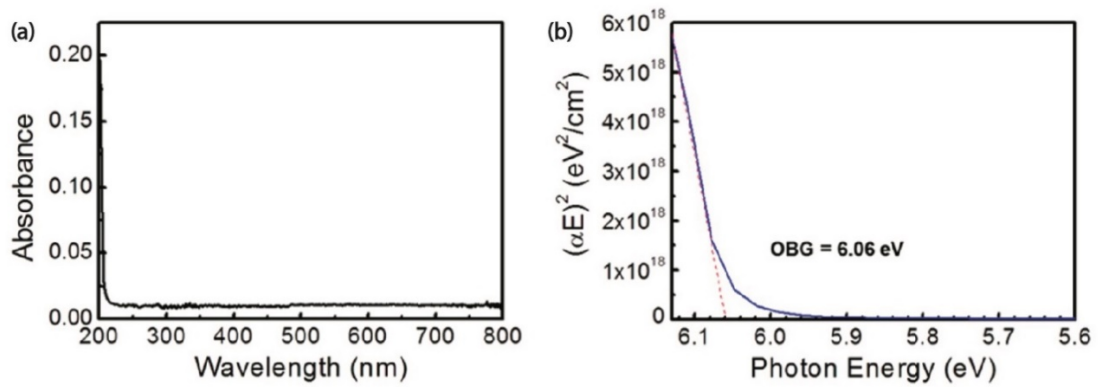


Figure 2.4 (a) UV-visible absorption spectrum of monolayer h-BN on a quartz substrate. (b) Optical band gap analysis of monolayer h-BN in (a). Reprint (adapted) with permission form: (a and b), ref (40), © 2013 American Chemical Society.

Vibrational Properties

The vibrational properties of h-BN reveal its lattice dynamics and thermodynamic properties in terms of elasticity, heat capacity and thermal expansion. Generally, researchers apply the following approaches to investigate these properties, such as *ab initio* calculations, inelastic x-ray scattering (IXS), electron-energy loss spectroscopy (EELS),⁴⁴ and Raman scattering.⁴⁵⁻⁴⁷ Serrano *et al.* investigated the phonon dispersion of bulk h-BN using inelastic x-ray scattering measurements (IXS) and *ab initio* calculations.⁴⁴ As shown in Figure 2.5 (a), the results of experimental IXS and the *ab initio* calculation (solid lines) are well matched. A splitting is observed at the Γ point between the longitudinal and transverse optical modes (LO-TO splitting).⁴⁴ Moreover,

the difference between the EELS and IXS results is attributed to the bonding when deposit h-BN on Ni metallic substrates, as shown in Figure 2.5 (b).⁴⁴ Raman spectroscopy in the UV and visible range is another frequently used method to investigate the vibrational properties of h-BN. Figure 2.5 (c) shows Raman spectra of mono-, bi-, and tri- layer BN using a green laser with 514.5 nm wavelength, reported by Gorbachev *et al.*⁴⁸ The integrated intensity I_T is proportional to the h-BN sample's layer numbers. The in-plane boron and nitrogen atoms move in opposite directions, and the atomic displacements are combined symmetrically. The Raman peak of bulk h-BN occurs at about 1366 cm^{-1} , while the monolayer h-BN has a Raman peak around 1370 cm^{-1} .⁴⁸ *Ab initio* calculations reveal that the lower frequency of bulk h-BN is related to softening sp^2 bonds in the bulk caused by interlayer interactions.⁴⁵

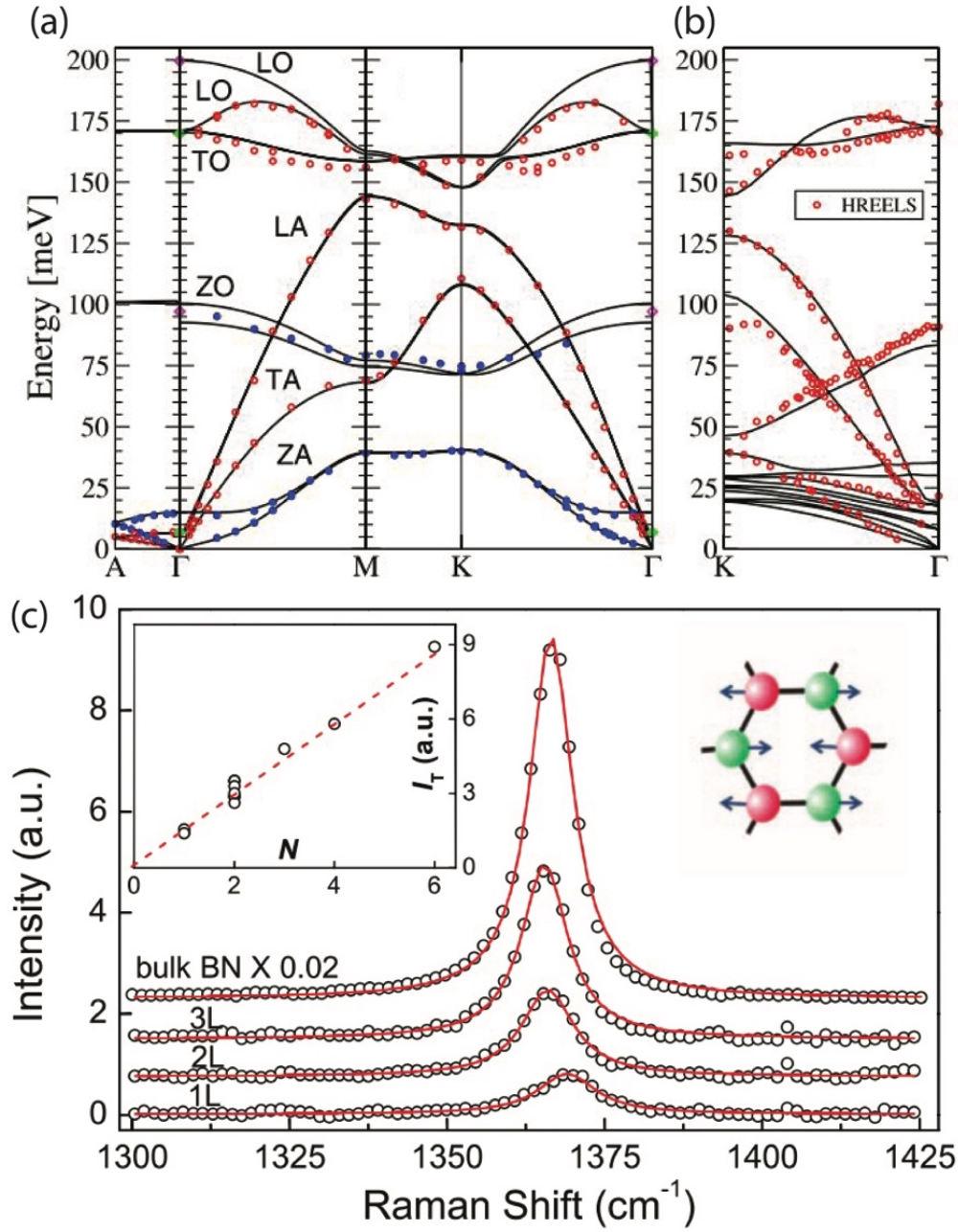


Figure 2.5 (a) Phonon dispersion relations of h-BN along high-symmetry lines. The open (red) circles display modes polarized in the hexagonal plane. The solid (blue) circles correspond to modes polarized along the c-axis. The solid curves represent the calculated phonon dispersion. (b) Calculated phonon dispersions of a monolayer h-BN deposited on three-layer Ni (solid lines) compared with the EELS data (red open circles). (c) Raman spectra of atomically thin BN. Left inset shows the changes in integrated intensity I_T with the number of layers N . The right schematic shows the phonon mode of h-BN. Reprint

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2.2.1 Chemical Vapor Deposition of Hexagonal Boron Nitride

Even though monolayer and few-layer h-BN have the mentioned properties, it is still a challenge to synthesise h-BN with controllable domain size, layer number, and morphology. Various methods have been used to synthesize 2D BN material. Most of them are similar to the growth of graphene sheets. In general, three main methods are used to prepare h-BN material: (1) mechanical exfoliation, (2) chemical exfoliation, and (3) chemical vapor deposition.

The mechanical exfoliation method is the first technique to obtain high quality 2D crystal sheets with atomic thickness.^{37,49} This method is used to obtain graphene sheets by Novoselov *et al* in 2004.¹ Mechanical exfoliation utilises adhesive tape to peel off thin h-BN sheets from its bulk material. The obtained sheets are then attached to SiO₂/Si substrates. Next the exfoliated h-BN sheets can be quickly examined using an optical microscope. The obtained nanosheets have low thickness and large lateral size. They are suitable for the fundamental studies.^{16,21,37,50} Pacile *et al.* successfully exfoliated h-BN sheets with average 10 µm size and about 3.5 nm thickness in 2008.⁵¹ The drawback of this technique is obvious. It is not able to control the number of layers, thickness, morphology and crystal edges. In contrast to the case of graphene, this technique has not been effective in producing few-layer and monolayer BN.³⁷

The chemical exfoliation method is a viable route to obtain high volume production of h-BN. Unlike mechanical exfoliation, this method employs chemicals to intercalate BN powders and creates BN-solvent interactions, which can overcome the Van der Waals forces between BN layers.³⁷ Han *et al.* used this technique to obtain h-BN with the lateral size of several micrometres and single, double, and triple layers thickness.⁵² BN powder

is placed in a 5 ml 1,2-dichloroethane solution of poly (m-phenylenevinylene-co-2,5-dioxy-p-phenylenevinylene) (1.2mg/10ml) and sonicated for 1 hour to disperse and break up the BN crystals. Thereafter more solvents are successfully used to realize the chemical exfoliation of h-BN, such as N,N-dimethylformamide (DMF), methanesulfonic acid, 1, 2-dichloroethane,⁵³ water⁵⁴ and so on.⁵⁵⁻⁵⁷ Milligram batches of pure BN nanosheet can be produced, and the majority of them have thicknesses between 2 and 10 nm.³⁷ This method has the potential to produce h-BN on a large scale and open up its polymer matrices application.

Deposition techniques have been applied to grow epitaxial BN thin film for several decades. The chemical vapor deposition method offers both large scale and high-quality production of mono or few layers h-BN film. For example Song *et al.* reported the large area synthesis of few-layered BN film (2-5 atomic layers) grown on copper substrates in 2010.⁵⁸ In order to obtain high quality h-BN film, it is necessary to investigate the growth parameters such as temperature, deposition time, amount of precursor, and growth environment. The growth environment includes atmospheric pressure, low pressure (0.1-1 Torr) and ultrahigh vacuum (UHV) conditions. Both low pressure and atmospheric pressure CVD have been widely used to synthesis h-BN recently. The advantages of using LPCVD are that: the synthesis of h-BN is surface limited growth and the growth process is less affected by the geometry of the substrate or by gas flow rates.⁵⁹ In the low pressure environment, the Cu substrates tend to deform at high temperature and lead to an increase in surface roughness.⁶⁰ It causes low quality h-BN thin film.

The APCVD system has a lower operating cost and is generally simple in design. It is also a preferred industrial production technique of h-BN film. The main disadvantage is that the grown h-BN thin film does not have a uniform density distribution because it is operated in the mass transport limited regime.⁶¹ However, the APCVD growth of h-BN on Pt foils shows its number can be controlled by changing the growth temperature of

precursor. Multilayer h-BN films are reported on polycrystalline Cu and Ni substrates.³⁹ In the following sections, the CVD growth parameters of h-BN thin film are discussed, such as chemical precursors, transition metal catalysts, and grown h-BN domains.

Precursors

There are two approaches of using chemical precursors in the CVD synthesis of h-BN. They are the mixed precursors approach and the single source precursor approach. The mixed chemical precursors include BF_3/NH_3 ,⁶² BCl_3/NH_3 ⁶³ and diborane/ammonia ($\text{B}_2\text{H}_6/\text{NH}_3$) mixtures.⁶⁴ The single source precursors include borazine $\text{B}_3\text{N}_3\text{H}_6$,⁶⁵ ammonia borane H_3NBH_3 , trichloroborazine $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$,⁶⁶ and hexachloroborazine $\text{B}_3\text{N}_3\text{Cl}_6$.⁶⁷ For the mixed chemical precursors, controlling the ratio between the boron source and NH_3 is critical in order to obtain stoichiometric h-BN layers.⁶⁸ The advantages of single source precursors are: (1) a direct pyrolysis process leads to the growth of h-BN film, and (2) the B/N stoichiometric ratio is 1:1. Borazine and ammonia borane precursors are not toxicity unlike other boron precursors, for examples BF_3 and BCl_3 . In recent publications, borazine and ammonia borane are the most used precursors to synthesise h-BN.^{39,58,68,69,70-73}

The mixed precursors ammonia and diborane are used to grow h-BN by Ismach *et al.* They reported that a controllable synthesis of h-BN can be achieved on Ni substrate in a LPCVD system.⁷⁴ The thickness of the h-BN film has a linear dependence with growth time, as shown in Figure 2.6 (a). The growth of h-BN on single crystal is reported to be surface limited.⁷⁵ Once a monolayer of h-BN is formed, the growth rate is significantly decreased or even completely stopped.⁷⁶ The results from sequential growth (sequential dosing diborane and ammonia) and X-ray photoelectron spectroscopy (XPS) reveal the h-BN growth mechanism. During the synthesis process, diborane precursor decomposes initially and boron reacts with Ni substrate forming a Ni-B bond. After that it reacts with

ammonia leading to the formation of h-BN.⁷⁴ The XPS spectra are presented in Figure 2.6 (b), (c) and (d).

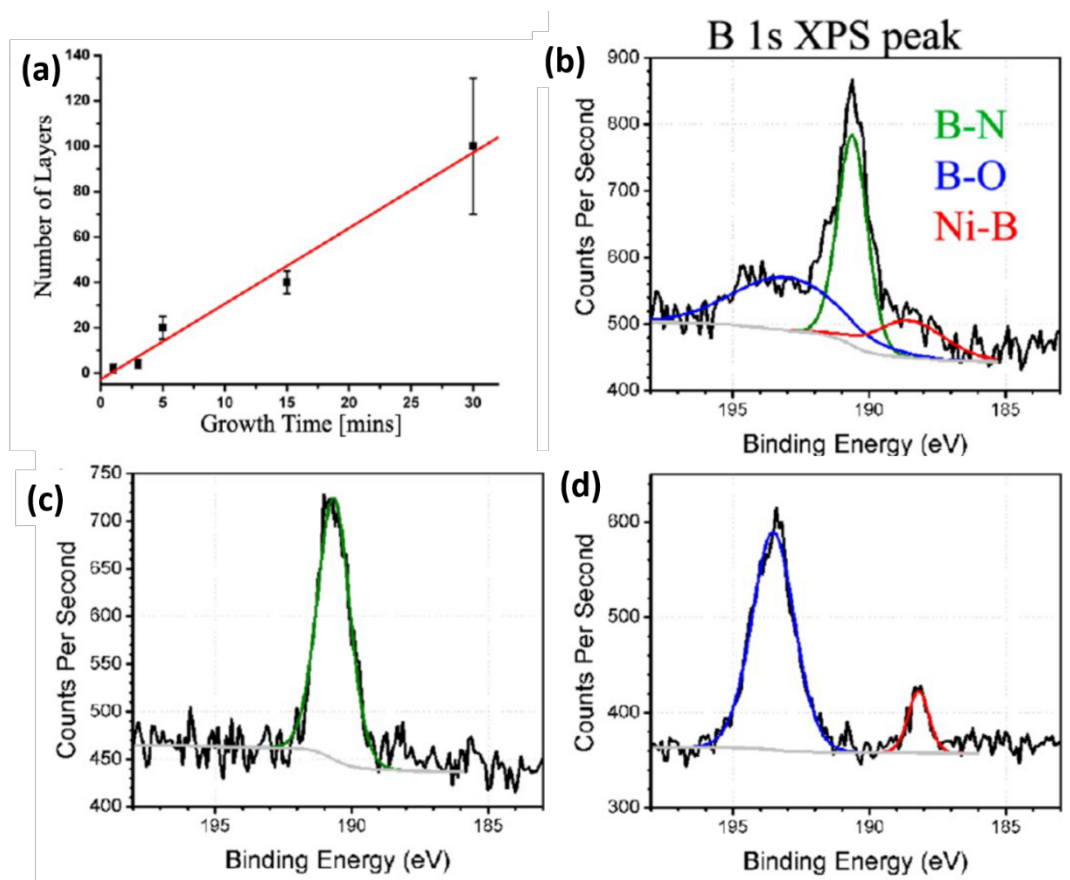


Figure 2.6 (a) This plot represents the layer number of h-BN as a function of growth time. XPS spectra for (b) sequential growth with diborane shows the peak deconvolution into B-N, B-O, and Ni-B states; (c) sequential growth with ammonia exhibits only B-N bonding state; and (d) Ni-B and B-O peaks when the Ni foil is exposed to diborane. Reprint (adapted) with permission from: (a-d), ref (74), ©2007 The American Physical Society.

The borazine is used by Shi *et al.* to grow large scale (20 μm), few-layer (5-50 nm thickness) h-BN on polycrystalline Ni in an APCVD system.⁶⁸ The grown h-BN fully covers the substrate surface with uniform thickness, however the h-BN domain size is limited by the Ni grain size. During the h-BN growth, the dehydrogenation reaction of

borazine occurs over a broad temperature range.⁷⁷ At 70°C, borazine is converted to polyborazylene, the resulting polymer undergoes weight loss and finally forms elementally pure boron nitrides. The initial weight loss of polyborazylene occurs between 125 °C and 300 °C. The cross-linking reaction of B-H and N-H groups takes place on adjacent chains.⁷⁸ After that, the second weight loss occurs between 400 °C and 1200 °C. The hydrogen is lost from the unaligned chain branches of polyborazylene.^{78,79} This process is illustrated in Figure 2.7 (a). Ammonia borane precursor is reported to synthesise h-BN film on Cu substrates by Song *et al.*⁵⁸ The obtained h-BN thin film is in the centimetre scale with about 1.3 nm thickness. Later on, Kim *et al.* also successfully synthesised large area monolayer h-BN from ammonia borane precursor on Cu substrates in an LPCVD system.⁷⁰ Ammonia borane precursor is more stable than borazine in ambient conditions. It is more widely used since borazine is moisture sensitive and hydrolyzes to boric acid, ammonia and hydrogen.⁸⁰⁻⁸² The dehydrogenation reaction of ammonia borane takes place over a temperature range between 77 °C and 137 °C. The decomposition of ammonia borane produces hydrogen, monomeric aminoborane (BH_2NH_2) and borazine, as illustrated in Figure 2.7 (b). However, the monomeric aminoborane is very active and it forms polymeric aminoborane (BH_2NH_2). It is a white noncrystalline solid and stable at room temperature. The BN nanoparticles (50-100 nm in diameter) is formed through the evaporation process of borazine. These nanoparticles are the main contaminants on the grown h-BN surface.⁸³ In order to eliminate the undesirable by-products, two simple arrangements of the CVD setup are used. Such as (1) a filtering system is employed and (2) the precursor can be placed below the reaction quartz tube.^{71,70} Both methods result relatively clean h-BN surface by restricting the nanoparticles to reach the substrates. It is hard to obtain uniform single layer h-BN due to the thermal decomposition rate of precursor is high.⁷⁴ The ammonia borane has a lower growth rate since it is in powder form. However, the ammonia borane precursor generates

undesirable polymetric aminoborane white particles. They are all over the substrate surface and reduce the quality of h-BN film in term of high roughness.

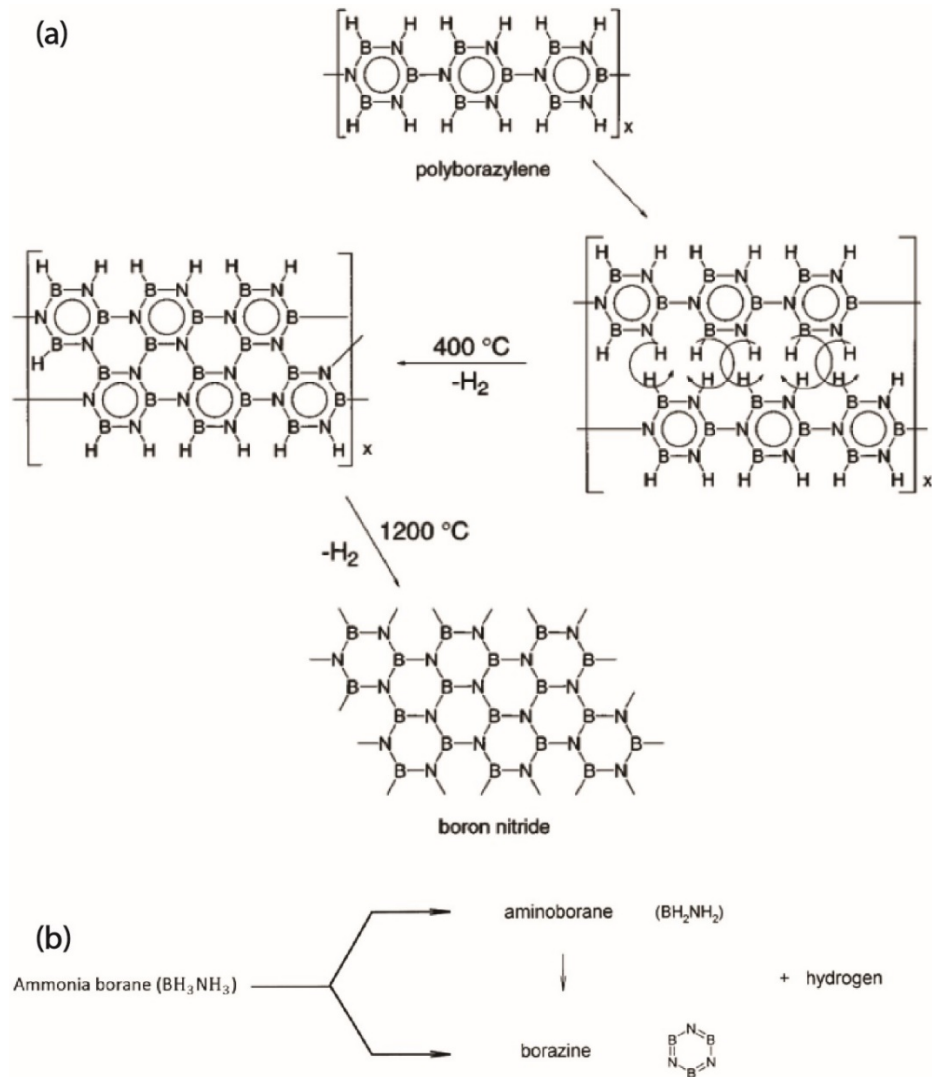


Figure 2.7 Proposed conversion process from (a) polyborazylene and (b) ammonia borane to h-BN formation. Reprint (adapted) with permission from: (a), ref (78), ©2007 The American Physical Society; (b), ref (80), ©2000 Elsevier Science B. V.

Transition Metal Catalysts as Substrates

Monolayer h-BN has been successfully synthesised on numbers of transition metal surfaces including Ni, Cu,⁸⁴ Pt, Pd,^{86,87} Fe,⁸⁸ Mo,⁸⁹ Cr,⁹⁰ Rh,^{75,85} and Ru.⁹¹ Among these transition metal catalysts, polycrystalline Ni, Pt, and Cu are often utilized as substrates for the synthesis of h-BN. Although prior work on h-BN growth uses single crystal transition metals, they are not ideal for future scalable fabrication.^{40,84,92,93} During the wet chemical transfer process, these single crystal substrates require sacrificial etching and result in high cost, especially for Pt substrates. The catalytic activity and surface morphology of the transition metal catalysts can influence the growth of h-BN film. In this section, the Ni, Pt and Cu substrates are reviewed in more details.

The study of the electronic dispersion relations of h-BN on Ni (111) surface is performed by Nagashima *et al.* in 1994.⁷⁶ The monolayer h-BN is synthesised by decomposition of borazine gas precursor at 800 °C in ultrahigh vacuum (UHV) condition. In this environment, the growth of h-BN follows the Stranski-Krastanov mode meaning it doesn't follow a layer-by-layer fashion after the formation of the first layer. Its structure of the valence and conduction band on Ni (111) indicates that there is no substantial mixing of Ni d states with h-BN π states, and it explains the weak bonding between the metal surface and monolayer. This result is obtained by angle-resolved ultraviolet photoelectron spectroscopy (ARUPS). On the other hand, Perobrajenski *et al.* reported a strong hybridization between Ni d states and h-BN π states indicating interaction between the Ni (111) surface and monolayer h-BN.⁹⁴ Furthermore Laskowski *et al.* utilized density functional theory (DFT) and reported that the interaction between h-BN and metal surface depends on B and N atom positions.⁹⁵ When N sits on top of the metal and B

occupies fcc or hcp hollow sites, the B attraction dominates the N repulsion and h-BN is bound to the surface.⁹⁵

Kim *et al.* demonstrated the growth of single layer h-BN film (8 mm × 25 mm) on recyclable Pt foil in a LPCVD process.⁴⁰ Later, Park *et al.* reported the LPCVD synthesis of large area (2 cm × 5 cm) monolayer h-BN film on polycrystalline Pt foil using borazine precursor.⁹⁶ In this study, the thickness of h-BN is not affected by cooling rate, assuring that the monolayer h-BN is formed by the surface mediated growth mechanism. Pt has a boron solubility of 1 at% at temperature around 1100 °C. The Pt₃B or Pt₂B compound phase is formed in a wide temperature range.⁹⁷ At high pressure, thick h-BN film is preferentially grown on Pt (111), while a thin h-BN film is grown on Pt (001). Because that the higher density of the Pt atoms leads to a more efficient decomposition of the borazine precursor.⁹⁶ Since Pt foil is a noble metal substrate, the commonly used etching-based transfer method is not suitable. The bubbling-based transfer method is developed. The grown h-BN on Pt foil is successfully transferred to arbitrary substrates. There is no change in the quality of the grown h-BN when the Pt foil is recycled up to 100 times.

Tay *et al.* reported a systematic study of the APCVD method grown h-BN film on Cu substrates using ammonia borane as precursor.⁶¹ In this study, most of the CVD growth parameters are discussed including substrate position (distance between precursor and substrate), growth temperature, growth time, precursor temperature, and the amount of ammonia borane precursor. The h-BN film coverage increases downstream along the copper substrate from triangular domains to continuous film, as shown in Figure 2.8 (a). The dramatic change in h-BN domain size and nucleation density is caused by the temperature gradient of the gas molecules and the concentration of the active species. Higher growth temperature increases the growth rate and crystallinity, as shown in Figure 2.8 (b). The longer deposition time results in thicker h-BN films with enhanced roughness.

Because the film grows both laterally and vertically under ambient pressure condition, as seen in Figure 2.8 (c). The precursor temperature has an interesting influence on the h-BN film growth. At about 60 °C, the formed h-BN films have the largest domains, however domain size reduces when the precursor temperature is beyond 60 °C, as shown in Figure 2.8 (d). This phenomenon is also reported by Gao *et al.* when grow h-BN on Pt foils using an APCVD setup.³⁹ Large amount of precursor results in thicker h-BN films with small domain sizes, as shown in Figure 2.8 (e) and (f), respectively. Next, Tay *et al.* demonstrated large hexagon shaped h-BN domains (35 μm^2) grown on electropolished Cu substrates using APCVD with ammonia borane precursor.³² As the domains coalesce to form a continuous film, the large h-BN domain size offers more pristine and smoother film with less grain boundaries and induced defects. The Cu substrate is smoother with an RMS of 4.42 nm due to electropolish than the purchased Cu foil (RMS = 314 nm). It is also observed that a higher nucleation density of triangular domains occurs along the scratched regions and grain boundaries, while fewer domains are found at remote areas.

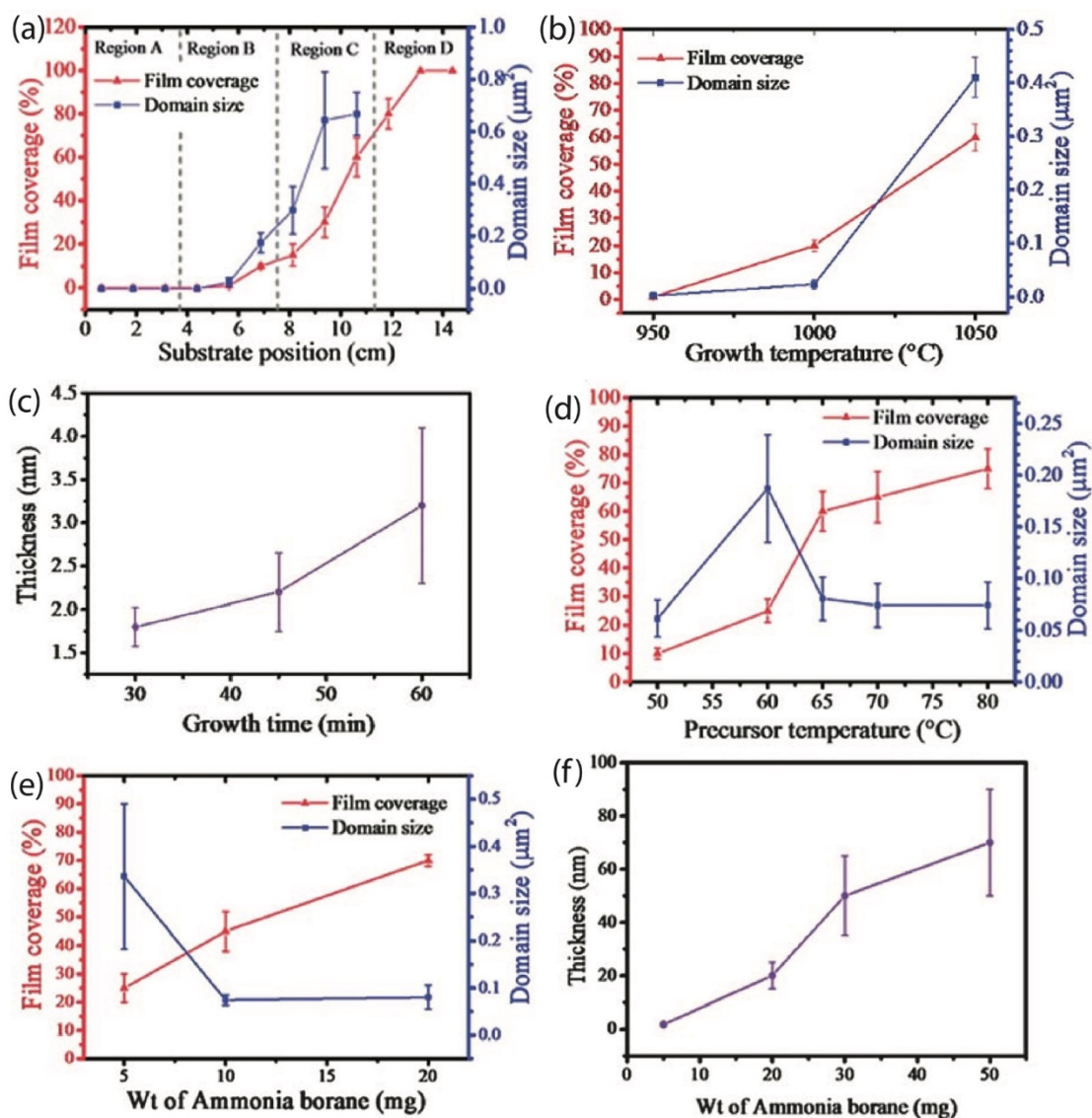


Figure 2.8 CVD parameters investigation of h-BN grow on Cu substrate. (a) Plots showing substrate-position-dependent film coverage (red) and size of h-BN domains (blue). (b) Plots of film coverage (red) and domain size (blue) vs. growth temperature. (c) Plots of film thickness vs. growth time. (d) Plot of film coverage (red) and domain sizes (blue) vs. precursor temperature. (e) Plot of film coverage (red) and domain sizes (blue) vs. weight of ammonia borane. (f) Plot of film thickness vs. weight of ammonia borane. Reprint (adapted) with permission from: (a-f), ref (61), © 2014 The Royal Society of Chemistry.

Domain Shapes and Orientations

Unlike the hexagon shaped graphene domains, the most commonly observed shapes of h-BN domains are triangle,⁷⁰ asymmetric diamond⁹⁸ and hexagon.⁹⁹ It is reported that the edges of triangular h-BN domains on Ni (111) are nitrogen terminated, because the nitrogen-terminated triangles have a lower edge energy than that of the boron-terminated edge.^{31,66} For the asymmetric diamond shaped h-BN, the origin of the shape is not clear. The hypothesis is that the equilateral triangle side is nitrogen terminated and the other side is terminated by both nitrogen and boron.⁷⁰ In APCVD growth, the h-BN domains have curved edges and rounded apexes due to the non-uniform density distribution in the gas flow.⁶¹ The hexagonal shaped h-BN domains are observed on electropolished copper substrates *via* APCVD growth. During the electropolish process, oxygen is induced on the Cu surface and the energy barrier of edge attachment is reduced. The BN radicals have sufficient energy to bond both N and B terminated edges, thus forming hexagon shaped h-BN domains.³² In the APCVD growth of h-BN on Pt foils, the domains are in triangle shapes with curved edges. It is different from the prefect triangular shape of the h-BN domains grown on Cu and Ni substrates, this is caused by the large lattice mismatch between h-BN and Pt.^{39, 100}

The size of CVD grown h-BN domains is an important factor and it is progressively increasing from micrometre to the millimetre scales recently. The typical size of CVD grown h-BN domains is in the order of several micrometres. Several groups reported h-BN domains have lateral size around 100 μm . For example, Lu *et al.* achieved single h-BN domain up to 7500 μm^2 on designed Cu-Ni alloy substrate;¹⁰¹ Caneva *et al.* reported the CVD grown h-BN crystal has lateral dimension of 300 μm on Si-doped Fe substrate;¹⁰² and Meng *et al.* successfully obtained h-BN domain up to 0.6 mm in edge

length on Ni (111)/sapphire substrate.¹⁰³ Most recently, Ji *et al.* reported an integrated method to grow h-BN with nucleation density below 1 per mm² by low-pressure CVD on polycrystalline copper substrate.⁹⁸ The inner surface of an enclosed Cu foil with 127 μm thickness shows (1) ultralow nucleation density; (2) about 300 μm h-BN domain size; (3) controllable nucleation density; and (4) the size of grown h-BN is proportional to the growth time, as shown in Figure 2.9 (a-g). In addition, the overlapping grain boundaries in monolayer h-N film do not have defect lines, and they are composed of self-sealing bilayer regions with limited width, as shown in Figure 2.9 (h and i).¹⁰⁴

The orientation of h-BN domains depends on the transition metal surface. After a high temperature annealing process, the Cu substrate has an increased grain size and is recrystallized predominantly to the (100) surface orientation. The h-BN triangular islands nucleate in random orientations on the Cu surface. The growth of h-BN on Ni (111) is observed with two different orientations where boron atoms are bonded on either Ni hcp or fcc sites, respectively.¹⁰⁵ This is because the symmetry of the (111) surface fcc crystal is hexagon shaped while the symmetry of the (100) surface is a square shaped. Moreover, the lattice mismatch between Cu (100) and h-BN domains is higher than Cu (111) and Ni (111), which causes more misalignments.⁶¹ Similar to Cu substrates, h-BN domains are randomly oriented in the same Pt grain, and the Pt grain orientation does not show an obvious influence on the shape and nucleation density of h-BN domains. It also indicates weak interactions between h-BN and Pt surface.¹⁰⁰ In order to obtain epitaxial growth of h-BN, it requires initial interaction between h-BN and metal surface. The interaction should be weaker than the strong σ bonds between N and B atoms. Lastly, the lattice size of the metal surfaces should be approximately matched with the h-BN domains.⁹⁵

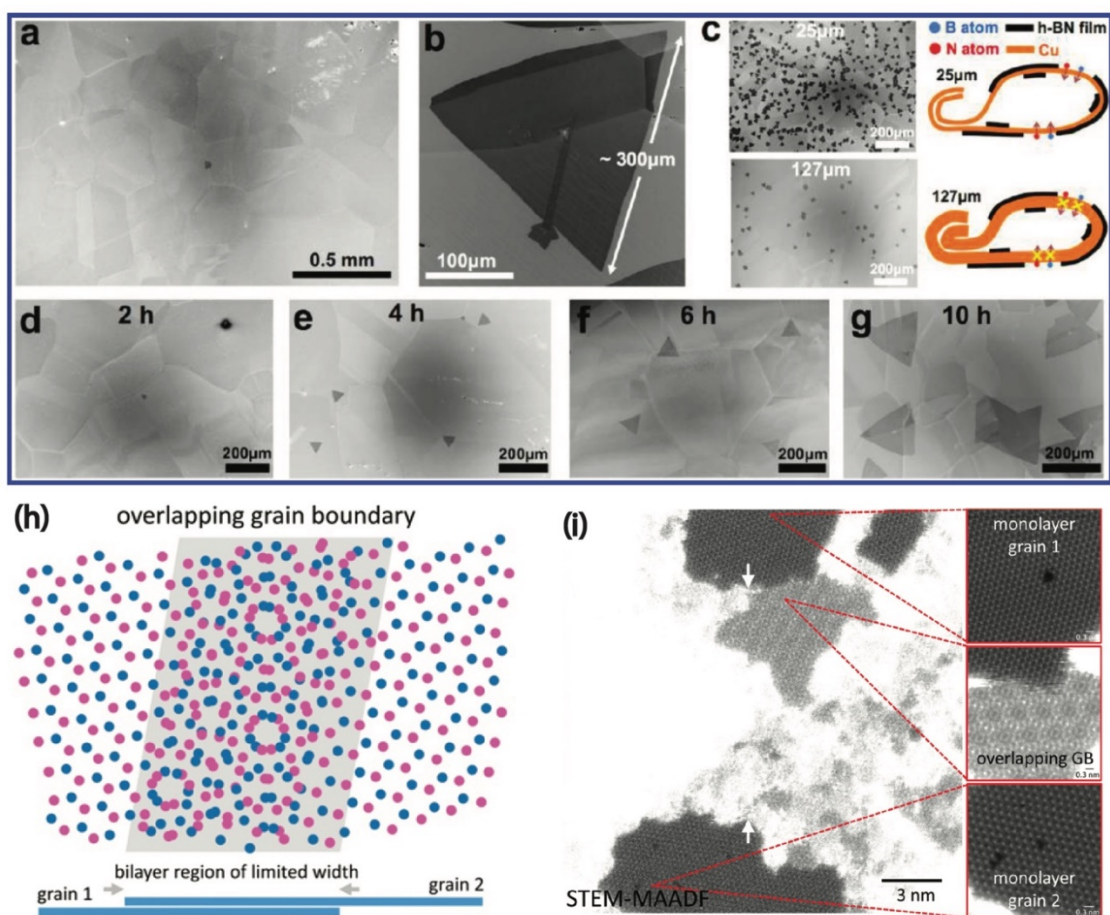


Figure 2.9 (a) SEM image shows the ultralow initial nucleation density of h-BN. (b) SEM image of a large triangular h-BN domain. (c) SEM images of the h-BN grown on 25 μm and 127 μm Cu enclosure, respectively. Illustrations of Cu enclosures and growth mechanism. (d-g) SEM images showing the CVD grown h-BN for 2, 4, 6, and 10 hours, respectively. (h) Illustration of overlapping grain boundary that has Van der Waals type interface where two monolayer h-BN grains merge *via* a turbostratically stacked bilayer region of limited width. (i) Corresponding STEM images show the illustration in (h). Reprint (adapted) with permission from: (a-g), ref (98), ©2017 American Chemical Society; (h and i), ref (104), ©2017 American Chemical Society.

2.2.2 Beyond CVD the Growth of h-BN

Novel 2D isolated atomic planes can be reassembled into heterostructures layer by layer through Van der Waals interactions. Another configuration is in-plane heterostructures and it is formed by the covalent bonding of 2D materials. Beyond the CVD growth of h-BN, researchers explore the direct synthesis of h-BN thin film with other 2D materials in both configurations. In this section, the heterostructures between h-BN thin film and other 2D materials are reviewed, such as graphene, transition metal dichalcogenides (TMDs), and boron carbon nitride (BCN).

Commonly graphene/h-BN hybrid structures exist in two configurations. One is the vertically stacked graphene and h-BN heterostructures, and the other one is in-plane graphene/h-BN atomic layer where the two materials are seamlessly integrated into lateral heterostructures. It is feasible that graphene and h-BN 2D crystals can be sequentially grown on substrates to create graphene/h-BN stacked layers *via* CVD methods.¹⁰⁶ This technique is able to reduce fabrication complexity and structural uncertainties such as lattice orientation, sample uniformity and interface contamination.

Liu *et al.* demonstrated the two-step direct CVD growth of h-BN on graphene.¹⁰⁷ Firstly, the graphene is synthesised on a Cu substrate using the liquid carbon source n-Hexane; after that, this graphene/Cu sample is loaded into another CVD system for the growth of h-BN film on top. Similarly, Ding *et al.* reported the direct growth of few layer graphene on h-BN flakes *via* an APCVD method. Both methods do not require the assistance of metal catalysts because their lattice mismatch is about 1.7 %.¹⁰⁸ In order to control the thickness of the grown graphene on h-BN substrate, Yang *et al.* successfully grew monolayer and bilayer graphene on 20-120 nm thick exfoliated h-BN flakes *via* a plasma assisted LPCVD method.¹⁰⁹ The overall size of the as-grown graphene is limited by the

size of h-BN flakes, and the graphene domains have the same orientation with respect to the h-BN substrate. Wang *et al.* reported that monolayer graphene can be directly grown on h-BN/Cu sample using LPCVD. The grown graphene/h-BN has a defect free interface, as shown in Figure 2.10 (a).¹¹⁰ Furthermore Wang *et al.* revealed the growth mechanism between h-BN and graphene on Cu by measuring the effect of h-BN film thickness, as shown in Figure 2.10 (b).¹¹¹ The results show that Cu foil covered with less than 3 nm h-BN film can catalyse the decomposition of methane and are used to grow graphene. The catalytic effect of growing graphene is inversely proportional to the thickness of the covered h-BN film.

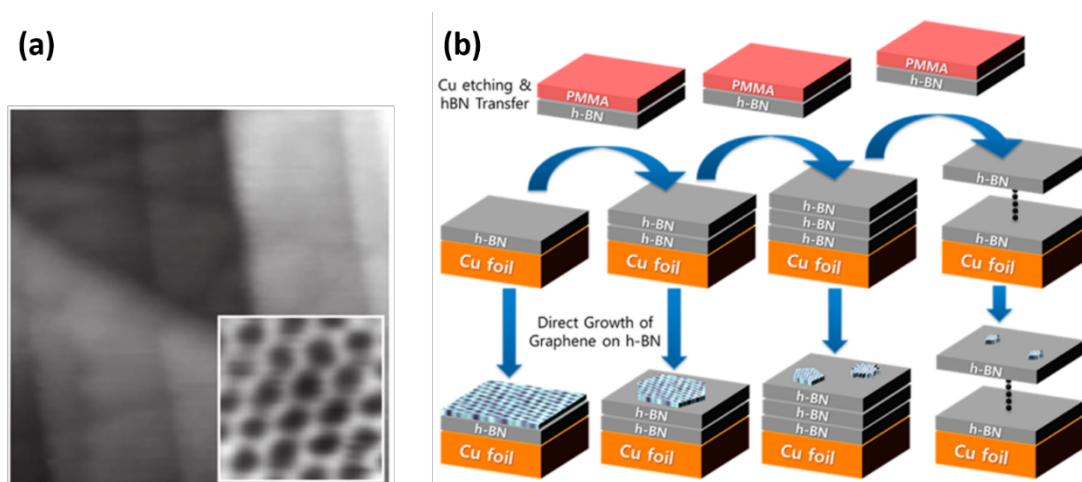


Figure 2.10 (a) Scanning tunnelling microscopy (STM) image of graphene on BN/Cu foil. Inset STM image of the graphene honeycomb lattice. (b) Illustrations of the CVD grown graphene on stacks of h-BN films with different thickness. Reprint (adapted) with permission form: (a), ref (110), © 2013 WILEY-VCH Verlag GmbH & Co.; (b), ref (111), ©2014 American Chemical Society.

Graphene and h-BN heteroepitaxial structures have been achieved through the patterned regrowth method and the bottom up synthesis method. The advantages of the patterned regrowth method include control the size and the shape of the second grown 2D crystals. The bottom up synthesis method can fabricate high quality graphene/h-BN heterostructures in the nanometre scale. But the growth requires noble metal substrates and harsh growth conditions. Liu *et al.* reported the fabrication of in-plane heterostructures of graphene and h-BN with controlled domain size *via* patterned regrowth method.¹¹² Similarly, Levendorf *et al.* produced lateral junctions between h-BN and graphene.¹¹³ The graphene is synthesised on the Cu surface, then the photolithography and reactive ion etching are used to pattern shapes on the grown graphene, lastly h-BN is deposited on the area where graphene is removed. This process is presented in Figure 2.11 (a).

Liu *et al.* reported monolayer h-BN synthesis from the graphene domain edges.¹¹⁴ This growth involves several steps: monolayer graphene film is deposited on Cu foil, hydrogen is then utilised to etch the graphene leaving equiangular hexagonal holes with zigzag edges, and finally monolayer h-BN is grown within the etched holes. Similar to the above method, Han *et al.* demonstrated another approach for growing heteroepitaxial graphene and h-BN. Single crystal h-BN is directly grown from the orientated edge of hexagonal graphene domains on Cu substrates using the APCVD method.¹¹⁵ This process is presented in Figure 2.11 (b). The width of the BN ribbons is between 180 and 530 nm. These results suggest that the graphene edges have higher reactivity than bare Cu foil. It is also observed that BN triangular domains nucleate away from graphene on the Cu foil. Later, Sutter *et al.* demonstrated a bottom up approach using UHVCVD method, lateral heteroepitaxial sequential synthesis of graphene and h-BN stripes at the edge of 2D seed crystals on Ru substrates, as shown in Figure 2.11 (c).¹⁰⁶

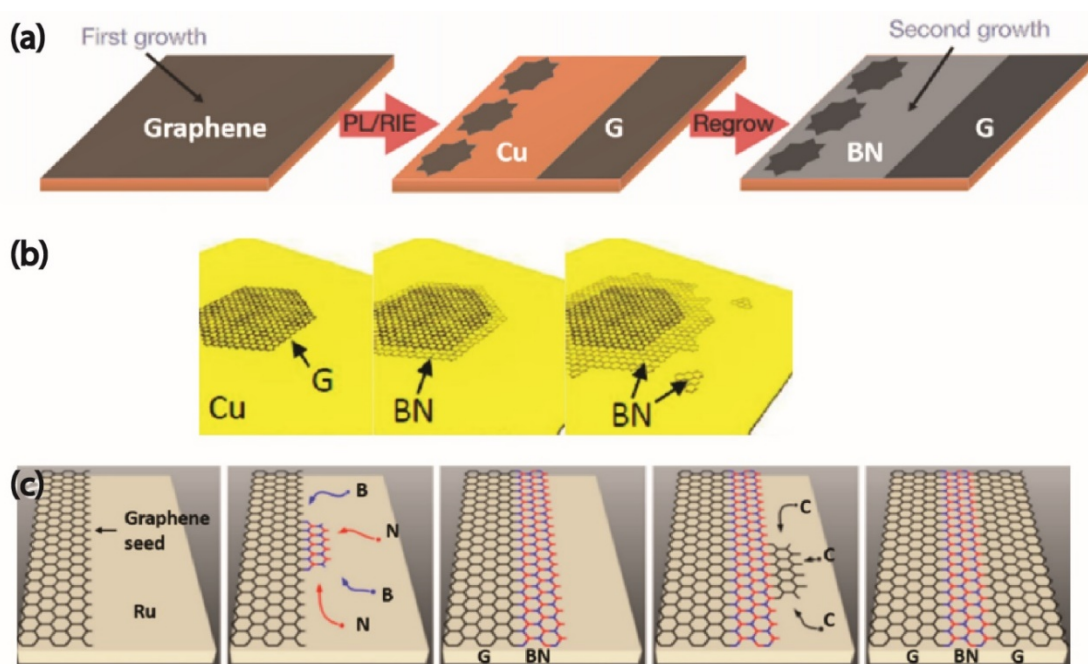


Figure 2.11 (a) Schematic shows the formation of atomically thin lateral heterostructures of graphene and h-BN using photolithography and reactive ion etching techniques. (b) Illustrations of epitaxial growth of BN ribbons around graphene domain. (c) Illustrations of sequential growth of h-BN and graphene strips from graphene seeds. Reprint (adapted) with permission from: (a), ref (113), ©2012 Macmillan Publisher Limited; (b), ref (115), ©2013 American Chemical Society; (c), ref (106), ©2014 American Chemical Society.

Various approaches are used to open a bandgap in graphene, and therefore it is converted from a semimetal to a semiconductor. Chemical doping is one of the feasible method, this involves using B and N atoms to replace C atoms in graphene.^{116,117} Ci *et al.* reported the synthesis of atomic layer thick h-BNC film on Cu substrates using LPCVD method.¹¹⁸ The B/N ratio is unity due to the ammonia borane precursor, while the atomic percentage of C can be tuned from 10 to 100. The structure is confirmed by high resolution transmission electron microscopy (HRTEM), and a clear Moiré pattern indicates the turbostratic stacking configuration. A fast Fourier transform (FFT) pattern shows the rotational angle is 16° between these two layers, as shown in Figure 2.12 (a). Electron energy-loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS) indicate

the sp^2 hybridisation among B, N and C atoms and also the C-B and C-N covalent bonds. A schematic drawing of the structure is displayed in Figure 2.12 (b) and it indicates the separated regions of graphene and h-BN. Later Gong *et al.* reported a topological substitution reaction, it converts graphene to h-BNC and h-BN.¹¹⁹ This growth technique is quite complex. In brief, the as-grown graphene on silicon substrate is loaded into a LPCVD system. Solid boric acid powder and ammonia gas are used as precursors to convert graphene, as shown in Figure 2.12 (c). The atomic sheet contains hybridized bonds among boron, nitride, and carbon elements. The new h-BNC material has properties complementary to graphene and h-BN.

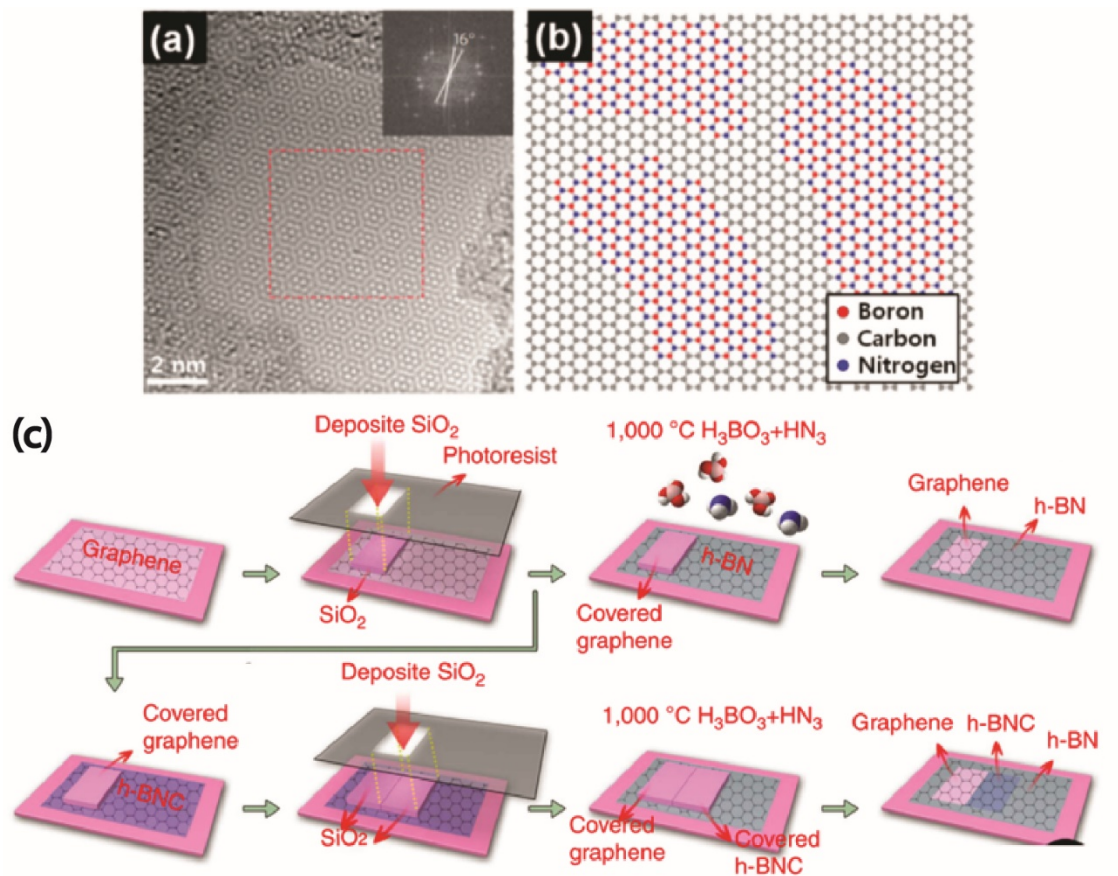


Figure 2.12 (a) HRTEM image of h-BNC film, inset FFT pattern of the marked region. (b) Schematic of the h-BNC film with hybridized h-BN and graphene regions. (c) Schematics of the spatially controlled conversion process of graphene into h-BN, and two-step process that converts graphene into a graphene/h-BNC/h-BN heterostructure thin film. Reprint (adapted) with permission from: (a and b), ref (118), ©2010 Macmillan Publishers Limited; (c), ref (119), ©2014 Macmillan Publishers Limited.

Transition metal dichalcogenides (TMDs) such as WS₂ and MoS₂ exhibit significant spin-valley coupling and optoelectronic performance because of their unique structural symmetry and band structures.^{120,121} In addition, layered TMDs are considered to be as the thinnest semiconductor and have great potentials for advanced short-channel devices.¹²² When combined with h-BN, their intrinsic properties can be further explored. The following section summaries the direct CVD growth of TMDs on h-BN material.

Okada *et al.* reported the direct CVD growth of WS₂ on exfoliated h-BN flakes, as shown in Figure 2.13 (a).¹²³ The supply rate of precursors is independently controlled by a 3-furnace CVD setup. The h-BN flakes are obtained from an ultrapure single crystal h-BN material. The quality of the grown WS₂ on h-BN flakes is characterised by Raman and photoluminescence (PL) spectroscopy. The Raman peak positions are at 356.3 and 419.4 cm⁻¹ and the PL peak position is at 2.01 eV, as shown in Figure 2.13 (b) and (c). Ling *et al.* demonstrated direct CVD growth of monolayer MoS₂ on h-BN film, as shown in Figure 2.13 (d).¹²⁴ The growth is assisted by the seeding promoters. They are deposited on the exfoliated h-BN flakes *via* thermal evaporation. After the CVD growth, the h-BN flakes and the rest of the SiO₂ surface is covered by continuous MoS₂ thin film. Raman and photoluminescence (PL) spectra are used to confirm the as-grown MoS₂ thin film. The Raman modes have 383 and 404 cm⁻¹ peak position which are corresponding to E_{2g} and A_{1g}. The PL peak position is at 1.85 eV, as shown in Figure 2.13 (e) and (f). Later, all CVD growth of MoS₂:h-BN vertical heterostructure is achieved and the grown MoS₂ thin film is monolayer.^{125,126}

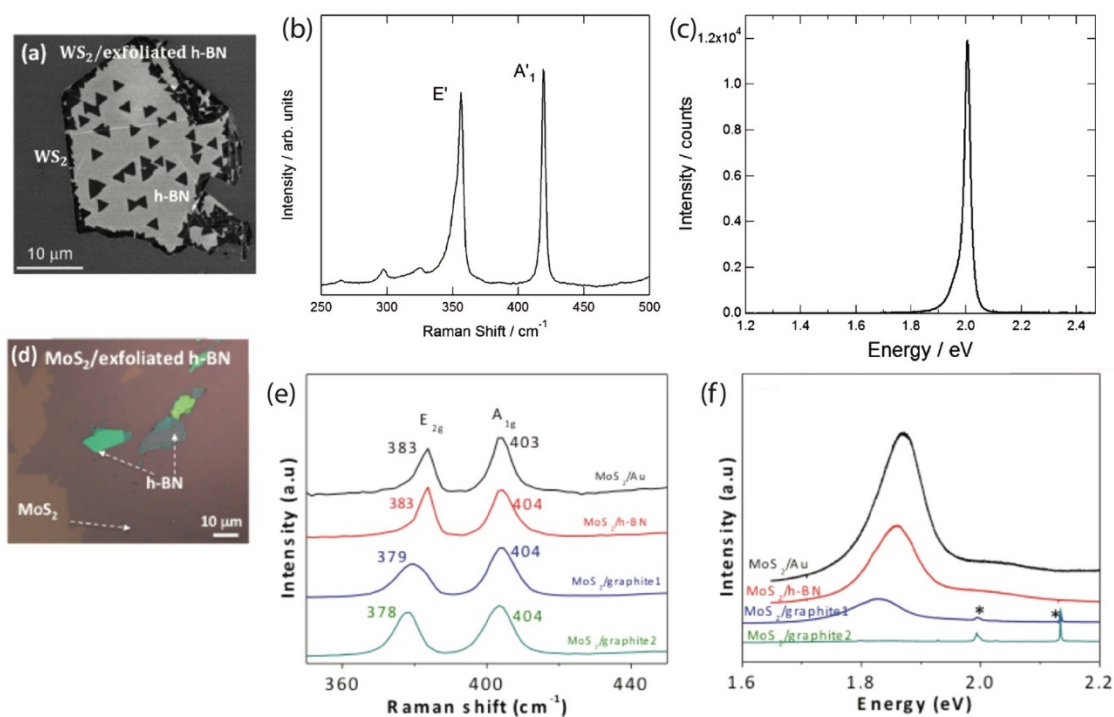


Figure 2.13 (a) SEM image of CVD grown WS₂ on h-BN flake. (b and c) Corresponding Raman spectrum and PL spectrum of the CVD grown WS₂ on h-BN flake. (d) Optical image of CVD grown MoS₂ on h-BN flake. (e and f) Corresponding Raman spectrum and PL spectrum of the CVD grown MoS₂ on h-BN flake. Reprint (adapted) with permission form: (a-c), ref (123), ©2014 American Chemical Society; (d-f), ref (124), ©2014 American Chemical Society.

2.2.3 Applications for Hexagonal Boron Nitride

In this section, the applications of the CVD grown h-BN materials and its related Van der Waals heterostructures are reviewed. They have attracted attention in the scientific community for a long time because of their distinguishing properties. The h-BN is applied to various applications such as ultraviolet lasers, aerogels, coatings, dielectric substrates in graphene electronic devices, and so on.¹²⁷

Yin *et al.* synthesised three dimensional (3D) boron nitride foams in an LPCVD system.¹²⁸ This 3D boron nitride foam has a permittivity of 1.03, 1.6 mg/cm³ density, and thermal stability up to 1200 °C. It exhibits complete recovery after compression, as shown in Figure 2.14 (a) and (b). Li *et al.* demonstrated that the Cu substrate covered by h-BN film has low friction and surface roughness.¹²⁹ In contrast to the oxidation of graphene, h-BN is chemically stable in high temperature. Ni, Cu and stainless steel are protected by h-BN films when study their oxidation resistance at high temperature. The h-BN films are not only impervious to oxygen diffusion but also can serve as oxidation resistant coatings up to 1100 °C, as shown in Figure 2.14 (c) and (d).¹³⁰ The exfoliated h-BN film performs less well, its oxidation begins at 700 °C, and it can only survive up to 850 °C in air.²¹ The theoretical study of h-BN oxidation reveals that oxygen atoms stretch and break B-N bonds results in O domains or O chains on the h-BN sheet. Finally the h-BN sheet is subsequently unzipped in the zigzag direction.¹³¹

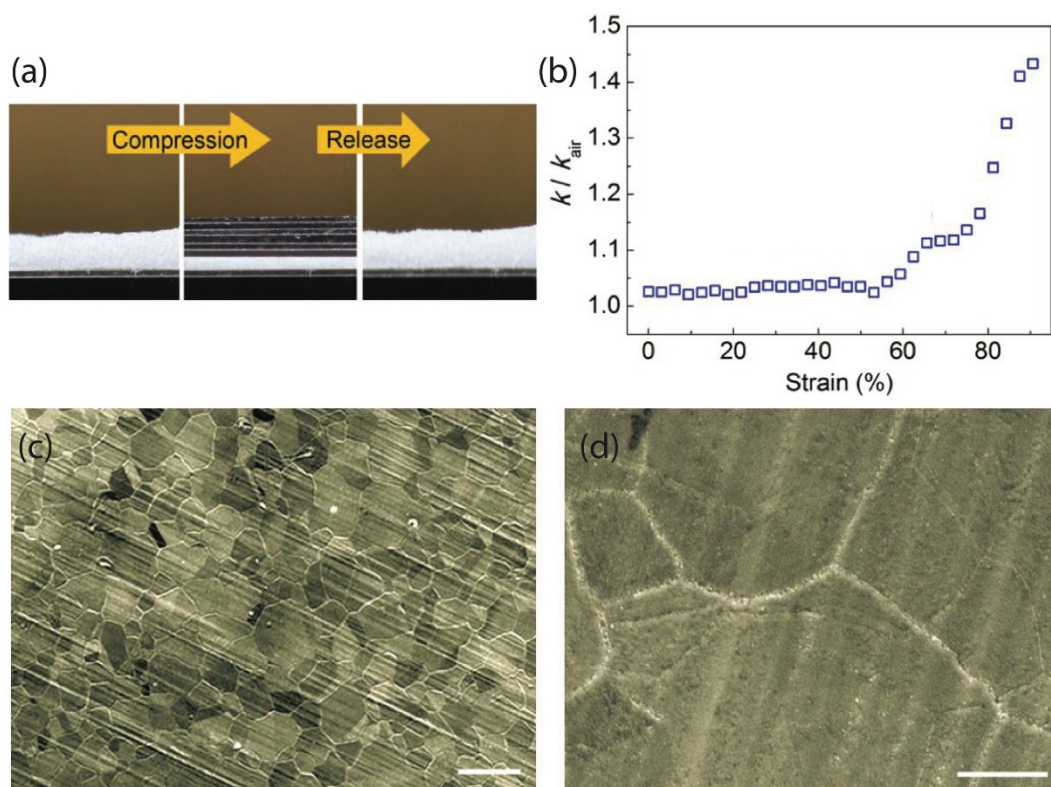


Figure 2.14 (a) Photographs showing the BN foam recovers to its original shape after compression. (b) Ratio of the dielectric constant of the BN foam at 100 kHz to that of air as a function of the strain. (c and d) Low-magnification and high-magnification SEM images of the h-BN-coated Ni foils after oxidization in 300 mTorr oxygen at 1100 °C for 30 min. Scale bars represent 100 μm and 10 μm , respectively. Reprint (adapted) with permission from: (a and b), ref (128), ©2013 American Chemical Society; (c and d), ref (130), ©2013 Macmillan Publisher Limited.

Graphene and h-BN are complementary 2D materials. They have similar structures, but they have different electronic properties. The carrier mobility of graphene on SiO₂/Si substrate is lower than it is on h-BN substrate, because the surface of h-BN is relatively free from dangling bonds and trapped charges. The h-BN films are excellent dielectric layers to complement graphene-based electronic devices. Furthermore, the in-plane h-BN and graphene heterostructures are fabricated into devices and have interesting properties. The measured mobility of Graphene/h-BN device is about 60000 cm²V⁻¹S⁻¹, and it is three times larger than the similar graphene-based device on SiO₂/Si substrate. Field effect transistors (FET) fabricated by LPCVD grown graphene on h-BN exhibit a carrier mobility of 4000 cm²V⁻¹S⁻¹.^{110,132} A shift of the Dirac point is observed, it indicates a low level concentration of charged impurities. The measured device has a higher mobility compared to the transferred graphene on SiO₂/Si and transferred graphene/h-BN on SiO₂/Si. These results are shown in Figure 2.15 (a) and (b). In addition, the boron nitride ribbons and graphene domains are also used to fabricate the side gate device on silicon substrate.¹¹⁵ Its electronic properties are measured in ambient and vacuum (1 × 10⁻⁶ Torr) conditions, as shown in Figure 2.15 (c) and (d). The device exhibits p-type doping due to atmospheric impurities. In ambient condition, its Dirac point is measured at 15 V. In vacuum condition, the charge neutrality point of the back gate is -5 V. The side gate in vacuum condition has a more negative Dirac point (around -22 V). The lateral heteroepitaxial graphene and h-BN are also used to make FETs with alternative stripes of pristine graphene and h-BN.¹¹² When 1 mV voltage is applied, the measured mobility is between 520 and 1700 cm²V⁻¹S⁻¹.

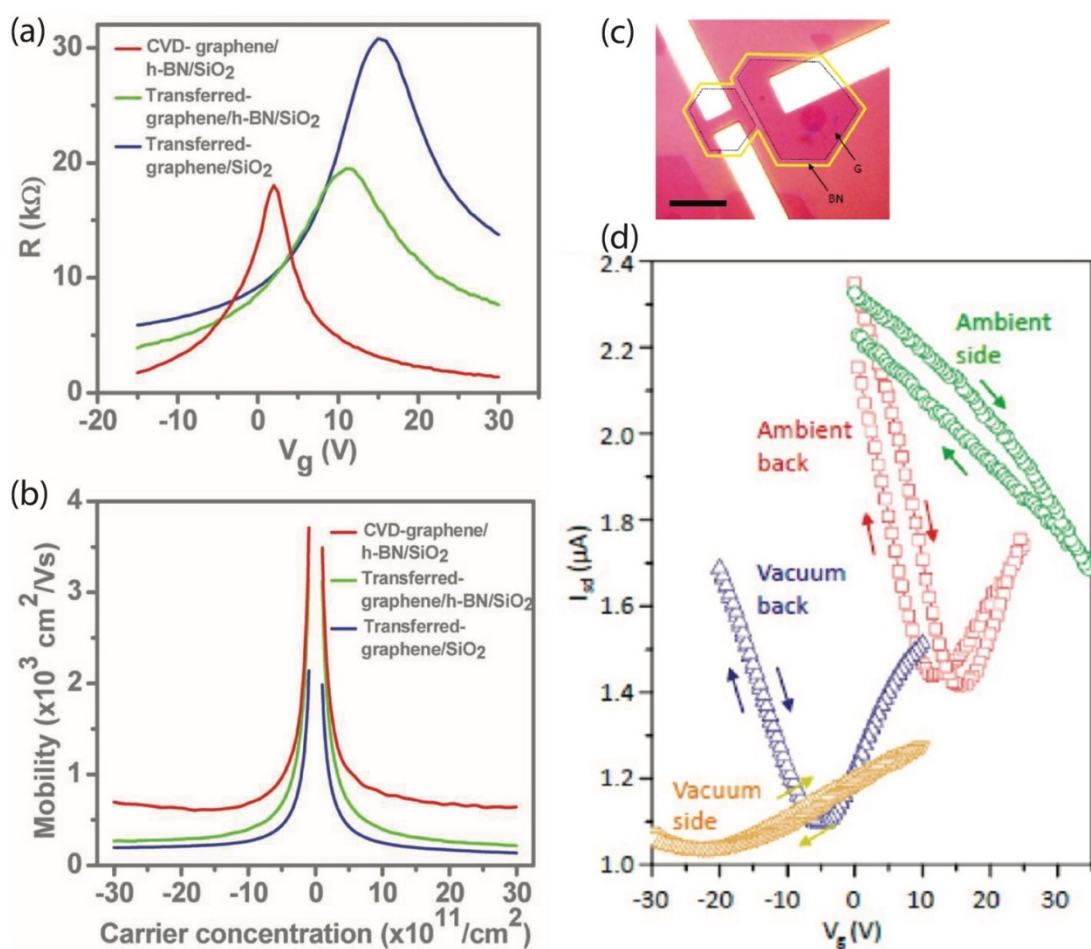


Figure 2.15 (a) Resistance versus applied gate voltage for CVD-grown graphene/h-BN, mechanically transferred graphene/h-BN, and graphene on silicon substrate. (b) Carrier mobility as a function of charge carrier density for the three devices. (c) Optical image shows two graphene domains are separated by a boron nitride gate dielectric region. Scale bar is 10 μ m. (d) I-V characteristics for the device in (c). Reprint (adapted) with permission from: (a and b), ref (110), © 2014 American Chemical Society; (c and d), ref (115), © 2013 Wiley-VCH Verlag GmbH & Co.

2.2.4 Conclusion for Hexagonal Boron Nitride

The current research on h-BN 2D crystals is summarised in the first part of this literature review. To summarise, the h-BN material has many interesting properties such as electrically insulating, atomically flat, chemical inert and so on. The h-BN plays an important role in the 2D semiconducting field as dielectric layer or substrate. The chemical vapor deposition (CVD) method enables the large-scale production of h-BN with low cost. The initial utilization of mixed chemical precursors has moved to single source chemical precursor such as borazine and ammonia borane. The Cu substrates are mainly used instead of noble metal substrates such as Pt. However, the CVD growth mechanism of h-BN still remains unclear. Further investigation of h-BN is required in order to achieve controllable growth. In addition, the h-BN heterostructures with other 2D crystals can be formed through Van der Waals interactions. At last, the systematic study of h-BN 2D crystals is highly desirable.

2.3.0 Gallium Sulfide

In addition to graphene and h-BN, transition metal dichalcogenides (TMDs) and layered group III metal chalcogenides such as MoS₂,¹³⁶ MoSe₂,¹³⁹ WS₂,^{133-135,137} WSe₂,¹³⁸ and GaS have been explored recently. These materials first interest scientific community because they are semiconductors. Graphene has a zero bandgap and h-BN is an insulator. A periodic table highlighting both the TMDs and layered group III metal chalcogenides is presented in Figure 2.16 (a). TMDs have gained attention due to their unique properties and potential applications.¹⁴⁰⁻¹⁴² They cover the whole range of electronic properties, including insulators (*e.g.* HfS₂), semiconductors (*e.g.* MoS₂ and WS₂), semi-metals (*e.g.* WTe₂ and TiSe₂), and metals (*e.g.* NbS₂ and VSe₂).¹⁴³ The TMDs have a general formula: MX₂, where M represents a transition metal element (*e.g.* Ti, V, Nb, Mo, Hf, Ta, and W) from group IV to X in the periodic table and X represents a chalcogen (*e.g.* S, Se, and Te).¹⁴⁴ The transition metal atoms are sandwiched between two layers of chalcogen atoms, altogether these three-atomic thick (X-M-X) TMDs are referred as monolayer. Like few-layered graphene, TMDs have all covalent bonding within each layer, and adjacent layers are interacted *via* Van der Waals forces.

Layered group III metal chalcogenides have drawn attention recently, because of their earth-abundance, low-cost, and environmentally friendly characteristics. In addition, their promising applications includes photodetectors,¹⁴⁷ transparent conductors,¹⁵¹ and terahertz generation and tuning devices.^{145,146,148-150} Similar to the structure of TMDs, layered group III metal chalcogenides have the monochalcogenide form such as MX, where M = Ga, In, Ti, and X = S, Se, Te.¹⁵²⁻¹⁵⁴ The GaS flakes are thermodynamically stable in ambient condition. The first exfoliated GaS flakes on silicon substrates is shown in Figure 2.16 (b). Single layer GaS has a hexagonal crystal structure with four atomic layers. Two layers of Ga metal atoms are sandwiched between two layers of S atoms in the sequence of S-Ga-Ga-S. It is known that the β -phase GaS layer has 2Hb polytypic

arrangement. Figure 2.16 (c) shows a schematic diagram of a monolayer GaS nanosheet. There are two layers of GaS in a unit cell and its dimensions are: $a = b = 3.587 \text{ \AA}$, and $c = 15.492 \text{ \AA}$ build by six-membered Ga_3S_3 rings.¹⁵⁵ In more detail, the calculated Ga-Ga bond distance is $2.48 \text{ \AA}$, the Ga-S bond distance is $2.37 \text{ \AA}$, the bond angle of Ga-Ga-S is 115.76° , and the bond angle of S-Ga-S is 102.51° .¹⁵⁶ Again, the in plane Ga and S atoms are connected by covalent bonds with each other, and the individual layers are held together by weak Van der Waals interactions. The metastable rhombohedral polymorph of GaS is known as γ -phase. It is formed when growth condition has excess of sulphur.¹⁵⁷ The γ -GaS is predicted in bulk crystals or nanotubes.¹⁵⁸

In the following sections, I aim to focus on research activities regarding GaS 2D layered materials. First, the band structures of GaS 2D materials are outlined, then the electronic and optical properties are summarised, followed by its vibrational properties. In addition, various synthesis strategies of GaS are discussed. Finally, the applications of GaS 2D materials are reviewed.

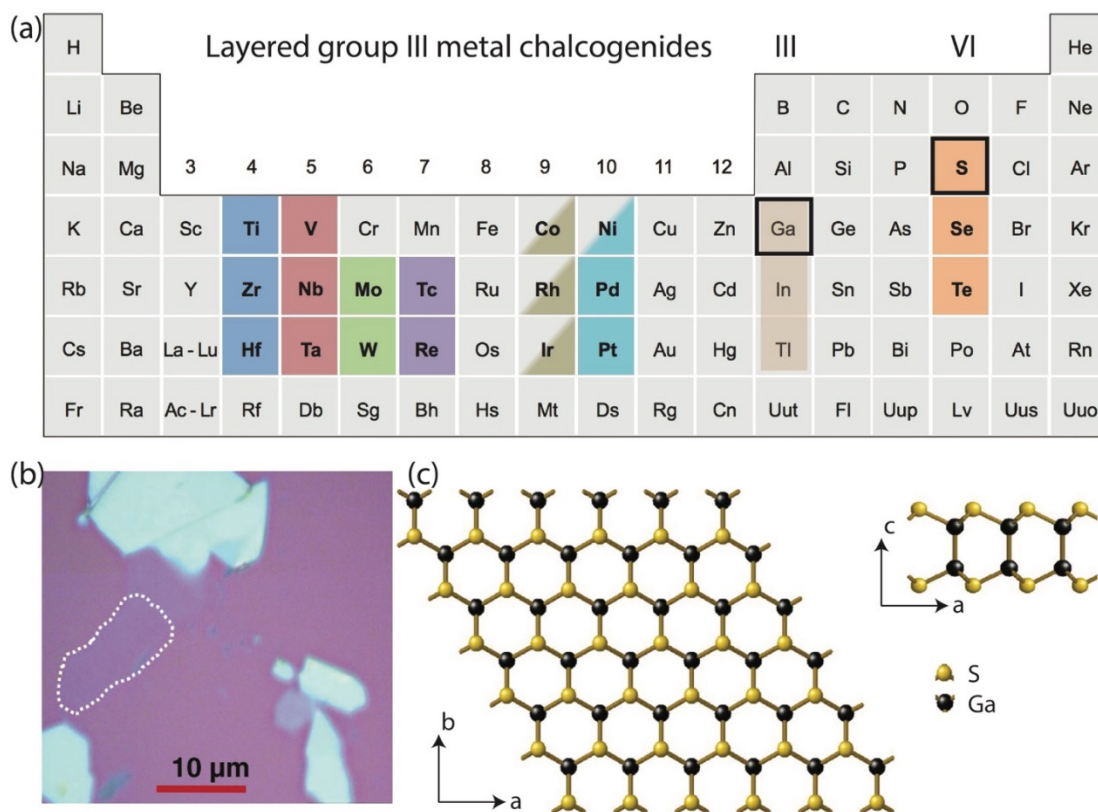
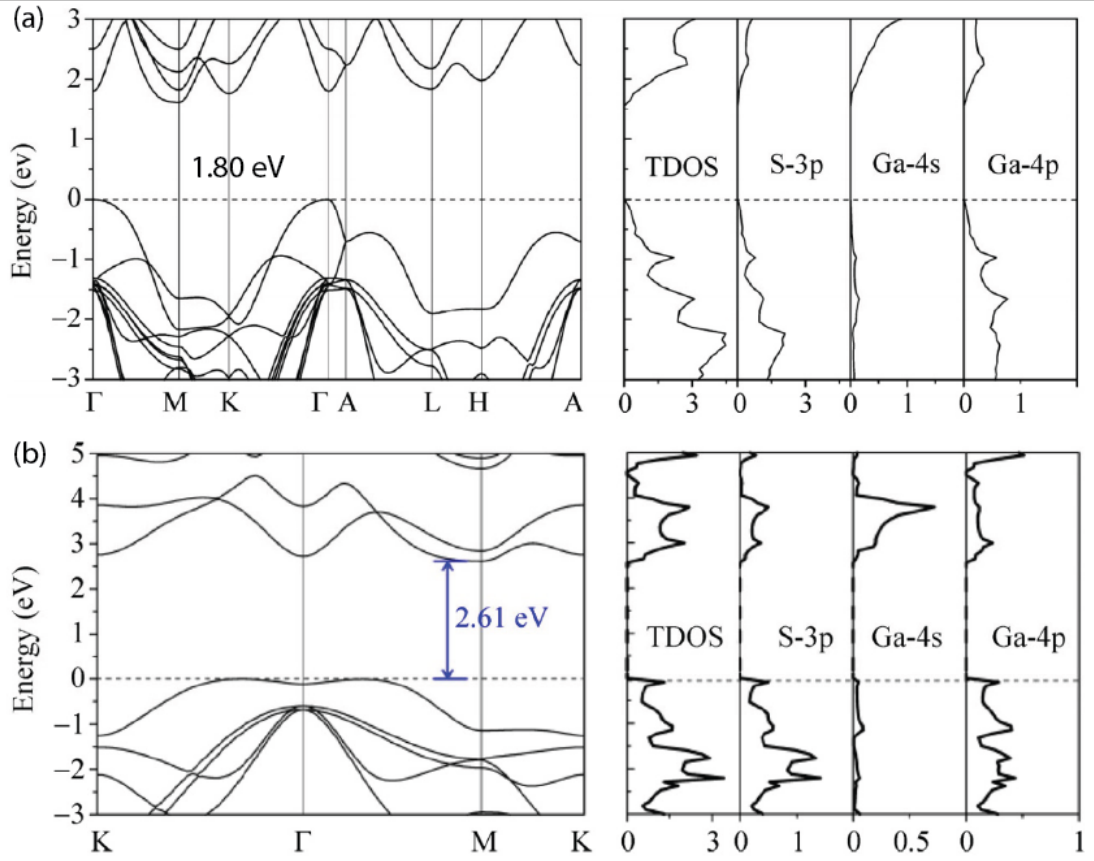


Figure 2.16 (a) Periodic table highlighting the TMDs and the layered group III metal chalcogenides. The positions of gallium and sulphur are outlined. (b) Optical image of ultrathin layer GaS flakes on SiO₂/Si substrate (highlighted by a dashed line). The structure of monolayer GaS (top view and side view), where yellow and black spheres represent sulphur and gallium atoms, respectively. Reprint (adapted) with permission form: (a), ref (143), © 2013 Macmillan Publishers Limited; (b), ref (154), ©2012 WILEY-VCH Verlag GmbH & Co; (c), ref (156), ©2004 The American Physical Society.

Electronic Properties

Monolayer GaS is a semiconducting 2D material with an indirect band gap. The difference between its direct and indirect band gap is so small, electrons can easily transfer with a small amount of thermal energy.^{159,160} The indirect band gap of GaS is around 2.59 eV at room temperature and the direct band gap is at approximately 0.45 eV higher in energy.^{161,162} Density function theory (DFT) studies reveal both the bulk and single layer band structures of GaS material and their corresponding density of states is shown in Figure 2.17.^{151,158} For bulk GaS crystals, the minimum values of the conduction band (CBM) and maximum value of the valence band (VBM) can be found at points M and Γ of the Brillouin zone, respectively. For monolayer GaS, although the CBM behaves the same as bulk GaS at M point, the VBM symmetrically splits at the Γ point. In the 2D GaS density of states, the top conduction bands are mainly contributed by S-3p and Ga-4s states because of the covalent Ga-S bonding.¹⁵¹ On the other hand, the bottom valence states are formed by the Ga-4p orbitals due to covalent intralayer Ga-Ga bonding and the antibonding S-3p orbitals.^{151,158} Similar to the TMDs, the electronic properties of GaS vary drastically with number of layers. The two calculated VBMs in monolayer GaS move towards the Γ point when the layer number increases. At a thickness of around 4-6 layers, there is no difference in VBMs between bulk and few-layered GaS materials.¹⁵¹ The calculated indirect band gap for monolayer GaS is between 2.50 and 2.61 eV, while the indirect band gap of bulk GaS is between 1.59 and 1.80 eV.¹⁶³ These calculated band gaps of GaS are in agreements with experimental results.



Optical Properties

Photoluminescence (PL) spectroscopy is a suitable and widely used technique for studying the electron-hole interaction in few-layer GaS 2D crystals.¹⁶⁴⁻¹⁶⁶ Figure 2.18 (a) shows the temperature dependence of PL spectra obtained from a GaS single crystal. Three PL bands are observed at 9K, centred at 558 nm (2.22 eV), 614 nm (2.02 eV), and 780 nm (1.59 eV), and these are marked as A, B, and C, respectively. When the temperature increases, the A and B bands gradually decrease and eventually disappear; although the C band shows similar behaviour as A and B bands, the peak energy of C band increases by almost 120 meV.¹⁶⁷ The bands A and B exhibit quenching effect at low temperature due to donor-acceptor pair recombination process. The behaviour of the C band is explained by the configuration coordinate model of defects.^{167,168} In addition, the room temperature photoluminescence (PL) spectrum of a synthesised GaS tube has two strong emission bands which are centred at 585 nm (2.12 eV) and 615 nm (2.02 eV), respectively.¹⁶⁹

The optical properties of GaS have also been characterised using temperature-dependent absorption and piezoreflectance (PzR) measurements reported by Ho *et al.* The low temperature PzR spectrum of GaS at 15 K has these exciton series in A, B, and C and they are shown in Figure 2.18 (b). The A series is related to Ga-S bonds at Γ point, the B series mainly come from the bonds of Ga-Ga, and C series come from the mix of S-S and Ga-S states.¹⁶¹ The band gap energies (E_g) and average photon energies (E_p) of GaS crystals can be both determined *via* analysis of the absorption coefficient and the energy of incident photon. The absorption coefficient α is proportional to the term $(h\nu - E_g + E_p)^2$, as shown in Figure 2.18 (c). The phonon energy E_p at different temperatures is invariant and the determined value is about 26 meV.

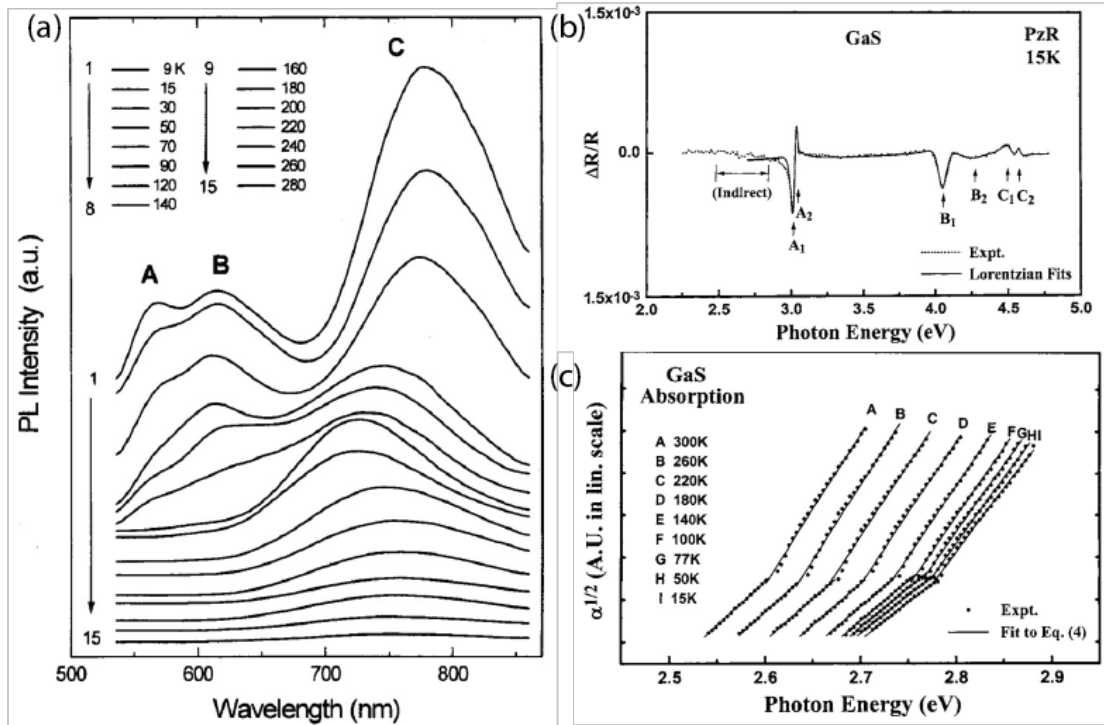


Figure 2.18 Temperature dependence of PL spectra from a GaS single crystal in the 525-860 nm range. (b) Low-temperature PzR spectrum of GaS at 15 K. The interband transition energies of the excitonic series A, B, and C are indicated by arrows. (c) $\alpha^{1/2}$ versus $h\nu$ of GaS single crystal. The solid circles are representative experimental points deduced from the absorption spectra and the solid lines are the least square fits. Reprint (adapted) with permission from: (a), ref (167), © 2000 American Institute of Physics; (b and c), ref (161), © 2006 American Institute of Physics.

Vibrational Properties

The vibrational properties of GaS have been studied by Raman spectroscopy. It is a widely-used technique for the non-destructive characterisation and identification of layered 2D materials. Three schematics are presented in Figure 2.18 (a). They are the atomic displacement vectors of GaS for both interlayer and intralayer displacements, known as A^1_{1g} , E^1_{2g} , and A^2_{1g} . All the gallium and sulphur atoms vibrate in either perpendicular or parallel directions. In the E^1_{2g} shear mode, atoms move in the direction of bending bonds, while the A^1_{1g} and A^2_{1g} compressional modes stretch the bonds. These three phonon modes are commonly observed in the Raman spectrum of bulk GaS material at 187.93 cm^{-1} (A^1_{1g}), 295.41 cm^{-1} (E^1_{2g}), and 359.58 cm^{-1} (A^2_{1g}). Similar to other layered 2D crystals, the Raman modes of GaS also show a dependence on layer numbers.^{154,170,163} For example, the frequency of ultrathin GaS are found to be at 185.53 cm^{-1} , 302.5 cm^{-1} , and 361.18 cm^{-1} corresponding to A^1_{1g} , E^1_{2g} , and A^2_{1g} , respectively. But the monolayer GaS only has the E^1_{2g} mode which is centred at 303.5 cm^{-1} and the intensities of the other peaks are too weak to be observed.¹⁵⁴ As the number of layers increases, the A^1_{1g} and A^2_{1g} modes experience red shifts, while the E^1_{2g} mode exhibits a blue shift. Since the GaS 2D crystals are stacked through weak Van der Waals forces, the unexpected shift of E^1_{2g} may relate to the changes in interlayer bonding.¹⁶³ The temperature dependence of the Raman modes in GaS crystals between 15-293 K reveals that the frequency shifts and the broadening of linewidths are caused by thermal expansion.¹⁷¹

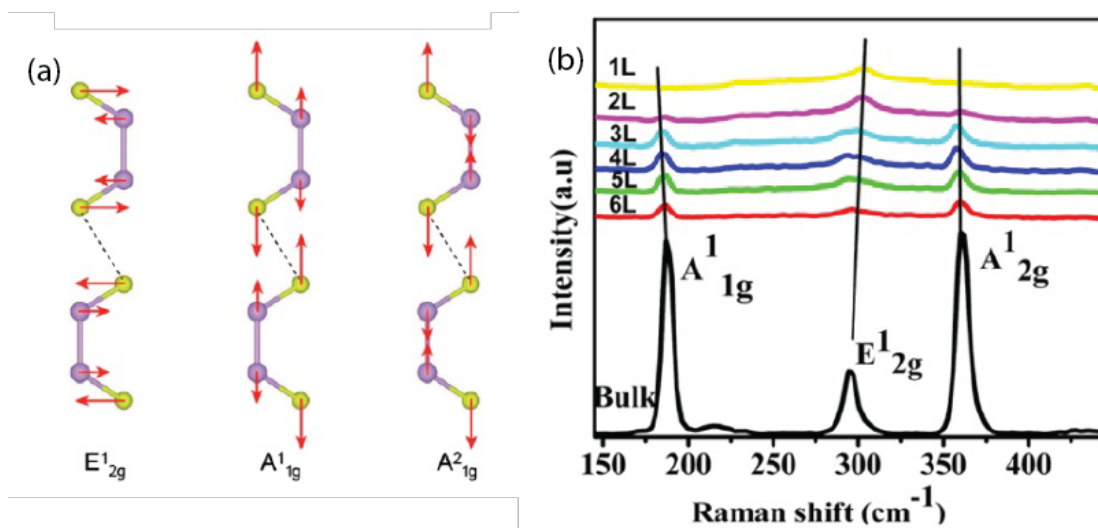


Figure 2.18 (a) Illustrations of the GaS phonon modes. (b) Raman spectra of bulk and GaS with various layer numbers on silicon substrate. Reprint (adapted) with permission from: (a), ref (170), © The Royal Society of Chemistry 2014; (b), ref (163), © 2013 American Chemical Society.

2.3.1 Synthesis of Gallium Sulfide

In order to realise the potential applications, methods which can provide large-scale and controllable fabrication of GaS are desirable. General production routes can be categorized into top-down and bottom-up approaches. The most desirable processes are those which are low cost, simple, and environmentally friendly. Gaining an understanding of the growth mechanism of GaS material is another goal. All the reported synthesis methods of GaS are reviewed in this section.

The top-down approach involves breaking down the bulk material into small pieces with the desired thickness. Monolayer and multilayer GaS nanosheets are first obtained using the mechanical cleavage technique, through repeated peeling from the bulk material and placing the detached sheets onto SiO_2/Si substrates. This technique has been proven to be an easy and relatively straightforward way to produce few-layer GaS flakes. The produced GaS flakes usually have high crystallinity, relative large size (tens of

micrometres), and various thicknesses.¹⁵⁴ Figure 2.19 (a-c) shows the mechanically exfoliated GaS ultrathin layers on SiO₂/Si substrate and its atomic force microscope (AFM) image of selected GaS flakes. Its height profile is measured along the marked line. This GaS flake has a thickness of 0.98 nm and it is clearly seen that the optical contrast difference in various thick GaS flakes. Therefore, optical microscopy is suitable to identify the layer numbers of GaS sample. The advantages include fast, non-destructive, and easy-to-use. Following this, the exfoliated GaS flakes are fabricated into photodetectors and field emission transistors (FETs) and their fundamental properties can be studied.

The liquid exfoliation technique is used to obtain thin sheets of layered materials.^{173,174} Generally this method involves the delamination of layered bulk crystal *via* sonication or apply high shear rates to form large quantities of 2D nanosheets in solution. After that, the remaining bulk material can be separated from the exfoliated nanosheets using centrifugation. The micromechanical cleavage method suffers low throughput. And the produced material is suitable for the fundamental studies. The liquid exfoliation method demonstrates large quantity production of GaS in terms of concentration, up to 0.2 mg/mL with 50 - 1000 nm lateral size and 3 - 80 layers thickness.¹⁷² Figure 2.19 (d) show a photograph of GaS nanosheets in solution. The yellow colour at the top of the vial indicates the separation between bulk and layered GaS materials. Figure 2.19 (e) shows three low-resolution transmission electron microscopy (LRTEM) images of liquid exfoliated GaS nanosheets. The liquid exfoliation technique has several advantages such as large-scale production, low-cost, and easy implementation.

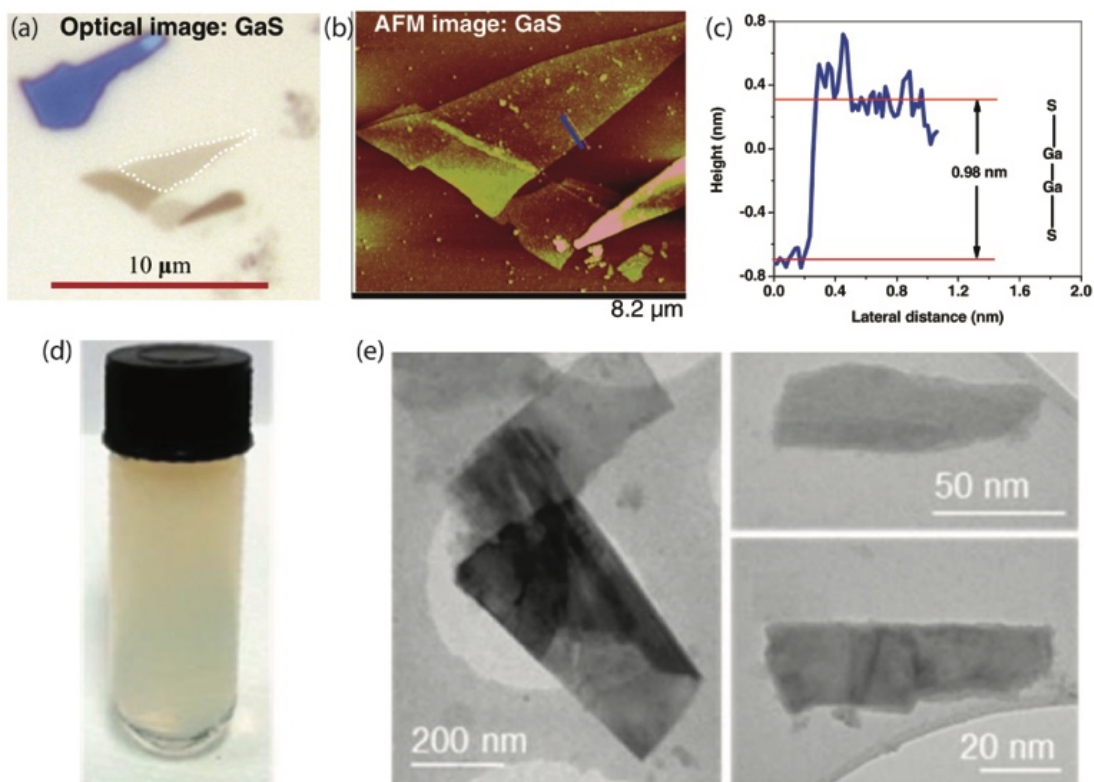


Figure 2.19 (a) Optical image of an ultrathin GaS layer (highlighted by a dashed line) on SiO₂/Si substrate. (b) AFM images of corresponding GaS layer in (a). (c) AFM height profile of the GaS layer shown in (b) measured along the marked line. (d) Photograph of layered GaS in solution. (e) LRTEM images of liquid exfoliation obtained GaS nanosheets with various scale. Reprint (adapted) with permission from: (a-c), ref (154), © 2012 WILEY-VCH Verlag GmbH & Co; (d and e), ref (172), © 2015 American Chemical Society.

The bottom-up approach involves building the layered group III metal chalcogenides from small to large scales, like Lego, and involves various technique such as epitaxial growth, physical vapor deposition, chemical vapor deposition (CVD), and atomic layer deposition (ALD). These techniques can not only produce monolayer or multilayer GaS 2D materials, but also various morphologies, including bulk material, nanobelts, and nanotubes. Kokh *et al.* demonstrated a modified Bridgman-Stockbarger technique to

grow bulk GaS material.¹⁷⁵ Purified gallium and sulphur precursors are loaded at the opposite ends of an ampoule. The ampoule is partially inserted into a single zone furnace with a small tilt angle. The precursors are slowly melted and homogeneously mixed together. When no liquid sulphur precursor is in the cold part of the ampoule, the ampoule is entirely pushed into the furnace. Figure 2.20 (a and b) illustrates this process. Finally, a bulk polycrystalline GaS ingot is produced, as represented in Figure 2.20 (c). These bulk GaS materials are mainly used to study the fundamentals.^{161,160,176}

The GaS nanotubes start to draw attentions following the discovery of carbon nanotubes.¹⁷⁷ The synthesis methods for making GaS nanotubes include annealing lamellar precursor,¹⁷⁹ thermally induced exfoliation with laser assistance,¹⁷⁸ and the high temperature thermal reaction route.^{156,169} Hu *et al.* demonstrated the synthesis of GaS tubes with uniform size, up to tens of microns in length *via* a high temperature reaction route, as shown in Figure 2.20 (d).¹⁶⁹ In this synthesis process, a mixture of Ga₂O₃, ZnS and active carbon powders are heated to 1400-1500 °C by a high speed furnace, then maintained for 1.5 hour growth time, and rapid cooled to room temperature. Hexagonal GaS nanobelts are prepared through a thermal evaporation method, and the schematic is presented in Figure 2.20 (e). Sulphur and gallium precursors are placed inside a two-zone furnace. The evaporation temperature is at 450 °C and 950 °C, respectively. The Au film deposited SiO₂/Si substrate is placed on top of the gallium metal precursor at a distance of 5 mm away. The Au catalysts provide energetically favoured sites for the absorption of Ga and S vapor. Eventually a stable GaS phase grows along c axis *via* a vapor-liquid-solid mechanism.¹⁸⁰ A low resolution TEM image in Figure 2.20 (f) shows the uniform GaS nanobelts with 20-50 nm width and have smooth surface. High resolution TEM image shows the crystal structure of GaS belts with the d-spacing of 3.8 Å, and the distance between Ga-S layers is 7.5 Å in Figure 2.20 (g).

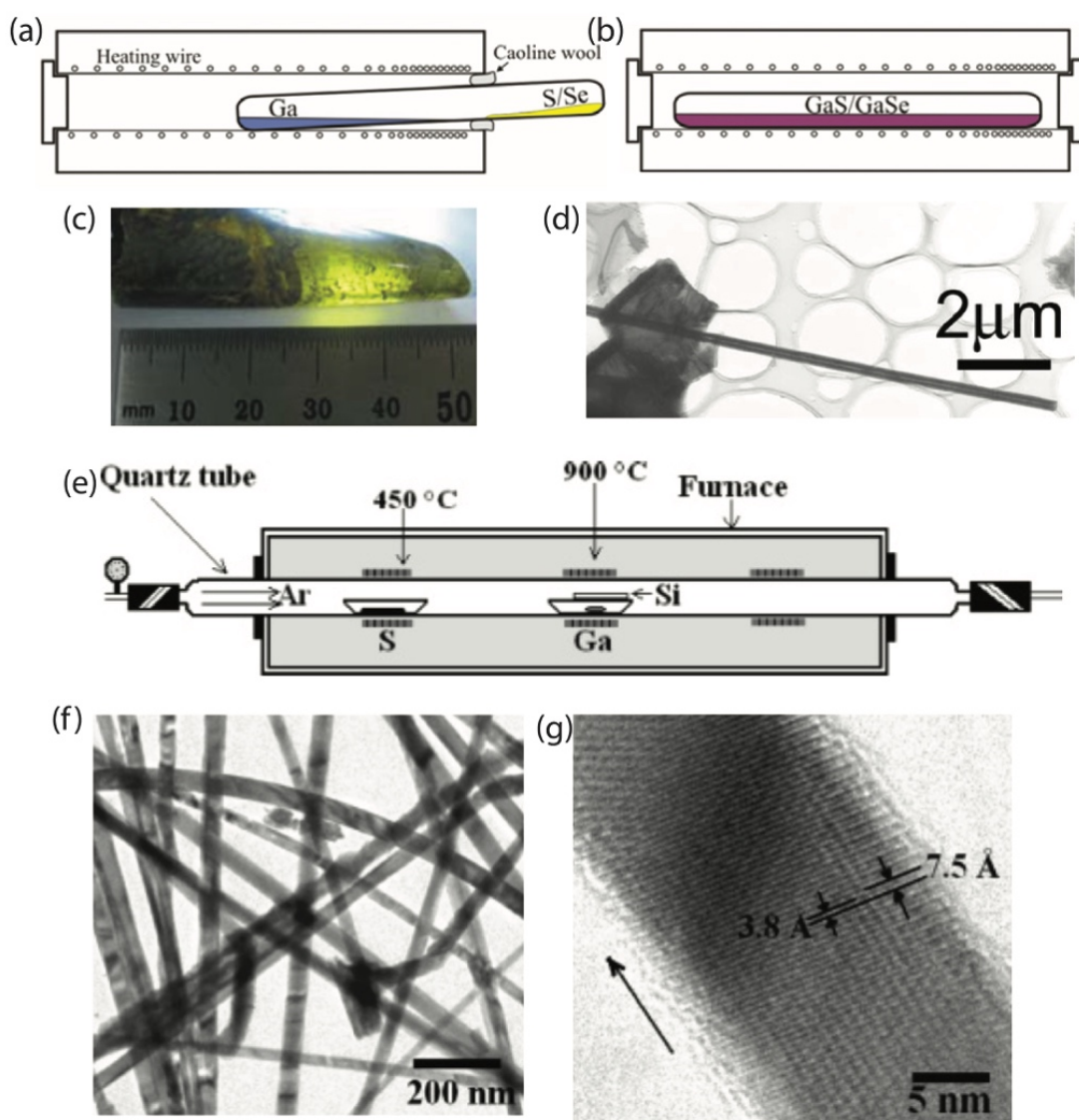


Figure 2.20 (a-b) Schematic process of the modified Bridgman-Stockbarger method. (c) Photo of a synthesised polycrystalline GaS ingot. (d) LRTEM image of a GaS nanotube. (e) Schematic diagram of the thermal evaporation method. (f) LREM image of GaS nanobelts with uniform width. (g) HRTEM image of a GaS nanobelt shows the layered structure with lattice fringe spacing. Reprint (adapted) with permission from: (a-c), ref (175), © 2011 WILEY-VCH Verlag GmbH & Co; (d), ref (130), © 2005 American Institute of Physics; (e-g), ref (180), ©2008 American Chemical Society.

Chemical vapor deposition (CVD) methods are used to produce atomically thin GaS sheets. The family of tert-butyl gallium sulfide compounds are used to produce different GaS materials. Such as crystalline GaS is grown from the $[(^t\text{Bu})_2\text{Ga}(\text{S}^t\text{Bu})]_2$ precursor, amorphous GaS materials is grown from $[(^t\text{Bu})\text{GaS}]_7$, and cubic GaS materials is grown from $[(^t\text{Bu})\text{GaS}]_4$.^{181,182} Recently, Shen *et al.* reported the CVD synthesis of GaS nanostructures on graphite substrates with various morphologies. They are thin nanowires, nanobelts, zigzag nanobelts, microbelts, and hexagonal microplates, as represented in Figure 2.21 (a).¹⁸³ The GaN and Bi_2S_3 precursors are placed in the centre of the furnace, and Ar gas is used as the carrier gas throughout the synthesis. Due to the single furnace system, the temperature distribution is symmetric at the centre, therefore the synthesised GaS has various morphologies. Then, Jung *et al.* successfully synthesised multilayer and monolayer of $\text{GaS}_{1-x}\text{Se}_x$ ($0 \leq x \leq 1$) alloy using a CVD method. The grown alloys have a linearly tuned emission from red-to-green.¹⁸⁴ The SEM images in Figure 2.21 (b) reveal that the grown triangular GaS domains cover a large region. The EDX spectrum is taken from one selected triangular GaS domain. And it confirms the 1:1 chemical compositional between Ga and S, as shown in Figure 2.21 (c and d). This is the first time that the triangular GaS domains are grown on silicon substrate. Furthermore, Sinha *et al.* demonstrated the synthesis of 1D GaS nanohorn arrays on thin Au film coated silicon substrates.¹⁸⁵ In Figure 2.21 (e), the SEM images show the vertically aligned GaS nanohorn arrays with 2 μm basal, 200 nm tip diameter, and 25 μm in length.

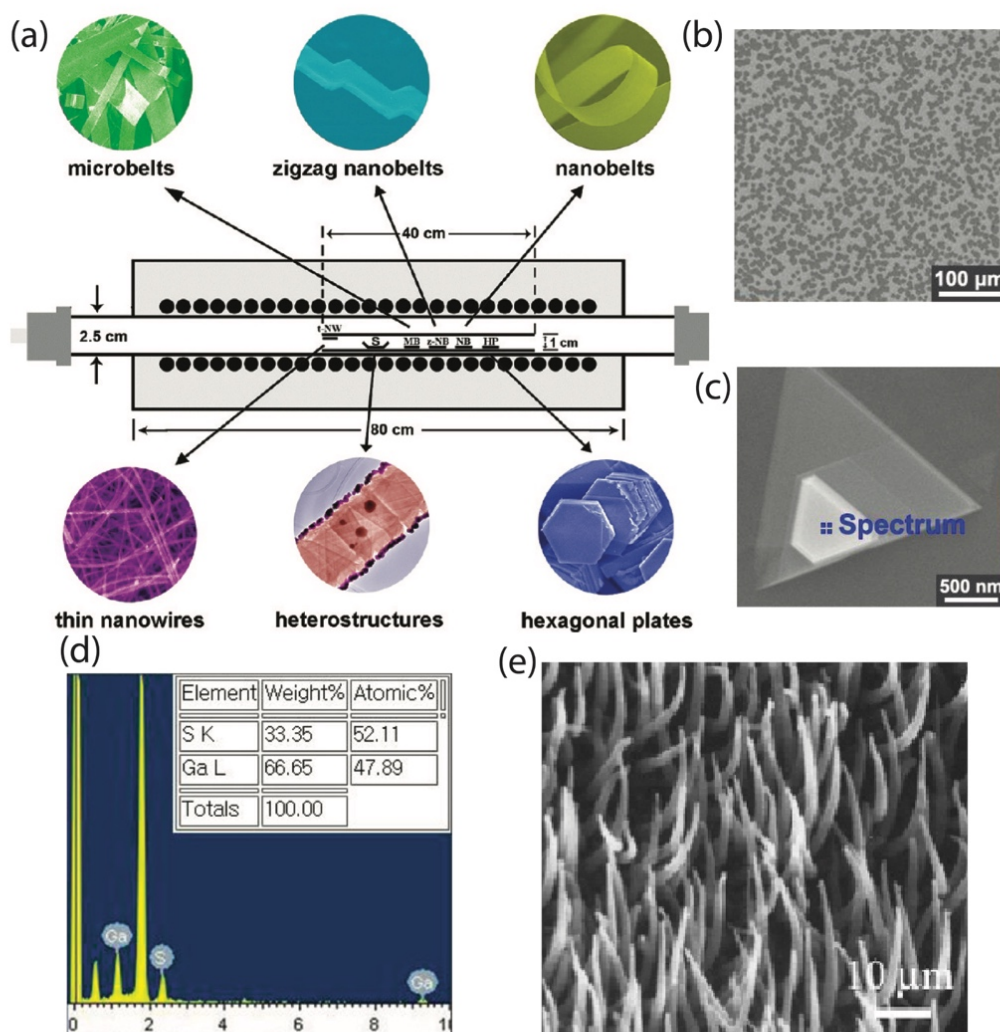


Figure 2.21 (a) Schematic of the experimental setup and various morphologies of the grown GaS materials. (b) SEM image of the GaS monolayers grown on a silicon substrate. (c) SEM image of a selected triangular GaS domain indicates where the EDX spectrum is obtained. (d) The EDX spectrum recorded from the area shown in (c). (e) SEM image of GaS nanohorn arrays. Reprint (adapted) with permission from: (a), ref (183), © 2009 American Chemical Society; (b-d), ref (184), © 2015 American Chemical Society; (e), ref (185), © 2011 American Chemical Society.

Meng *et al.* reported the atomic layer deposition (ALD) of GaS films by alternate exposure the substrate to $\text{Ga}_2(\text{NMe}_2)_6$ and H_2S precursors in the temperature range of 125 - 225 °C.¹⁸⁶ Unlike the CVD method, the self-limiting nature of ALD not only provides atomic-level precision in term of thickness and composition, but also achieves uniform film thickness and complex geometry. The ALD method is not easy to implement. It requires a hot-walled ALD reactor, highly reactive precursors, and ultra-high vacuum condition. The SEM images in Figure 2.22 (a) show the deposited GaS on a micromachined silicon trench substrate with an aspect ratio of 6:1. Zoomed in SEM images reveal that this ALD synthesised GaS film is uniformly covered the trench from top to bottom, as shown in Figure 2.22 (b and c). The production of bilayer GaS film is reported using screen printing method, by Carey *et al.*¹⁸⁷ This novel process is quite complex, as illustrated in Figure 2.20 (d). First, the melted liquid gallium is homogeneously spread across the substrate using soft PDMS, and a thin layer of gallium oxide film is formed *via* self-limiting reaction. Next, the printed wafer is baked in a HCl environment for 5 min forming GaCl_3 film. The hydrochloric acid vapor treatment is used as an intermediary step and it helps to reduce the sulfurization temperature from 900 °C to 300 °C. In the final sulfurization step, the formed GaCl_3 film is placed in a sulphur environment for 90 minutes, where it is fully transformed into bilayer GaS thin film. Figure 2.22 (e and f) display the AFM images of GaS thin film fabricated by this screen printing method. The corresponding height profile confirms that the thickness of grown GaS is bilayer and it is 1.5 nm.

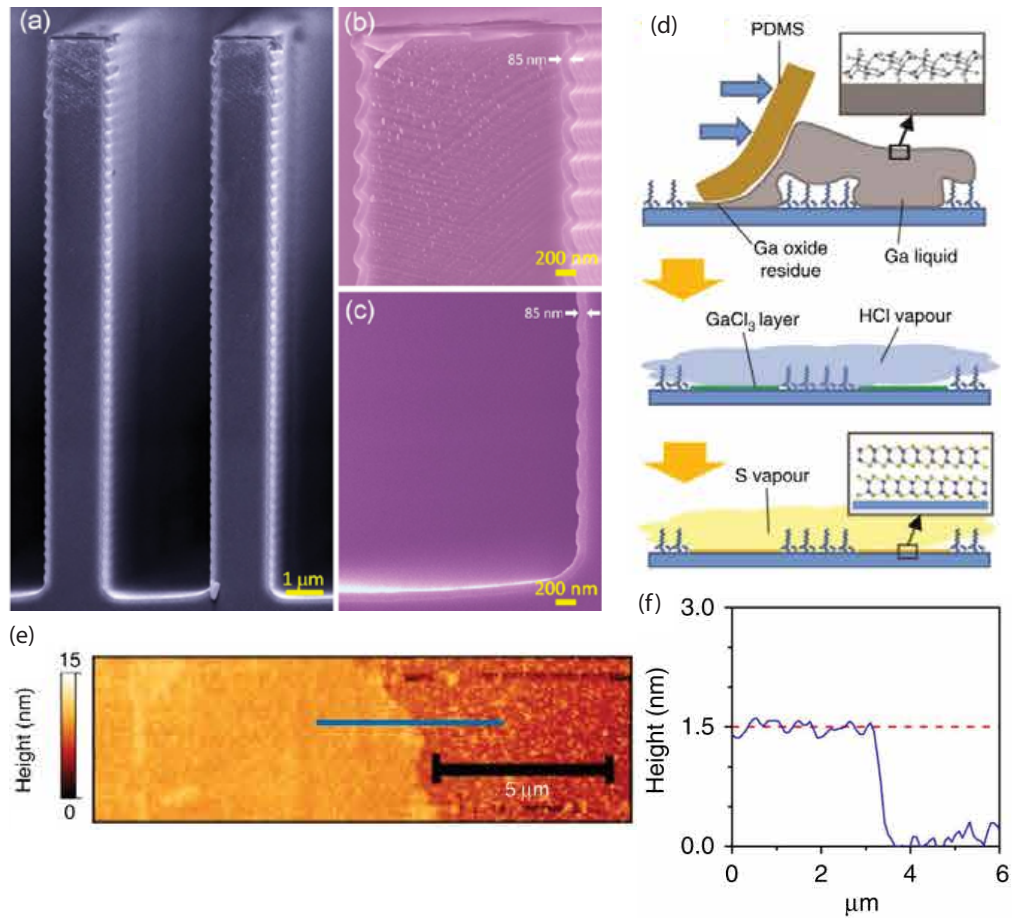


Figure 2.22 SEM images of ALD fabricated GaS film deposited on a silicon trench, (a) shows the silicon trench, (b and c) show the zoomed-in top and bottom of the trench, respectively. (d) The schematic process of the screen printing method. (e and f) AFM image and the corresponding height profile of the printed bilayer 2D GaS. Reprint (adapted) with permission from: (a-c), ref (186), © 2013 American Chemical Society; (d-f), ref (187), © 2017 Spring Nature.

2.3.2 Applications of Gallium Sulfide

2D layered semiconducting materials offer extraordinary properties such as atomic smoothness,¹⁸⁸ thermal stability,¹⁸⁹ absence of dangling bonds,¹⁹⁰ and uniform thickness.¹⁹¹ Research show that monolayer TMDs exhibit wider band gap than their bulk form.^{143,149} In addition, the indirect-to-direct band gap transition is the most distinguishing feature of 2D TMDs.^{189,192} The GaS 2D crystals are studied because of its promising applications in field effective transistors (FETs), energy storage materials,¹⁹³ catalysts for the hydrogen evolution reaction (HER),¹⁷² and photodetectors.^{163,184}

2D heterostructures offer the ability to adjust the band structures through wake Van der Waals interactions.^{194,195} Their planar nature is compatible with the present manufacture technology.^{194,196} The first GaS FETs are fabricated based on the mechanical exfoliated GaS materials. The measurements are carried out by applying the drain-source voltage V_{ds} to electrodes, and the back-gate voltage V_{gs} is applied to the silicon substrate. In Figure 2.23 (a and b), the single-sheet GaS FET shows n-type channel conductance and its calculated mobility is about $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with $10^4 - 10^5$ on/off current ratios.¹⁴⁸ Moreover, the calculated mobility of a bilayer GaS FET is about $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with 150 on/off ratio.¹⁸⁷ The schematic of bilayer GaS FET is represented in Figure 2.23 (c).

GaS nanobelts and nanohorns have excellent field emission properties because of their low turn on voltage and emission current durability in ultra-high vacuum condition. The field emission is related to the work function of the materials and the field enhancement factor. The former is an intrinsic property and the latter one depends on the ratio between local and applied field. The field enhancement factor can be modified by altering the tip diameter of the nanostructure. The GaS nanobelts have a low turn-on field about $2.9 \text{ V}/\mu\text{m}$ and a field enhancement factor about 2.0×10^{14} . Its duration is more than 2 hours with $4 \mu\text{A}$ emission current.¹⁸⁰ Figure 2.23 (d) shows the field emission current density

against the applied field of GaS nanohorns. Its turn-on field is found to be about $4.2 \text{ V}/\mu\text{m}$ with $0.1 \mu\text{A}/\text{cm}^2$ current density. The Fowler-Nordheim plot in Figure 2.23 (e) shows a linear behaviour with negative slope. The emission current stability measurement indicates the GaS nanohorns have a duration over four hours.¹⁸⁵

GaS 2D crystals are also applied in photodetectors.^{184,197} For example, Hu *et al.* reported the GaS based photodetectors fabricated on both rigid substrate (SiO_2/Si) and flexible plastic (polyethylene terephthalate PET) substrate, as shown in Figure 2.24 (a).¹⁶³ The GaS photodetector has two electrodes and the GaS nanosheet is fabricated in $20 \mu\text{m}$ long and $10 \mu\text{m}$ wide. Figure 2.23 (b) indicates the GaS photodetector is highly responsive. The on/off switching ratio is 2.94×10^4 , the dark current is $1.36 \times 10^{-4} \text{ nA}$, and the high current is 4 nA . The flexible GaS photodetector exhibits the photoresponsivity of 19.2 AW^{-1} and external quantum yields (EQE) up to 9371%.¹⁶³ In addition, Yang *et al.* reported that a few-layer GaS photodetector with photoresponsivity of 64.43 AW^{-1} and EQE of 12621 % is measured in ammonia environment.¹⁷⁰

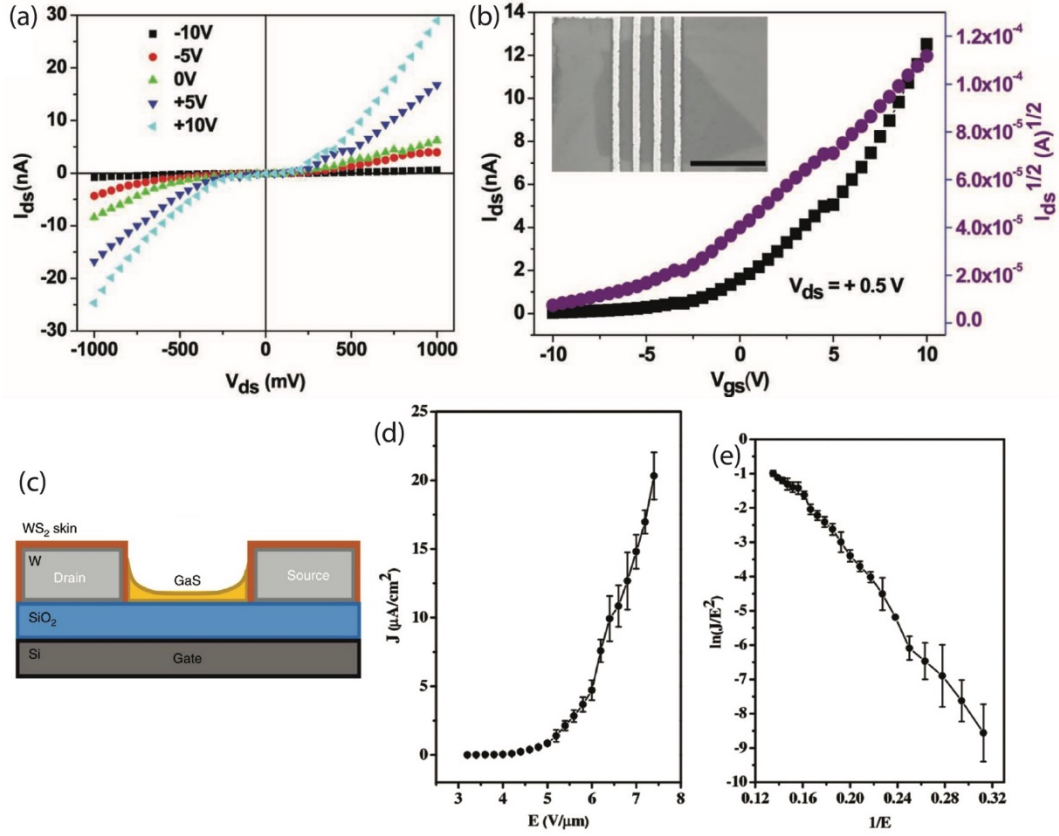


Figure 2.23 (a) Gate dependent current-voltage (I-V) characteristics of a single-sheet GaS measured at room temperature. (b) I-V characteristics of a single-sheet GaS FET. Inset shows an SEM image of the device with a 10 μm scale bar. (c) Schematic of back gated bilayer GaS FET with tungsten/WS₂ electrodes. (d) Field emission current density-applied field plot of the GaS nanohorns. (e) The corresponding Fowler-Nordheim plot of the GaS nanohorns. Reprint (adapted) with permission from: (a and b), ref (148), © 2012 WILEY-VCH Verlag GmbH & Co; (c), ref (187), © 2017 Spring Nature; (d and e), ref (185), © 2011 American Chemical Society.

The liquid exfoliated GaS nanosheets show favourable performance as hydrogen evolution reaction (HER) catalysts.¹⁷² Figure 2.24 (c) represents the current density versus potential relative to reversible hydrogen electrode of GaS nanosheets. The GaS nanosheets with 180 nm size have a -0.58 V onset potential, the 280 nm sized sheets have a -0.62 V onset potential, and the 450 nm sized sheets have a -0.72 V onset potential. The corresponding Tafel plots of overpotential versus current density are plotted in Figure 2.24 (d). The deduced Tafel slopes are 106, 85, and 85 mV/dev for 450, 280 and 180 nm sized GaS nanosheets, respectively. In addition, the atomic layer deposited GaS nanomaterial is used as electrode in lithium ion battery. It has a sustained and stable capacity of 650 mAh/g after 160 charge-discharge cycles under a current density of 640 mA/g.¹⁸⁶ While the capacity of commercial Ga₂S₃ electrode reduces to 100 mAh/g after 100 charge-discharge cycles.

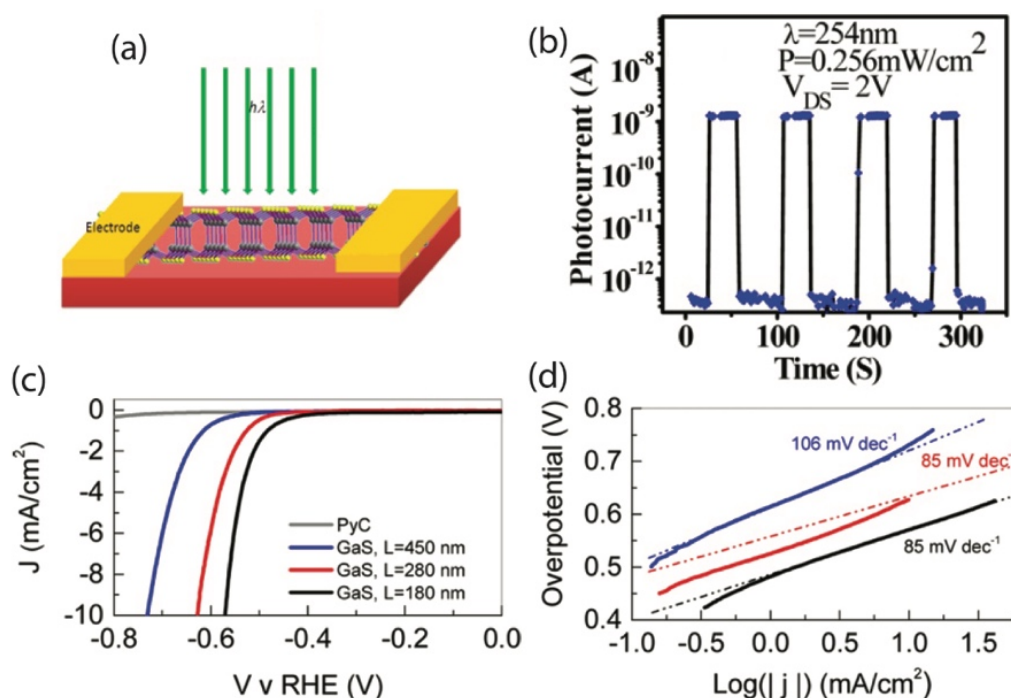


Figure 2.24 (a) Schematic of the GaS nanosheet photodetector on SiO₂/Si substrate. (b) Photocurrent as function of time under pulse illumination at a bias voltage of 2 V. (c) Linear sweep voltammograms (5 mV s⁻¹) of vacuum-filtered GaS nanosheets transferred onto pyrolytic carbon with a reversible hydrogen (RHE) reference electrode. The electrocatalytic response toward the hydrogen-evolution reaction is compared for size-selected GaS with three different mean sizes. (d) Corresponding overpotential versus log ($|j|$) plot from (c) and the Tafel slopes are determined in millivolts per decade (mV dec⁻¹). Reprint (adapted) with permission from: (a and b), ref (163), © 2013 American Chemical Society; (c and d), ref (172), © 2015 American Chemical Society.

2.3.3 Conclusion for Gallium Sulfide

Since the discovery of graphene, the 2D material family has expanded significantly. The current research on GaS 2D crystals is summarised in the second part of this literature review. The GaS is from the layered group III metal chalcogenides and has distinguished electronic, optical and vibrational properties. The indirect band gap of monolayer GaS is around 2.59 eV and the direct band gap is at approximately 0.45 eV higher in energy. Many techniques are reported to successfully synthesise GaS 2D crystals based on top-down or bottom-up approach. They include conventional exfoliation method, chemical vapor deposition (CVD) method, atomic layer deposition (ALD) method, and the novel screen printing method. In addition, the GaS 2D materials attract attentions from scientific community because of its potential applications such as field effect transistors (FETs) and hydrogen evolution reaction (HER) catalysts. In summary, the systematic investigation of GaS 2D crystals is highly desirable.

2.4.0 Conclusions

Two novel 2D materials are reviewed in this chapter; the hexagonal boron nitride (h-BN) and gallium sulfide (GaS). They are quite different in terms of crystal structures, band structures, optical properties, and potential applications. The crystal structure of h-BN is an analogous to graphene with exactly one atomic thickness. It is known as an insulator in 2D materials and it has an indirect band gap of about 6.0 eV. The GaS is from the layered group III metal chalcogenides. Monolayer GaS consists 4 layers of atoms in the S-Ga-Ga-S sequence. It has an indirect band gap at about 2.61 eV and a direct band gap at about 3 eV. The research pace on 2D materials is quite rapid nowadays. This is attributed to the following reasons: (1) the transferable synthesis method among 2D materials. For examples the developed synthesis methods for graphene are applied to the synthesis of h-BN, and the synthesis methods for TMDs are also used to grow GaS. (2) The well-built frameworks for graphene and TMDs applications are also used in the novel developed 2D materials, such as field effective transistors (FETs) and photodetectors. Lastly, (3) the concept of heterostructures provides more diverse and even tailored properties for the current 2D materials. The next step is to develop the synthesise methods for h-BN and GaS 2D materials. In this context the following requirements shall be considered: feasible synthesis scheme, cost-effective production, environment-friendly synthesis route, scalability, and high-quality continuous film. In this thesis, the CVD synthesis of h-BN and GaS materials are explored with the mentioned requirements in mind, and their growth mechanism are discussed.

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Chapter 3

Methodology

The goal of this chapter is to describe the experimental and characteristic methods. They are used to carry out the work in this thesis. The chemical vapor deposition (CVD) methods are developed and used to grow h-BN and GaS 2D materials, respectively. A series of characterisation is used to evaluate the grown materials, including optical microscopy, scanning electron microscopy (SEM), Raman and photoluminescence (PL) spectroscopies, atomic force microscopy (AFM) and transmission electron microscopy (TEM). All above mentioned techniques are covered in this chapter.

3.1 Chemical Vapor Deposition Synthesis of Hexagonal Boron Nitride

A chemical vapor deposition (CVD) system is built to grow the hexagonal boron nitride (h-BN) materials. The CVD system has three main components, such as an isolated precursor chamber surrounded by a heating belt, a furnace, and two mass flow controllers, as seen in Figure 3.1. In my first project, multilayer h-BN films are synthesised on copper substrates at ambient pressure from three precursors. They are the ammonia borane ($\geq 97\%$, Sigma-Aldrich Co.), diborazane, $\text{H}_3\text{B}\cdot\text{NH}_2\text{BH}_2\cdot\text{NH}_3$ (DAB), and triborazane (TAB). The last two precursors are newly synthesised by collaborators from the Chemistry Department, University of Oxford. All three precursors are white crystalline solids and have a 1:1 of B to N stoichiometric ratio. For each synthesis of h-BN continuous films, 10 mg precursor is loaded into the isolated chamber with a valve. After heating the precursor to 80-90 °C using the heating belt, it begins to dissociate, and its products are carried into the reaction tube with 120 sccm of hydrogen carrier gas (~25% in Ar). The growth temperature is about 1040 °C for 10 - 30 minutes growth. The flow of carrier gas is characterised as the lamina flow because of 403 Reynolds number. The

calculation of Reynolds number is in the Appendix A. Figure 3.2 shows the SEM images of copper substrate surfaces after the CVD process, where (a) represents the copper surface without h-BN film, and (b) represents the copper surface covered by the grown h-BN film.

Prior to the growth, copper foils are cut into 1 cm² pieces and cleaned in 1 M hydrochloric acid (HCl) to eliminate the oxide layer, followed by rinsing successively in 80 ml of deionized water, acetone, and IPA solutions. Then, the copper foils are placed in the middle of the furnace. These copper foils are annealed at 1000 °C for 1h with a mixed flow of 75 sccm hydrogen (~25% in Ar) and 425 sccm argon gas. Directly after h-BN deposition, the valve is switched off, the samples are quickly moved out of the hot zone and rapid cooled to room temperature. The gas flow is turned back to the annealing flow rate. Multilayer h-BN films are successively produced using this method. More results and discussions can be found in Chapter 4.

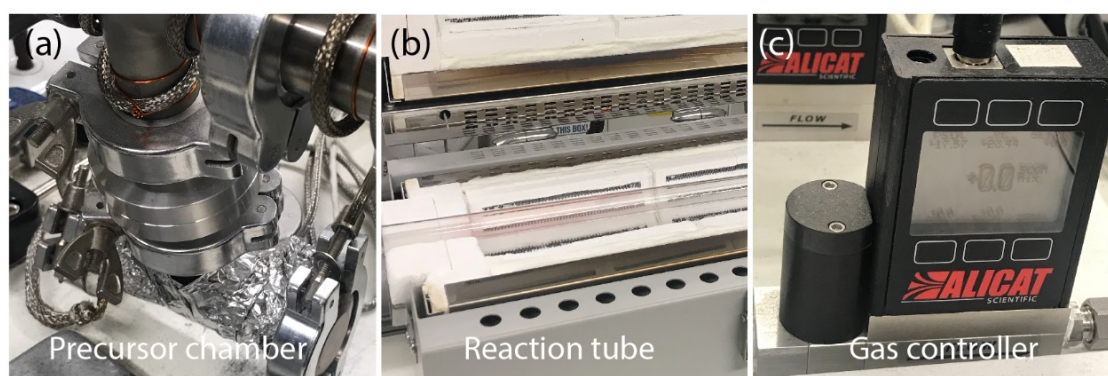


Figure 3.1 Photographs of h-BN chemical vapor deposition system setup: (a) precursor chamber, (b) tubular furnace with 1-inch quartz tube, and (c) mass flow controller.

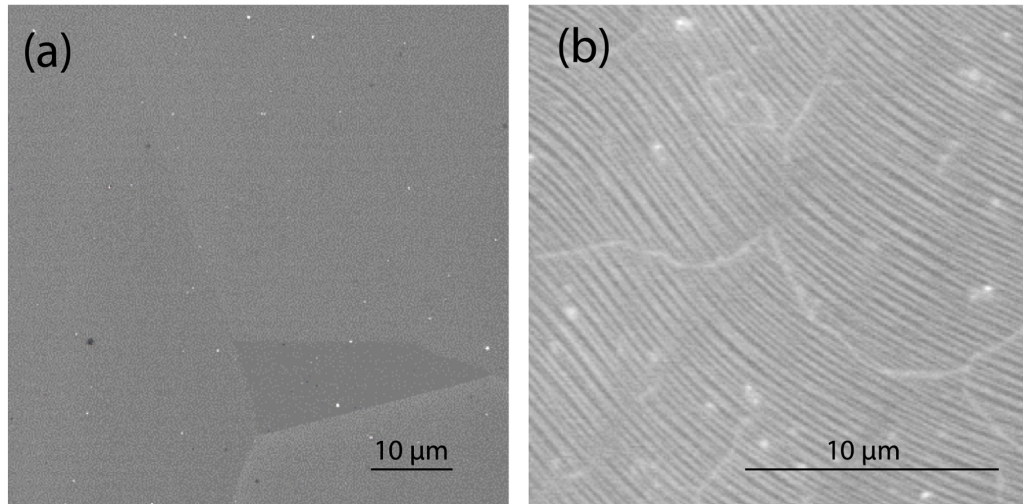


Figure 3.2 (a) SEM image of the Cu substrate surface without h-BN film, and (b) SEM image of the Cu substrate surface covered by the CVD grown h-BN film.

Wet chemical transfer method is used to transfer the h-BN film to arbitrary substrates. Firstly, the sample is coated with a layer of 495 K A8 poly (methyl methacrylate) (PMMA) at 4500 rpm for 60 second using a spin coater (Laurell-WS-650MZ-23NPP). Next, the PMMA/h-BN/Cu sample is baked on a hot plate (Stuart-SD 160) at 180 °C for 90 second to enhance the adhesion between the PMMA layer and h-BN film. Subsequently, the copper substrate is etched away by floating on a 3 M ammonia persulfate solution. The PMMA/h-BN sample is washed by deionized water several times before scooping it onto SiO₂/Si substrate. The final step is to remove the top PMMA layer by dissolving it in 80 ml acetone solution overnight. After that the h-BN film is on the SiO₂/Si substrate and ready for further characterisation.

3.2 Chemical Vapor Deposition Synthesis of Gallium Sulfide

The synthesis of Ga₂S₃/GaS mixture phase thin film and monolayer GaS is performed in another CVD system. The Ga₂S₃/GaS mixture phase thin film is synthesised on two different substrates, such as silicon wafers (University Wafer, 300 nm thick amorphous SiO₂ coated on the p-doped Si) and glassy carbon substrates. For each growth, 10 mg of Ga₂S₃ precursor (Sigma-Aldrich Co.) is placed in middle of the furnace and the substrate is vertically placed downstream to the precursor. The distance between precursor and substrate can be adjusted. The typical growth process has three stages: first the system is flushed with 500 sccm Ar gas for 30 minutes to reduce the oxygen content; then the main growth stage takes place at 800 °C, growth time is between 10 and 60 minutes, carrier gas is 30 sccm H₂ (~25% in Ar); finally the substrate and precursor are fast cooled by switching off the furnace and moving the substrates out of the hot zone, and the carrier gas is 150 sccm Ar. The Ga₂S₃/GaS mixture phase thin film is observed on the SiO₂/Si substrate. At the main growth stage, the flow of carrier gas is lamina flow with 101 Reynolds number. This calculation is in the Appendix A.

The CVD synthesis of monolayer GaS film is similar to the synthesis of Ga₂S₃/GaS mixture phase thin film. The 2 by 2 cm sized SiO₂/Si substrates are used horizontally and placed at 8.5 cm away downstream from the precursor. The SiO₂/Si substrate is washed by isopropanol (IPA) for 15 minutes with sonication. Then the whole furnace system is flushed with 500 sccm Ar gas for 30 minutes to reduce the oxygen content. Once the growth temperature reaches to 800 °C, the carrier gas is switched to 70 sccm H₂ (~25% hydrogen in Ar) and GaS is grown for a certain period of time. At the main growth stage, the gas flow is characterised as the lamina flow with 235 Reynolds number. The calculation of Reynolds number is presented in the Appendix A. Finally, a fast cooling

process takes place in order to arrest any further growth with 150 sccm Ar gas. Now the as-grown monolayer GaS film is ready for characterisation.

The as-grown GaS samples can be transferred onto any arbitrary substrates, such as silicon wafer with metal contacts, or TEM grids. First, the sample is spin-coated with a 495 K A8 poly (methyl methacrylate) (PMMA) scaffold at 4500 rpm for 60 seconds and baked at 180 °C for 90 seconds on a hot plate. The SiO₂/Si substrate is detached from the PMMA/GaS stack by floating the sample on a 1 M potassium hydroxide (KOH) (Sigma-Aldrich Co.) solution. The PMMA/GaS film is rinsed successively in deionized water. Then the sample is ready to be transferred onto any substrates. Taking a holey-carbon TEM grid as example, the PMMA/GaS sample is scooped onto the TEM grid, left to dry in a fume hood overnight, and then baked on a hot plate at 150 °C for 15 minutes. Finally, the PMMA is removed by leaving the sample in 80 ml of acetone solution.

3.3 Optical Microscopy

Optical microscopy is a convenient and quick tool to examine 2D materials. Two optical microscopes are used in my projects. The first optical microscope is built in the group and equipped with a Mitutoyo objective lens with 50x magnification, and a CMOS camera (DCC1645C Thorlab high-resolution CMOS camera with colour sensor). The obtained optical images are used to compare the oxidised copper surface between with and without h-BN film. These results are shown in Chapter 4. The other optical microscope is an Eclipse LV100ND from Nikon. It is used to conduct a preliminary examination of the CVD grown Ga₂S₃/GaS mixture phase thin film and GaS 2D materials on silicon substrates. These results can be found in Chapter 5 and 6, respectively. The optical images obtained from both microscopes are adjusted in term of contrast and brightness using the ImageJ software.

3.4 Raman and Photoluminescence Spectroscopy

The CVD grown h-BN and GaS materials are characterised using Raman spectroscopy. The Raman results in this project are obtained from a JY Horiba Lab RAM Aramis imaging confocal Raman microscope, under an excitation wavelength of 532 nm with an estimated laser spot size of 1 μm . Before taking any measurements, the Raman spectrometer is calibrated with a standard silicon chip, which exhibits a peak at 520.7 cm^{-1} to eliminate any instrument introduced error. The Raman spectrum of h-BN film is obtained after the h-BN film is transferred onto silicon substrate *via* the wet chemical transfer method. Raman spectra are recorded with a range of 1200 to 1500 cm^{-1} and a grating of 1800 slits per mm. The incident laser intensity is set to 100%, accumulation number is 10, and the acquisition time is kept at 30 seconds. Raman spectra of h-BN can be found in Chapter 4.

The 1800 slits per mm grating is also selected for CVD grown $\text{Ga}_2\text{S}_3/\text{GaS}$ mixture phase thin film, multilayer GaS flakes and GaS monolayer domains for their Raman characterisation. The Raman spectra are taken from 100 to 500 cm^{-1} , with an acquisition time of 5 second, and an accumulation number of 5. Photoluminescence (PL) spectra are captured for multilayer GaS flakes between 500 and 800 nm using a coarse resolution of 600 slits per mm grating with the same acquisition time and accumulation number as mentioned before. Raman spectra of CVD synthesised $\text{Ga}_2\text{S}_3/\text{GaS}$ mixture phase thin film, GaS flakes, and domains can be found in Chapter 5 and 6. The PL measurements of GaS flakes and domains are in Chapter 6.

3.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a powerful tool to study the morphologies of CVD grown materials. Two SEMs are operated during my projects, they are Hitachi S-4300 model and Zeiss Merlin model. Both SEMs are used to characterise micrometre-scaled features of the as-grown h-BN on copper substrates. The Hitachi S-4300 is operated under an accelerating voltage of 3.0 kV and a beam current of 10 μ A. The Zeiss Merlin is operated under an accelerating voltage of 3.0 kV and a beam current of 179 pA. The CVD as-grown Ga₂S₃/GaS mixture phase thin film and monolayer GaS are mainly characterised using the Zeiss Merlin SEM. A low accelerating voltage is used for high quality images and the effects of charging and irradiation damages are minimised. The Zeiss Merlin SEM is equipped with an energy-dispersive X-ray spectrometer (EDX) (Oxford Instruments), the chemical composition is analysed under an accelerating voltage of 5.0 kV and a beam current of 200 pA. All SEM samples are mounted onto sample stubs using carbon sticky pads.

3.6 Atomic Force Microscopy

The thickness and surface topology of CVD grown h-BN and GaS are carried out using atomic force microscopy (Asylum Research MFP-3D). The results from AFM measurement are comprehensive, although only small areas can be examined. AFM scans are conducted in tapping mode (AC mode) with a silicon AC160TS cantilever (Olympus, spring constant of about 42 N/m and resonant frequency of $\sim$ 300 kHz). The as-grown h-BN on copper substrates is not ideal for AFM measurements. Therefore, the h-BN has to be transferred onto silicon substrates. The AFM measurements are performed at the edges of h-BN film. Since the GaS 2D materials are directly formed on silicon substrates, AFM measurements can be carried out on as-grown samples. Various morphologies of GaS are

scanned by AFM such as triangular domains, edges of continuous film, and flakes. The Gwyddion software is used to process all the AFM results, including height profile and surface roughness measurements.

3.7 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is not only used to count the layer number of as-grown 2D materials, but also study their crystal structure. The TEM images and corresponding selective area electron diffraction (SAED) patterns of h-BN films are recorded using a JEOL 2100 TEM operated at 80 kV. The TEM measurements are conducted by Dr Tom Samuels using the JEOL 2100 TEM and the results are represented in Chapter 4. The study of GaS materials is carried out using the aberration-corrected transmission electron microscope (AC-TEM) and the JEOL 2100 high-resolution TEM. Both TEMs are operated at an accelerating voltage of 80 kV. The high resolution TEM (HRTEM) images reveal the crystal structure and lattice spacing of GaS materials. The corresponding Fast Fourier Transfer (FFT) can be extracted from these HRTEM images using the ImageJ software. Ms Sha Li and Dr Jakung Lee helped me characterise the as-grown GaS materials, and these results are shown in Chapter 5 and 6, respectively.

Chapter 4

Oligomeric Aminoborane Precursors for the Chemical Vapor Deposition Growth of Few-Layer Hexagonal Boron Nitride

In this chapter, I explore the use of stable, pre-formed oligomeric aminoboranes as precursors for the CVD growth of few-layered h-BN film on Cu foils under atmospheric pressure condition. Dimeric diborazane, $\text{H}_3\text{B}\cdot\text{NH}_2\text{BH}_2\cdot\text{NH}_3$ (DAB), and trimeric triborazane $\text{H}_3\text{B}\cdot(\text{NH}_2\text{BH}_2)_2\cdot\text{NH}_3$ (TAB), derivatives of ammonia borane, $\text{H}_3\text{B}\cdot\text{NH}_3$ (AB), are compared with the AB, a commonly used precursor for the CVD growth of h-BN. The DAB and TAB precursors are newly synthesised by collaborators from the Department of Chemistry, University of Oxford. Both DAB and TAB show similar effectiveness to AB in growing few layered h-BN films. Using DAB as the precursor instead of AB leads to fully continuous h-BN films in a shorter period of time. Analysis of the surface of the h-BN films reveals that DAB and TAB precursors deposit more nanoparticles on the surface within the same time period as when using AB. The viability of these two new h-BN precursors (DAB and TAB), opens up a wider range of solid-state sources for growing h-BN film using CVD technique. The h-BN growth mechanism on copper substrate is discussed here based on the approach of different precursor molecular form.

4.1 Introduction

The wide band gap of h-BN, making it an insulating 2D crystal that can be used as a substrate for graphene or as a dielectric barrier.^{1,2} Growing large area continuous film of h-BN is needed for new applications in electronics and opto-electronics. Chemical vapor deposition (CVD) is a leading approach to produce such high quality material.^{3,4} There are many similarities between the growth of graphene and h-BN by CVD method, as they both can be grown on Cu foil and are influenced by the growth temperature, deposition time, and the precursor form.^{5,6} In both graphene and h-BN CVD synthesis, individual domains nucleate at the beginning and then grow in size until they coalesce to eventually form a complete polycrystalline h-BN film.⁷ There have been several precursors explored for the growth of BN by CVD, ranging from gas, liquid to solid.⁸⁻¹⁰ Generally, the commercial solid state precursor $\text{H}_3\text{B}\cdot\text{NH}_3$ (AB) has been widely used in the atmospheric pressure CVD (APCVD) synthesis of h-BN.¹¹⁻¹⁴ In particular, H_2 loss from AB, encouraged by non-classical $\text{B}-\text{H}\cdots\text{H}-\text{N}$ hydrogen bonds, is first likely to lead to reactive, transient aminoborane, $\text{H}_2\text{B}=\text{NH}_2$, which then undergoes a further dehydrocoupling/oligomerisation/ H_2 -loss processes.¹⁵⁻¹⁹

Given that the studies into using solid-state precursors for h-BN growth are limited, in terms of the different precursor molecular form, it is important to explore new opportunities in this area. Noting, in particular, the first fragmentation event in the thermolysis of $\text{H}_3\text{B}\cdot\text{NH}_3$ (AB) is loss of H_2 to form $\text{H}_2\text{B}=\text{NH}_2$. I seek stable precursors that acted as masked agents for this very reactive species in the anticipation that this would result in different, possibly enhanced, film-growth. Two novel precursors linear di- and tri-borazanes, $\text{H}_3\text{B}\cdot\text{NH}_2\text{BH}_2\cdot\text{NH}_3$ (DAB) and $\text{H}_3\text{B}\cdot(\text{NH}_2\text{BH}_2)_2\cdot\text{BH}_3$ (TAB) are implemented in this project, and they are provided by collaborators from the Department of Chemistry, University of Oxford. The synthesis of DAB and TAB is reported by Shore and Sneddon respectively and offer such a motif.^{20,21} They offer one and two equivalents

of $\text{H}_2\text{B}=\text{NH}_2$ respectively. The DAB and TAB are both potential hydrogen storage materials. The DAB is produced from the reaction between ammonia borane and tetrahydrofuran borane *via* the formation of dihydrogen bond. The DAB is in white crystalline solid powder form at room temperature with a melting point of 62 °C.²⁰ The TAB is produced through the reactions between NaHMDS and amine borane. The solid-state TAB undergoes a two-step decomposition. The initial 30% weight loss begins at 110 °C, followed by a second 30% loss begins at 142 °C.²¹ This decomposition profile is similar to that of AB. The AB shows an initial weight loss beginning at 110 °C, followed by a second loss at 130 °C.³⁷ Both DAB and TAB are predicted to be intermediates in the thermal dehydrogenation of AB.^{22,23}

Here, I examine the use these two B-N precursors DAB and TAB and compare them with AB for growth of h-BN films on Cu by APCVD method. The morphology of h-BN films is investigated as a function of growth time. These AB, DAB and TAB precursors lead to a notable dependence in the film coverage for various growth times. The h-BN films are characterised by transmission electron microscopy (TEM), Raman spectroscopy, atomic force microscopy (AFM), optical microscopy, and scanning electron microscopy (SEM).

4.2 Results and Discussion

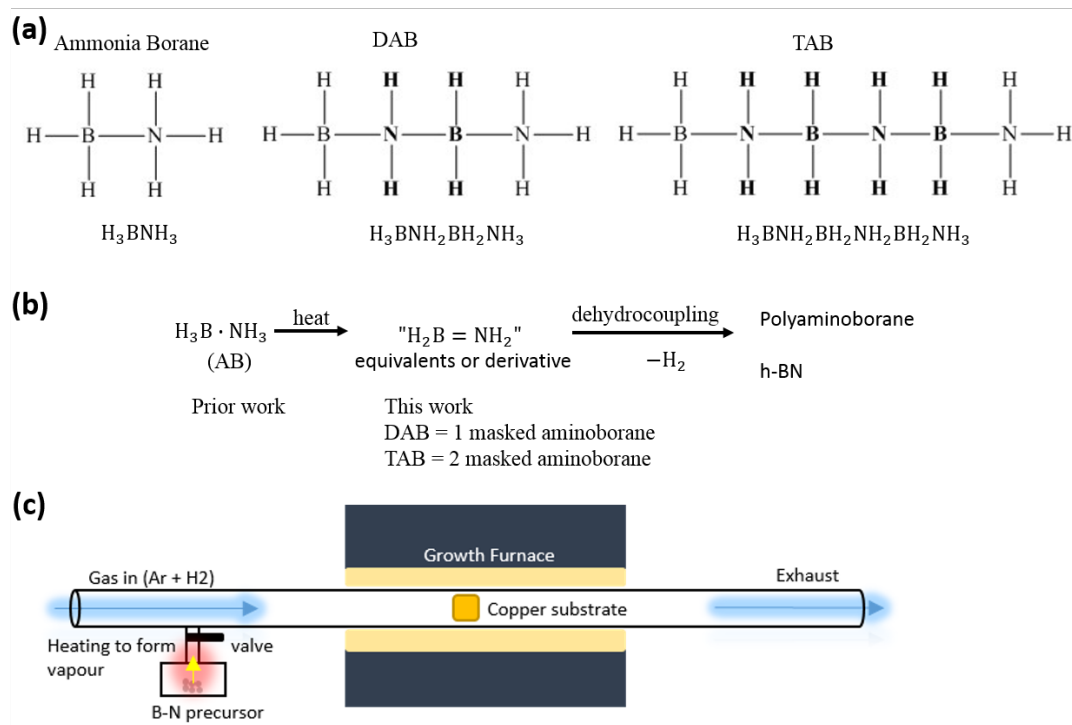


Figure 4.1 Atmospheric pressure CVD synthesis of h-BN on a Cu substrate using three different chemical precursors. (a) Structure of h-BN grown precursors, as $\text{H}_3\text{B} \cdot \text{NH}_3$, $\text{H}_3\text{B} \cdot \text{NH}_2\text{BH}_2 \cdot \text{NH}_3$ (DAB) and $\text{H}_3\text{B} \cdot (\text{NH}_2\text{BH}_2)_2 \cdot \text{BH}_3$ (TAB). (b) AB precursor is thermally decomposed to equivalents or derivatives of $\text{H}_2\text{B}=\text{NH}_2$ and produce h-BN and polyaminoborane *via* dehydrocoupling. (c) APCVD experimental setup for h-BN growth; the precursor is in an isolated chamber with a valve to control the vapor gas; the chamber is surrounded by a separated heating belt. Copper substrates are placed at the middle of a 1 inch quartz tube.

Figure 4.2 shows the SEM images of the samples on Cu for the three different precursors (AB, DAB and TAB) with different growth times (10min, 15min and 30min). For AB, Figure 4.2 (a-c), 10 minutes growth results in h-BN domains (in Appendix B Figure A 1 a), and for the 15 minutes and 30 minutes growth a complete film is produced. The change from 10 to 15 minutes growth duration with the AB precursor results in a significant

increase in the film coverage from single h-BN domains to continuous film. Similar to a recent report, the longer growth time results in h-BN crystals coalescing with subsequent growth into a complete film.¹⁴ The diborazane precursor, DAB, results in continuous h-BN films on the Cu substrate, Figure 4.2 (d-f), for all three growth durations: 10 minutes, 15 minutes, and 30 minutes, respectively. The triborazane precursor, TAB, does not produce any h-BN within the 10 minutes and 15 minutes growth periods, Figure 4.2 (g and h). However, after 30 minutes growth time a fully continuous h-BN film on the Cu substrate is obtained Figure 4.2 (i). Different contrast within the SEM images is attributed to slight variations in the layer thickness. In addition to the 30 minutes growth time, small triangular h-BN domains are observed for all three precursors above the grown h-BN film (see in Appendix B Figure A 4), this could possibly be because the growth mode follows the combination of a layer by layer growth and island growth, similar to the previously described reports.^{13,24} The CVD grown h-BN films all have white nanoparticles deposited onto the surface which are presumed to be polyaminoborane arising from the dehydrocoupling of the precursors, such a $\text{H}_2\text{B}=\text{NH}_2$, as shown in Figure 4.2.^{24,25}

Comparing results from all three precursors in the 10 minutes growth window, Figure 4.2 (a, d, and g), shows h-BN domains for the AB precursor, a fully continuous film for the DAB, and nothing for the TAB. This provides insights into the different reactivity of these three precursors and surprisingly doesn't follow a simple trend with increasing molecular weight. The thermal decomposition of AB is quite complex, but is well studied, and results in borazine ($\text{B}_3\text{N}_3\text{H}_6$), transient aminoborane (H_2BNH_2) and hydrogen gas.^{18,26,27} The major volatile products are then delivered into the growth furnace for further reactions at high temperature (1040 °C), resulting in the formation of h-BN film on Cu substrates, as illustrated in Figure 4.1 (b). The byproducts are likely polyaminoborane and noncrystalline polyiminoborane.²⁸ The proposed mechanistic details of dehydrogenation of all the precursors is based on transient and reactive

$\text{H}_2\text{B}=\text{NH}_2$, which then undergoes metal catalyst mediated B-N coupling at the Cu substrate surface.²⁹⁻³² The morphology of the CVD grown h-BN on Cu substrates using the precursors DAB and TAB is different compared with h-BN grown using ammonia borane. In term of the growth rate, the DAB is the most active precursor; while on the contrast the TAB is the least active precursor. I repeat the growth several times for each precursor and obtained similar results each time, confirming the reproducibility of the experimental synthesis methods with different precursors.

In addition to the CVD grown h-BN multilayer films on copper substrate using three different precursors, hydrogen (25%) carrier gas is used during above mentioned h-BN growth. It is worth to discuss the role of hydrogen in the CVD grown h-BN on copper substrate. Firstly, copper substrates are annealed in hydrogen environment at ambient pressure and it supresses the effect of copper substrate morphology. For example, the copper grains are enlarged, and the grain boundaries are removed. Secondly, hydrogen has shown an etching effect not only in the grown graphene but also in the grown h-BN.³⁸ The hydrogen gas reduces the nucleation sites of h-BN and results large crystal size h-BN domains.³⁹ The study of hydrogen etching reveals that it starts form the point defects and it helps to define the crystalline orientations.⁴⁰ In addition, by comparing the hydrogen and nitrogen carrier gas in the CVD grown h-BN films, more defects exist and higher surface roughness are resulted in the h-BN film when nitrogen gas is used. On the contrast, using hydrogen carrier gas shows improvement in the crystallinity of the grown h-BN.⁴¹ In conclusion, the hydrogen gas has three roles in the CVD grown h-BN thin film, it supresses the copper morphology during annealing process, it reduces h-BN nucleation sites, and finally it helps to remove the defects from the grown h-BN film.

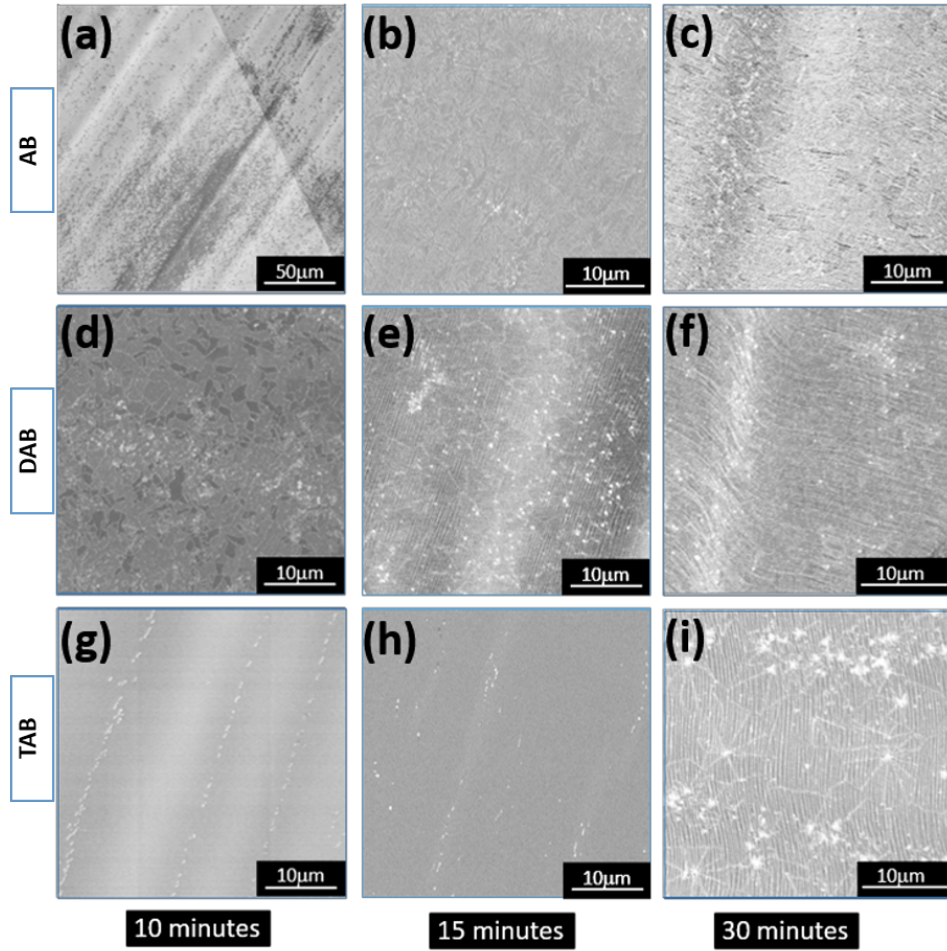


Figure 4.2 SEM images of the Cu substrate surface after h-BN CVD growth for various durations and with the AB (a-c), DAB (d-f), and TAB (g-i), three different molecular weight precursors, respectively. The x-axis represents the growth time *i.e.* 10, 15, and 30 minutes and the y-axis represents precursor type *i.e.* AB, DAB, and TAB.

Further insight into the degree of h-BN coverage on the Cu substrate after CVD growth can be obtained by heating the samples in air to oxidize any region of Cu–substrate that is not covered by h-BN. This approach has been utilized before for graphene layers grown on Cu by CVD. Figure 4.3 shows optical microscope images of the baked copper foils for 10 minutes, 15 minutes, and 30 minutes CVD growth, respectively. These h-BN grown samples are placed on a hot plate and baked at 200 °C for 2 minutes in air. The optical images are complimentary to the SEM images shown in Figure 4.2. Oxidization of the Cu results in a colour change from orange to red forming a layer of CuO on the original surface, and thus enables convenient optical analysis of the large area h-BN coverage, as demonstrated in Figure 4.3 (b, d, e, g, h, and j). All samples that showed continuous film coverage in the Figure 4.2, show no signs of Cu oxidization in Figure 4.3, confirming that the h-BN films are present across the large areas and protect the Cu from reacting in air.

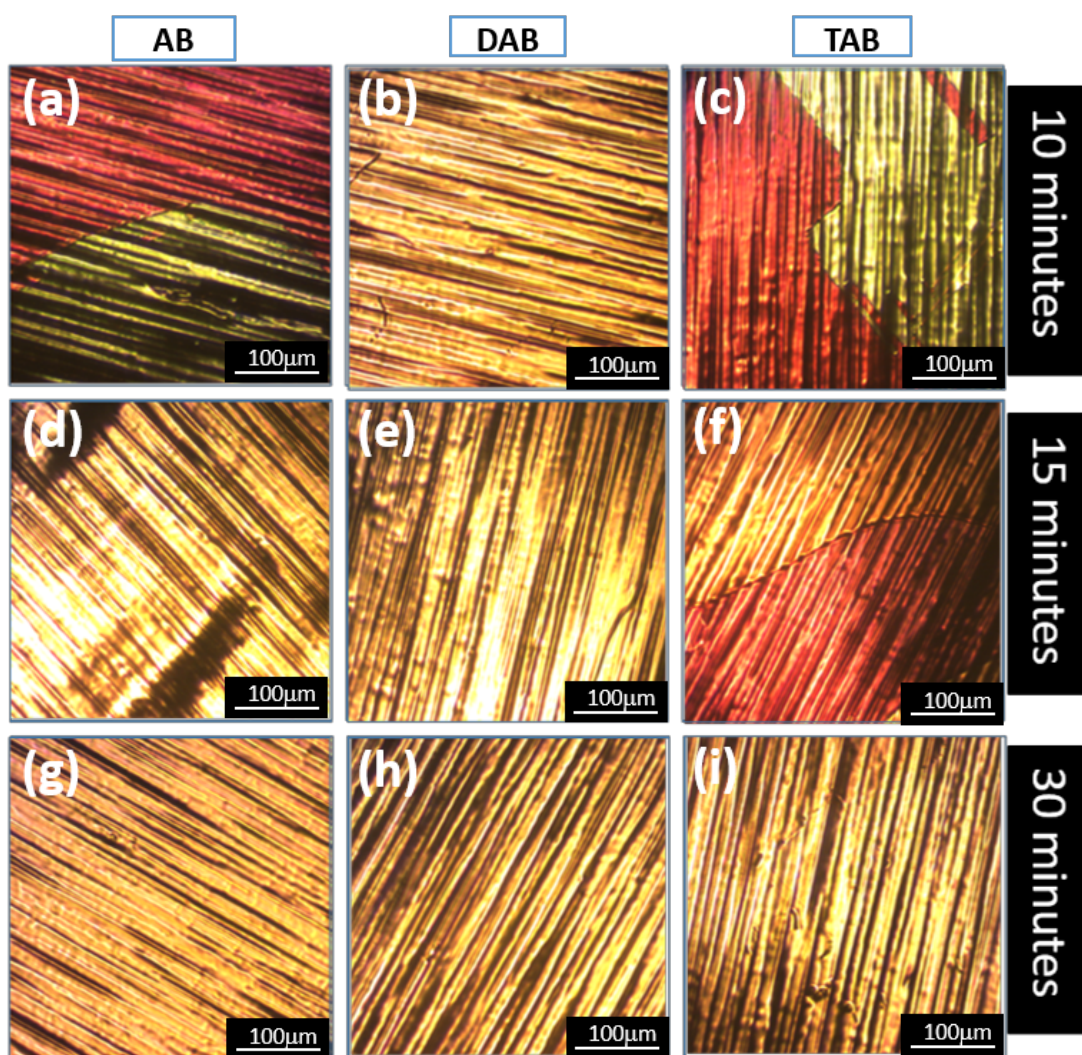


Figure 4.3 Optical images of oxidized Cu surface after the CVD growth of h-BN with various growth time and various types of precursor. AB grown h-BN on Cu with (a) 10 min, (d) 15 min, and (g) 30 min growth time. DAB grown h-BN on Cu with (b) 10 min, (e) 15 min, and (h) 30 min growth time. TAB grown h-BN on Cu with (c) 10 min, (f) 15 min, and (i) 30 min growth time.

It is also important to examine the deposition of the proposed BN-containing nanoparticles on the surface of the h-BN films. Figure 4.4 (a-c) shows SEM images of CVD grown h-BN films for 30 minutes growth time, which are used to analyse the coverage of the surface nanoparticles. As discussed earlier, these nanoparticles are likely formed by dehydrocoupling of the chemical precursors *i.e.* polymeric aminoborane.^{28, 33}

Figure 4.4 (g) shows the statistical information about the relationship between the precursor type and the coverage of surface nanoparticles, obtained from the images in Figure 4.4 (d, e and f), where the nanoparticles are white in colour. The overall surface nanoparticle coverage is proportional to the precursor molecular weight. For example, the ammonia borane grown h-BN film has 5% coverage of the nanoparticle, the DAB grown h-BN film has about 15%, and the TAB grown h-BN film has the highest impurity coverage which is 25%. During this CVD synthesis of h-BN, the TAB precursor is likely producing a larger amount of polyaminoborane compared to the DAB and the ammonia borane precursor.

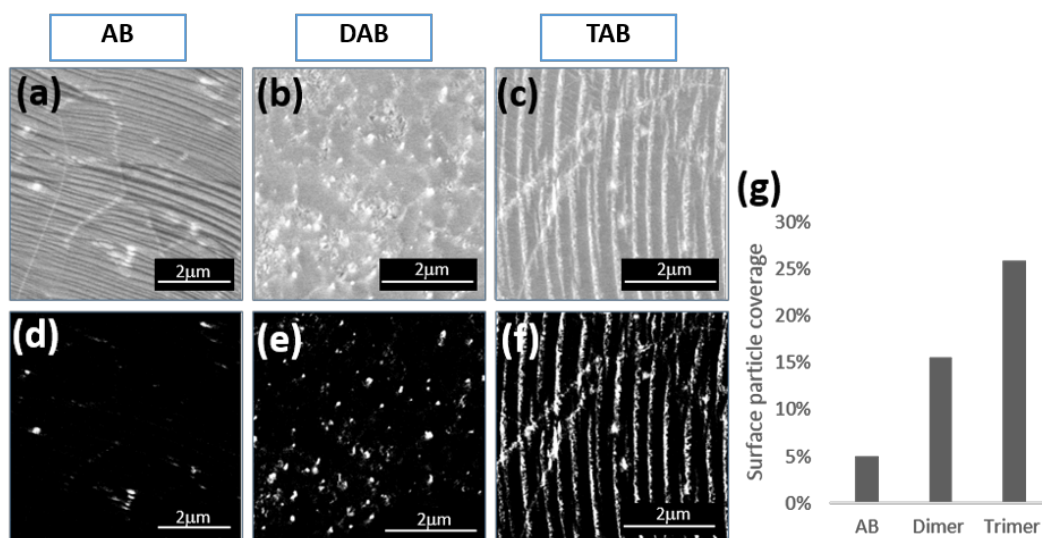


Figure 4.4 SEM images (a, b, and c) of synthesised continuous h-BN films with ammonia borane, DAB, and TAB precursors and 30 minutes growth time, respectively. Binary threshold SEM images (d, e, and f) of the corresponding surface nanoparticles are shown in white colour. (g) Plot showing the precursor type dependent surface nanoparticle coverage.

To examine the quality of the h-BN films, Raman spectroscopy and atomic force microscopy (AFM) are performed after transferring onto silicon substrates. Raman spectroscopy is a powerful technique to analyse the characteristics of 2D materials including h-BN layers. It is well known that the Raman peak of bulk of h-BN is at 1366 cm^{-1} and shifts to a higher frequency as the number of h-BN layers decreases.³⁴ For a monolayer h-BN film the peak is around 1370 cm^{-1} . All three h-BN films have Raman peaks, as shown in Figure 4.5 (a). The E_{2g} phonon vibration modes are between $1366\text{--}1369\text{ cm}^{-1}$, indicating few layers h-BN. These Raman peaks are symmetric and have narrow width, indicating high purity of h-BN film. Since the deleterious by-products of precursor, *i.e.* cubic-BN, $B_xC_yN_z$ and BN nanoparticles, the Raman spectra would have asymmetric peak positions.^{11,35} Gaussian curve fitting are used to show the symmetry of the three Raman peaks obtained from different precursor grown h-BN films. The FWHM value (14 cm^{-1}) of DAB-grown h-BN film is the lowest compared to the TAB

(FWHM=20 cm^{-1}) and AB (FWHM=16 cm^{-1}) grown h-BN. Although Figure 4.4 estimates the highest nanoparticles coverage of the whole film for TAB precursor, ~25%, 75% of the grown h-BN film is not covered by nanoparticles, therefore these Raman spectra show signals primarily from h-BN material. The wet chemical transfer method may help remove the byproducts *i.e.* $\text{B}_x\text{C}_y\text{N}_z$ and BN nanoparticles. The thickness of the as grown h-BN films is further characterised by atomic force microscopy (AFM). Figure 4.5 (c, e, and g) provide AFM height profiles from the measured edges of the transferred h-BN film. The thickness of the ammonia borane grown h-BN film is ~4 nm, and the thickness of DAB and TAB precursor grown h-BN film are both ~7 nm. Indicating that all the grown h-BN films from these precursors are few-layered. These AFM measurements does directly characterise the thickness of the CVD grown h-BN films. Because the wet chemical transfer method involves a layer of PMMA coating on the h-BN films, and it cannot be removed by the acetone solution. These results overestimate the thickness of the grown h-BN film.

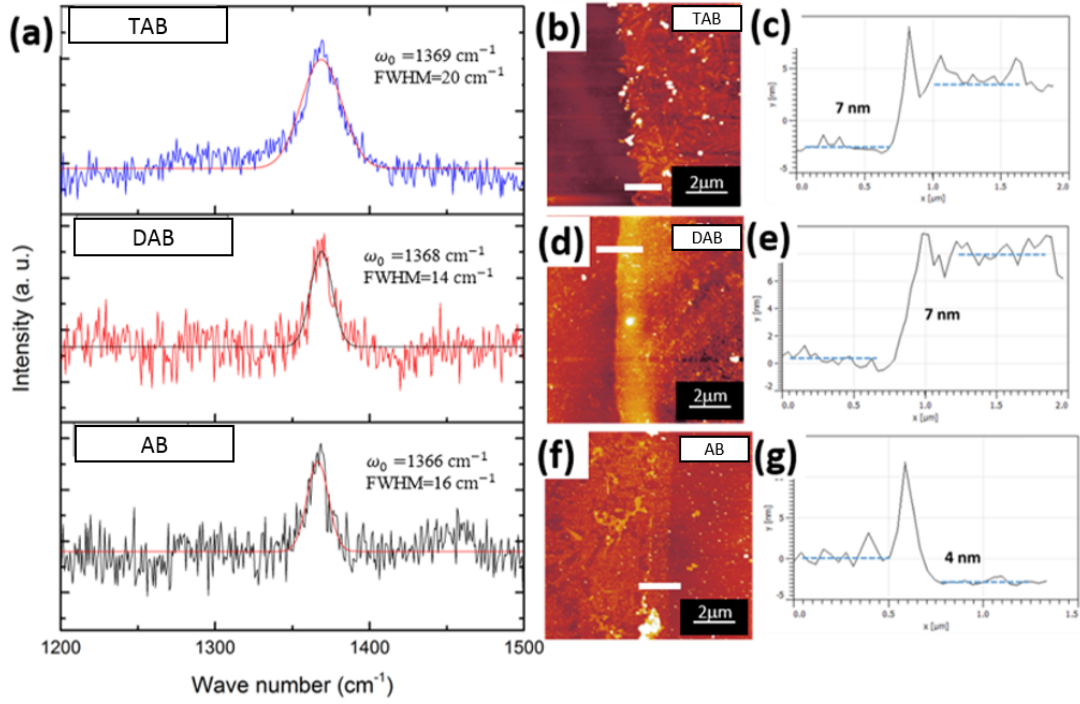


Figure 4.5 (a) Raman spectra of h-BN films transferred to silicon substrates grown by AB, DAB, and TAB, respectively. AFM images of h-BN films transferred to silicon substrate, (b) TAB grown h-BN sample, (d) DAB grown h-BN sample, and (f) AB grown h-BN sample. Corresponding height profiles (c) for TAB, (e) for DAB, and (g) for AB samples and are taken from the white lines indicated in the corresponding AFM images, respectively.

The layer number is further investigated using transmission electron microscopy (TEM) to image the back folded edge regions of the 30 minutes grown h-BN films. Imaging folded edges provide lines of contrast that enable the counting of the layer numbers. The TEM images, Figure 4. 6 (b, e, and h), show 2 lines of contrast typical for AB grown samples and 3 lines of contrast for the DAB samples, and 4 lines of contrast for TAB samples. The line profiles taken across these edges, Figure 4.6 (c, f, and i), confirm this. The Figure A9 in Appendix B presents the statistical variation in the edge number for these samples. The crystalline structure of the h-BN films is characterised using selected area electron diffraction (SAED) taken from the regions shown in the corresponding low-

magnification TEM images in Figure 4.7 (a and c) for AB precursor, Figure 4.7 (e and g) for DAB precursor, and Figure 4.7 (i and k) for TAB precursor samples. The SAED patterns show a systemic hexagonal diffraction pattern, indicative of h-BN lattice structure.²⁸ A single crystal SAED pattern is typically found for AB grown h-BN, seen in Figure 4.7 (b and d). The SAED pattern of DAB and TAB precursor grown h-BN films shows both single and multiple sets of diffraction spots rotated with respect to each other. The turbostratic stacking takes place in Figure 4.7 (f and h) for DAB precursor, and Figure 4.7 (j and l) for TAB precursor. The observed interlayer distance for all h-BN films is ~ 3.5 Å, which is similar to that of bulk h-BN.³⁶

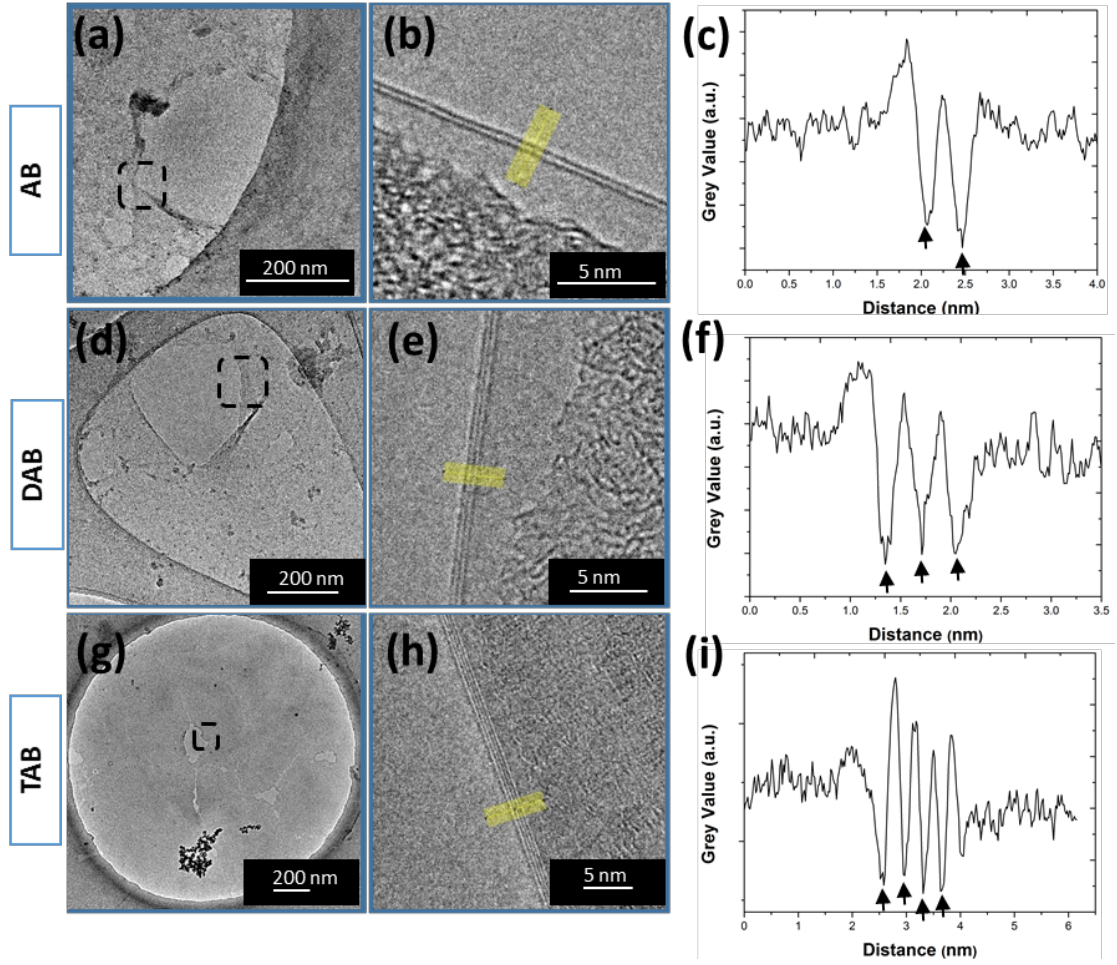


Figure 4.6 TEM images show the layer number of the grown h-BN films. Low-magnification TEM images show the folded edges of (a) AB, (d) DAB, and (g) TAB precursor 30 minutes grown h-BN film. (b, e, and h) are the zoomed-in regions marked in (a, d, and g), respectively. The line contrast line intensity profiles (c, f, and i) record along the marked regions in (b, e, and h). The black arrows point to the counted layers.

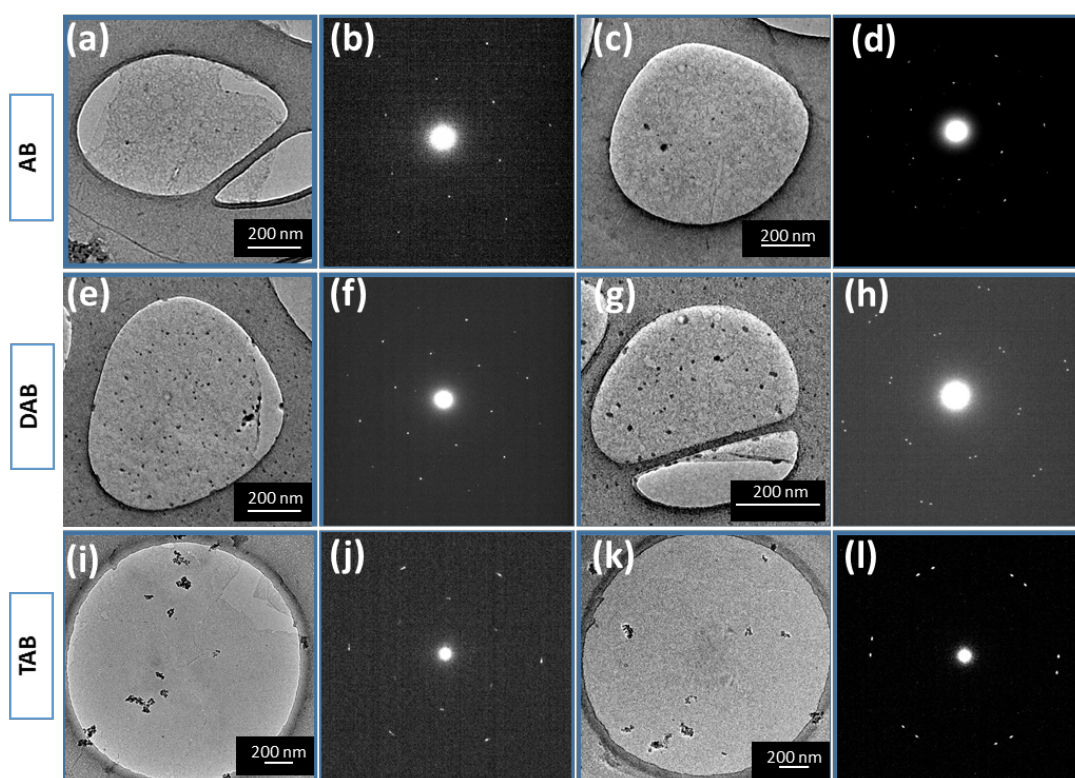


Figure 4.7 Low-magnification TEM images of three precursor grown h-BN films and their corresponding SAED patterns. Low-magnification TEM images of (a and c) AB precursor 30 minutes grown h-BN samples and single set of SAED pattern (b and d). TEM images (e and g) show DAB precursor 30 minutes grown h-BN samples and single crystal and multiple sets of SAED patterns (f and h), respectively. TEM images (i and k) show TAB precursor 30 minutes grown h-BN samples and single crystal and multiple sets of SAED patterns (j and l), respectively.

4.3 Conclusion

In summary, I grow few-layered h-BN films on Cu substrates by the APCVD method using three different precursors. Two precursors, diborazane, $\text{H}_3\text{B}\cdot\text{NH}_2\text{BH}_2\cdot\text{NH}_3$ (DAB), and trimeric triborazane $\text{H}_3\text{B}\cdot(\text{NH}_2\text{BH}_2)_2\cdot\text{NH}_3$ (TAB), both derivatives of ammonia borane, $\text{H}_3\text{B}\cdot\text{NH}_3$ (AB), show success in growing h-BN. The 30 minutes growth duration results in continuous h-BN film formation on Cu substrates for all three precursors. The overall surface nanoparticle coverage shows dependence about the precursor molecular weight. The grown h-BN films are characterised *via* Raman microscopy, AFM, and TEM, indicating that the grown h-BN films are 2 – 5 nm thick and their crystallinity. Because the surface of Cu is the same for all three precursors, the difference in growth rates is associated with the precursor decomposition process. Future work incorporating mass spectroscopy to measure the chemical species emitted from each precursor upon heating may help shed more light on this topic. This work offers an insight into the variety of precursors that can be used for the CVD growth of h-BN.

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Chapter 5

Chemical Vapor Deposition Synthesis of Gallium Sulfide Mixture Phases (GaS/Ga₂S₃) Thin Film and Their Application as Hydrogen Evolution Catalysts

In this work, I establish the synthesis method of GaS/Ga₂S₃ thin film using a CVD method. The thin film is produced by a single-step scalable thermolysis of Ga₂S₃ precursor under atmospheric pressure condition. Structural analysis shows that the prepared material has triangular and hexagonal GaS/Ga₂S₃ flakes. The optimized growth recipe provides continuous film on both SiO₂/Si and glassy carbon substrates, and the GaS/Ga₂S₃ flakes exhibit thickness ranging from 4.5 to 30 nm depending on the growth time. Then the systematic study is performed about its catalytic activity in hydrogen evolution reaction (HER). One of the GaS/Ga₂S₃ samples exhibits an outstanding performance with a Tafel slope of 126 mV/dec and 5.50 $\mu\text{A}/\text{cm}^2$. Further post annealing process results an improvement in Tafel slope of 109 mV/dec and 3.07 $\mu\text{A}/\text{cm}^2$. This work provides important insights into the fabrication of layered group III metal chalcogenide catalysts and an understanding of their HER performance.

5.1 Introduction

Hydrogen is a promising future energy source. The hydrogen evolution reaction (HER) allows the extraction of hydrogen from water, however the most active catalyst platinum is expensive and rare.¹ Transition metal dichalcogenides (TMDs) have been attracted attentions and proven catalytically active for the HER.^{2–8} Moreover, materials such as MoS₂, WS₂, h-BN, and SnS₂ have potentials in nanoelectronic devices.^{9–14} The properties of these layered nanomaterials include high surface-to-volume ratio, distinguished electrical, magnetic, and optical properties.^{15–24}

Voiry *et al.* demonstrate that both WS₂ and MoS₂ nanosheets act as catalysts for the HER due to their concentration of the strained metallic 1T phase, and distorted local lattices.^{3,4} Chen *et al.* report that the crystalline WS₂ is an active catalyst, and in the MoS₂ system amorphous MoS₂ and S₂²⁻ species are key components.²⁵ Wu *et al.* demonstrate that WS₂ has a higher electrocatalytic activity than MoS₂ because the loosely stacked layers in WS₂ provide larger active sites than the densely stacked MoS₂ layers.²⁵ Yang *et al.* report using hydrothermal synthesis method to fabricate WS₂ on reduced graphene oxides. The hybrid material exhibits excellent performance in HER, because of the interconnected conducting support material facilitates rapid electron transfer between the electrode and catalyst.²⁶ MoS₂ nanoparticles on reduced graphene oxide sheets exhibits excellent HER activity. Its overpotential is 0.1 V and Tafel slope is 41 mV/dec.²⁷ The GaS materials from the layered group III metal chalcogenides, has recently shown its catalyst activity in HER.⁶ The other potential applications of GaS include photodetectors, anode materials in lithium-ion battery and transistors.^{30,31,38} Like those of other 2D materials, the production methods can be generally classified as mechanical cleavage, chemical vapor deposition (CVD), and liquid exfoliation.^{6,20–37}

In this chapter, an ambient pressure CVD synthesis method is used to grow GaS/Ga₂S₃ thin film, and they are utilized as catalysts in the HER application. The GaS/Ga₂S₃ thin films are deposited on both SiO₂/Si and glassy carbon substrates. Their surface structures are studied and characterised by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), Raman spectroscopy, and transmission electron microscopy (TEM). The results demonstrate that the catalytic performance of CVD grown GaS/Ga₂S₃ thin film in the HER application.

5.2 Results and Discussion

Researchers have made efforts to discover and develop new precursors in order to synthesize the GaS thin film.^{39,40,41} The Ga₂S₃ compound is stable in air, easy to handle and contains all the desired elements in a single molecule.²⁹ It is used as precursor for the production of GaS/Ga₂S₃ film in the following projects. The formation of the GaS/Ga₂S₃ flakes occurs *via* the following reaction:



The Ga₂S₃ precursor is thermally decomposed and reduced by hydrogen gas at high temperature. Then the generated vapor gas is carried to the lower temperature region of the furnace and the deposition occurs at the substrate. The substrate is vertically placed in the quartz tube, and it experiences homogeneous vapor concentration from the precursor without the influence of geometric effect.¹³ Micrometre-scale GaS/Ga₂S₃ flakes are consistently synthesised using this method. The distance between the precursor and substrate can be adjusted. It provides the control of the nucleation density since the temperature of the vapor can be adjusted by moving the substrate.

Figure 5.1 (a) shows a schematic diagram of a typical CVD growth of GaS/Ga₂S₃ materials. 10 mg of Ga₂S₃ is loaded into the furnace. A bare SiO₂/Si substrate is placed vertically in the middle of the furnace. The distance between the precursor and substrate

is 8.5 cm. After 30 minutes growth, a continuous GaS/Ga₂S₃ film is deposited on the substrate. The overall CVD synthesis of GaS/Ga₂S₃ has three main stages. Stage I involves increasing the furnace temperature, for example to 800 °C, the 150 sccm Ar and 30 sccm H₂ as carrier gas are passed through the furnace. The second stage maintains the target temperature for a period of time, such as 30 minutes, and carrier gas is 30 sccm H₂. The final stage involves fast cooling the substrate with flowing 150 sccm Ar to immediately stop the growth. These three stages are presented in Figure 5.1 (b). Both SiO₂/Si wafer and glassy carbon are used as substrates in the CVD synthesis, as shown in Figure 5.1 (c). The grown GaS/Ga₂S₃ is well deposited on the SiO₂/Si substrate, it appears green colour, while the glassy carbon substrates with GaS/Ga₂S₃ appears black. Figure 5.1 (d) shows the zoomed-in optical image of GaS/Ga₂S₃ on SiO₂/Si substrate where the grown flakes are homogeneously deposited on the substrate surface.

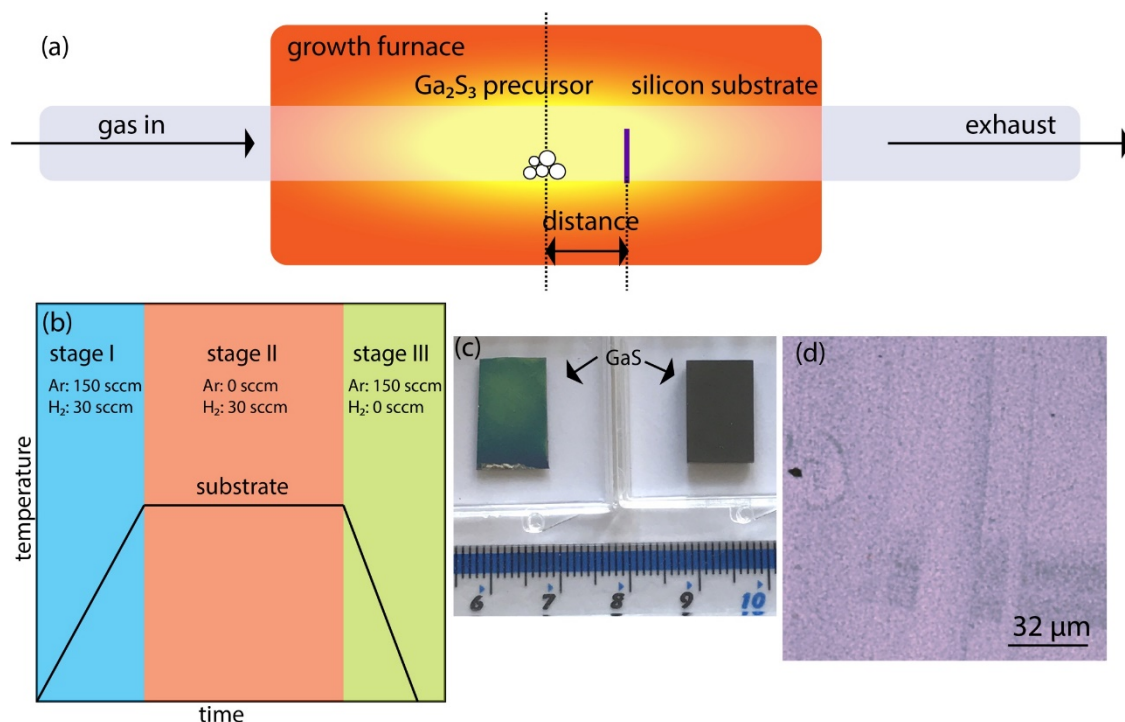


Figure 5.1 (a) Schematic illustration of the CVD synthesis setup of GaS/Ga₂S₃. (b) Temperature against growth time profile of the CVD synthesis of GaS/Ga₂S₃. (c) Photograph showing the GaS/Ga₂S₃ thin film grown on SiO₂/Si and glassy carbon substrates with a scale ruler (both GaS/Ga₂S₃ films are deposited using the same growth conditions). (d) Optical image shows GaS/Ga₂S₃ film grown on an SiO₂/Si substrate.

Figure 5.2 shows series of SEM images of the CVD grown GaS/Ga₂S₃. They demonstrate the growth depends on two parameters: growth time and substrate position. The surface morphology is complete different for the presented 9 samples. In Figure 5.2 (a), (b), and (c), the substrate position is 8.5 cm, when the growth time increases from 10 to 30 minutes, the GaS/Ga₂S₃ shows from small crystals to continuous thin film. When the growth time is fixed, and the substrate distance is decreased, less GaS/Ga₂S₃ is deposited on the SiO₂/Si substrate. As shown in Figure 5.2 (b), (e), and (h), all samples have same 15 minutes growth time, the morphology changes from partially film coverage to small domains, and eventually to dendritic structures, because of the reduced substrate distance. For a growth time of 30 minutes and 8.5 cm distance, the sample shows a complete film

coverage on the SiO_2/Si substrate. Similarly, the 30 minutes and 8.0 cm substrate sample has some well crystallized domains, and this will be discussed in more details. The closest substrate (7.5 cm) after 30 minutes growth results the formation of white particles. The above mentioned three samples are shown in the Figure 5.2 (c), (f), and (i), respectively. These white particles are attributed to the rapid change of the growth temperature and the incomplete reduction from the Ga_2S_3 precursor to GaS vapor. The medium substrate position (8 cm) and 30 minutes growth time sample does not have complete film coverage. Only 30 minutes growth time and 8.5 cm sample has a complete film coverage, as shown in Figure 5.2 (c).

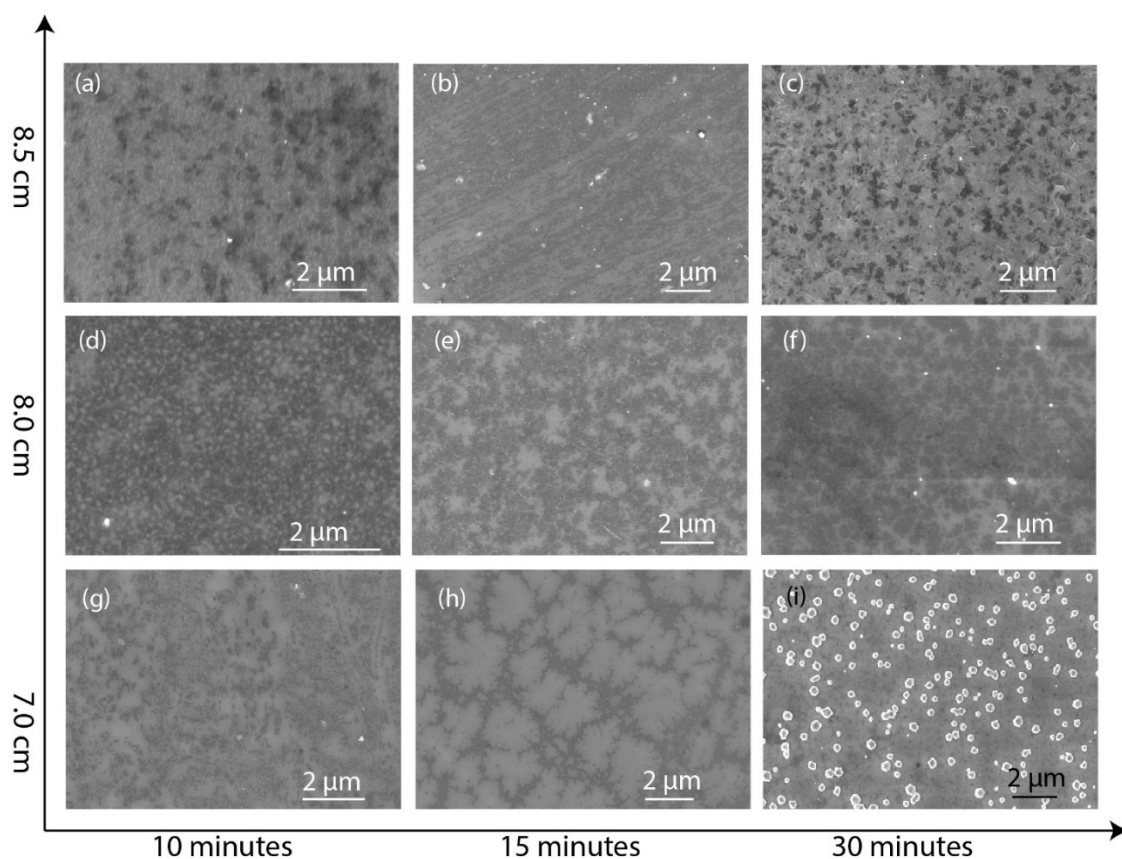


Figure 5.2 SEM images showing the morphology dependence of CVD grown GaS/Ga₂S₃ as a function of growth time and substrate position at a fixed growth temperature of 800 °C.

To understand the growth mechanism of the GaS/Ga₂S₃ films, several modifications are made based on the recipe of 8 cm substrate distance, 800 °C growth temperature and 30 minutes growth time, such as extending the growth time and tuning the growth temperature in a step-by-step process. The growth time is increased from 15 minutes up to 60 minutes; and the growth temperature is varied between 700 °C and 900 °C. Both sets of experiments give interesting results. In Figure 5.3 (a-c), when the growth temperature is 800 °C, the longer growth time results in crystalline domains, and they have mixtures of triangular and hexagonal domains with sharp edges. The shape of grown domains is hexagon with sharp edges when the growth temperature is 800 °C, as shown

in Figure 5.3 (e). The hexagonal shaped flakes are consistent with previously reported CVD grown GaS materials in low temperature.³⁵ At the 900 °C growth temperature, the reaction is more vigorous and the crystallised domains are stacked together, as shown in Figure 5.3 (f). At the lowest 700 °C growth temperature, Figure 5.3 (d) shows the initial growth stage of the CVD grown GaS/Ga₂S₃ on silicon substrate. Figure 5.3 (b) and (e) are obtained from the same sample, but the images are taken from separate positions, where (b) is taken at bottom of the substrate and (e) is taken at the top of the substrate. It clearly shows the difference in vapor concentration from the Ga₂S₃ precursor and the mean free path of the reacted species. During the growth stage, a higher concentration of GaS vapor arrives at the top of the substrate and deposits initial nucleation sites. Next, GaS/Ga₂S₃ crystals start to grow and eventually form continuous film. However, the bottom of substrate experiences a low concentrate of GaS vapor, and it causes the nucleation of triangle shaped domains. Figure 5.3 (b) and (e) are consistent with the optical image of GaS/Ga₂S₃ thin film on the SiO₂/Si substrate, as shown in Figure 5.1 (c). It also explains the observed colour difference.

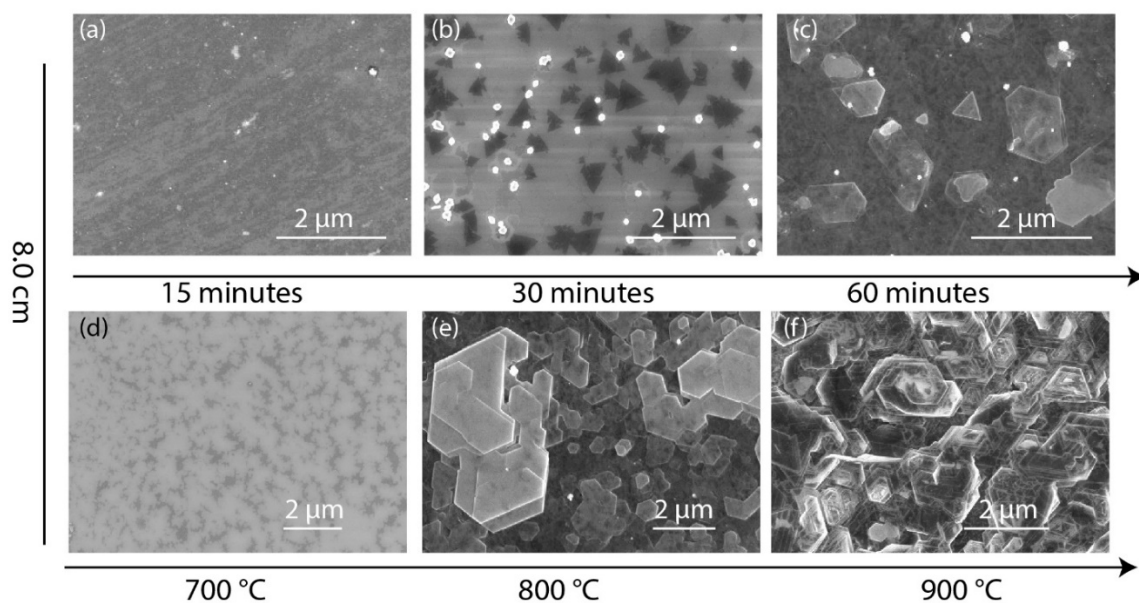


Figure 5.3 SEM images of GaS/Ga₂S₃ depending on the growth time and growth temperature with a fixed substrate position of 8 cm. (a-c) The CVD grown GaS/Ga₂S₃ with fixed 800 °C growth temperature and 15 minutes, 30 minutes, and 60 minutes growth time, respectively. (d-f) The CVD grown GaS/Ga₂S₃ with fixed 30 minutes growth time and 700 °C, 800 °C, and 900 °C growth temperature, respectively.

Three phonon modes exist in the first-order Raman spectrum of GaS. The typical bulk GaS has Raman peaks at 187-188, 289-295, and 360 cm⁻¹.^{30,36} The CVD grown GaS on SiO₂/Si substrate exhibits the Raman peaks at 185, 288, and 357 cm⁻¹, as shown in Figure 5.4 (b). Comparing with mechanical exfoliated GaS nanosheets, all three phonon modes decrease for the CVD grown GaS at room temperature. The reduced E_{2g}¹ mode is due to the induced strain. It is occurred during the fast cooling stage and the different thermal expansion coefficients of deposited materials and SiO₂/Si substrate. The liquid exfoliated GaS sample has Raman position at 195, 300, and 370 cm⁻¹.⁶ The GaS grown by CVD method is close to mechanical exfoliated GaS nanosheet. Above mentioned Raman modes are summarized in Table 5.1. However, the Ga₂S₃ Raman peaks are also found on the CVD grown sample at various spots, as shown in Figure 5.4 (a). This is because that

the CVD growth method could not convert all the Ga_2S_3 precursor to the GaS vapor. Therefore, a mixture phase thin film is formed on the substrate. A systematic study about the area covered by GaS/ Ga_2S_3 thin film is investigated and it is in Appendix C supporting information. The 15 minutes growth sample has 0% Ga_2S_3 coverage, while the 30 minutes growth sample has roughly 84% Ga_2S_3 coverage, and the 60 minutes sample has about 52% Ga_2S_3 coverage. In conclusion, this method produces a mixture phases GaS/ Ga_2S_3 thin film.

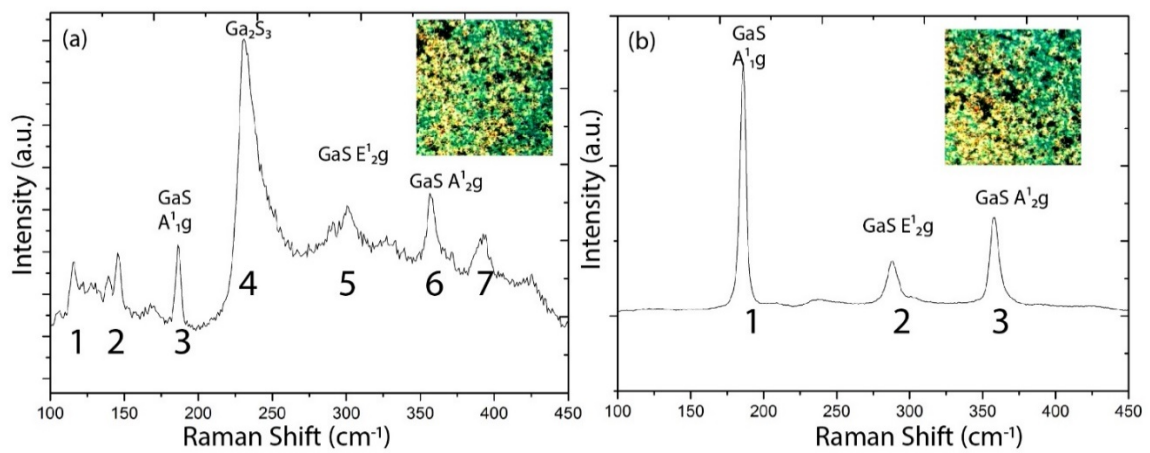


Figure 5.4 (a) The Raman spectrum of both GaS and Ga_2S_3 characteristic peaks. (b) The Raman spectrum of GaS characteristic peaks. Insets are the optical images of the samples.

Table 5.1 Contains the GaS and Ga₂S₃ Raman peak positions obtained from this work and literatures.

<i>Sample name</i>	<i>Peak Position</i>		A^1_{1g}		E^1_{2g}	A^2_{1g}		<i>ref</i>
(a)	115	145	186	232	301	357	392	This work
(b)			185		288	357		This work
<i>Bulk GaS</i>			187		289	368		30,36
			188		295	360		
<i>0.85 nm mechanical exfoliated GaS ultrathin layer</i>			186		303	361		36
<i>Liquid exfoliated GaS flakes</i>			195		300	370		6
<i>Ga₂S₃</i>		140	180	230	325	352	380	42

The morphology of the GaS/Ga₂S₃ sample (recipe of the 800 °C growth temperature and 30 minutes growth time) is further characterised by the AFM. Figure 5.5 (a) shows an overall AFM scanned region of this sample. Large particles are randomly dispersed on the surface. These particles are either from the solid Ga₂S₃ precursor or are pure gallium metal. The presence of Ga₂S₃ is confirmed by the Raman results, as discussed earlier. Figure 5.5 (b) shows the measured surface roughness of the dashed region and its RMS is 5.35 nm. The corresponding 3D AFM height profile represents the diameter of the white particle is about 0.14 µm, as shown in Figure 5.5 (c). Three individual flakes of the CVD grown GaS/Ga₂S₃ are measured, as shown in Figure 5.5 (d-f). Along the indicated lines, their associated step height profiles are plotted in Figure 5.5 (g, h, and i). The measured sharp edge of the GaS/Ga₂S₃ domain is 0.6 nm and this step height does not match with the 0.75 nm thickness of GaS monolayer.²⁸ The thickness of the CVD grown GaS/Ga₂S₃ flakes is between 6 and 11 nm in general.

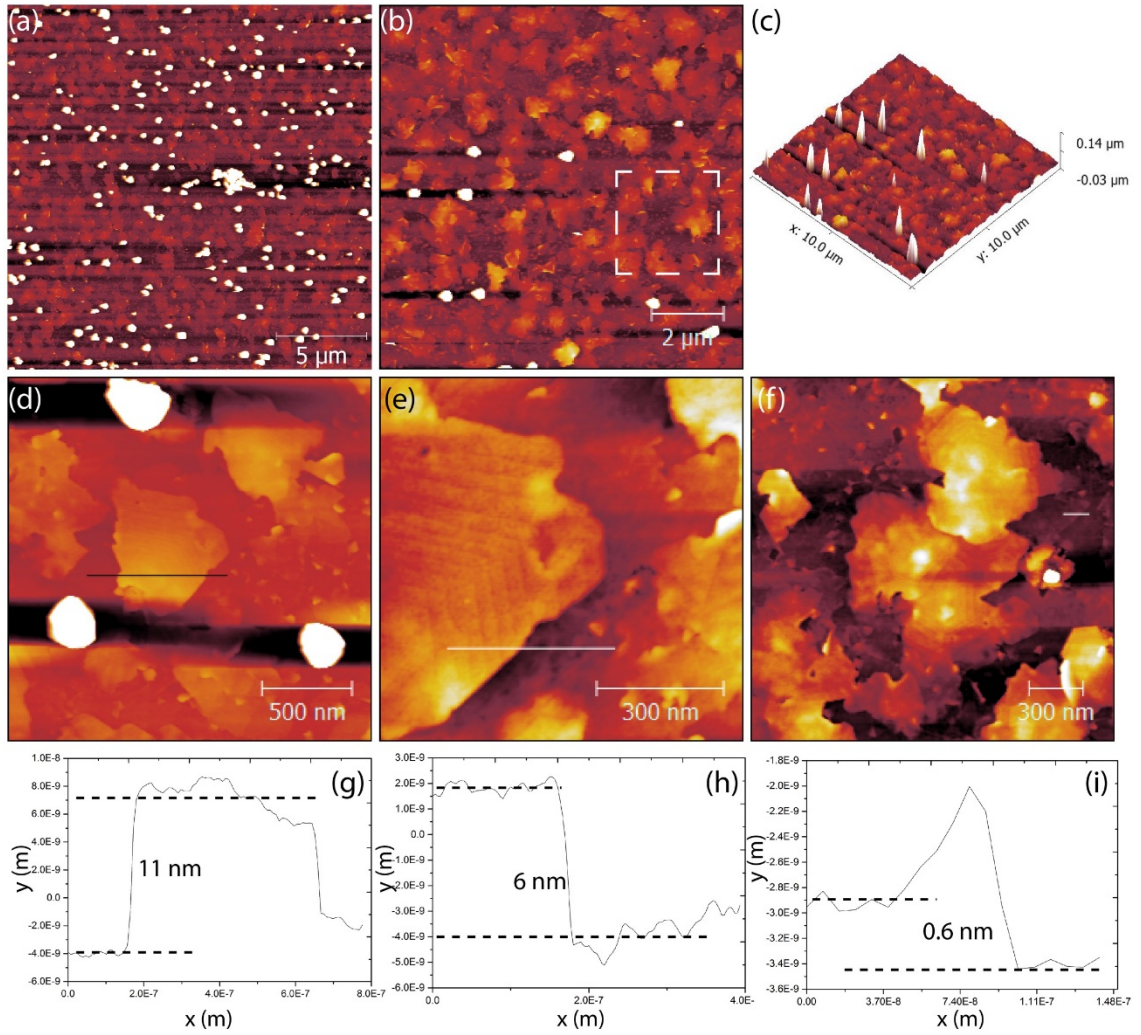


Figure 5.5 AFM images of measured CVD grown GaS/Ga₂S₃ on SiO₂/Si substrates. (a) 20 × 20 μm large area scan, (b) Zoomed-in scan with measured surface roughness of the dashed region. (c) The 3D AFM image of (b) indicating the scale of large particles. (d-f) Three zoomed-in AFM images show the measurement of the grown GaS/Ga₂S₃ flakes along the marked lines. The corresponding measured height profiles (g-i) of the CVD grown GaS/Ga₂S₃ flakes in (d-f).

The CVD growth recipe (8.5 cm substrate distance, 15, 30, and 60 minutes growth time and 800 °C growth temperature) is then used to grow GaS/Ga₂S₃ on glassy carbon substrates, in order to test its catalytic ability in the hydrogen evolution reaction (HER). Before the HER test, the three CVD grown GaS/Ga₂S₃ samples are characterised by SEM,

as shown in Figure 5.6 (a-c). It is shown that the longer the growth time the more particles appear on the surface. These particles are discussed in later section.

Electrochemical testing is performed in 0.5 M H_2SO_4 Ar-purged electrolyte. The Ag/AgCl/KCl (3M) is used as the reference electrode ($E(\text{RHE}) = E(\text{Ag/AgCl/KCl (3M)}) + 0.059 \times \text{pH}$). An activated carbon counter electrode is used. A 3 mm thick glassy-carbon plate (Sigma-Aldrich Company Ltd.) with the CVD-grown GaS/Ga₂S₃ film is used as the working electrode. The effective area ($1 \times 0.8 \text{ cm}$) of the working electrode is defined by applying electrochemically inert hydrophobic wax and pure polytetrafluoroethylene (PTFE) tape. A metal clip is used to connect the working electrode with an external circuit. Linear sweep voltammetry (LSV, scan rate of 1 mV/s) under quasi-equilibrium conditions is recorded by a Biologic VMP3 potentiostat. Cyclic voltammetry (CV) is conducted at 100 mV/s to investigate the cycling stability. Electrochemical impedance spectroscopy (EIS) is carried out from 200000 to 1 Hz with an amplitude of 10 mV.

The cathodic polarization curves are shown in Figure 5.6 (d). The 15 minutes grown sample requires a large overpotential in order to generate current, while the other 30 and 60 minutes grown samples exhibit exchange current through applied potentials between -1.0 V and -0.7 V. The corresponding Tafel plots are shown in Figure 5.6 (e). The exchange current densities are determined by fitting the liner portion of the Tafel plot at low cathodic current to the Tafel equation. The calculated Tafel slopes of the 30 and 60 min samples are 126 mV/dec with $5.50 \mu\text{A}/\text{cm}^2$ and 167 mV/dec with $10.57 \mu\text{A}/\text{cm}^2$, respectively, as seen in Figure 5.6 (e). There is almost no change in the cathodic current after a 1000 cycle durability test for the 30 minutes CVD grown sample, and this result is shown in Figure 5.6 (f). Electrochemical impedance spectroscopy (EIS) is used to study the electrode kinetics and interface reactions during the HER process, as shown in Figure 5.6 (g).

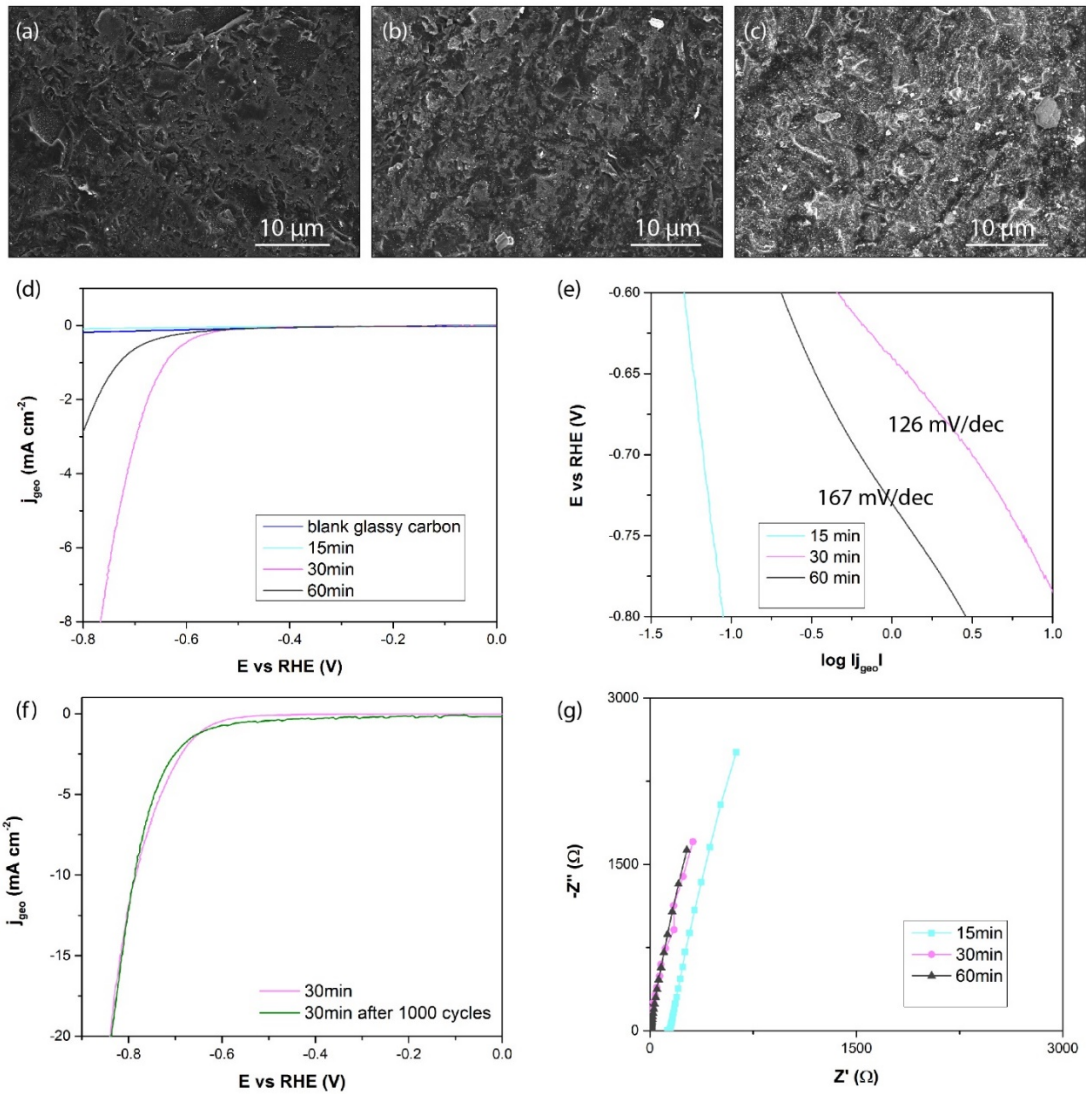


Figure 5.6 (a-c) SEM images show the GaS/Ga₂S₃ grown on glassy carbon substrates with 15, 30, and 60 min growth times, respectively. (d) Cathodic polarization curves at a scan rate of 1 mV/s and their corresponding Tafel plots as shown in (e). (f) Electrochemical stability test of the 30 min CVD synthesised GaS/Ga₂S₃ thin film before and after 1000 cycles. (g) Electrochemical impedance spectroscopy (EIS) of the CVD grown GaS/Ga₂S₃ films on glassy carbon substrates.

GaS/Ga₂S₃ samples produced on glassy carbon are subjected to a post annealing process. This post annealing process involves baking the samples in a H₂ environment for 30 minutes at 600 °C in order to increase their active surface area. Figure 5.7 (a-c) show the surface of the samples after the post annealing process. It is obvious that the overall

particles density of 30 min and 60 min samples is significantly reduced. When the HER test is conducted as before under the same conditions, the 15 minutes CVD grown sample now exhibits electrocatalytic activity towards hydrogen evolution. Overall the HER catalytic ability of all sample is enhanced, as shown in Figure 5.7 (d). The calculated Tafel slopes of post-growth annealed 15, 30, and 60 min CVD grown samples are 112 mV/dec with $2.17 \mu\text{A}/\text{cm}^2$, 109 mV/dec with $3.07 \mu\text{A}/\text{cm}^2$, and 171 mV/dec with $14.55 \mu\text{A}/\text{cm}^2$, respectively, as shown in Figure 5.7 (e).

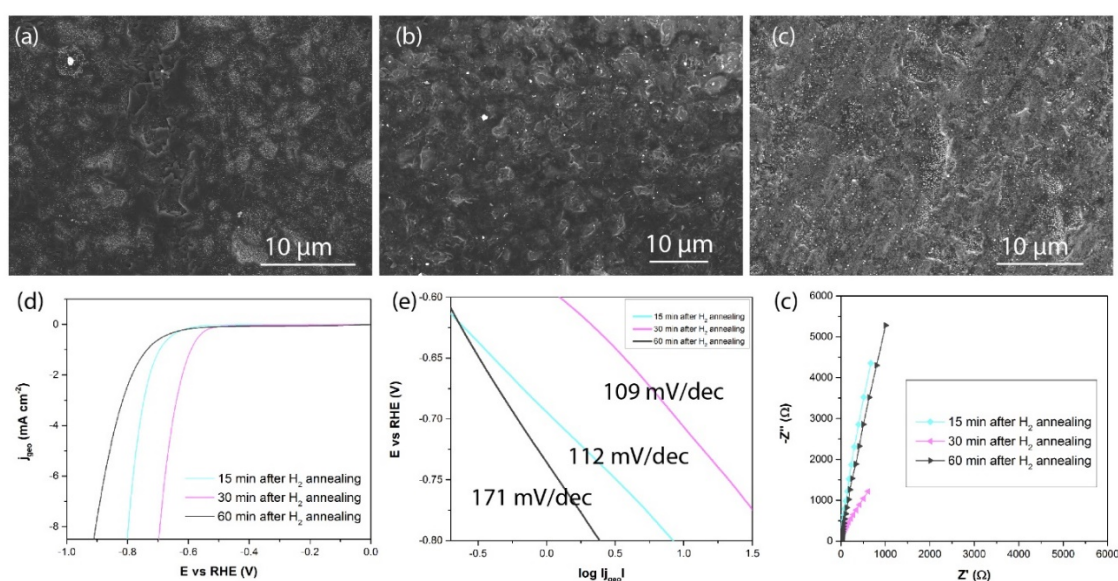


Figure 5.7 (a-c) SEM images of the GaS/Ga₂S₃ grown on glassy carbon substrates with 15, 30, and 60 min growth times after the post annealing process, respectively. (d) Cathodic polarization curves at a scan rate of 1 mV/s and their corresponding Tafel plots as shown in (e). (f) Electrochemical impedance spectroscopy (EIS) of post annealing processed GaS/Ga₂S₃ films on glassy carbon substrates.

Further investigations on the CVD grown GaS/Ga₂S₃ films produced with different growth times (15, 30, and 60 minutes) are carried out using SEM with EDX, Raman, and AFM. All the samples are grown on the silicon substrates. The EDX mappings suggest that Ga and S are homogeneously distributed over the surface on both silicon and glassy carbon substrate (see Figure B 4 in Appendix C supporting information). Figure 5.8 (a-c)

shows the morphology of the CVD grown GaS/Ga₂S₃ with 15, 30, and 60 min growth time. All the samples contain both flakes and white particles. These white particles are highlighted using the ImageJ software, as presented in Figure 5.8 (d-f). The relation between particle coverage and growth time is plotted in Figure 5.8 (g). The coverage of white particles is proportional to the growth time. The particle coverage increases from 0.02%, 0.85%, and eventually to 1.73% for 15, 30, and 60 min growth time, respectively. Furthermore, these white particles and flakes are characterised by EDX and the spectra are shown in Figure 5.8 (i and j). The flakes have about 52.4 wt% of Ga and 47.6 wt% of S, indicating the deposition of the Ga₂S₃ materials. The EDX spectrum of white particle results about 95.6 wt% of Ga and 4.4 wt% of S which is correspond to the pure gallium metal.

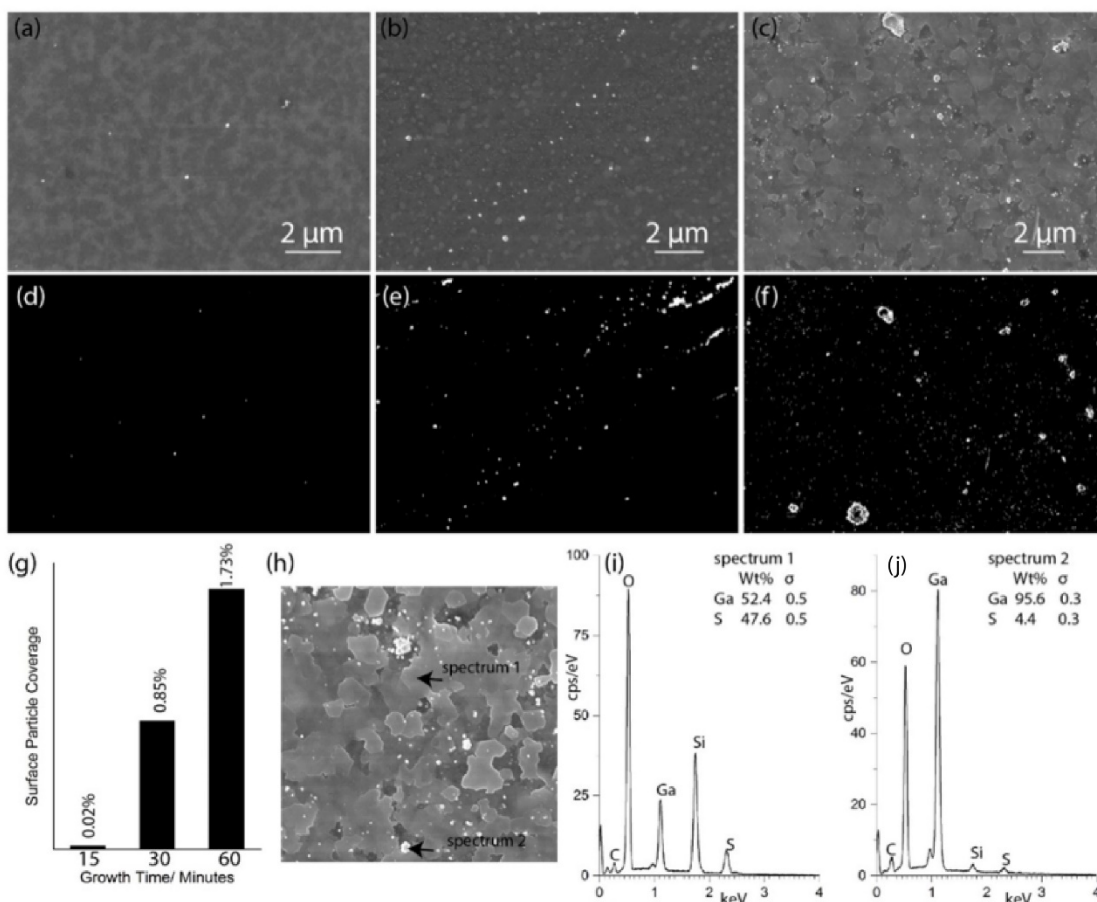


Figure 5.8 SEM images (a-c) show the synthesised GaS/Ga₂S₃ on silicon substrates with 15, 30, and 60 minutes growth time, respectively. Binary threshold SEM images (d-f) of the corresponding surface nanoparticles which are labelled in white colour. Plot (g) represents the growth time against surface nanoparticle coverage for the corresponding 15, 30, and 60 minutes CVD grown samples. Two EDX spectra (i and j) represents the flake and particle form the 30 min sample. The SEM image (h) shows the 30 min sample and indicates the positions of the EDX spectra are recorded from.

Figure 5.9 (a) shows the Raman spectra of the 15, 30, and 60 minutes CVD grown GaS/Ga₂S₃ samples on silicon substrates. The three CVD grown GaS/Ga₂S₃ on SiO₂/Si substrate reveals the characteristic features of GaS, such as the A_{1g}¹ (185 cm⁻¹), E_{2g}¹ (288 cm⁻¹), and A_{2g}¹ (357 cm⁻¹) peaks. The Raman spectra of 15 min and 30 min samples

contain the Ga_2S_3 characteristic peak around 230 cm^{-1} . AFM images show the measured GaS/ Ga_2S_3 thin films in Figure 5.9 (b-d). The thickness of the as-grown films is proportional to the growth time. The 15 minute grown film has a thickness of about 4.5 nm, the 30 minute grown film has a thickness of about 9 nm, and the 60 minutes grown film has a thickness of about 30 nm, the corresponding step height profiles are presented in Figure 5.9 (e-g).

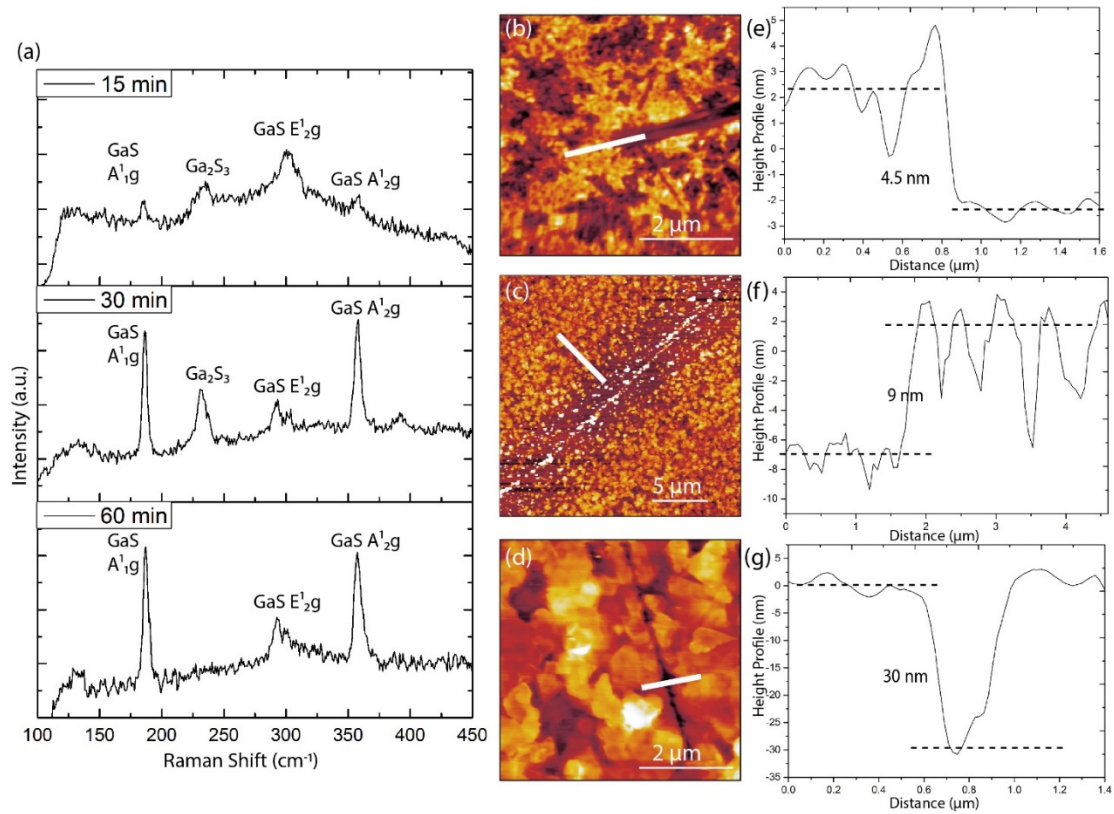


Figure 5.9 (a) Raman spectra of GaS/ Ga_2S_3 grown on silicon substrate for 15, 30, and 60 min growth times, respectively. The step height profiles (e-g) of 15, 30, and 60 min samples corresponding to the AFM images, and they are measured along the white lines in (b-d).

The CVD grown GaS/Ga₂S₃ continuous films are further investigated using transmission electron microscopy (TEM) to examine their lattice spacing, as shown in Figure 5.10 (a-c). In Figure 5.10 (b), the contrast difference suggests the sample contain multilayers and they are stacked together. The Figure 5.10 (c) reveals the triangular shape contrast difference in the 60 min grown sample. Figure 5.10 (d-f) represent the line contrast intensity profiles from the labelled yellow boxes in Figure 5.10 (a-c). The measured lattice spacing for the 15 and 60 min samples are the same and they are around 0.31 nm.^{43,35} The measured lattice spacing for the 30 min sample is about 0.24 nm.³⁵

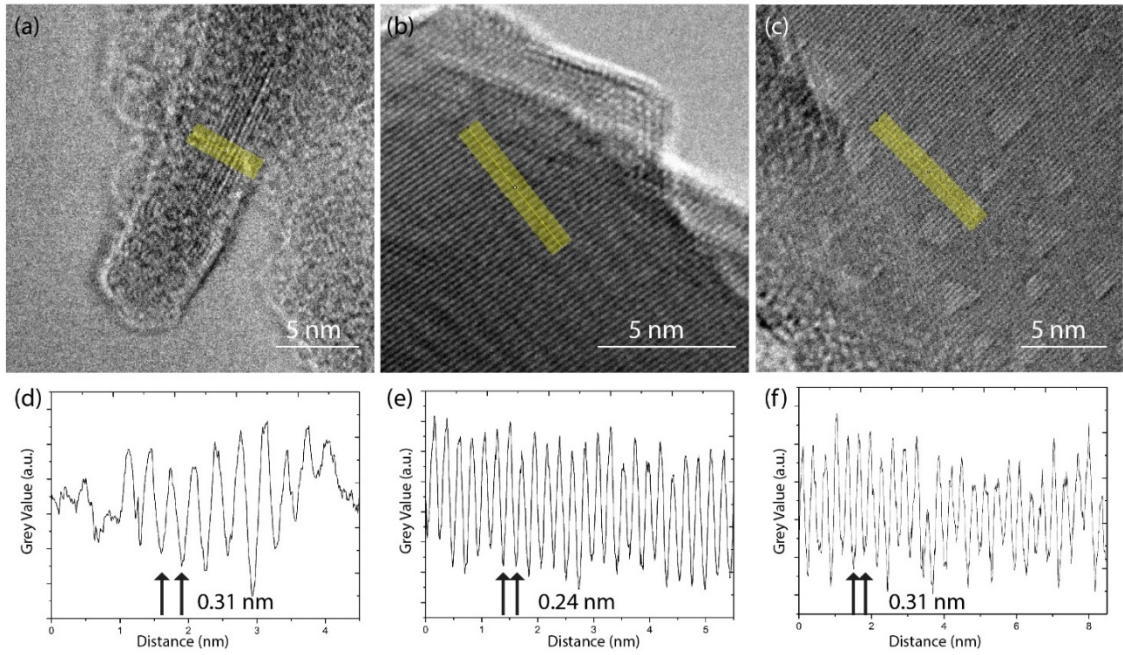


Figure 5.10 TEM images of the GaS/Ga₂S₃ samples with: 15 minutes growth time (a), 30 minutes growth time (b), and 60 minutes growth time (c). The corresponding line contrast intensity profiles are measured along the yellow boxes and presented in plots (d-f), respectively.

5.3 Conclusion

In conclusion, I have systematically studied the growth of GaS/Ga₂S₃ thin films using an ambient pressure chemical vapor deposition (CVD) method. Growth parameters, such as growth time, temperature, and substrate distance are investigated. The optimized growth condition can provide continuous GaS/Ga₂S₃ thin film with thickness between 4.5 and 30 nm. These GaS/Ga₂S₃ flakes are well crystallised with triangle and hexagon shapes. Subsequently the as-grown GaS/Ga₂S₃ thin films with 15, 30, and 60 minutes growth time are tested as catalysts for the hydrogen evolution reaction (HER). Among these samples, the 30 min CVD grown sample performs the best and it has calculated 126 mV/dec Tafel slop and 5.50 $\mu\text{A}/\text{cm}^2$. After a post annealing process, the catalytic activity of all three samples are improved. The 30 min sample then exhibits a 109 mV/dec Tafel plot and 3.07 $\mu\text{A}/\text{cm}^2$. This work paves the way for the future CVD growth of pure GaS on silicon substrate. It not only provides important insights for the CVD growth of GaS/Ga₂S₃ but also shows the HER catalytic activity of the CVD grown GaS/Ga₂S₃ thin film.

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Chapter 6

Chemical Vapor Deposition Growth of Two-Dimensional Monolayer Gallium Sulfide Crystals Using Hydrogen Reduction of Ga₂S₃

In previous chapter, I establish a CVD method to grow GaS/Ga₂S₃ thin film. In this chapter, the CVD method is further improved, and the formation of monolayer GaS film is produced. This is achieved by increasing the flow rate of hydrogen carrier gas and placing the substrate horizontally in the reaction tube. The as-grown GaS film is merged by individual domains and it has 0.7 cm diagonal size. In addition, the synthesised GaS materials exhibit triangular domains and multilayer flakes with thicknesses of 1 and 15 nm, respectively. A series of characterisation methods is applied to examine the as-grown GaS 2D material. These results provide a novel approach to grow high quality GaS 2D material, and this work contributes to the understanding of its growth mechanism.

6.1 Introduction

Transition metal dichalcogenides (TMDs) have attracted great interest because of their unique properties and promising applications.^{1–14} The GaS is from layered group III metal chalcogenides and the monolayer GaS has an indirect bandgap about 2.59 eV, which lies between the semimetal graphene and insulating h-BN.^{15–20} The distinguished band structure make it a promising material in electronic and optoelectronic applications.^{21–23} The chemical vapor deposition (CVD) method is one of the most promising methods to produce large-area and high-quality 2D materials, as well as for the synthesis of GaS material.^{25–31} In Chapter 2, the other production methods of GaS are reviewed.^{18,19,24,32–34}

The controllable production of GaS monolayer film still remains a challenge. And its growth mechanism is not clear. In this work, I investigate the growth mechanism and improve the feasible CVD growth of 2D GaS material. The CVD growth process includes the evaporation and reduction of the Ga_2S_3 precursor and the use of hydrogen carrier gas. Continuous monolayer GaS film is achieved by controlling the growth temperature, substrate position, and the flow rate of carrier gas. The CVD as-grown GaS samples are characterised using optical microscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), photoluminescence (PL) and Raman spectrometers, and transmission electron microscopy (TEM).

6.2 Results and Discussion

Figure 6.1 (a) shows a schematic illustration of the CVD setup which is used to grow GaS 2D material on SiO_2/Si substrates. The whole chemical reaction takes place inside a 1-inch diameter quartz tube under ambient pressure. 10 mg of Ga_2S_3 precursor is placed at the centre of the growth furnace. The 2 by 2 cm substrate is horizontally placed downstream with a distance of 8.5 cm away from the precursor. Figure 6.1 (b) represents the temperature profile against time employed in this CVD process. The whole system is flushed with 500 sccm argon gas for 30 minutes. In stage I, the temperature of the precursor increases to 800 °C with a mixture of 70 sccm of hydrogen gas and 150 sccm of argon gas. In stage II, only 70 sccm hydrogen gas is flow through the furnace for a certain period of time. After that, a fast cooling process is applied with 150 sccm argon gas flow. By optimizing the reaction parameters, it is possible to produce GaS domains and monolayer continuous GaS film based on two primary modifications in stage II. The first modification involves placing the substrate horizontally, and it creates a precursor concentration gradient and an inhomogeneity of the precursor feed-stock on the substrate surface. The other modification involves increasing the hydrogen gas flow rate during the growth stage, and it tunes the Ga_2S_3 precursor decomposition. In Figure 6.1 (c), the

U-shaped pattern is caused by the sharp precursor concentration gradient and a change in the kinetic growth dynamics at substrate edge. This pattern is also observed in the CVD growth of other 2D TMD growth such as WS₂ and MoS₂.^{25,26} Figure 6.1 (d) and (e) show two optical images of selective regions in Figure 6.1 (c). They indicate stacked GaS flakes and two individual triangular GaS domains with the size of 4 μm .

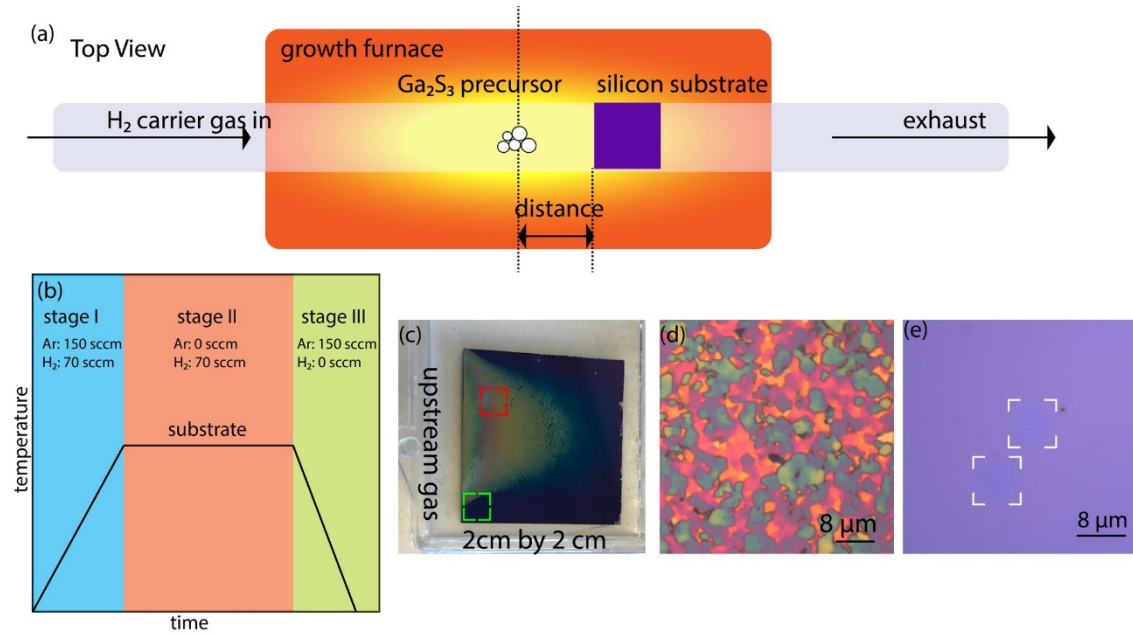


Figure 6.1 Atmospheric pressure CVD synthesis of large-area gallium sulfide (GaS) on SiO₂/Si substrates. (a) Top view schematic of the CVD setup. Ga₂S₃ precursor is placed at the middle of the growth furnace. (b) Temperature against time profile of the substrate with three stages. (c) Photo shows the U-shaped pattern on the 2 by 2 cm SiO₂/Si substrate. The contrast different results from the various thicknesses of the grown GaS materials. Two optical images labelled in (c), (d) shows the stacked GaS flakes and (e) shows two individual triangular GaS domains with a size around 4 μm .

To study the U-shaped morphology of the as-grown GaS 2D material, SEM is applied to examine the whole silicon substrate. Several distinct morphologies are observed on the surface of the substrate. Figure 6.2 (a) presents a schematic of the U-shaped pattern and 6 selected regions with labelled numbers indicating where the SEM images are taken.

These 6 regions clearly reveal the dependence of the shape change due to the Ga_2S_3 precursor vapor concentration. Figure 6.2 with position 1 shows the centre and upstream region where multilayer GaS flakes are formed. Toward the edge of the substrate at positions 2, 3, and 4, isolated triangular GaS domains with the sizes from 8 to 2 μm are observed. In addition, at position 4-1, the transition between individual domains and the continuous monolayer GaS film is found. Half of the region shows continuous film and the other half shows the GaS domains. The monolayer GaS film is merged by individual domains and their sizes are between 2 and 6 μm , as shown in SEM images 4-2, and 4-3, respectively. Further downstream on the substrate, there is a dramatically change in the size of GaS domains. At position 5 and 6, the GaS domain size is reduced to less than 2 μm and rounded nucleation sites are observed. Eventually the size is too small to distinguish the domain shape at the end of substrate. It can be seen that with the increase in the distance between precursor and the growth location, the GaS domains experience a transformation in terms of size and shape.

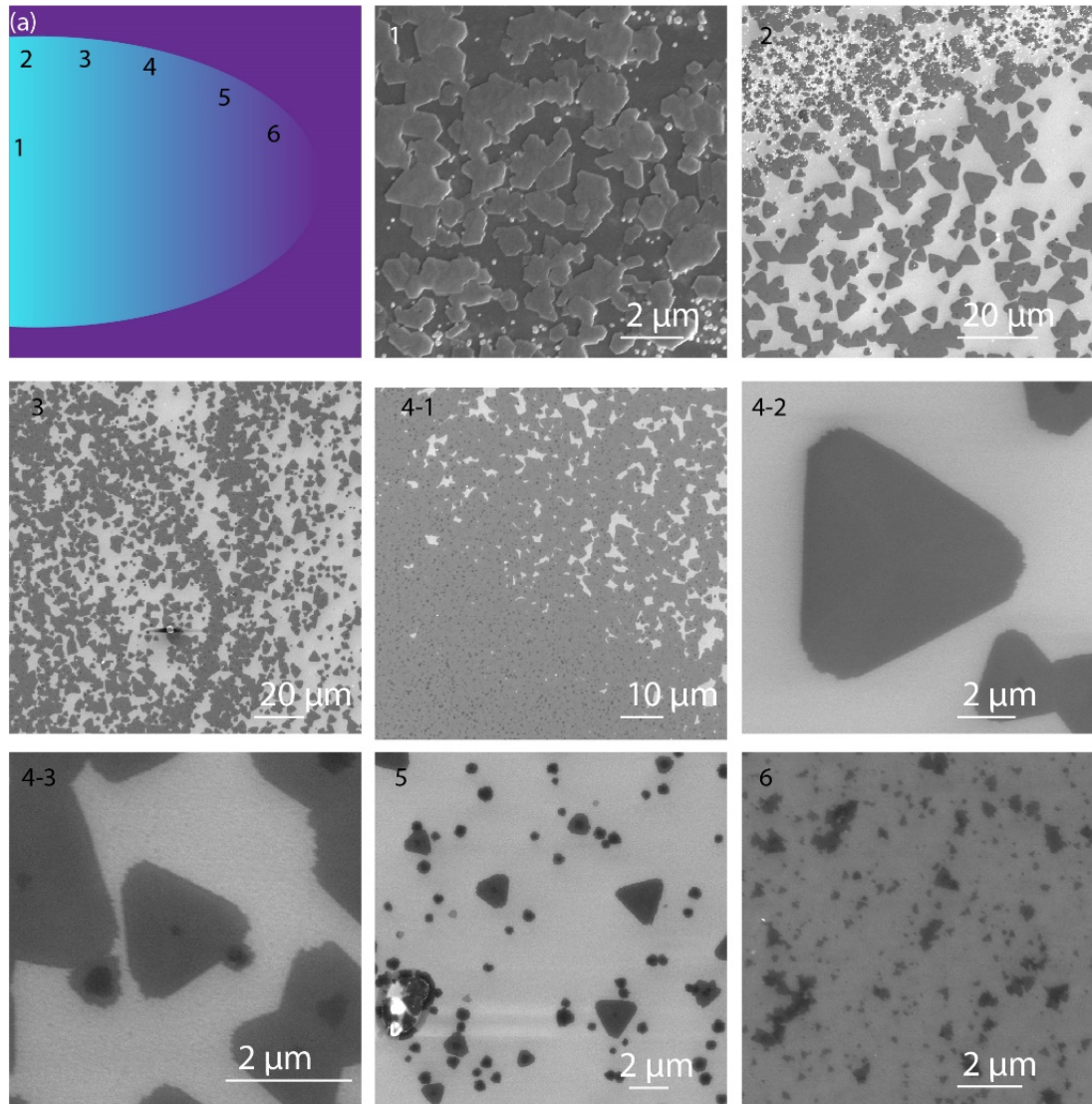


Figure 6.2 The SEM morphology study of the U-shaped as-grown GaS on silicon substrate. (a) Schematic of the U-shaped region with number labels. Each number label represents the selected regions in (a) and the corresponding SEM images are shown.

The continuous region of GaS is further investigated because achieving continuous film is vital for its future applications. Figure 6.3 (a) shows the large scale of the continuous GaS region on the silicon substrate, and the left corner has partially covered triangular GaS domains. The complete film coverage of GaS is presented in Figure 6.3 (b) with a size of 700 μm . It is observed that the large white particles are deposited first and then gradually enclosed regions on the substrate. Next, small triangular domains are nucleated

preferentially at certain locations, such as edges, scratches, dust particles, and rough surfaces.³⁷ More SEM images are shown in the Appendix D. Then, from the initial nucleation sites, triangular GaS domains continue to grow epitaxial and the boundaries are formed when domains meet. The domains eventually are coalesced and merged into a monolayer GaS film with sufficient precursor supply and sufficient density of nucleation sites. Figure 6.3 (c) represents the further zoomed-in SEM image of GaS film, the small dark regions indicate the second layer nucleation sites.

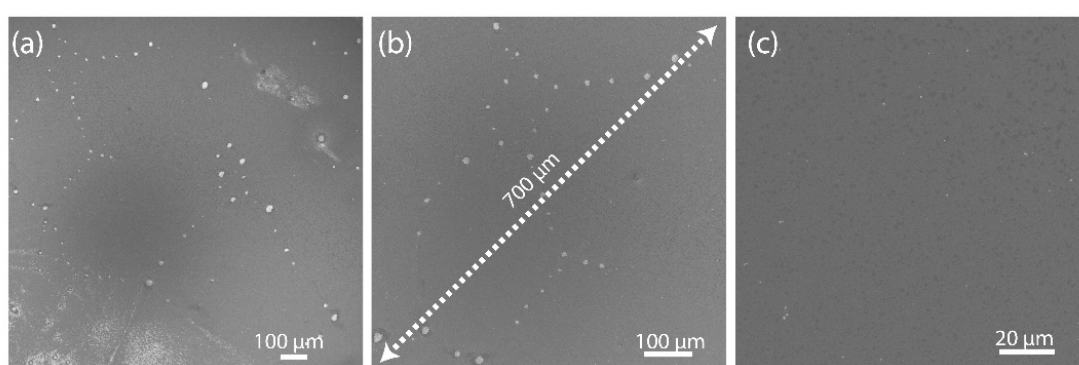


Figure 6.3 Surface morphology of monolayer GaS film. (a) SEM image of large area monolayer GaS film. (b) SEM image of selected uniform region of monolayer GaS film. (c) SEM image of monolayer GaS film with second layer nucleation sites.

EDX spectroscopy is used to evaluate the chemical composition of the as-grown GaS 2D material. The typical EDX spot spectra of as-grown GaS flakes and monolayer regions are shown in Figure 6. 4 (a) and (b), respectively. The corresponding insets are the SEM images indicating where the EDX spectrum are taken from. The intensity of Ga and S from GaS flakes is significantly stronger than the monolayer GaS due to their difference in thickness. The ratios of GaS flakes have the value of 1.2, while the ratios of GaS monolayer region has the value between 1.9 and 1.4. Because of the ultrathin property of the monolayer GaS film, it is difficult to detect subtle variations when using EDX spectroscopy. The atomic percentages and the ratios of the as-grown GaS material are summarised in Table 1 C in Appendix D. In addition, the shape of the CVD synthesised

GaS domains is quite consistent and they all exhibit truncated triangular shapes. In previously work, the hexagonal and triangular flakes are observed and they all have sharp edges. The hexagonal shaped flake has 3 Ga and S terminated edges, and the triangular flake only has either S or Ga terminated edges.^{33,34} The exact ratio between Ga and S could influence the energetic stability of Ga and S terminated edges. Moreover, the single source precursor Ga_2S_3 is reduced by a higher amount of hydrogen gas, the vaporised free S and Ga sources may be in balance. These explain why the resulted GaS domains are truncated. Similar results are reported for the CVD synthesis of WS_2 .²⁶

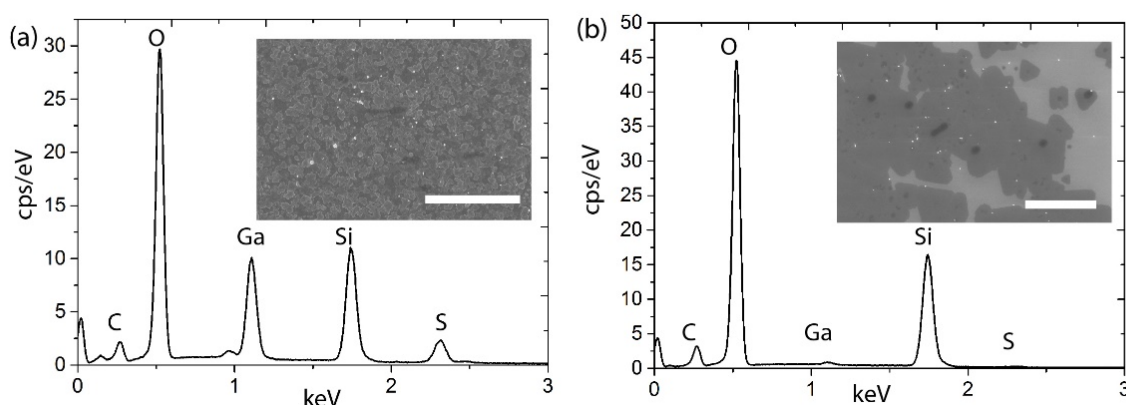


Figure 6.4 Typical EDX spectra of GaS flakes (a) and GaS monolayer regions (b), respectively. Both inset SEM images show where the EDX spectra are obtained and the scale bar is 8 μm .

The roughness and thickness of the GaS continuous film, flakes and domains are characterised by AFM. Figure 6.5 (a) is a 20 by 20 μm AFM scan of monolayer GaS region. This scanned region is densely covered by triangular GaS domains. Figure 6.5 (b) shows the AFM scan of the selected region in Figure 6.5 (a), the GaS domains are about to coalesce into a continuous film. The merged grain boundaries and the second layer nuclei are observed. The Figure 6.5 (c) is the further zoomed-in AFM scan from the selected area in Figure 6.5 (b) and the 0.19 nm RMS is measured from the indicated green box. Figure 6.5 (d) represents the height profile of the as-grown GaS continuous film,

and it is measured along the black line in Figure 6.5 (c). The 1 nm thickness of the as-grown GaS film is in agreement with monolayer GaS flakes on silicon substrate.¹⁹ The height profile of GaS flakes is also measured along the black line indicated in Figure 6.5 (e). Two thickness steps are measured such as 25 nm and 10 nm, as shown in Figure 6.5 (f). Finally, two individual triangular GaS domains have a step height of about 0.6 nm, although the measured RMS of silicon substrate is 0.48 nm, as shown in Figure 6. 5 (g) and (h), respectively. In addition, the 0.16 nm RMS on the triangular GaS domain is closely matched with the monolayer GaS film.

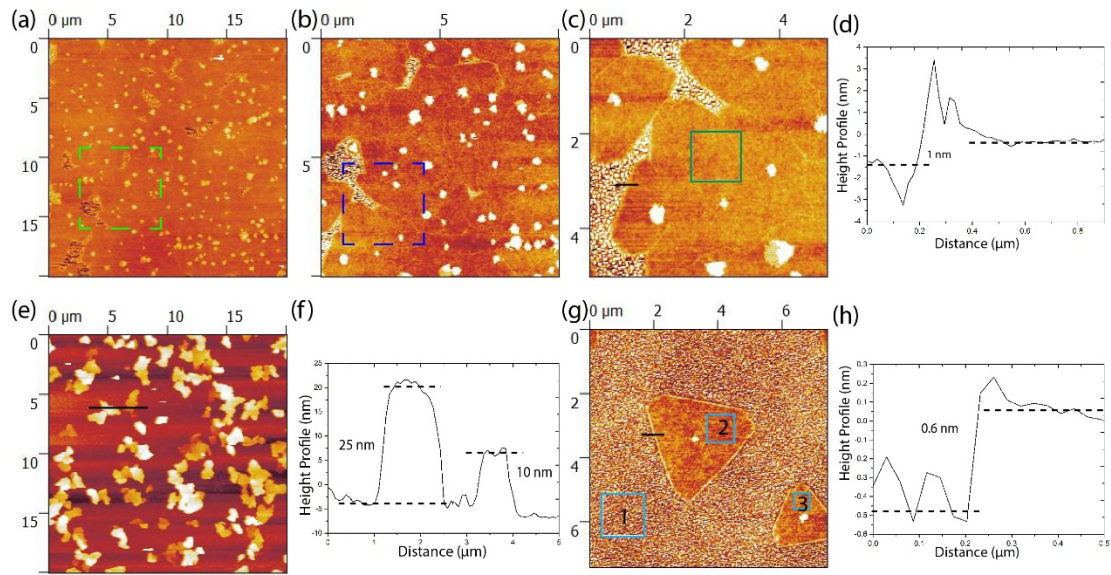


Figure 6.5 (a-c) Series of AFM images about monolayer continuous GaS film. The zoomed-in regions are labelled in green and blue dashed boxes. The highlighted green colour region has a RMS of 0.19 nm. (d) The height profile of the continuous GaS film is measured across the black line in (d). (e) AFM image of as-grown GaS flakes. (f) The corresponding height profile of selected GaS flakes is measured across the black line in (e). (g) AFM images of two GaS domains. Box 1 has the RMS of 0.48 nm about the silicon substrate, the boxes 2 and 3 have the same RMS of 0.16 nm about the GaS domains. (h) The corresponding height profile of GaS domain is measured across the black line in (g).

The as-grown GaS flakes and monolayer domains are further investigated by Raman and PL spectroscopy with a 532 nm laser source. Bulk GaS has three first-order phonon modes in the Raman spectrum. They are two out-of-plane A^1_{1g} and A^2_{1g} modes, and one in-plane E^1_{2g} mode. Spot Raman spectra are taken from both the GaS flakes and domains, as shown in Figure 6.6 (a) and (b), respectively. The as-grown GaS flakes show all three Raman modes where A^1_{1g} is centred at 188 cm^{-1} , A^2_{1g} is centred at 360 cm^{-1} , and E^1_{2g} is centred at 294 cm^{-1} . In addition, the full width at half-maxima (fwhm) of the A^1_{1g} and A^2_{1g} are 5 and 6 cm^{-1} , respectively. The Raman spectrum of as-grown GaS domain only exhibits the A^1_{1g} (179 cm^{-1}) and E^1_{2g} (297 cm^{-1}) modes. The A^2_{1g} peak is not observed in the spectrum. The 303 cm^{-1} Raman peak corresponds to the silicon substrate in both cases. It results in a broad peak in the Raman spectrum of GaS domain. Since the thickness decreases from the flake to the monolayer domains, the frequency of the E^1_{2g} mode increases slightly and the A^1_{1g} mode decreases. Also, the overall intensity is observed in Figure 6.6 (b) decreases as well. These results are in agreement with previously reports.^{17,19,22,37} The PL measurement of the GaS flakes shows a broad peak between 550 and 800 nm with a centred position at 622 nm in Figure 6.6 (c). This peak is associated with the defects in GaS flakes and the deep trap recombination states.³⁸ However, the monolayer GaS domain does not have this peak, as shown in Figure 6.6 (d).

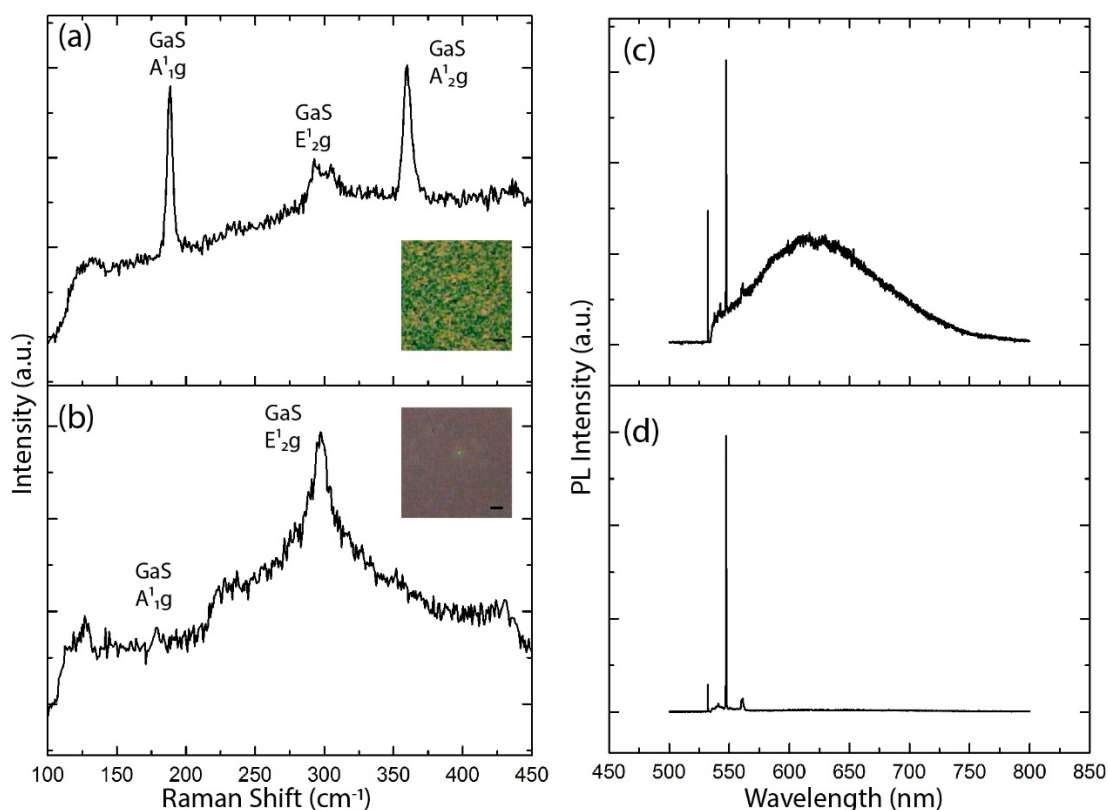


Figure 6.6 Raman spectra and PL measurements of CVD grown GaS flakes and GaS domains on SiO₂/Si substrate. (a) Raman spectrum and (c) PL emission spectrum of the multilayer stacked GaS flake region. (b) Raman spectrum and (d) PL emission spectrum of a monolayer GaS domain. Both insets are the corresponding optical images and the scale bars are 5 μm .

TEM is used to further characterise the layered structure of the as-grown GaS materials. They are transferred onto TEM grids using the wet chemical transfer method. Figure 6.7 (a) shows a low magnification TEM image of the GaS flakes on lacey carbon grid. Figure 6.7 (b) shows a high magnification TEM (HRTEM) image of GaS flakes. It reveals the crystalline nature of the CVD grown GaS flakes. The line intensity profile from the yellow box in Figure 6.7 (b) is plotted in Figure 6.7 (c). The measured d-spacing between the neighbouring (100) planes of the GaS is about 0.31 nm, and it is close to the value for β -GaS ($a=3.587 \text{ \AA}$).^{14,33} The inset in (b) shows the corresponding fast Fourier-transform (FFT) image indicating the GaS sheet is orientated along the [0001] zone axis and the

hexagonal structure is confirmed.³⁴ A further zoomed-in HRTEM image is shown in Figure 6.7 (d) from the selected area in Figure 6.7 (b). The schematic diagram of top view and side view GaS crystals are presented in Figure 6.7 (e). These characterisation results help us understand the as-grown GaS material and compare the quality with exfoliated GaS flakes.¹⁴

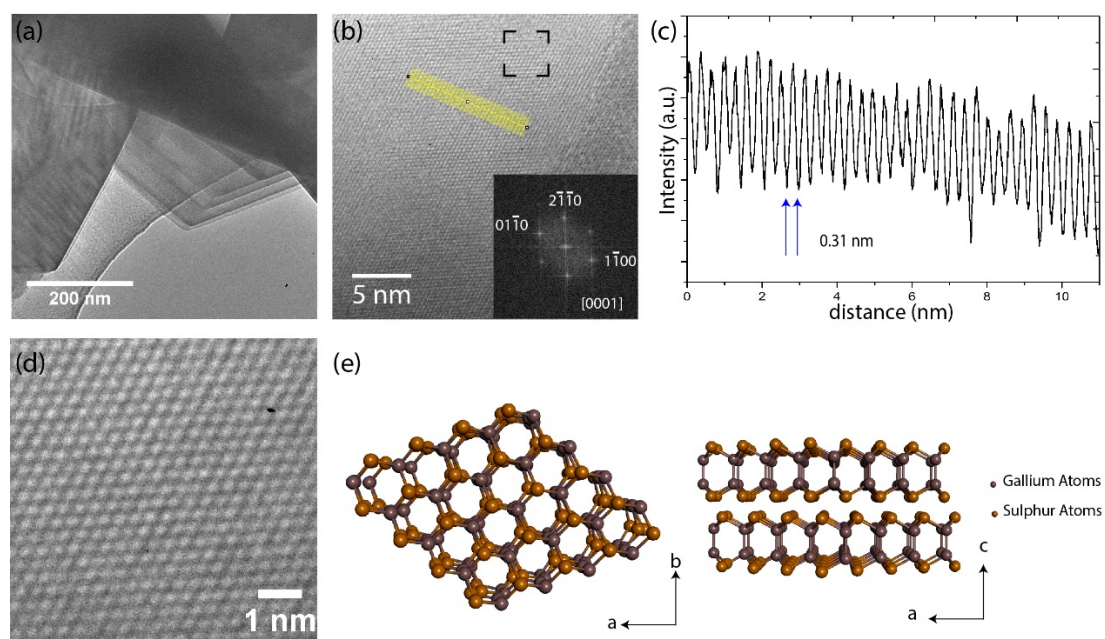


Figure 6.7 TEM images of GaS multilayer flakes. (a) Low magnification TEM image of GaS flakes with the layered structures. (b) HRTEM image of GaS monolayer region at the zone axis of $[0001]$, indicating the single crystalline nature. Inset is the corresponding FFT image. (c) The corresponding line intensity profile is taken from the yellow marked region in (b). It indicates the (100) planes of GaS are separated by 0.31 nm. (d) Zoomed-in HRTEM image is from the selected area in (b). (e) Schematic diagrams show the top and side view of GaS crystal structure.

6.3 Conclusion

In conclusion, I report a simple approach to grow both monolayer and multilayer high-quality GaS film on SiO₂/Si substrate. The CVD growth method takes place at atmospheric pressure with hydrogen carrier gas and single source non-toxicity precursor. Two modifications are made based on previously established CVD growth method. It creates a sharp precursor concentration gradient and a change in the kinetic growth dynamics at substrate edges. The as-grown GaS film is characterised by series of characterisation methods. These results show how sensitive the growth of GaS is to minor variations in the CVD parameters and the drastic improvements can be easily achieved by simple optimizations. This approach has potential in scale-up and meets safety requirements for commercial implementation, and eventually towards the controllable growth of 2D GaS materials.

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Chapter 7

Conclusions and Outlook

7.1 Conclusions

The subject of this DPhil thesis involves making contributions to the synthesis of novel 2D materials and understanding of their growth mechanism. The novel 2D materials hexagonal boron nitride (h-BN) and gallium sulfide (GaS) are grown through a chemical vapor deposition (CVD) method and followed by characterisation to investigate their morphology and crystallinity.

The insulating h-BN 2D material has one atom thickness and its structure is analogous to graphene, showing potential applications in electronics, optoelectronics and flexible devices. To meet the forthcoming demand, the synthesis of large-area h-BN films with effective, low cost, and environment friendly method is required. The CVD method has not only shown the potential to meet the goals but also provides the ability for delicate control of reaction parameters. I first established and developed growth strategies capable of producing multilayer h-BN film. The ammonia borane (AB) is used as precursor with independent temperature control. The gaseous AB precursor is then delivered to main reaction chamber by a mixture of hydrogen and argon carrier gas. Eventually, multilayer h-BN film is formed on the copper substrates under ambient pressure condition. Since the designed CVD system provides a platform to explore the impact of precursors, the CVD synthesised h-BN films from AB precursor are compared to those produced using dimeric diborazane (DAB) and trimeric triborazane (TAB) precursors. Although all three precursors lead to continuous h-BN film growth, the DAB requires a shorter period of time, and both the DAB and TAB precursors result in more volatile growth in a certain

period of growth time. All the multilayer h-BN films from various precursors are characterised by SEM, AFM, Raman, and TEM techniques.

The second part of the thesis explores gallium sulfide materials. The GaS/Ga₂S₃ thin film is synthesised on SiO₂/Si and glassy carbon substrates with between 4.5 and 30 nm thickness using a CVD method in ambient pressure condition. In order to reduce the spatial gradient from the gaseous precursor, the substrates are placed vertically. After 15 to 30 minutes growth, the GaS/Ga₂S₃ thin film is formed and merged by flakes. The morphologies of the flakes show distinguished triangular and hexagonal shapes. A systematic study is carried out to investigate a range of synthesis parameters about the GaS/Ga₂S₃ thin film, such as the evaporation temperature of the Ga₂S₃ precursor, growth time, and the distance between the substrate and precursor. Subsequently, the GaS/Ga₂S₃ thin film are used as catalysts for the hydrogen evolution reaction (HER). The 30 minutes CVD grown sample exhibits a 126 mV/dec Tafel plot with 5.50 A/cm². Moreover, there is almost no change in the cathodic current after a 1000 cycle durability test.

In addition, the monolayer GaS film is attracted for potential applications due to its indirect band gap at around 2.6 eV. This incentive is the driving force for the further investigation about GaS growth *i.e.* optimise the CVD method to grow monolayer, large-area, and continuous film. It is achieved by two primary modifications of the previously established CVD procedure. The first modification is placing the substrate horizontally and it creates a precursor concentration gradient and inhomogeneity of the precursor feed-stock on the substrate surface. The other modification involves increasing the hydrogen gas rate during the growth stage and it tunes the Ga₂S₃ precursor decomposition. Finally, GaS film is synthesised coalesced by monolayer domains.

In conclusion, this thesis covers three sections: (1) in Chapter 4, I establish versatile APCVD synthesis methods to produce multilayer h-BN film on copper substrate and have

gained insights into the growth mechanism by comparing the different precursors; (2) in Chapter 5, I develop versatile APCVD method to synthesis thin film GaS/Ga₂S₃ materials on SiO₂/Si and glassy carbon substrates, and explore its application in hydrogen evaluation reaction (HER) as catalyst; and (3) in Chapter 6, the APCVD method synthesis of monolayer GaS film is achieved, and insights of the growth mechanism are gained.

7.2 Outlook

For the first h-BN project, the future works could involve adding low pressure capability to the existing CVD system and replacing the heating belt with an advanced heating system. In addition, *in-situ* measurements would allow the study of h-BN real-time growth mechanism during the APCVD process.

The procedure established for the CVD synthesis of GaS materials are transferable to the other layered group III metal chalcogenides materials. And the next step is to optimise the current growth recipe and eventually it may achieve a controllable growth. In addition, photoluminescence study should be carried out on the CVD grown monolayer GaS film. Electronic devices such as photodetectors, FETs and LEDs based on CVD grown monolayer GaS have not been fabricated to date, and it would be an interesting direction for future work.

Appendix A Supporting Information for Chapter 3

Methodology

The Reynolds number of the CVD method grown h-BN on copper substrate is calculated.

The equation is used as follow:

$$Re = \rho \cdot V \cdot D / \mu$$

where Re is the Reynolds Number (non-dimensional), ρ is the density (kg/m^3) of the mixed gas (25% H_2 and 75 % Ar), V is mean velocity (m/s), D is the tube diameter (m), and μ is the absolute viscosity of the fluid ($\text{kg/m}\cdot\text{s}$).

The constants are shown in below:

hydrogen gas density is 0.0899 kg/m^3 ,

argon gas density is 1.6610 kg/m^3 ,

hydrogen gas absolute viscosity is $0.8800 \times 10^{-5} \text{ kg/m}\cdot\text{s}$,

argon gas absolute viscosity is $2.2300 \text{ kg/m}\cdot\text{s}$,

the tube diameter is 1 inch and it is equal to $2.5400 \times 10^{-2} \text{ m}$.

Therefore, the mixture gas density is 1.2682 kg/m^3 ($0.25 \times 0.0899 + 0.75 \times 1.6610$), and

the mixture gas absolute viscosity is $1.8925 \times 10^{-5} \text{ kg/m}\cdot\text{s}$ ($0.25 \times 0.8800 + 0.75 \times 2.2300$).

During the h-BN CVD deposition stage, the carrier gas flow rate is 120 sccm. The flow rate of the carrier gas is calculated as following:

$$V = \text{gas flow rate} \times 1/\text{the cross-section area of tube} = 120 \times 1/ (0.25 \times \pi \times (2.5400)^2) = 0.2368 \text{ m/s}$$

After substituting the values to the above equation:

$$Re = \rho \cdot V \cdot D / \mu = (1.2682 \times 0.2368 \times 2.5400 \times 10^{-2}) / 1.8925 \times 10^{-5} = 403$$

The Reynolds number of the CVD grown h-BN is 403, which indicates the lamina flow in the system.

Similarly, the Reynolds number of the CVD grown mixture Ga₂S₃/GaS thin film with 30 sccm carrier gas is calculated as following:

$$V = \text{gas flow rate} \times 1 / \text{the cross-section area of tube} = 30 \times 1 / (0.25 \times \pi \times (2.5400)^2) = 0.05921 \text{ m/s}$$

$$Re = \rho \cdot V \cdot D / \mu = (1.2682 \times 0.0592 \times 2.5400 \times 10^{-2}) / 1.8925 \times 10^{-5} = 101$$

The Reynolds number of the CVD grown mixture Ga₂S₃/GaS thin film is 101, which indicates the lamina flow in the system.

Finally, the Reynolds number of the CVD grown GaS thin film with 70 sccm carrier gas is calculated as following:

$$V = \text{gas flow rate} \times 1 / \text{the cross-section area of tube} = 70 \times 1 / (0.25 \times \pi \times (2.5400)^2) = 0.1381 \text{ m/s}$$

$$Re = \rho \cdot V \cdot D / \mu = (1.2682 \times 0.1381 \times 2.5400 \times 10^{-2}) / 1.8925 \times 10^{-5} = 235$$

The Reynolds number of the CVD grown GaS thin film is 235, which indicates the lamina flow in the system.

Appendix B Supporting Information for Chapter 4

Oligomeric Aminoborane Precursors for the Chemical Vapor Deposition Growth of Few-Layer Hexagonal Boron Nitride

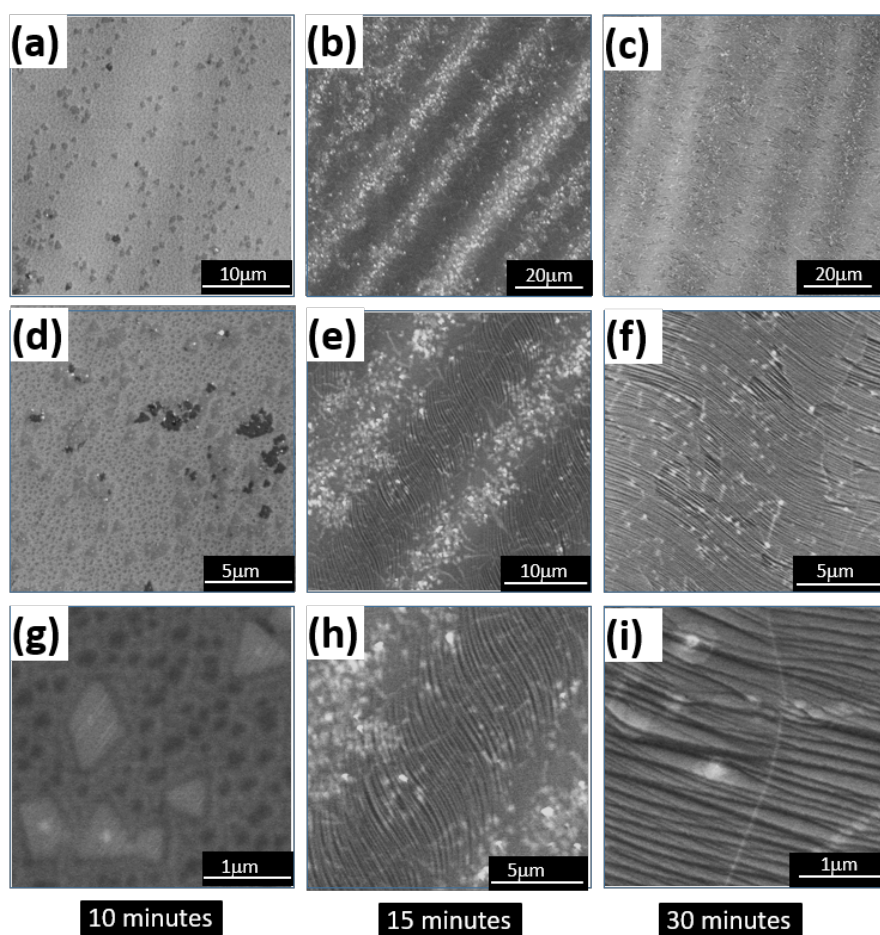


Figure B 1. SEM images of the Cu substrate surface after h-BN CVD growth with ammonia borane precursor with (a), (d), and (g) 10, (b), (e), and (h) 15, and (c), (f), and (i) 30 minute growth durations.

For the 10 minutes growth duration, the h-BN crystals are formed on the copper substrate surface as shown in Figure B 1 (d). Moreover, the Figure B 1 (g) shows the triangle shapes of the h-BN crystals on copper surface. While for the 15 and 30 minutes growth duration, continuous h-BN film is formed, as shown in Figure B 1 (e), (h), (f), and (i).

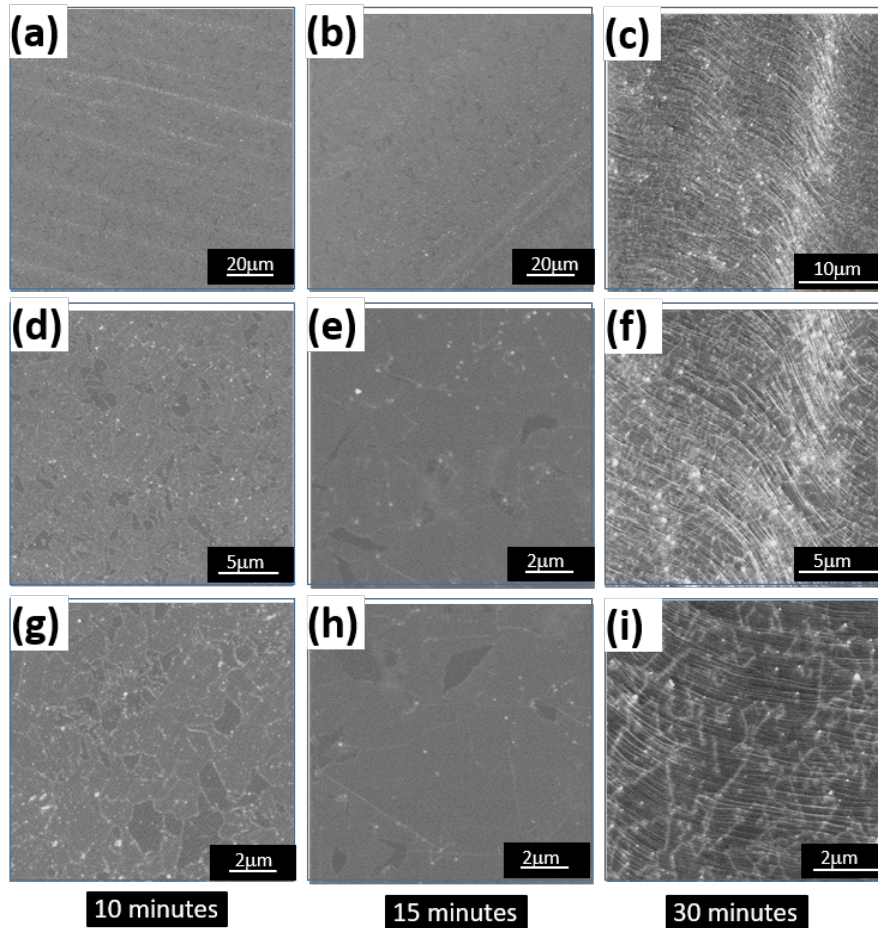


Figure B 2. SEM images of the Cu substrate surface after h-BN CVD growth with DAB precursor with (a), (d), and (g) 10, (b), (e), and (h) 15, and (c), (f), and (i) 30 minute growth durations.

Figure B 2 provides more SEM images of the DAB precursor grown h-BN continuous film on copper substrates with 10, 15, and 30 minutes growth duration. Figure B 2 (g), (h), and (i) are the zoomed in SEM images and show the white grain boundaries all over

the surface. Unlike 10 minutes ammonia borane grown h-BN, no triangle shaped h-BN domains are found.

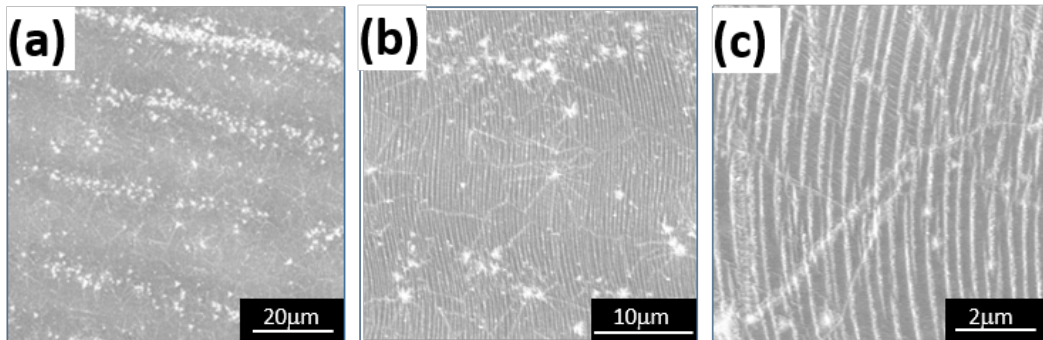


Figure B 3. SEM images of the Cu substrate surface after h-BN CVD growth with TAB precursor with 30 minutes duration.

Figure B 3 show high, medium and low magnification SEM images of the TAB precursor grown h-BN film with 30 minutes duration.

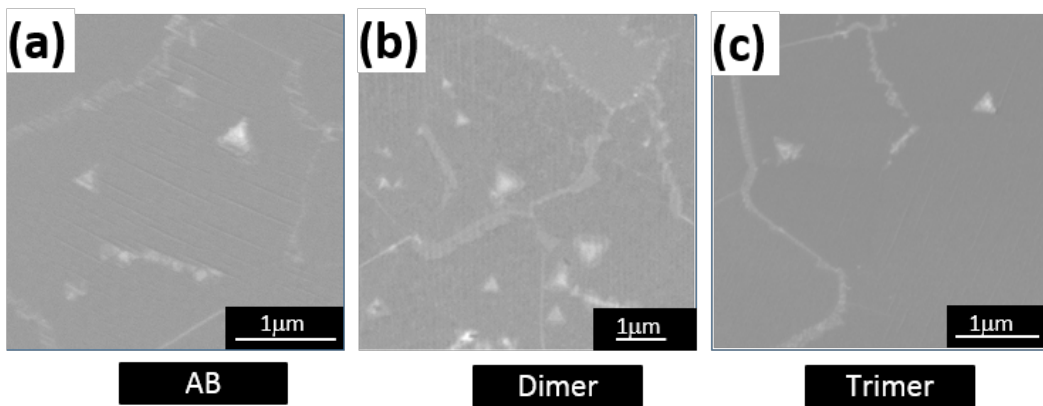


Figure B 4. SEM images of the small triangle h-BN domains after CVD growth with (a) ammonia borane, (b) DAB, and (c) TAB precursor with 30 minute durations.

Figure B 4 illustrates the small triangle domains which are observed on all the grown h-BN continuous film by the three different molecular weight precursors with 30 minutes growth duration. This suggests that the formation of h-BN follows a combination of a layer by layer growth and island growth mechanism.

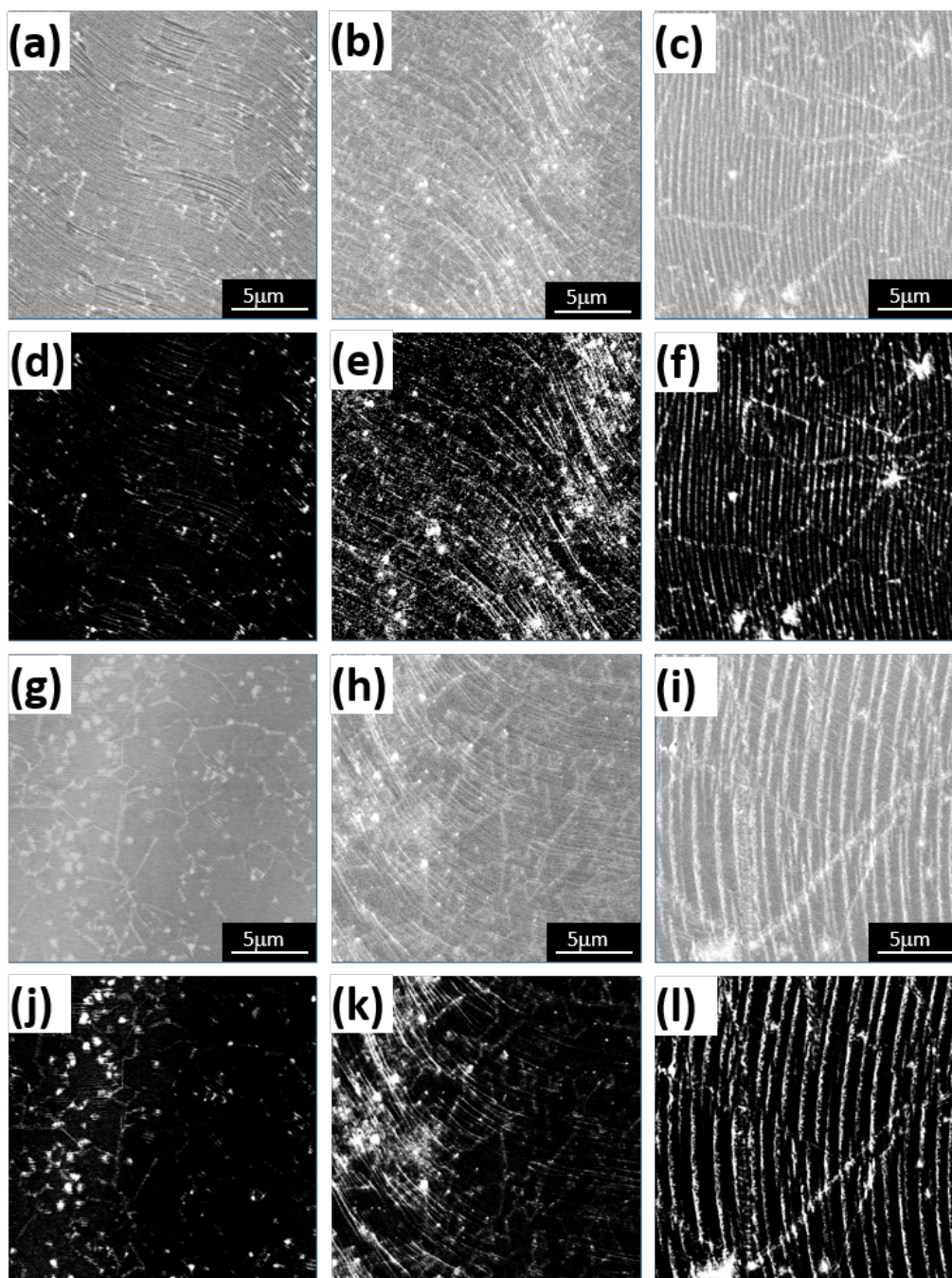


Figure B 5. SEM images of the Cu substrate surface after h-BN CVD growth with ammonia borane (a) and (g), DAB (b) and (e), and TAB (c) and (i) precursor with 30 minute growth duration. The corresponding lowered images (d), (e), (f), (j), (k), and (l) are ImageJ processed figures and used to calculate the percentage of nanoparticles as the related surface, respectively.

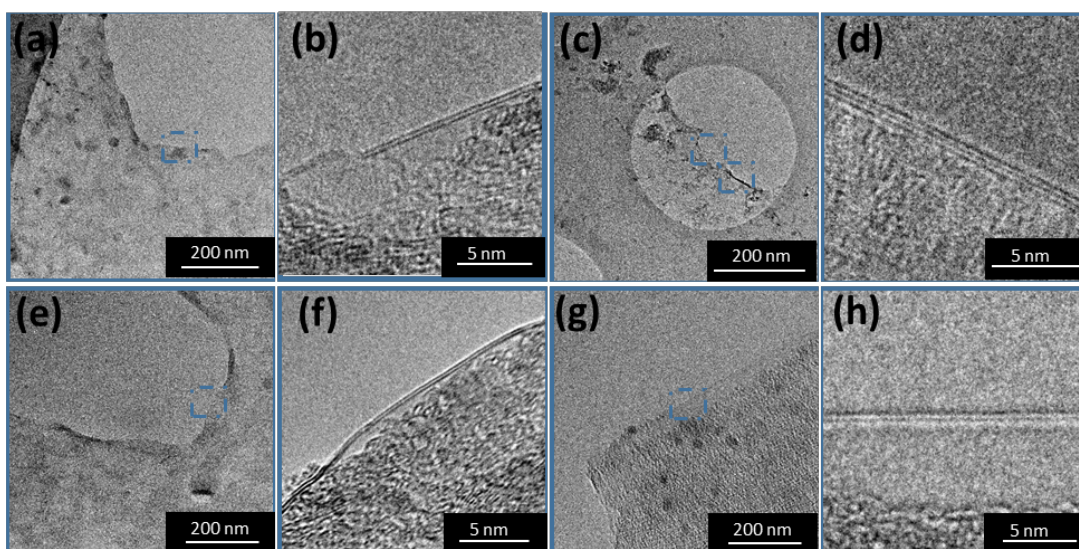


Figure B 6. TEM images show number of layers of AB precursor 30 minute grown h-BN films near their folded edges. Low-magnification TEM images (a, c, e, and g) shows the folded edges of AB precursor 30 minutes grown h-BN film and the corresponding zoomed-in images (b, d, f, and h) from the marked regions.

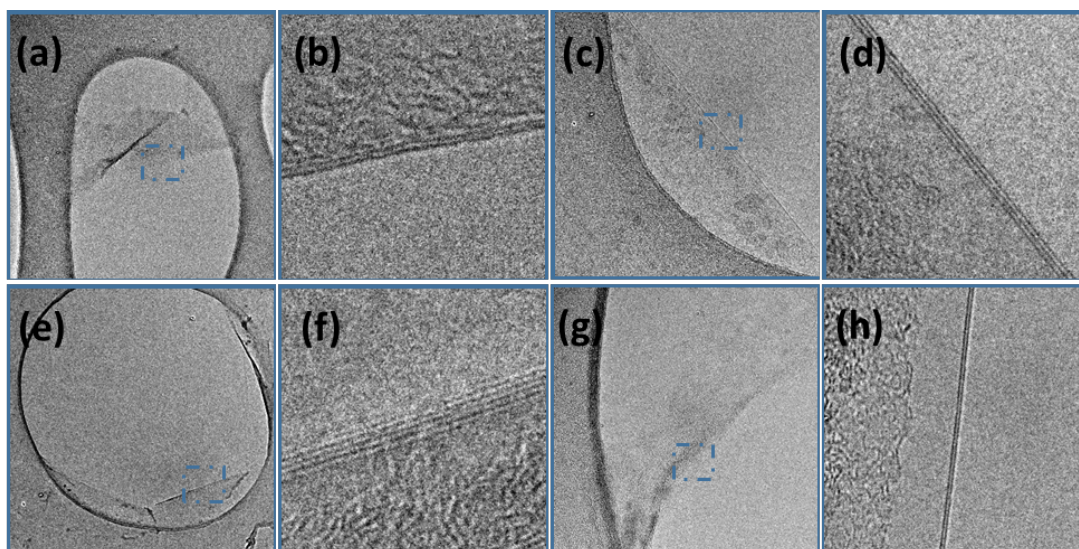


Figure B 7. TEM images show number of layers of DAB precursor 30 minute grown h-BN films near their folded edges. Low-magnification TEM images (a, c, e, and g) shows the folded edges of AB precursor 30 minutes grown h-BN film and the corresponding zoomed-in images (b, d, f, and h) from the marked regions.

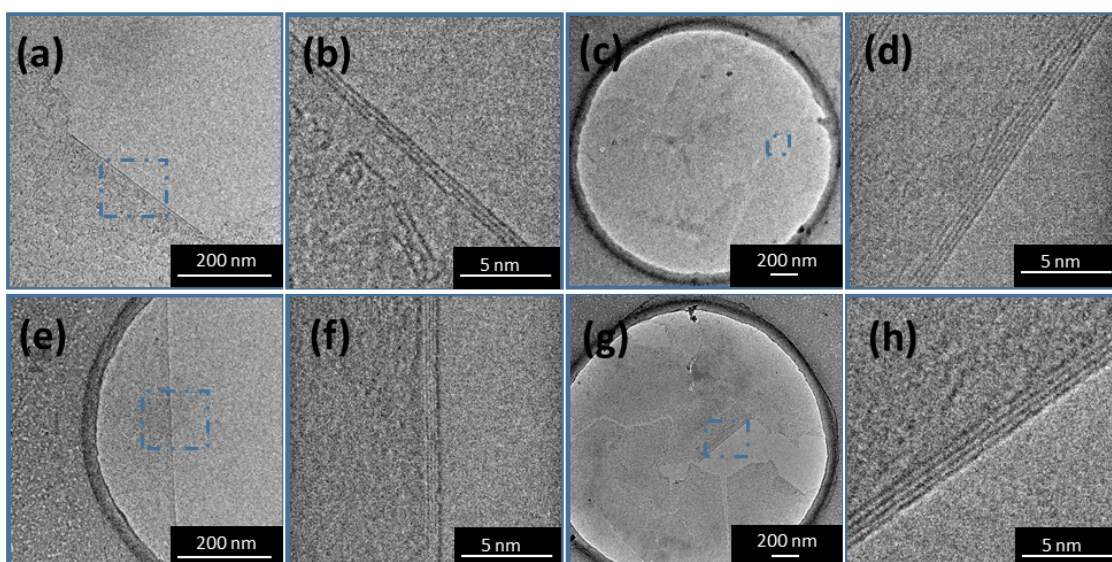


Figure B 8. TEM images show number of layers of TAB precursor 30 minute grown h-BN films near their folded edges. Low-magnification TEM images (a, c, e, and g) shows the folded edges of AB precursor 30 minutes grown h-BN film and the corresponding zoomed-in images (b, d, f, and h) from the marked regions.

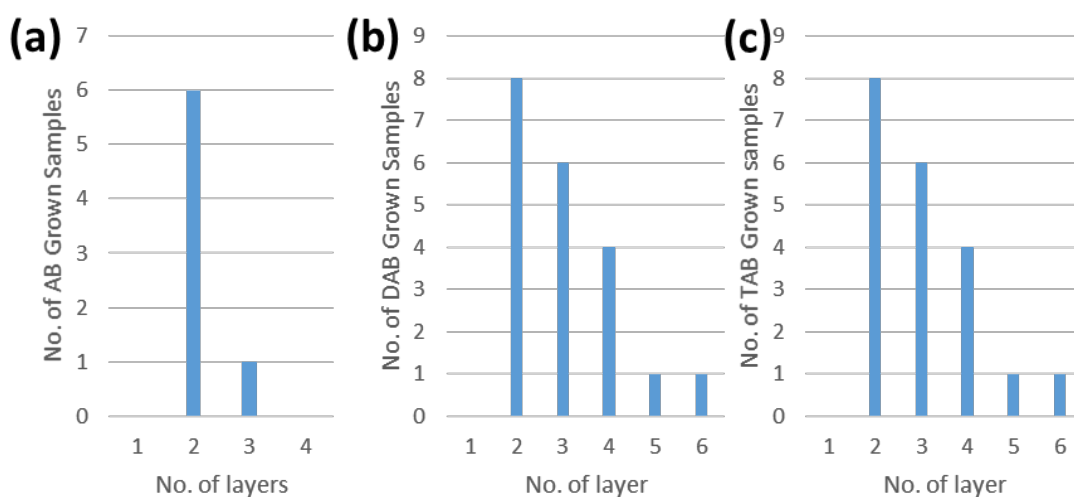


Figure B 9. Statistics about the number of layers against the number of grown h-BN samples, such as (a) for AB precursor, (b) for DAB precursor, and (c) for TAB precursor.

Appendix C Supporting Information for Chapter 5

Chemical Vapor Deposition Synthesis of Gallium Sulfide Mixture Phases (GaS/Ga₂S₃) Thin Film and Their Application as Hydrogen Evolution Catalysts

The Raman spectra are recorded about the CVD synthesised GaS/Ga₂S₃ samples on silicon substrate with various growth time such as 15, 30, and 60 minutes. For each sample, 25 Raman spectra are taken at relevant positions, as shown in the schematic diagram Figure C 1 (a) as an example. Each of the Raman spots are labelled as 1.1, 1.2, 1.3 and so on, and the summarized Raman characterisation spectra are plotted row by row, as shown in Figure C 1 (b), (c), (d), (e) and (f) as examples.

The CVD grown GaS/Ga₂S₃ on SiO₂/Si substrates have the Raman peaks at 185, 288, and 357 cm⁻¹ for this study. The 15 minutes CVD grown samples does not show any other Ga₂S₃ peaks which may be introduced by the precursor at the growth stage. The Ga₂S₃ may from precursor and it has characteristic Raman peaks at about 230 cm⁻¹ and 380 cm⁻¹. It appears that GaS is homogeneously deposited for 15 minutes growth time. Comparing for all the Raman spectra recorded from 30 minutes CVD grown sample, Ga₂S₃ peaks are observed on most of the spots. In total, 21 spots with the Ga₂S₃ characteristic Raman peaks are observed for the 30 minutes CVD grown sample. Similiarly, 13 spots with the Ga₂S₃ characteristic Raman peak positions are observed for the 60 minutes CVD grown sample. In summary, the 15 minutes CVD grown GaS has estimated 0% Ga₂S₃ coverage, the 30 minutes sample has estimated 84% Ga₂S₃ coverage, and the 60 minutes sample has about 52% Ga₂S₃ coverage.

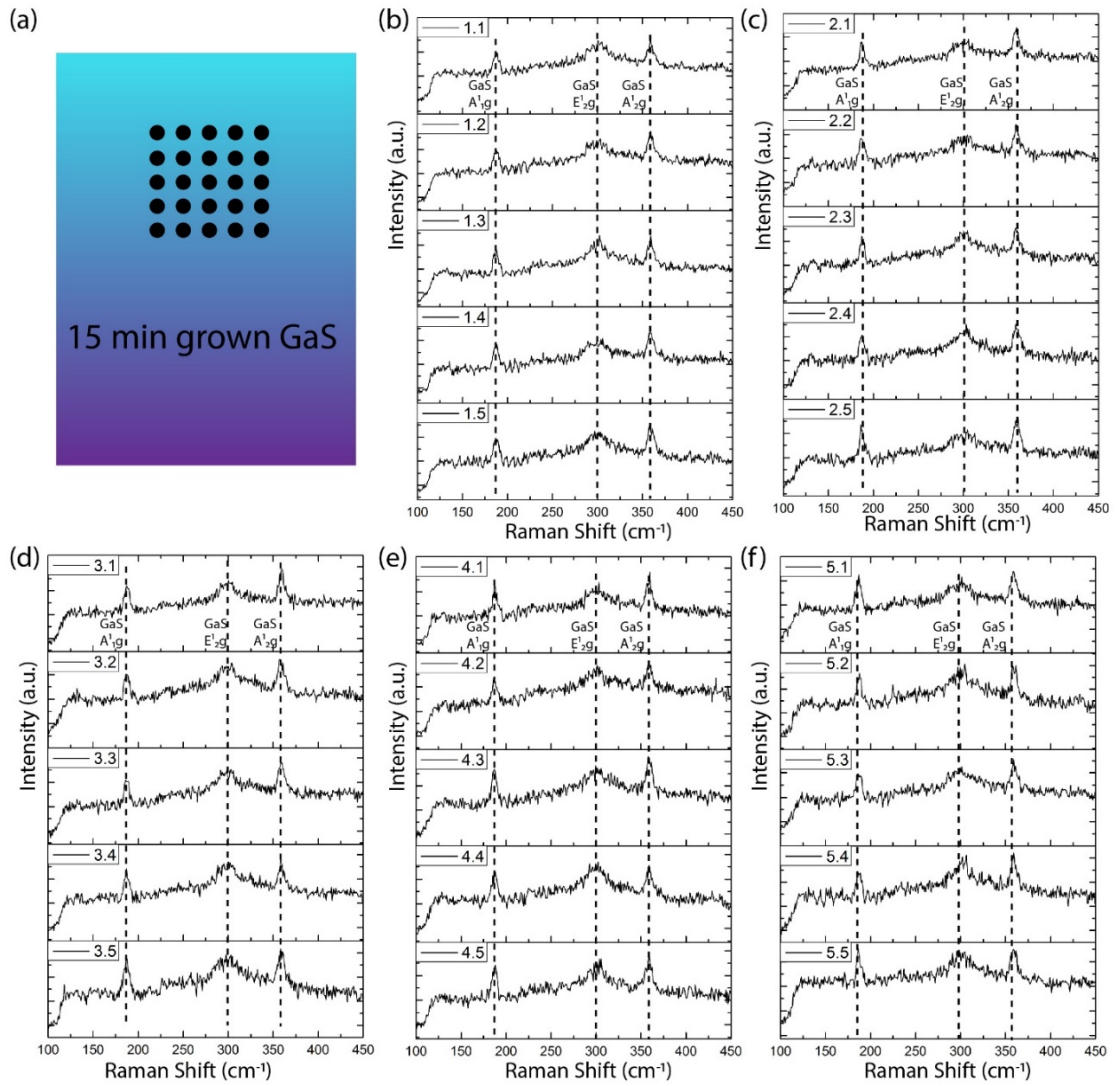


Figure C 1. Raman characterisation of 15 minutes CVD grown continuous GaS film on silicon substrate. (a) Illustration of how the Raman spectra are recorded across the sample. (b-f) Each shows the summarised stack plot of the Raman spectrum and the dashed lines indicate the typical Raman characteristic peaks of GaS.

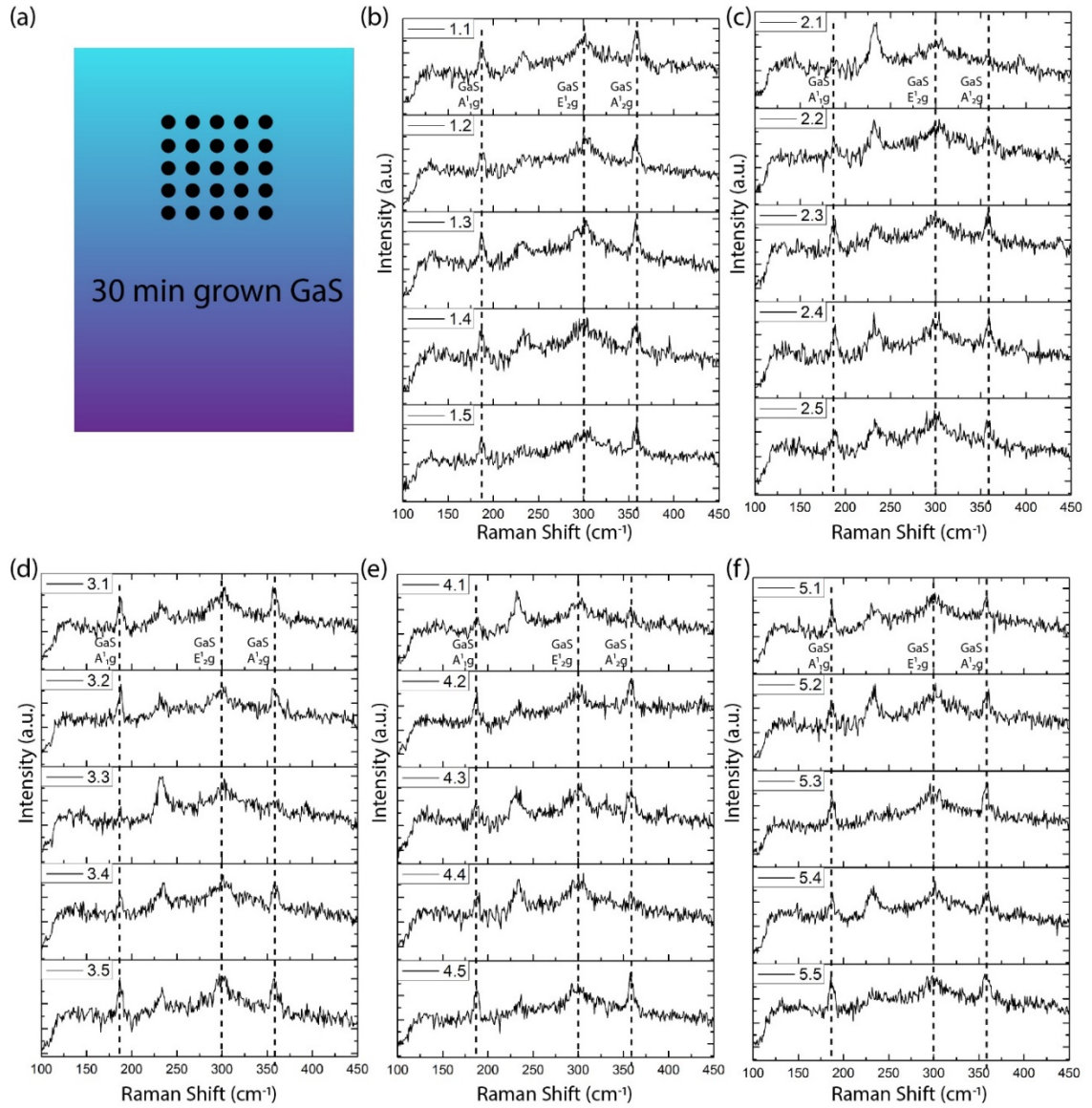


Figure C 2. Raman characterisation of 30 minutes CVD grown continuous GaS/Ga₂S₃ film on silicon substrate. (a) Illustration of how the Raman spectra are recorded across the sample. (b-f) Each shows the summarized stack plot of the Raman spectrum and the dash lines indicate the typical Raman characteristic peaks of GaS.

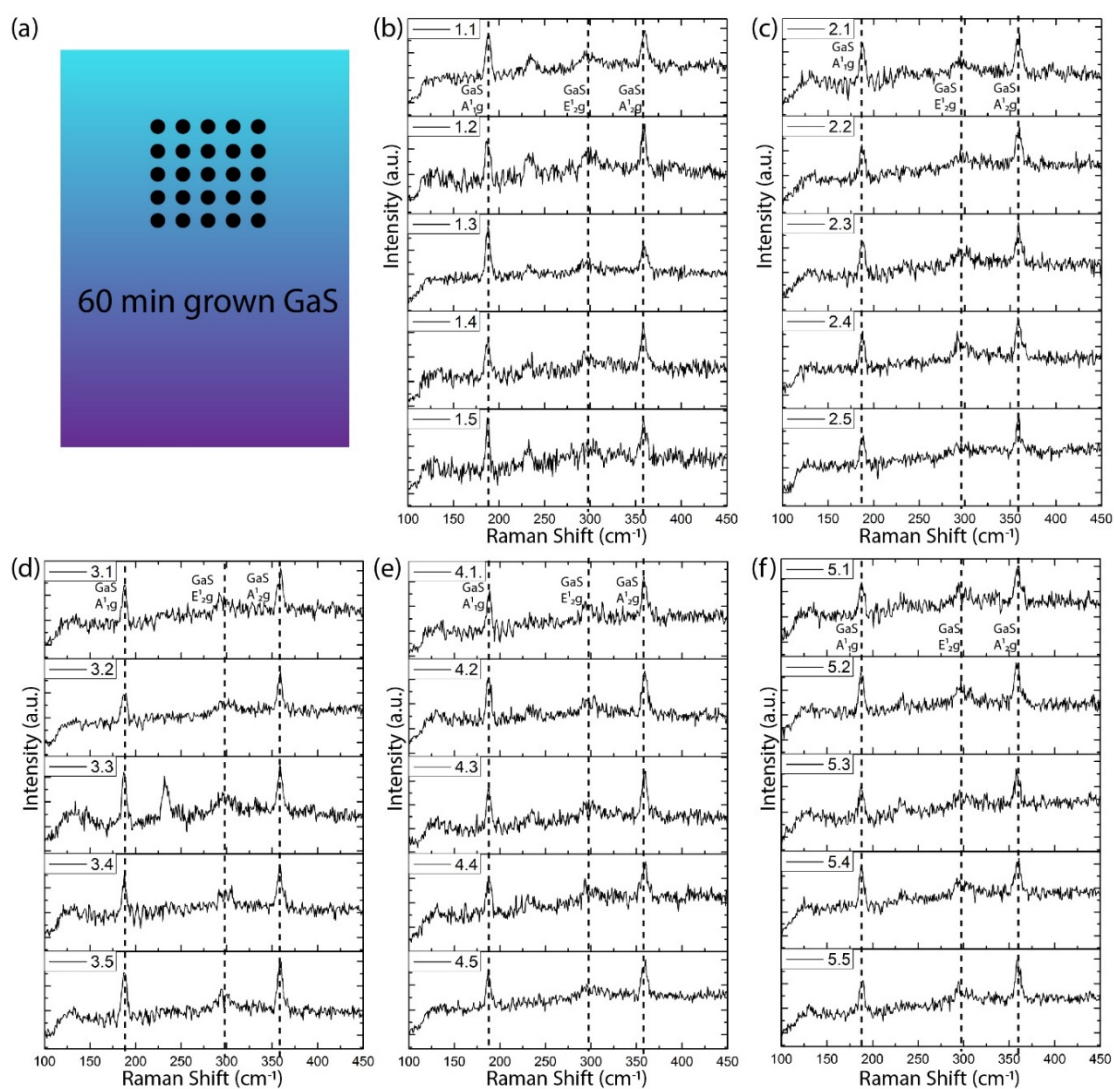


Figure C 3. Raman characterisation of 60 minutes CVD grown continuous GaS/Ga₂S₃ film on silicon substrate. (a) Illustration of how the Raman spectra are taken across the sample. (b-f) Each shows the summarized stack plot of the Raman spectrum and the dash lines indicate the typical Raman characteristic peaks of GaS.

Supporting Figure C 4 (a-d) and (e-h) represent the CVD grown GaS/Ga₂S₃ on SiO₂/Si and glassy carbon substrates, respectively. The EDX maps show the difference between substrates such as silicon and carbon signals, as shown in Figure C 4 (b) and (f), respectively. The rest of the EDX maps show the homogeneous compositional distributions of Ga and S signals all over the substrate surface, as shown in Figure C 4 (c, d, g and h).

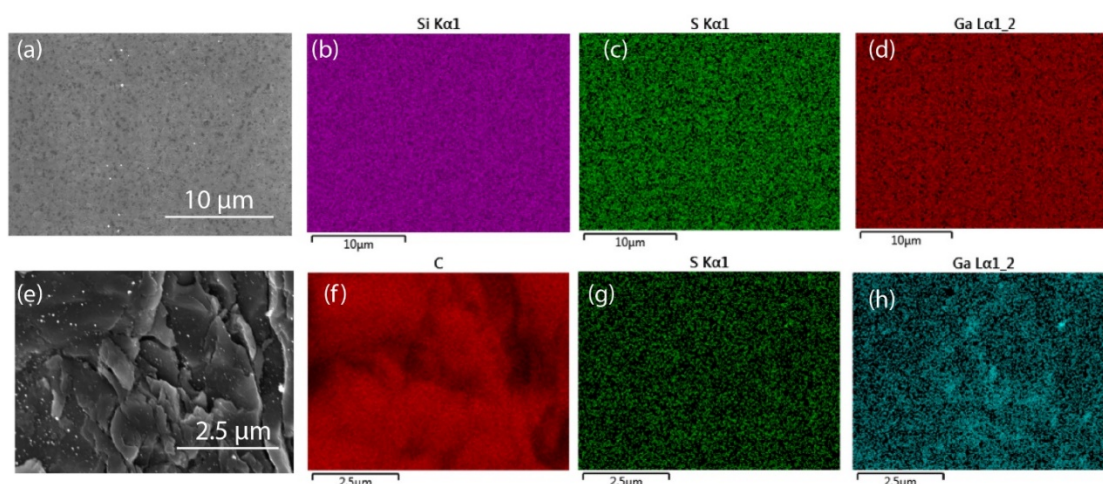


Figure C 4. EDX maps of gallium, sulphur, silicon, and carbon elements acquired on the GaS/Ga₂S₃/SiO₂/Si (b-d) and GaS/Ga₂S₃/glassy carbon (h-f) samples. The corresponding SEM images are shown in (a) and (e) for the silicon and glassy carbon substrates, respectively.

Appendix D Supporting Information for Chapter 6

Towards a Controllable Chemical Vapor Deposition

Method to Grow Gallium Sulfide Domains and

Monolayer Continuous Film

Table D 1. contains five spot EDX spectra data about the atomic percentage of sulphur and gallium obtained from multilayer and monolayer regions of GaS samples.

<i>Position</i>	<i>Multilayer Region</i>			<i>Monolayer Region</i>		
	S At%	Ga At%	S:Ga Ratio	S At%	Ga At%	S:Ga Ratio
1	55.3	44.7	1.24	60.6	39.4	1.54
2	56.0	44.0	1.27	65.0	35.0	1.86
3	55.5	44.5	1.25	65.1	34.9	1.87
4	55.4	44.6	1.24	57.6	42.4	1.36
5	55.5	44.5	1.25	64.5	35.5	1.82

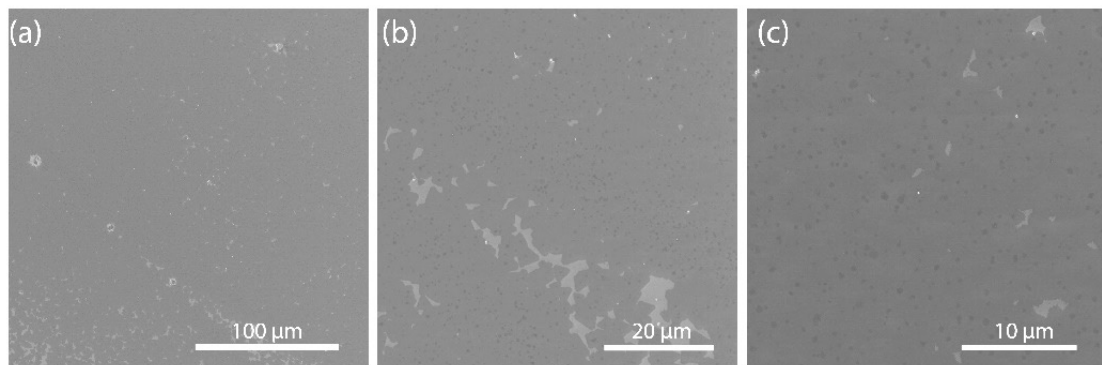


Figure D 1. SEM images of the GaS monolayer continuous film. (a) SEM image of GaS continuous film region. (b) Zoomed-in SEM image of the GaS continuous film where the triangular domains are about to coalesce into continuous film. (c) Zoomed-in SEM image shows the secondary nucleation sites on the film.

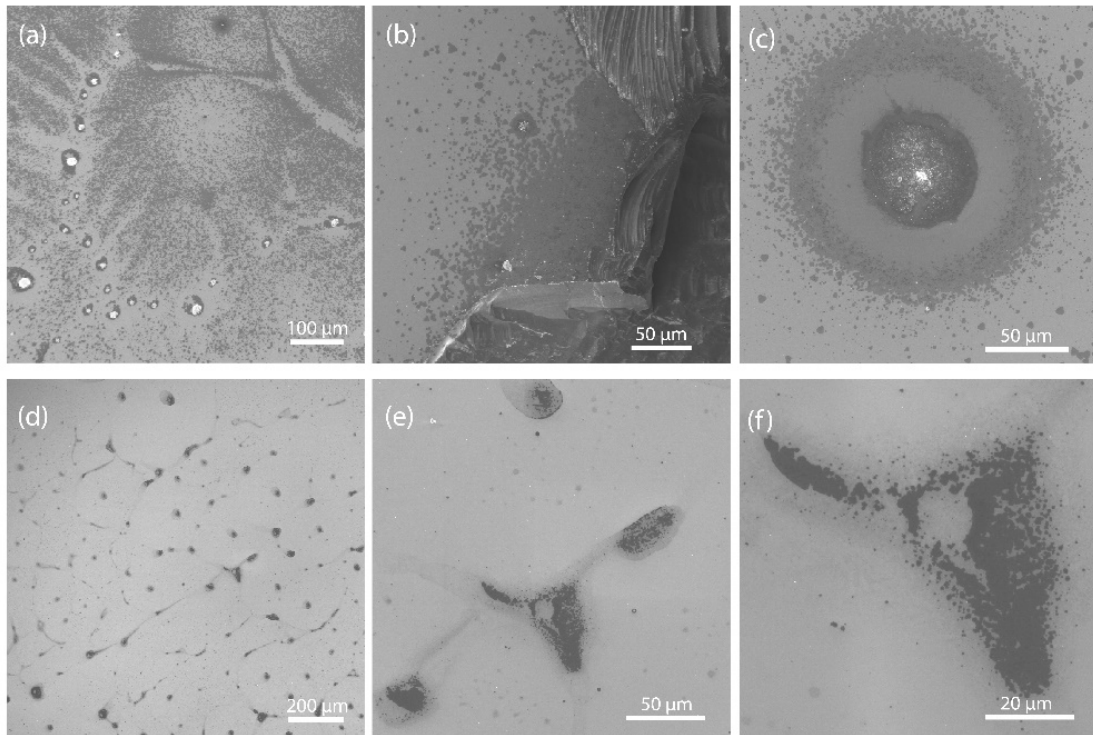


Figure D 2. SEM images reveal preferred growth sites and initial nucleate sites. (a) shows the GaS domains are surrounded by large white particles. (b) shows high coverage of GaS at the edge of silicon substrate. (c) SEM image of high-density formation of GaS around a dust particle. (d-f) Series of SEM images showing the initial GaS nucleation sites on silicon substrate from low to high magnification.

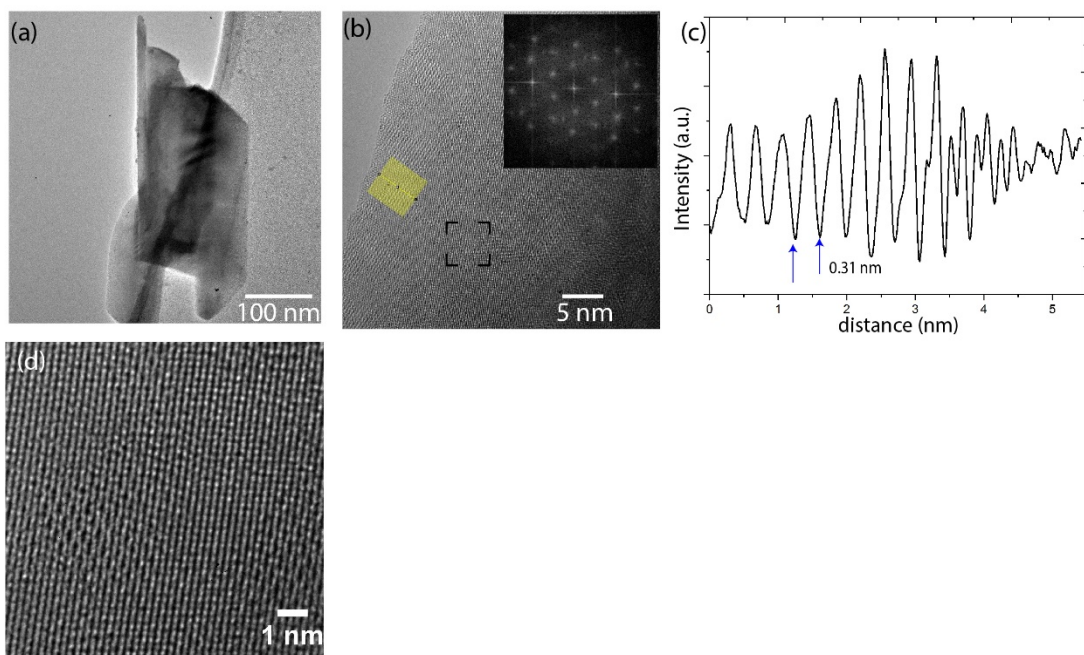


Figure D 3. (a) Low magnification TEM image shows the GaS flake is attached to lacey carbon TEM grid. (b) HRTEM and corresponding FFT image indicates the GaS crystal orientation. (c) The line intensity profile is taken from the yellow coloured region in (b), and the d-spacing of the flake is about 0.31 nm. (d) HRTEM image of the GaS flake corresponding to the selected area in (b).