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Vapor-Phase Synthesis of Two-Dimensional Metal Chalcogenide Semiconductors

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Abstract

As demonstrated by efforts in graphene commercialization, scalable synthesis and high-quality material availability are primary limiting factors for the realization of technologies based on two-dimensional (2D) materials. Thus, in considering the fate of emergent 2D materials such as the metal chalcogenides, the challenge of scalable synthesis is a highly relevant if not prohibitive one. Of the available synthesis methods, vapor-phase techniques are best suited for the wafer-scale fabrication of high-quality 2D materials. The development of vapor-phase synthesis methods for 2D metal chalcogenides is thus a vital effort for the realization of the novel and high-performance electronic and optoelectronic applications lauded by the 2D material literature. While more established 2D metal chalcogenides (*e.g.*, MoS₂) have several vapor-phase methods at their disposal, others are more difficult to grow (*e.g.*, InSe) and call for systematic studies to devise a reliable synthesis method. Additionally, vapor-phase growth can be leveraged to assemble 2D materials into diverse heterostructures *via* a van der Waals (vdW) interface without the substrate lattice matching constraints that govern the growth of conventional three-dimensional (3D) materials. This capability will facilitate a crucial step in the technological implementation of 2D semiconductors – their integration with 3D materials. Hence, in addition to expanding the variety of 2D metal chalcogenides which can be synthesized *via* vapor-phase methods, further exploration into their vapor-phase integration with functional 3D materials is warranted.

This thesis first focuses on the use of vapor-phase synthesis for the vdW-mediated assembly of monolayer MoS₂ into a heterostructure with amorphous Al₂O₃, which is a bulk-like material with a high dielectric constant (κ). The presented work demonstrates the value of integrating a 2D semiconductor with an existing 3D technology. In particular, the use of high- κ dielectrics such as atomic layer deposition (ALD)-derived amorphous Al₂O₃ is ubiquitous for low-power

electronics. Here, the hybrid 2D MoS₂/3D Al₂O₃ heterostructure was achieved by the direct growth of monolayer MoS₂ using chemical vapor deposition (CVD) onto 20-nm-thick Al₂O₃ grown using ALD. The resulting MoS₂/Al₂O₃ heterostructures were fabricated into enhancement-mode field-effect transistors (FETs) which exhibit high performance in low-power electronics metrics. The tactic of direct growth of MoS₂ on the dielectric, which avoids the deleterious doping effect of dielectric deposition onto MoS₂, is a tactic not easily accessible to 3D semiconductors which struggle to grow on amorphous substrates. The presented work thus substantiates the prospect of scalable MoS₂/high- κ structures for low-power electronics and illustrates the advantage of vdW-mediated vapor-phase growth in accessing new fabrication schemes.

The latter part of the thesis presents the development of a vapor-phase synthesis method for large-area InSe films. So far, the complicated indium–selenium phase diagram has presented a significant hurdle to the growth of ultrathin films of InSe. This hurdle is one not easily overcome by the tedious trial-and-error experimental design which is characteristic of 2D material synthesis development, a process colloquially referred to as a “dark art” rather than a science. In this work, a synthesis method was rationally determined by elucidating the structural and compositional evolution of ultrathin InSe films deposited using pulsed laser deposition (PLD) and subsequently processed *via* vacuum thermal annealing. The method yielded thickness-tunable ultrathin InSe films with high crystallinity and no detectable impurity phases. The InSe films demonstrated high responsivity in phototransistors and were patterned for high-yield arrays of top-gated enhancement-mode InSe FETs. This work accomplishes the large-area device implementation of ultrathin InSe films and achieves a level of electronic uniformity yet to be demonstrated in 2D InSe synthesis. Moreover, it demonstrates the merit of phase exploration in 2D materials for the purpose of rational synthesis design and advocates for systematic studies into 2D material growth in the hope of enlightening a “dark art” with rationality and reproducibility.

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List of Abbreviations

κ dielectric constant

κ_{eff} effective dielectric constant

μ_{FE} field-effect mobility

2D two-dimensional

3D three-dimensional

AFM atomic force microscopy

AFRL Airforce Research Laboratory

ALD atomic layer deposition

ARES Autonomous Research System

C-V capacitance-voltage

CMOS complementary metal-oxide-semiconductor

CVD chemical vapor deposition

CVT chemical vapor transport

DFT density functional theory

EBL electron-beam lithography

EDS energy-dispersive X-ray spectroscopy

FET field-effect transistor

FWHM full width at half maximum

GIIIMC group III metal chalcogenide

GO graphene oxide

***h*-GaTe** hexagonal-GaTe

HAADF high-angle annular dark-field

I_{dark} drain current in the dark

I_{light} drain current under illumination

I_{pc} photocurrent

I_{off} source-drain current at the device OFF state

I_{on} source-drain current at the the device ON state

IPA isopropyl alcohol

IR infrared

L channel length

LPE liquid-phase exfoliation

***m*-GaTe** monoclinic-GaTe

MBE molecular beam epitaxy

MFC mass flow controller

MIBK methyl isobutyl ketone

MIS metal-insulator-semiconductor

MOCVD metal-organic chemical vapor deposition

NMP *n*-methyl-2-pyrrolidone

P illumination power

PL photoluminescence

PLD pulsed laser deposition

PMMA poly(methyl methacrylate)

PTAS perylene-3,4,9,10-tetra-carboxylic acid tetrapotassium salt

PVD physical vapor deposition

PVT physical vapor transport

R responsivity

RMS root mean square

RT room temperature

SAED selected area electron diffraction

SEM scanning electron microscopy

SHG second harmonic generation

STEM scanning transmission electron microscopy

STM scanning tunneling microscopy

TEM transmission electron microscopy

TMA trimethylaluminum

TMD transition metal dichalcogenides

TMDAH tetrakis(ethylmethylamino)hafnium

UHV ultra-high vacuum

V_{BG} bottom-gate voltage

V_D source-drain voltage

V_G gate voltage

V_{TG} top-gate voltage

V_{TH} threshold voltage

vdW van der Waals

W channel width

XPS X-ray photoelectron spectroscopy

XRD X-ray diffraction

XRR X-ray reflectivity

À mon père, Jean – mon guide sur Terre
À mon frère, Mathieu – mon guide au delà

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Part I

Background and Literature Review

Chapter 1

Two-Dimensional Metal Chalcogenide Semiconductors

Beyond graphene

Though originally thought to be thermodynamically unstable, 2D crystals have become an intense field of research since their discovery in the form of atomically-thin graphene exfoliated from bulk graphite.¹ The superlative electronic,² mechanical,³ and thermal⁴ properties of graphene have generated abundant studies into its rich physics⁵ and unveiled the advantages of 2D materials in a breadth of applications from nanoelectronics to composites. The graphene global market is now expected to surpass US\$ 100 million in sales by 2021.⁶ The path forged by graphene presents a roadmap for emerging semiconducting 2D materials. In particular, the scalable synthesis and availability of the material is consistently identified as a limiting factor for graphene commercialization.⁶⁻⁸ Thus, in considering the fate of emergent 2D materials such as the metal chalcogenides, the challenge of scalable synthesis is a highly relevant, if not prohibitory, one.

Shortly after the discover of graphene, the field of 2D materials greatly expanded its repertoire.⁹⁻¹¹ The 2D material library now contains insulators (*e.g.*, hexagonal boron ni-

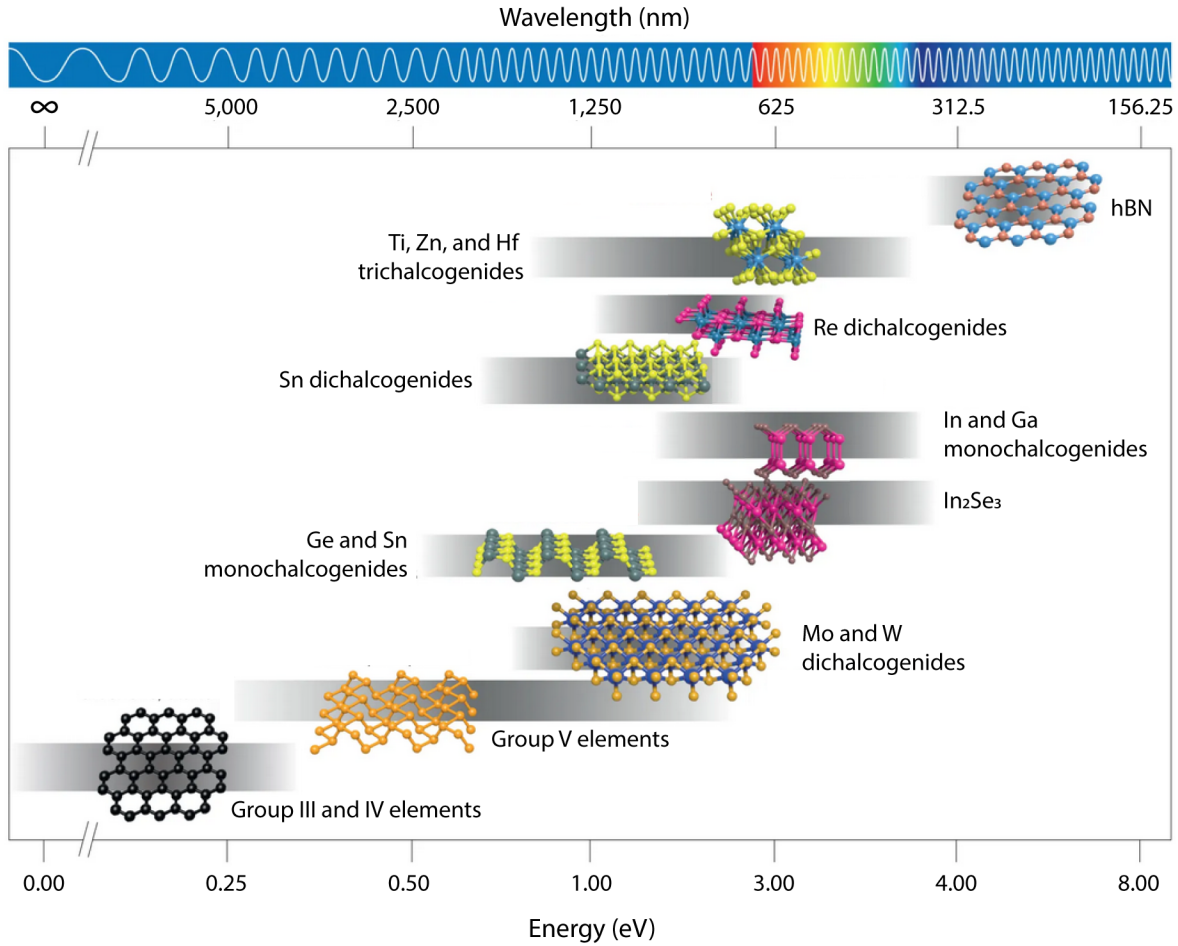


Figure 1.1: Bandgap values spanned by various 2D material classes. The materials range from metals to insulators. The list of materials included in the graphic is not exhaustive of all accessible 2D materials. Figure adapted with permission from [15].

tride),¹² semiconductors (*e.g.* MoS_2),¹³ and metals (*e.g.*, borophene)¹⁴ to enable a range of properties for the pursuit of electronic, optoelectronic, and energy demands. The illustration in Figure 1.1 provides an idea of the range of bandgap values spanned by a non-exhaustive subset of 2D materials. The 2D material family is ever-growing; while the tabulation of 2D material classes and their properties used to be a simple task, the field has expanded to a scale where exhaustive classifications are no longer feasible or relevant.

Though the specific properties of 2D materials can differ greatly, they share the commonality of having no out-of-plane dangling bonds. As a result, 2D materials have the ability

to establish pristine interfaces in heterostructures. Most 2D materials originate from bulk analogues (*i.e.*, vdW solids) consisting of atomic layers with strong intralayer bonds that are stacked in the out-of-plane direction with weak vdW interlayer interactions. For example, the interlayer vdW bonding energies are typically ~ 20 meV/Å² for the transition metal dichalcogenides (TMDs). This weak out-of-plane coupling makes it possible to delaminate 2D sheets from the bulk crystal and has led to mechanical exfoliation being the primary means of isolating new 2D materials.^{2,9} Notable exceptions are group III elements (borophene)¹⁴ and non-carbon group IV elements (*e.g.*, silicene,¹⁶ germanene,¹⁷ stanene,¹⁸), which do not form bulk layered structures. As a result, the aforementioned 2D materials require the stabilization of a substrate and are currently obtained exclusively through vapor-phase methods such as molecular beam epitaxy (MBE). The most prominently studied 2D semiconductors are the TMDs. Though not as prevalent in the 2D material literature, group III metal chalcogenide (GIIIMC)s (*e.g.*, GaS, GaSe, InSe, In₂Se₃, etc.) consist another class of semiconducting layered materials growing in interest and demonstrating interesting electronic properties in the ultrathin limit.^{9,19}

1.1 Transition metal dichalcogenides

TMDs have a formula of MX_2 , where M is a transition metal and X is a chalcogen, and many of them are semiconductors. The re-discovery of layered semiconducting TMDs as 2D materials has opened up a new playing field for nanoelectronics, enabling the engineering of 2D analogues of standard devices of the semiconductor industry as well as entirely novel devices based on their atomically-thin semiconducting quality. The TMDs have become the “standard” for 2D semiconductors, with MoS₂ as its most ubiquitous representative. While room-temperature the charge carrier mobilities of 10-500 cm²/Vs are lower in comparison to other 2D materials (*i.e.*, graphene, black phosphorus), the sizeable bandgaps of many

TMDs yields FETs with large switching ratios of up to 10^8 .^{20,21} Moreover, their stability in ambient conditions impart a hardness that makes them easy to work with and thus more prolific. In addition to the advantages of their ultrathin nature (*e.g.*, excellent gate-tunability, flexibility), 2D TMDs exhibit quantum confinement effects and thickness-dependent evolution of properties that are relevant to electronics applications. For example, monolayer semiconducting TMDs have exciton binding energies up to hundreds of meV, which are orders of magnitude larger than typical bulk semiconductors.^{22,23} Furthermore, many TMDs (*e.g.*, MoS₂, MoSe₂, WS₂) transition from an indirect to direct bandgap in the monolayer limit.^{24,25} As a result, TMDs are being explored for novel optoelectronic devices.^{20,26} Tunability of the bandgap of 2D TMDs is also achievable *via* strain engineering^{25,27} while their high surface to volume ratio enables tunable Fermi level doping via surface functionalization with physisorption or chemisorption of molecules.^{28,29}

The TMDs exhibit two main polymorphs: 2H and 1T. Both of these structures are composed of a hexagonally arranged atomic sheet of molybdenum atoms between two hexagonally arranged atomic sheets of sulfur atoms (Figure 1.2a). In the 2H structure, the metal atoms have trigonal prismatic coordination to the chalcogen, while in the 1T structure, the chalcogens are octahedrally coordinated to the metal atoms. The 2H and 1T polymorphs correspond to the $P6_3/mmc$ and $P\bar{3}m1$ spaces groups, respectively. The commonly observed structures of monolayer TMDs are summarized in Figure 1.2, along with their notable electronic properties. It should be clarified that the 2H and 1T notation are used to refer to the structure of a single vdW layer composed of three atomic layers. Additionally, the TMDs exhibit several stacking polytypes, namely, 2H_a, 2H_b, 2H_c, 3R, as well as various 4H stacking schemes.³¹ While the Nb and Ta dichalcogenides exhibit rich polytypism, the Mo and W dichalcogenides only stack in the 2H_c and 3R polytypes. For MoS₂, which is the focal TMD of this document, the 2H monolayer structure with a 2H_c stacking polytype is most common and stable,³² though the 3R polytype has also been somewhat explored in

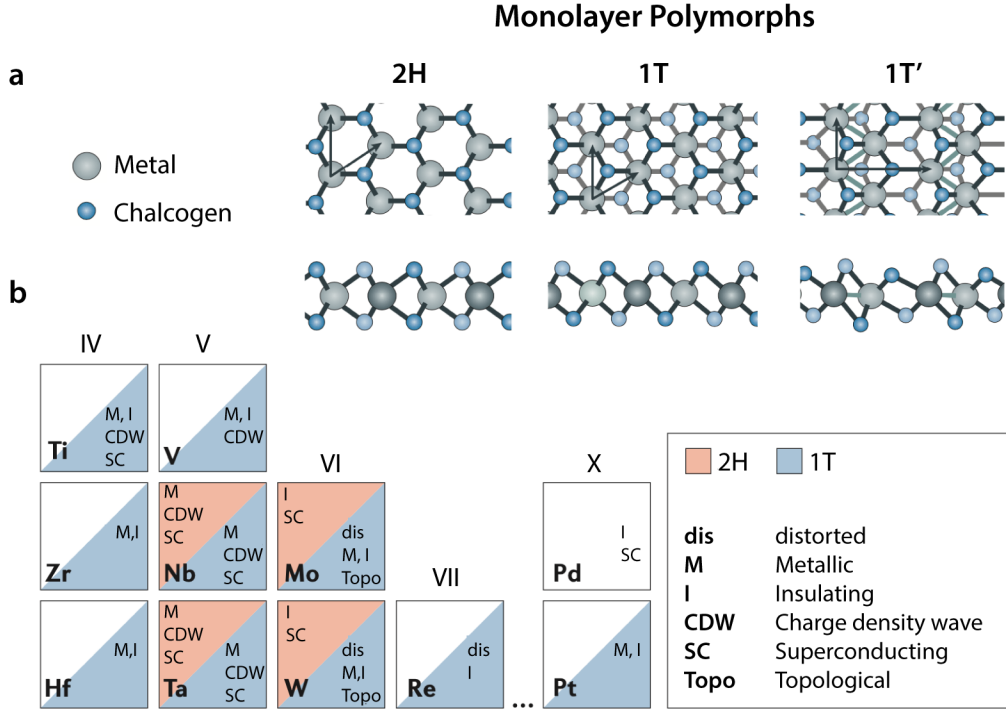


Figure 1.2: Structures and electronic properties of transition metal dichalcogenides. (a) The structures of the most commonly observed monolayer polymorphs of TMDs are pictured. (b) Summary of the structures exhibited by the TMDs (by transition metal element) and their notable electronic properties. The classification of “insulating” encompasses anything other than a metal. Adapted with permission from [30].

2D literature.³³ The 2H_c polytype corresponds to an AbABaB atomic layer stacking scheme. Phase transitions between the polymorphs can be observed in the TMDs. For example, MoS₂ can adopt a metastable and metallic 1T structure if perturbed with external forces such as lithiation, irradiation, or plasma treatment.³⁴ Monolayer MoS₂ is also reported to form a rarer distorted 1T' phase.³⁵ Notably, a few TMDs have ground states that are neither 2H or 1T. Some TMDs crystallize in the monoclinic 1T' (*e.g.* TaTe₂) or 1T'' (*e.g.* ReS₂) polymorphs, and the stable bulk phase of WTe₂ is the orthorhombic T_d phase.^{30,36}

1.1.1 2D molybdenum disulfide (MoS_2)

MoS_2 is the most widely studied of the 2D TMDs and has become a reference point for this class of materials. In addition to its semiconducting nature, the popularity of 2D MoS_2 can be partially attributed to its accessible synthesis *via* solid-precursor CVD (see subsection 2.4.1). Consequently, monolayer MoS_2 is one of the most available 2D materials. In the bulk, MoS_2 has an indirect bandgap of 1.29 eV which increases in the few-layer limit until a transition to a direct bandgap of 1.9 eV in the monolayer.^{13,37} The direct bandgap leads to high intensity photoluminescence (PL) and much higher quantum yield in the monolayer than in multilayer MoS_2 , since PL arises from radiative recombination of in-plane excitons *via* direct electronic transitions. In addition to integration of 2D MoS_2 into ubiquitous devices such as FETs and photovoltaics,^{20,21,38–40} it has also been used to generate novel technologies. For example, the breaking of inversion symmetry in monolayer MoS_2 results in observation of the valley Hall effect, which is promising for next-generation information storage and processing using valleytronics.^{41–43} However, it should be noted that multilayer MoS_2 recovers its inversion center. Defect migration in 2D MoS_2 has recently been shown to facilitate novel gate-tunable 2D memristors, known as memtransistors.⁴⁴ Furthermore, monolayer MoS_2 has been used to fabricate Gaussian heterojunction transistors with unprecedented tunability for spiking neurons.⁴⁵ As a result, monolayer MoS_2 has been leading the way in 2D hardware implementations for neuromorphic computing.⁴⁶

1.2 Group III metal chalcogenides

The GIIMCs are class of layered materials growing in interest from the nanoelectronics community. While their interlayer bonding is weak and permits mechanical exfoliation, it is about an order of magnitude stronger than that of TMDs and graphite.⁴⁷ In the multilayer form, many of these materials exhibit a direct bandgap, which makes them of particular

interest for applications in photodetectors and photovoltaics.^{48,49} Furthermore, as discussed in more detail in the following subsections, several of the GIIIMCs are noncentrosymmetric in the multilayer form, which imparts them with spontaneous polarizations such as piezoelectricity and ferroelectricity, as well as second harmonic generation (SHG) capabilities for nonlinear optics. Overall, many of the GIIIMCs are most interesting in the multilayer regime, rather than the monolayer limit, in contrast to the TMDs.

The GIIIMCs adopt many stoichiometries with a general formula M_aX_b , where $M = \text{Ga, In}$ and $X = \text{S, Se, Te}$. However, most of the layered GIIIMCs are of the stoichiometry $M_2X_2 = MX$ and M_2X_3 . These structures consist of vdW-bonded hexagonal single layers with internal atomic layer of the form $X-M-M-X$ and $X-M-X-M-X$, respectively (Figure 1.3a). GIIIMCs which demonstrate layered polymorphs but have not been significantly studied in the 2D materials community include In_2S_3 ,⁵⁰ In_3Se_4 ,⁵¹ In_4Se_3 ,⁵² InTe ,⁵³ In_2Te_3 ,⁵⁴ and Ga_2Te_3 .⁵⁴ The following discussions will instead focus on the layered GIIIMCs which have growing interest among the 2D community, namely, GIIIMCs of composition $MX = \text{GaS, GaSe, InSe}$ and $M_2X_3 = \text{In}_2\text{Se}_3$.

The layered GIIIMCs demonstrate various stacking polytypes.⁵⁵ This phenomenon is well documented for InSe , GaSe , and $\alpha\text{-In}_2\text{Se}_3$ and $\beta\text{-In}_2\text{Se}_3$. In particular, the 2H and 3R stacking polytypes are among the most commonly observed. It is also possible to observe other stacking orders, such as 4H,⁵⁵ but these are more uncommon. The commonly observed stacking polytypes for the 2D GIIIMCs are summarized in Figure 1.3d. Furthermore, a summary of the structures and bandgaps for the discussed GIIIMCs can be found in Table 1.1 and Table 1.2.

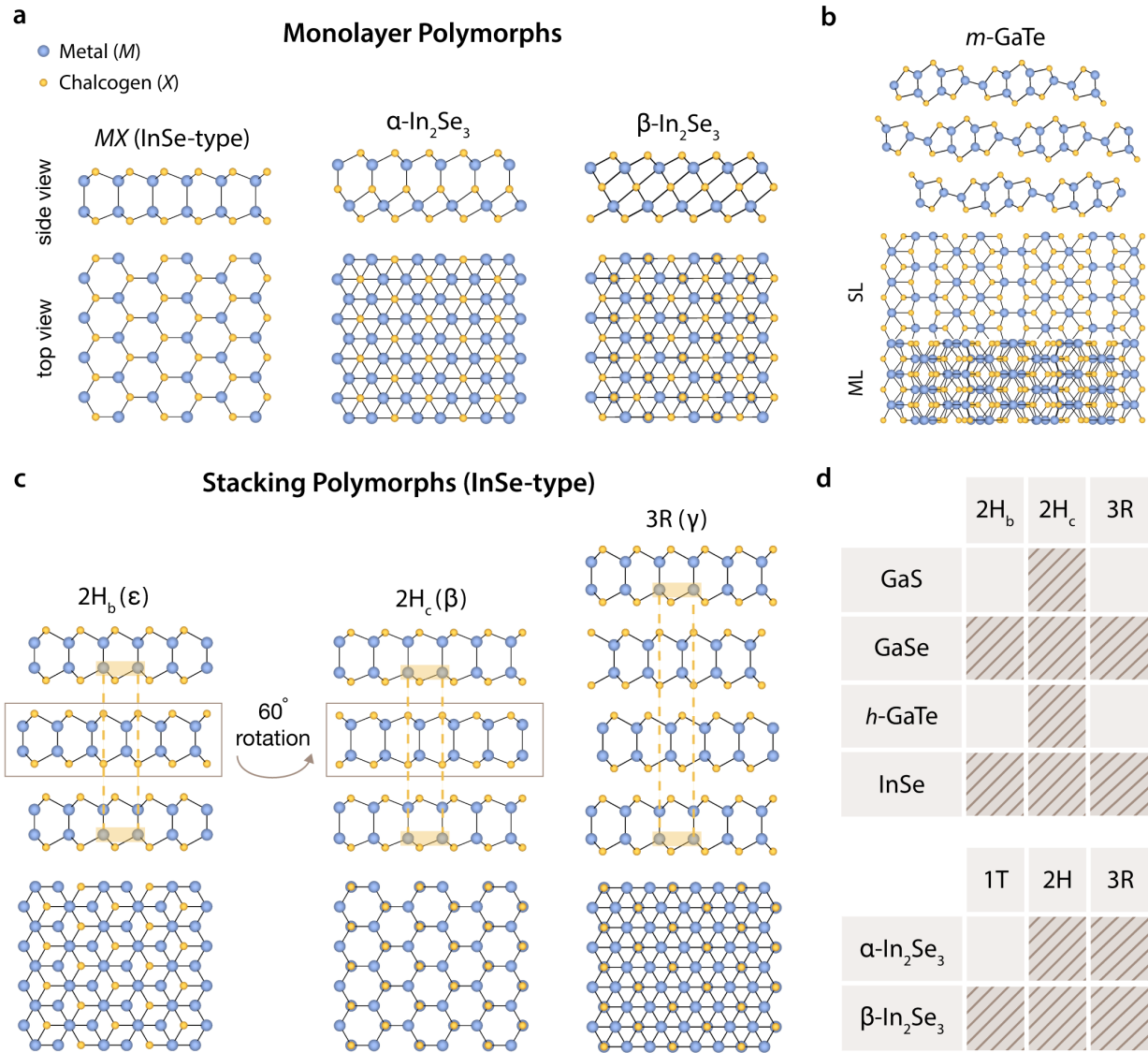


Figure 1.3: 2D polymorphs of group III metal chalcogenides. (a) Monolayer polymorphs of layered GIIIMCs with composition *MX* (*i.e.*, GaS, GaSe, hexagonal-GaTe (*h*-GaTe), and InSe) and M_2X_3 (*i.e.*, In_2Se_3), as well as (b) monoclinic GaTe (*m*-GaTe). (c) Stacking polytypes for the InSe-type structures. The yellow rectangle and dashes lines indicate the stacking to equivalent layers. The $2H_b$ and $3R$ polytypes corresponds to AB and ABC stacking, respectively. The $2H_c$ polytype corresponds to AA' stacking where the alternating layers are 60° rotated such that the metal atoms are stacked directly on top of the chalcogen atoms. The stacking polymorphs for In_2Se_3 are not shown here but are given by the 1T (AA stacking), 2H (AB stacking with 60° rotations between alternating layers), and 3R (ABC stacking with translational offset between layers) polytypes. (d) Summary of commonly observed 2D GIIIMC stacking polytypes.

1.2.1 2D gallium and indium monochalcogenides (MX)

The layered MX compounds exhibit an InSe-type intralayer structure and include GaS, GaSe, and InSe. While GaTe can exist in a hexagonal InSe-type structure at high pressures, here referred to as h -GaTe, its more stable structure in the bulk is the more complex layered monoclinic structure, here referred to as monoclinic-GaTe (m -GaTe) and depicted in Figure 1.3b.^{56,57} For the InSe-type structures, there are three commonly observed stacking polytypes: $2H_b$, $2H_c$, and $3R$, which are known as the ϵ , β , and γ polytypes, respectively. The differentiation in the $2H$ structures ($2H_b$ and $2H_c$) is in analogy to the TMD literature, wherein the $2H_b$ and $2H_c$ polytypes have AbACaC and AbABaB stacking motifs, respectively.³¹ The β and γ characters are also used in the M_2X_3 literature but denote different intralayer structures instead of stacking polytypes. Both the $2H_b$ and $3R$ polytypes corresponds to translational offsets between layers with AB and ABC vdW layer stacking, respectively. The $2H_c$ polytype has a 60° rotation between layers, such that the chalcogen atom column lies above the metal atoms and vice versa (AA' vdW layer stacking). In terms of the individual atomic layers, the $2H_b$ and $2H_c$ stacking in InSe-type GIIIMCs exhibit AbbACaaC and AbbABaaB arrangements, respectively. The $2H_b$, $2H_c$, and $3R$ stacking polytypes for InSe-type GIIIMCs are depicted in Figure 1.3c, and the polytypes most commonly observed for the materials discussed are summarize in Figure 5d. While most of them demonstrate polytypism, GaS and h -GaTe have only been dominantly observed in the $\beta(2H_c)$ form.⁵⁸ Additionally, a first-principles calculation report by Kou *et al.* suggests that monolayer InSe may exist as other stable monolayer polymorphs, however these have not been observed experimentally.⁵⁹

Since the polymorphism in most of the MX GIIIMCs arises from differences in stacking, the distinction in their properties is primarily encompassed by the distinction in their symmetries. Both InSe-type and m -GaTe monolayers are noncentrosymmetric. However, different symmetries can be achieved *via* the different stacking orders in the InSe-type MX s. In partic-

ular, the $2H_b$ and $3R$ polytypes for the MX s are noncentrosymmetric while the $2H_c$ stacking is centrosymmetric for even numbers of vdW layers. Since noncentrosymmetric materials are anticipated to be applicable for nonlinear optics⁶⁰ and display spontaneous polarization,⁶¹ much attention has been directed at studying the noncentrosymmetric polytypes. Indeed, noncentrosymmetric monolayer MX s are predicted by Li *et al.* to demonstrate piezoelectricity, and in contrast to centrosymmetric TMDs, the $2H_b$ and $3R$ polytypes of MX s could sustain a piezoelectric response in the multilayer form.⁶² In-plane piezoelectricity was confirmed in $3R$ -InSe by Dai *et al.*⁶³ Furthermore, SHG in the MX s has been the subject of many recent investigations. By directly synthesizing bilayer $2H_b$ -GaSe and $2H_c$ -GaSe using CVD, Zhou *et al.* observed enhanced SHG in the $2H_b$ -GaSe bilayers and nearly zero SHG signal in the $2H_c$ -GaSe.⁶⁴ This result demonstrates the promise of multilayer noncentrosymmetric MX s in high intensity SHG, which has since been investigated further computationally^{65,66} and confirmed experimentally in multilayer $3R$ -InSe⁶⁷ and $2H_b$ -InSe.^{68–70} Electronically, the $2H_b$, $2H_c$, and $3R$ polytypes of the InSe-type MX s are expected to be similar.^{71–73} However, Sun *et al.* reported that the computed charge carrier mobilities of $2H_c$ -InSe are larger than $3R$ -InSe (up to $\sim 1.5\times$ in the thick limit).⁷⁴

In contrast to the InSe-type monolayer structure, m -GaTe exhibits in-plane anisotropy, which was studied in exfoliated 2D flakes of m -GaTe by Huang *et al.* via optical extinction and Raman spectroscopy.⁷⁵ Since m -GaTe also has broken inversion symmetry, it has been shown to exhibit SHG.⁷⁶ As for the in-plane isotropic h -GaTe polymorph, a recent density functional theory (DFT) study by Kosobutsky *et al.* suggests that it shows a higher degree of bandgap tunability as a function thickness than m -GaTe.⁷⁷

1.2.2 2D indium sesquiselenide (In_2Se_3)

For layered In_2Se_3 , two monolayer polymorphs are observed and correspond to α - In_2Se_3 and β - In_2Se_3 , the latter of which shares the same intralayer structure as Bi_2Te_3 . In_2Te_3 and

Ga_2Te_3 can also exist in a layered polymorph of $\beta\text{-In}_2\text{Se}_3$ (Bi_2Te_3 -type), but it is metastable and observed at high pressures.⁵⁴ Similar to the MX compounds, the layered polymorphs of In_2Se_3 show stacking polytypes. $\alpha\text{-In}_2\text{Se}_3$ stacks in both the 2H and 3R polytypes while $\beta\text{-In}_2\text{Se}_3$ stacks in the 1T, 2H, and 3R polytypes (Figure 1.3d).^{78,79} The 1T polytype corresponds to AA stacking where the single layers are stacked directly on top of each other with no offset. The 2H polytype has an AB stacking pattern with a 60° rotation between layers and the 3R polytype has an ABC stacking pattern with only a translational offset between the layers. Additionally, distorted β structures, denoted as β' , have also been observed for 2D In_2Se_3 . One of the structures reported is the result of a 1D periodic modulation along the high-symmetry direction,^{80,81} and the other is a new structure with a rectangular lattice, though they are not yet fully understood.⁸²⁻⁸⁴

Since the $\alpha\text{-In}_2\text{Se}_3$ structure is noncentrosymmetric and $\beta\text{-In}_2\text{Se}_3$ is centrosymmetric, the two polymorphs have significant distinctions in properties. Firstly, $\alpha\text{-In}_2\text{Se}_3$ is predicted to demonstrate robust room-temperature spontaneous polarization,⁸⁵ including intrinsic in-plane and out-of-plane ferroelectricity which persists to monolayer thickness.⁸⁶ This is in contrast to conventional ferroelectric thin films in which the effect is suppressed past a critical thickness. Xiao *et al.* recently confirmed the out-of-plane ferroelectricity of 2D $\alpha\text{-In}_2\text{Se}_3$ at room temperature,⁸⁷ while Xue *et al.*⁸⁸ and Cui *et al.*⁶¹ also confirmed in-plane ferroelectricity of 2D $\alpha\text{-In}_2\text{Se}_3$ under such conditions. Additionally, out-of-plane and in-plane piezoelectricity have also been experimentally confirmed for 2D $\alpha\text{-In}_2\text{Se}_3$.^{63,89,90} In contrast, $\beta\text{-In}_2\text{Se}_3$ does not exhibit ferroelectricity or piezoelectricity. However, if the $\beta\text{-In}_2\text{Se}_3$ structure is distorted and the inversion symmetry broken, it could result in spontaneous polarizations. In particular, Zheng *et al.*⁸⁰ showed room-temperature in-plane ferroelectricity in distorted $\beta'\text{-In}_2\text{Se}_3$ layers. As for electronic transport properties, Tao and Gu⁹¹ and Feng *et al.*⁹² both found $\beta\text{-In}_2\text{Se}_3$ to be more conductive than $\alpha\text{-In}_2\text{Se}_3$.

Material	Monolayer			Multilayer			
	Structure Type	Lattice Parameters (Å)	Bandgap (eV)	Polymorph/ Polytype	Space Group	Lattice Parameters (Å)	Bulk Bandgap (eV)
GaS	InSe-type	$a = 3.63^* [93]$	2.48-3.19* (I) [93]	β (2H _c)	P6 ₃ /mmc	$a = 3.592$ $c = 15.465$ [94]	2.53 (I) [95]
				ϵ (2H _b)	P $\bar{6}$ m2	$a = 3.755$ $c = 15.946$ [99]	1.928* (D) 2.065 (D) [73, 100]
GaSe	InSe-type	$a = 3.82^* [96]$	2.352* (I) 3.001* (I) [97, 98]	β (2H _c)	P6 ₃ /mmc	$a = 3.755$ $c = 15.940$ [99]	1.881* (D) 2.117 (D) [73, 100]
				γ (3R)	R3m	$a = 3.755$ $c = 23.920$ [99]	1.931* (D) 2.065 (D) [73, 100]
InSe				ϵ (2H _b)	P $\bar{6}$ m2	$a = 4.00$ $c = 16.640$ [103]	1.198* (D) [73]
	InSe-type	$a = 4.10^* [96]$	2.97* (I) 2.11 (I) [101, 102]	β (2H _c)	P6 ₃ /mmc	$a = 4.00$ $c = 16.640$ [103]	1.172* (D) [73]
GaTe				γ (3R)	R3m	$a = 4.00$ $c = 25.320$ [103]	1.132* (D) 1.26 (D) [73, 104]
	m -GaTe	$a = 23.14^*$ $b = 4.05^*$ [105]	1.370*-2.063* (D) [105]	m -GaTe	C2/m	$a = 17.32$ $b = 4.05$ $c = 10.59$ [105]	1.098* (D) 1.66 (D) [57, 106]
	h -GaTe (InSe-type)	$a = 4.13^*$ [96]	1.44*-2.02* (I) [93]	β (2H _c)	P6 ₃ /mmc	$a = 4.06$ $c = 16.96$ [107]	1.44-1.46 (I) [107]

Table 1.1: Structures and bandgaps of group III metal monochalcogenides. Calculated values are denoted by * and the nature of the bandgap is denoted by (D) = direct and (I) = indirect.

Material	Monolayer			Multilayer			
	Structure Type	Lattice Parameters (Å)	Bandgap (eV)	Polymorph/ Polytype	Space Group	Lattice Parameters (Å)	Bulk Bandgap (eV)
In ₂ Se ₃	α-In ₂ Se ₃	$a = 4.106^* [86]$	1.46* (I) 1.92* (I) 1.55 (I) [86, 101, 108]	2H-α	P6 ₃ mc	$a = 4.023$ $c = 19.217$ [78]	-
				3R-α	R3m	$a = 4.026$ $c = 28.750$ [78]	1.365 (D) [109]
	β-In ₂ Se ₃ (Bi ₂ Te ₂ -type)	$a = 4.048^* [86]$	1.15* (I) 1.55 (I) [83, 110]	1T-β	P3̄m1	$a = 4.04$ $c = 9.76$ [79]	-
				2H-β	P6 ₃ mc	$a = 4.06$ $c = 19.48$ [79]	-
				3R-β	R3̄m	$a = 4.05$ $c = 29.41$ [111]	1.62* (D) 1.3 (D) [109]

Table 1.2: Structures and bandgaps of indium sesquiselenide (In_2Se_3). Calculated values are denoted by * and the nature of the bandgap is denoted by (D) = direct and (I) = indirect.

Chapter 2

Vapor-Phase Synthesis of Metal Chalcogenides

2.1 Synthesis of 2D materials

The synthesis of 2D materials can be achieved *via* two pathways: top-down and bottom-up. The top-down approach entails the separation of atomically-thin layers from a bulk crystal through mechanical or chemical exfoliation. Micromechanical exfoliation of 2D nanoflakes using scotch tape can yield high-quality monolayer single crystals up to microns in size but in minute quantities. While liquid-phase exfoliation (LPE) is scalable, the films assembled from the solution-processed flakes are generally thick (>100 nm) and of poor connectivity, which compromises the overall electronic quality of the films. As shown in Figure 2.1 for graphene products, the LPE of 2D materials has a role in the supply of low-cost 2D materials which is more or less orthogonal to bottom-up vapor-phase synthesis. Bottom-up vapor phase synthesis can yield wafer-scale ultrathin films of 2D materials with high quality, and is thus necessary for the technological realization of novel or high-performance electronic and optoelectronic applications. As reported by Lin *et al.*, only CVD-derived graphene films are currently used in transistor applications. For semiconducting 2D materials, vapor-phase

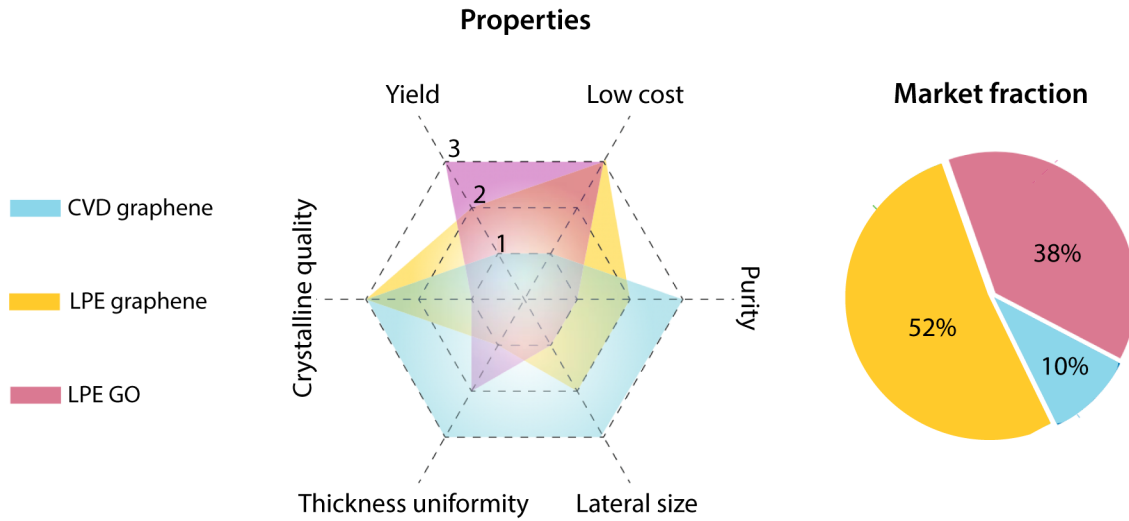


Figure 2.1: Attributes and market fraction of commercial graphene products by manufacturing technique. Left: Attributes of the graphene products obtained using CVD and LPE. Graphene oxide (GO) products, which are obtained using LPE are also included. The crystalline quality is evaluated in terms of defect density. The values of 1, 2, and 3 correspond to low, medium, and high levels, respectively. CVD and LPE yield products which are complementary in properties. Right: Market fraction of graphene products. Adapted from [7].

synthesis is even more crucial given the quality and homogeneity required for their anticipated electronic applications, many of which are transistor-based.

The vapor-phase synthesis of 2D materials entails the assembly of ultrathin films from precursors in the gas phase. Vapor-phase synthesis techniques include both physical and chemical vapor deposition processes, wherein gas-phase reactions form the basis of the latter but the not the former. A summary of the various synthesis techniques for 2D materials is depicted in Figure 2.2. Specifically, vapor-phase techniques include chemical vapor transport (CVT), physical vapor transport (PVT), CVD, ALD, MBE, and sputtering techniques such as PLD or magnetron sputtering. Additionally, the vapor-phase conversion of deposited films (*e.g.*, chalcogenization of transition metal or oxide films deposited using thermal evaporation) can also be considered a vapor-phase method, though the resulting films typically exhibit nanocrystallinity. There are also liquid-phase bottom-up methods such

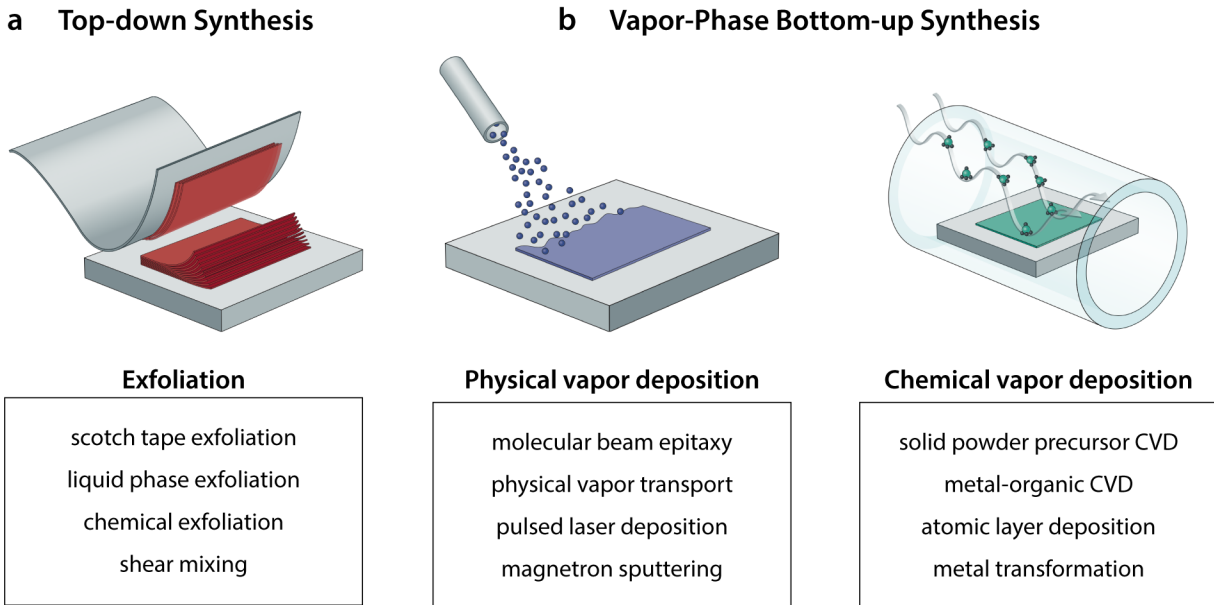


Figure 2.2: Summary of synthesis techniques for 2D materials. (a) Top-down synthesis methods are based on exfoliation from a bulk crystal. Techniques range from low-yield micromechanical exfoliation with scotch tape to shear mixing, which produces large volumes of exfoliated crystals. (b) Vapor-phase bottom-up synthesis methods, categorized by physical or chemical vapor deposition. Adapted with permission [112].

as colloidal synthesis,¹¹³ but they are not discussed in this document. The main advantages of vapor-phase deposition methods for 2D materials are the tunability, uniformity, continuity, and high quality of the synthesized films. As bottom-up approaches, these techniques also enable a higher level of control in the resulting films' properties but are correspondingly more difficult to develop and optimize due to a vast parameter space. Over the past 5 years, there have been significant advances in the vapor-phase synthesis of 2D semiconducting metal chalcogenides. Among them, the realization of wafer-scale monolayer molybdenum and tungsten dichalcogenides *via* metal-organic chemical vapor deposition (MOCVD) by Kang *et al.* stands out as an important step towards the technological implementation of 2D semiconductors.¹¹⁴ A remaining challenge is the achievement of self-limited monolayer TMD growth, which has been reported but requires further investigation.¹¹⁵

Additionally, when considering the vapor-phase deposition of 2D materials onto substrates, the conventional rules of 3D epitaxy do not necessarily apply. As vdW materials with no out-of-plane dangling bonds, the growth of 2D materials is facilitated by vdW epitaxy, which foregoes the strict lattice matching requirements for interfacing with a substrate. The implications of vdW epitaxy are significant; a plethora of heterostructures can be directly assembled regardless of lattice parameter compatibility.

2.2 Van der Waals epitaxy

In conventional 3D epitaxy, there are dangling bonds at the surface of the substrate or epilayer which result in a covalent bonding between the substrate and overlayer. Since lattices are rarely perfectly lattice-matched in heteroepitaxy, the deposited film is strained to adopt the periodicity of the substrate. In cases where the in-plane lattice constants are not too mismatched, the growth is pseudomorphic and accommodates the strain. Beyond a critical deposited film thickness, or for high misfits, the strain is relieved through the formation of dislocations which degrade the integrity of the interface and deposited crystal quality (Figure 2.3a). As a result, the range of high-quality heterostructures (*i.e.*, film-substrate pairings) is quite limited since the quality of the deposited crystals is highly dependent upon lattice compatibility.¹¹⁶

If the dangling bonds are passivated or absent, the film-substrate interaction is instead vdW in nature and can accommodate large lattice mismatches with an atomically abrupt and defect-free interface. Due to their lack of dangling bonds, the vapor-phase growth of 2D materials on various substrates proceeds *via* vdW epitaxy facilitated by a vdW gap (Figure 2.3b). This concept was detailed and demonstrated by Koma *et al.* in the mid 1980's.¹¹⁷ They obtained strain-free TMDs on both vdW substrates (*e.g.*, MoSe₂/mica, lattice mismatch of 58%) and quasi vdW adatom-passivated 3D substrates (*e.g.*, MoSe₂ on F-terminated

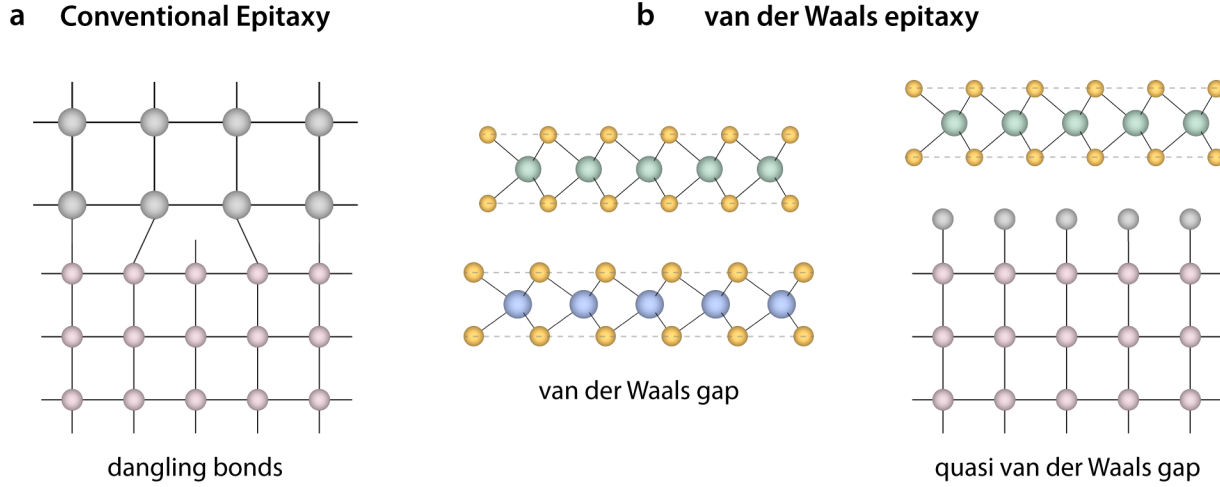


Figure 2.3: Conventional versus van der Waals epitaxy. (a) In conventional epitaxy, the dangling bonds at the film-substrate interface result in strain and defect formation. (b) In vdW epitaxy, the dangling bonds are absent, resulting in a vdW interaction and corresponding gap at the film-substrate interface. Quasi vdW epitaxial growth can also be achieved by passivating the dangling bonds of a 3D substrate. Adapted with permission from [117].

CaF_2 , lattice mismatch of 17%). VdW epitaxy accommodates more relaxed forms of registry such as rotational commensurability, wherein the lattices of two materials are rotationally aligned without requiring atomic coincidence. The alignment of crystallographic orientation in vdW heterostructures has been demonstrated between 2D materials with large lattice mismatches such as graphene/hBN,¹¹⁸ MoS_2 /hBN,¹¹⁹ MoS_2 /graphene,¹²⁰ WSe_2 /graphene,¹²¹ and GaSe/graphene.¹²² In the case of amorphous substrates, the growth is polycrystalline since no template is present to favor the nucleation of a particular orientation. However, 2D material growth can still proceed *via* Stranski-Krastanov (layer-plus-island) or Frank Van der Merwe (layer-by-layer) growth modes,¹²³ with domains sizes up millimeters in edge length.¹²⁴ In contrast, growth of 3D semiconductors on amorphous substrates is a challenge which requires complex schemes to steer away from disordered nanocrystalline growth.^{125–127} As a result, 2D materials can be directly assembled into diverse heterostructures without lattice matching constraints. Alternatively, the weak coupling between the 2D material and the

substrate also enables ease of transfer onto arbitrary substrates. These factors will facilitate their integration into existing 3D technologies.¹²⁸ Moreover, Kim *et al.* exploited vdW epitaxy for the growth of 3D crystals in a concept known as remote epitaxy.¹²⁹ The authors use a graphene layer to mediate the homoepitaxy of costly semiconductors films such as GaAs. By utilizing a single-crystal GaAs(001) substrate, single-crystal films of GaAs(001) can be grown through the monolayer graphene interfacial layer, which serves to then easily decouple the GaAs(001) epilayer for a target application. Hence, vdW epitaxy is a significant 2D material advantage that is accessible through vapor-phase growth.

2.3 The role of substrates in the vapor-phase synthesis of 2D materials

While the growth of 2D vdW materials is more flexible than conventional 3D materials, the role of the substrate is substantial. In fact, since the “bulk” of a 2D material is dominated by the surface, the interaction of the 2D material with its substrate can significantly alter its properties. The engineering of growth substrates is thus a critical area of development for 2D materials. The importance of growth substrates is dramatically illustrated by the synthesis of group III and group IV monoelemental 2D materials. In contrast to pure vdW materials, these materials (*e.g.*, borophene, silicene, germanene, stanene) require additional stabilization to obtain the metastable 2D polymorphs instead of the more stable non-layered bulk structures. Consequently, metal substrates have been the prolific substrate of choice. In a study by Gao *et al.* into the growth mechanism of silicene on Ag (111), the authors found that initial silicene clusters were stabilized by the Ag(111) surface as a result of the passivation of unsaturated edge Si atoms by the free electrons of the metal and the $p-d$ hybridization between inner Si atoms and the metal substrate.¹³⁰ Hence, strong film-substrate interactions are necessary to obtain the 2D structure in group IV elements.¹³¹ When weakly interacting vdW substrates are

used, the formation of silicon or germanium clusters is reported.^{132–134} While metal substrates can provide the strength of interaction necessary for the stabilization of 2D material growth, they can strongly perturb the intrinsic properties of the 2D material. In particular, group IV monoelemental 2D materials are predicted to exhibit 2D Dirac cones.^{135,136} However, the hybridization between the Ag(111) substrate and silicene film is believed to destroy the intrinsic Dirac-like cones in silicene,^{137–141} though the topic is still debated.¹⁴² Similarly, a computational study by Wang *et al.* suggests that many metal substrates destroy the Dirac cones in germanene,¹⁴³ and the conclusive experimental observation of Dirac-like cones in germanene has not been achieved. For the growth of borophene, the substrate is predicted to determine the polymorph of the obtained film.¹⁴⁴ In the case of borophene, it is not a templating mechanism, but rather the nature of the electrostatic interaction between the borophene layer and the substrate which dictates the systematic vacancy concentration (*i.e.*, structure) of the borophene. Hence, the substrate used in the vapor-phase synthesis of 2D materials can alter both their structure and intrinsic properties.

Through vdW epitaxy, substrates can be used to template the vapor-phase growth of 2D materials and even select among 2D polymorphs. As mentioned in section 2.2, graphene is a commonly-used six-fold symmetric substrate to template the growth of other hexagonal 2D materials such as the metal chalcogenides. Similarly, *c*-plane sapphire is also frequently used substrate to template hexagonal 2D TMDs^{145–147} or GIIIMCs¹⁴⁸ with rotational commensurability. In the group V monoelemental materials, and antimonene in particular, the substrate symmetry and strength of interaction has been leveraged to manipulate the synthesized polymorph. Three different polymorphs of antimonene were realized *via* the use of different substrates: hexagonally buckled Sb (space group $P\bar{3}m1$), asymmetric washboard Sb (orthorhombic space group $Pmn2_1$), and planar hexagonal Sb (space group $P6/mmm$). Many substrates with hexagonal symmetry have been used with vapor-phase synthesis to yield hexagonally buckled antimonene, including Bi_2Te_3 and Sb_2Te_3 ,¹⁴⁹ $\text{Ge}(111)$,¹⁵⁰ PdTe_2 ,¹⁵¹ Cu

(111),^{152,153} and graphene.¹⁵⁴ However, when a rectangular-latticed T_d -WTe₂ substrate was used, the orthorhombic asymmetric washboard polymorph of antimonene was formed.¹⁵⁵ Furthermore, when a more strongly interacting substrate such as Ag(111) substrate was used, planar hexagonal antimonene was reported.¹⁵⁶ Hence, the use of the growth substrate as a structural template is a promising method for stabilizing particular 2D materials structures.

Even in cases of minimal 2D material-substrate coupling, such as the placement of mechanically exfoliated flakes onto a substrate, the substrate can significantly affect the electronic properties of the material. This is exemplified by the sensitivity of 2D InSe charge carrier mobility to the nature of the substrate. The field-effect mobility of exfoliated InSe flakes on poly(methyl methacrylate) (PMMA) ($> 1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) was measured to be significantly higher than on Si_3N_4 , amorphous SiO_2 , or amorphous Al_2O_3 (50-200 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$).^{157,158} Similar trends were observed for exfoliated 2D MoS₂ on PMMA.¹⁵⁹ The increased mobility of PMMA is attributed to the reduction of interfacial Coulomb scattering sites. Indeed, the scattering of InSe charge carriers on SiO_2 worsens with decreased InSe thickness,¹⁵⁷ illustrating how the interface dominates the “bulk” behavior in 2D materials. In summary, the choice of substrate is critical and should be regarded as powerful degree of freedom in engineering 2D materials.

2.4 Chemical vapor deposition of metal chalcogenides

The most prevalent vapor-phase method for TMD synthesis is CVD. The development of CVD for 2D GIIMCs has also been pursued, but the results mostly fall short of the homogeneity and reproducibility required for academic research purposes. 2D InSe is especially difficult to synthesize using CVD due to its phase complexity, though attempts have been made. The work presented in Part III provides insight into the challenges of InSe synthesis and develops a physical vapor deposition (PVD) scheme using PLD (see subsection 2.5.1) to

realize ultrathin films of crystalline InSe. The CVD and MOCVD of 2D GaSe and In₂Se₃ has been more fruitful, but progress on that front is still years behind the TMDs.^{148,160} The following discussions on CVD will mostly focus on the TMDs.

2.4.1 Solid precursor chemical vapor deposition

The CVD of monolayer metal chalcogenides first originated in 2012 with a technique known as solid precursor CVD.¹⁶¹ In this method, the metal and chalcogen precursors consist of solid powders which are directly placed in the reaction zone. The powders are vaporized, react in the gaseous phase, and deposit on a substrate. This powder-based method is the one typically alluded to when discussing the “CVD” of TMDs. However, due to the development MOCVD for 2D TMDs in 2015, a distinction should be made. The powder-based CVD method is far more accessible than MOCVD, but has comparatively lower controllability, yield, homogeneity, and reproducibility. While the details of the solid precursor-based CVD method can vary, the approach used in our research lab and among several research groups utilizes solid powders of the metal oxide and pure chalcogen as precursors (Figure 2.4). For example, the CVD of monolayer MoS₂ can be achieved by evaporating sulfur powder from an upstream heating zone, which is carried downstream with an argon carrier gas to a heated MoO₃ source. Alternative metal sources include metal chlorides (*e.g.*, MoCl₅) or metal foils which are oxidized *in situ* to form metal oxides.¹⁶² TMD CVD setups can be operated at atmospheric or low pressures, though low pressures make the reaction more controllable.¹⁶²

Given the lack of *in situ* capabilities during CVD, the exact growth mechanism is not well-understood. Two proposed pathways include: (1) the adsorption of MoO_{3-x} species onto the substrate which then react with sulfur to form MoS₂ and (2) the direct reaction of MoO_{3-x} with sulfur in the gas phase, followed by adsorption and growth of MoS₂ clusters on the substrate.¹⁶³ Both are depicted in Figure 2.4. Subsequent studies point to the former as the favored pathway. In detail, the sulfur powder reduces the vaporized MoO₃ step-wise to

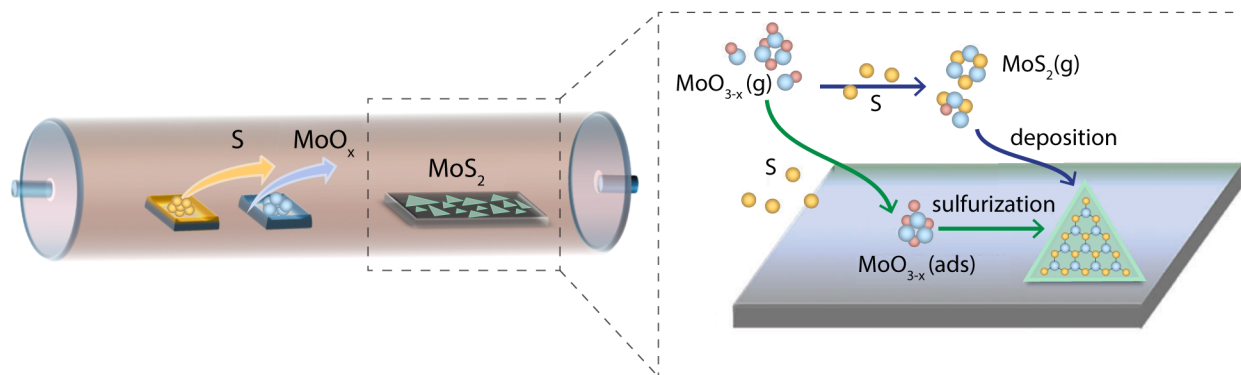


Figure 2.4: Solid precursor CVD of 2D MoS₂ and potential deposition mechanisms. Schematic of the CVD of 2D MoS₂ using sulfur and molybdenum oxide powders. Potential growth mechanisms are pictured on the right, which include reaction of MoO_x species with sulfur (1) on the substrate (green arrows) or (2) directly in the gas phase (blue arrows). The image on the left is adapted with permission from [123] and the one on the right is adapted with permission from [163].

form sub-oxides which condense on a substrate. These sub-oxide seeds act as nucleation sites and transition metal feedstocks for further growth/sulfurization.^{164,165} Solid precursor CVD is limited by the heterogeneity of its products, sometimes forming a mixture of MoS₂ and MoO_x suboxides with spatial variance so that only a small region on the substrate is covered in pure MoS₂.^{166–168} This is due to an inherent precursor concentration gradient due to the highly localized solid sources. These concentration gradients can be significantly improved using gaseous precursors (*i.e.*, MOCVD). However, powder-based CVD can still produce high-quality material for electronic and optoelectronic applications.^{169–172}

Several modifications to solid precursor CVD have been developed over the years. Firstly, the use of seeding promoter was reported shortly following the initial development of solid precursor CVD of TMDs. The most commonly used seed is perylene-3,4,9,10-tetra-carboxylic acid tetrapotassium salt (PTAS), which is reported to promote the growth of TMDs. However, there are many others which have been investigated.¹¹⁵ More recently, the use of alkali metal halides (*e.g.*, NaCl, KCl, KI) has become popular for obtaining layer-by-layer growth of TMDs. Several groups have reported large increases in single crystal domain size and

relative suppression of multilayer growth. Zhou *et al.* recently reported the synthesis of 47 TMD compounds, including those typically difficult to produce (*e.g.*, Nb or Pb dichalcogenides) by adding NaCl or KI to their metal oxide powder.¹²⁴ The authors attributed the successful synthesis of these materials to overall increase reaction rates due to lowered melting point of the reactants and improved intermediate product formation. However, the role of alkali metal halides is not well-understood, with several research groups reporting different mechanisms.^{115,173} Recently, Yang *et al.* used soda-lime glass to grow MoS₂ and reported dramatically increase monolayer single crystal domain sizes, which they attributed to the presence of sodium in the substrate released upon heating the substrate to near melting-point temperatures. This finding is supported by a preceding report of improved MoSe₂ synthesis on molten glass.¹⁷⁴ However, in the account by Chen *et al.*, the larger crystal domains were attributed to decreased nucleation sites due to a molten substrate surface. Yang *et al.* also claimed that the growth is self-limited due to quenching of the sodium source by the deposited MoS₂.¹⁷⁵ Since attempts at reproducing this effect have not been fruitful in our research lab, further work is necessary to evaluate the prospect of alkali metal halides in the quest for self-limited growth of TMDs. Additional attempts at self-limited CVD-growth of TMDs include the use of Au foil substrates for WS₂ growth¹⁷⁶ and the introduction of Cu atoms to quench the active reaction sites on the surface of WSe₂ and promote edge attachment.¹⁷⁷ For the use Cu or alkali metal halides additives, it is unclear how the presence of these extraneous elements affects the resulting quality and if they will ultimately hinder the achievement of wafer-scale electronic grade TMDs. A report by Zhang *et al.* on the effects of NaCl in the MOCVD of MoS₂ suggests that its use results in significant electronic and optical heterogeneities of the films¹⁷⁸ while the work of Kang *et al.* does not indicate such issues.¹¹⁴ Consequently, the use of alkali metal halides and the self-limited CVD growth of TMDs is a research direction which requires more attention.

2.4.2 Metal-organic chemical vapor deposition

In 2015, Kang *et al.* reported the MOCVD of the monolayer TMDs of MoS₂ and WS₂.¹¹⁴ In comparison to solid precursor CVD, MOCVD provides much better control over the growth of metal chalcogenide layers in addition to improved scalability. This is due to the supply of precursors being introduced in the gaseous phase, instead of using solid sources. For the MOCVD of TMDs, the transition metal precursor is usually the metal hexacarbonyl (*e.g.*, Mo(CO)₆) or metal chloride (*e.g.*, (MoCl₅)₂) while the chalcogen precursor is a chalcogen hydride (*e.g.*, H₂S) or chalcogen containing organic compound (diethyl sulfide (C₂H₅)₂S).¹⁷⁹ At ambient conditions, none of these precursors are in the gas phase. However, they have high vapor pressures which allows them to be carried into the reaction chamber *via* a carrier gas which bubbles through the precursor. The concentration of the precursors in the chamber can thus be carefully controlled using the precursor bubbler temperature, pressure, and carrier gas flow rate.

The precursors used for MOCVD by Kang *et al.* in the Park Research Group at the University of Chicago, as well as in our lab, are Mo(CO)₆ and diethyl sulfide. Using these precursors, Kang *et al.* demonstrated wafer-scale growth of high-quality monolayer MoS₂ (field-effect mobility of 30 cm²V⁻¹s⁻¹) with precise control over coverage and lateral domain sizes (hundreds of nanometers to 10 μm). A schematic of an MOCVD setup and images of MOCVD-grown MoS₂ are shown in Figure 2.5. The monolayer TMD films can then be transferred to arbitrary substrates due to weak vdW coupling to the substrate. Kang *et al.* demonstrated multilayer heterostructures of artificially stacked TMDs (*e.g.*, MoSe₂/MoS₂/WS₂) using a vacuum-assisted transfer method.¹⁸⁰ To achieve layer-by-layer growth, the authors had to use slow deposition rates, requiring a total deposition time of >26 hours for a monolayer. Further optimization reduced the time to ~10 hours. Notably, the Park Research Group uses NaCl in their MOCVD process, while the Redwing Research Group

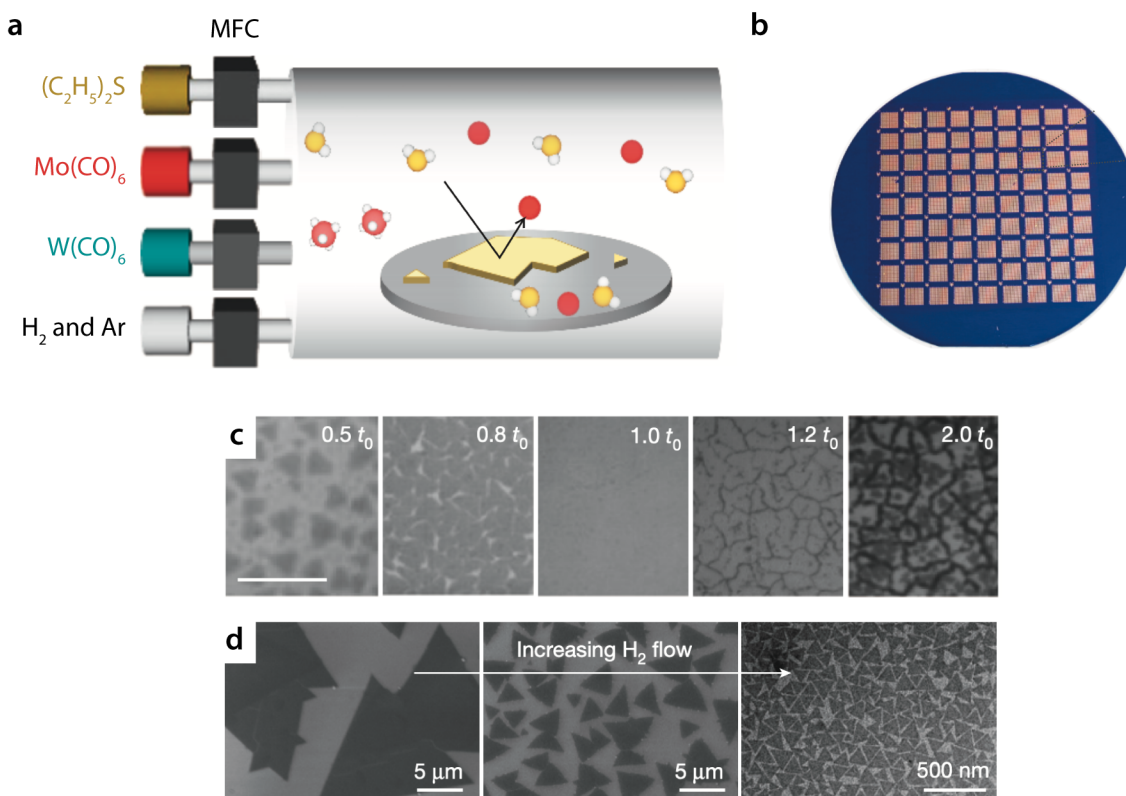


Figure 2.5: Metal-organic chemical vapor deposition of 2D TMDs. (a) Schematic of an MOCVD setup where the input of precursors into the reaction chamber is in the gaseous phase and is controlled using mass flow controllers (MFCs). (b) Picture here are 8,100 FETs fabricated from monolayer MoS₂ deposited using MOCVD over an entire 4-inch wafer. (c) Optical images of MoS₂ grown on SiO₂ using MOCVD at various growth times, where t_0 was the deposition time for a continuous monolayer. The scale bar is 10 μm . (d) scanning electron microscopy (SEM) images of the sizes of single-crystal monolayer MoS₂ domains grown on SiO₂ using MOCVD. The grain size can be varied using the H₂ flow into the reaction chamber. All of the figures are reproduced or adapted from [114].

and her 2D Crystal Consortium at Penn State do not. Furthermore, Zhang *et al.* from the Redwing Research Group use cold-wall MOCVD reactors which reduce parasitic deposition on chamber walls by only heating the substrate using a susceptor.¹⁴⁵ As presented in their report, the authors developed a multi-step growth procedure which results in a full monolayer of WSe₂ on sapphire in 45 minutes. Their procedure entails specific steps targeting (1) nucleation, (2) ripening of nuclei, and (3) lateral growth from ripened nuclei. The multi-step procedure is

enabled by the control of precursor flow, which illustrates the enhanced controllability of this technique. Fine control is further underscored by the work of Xie *et al.*, in which the authors alternate between precursors to build in-plane atomically-detailed superlattices of WS₂ and WSe₂.¹⁸¹ More recently, Zhang *et al.* also demonstrated the MOCVD of 2D β -In₂Se₃ on sapphire.¹⁴⁸ Their work provides a substantial improvement over previous demonstrations of the MOCVD of indium chalcogenide thin films,¹⁸² and indicates that MOCVD is a promising method for other 2D metal chalcogenides.

The increased capabilities of MOCVD also come with increased cost and safety concerns. Currently, the number of research groups with access to this technique is still quite limited due to the high cost of the equipment and accompanying safety mechanisms. In particular, several of the precursors are pyrophoric or toxic. While these concerns make the MOCVD of metal chalcogenides less accessible, it is the most promising pathway to the synthesis of high-quality 2D semiconductors on a technologically relevant scale. Given that the MOCVD of 2D metal chalcogenides has only been pursued for 5 years, and that few research groups can undertake it, there is still much work to be done on this front.

2.5 Physical vapor deposition of metal chalcogenides

PVD techniques entail the removal of atoms from a solid or liquid source material into vapor form, followed by transport of the vaporized species to a substrate where it condenses. While chemical reactions can occur in PVD processes, the general process is encompassed by a physical process of a solid-vapor-solid transformation, rather than the chemical transformations in CVD. The vaporization of condensed sources is can be achieved through thermal heating (*e.g.*, Knudson cell) or ablation (*e.g.*, laser heating or ion bombardment).^{183,184} Since PVD processes do not rely on chemical transformations, the control over the phase and purity of the films can be easier than with CVD. Furthermore, some PLD techniques (*e.g.*, PLD) can

access metastable structure away from chemical or thermal equilibrium.

(borophene)¹⁴ and non-carbon group IV elements (*e.g.*, silicene,¹⁶ germanene,¹⁷ stanene,¹⁸), which do not form bulk la

PVD includes processes such as MBE, PLD, sputtering, PVT, and thermal evaporation in vacuum. The use of MBE has been crucial for the development of synthetic 2D materials such as borophene,¹⁴ silicene,¹⁶ germanene,¹⁷ and stanene¹⁸ MBE uses high-purity source materials to grow thin films in an ultra-high vacuum (UHV) environment. For binary compounds, the elemental sources are usually decoupled, giving great precision over the film's composition. As a result, MBE is a highly controlled deposition method which can produce high-quality 2D materials. MBE has been used to synthesize several 2D TMDs,¹⁸⁵ as well as InSe,¹⁸⁶ GaSe,^{187–191} and GaTe.¹⁹² However, the UHV and source purity constraints make MBE technologically impractical due to high cost and low yield. For the synthesis of 2D GIIMCs, and especially the monochalcogenides, the use of PVT is prevalent. Since PVT does not rely on careful stoichiometric tuning of the reactants, it has been more commonly reported than CVD. In this technique, researchers have used stoichiometric powders of GaSe, GaTe, and InSe to yield 2D crystals of GaSe,^{122,193–196} GaTe,^{197–199} and InSe,^{70,200} respectively, though some also use a small amount of Ga₂Se₃ or Ga₂Te₃ to counteract chalcogen loss. However, the monochalcogenide films resulting from PVT suffer from inhomogeneities and poor coverage. Similar to solid-precursor CVD, the localized solid sources create an inherent precursor concentration gradient which makes phase control more difficult.

Alternatively, the PVD of metal chalcogenides can also be achieved using ion impact (*i.e.*, sputtering) or laser ablation (*i.e.*, PLD). Specifically, magnetron sputtering has been used to grown 2D materials such as hBN²⁰¹ and Mo and W dichalcogenides^{202–204} with high deposition rates and low growth temperatures.^{185,205} However, the thickness control and crystallinity of the resulting materials are poor. On the other hand, PLD enables great thickness control and has been reported to yield 2D materials with good crystallinity.

2.5.1 Pulsed laser deposition

PLD is a PVD technique in which a pulsed high-power laser is incident on a solid target, ejecting a vaporized plume of ions and atoms which condense on a substrate in front of the target. A schematic of the process is shown in Figure 2.6. When a high intensity laser pulse is incident on the target, a plasma is generated from the ionization of the target material, resulting in ablated species between 1 eV and 100 eV in kinetic energy. The composition of the ejected material plume can be complex, including ionic species, electrons, and neutral atoms or clusters. Due to the energetic ablation process, the vaporized material condenses on the substrate with substantial kinetic energy, even with the substrate at room temperature. The substrate temperature can be adjusted to manipulate the structure of the resulting film from amorphous to crystalline. PLD takes place in a high vacuum chamber, though inert or reactive gases can be introduced to further control the deposition.

One of the greatest strengths of PLD is the ability for congruent material transfer, meaning that the stoichiometry of the target is translated to the stoichiometry of the deposited film. For this reason, PLD has been successfully employed for the deposition of multielemental films such as complex oxides^{206–208} and ceramic superconductors.^{209,210} However, congruent deposition is not guaranteed and sometimes requires enriching of the target with elemental components to achieve the desired film composition. Additionally, PLD is applicable to many materials since almost any solid can be ablated. The method also has fine control over the resulting film thickness *via* the number of pulses and can yield highly homogeneous films over large areas ($> 1 \text{ cm}^2$). An important distinction of PLD from many of the previously discussed methods is that the high-energy plasma generation shifts the reaction away from thermal/chemical equilibrium to access metastable structures.^{211–215} The vaporized material and the substrate temperatures can be vastly different. This is in direct contrast to CVD, where all the degrees of freedom are at the same temperature.

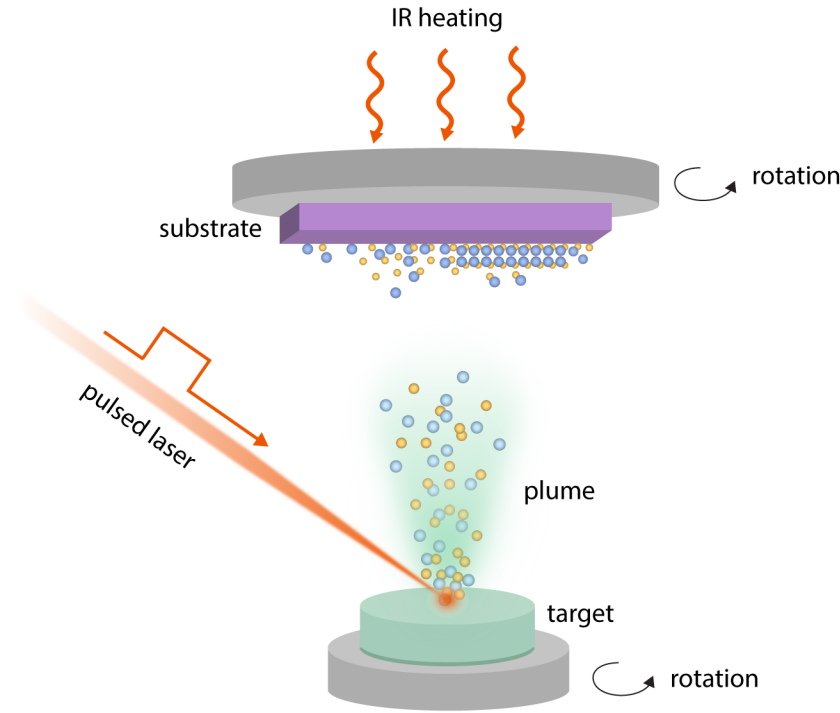


Figure 2.6: Schematic of pulsed laser deposition. PLD is a PVD process in which a high-power pulsed is focused onto a solid target. Incoming laser pulses locally heat the target and eject a plume of material which condenses on a substrate facing the target. The deposition is performed in high vacuum and the substrate can be heated using IR irradiation. The target and substrate are rotated to ensure even deposition.

PLD has been successfully applied to several 2D materials. The use of PLD for the synthesis of MoS₂ thin films dates back to 1988²¹⁶ but has only recently been tailored for atomically-thin deposition on metallic and insulating substrates. The PLD of graphene was first accomplished in 2005,^{217–221} prior to the optimization of the graphene CVD process. The list of 2D materials which have been successfully synthesized by PLD includes hBN,^{217,222} MoS₂,^{223–226} WS₂,^{227–229} WSe₂,^{230,231} WTe₂,²³² ReS₂,²³³ GaSe,²³⁴ InSe,^{235,236} and black phosphorus.²³⁷ However, many of these efforts report amorphous or nanocrystalline films. The morphology of PLD-derived 2D material films is far from CVD-derived TMD growth. PLD-grown single-crystalline films have been obtained in the past for bulk materials, but the quality of the films is highly dependent on the experimental parameters. In particular, the substrate temperature, target-substrate

distance, chamber pressure, and several laser source parameters (*e.g.*, laser wavelength, laser fluence, pulse frequency, etc.) all have significant effects on the resulting film and require optimization for each material. Furthermore, in most reports of 2D metal chalcogenide PLD synthesis, there is significant loss of chalcogen, requiring the addition of the chalcogen into the target or post-growth annealing in a chalcogen-rich environment. Hence further work is necessary to assess the prospect of PLD in the scalable and high-quality synthesis of 2D metal chalcogenides. PLD may be particularly useful for 2D materials which are hard to produce *via* CVD, as is the case with the GIIIMCs which exhibit a range of stoichiometries and suffer from poor synthetic phase control.

Chapter 3

Phase Control in Group III Metal Chalcogenides

Since the GIIIMCs can exhibit structural and compositional variety, a discussion on the current methods available to control the phases of GIIIMCs is warranted. In particular, as will be explored in Part III, the indium-selenium phase space is especially complex, including many stable compositions (*e.g.*, In_4Se_3 , InSe , In_6Se_7 , $\text{In}_9\text{Se}_{11}$, In_5Se_7 , In_2Se_3), many of which with their own polymorphic structural variations.^{238,239} In contrast, the accessible compositions for transition metal chalcogenides, especially those based on Mo and W, are more limited and the polymorphic variations are more energetically distinct.^{240–242} The challenge of vapor-phase synthesis in GIIIMCs is therefore largely one of phase control.

3.1 Synthesis conditions

Due to competing polymorphs and stoichiometries, small changes synthesis conditions can significantly affect the phase of the resulting GIIIMC. In a study by Huang *et al.*, the successful CVD of 2D InSe was restricted to a narrow region with low Se sublimation temperature and high H_2 content in an Ar carrier gas (Figure 3.1a).⁶⁸ The excess of Se from high sublimation temperatures favors the formation of In_2Se_3 , as does the absence of H_2 . However, too low

a concentration of Se, or too high a concentration of H_2 , results in poor quality growth. Especially for the indium-selenium system, it is common to observe the formation of different compositional phases and the reaction temperature is one of the primary parameters used to control the phase of the deposited material. This method of control is well illustrated by the work of Balakrishnan *et al.*, wherein four different phases of indium chalcogenides are obtained by varying the PVD growth temperature.²⁰⁰ They exploit the temperature gradient of a tube furnace to obtain nanoscale thickness γ - In_2Se_3 (a nonlayered polymorph), β - In_2Se_3 , α - In_2Se_3 , and 3R- $InSe$ along a substrate temperature gradient of 580 °C to 500 °C. It is important to note here that there is also an implicit precursor concentration gradient in the PVD method used. Similarly, the CVT of 2D $2H_c$ - $InSe$ on mica was achieved using a substrate temperature of 400°C while 2D α - In_2Se_3 was obtained at 450 °C.²⁴³ Both of these reports suggest a narrow temperature region in which these varied structures can be obtained, which illustrates the difficulty in achieving single-phase growth. In the MBE of 2D GaSe, higher temperatures of 575 °C resulted in pure epitaxial $2H_b$ -GaSe on GaN while lower temperatures improved continuity of the films but resulted in a mixture of $2H_b$ -GaSe and $2H_c$ -GaSe.¹⁹⁰ This behavior is consistent with reports that the $2H_b$ polytype of GaSe is more stable than $2H_c$ -GaSe.²⁴⁴ Similarly, h -GaTe is metastable²⁴⁵ but can be obtained using PVD on mica at lower temperatures (600 °C) than the more stable m -GaTe polymorph obtained at 760 °C.¹⁹⁹

A recent report on the CVD of indium chalcogenides demonstrates the combination of various parameters to target specific polymorphs. Using both a higher temperature for the In source (In_2O_3) and substrate, Liu *et al.* obtained nanoscale structures of 2H α - In_2Se_3 on SiO_2 at upstream substrate positions and γ - In_2Se_3 when the substrate was positioned further downstream.⁷⁹ By decreasing the temperature of the In source and substrate by ~ 100 °C, 1T β - In_2Se_3 was obtained. By switching the substrate to HOPG under those same conditions, 2H β - In_2Se_3 was synthesized. However, a precise level of control over these In_2Se_3 polymorphs

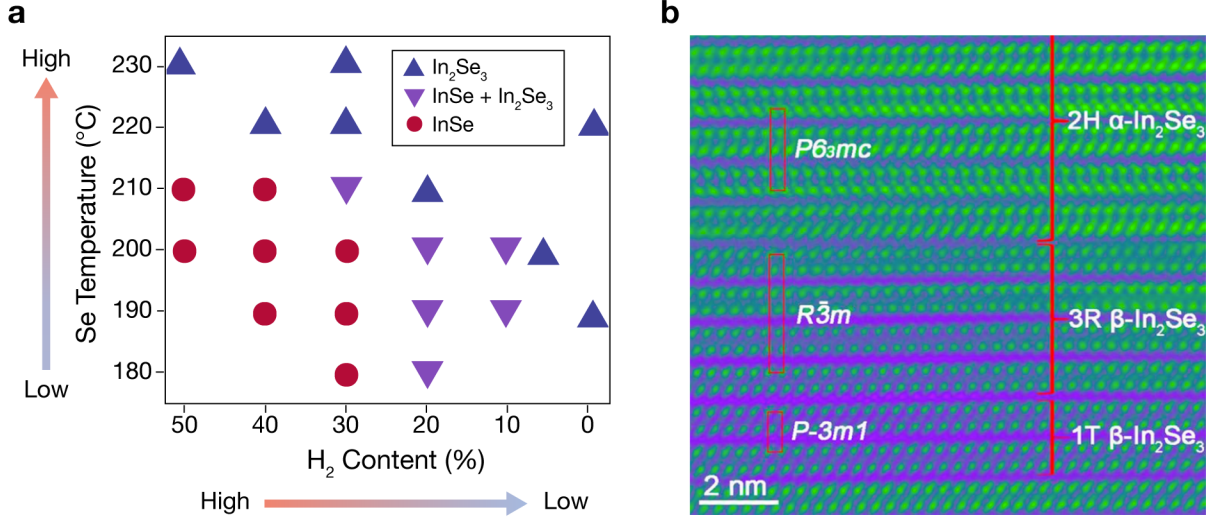


Figure 3.1: Synthesis-based polymorphic control in 2D GIIIMCs.(a) Synthesis conditions for the CVD growth of InSe and In₂Se₃. InSe is favored at low Se sublimation temperatures and high H₂ concentrations while In₂Se₃ is favored in the absence of H₂ with high Se sublimation temperatures. The plot is adapted with permission from [68]. (b) Atomic scale high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM) image of the coexistence of α-In₂Se₃, β-In₂Se₃, and their stacking polytypes in a crystal synthesized *via* CVD. The image illustrates the difficulty in obtaining phase-pure In₂Se₃. The image is reproduced with permission from [79].

and polytypes is difficult to achieve. As demonstrated in Figure 3.1b, the CVD of In₂Se₃ on SiO₂ can result in a mixture of 1T β-In₂Se₃, 3R β-In₂Se₃, and 2H α-In₂Se₃ in a single crystal, presenting a challenge for the development more stringent structural control in the growth of GIIIMCs.

The cooling rate of materials grown at high temperatures can also affect the ultimate structure of the 2D crystals. In a report on the CVD of 2D In₂Se₃ by Cui *et al.*, slow cooling (0.1 °C/min) favored the formation of α-In₂Se₃ in comparison to β-In₂Se₃.⁶¹ Crystals synthesized with fast cooling were instead dominated by β-In₂Se₃. This result is consistent with previous accounts of β-In₂Se₃ as a high-temperature phase of α-In₂Se₃, which reverts back to α-In₂Se₃ in the bulk.²⁴⁶ In combination with a 2D thickness effect,⁹¹ quenching may help to stabilize the high-temperature form at room temperature. Similarly, Lin *et al.*

observed that slow cooling rates (<5 °C/min) following PVD resulted in α -In₂Se₃ while fast cooling rates (>100 °C/min) resulted in the formation of an In₂Se₃ superlattice phase.²⁴⁷ This superlattice phases resembles a structure later reported as a β -In₂Se₃ superstructure^{80,83} and exhibits metallic rather than the semiconducting behavior expected for β -In₂Se₃.

3.2 Substrates

The substrate used in the synthesis of 2D GIIMCs can have a significant influence on the resulting structure. By using *c*-plane sapphire and Si(111) substrates in the MOCVD of In₂Se₃, Zhang *et al.* obtained epitaxial 2D β -In₂Se₃.¹⁴⁸ In contrast, the authors obtained a nonlayered γ -In₂Se₃ phase when using an amorphous SiO₂ substrate. Similarly, Bae *et al.* attributed the formation of *h*-GaTe on GaAs(001) *via* MBE to the better match in symmetry of the GaAs(001) surface to the *h*-GaTe structure rather than *m*-GaTe.¹⁹² However, upon further GaTe deposition, the additional growth is monoclinic, presumably due to relaxation of the structure into its more stable form as the epitaxial strain located to the interface with GaAs is diminished. Despite the existence of a quasi vdW gap, Yonezawa *et al.* reported the observation of GaSe on Ge(111) with an alternative structure to the InSe-type structure (also referred to as “wurtzite-like”) typically observed.²⁴⁸ Instead, the GaSe layers near the interface with a Ge(111) substrate showed a zinc blende-like structure where the top and bottom Ga-Se bonds point in opposite directions. The authors thus make the case that despite the vdW gap, the substrate can still significantly influence the structure of the deposited 2D material. Structural preferences can also be affected by substrate pre-treatments. As reported by Diep *et al.*, the direct deposition of GaSe *via* MBE on GaAs(001) favors the 2H_b (ϵ) polytype of GaSe.¹⁸⁹ By pre-treating the surface of the GaAs with selenium, the authors instead grow the 2H_c (β) polytype.

3.3 Post-synthesis processing

The processing of 2D GIIMCs after synthesis is a frequently used method of polymorph conversion. In particular, thermal annealing is a prevalent way to transform one 2D GIIMC into another. By annealing at $\sim 350^\circ\text{C}$ in argon, Tao and Gu converted exfoliated $\alpha\text{-In}_2\text{Se}_3$ into $\beta\text{-In}_2\text{Se}_3$.⁹¹ In the bulk, the high temperature $\beta\text{-In}_2\text{Se}_3$ phase would normally revert back into $\alpha\text{-In}_2\text{Se}_3$,²⁴⁶ but this study suggests that the nanoscale thickness of the crystal may stabilize the metastable phase at room temperature. Tao and Gu observed that the annealing temperature required for the phase transformation demonstrated a clear thickness-dependence, with higher temperatures required for thinner crystals. Furthermore, a dramatic decrease in resistivity is accompanied with the conversion into $\beta\text{-In}_2\text{Se}_3$. This result was corroborated by Feng *et al.*⁹² The authors followed the same procedure to obtain higher charge carrier field-effect mobilities ($18\times$ greater) and better photodetector performance from multilayer $\alpha\text{-In}_2\text{Se}_3$ converted to $\beta\text{-In}_2\text{Se}_3$. A similar large increase in current was observed, but the $I_{\text{on}}/I_{\text{off}}$ ratio was severely compromised due to metallic behavior. This behavior was also observed in exfoliated 2D $2\text{H}_c\text{-InSe}$ processed *via* thermal annealing. Feng *et al.* annealed 2D $2\text{H}_c\text{-InSe}$ at $\sim 350^\circ\text{C}$ in an H_2 /argon reducing atmosphere and demonstrated an increased mobility ($4\times$ greater) and photoresponsivity, but orders of magnitude lower $I_{\text{on}}/I_{\text{off}}$ ratio. In this report, Feng *et al.* determined the effect to be the result of the formation of an InSe superlattice. Thus, it is also possible that previous reports on the formation of metallic phases in In_2Se_3 are also attributable to a superstructure. In contrast, a prior report by Osman *et al.* on annealed 2D $2\text{H}_c\text{-InSe}$ instead found degradation of the mobility ($4\times$ lesser) and photodetector performance.²⁴⁹ In this case, the exfoliated $2\text{H}_c\text{-InSe}$ was annealed at $200\text{-}400^\circ\text{C}$ in an argon atmosphere without H_2 and resulted in partial conversion of the InSe to $\gamma\text{-In}_2\text{Se}_3$. Some phase transitions can also be monitored using the SHG signal intensity. This has been demonstrated for the conversion of noncentrosymmetric $\alpha\text{-In}_2\text{Se}_3$ to

centrosymmetric β -In₂Se₃. Xiao *et al.* observed the dramatic decrease of SHG signal intensity during annealing of a 4-layer thick exfoliated α -In₂Se₃ crystal to 427 °C⁸⁷ and Xue *et al.* observed a similar decrease after annealing a thick exfoliated α -In₂Se₃ crystal to 300 °C.⁸⁸ In addition to thermal annealing, laser annealing can be used to induce a phase transformation and holds the considerable advantage of patternable conversion. As shown in Figure 3.2a, Yu *et al.* demonstrated this concept using a femtosecond laser to partially convert *h*-GaTe into *m*-GaTe,¹⁹⁹ the more stable polymorph.²⁴⁵

Cooling can also lead to structural phase transformations in the 2D GIIMCs. Zhang *et al.* recently reported the reversible phase conversion between β -In₂Se₃ at room temperature and a distorted β' In₂Se₃ structure at 77 K.⁸³ As shown in the STM images of Figure 3.2b, the hexagonal lattice of β -In₂Se₃ transforms to a rectangular lattice at low temperatures. The hexagonal lattice is recovered upon warming to room temperature. A subsequent report by Dong *et al.* of β -In₂Se₃ grown on WS₂ demonstrated the thickness dependence of the phenomenon, with the transition temperature increasing with an increasing number of layers.⁸⁴

3.4 Thickness

Another factor which controls the structure of 2D GIIMCs is the thickness of the material. Upon exfoliation of bulk *m*-GaTe crystals, Zhao *et al.* observed its spontaneous transformation into *h*-GaTe.²⁵⁰ As shown in Figure 3.1c, the selected area electron diffraction (SAED) of the bulk GaTe and exfoliated 2D GaTe are of a monoclinic and hexagonal lattice, respectively. They found the transformation occurred below a critical thickness of 4 layers. Zhao *et al.* perform first-principles calculations which support the explanation that the transformation occurs due to the balance between the interlayer interactions and surface energy shifting toward *h*-GaTe as the surface energy contribution becomes more dominant in thinner layers.

3.5 Application of external forces

The application of hydrostatic pressure is a common method used in bulk crystals to observe various polymorphs in GIIIMCs. However, there are few of accounts on the use of pressure on 2D GIIIMCs. Su *et al.* recently used hydrostatic pressure to alter the symmetry of 2H_b-InSe.²⁵¹ They observed a continuous transition from three-fold symmetry to mirror symmetry as a hydrostatic pressure of up to 8.2 GPa was applied. The symmetry was monitored *via* the polarization of the SHG signal from the 2D 2H_b-InSe sample and was found to be reversible upon return to atmospheric pressures. Su *et al.* attribute the change in symmetry to the sliding of adjacent InSe layers under pressure. Furthermore, the application of a current can also be used to control between GIIIMCs polymorphs. Choi *et al.* demonstrated that reversible conversion between β -In₂Se₃ and γ -In₂Se₃ can be driven electrically due to Joule heating,²⁵² which follows previous understanding of γ -In₂Se₃ as a high-temperature phase of β -In₂Se₃.²⁴⁶ Starting with an exfoliated α -In₂Se₃ crystal, the device was annealed to 250 °C to convert the crystal to β -In₂Se₃. Pulses of 3 V and 0.7 V were then used to RESET or SET the device into its low (β -In₂Se₃) and high resistance (γ -In₂Se₃) states, respectively. Lastly, a report by Kou *et al.* presents that electrostatic forces, or charge doping, could be used to stabilize yet unrealized polymorphs of InSe with different intralayer structures.⁵⁹

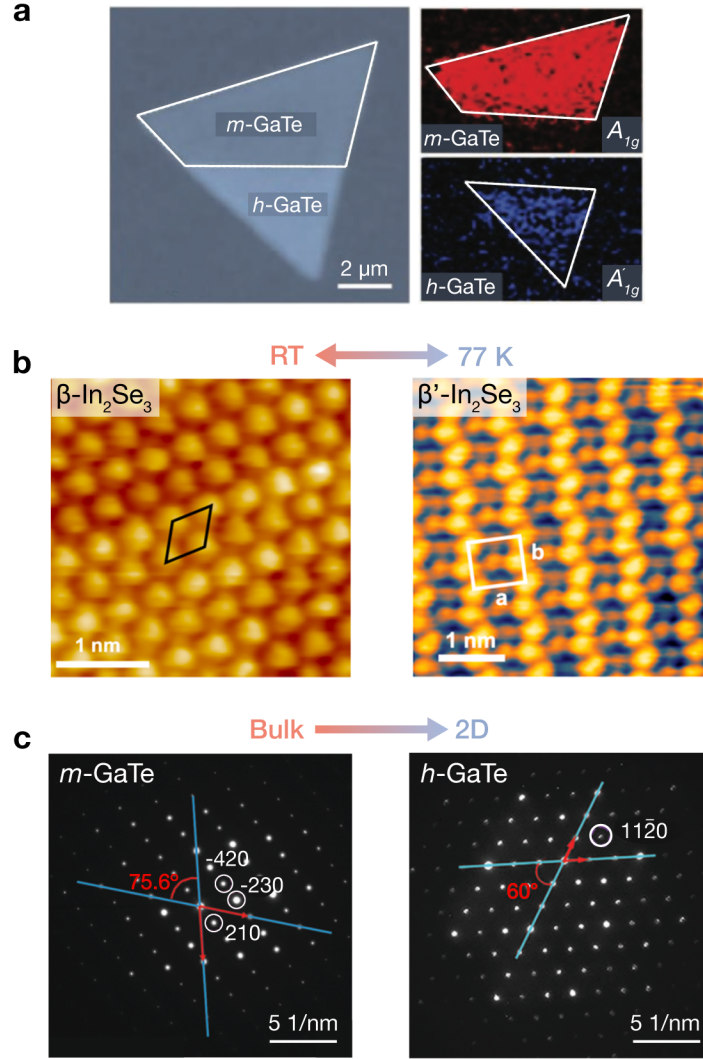


Figure 3.2: Non-synthesis-based methods of polymorphic control in 2D GIIMCs.

(a) The laser-induced transformation of a section of a monolayer h -GaTe crystal to m -GaTe. Left: optical microscopy image of the partially converted monolayer h -GaTe domain. Right: Raman spectroscopy maps of the two domains in the optical microscopy image, showing significant m -GaTe A_g Raman mode signal in the converted region (top) and h -GaTe Raman A'_g Raman mode signal in the pristine region (bottom). The images are adapted with permission from [199]. **(b)** Scanning tunneling microscopy (STM) image of exfoliated β - In_2Se_3 at room temperature (RT) (left) and distorted β' - In_2Se_3 at 77 K (right). The temperature-driven transformation is observed to be reversible. The images are adapted with permission from [83]. **(c)** The thickness-induced transformation of m -GaTe to h -GaTe upon exfoliation down to a few layers. The SAED patterns of the bulk (left) and exfoliated (right) crystals show the patterns expected for m -GaTe and h -GaTe, respectively. The images are adapted with permission from [250].

Part II

Hybrid MoS₂/Al₂O₃ Heterostructures for Low-Power Electronics

Chapter 4

Introduction

2D semiconducting materials have attracted significant interest for both high-performance and low-power electronic applications.^{253,254} Among the 2D TMDs, MoS₂^{13,255} has been specifically identified as a promising candidate for low-power devices.^{20,21,256,257} MoS₂ FETs exhibit high field-effect mobilities (30-480 cm²V⁻¹s⁻¹),^{114,159,169,258,259} high current on/off ratios (10⁸-10⁹),^{170,260} and low sub-threshold swings ($\sim$ 70 mV/decade) at room temperature.²⁵⁷ Moreover, the large-area synthesis of monolayer MoS₂ *via* chemical vapor deposition (CVD)^{161,171,261} and MOCVD¹¹⁴ provides a pathway to wafer-scale TMD-based circuitry. A crucial next step is the integration of 2D semiconductors with functional bulk materials for hybrid 2D/3D heterostructures.¹²⁸ In this work, 2D MoS₂ is integrated with a 3D high- κ dielectrics, an essential class of materials for low-power electronics, for a functional hybrid 2D/3D heterostructures targeted toward low-power FETs.

The synthesis and processing of new materials for low-power electronics is guided by key transistor figures of merit such as the threshold voltage V_{TH} , sub-threshold swing SS, and current I_{on}/I_{off} ratio.^{253,256,262} For modern complementary metal-oxide-semiconductor (CMOS) digital electronics, low power consumption is enabled by enhancement-mode devices that have minimal off-current at zero gate bias (*i.e.*, I_{off} is defined as the current at zero gate voltage).^{253,263} The CMOS I_{on}/I_{off} ratio is a relevant low-power electronics metric that

evaluates device performance while taking into account the standby power consumption. The optimization of CMOS performance metrics is achieved by integrating appropriately doped semiconducting materials with high- κ ultrathin dielectrics. Kim *et al.* demonstrated MoS₂/high- κ dielectric FETs by transferring micromechanically exfoliated MoS₂ onto 50-nm-thick amorphous Al₂O₃ grown by ALD, resulting in mobilities $> 30 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $I_{\text{on}}/I_{\text{off}}$ ratios $> 10^3$, and sub-threshold swings of $\sim 70 \text{ mV/decade}$.²⁵⁷ However, micromechanical exfoliation of MoS₂ is not suited for large-area processing. Instead, the integration of monolayer MoS₂ with ultrathin high- κ amorphous oxides must be pursued through scalable vapor-phase synthesis pathways.

As illustrated in Figure 4.1, there are several potential tactics based on vapor-phase methods to combine 2D MoS₂ with high- κ dielectrics. Most literature reports of 2D MoS₂/high- κ dielectric FETs have employed the first tactic: deposition of the high- κ material on top of the MoS₂ as a functional top-gate dielectric.^{264–267} Alternatively, some researchers have opted to transfer the MoS₂ onto the dielectric layer in a bottom-gate configuration.^{257,268} However, these aforementioned methods lack of control over MoS₂ doping, and thus the FET threshold voltage. For example, the growth of high- κ dielectrics on top of monolayer MoS₂ strongly increases electron doping and induces large negative shifts in V_{TH} , which significantly increase CMOS power consumption.^{265,269,270} Meanwhile, transfer processes lead to not only structural defects and wrinkles in the MoS₂ monolayer but also uncontrolled doping from processing residues.^{159,271,272}

In contrast to these previously established tactics, the capability of 2D materials for vdW-interfaced growth presents a third option: direct growth of the 2D semiconductor onto amorphous substrates. This tactic is not readily available for conventional 3D semiconductors due to dangling bonds which promote covalent bonding to the substrate. Direct growth of 3D semiconductors on amorphous substrates is sought-after but requires complex growth schemes and the results are generally nanocrystalline.^{126,127} Due to the lack of dangling bonds,

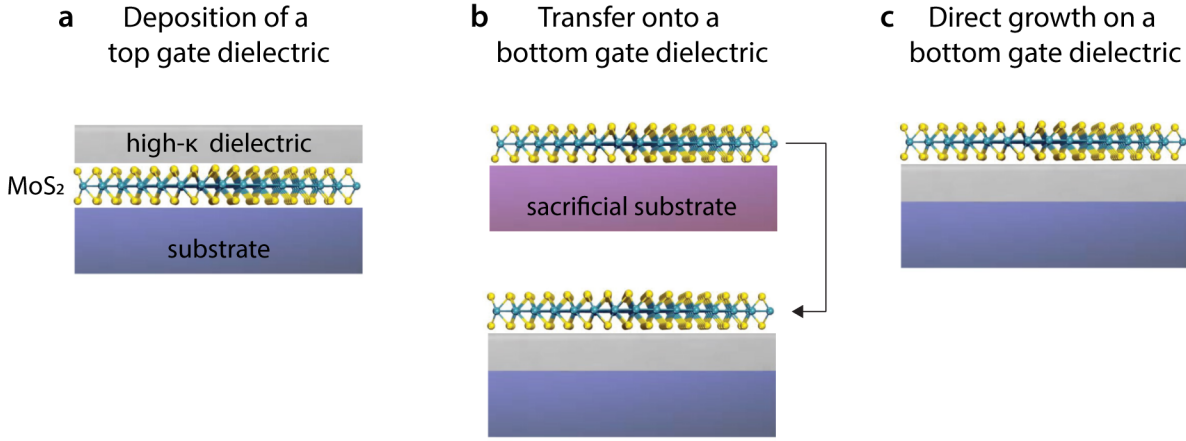


Figure 4.1: Tactics for combining 2D MoS₂ and Al₂O₃ using vapor-phase techniques.

2D semiconductors such as MoS₂ more easily assemble on bulk amorphous substrates in a layer-by-layer mode. Hence, direct growth of MoS₂ onto a high-κ dielectric is an accessible but under-explored heterostructure fabrication scheme. Kang *et al.* have reported the MOCVD of monolayer MoS₂ on amorphous Al₂O₃ and HfO₂, but the implications of the heterostructure in low-power nanoelectronics were not investigated.¹¹⁴ Thus, a scalable and transfer-free pathway for enhancement-mode FETs from CVD-grown hybrid MoS₂/high-κ dielectric heterostructures requires further investigation.

In this work, which is also presented in [273], we overcome previous issues in the integration of 2D MoS₂ with high-κ dielectrics and develop a method for the direct CVD growth of monolayer MoS₂ on 20-nm-thick ALD-derived amorphous Al₂O₃. The resulting MoS₂/Al₂O₃ heterostructures are characterized with a suite of microscopy and spectroscopy techniques including SEM, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), PL spectroscopy, and Raman spectroscopy. Furthermore, the integrity of the dielectric following CVD growth is verified with X-ray reflectivity (XRR) and capacitance-voltage (C-V) measurements. The high-quality interface between the MoS₂ and Al₂O₃ results in FETs with a CMOS $I_{\text{on}}/I_{\text{off}}$ ratio up to 10^4 , sub-threshold swing as low as 220 mV/decade,

and enhancement-mode threshold voltage of ~ 2 V. This overall set of device metrics for transfer-free FETs represents a significant improvement over literature precedent with direct implications for low-power electronics. Moreover, this work demonstrates the advantage of vdW-mediated interfaces in accessing new fabrication schemes for the successful integration of 2D atomic layers with bulk materials.

Chapter 5

Synthesis of $\text{MoS}_2/\text{Al}_2\text{O}_3$ Heterostructures

5.1 Chemical vapor deposition of monolayer MoS_2

The CVD growth of monolayer MoS_2 on ALD Al_2O_3 was achieved by adapting a procedure previously used for CVD growth on SiO_2/Si substrates.^{120,161,274} In detail, 12 mg of molybdenum trioxide powder (MoO_3 , 99.98% trace metal Sigma-Aldrich) was placed in an alumina boat in the middle of a hot zone Lindberg/Blue 1 inch quartz tube furnace. A schematic of the home-built CVD setup is depicted in Figure 5.1. A $1.5 \text{ cm} \times 4 \text{ cm}$ $\text{Al}_2\text{O}_3/\text{Si}$ substrate was placed 2 cm downstream of the MoO_3 boat. An alumina boat containing 150 g of sulfur powder was placed 30 cm upstream of the MoO_3 boat (outside of the furnace) under a proportional integral derivative temperature-controlled heating belt. Prior to growth, the quartz tube was evacuated to ~ 70 mTorr and then purged under a flow of 200 sccm of argon for 10 min. The growth occurred under a 25 sccm flow of Ar and pressure of 150 Torr following the temperature profiles shown in Figure 5.2.

Due to the high temperature of the substrate during CVD growth (800 °C for 20 minutes), substrate preparation is important in preventing degradation of the ultrathin dielectric. The Si substrates were solvent-cleaned and then further treated in a Piranha solution of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (3:1) to remove organic residues. Piranha cleaning of the substrate was necessary to prevent

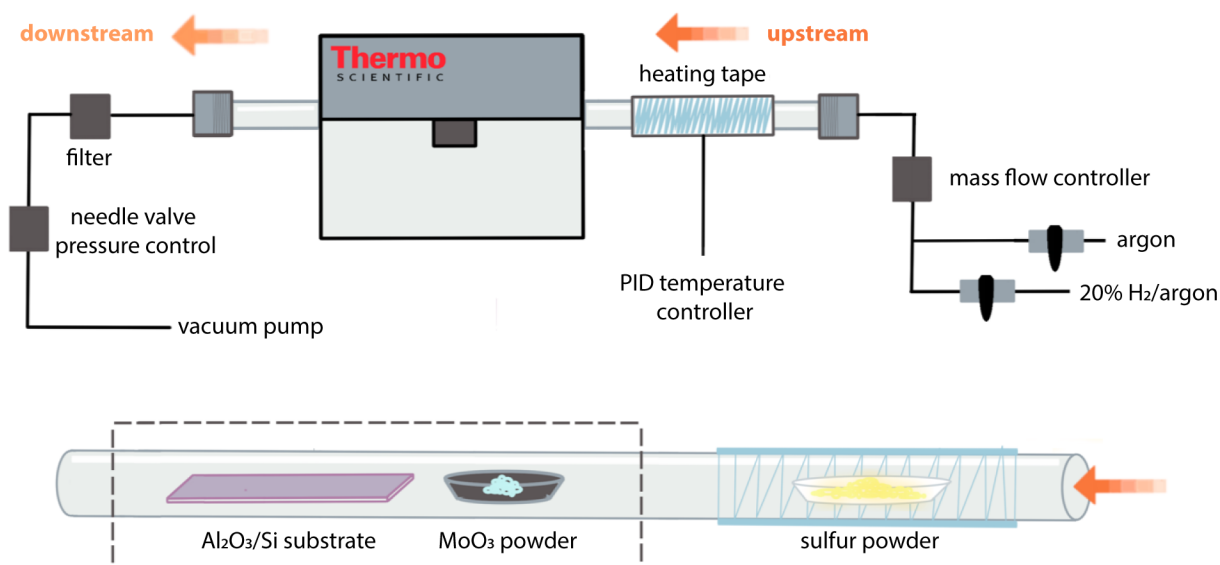


Figure 5.1: Schematic of the home-built CVD reactor for the growth of MoS₂. The overall setup is depicted in the top schematic while the bottom schematic shows the placement of the source powders and substrate inside the quartz tube in the furnace.

defects in the dielectric after high temperature processing, which led to high leakage current levels. The Si substrates were then directly taken to a Cambridge NanoTech ALD reactor for Al₂O₃ deposition with 200 cycles of trimethylaluminum (TMA) and H₂O at 200 °C (~20 nm of amorphous Al₂O₃). Deposition at lower temperatures (*e.g.*, 150 °C) resulted in higher leakage current and lower capacitance in the Al₂O₃ dielectric after high temperature processing. A more detailed discussion is presented later in section 5.2. After ALD growth, the substrates were again solvent-cleaned in acetone and isopropyl alcohol (IPA), followed by O₂ plasma cleaning for 2 minutes.

Figure 5.3a and b present SEM and optical images, respectively, of the resulting CVD-grown MoS₂ domains. Most of the MoS₂ domains possess lateral edge lengths of ~1-2 μm with some domains showing edge lengths up to 20 μm. An AFM topography image of a single domain (Figure 5.3c) reveals a step height of 0.72 nm, which is consistent with monolayer MoS₂.³⁷ A Raman spectrum obtained from the CVD-grown MoS₂ (Figure 5.3)

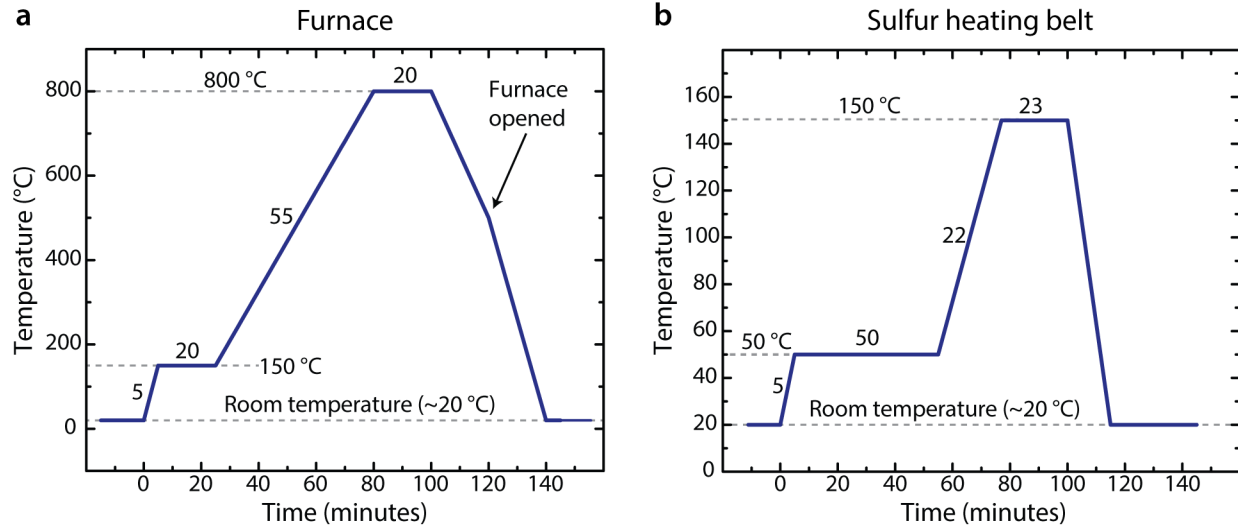


Figure 5.2: Temperature profiles for the CVD growth of MoS₂ on Al₂O₃. Temperature of the (a) furnace and (b) sulfur heating belt as a function of time for the CVD of MoS₂. The amount of time (in minutes) spent at each step is indicated. The cooling of both the furnace and heating belt occurred naturally by turning the heating off (the cooling rates in the figures are estimated).

further corroborates the single-layer thickness of the MoS₂. The MoS₂ in-plane (E_{2g}^1) and out-of-plane (A_{1g}) vibrational modes were each fit with a Lorentzian function to determine their spectral locations at 384.7 cm⁻¹ and 404.9 cm⁻¹, respectively. A difference of 20.2 cm⁻¹ between these modes is consistent with monolayer CVD MoS₂.^{161,275} The room-temperature PL spectrum of the MoS₂ (Figure 5.3d) exhibits a pronounced peak at ~669 nm and a minor peak at ~620 nm corresponding to the excitonic A and B direct-gap optical transitions in monolayer MoS₂, respectively.^{37,276,277} The presence of this sharp peak indicates that the synthesis on Al₂O₃ results in high quality crystals comparable to growth on other amorphous substrates such as SiO₂.

Lastly, the chemical composition of the MoS₂ is probed using XPS. The molybdenum core level spectrum is presented in Figure 5.3f. The position of the Mo 3d_{5/2} peak at ~230 eV is consistent with the Mo⁴⁺ formal oxidation state of MoS₂, whereas the minor doublet at higher binding energies corresponds to MoO_x.^{278,279} The relatively weak intensity of the

MoO_x peaks suggests minor MoO_x content, as observed in other MoS₂ CVD studies.^{120,280,281} From the fitting, the peaks positions were determined to be the following: S 2s, 227.5 eV; MoS₂ 3d_{5/2}, 230.9 eV; MoS₂ 3d_{3/2}, 233.4 eV; MoO_x 3d_{5/2}, 233.4 eV; and MoO_x 3d_{3/2}, 236.7 eV. The sulfur core level spectra also demonstrated peak locations consistent with MoS₂, with the S 2p_{3/2} located at 160.9 eV and the S 2p_{1/2} located at 162.2 eV.

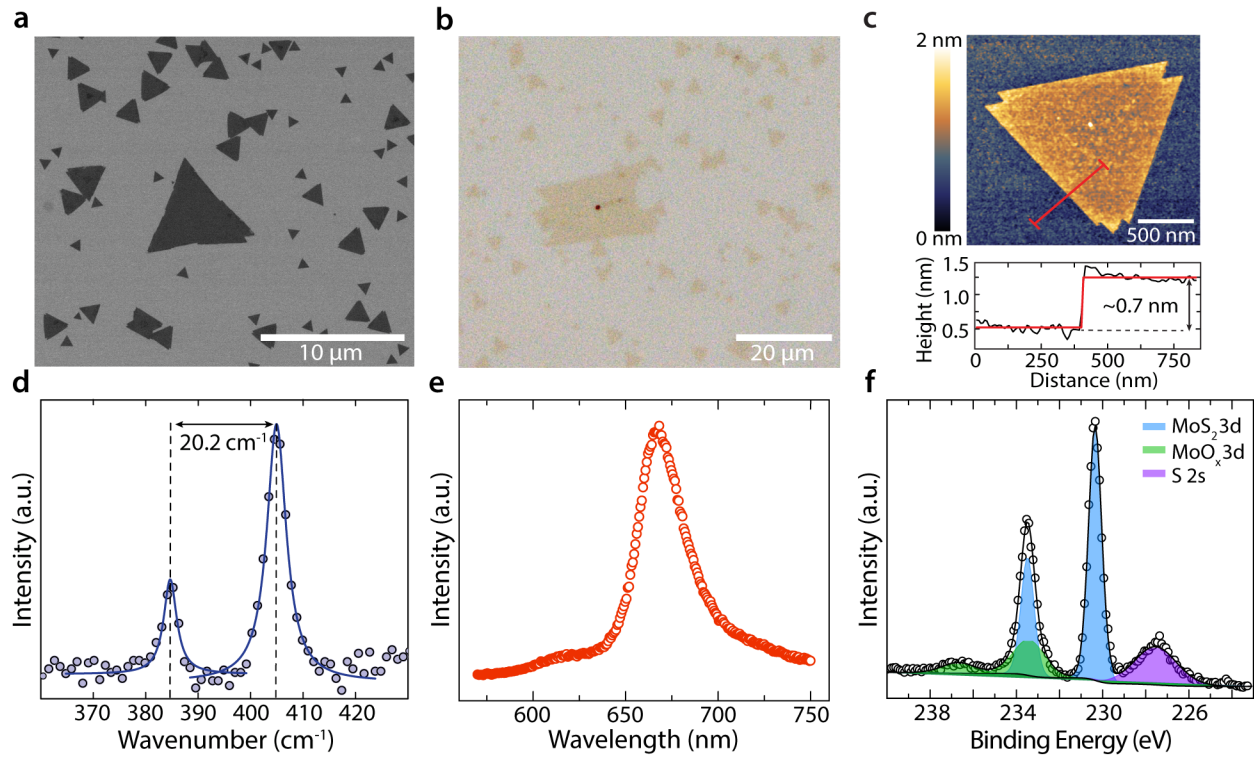


Figure 5.3: Characterization of CVD-grown monolayer MoS₂ on ALD Al₂O₃. (a) SEM image of CVD MoS₂ grown on ALD Al₂O₃ showing micron-scale single crystal domains. (b) Optical image of CVD MoS₂ on ALD Al₂O₃ (the image contrast was digitally enhanced since interference effects decrease the contrast of the MoS₂ domains on the Al₂O₃ layer in comparison to 300-nm-thick SiO₂). (c) AFM topography image of a single crystal of MoS₂. The height of the red line profile across the flake edge is shown below, where a step edge fit indicates a height of ~0.7 nm, which is consistent with monolayer MoS₂.³⁷ (d) Raman spectrum from the synthesized MoS₂, showing a separation of 20.2 cm⁻¹ between the A_{1g} and E_{2g}¹ modes, which is consistent with monolayer MoS₂.^{261,275} (e) PL spectrum from the MoS₂, showing direct-gap A and B exciton peaks from monolayer MoS₂.^{37,276,277} (f) XPS spectrum of the Mo 3d core level of the MoS₂.

5.2 Evaluation of the Al₂O₃ dielectric

The effects of the MoS₂ growth conditions on the electronic quality of the 20-nm-thick Al₂O₃ dielectric layer were investigated *via* metal-insulator-semiconductor (MIS) C-V measurements on an Al₂O₃/Si substrate annealed in a temperature cycle identical to that of the MoS₂ growth process (Figure 5.2). For these measurements, 200 $\mu\text{m} \times 200 \mu\text{m}$ metal contact pads (5 nm Ti/75 nm Au) were patterned over a $\sim 1 \text{ cm}^2$ area of the annealed Al₂O₃/Si substrates using shadow masking. The capacitance and leakage of Al₂O₃ grown at 150 °C and 200 °C was investigated. Presented in Figure 5.4a is a comparison of the capacitance of the annealed Al₂O₃ layers grown at the two different temperatures. The histograms of the capacitance were obtained at $V = 4 \text{ V}$ (*i.e.*, accumulation regime for the grounded *n*-type Si substrate). While the growth of amorphous Al₂O₃ is commonly performed at 150 °C, the dielectric layer grown at this temperature significantly degraded when annealed to 800 °C. The average capacitance of the 20-nm-thick Al₂O₃ layer grown at 150 °C was $329 \pm 8 \text{ nF/cm}^2$, corresponding to an effective dielectric constant (κ_{eff}) of 8.18 ± 0.2 . κ_{eff} was calculated using the Al₂O₃ thickness measured by XRR and a 1.8-nm-thick native silicon oxide.²⁸² On the other hand, using a higher substrate temperature of 200 °C during the ALD process resulted in a dielectric with better thermal endurance. The capacitance of the 20-nm-thick Al₂O₃ grown at 200 °C was $328 \pm 3 \text{ nF/cm}^2$, corresponding to a κ_{eff} of 8.45 ± 0.08 . While the means of the capacitance distributions are comparable, the spread is more pronounced in the dielectric grown at 150 °C. The leakage distributions of the two samples show a greater contrast (Figure 5.4b). Following annealing, over 55% of the devices from the dielectric deposited at 200 °C exhibited a leakage current less than 10^6 A/cm^2 . In other words, over 55% of the measured regions on the sample would be fit for use in an FET. In contrast, only 14% of the regions measured on the dielectric deposited at 150 °C showed a leakage current less than 10^6 A/cm^2 . Thus, the deposition of the 20-nm-thick Al₂O₃ layer requires higher substrate temperatures (200 °C) to preserve its

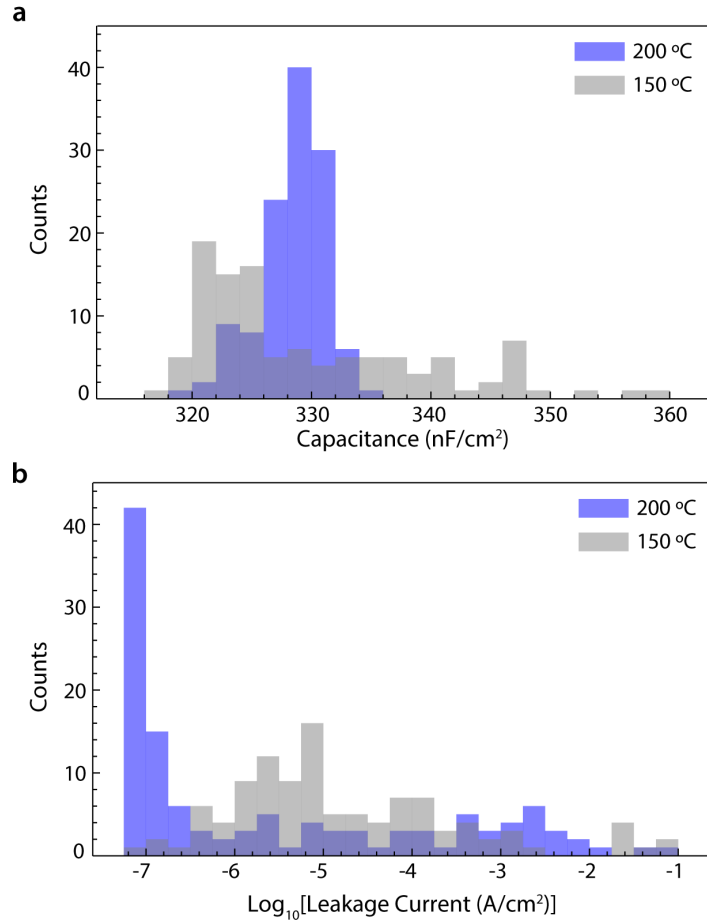


Figure 5.4: Capacitance and leakage current of annealed 20-nm-thick Al₂O₃ films deposited on Si at 150 °C and 200 °C. Histogram of (a) the capacitance at $V = 4$ V (accumulation regime) and (b) leakage current of 109 Au/Al₂O₃/Si MIS capacitors made from Al₂O₃ grown at 150 °C and 121 Au/Al₂O₃/Si MIS capacitors made from Al₂O₃ grown at 200 °C. The histograms show the values following annealing at 800 °C to mimic the MoS₂ deposition process. The means of the capacitance distributions are 329 ± 8 nF/cm² and 328 ± 3 nF/cm² for the Al₂O₃ grown at 150 °C and 200 °C, respectively. 14% and 56% of the devices show leakage currents below 10^6 A/cm² for the Al₂O₃ grown at 150 °C and 200 °C, respectively.

dielectric function following the high temperature processing involved in the direct growth of MoS₂.

A comparison of the pristine and annealed Al₂O₃ films deposited at 200 °C demonstrates that the annealed sample still functions well as a dielectric layer. The histograms of the capacitance values at $V = 4$ V for 130 devices on the pristine Al₂O₃ (Figure 5.5a) shows

a narrow distribution with an average value of 332 ± 3 nF/cm². κ_{eff} was calculated to be 8.25 ± 0.07 . Since the mean value of the capacitance was 328 ± 3 nF/cm² after the anneal, the thermal cycling did not significantly affect the dielectric quality (<2% reduction in capacitance). Furthermore, a κ_{eff} of 8.45 ± 0.08 after the anneal is consistent with values typically obtained for ALD Al₂O₃.²⁸³ However, the leakage appeared to be more significantly affected by the annealing process. The leakage distribution of a pristine 20-nm-thick Al₂O₃ layer deposited on Si at 200 °C is shown in Figure 5.5b. Over 99% of the regions measured showed a leakage less than 10^6 A/cm² and the distribution is very tight. The main degradation pathway of the dielectric layer during the annealing process is thus the formation of localized pinholes. To prevent the formation of these defects during annealing, more aggressive cleaning of the Si substrates could be performed (*e.g.*, HF etch) in addition to processing a cleanroom facility.

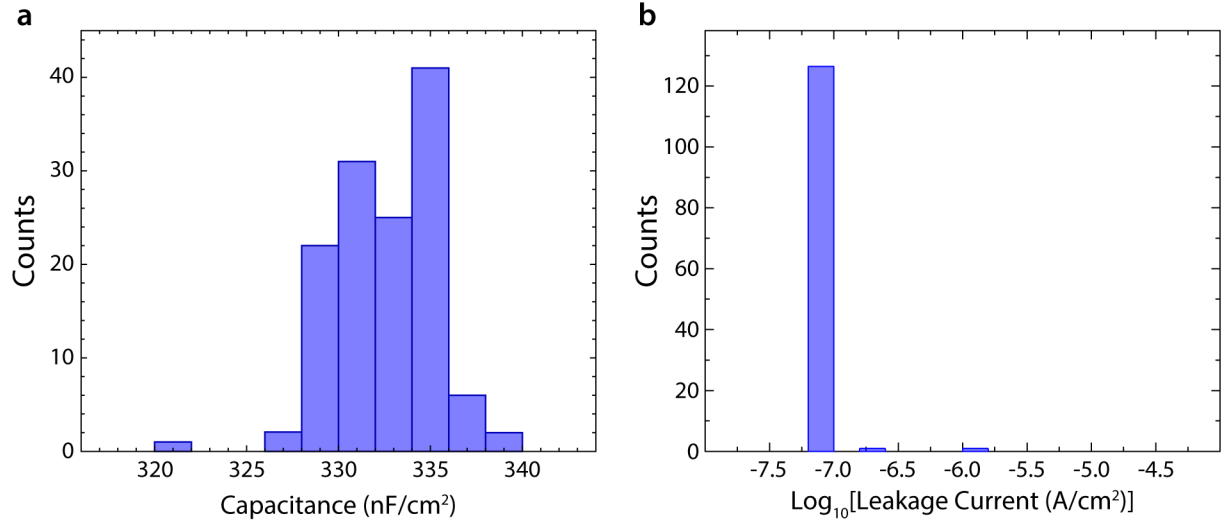


Figure 5.5: Capacitance and leakage current of pristine 20-nm-thick ALD Al₂O₃ deposited at 200 °C. Histogram of the (a) capacitance at $V = 4$ V (accumulation regime) and the (b) leakage current of 130 Au/Al₂O₃/Si MIS capacitors made from as-deposited Al₂O₃. The average capacitance of the pristine Al₂O₃ layer is 332 ± 3 nF/cm² and > 99% of devices show a leakage current below 10^6 A/cm².

The integrity of the Al₂O₃ and Al₂O₃/Si interface was further characterized using XRR.

Previously, XRR has been employed to probe the robustness and thickness of heterogeneous ultrathin dielectric stacks following chemical treatments.^{282,284} The depth-dependent electron density profile was extracted by fitting the XRR data with the parameters in Table 5.1. Figure 5.6a shows the XRR data collected from a sample of MoS₂ directly grown on Al₂O₃/Si, the corresponding model fit, and the depth-dependent electron density profile normalized to the electron density of the Si substrate. From this analysis, the thickness of the Al₂O₃ layer after MoS₂ deposition is found to be 20.0±0.3 nm with the addition of a 1.83±0.08 nm Al₂O₃/Si interfacial layer included to achieve the best fit. The presence of similar interfacial layers has previously been reported in annealed Al₂O₃ systems.^{285,286} A control sample of pristine ALD Al₂O₃/Si without MoS₂ showed a dielectric thickness of 20.7±0.1 nm (Figure 5.6c), which agrees well with the sample that underwent MoS₂ growth.

	Thickness (nm)		
	MoS₂/Al₂O₃/Si	Annealed Al₂O₃/Si	Pristine Al₂O₃/Si
Top layer	1.83 ± 0.08	1.92 ± 0.07	1.67 ± 0.10
Al ₂ O ₃	20.0 ± 0.3	21.1 ± 0.1	20.7 ± 0.1
Al ₂ O ₃ /Si Interface	2.0 ± 0.6	1.5 ± 1.2	2.2 ± 0.4
	Electron Density (SLD)		
	MoS₂/Al₂O₃/Si	Annealed Al₂O₃/Si	Pristine Al₂O₃/Si
Top layer	7 ± 1	8 ± 2	7 ± 2
Al ₂ O ₃	28 ± 4	28 ± 2	28 ± 1
Al ₂ O ₃ /Si Interface	23 ± 1	22 ± 2	21 ± 1
Si	20.04	20.04	20.04

Table 5.1: XRR fitting parameters for MoS₂/Al₂O₃/Si heterostructures

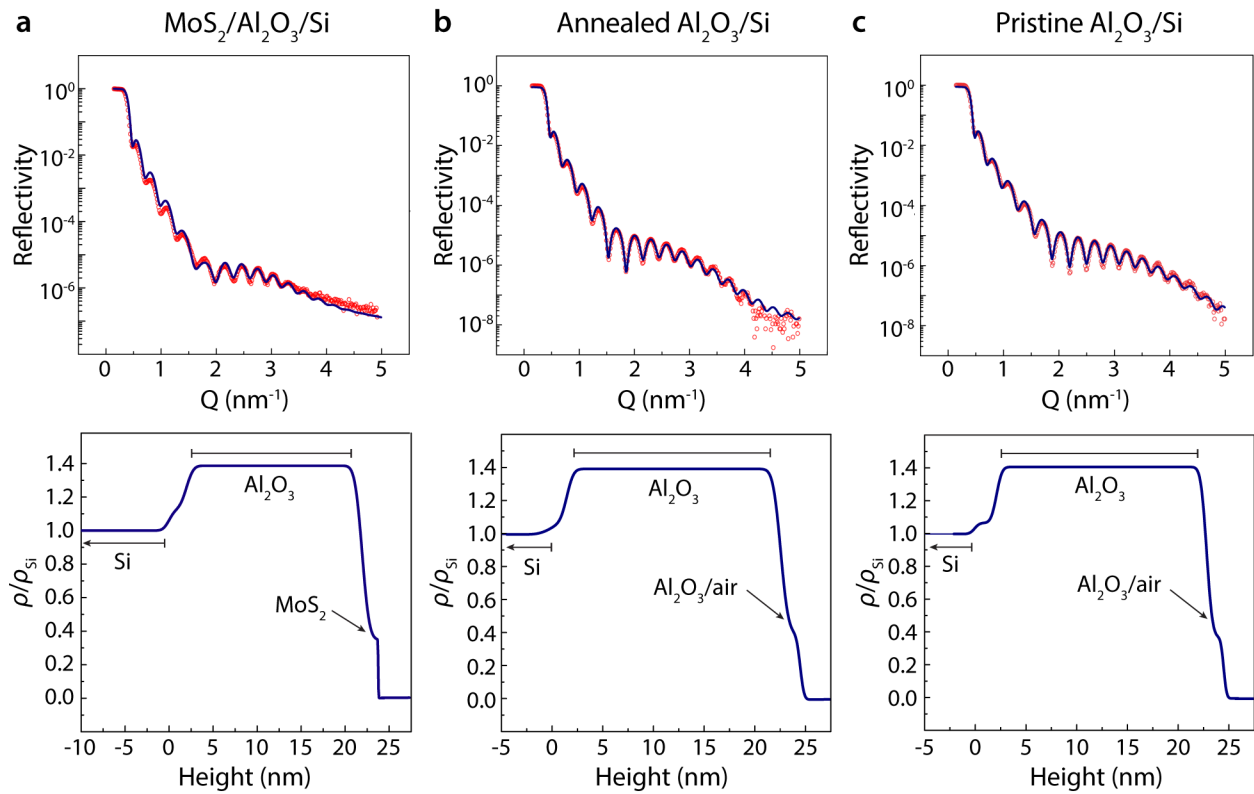


Figure 5.6: XRR of the MoS₂/Al₂O₃/Si and Al₂O₃/Si heterostructures. Top: XRR data (red circles) and model fits (blue line) of the (a) CVD MoS₂ on Al₂O₃/Si, (b) annealed Al₂O₃/Si, and (c) pristine Al₂O₃/Si heterostructures. Bottom: the thickness profile extracted from the XRR models, with the density normalized to the electron density of the Si substrate. The fitting parameters are given in Table 5.1.

Chapter 6

Low-Power Performance of MoS₂/Al₂O₃ Heterostructures

6.1 Bottom-gated MoS₂/Al₂O₃ FETs

To investigate electronic transport properties, FETs were fabricated from the monolayer CVD MoS₂ grown on 20-nm-thick ALD Al₂O₃, with the Al₂O₃ serving as the bottom-gate dielectric (schematic shown in Figure 6.1a). Both two-probe FETs and four-probe van der Pauw devices were studied to determine the effect of contacts on the transport characteristics. The devices were patterned with electron-beam lithography (EBL) and contact metallization (2.5 nm Ti/ 100 nm Au). All devices were measured at 25°C and $< 5 \times 10^{-5}$ Torr. The output characteristics of a typical two-probe MoS₂ FET (Figure 6.1b) are linear in the low bias range, which is consistent with previous studies of MoS₂ contacted with Ti/Au.^{260,287} The transfer characteristics of the same device exhibit a CMOS $I_{\text{on}}/I_{\text{off}}$ ratio $> 10^4$, sub-threshold swing ~ 220 mV/decade, and $V_{\text{TH}} = 2.1$ V (Figure 6.1c). The threshold voltage is defined here as the bottom-gate voltage (V_{BG}) axis intercept of the extrapolation of the linear region of the transfer curve. The transfer curve of a four-probe device is shown in Figure 6.1d. The linear field-effect mobility from the devices was calculated according to the following

equation:

$$\mu_{\text{FE}} = \frac{L}{C_{ox}W} \left(\frac{\partial G_D}{\partial V_G} \right) \quad (6.1)$$

where V_G and G_D are the gate voltage and channel conductance, respectively. L and W are the channel length and width, respectively, where the dimensions are defined by the area enclosed by the inner electrodes 2 and 3 for the four-probe devices (inset of Figure 6.1d). C_{ox} is the area-normalized capacitance of the gate-dielectric (328 nF/cm²). Measurements on two-probe and four-probe devices revealed comparable field-effect mobilities, indicating that the contact resistance does not dominate the overall transistor characteristics. The field-effect mobility of all six measured devices is found to vary from 0.4 to 4.1 cm²/Vs (extracted at a source-drain voltage (V_D) $\leq$ 1 V), in agreement with previous reports for CVD MoS₂ mobilities.^{280,288,289} The devices also show low hysteresis in comparison to other reports on 2D MoS₂^{280,290–292} (see Figure 6.1c) where the sweep direction dependent shift in V_{TH} is $\sim$ 10 mV. The direct deposition of monolayer MoS₂ on amorphous ALD Al₂O₃ *via* CVD thus results in MoS₂ of comparable quality to the more common synthesis on amorphous SiO₂. However, the ALD Al₂O₃ substrate is much more suitable for low-power electronic applications.

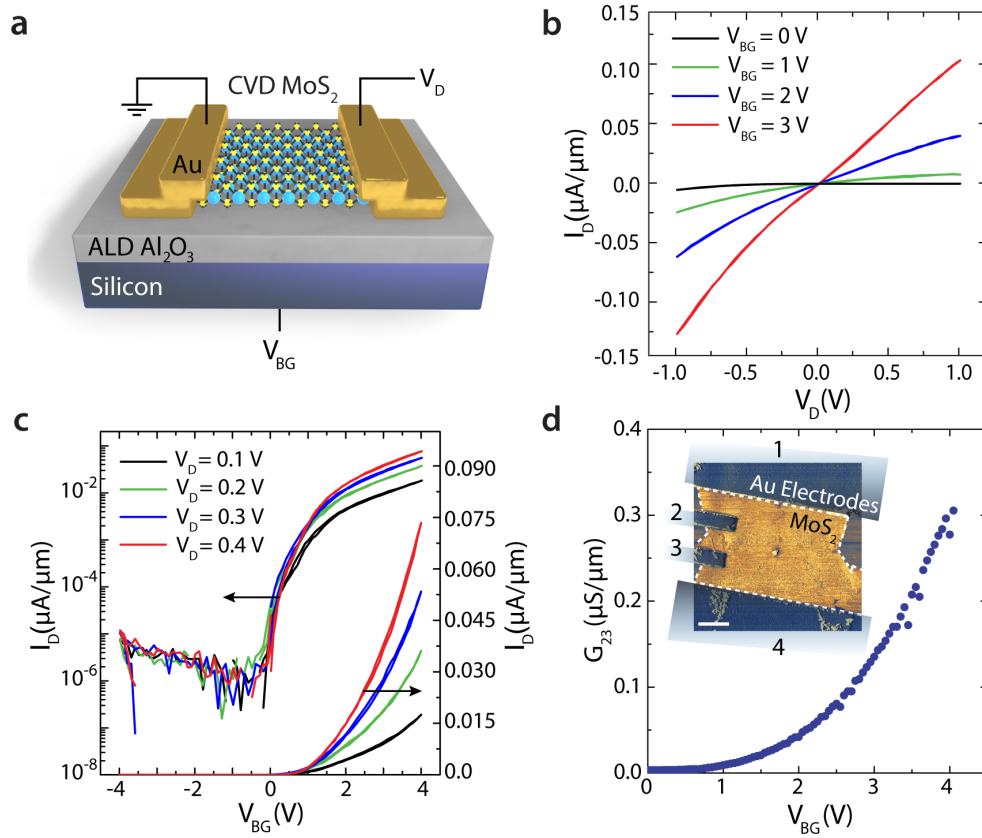


Figure 6.1: Characteristics of bottom-gated MoS₂/Al₂O₃ FETs. (a) Schematic of a two-probe FET fabricated from monolayer MoS₂ directly grown on 20-nm-thick ALD Al₂O₃ (b) Output plots of an FET at different gate voltages, normalized by device channel width ($L = 3 \mu\text{m}$, $W = 5.2 \mu\text{m}$). (c) Linear and semi-log transfer characteristics of the same device at different drain biases, including forward and backward sweeps. (d) Conductance versus gate bias of a four-probe device (normalized by device channel width $W = 7.5 \mu\text{m}$). The inset shows an AFM phase image of the four-probe device, with the MoS₂ highlighted by the white dashed lines. The scale bar is $2 \mu\text{m}$. The conductance G_{23} was measured between electrodes 2 and 3 while applying a constant current of 10 nA between electrodes 1 and 4.

6.2 Evaluation of low-power FET figures of merit

We now consider the specific transistor metrics relevant to low-power digital electronics applications. Figure 6.2 shows the simultaneous improvement in the CMOS $I_{\text{on}}/I_{\text{off}}$ ratio, threshold voltage (V_{TH}), and sub-threshold swing of the FETs in this work in comparison with previous literature for directly-grown CVD MoS_2 FETs.^{114,170,171,265,271,274,277,280,288,291,293–308} Unless explicitly reported in the literature, the metrics were extracted from published data using a figure digitizer. The majority of recent reports of transfer-free CVD MoS_2 FETs were included in this analysis, excluding electrochemically-gated devices. In particular, we highlight the CMOS $I_{\text{on}}/I_{\text{off}}$ ratio, where I_{on} is calculated at the maximum positive gate voltage reported and I_{off} at $V_{\text{G}} = 0$ V. For our devices, the maximum positive gate voltage ranges from $V_{\text{G}} = 3 - 4$ V and the resulting CMOS $I_{\text{on}}/I_{\text{off}}$ ratio ranges from 10^2 to 10^4 , which is a significant improvement over previous work on CVD MoS_2 . Furthermore, the low sub-threshold swing of our devices from 220 – 530 mV/decade, and the low V_{TH} from 1.3 – 2.7 V, also compare favorably with literature on CVD MoS_2 FETs.

The favorable low-power performance of the presented devices can be attributed to the direct growth of the MoS_2 on ALD Al_2O_3 . The pristine interface between the two materials minimizes the doping variability of transfer methods while maintaining the low-power advantages of ultrathin high- κ dielectrics. The as-grown doping of monolayer MoS_2 on Al_2O_3 results in enhancement-mode FETs with low operating voltages. As shown in Figure 6.2a, the ALD growth of ultrathin metal oxides on CVD MoS_2 has been reported to achieve low operating voltages in top-gated FET geometries. However, this approach increases n -type MoS_2 doping, often resulting in depletion-mode transistors ($V_{\text{TH}} < 0$ V) unsuitable for low-power CMOS applications. Thus, optimization of power consumption metrics (*i.e.*, CMOS $I_{\text{on}}/I_{\text{off}}$ ratio, threshold voltage, and sub-threshold swing) in this work is highly relevant to logic applications for circuits based on 2D semiconductors.

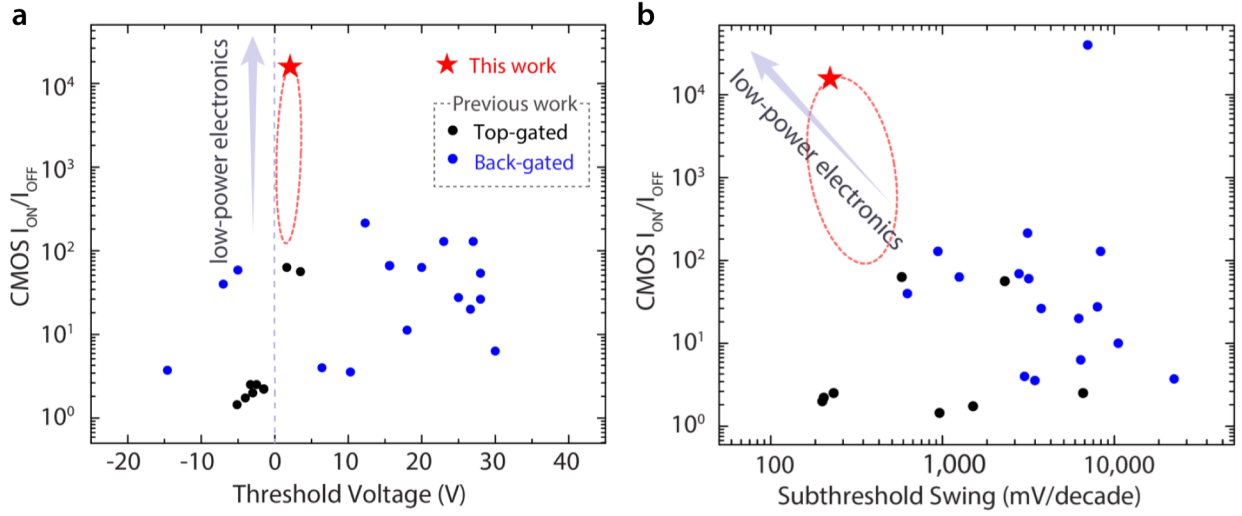


Figure 6.2: Comparison of the low-power performance of the MoS₂/Al₂O₃ FETs with literature. A plot of CMOS I_{on}/I_{off} ratio versus (a) threshold voltage and (b) subthreshold swing of the devices from this work in comparison to other directly-grown CVD MoS₂ FETs reported in the literature. Reports in which the threshold voltage could not be extracted or exceeded 45 V are not included. Reports in which the sub-threshold swing could not be extracted or exceeded 20,000 mV/decade are not included. The red star denotes the best device in this work while the red dashed oval depicts the range in the metrics for the six devices measured. The black and blue points represent previously reported top-gated and bottom-gated devices, respectively. The CMOS I_{on}/I_{off} was calculated with I_{on} as the current at the maximum positive gate voltage reported for each device and I_{off} at $V_G = 0$ V.

Chapter 7

Conclusions and Future Work

In conclusion, this work presents the direct growth of monolayer MoS₂ on 20-nm-thick ALD Al₂O₃ using solid precursor CVD. Both AFM and Raman spectroscopy confirm the growth of monolayer MoS₂. Annealing of the 20-nm-thick ALD Al₂O₃ deposited at 200 °C through a temperature cycle of 800 °C decreases capacitance by <2% in comparison to a control sample of as-deposited Al₂O₃/Si. XRR also confirms that the thickness of the dielectric does not significantly change after MoS₂ deposition. The resulting MoS₂ FETs exhibit high performance in low-power CMOS metrics such as a CMOS I_{on}/I_{off} ratio of 10² to 10⁴, sub-threshold swing = 220 – 530 mV/decade, and V_{TH} = 1.3 – 2.7 V, with negligible hysteresis. The low operating voltage enhancement-mode FETs fabricated from the MoS₂ grown on ALD Al₂O₃ demonstrate promise for the low-power *n*-type branch of CMOS in integrated circuits. The work presented here thus substantiates the prospect of scalable hybrid MoS₂/high- κ dielectric heterostructures for low-power electronics. Furthermore, it illustrates the advantage of vdW-mediated in accessing new fabrication schemes that are not readily available to 3D semiconductors. In this case, the direct growth approach circumvented of the deleterious effects of Al₂O₃ deposition and transfer processes on the MoS₂ doping level. In considering the advantages of 2D materials, the freedom afforded by the vdW interface is tantamount to their acclaimed intrinsic properties.

In addition to the fabrication of low-power FETs, the heterostructures developed in this work can serve as a starting point for the substrate engineering of self-limited growth of monolayer MoS₂. Since ALD Al₂O₃ is a thermally stable and easily deposited dielectric layer, it can serve as an essential interface for the development of more complicated catalytic substrates to advance the scalable synthesis of monolayer MoS₂ and other TMDs. A more detailed discussion on this future direction is presented in section 15.1.

Chapter 8

Experimental Methods

Scanning electron microscopy

SEM images were acquired on a Hitachi SU8038 cold source field emission SEM. The images were taken with an accelerating voltage of 2.0 kV and magnification of $\sim 3000\times$.

Atomic force microscopy

AFM was performed using an Asylum Cypher AFM in tapping mode. A NanoWorld NCHR-W Si cantilever with a resonant frequency of ~ 320 kHz was used. The images were taken with a pixel resolution of 512×512 at a scanning rate of ~ 1 Hz.

Raman and photoluminescence spectroscopy

Raman and PL measurements were performed with a Horiba Scientific XploRA PLUS Raman microscope in ambient conditions using a 532 nm laser with incident power of ~ 1 mW and spot size of $\sim 1 \mu\text{m}^2$. The signal was collected using a $100\times$ Olympus objective (NA = 0.9) to a Sincerity CCD. The Raman signal was dispersed by a 2400 grooves/mm grating (corresponding to a spectral resolution of $\sim 1 \text{ cm}^{-1}$) while the PL spectrum was dispersed

using an 1800 grooves/mm grating. The Raman and PL spectra were acquired for 10 s and 12 s, respectively. The Lorentzian fit on the Raman peak positions yielded an error of 0.5 cm^{-1} .

X-ray photoelectron spectroscopy

The XPS spectra were acquired using a Thermo Scientific ESCA Lab 250Xi scanning XPS equipped with a monochromatic KR Al X-ray source. The spot size was $\sim 500 \text{ }\mu\text{m}$ and the spectrum consists of an average of 5 spectra collected with pass energy of 15 eV and dwell time of 100 s. A flood gun was used for charge compensation. The analysis of the spectrum was performed using the Advantage (Thermo Scientific) software. The sub-peaks were fit using a modified Shirley background and were corrected for charge shifting using the adventitious carbon peak at 284.8 eV.

X-ray reflectivity

XRR measurements were taken using a Ragaku ATXG equipped with a Cu rotating anode generator ($\lambda = 0.154 \text{ nm}$) and a multilayer parabolic mirror. The beam was collimated using beam defining slits S1 and S2 set at $0.5 \times 2.0 \text{ mm (H} \times \text{V)}$ and $0.1 \text{ mm} \times 2.0 \text{ mm (H} \times \text{V)}$, respectively. Receiving slits S3 and S4 were set at $0.5 \times 10.0 \text{ mm (H} \times \text{V)}$ and 0.5 (H) , respectively. The resolution of the setup was found to be 0.08 nm^{-1} FWHM using a Si(111) single crystal and gave a straight through beam intensity of $8 \times 10^7 \text{ cps}$ at the sample surface. The samples were mounted vertically. The beam height was measured to be 0.15 mm , and a footprint correction was applied to the low- q data. The XRR data was background-subtracted using measures taken with a θ misalignment of $\pm 0.14 \text{ nm}^{-1}$. The XRR data was fit using the using the Motosfit software package.³⁰⁹

Device fabrication and measurement

The MIS devices were fabricated by depositing metal contacts (5 nm Ti/75 nm Au) onto the ALD $\text{Al}_2\text{O}_3/\text{Si}$ substrates using thermal evaporation through a shadow mask in a Nano38 thermal evaporator (Kurt J. Lesker, Inc.). The devices were measured in ambient conditions using a Cascade MicroTech semi-automated probe system with a Keithley 4200 semiconductor analyzer.

The FETs were fabricated using EBL in an FEI Quanta ESEM system. A resist of PMMA from MicroChem Corp. was spin-coated onto the $\text{MoS}_2/\text{ALD } \text{Al}_2\text{O}_3/\text{Si}$ heterostructure and was used to pattern the electrodes. The substrate was developed in a methyl isobutyl ketone (MIBK):IPA (1:3) solution followed by a rinse in IPA. The metal contacts (2.5 nm Ti/ 100 nm Au) were deposited using thermal evaporation. The electrical measurements were done at room temperature and in vacuum (5×10^{-5} Torr) using a probe station (LakeShore CRX 4K) connected with Keithley 2400 source-meters controlled with home-made LabVIEW programs.

Part III

Large-Area InSe Films via Controlled Phase Evolution

Chapter 9

Introduction

A common obstacle to the realization of novel electronic devices is the lack of high-quality material growth methods to enable these new designs. This is especially true for emerging 2D materials; their unique properties hold promise for unprecedented device functionality, but their synthesis methods and mechanisms are not well developed. In particular, InSe is a semiconducting vdW GIIIMC material that possesses exceptional band-gap tunability as a function of thickness in the ultrathin limit.^{104,310,311} This tunability is thought to be attributed to the strong vdW interlayer coupling, which is also responsible for the indirect-to-direct band gap transition with increasing layer thickness.⁷⁴ Moreover, ultrathin InSe has been shown to be suitable for high-performance electronics when interfaced with metallic indium^{312,313} and with high- κ dielectrics,^{310,314} polymethyl methacrylate,¹⁵⁷ or a combination of both.¹⁵⁸ As a result, ultrathin InSe is promising for application in devices such as FETs^{158,315} and photodetectors,^{316,317} in addition to serving as a platform for the study of low-dimensional physics.^{310,318,319}

Despite its desirable electronic properties, InSe is a relatively under-investigated 2D material, largely because high-quality samples have only been achieved *via* mechanical exfoliation as opposed to large-area thin film growth. The complex phase diagram of the indium-selenium material system³²⁰ makes synthesizing pure InSe over large areas a more

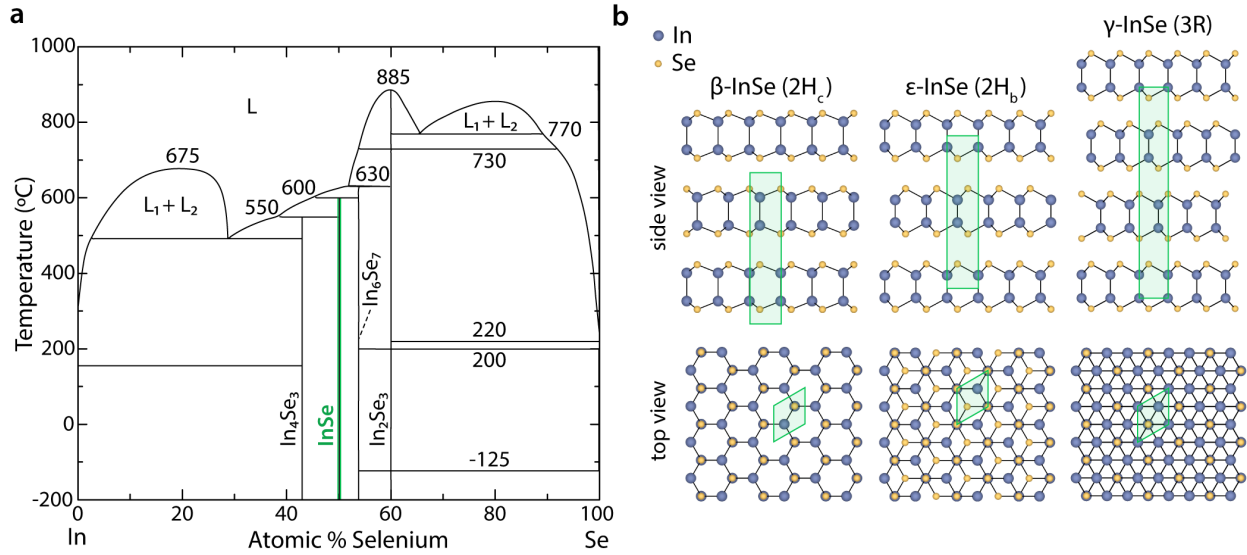


Figure 9.1: Indium-selenium phase diagram and polytypes of InSe (a) Phase diagram of the indium-selenium material system. Adapted with permission from [320]. The formation of InSe occurs on the line highlighted in green. (b) Structures of the various InSe polytypes with the unit cells highlighted in green.

difficult task than many of the extensively studied and vapor-phase synthesized vdW 2D material systems which have relatively simple phase diagrams (*e.g.*, MoS_2).³²¹ Thus, more fundamental studies aimed at characterizing and understanding growth mechanisms are needed. As shown in Figure 9.1a, the indium-selenium phase diagram contains many stable phases of various stoichiometries (*e.g.*, In_4Se_3 , InSe, In_6Se_7 , and In_2Se_3),²³⁸ and the targeted phase (InSe) only exists as a narrow line highlighted in green. In contrast, pure MoS_2 forms over a large region of the molybdenum-sulfur phase diagram (Figure 9.2). Moreover, the higher thermal stability of In_2Se_3 ³²² presents a significant barrier to achieving the high-quality synthesis of phase-pure InSe thin films. Pure InSe nanoflakes by CVD have only been observed in a very narrow parameter space,⁶⁸ and the fine stoichiometric control necessary for reliable spatial homogeneity is lacking in powder-based CVD methods.^{166,168}

In addition to stoichiometric variation, InSe also exhibits various stacking polytypes, namely, β -InSe, ϵ -InSe, and γ -InSe (Figure 9.1b). As stacking polytypes, all three structures

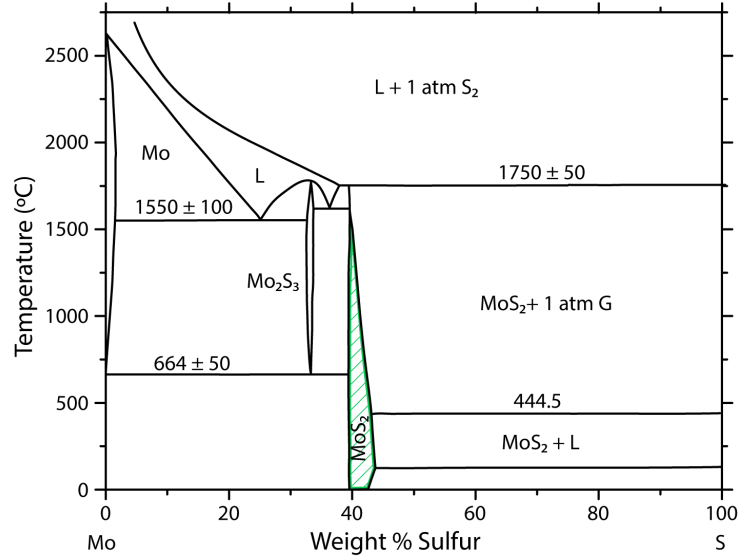


Figure 9.2: Molybdenum-sulfur phase diagram The region where pure MoS₂ is obtained is highlighted in green. Adapted with permission from [323].

have the same in-plane structure: a hexagonal single layer with lattice parameter $a = 4.00 \text{ \AA}$. In the out-of-plane direction, γ -InSe exhibits ABC stacking resulting in a 3R structure with $c = 25.32 \text{ \AA}$, while β -InSe and ϵ -InSe exhibit AB stacking for a 2H structure with $c = 16.64 \text{ \AA}$.¹⁰³ β -InSe differs from ϵ -InSe and γ -InSe in that alternating layers are rotated by 60° . As a result, β -InSe is centrosymmetric when even-layered while both ϵ -InSe and γ -InSe are noncentrosymmetric. The noncentrosymmetric structures of ϵ -InSe and γ -InSe make these particular polytypes attractive for nonlinear optics applications^{60,324} such as second harmonic generation.^{65,67–70}

Recent efforts toward the growth of ultrathin InSe films include techniques such as CVT,^{243,314} PVT,^{70,200} CVD,^{68,325} MBE,¹⁸⁶ PLD.^{235,236} However, device demonstrations from these efforts were limited to single devices rather than large-area statistical evaluation. Furthermore, the ambient instability of InSe^{326,327} requires careful synthesis and device fabrication schemes which limit ambient exposure. Consequently, the large-area growth and device implementation of electronic grade ultrathin InSe remains elusive.

Towards that end, we used *in situ* X-ray diffraction (XRD) and diverse surface characterization techniques to study the structural and compositional evolution of ultrathin InSe films deposited by PLD and subsequently processed *via* vacuum thermal annealing. By monitoring the material as a function of post-deposition annealing temperatures, we rationally determined the synthesis conditions to realize ultrathin ϵ -InSe films with high uniformity over large areas, controlled thickness, and no detectable impurity phases. Using this optimized deposition and post-annealing method, bottom-gated phototransistors were fabricated to explore the optoelectronic response of the films, and the resulting devices showed a high responsivity (10^3 A/W). Finally, to demonstrate large-area device implementation, ultrathin InSe films were patterned for an array of top-gated enhancement-mode FETs with high yield (91%) and consistent device behavior over an area of 1 cm^2 . Ultimately, our work provides a roadmap to navigate InSe synthesis and a method for the realization of large-area ultrathin InSe films with high crystallinity, thickness tunability, and generalizability to a wide range of substrates suitable for nanoelectronic applications.

Chapter 10

Phase Evolution of InSe Films

10.1 Pulsed laser deposition of InSe films

PLD is a physical vapor deposition technique in which a high-power laser pulse is incident on a solid target, ejecting a gas-phase plume of ions and atoms which condense on a substrate opposite the target. PLD enables fine control over the thickness of the deposited film *via* the number of laser pulses, which is important for leveraging the thickness-dependent tunability of InSe. More importantly, a considerable advantage of this growth technique is the stoichiometric ejection of material from the target.²¹³ In contrast, powder-based CVD methods suffer from stoichiometric variability that is problematic for the complex indium-selenium material system.

The starting films were deposited onto 1 cm $\times$ 1 cm 300-nm-thick amorphous SiO₂/Si substrates at RT and a pressure of 10^{-7} Torr, resulting in amorphous films of InSe. A 248 nm KrF excimer laser was used to ablate a target made from pressed InSe powder using 200 mJ pulses at a frequency of 1 Hz. Details on the deposition parameters can be found in chapter 14. Heating the substrate during the deposition process results in a significant deficiency of Se from the deposited film due to it being more volatile than In^{213,235,328} and the sticking coefficient of single Se species approaching zero at substrate temperatures higher

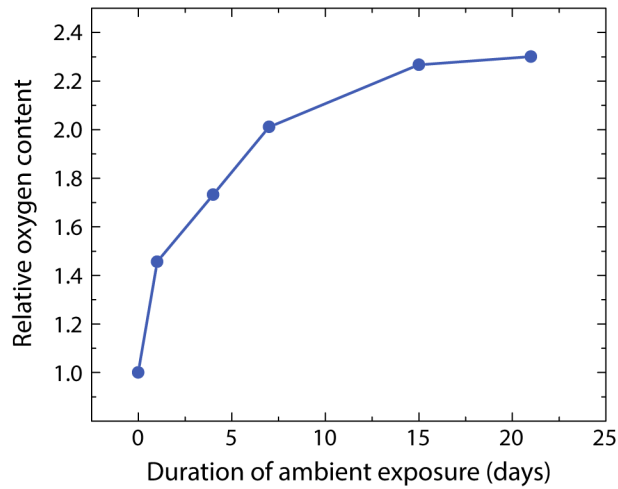


Figure 10.1: Oxidation of amorphous PLD InSe films over time. Relative oxygen content of an as-deposited amorphous InSe film on SiO₂ as a function of the time exposed to ambient conditions. The oxygen content is given as a multiplicative factor of the original concentration.

than 200 °C.³²⁹ This effect was also observed in previous reports of MBE -grown InSe thin films where an excess of Se was needed.^{329–331} Thus, deposition on a substrate at RT affords greater stoichiometric control of the deposited film given the composition of the PLD target.

The ambient stability of as-deposited amorphous InSe films on 300-nm-thick SiO₂/Si was studied using XPS. The concentration of oxygen in 8-nm-thick InSe films was determined from the intensity of the O 1s core level spectrum. Directly after deposition, the oxygen concentration was found to be 20%. However, this concentration is inaccurate due to the detectable presence of the supporting SiO₂ through the InSe film. Nonetheless, this value can be used as a baseline from which to compare the oxygen content of the film as a function of the time exposed to ambient conditions. Presented in Figure 10.1 is the oxygen content of the film relative to the initial concentration after deposition (day 0), as determined by XPS. After a single day, the oxygen content increased to about 1.5× its initial value, before saturating at ~2.3× after 15 days. The slope is steepest during the first day, indicating a significant oxidation of the film during the first 24 hours. This result is consistent with a study by Ho *et*

al. on the oxidation of exfoliated InSe flakes, wherein a large increase in oxygen content was observable by XPS following 24 hours in air.³³² Consequently, care was taken to minimize ambient exposure of InSe samples throughout the study, including transport of samples in an evacuated vessel and storage of samples in a nitrogen glovebox.

10.2 Structural and compositional evolution of InSe films

10.2.1 *in situ* X-ray diffraction

The crystallization of the PLD InSe films was achieved *via* vacuum thermal annealing and their structural evolution as a function of annealing temperature was studied using *in situ* XRD. A 30-nm-thick PLD InSe film was heated from RT to 500 °C at 30 °C/min at a pressure of 10^{-4} Torr in a furnace attachment. Diffraction patterns were collected in 10 °C and 25 °C intervals. The diffraction patterns at selected transitional temperatures are shown in Figure 10.2a. The film began in an amorphous state with no evident diffraction peaks, excluding a low intensity peak attributed to the Si substrate at $2\theta = 33^\circ$. At 250 °C, the film started to crystallize through the appearance of a weak diffraction peak at 27.8° . While this peak is consistent with the (330) plane of In_4Se_3 , as seen in previous studies on In_4Se_3 thin films,^{330,333} a robust identification of this phase requires additional information. In complement, *ex situ* Raman spectra (Figure 10.2b) collected from a 30-nm-thick InSe film annealed to 250 °C and cooled to RT reveals the structure to be a mixture of InSe and In_4Se_3 . The modes corresponding to InSe are located at 116 cm^{-1} (A'_1), 178 cm^{-1} (E'' and E' -TO), and 226 cm^{-1} (A'_1)^{334,335} while the modes at 71 cm^{-1} and 103 cm^{-1} , 150 cm^{-1} correspond to In_4Se_3 .^{330,336} Optical microscopy of the same film annealed at 250 °C (Figure 10.2c) shows two distinct phases, indicative of a partial crystallization of the film into an In_4Se_3 phase.

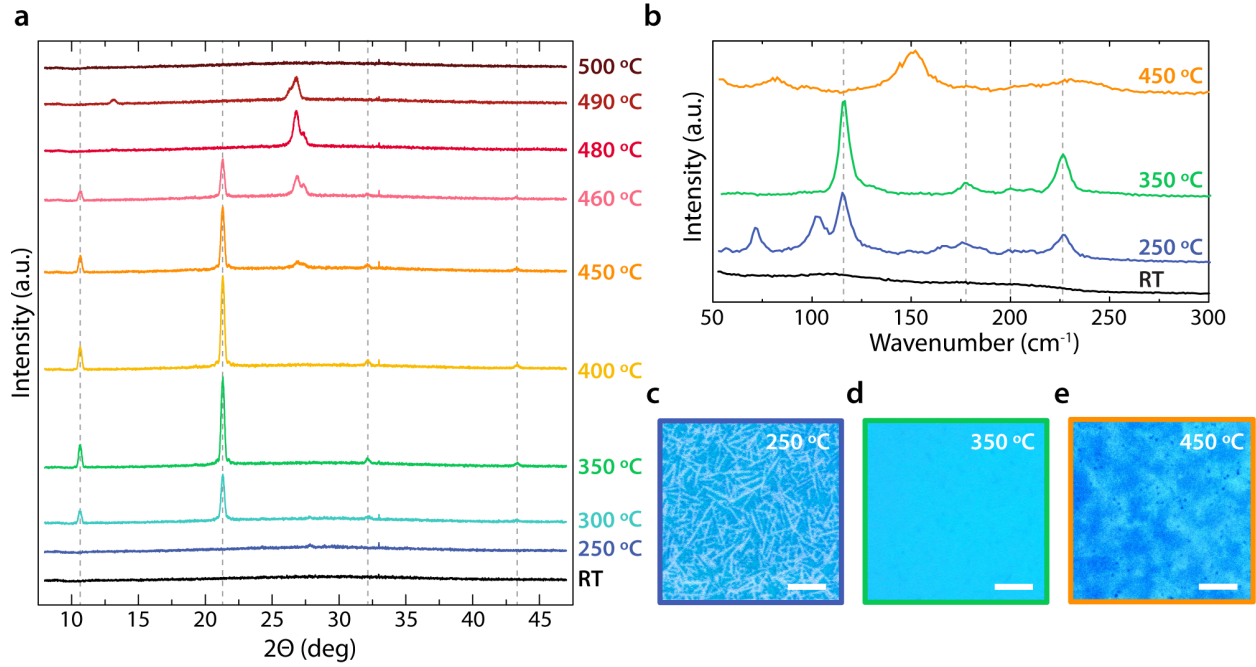


Figure 10.2: *In situ* XRD of InSe films being annealed (a) *In situ* XRD of an amorphous 30-nm-thick PLD InSe film being annealed from RT to 500 °. The peaks attributed to InSe are denoted by the dashed lines. (b) *Ex situ* Raman spectra from 30-nm-thick InSe films after annealing to various temperatures in the XRD instrument. The peaks attributed to InSe are denoted by the dashed lines. Optical micrographs of InSe films after annealing to (c) 250 °C, (d) 350 °C, and (e) 450 °C in the XRD instrument. The scale bar is 10 μm .

Between 300 °C and 400 °C, a pure InSe XRD pattern was achieved and matches well with standard patterns for InSe (PDF # 04-005-5113 and 04-004-6176) and other reports of synthesized InSe crystals and films.^{69,235,337} Specifically, the diffraction peaks at $2\theta = 10.6^\circ$, 21.3° , 32.1° , and 43.3° correspond to the (002), (004), (006), and (008) planes for β -InSe and ϵ -InSe, or the (003), (006), (009), and (0012) planes of γ -InSe. The observation of exclusively (00 l) diffraction peaks indicates strong texturing of the InSe crystal domains parallel to the SiO_2/Si substrate surface. As a result, this XRD pattern alone does not enable distinction between the InSe polytypes due to their similar d -spacing (spatial periodicity) in the out-of-plane c -axis direction. However, as further discussed in subsection 11.2.3, the crystalline InSe films are identified as ϵ -InSe using electron microscopy. The corresponding *ex situ* Raman

spectroscopy of a film annealed to 350 °C also shows a phase-pure spectrum of InSe. In particular, the presence of the InSe A_2'' Raman mode at 200 cm^{-1} indicates the identity of the crystalline film as either γ -InSe or ϵ -InSe, rather than β -InSe.^{338,339} Additionally, the optical microscopy of the film annealed to 350 °C shows a homogeneous film (Figure 10.2d).

Further annealing to 450 °C and above resulted in the appearance of diffraction peaks at $2\theta = 26.8^\circ$ and 27.3° . These peaks are consistent with previous studies on the post-annealing of In_2Se_3 thin films wherein the two peaks correspond to the (006) planes of κ - In_2Se_3 and γ - In_2Se_3 , respectively, the former of which is metastable.^{340–343} An additional diffraction peak located at $2\theta = 13.2^\circ$ emerged at 490 °C and matches well with the (003) plane of κ - In_2Se_3 . The *ex situ* Raman spectrum from a film annealed to 450 °C and cooled to RT reveals modes at 81 cm^{-1} , 150 cm^{-1} , and 231 cm^{-1} , which correspond to γ - In_2Se_3 .²⁰⁰ However, κ - In_2Se_3 exhibits similar Raman modes³⁴¹ and the possibility of its co-existence with γ - In_2Se_3 cannot be ruled out. The broadness of the Raman peaks (Figure 10.2b) and the inhomogeneity of the film (Figure 10.2e) both indicate material loss after annealing at 450 °C. At 500 °C, we observed complete material loss *via* sublimation. Altogether, the *in situ* XRD study demonstrates how the complexity of the indium-selenium system manifests itself through a post-deposition annealing process under vacuum and how various structures (*i.e.*, In_4Se_3 , InSe, In_2Se_3) can be accessed using the annealing temperature.

10.2.2 *in situ* post-annealing in the PLD chamber

The results from the *in situ* XRD study were used to guide the post-annealing of InSe films inside the PLD chamber (*i.e.*, *in situ* post-annealing). The annealing was performed using an infrared (IR) heating lamp immediately after deposition on 300-nm-thick SiO_2/Si at a pressure of 10^{-7} Torr. This procedure eliminates exposure of the films to ambient conditions between the deposition and annealing step. The Raman spectra at selected temperatures (Figure 10.3a) illustrates a structural evolution in 8-nm-thick InSe films which closely follows

the trends observed in the *in situ* XRD study. The onset of crystallization occurred at 220 °C with In_4Se_3 as identified by the Raman modes at 71 cm^{-1} , 103 cm^{-1} , and 150 cm^{-1} . At higher temperatures, the coexistence of InSe and In_4Se_3 was observed until a threshold temperature (370 °C) at which the In_4Se_3 phase disappears, leaving pure InSe. There appears to be a ~ 20 °C difference in this threshold temperature between the PLD and XRD instruments, presumably due to a significant difference in the chamber pressure and heating mechanism. Annealing to 450 °C resulted in the appearance of Raman modes at 110 cm^{-1} , 173 cm^{-1} , 204 cm^{-1} which correspond to $\beta\text{-In}_2\text{Se}_3$.^{79,91,200} Interestingly, $\beta\text{-In}_2\text{Se}_3$ was formed by post-annealing the 8-nm-thick films to high temperatures (≥ 450 °C) in the PLD instrument, while $\gamma\text{-In}_2\text{Se}_3$ was formed in 30-nm-thick films in the *in situ* XRD experiment. We attribute this discrepancy to the difference in thickness of the samples, since high temperature post-annealing of thicker films (~ 45 nm) in the PLD instrument resulted in $\gamma\text{-In}_2\text{Se}_3$ (Figure 10.3b). The effect of thickness on stabilizing different In_2Se_3 polymorphs has been studied recently and reports suggest that $\beta\text{-In}_2\text{Se}_3$ can only be obtained at room temperature in the 2D limit while $\beta\text{-In}_2\text{Se}_3$ has only been observed at high temperatures (> 200 °C) in the bulk form.⁹¹ Furthermore, Choi *et al.* demonstrated electrically-driven and reversible phase switching between $\beta\text{-In}_2\text{Se}_3$ and $\gamma\text{-In}_2\text{Se}_3$ in exfoliated 2D material, attesting to the existence of transitional pathways between the two structures.²⁵²

To study the compositional evolution of the 8-nm-thick InSe films, we used *ex situ* XPS. The Se:In ratios of the films following post-annealing at various temperatures are plotted in Figure 10.4a and match well with the structural evolution studied using Raman spectroscopy. The stoichiometry of a bulk single crystal of InSe was also measured for comparison. Initially, the as-deposited PLD InSe film at room temperature was Se-deficient with a Se:In ratio of 0.8. Hence, the PLD plume most likely contains single Se species with poor sticking coefficients. However, annealing of the films resulted in stoichiometric 1:1 InSe through the relative loss of In. Further annealing to 450 °C resulted in an increase in the Se:In ratio to 1.5, corresponding

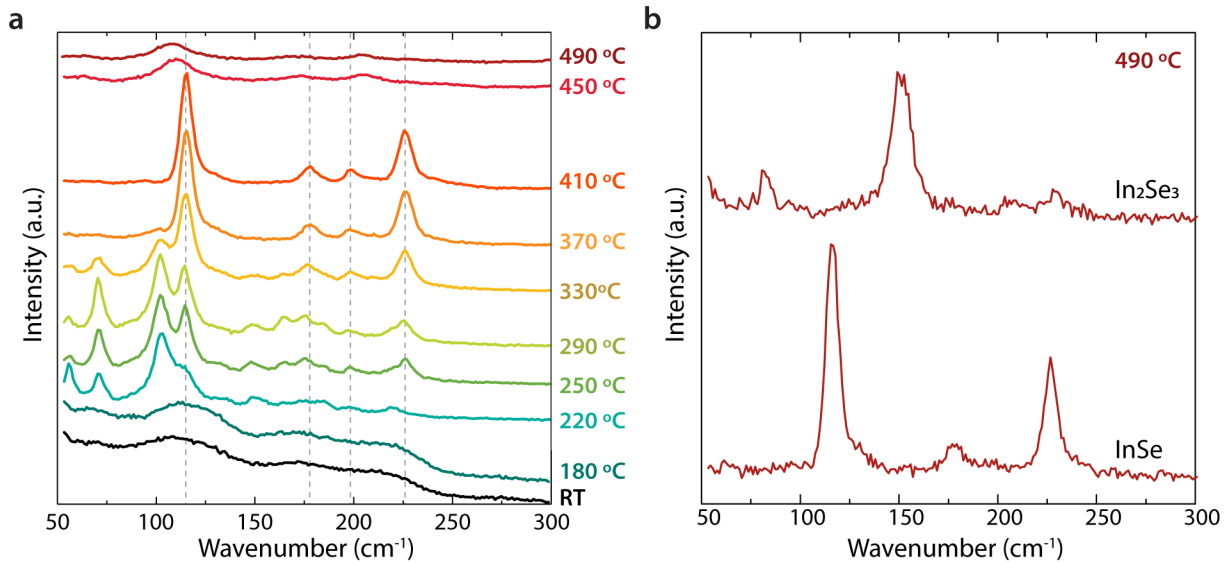


Figure 10.3: Raman spectra from InSe films on SiO₂ following post-annealing in the PLD chamber. (a) Raman spectra from 8-nm-thick InSe films following post-annealing at various temperatures. The annealing was performed *in situ* directly after deposition in the PLD chamber and shows a similar trend to the *in situ* XRD annealing study. The peaks attributed to InSe are denoted by dashed lines. (b) Raman spectra from a ~45-nm-thick InSe film annealed at 490 °C in the PLD instrument. Annealing to high temperatures in thicker films resulted in the formation of γ -In₂Se₃ domains in coexistence with InSe, instead of the β -In₂Se₃ seen in thinner films. The spectra are from two different locations on the same sample.

to In₂Se₃. Additional annealing to 490 °C results in Se loss.

Since the vapor pressure of In is lower than both InSe and In₂Se₃, which in turn have lower vapor pressures than elemental Se,³²⁹ it is unlikely that the In loss proceeds *via* elemental In. Instead, previous studies elucidated the evaporation products of both InSe and In₂Se₃ as In₂Se and Se₂.^{344–346} Therefore, we conclude that the relative loss of indium in the annealed films most likely occurs through the evaporation of In₂Se. The decrease in the Se:In ratio to 1.4 at 490 °C is then enabled by preferential evaporation of Se₂ from In₂Se₃. The formation of In₂Se₃ from InSe using thermal annealing has been previously reported.^{249,347} Additionally, we cannot preclude the possibility that the film passes through alternative stoichiometries such as In₅Se₇ or In₆Se₇ on the way to In₂Se₃ from InSe. However, the characterization of

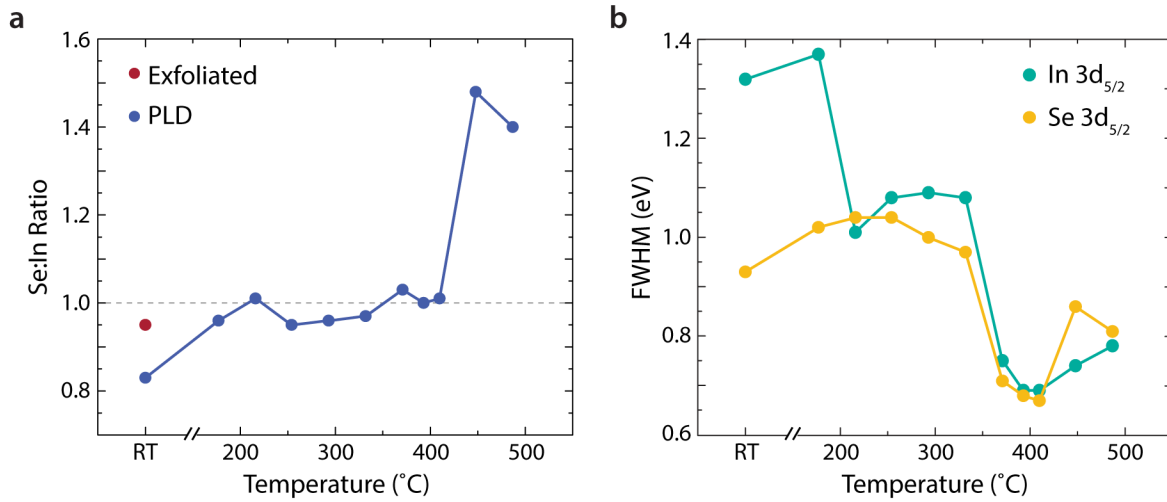


Figure 10.4: XPS spectra from InSe films on SiO₂ following post-annealing in the PLD chamber. (a) The selenium to indium ratio, as determined by XPS, and the (b) full width at half maximum (FWHM) of the In 3d_{5/2} and Se 3d_{5/2} XPS peaks from 8-nm-thick InSe films following post-annealing at various temperatures. The targeted Se:In ratio of 1:1 for InSe is denoted by the dashed line.

the cooled films matches well with In₄Se₃, InSe, and In₂Se₃ at the various post-annealing temperatures.

Additional insight into the purity of the chemical coordination of the In and Se atoms was obtained from the FWHM of the In 3d_{5/2} and Se 3d_{5/2} XPS peaks (Figure 10.4b). Due to the amorphous nature of the as-deposited film, the FWHM for the peaks of both elements were initially large in value (> 0.9 eV). The initially larger In 3d_{5/2} FWHM could be due to the relative deficiency of Se upon RT deposition; the lack of single Se species could result in more uniform Se coordination, while the excess In could result in a mixture of In coordination. Upon the onset of crystallization at 220 °C, the In 3d_{5/2} peak sharpened, indicating a significant alignment in the chemical coordination of In which coincided with the relative loss of excess In to achieve a 1:1 Se:In ratio. This behavior is consistent with the partial crystallization of the film into In₄Se₃ observed with Raman spectroscopy. Full minimization of the FWHM for both elemental peaks occurred between 370 °C and 410

°C, coinciding with the temperature range for pure InSe. Post-annealing to 450 °C then broadened the In 3d_{5/2} and Se 3d_{5/2} again due to degradation and material loss. The FWHM of the XPS peaks were minimized for films annealed at 410 °C, reaching a minimum value of 0.7 eV for both In 3d_{5/2} and Se 3d_{5/2}. For comparison, the FWHM measured for the In 3d_{5/2} and Se 3d_{5/2} peaks of bulk single-crystal InSe were also 0.7 eV, attesting to the purity of the synthesized films.

10.2.3 Generalizability of optimal post-annealing temperatures

The generalizability of the PLD deposition and vacuum post-annealing procedure in obtaining crystalline InSe was investigated on (1) a different substrate and (2) using a different annealing method. Firstly, we studied the crystallization of 8-nm-thick InSe films deposited on *c*-plane sapphire and post-annealed in the PLD chamber. As deduced from the *ex situ* Raman spectroscopy study (Figure 10.5a), the optimal post-annealing temperature for InSe films on *c*-plane sapphire substrates was ~390 °C, which agrees with the optimal temperatures for InSe films on 300 nm SiO₂/Si obtained in the preceding discussion (~400 °C). Secondly, we investigated the effect of vacuum laser annealing on PLD InSe films. In this study, 8-nm-thick amorphous PLD InSe films were deposited on Si micro-pillars which were then individually heated using laser irradiation in an Autonomous Research System (ARES), as described in a previous report.^{348,349} The crystallization of the InSe films was monitored using *in situ* Raman spectroscopy as each pillar was heated individually by the laser to a certain temperature and annealed for 90 s at a pressure of 10⁻⁴ Torr. The ratio of the intensity of the InSe A₁' Raman peak at ~116 cm⁻¹ to the intensity of the Si substrate Raman mode at ~520 cm⁻¹ was maximized at an optimal annealing temperature of ~400 °C (Figure 10.5b,c), corresponding well to optimal temperatures for annealing the InSe films in the PLD chamber and suggesting that these temperatures are generalizable to other annealing treatments.

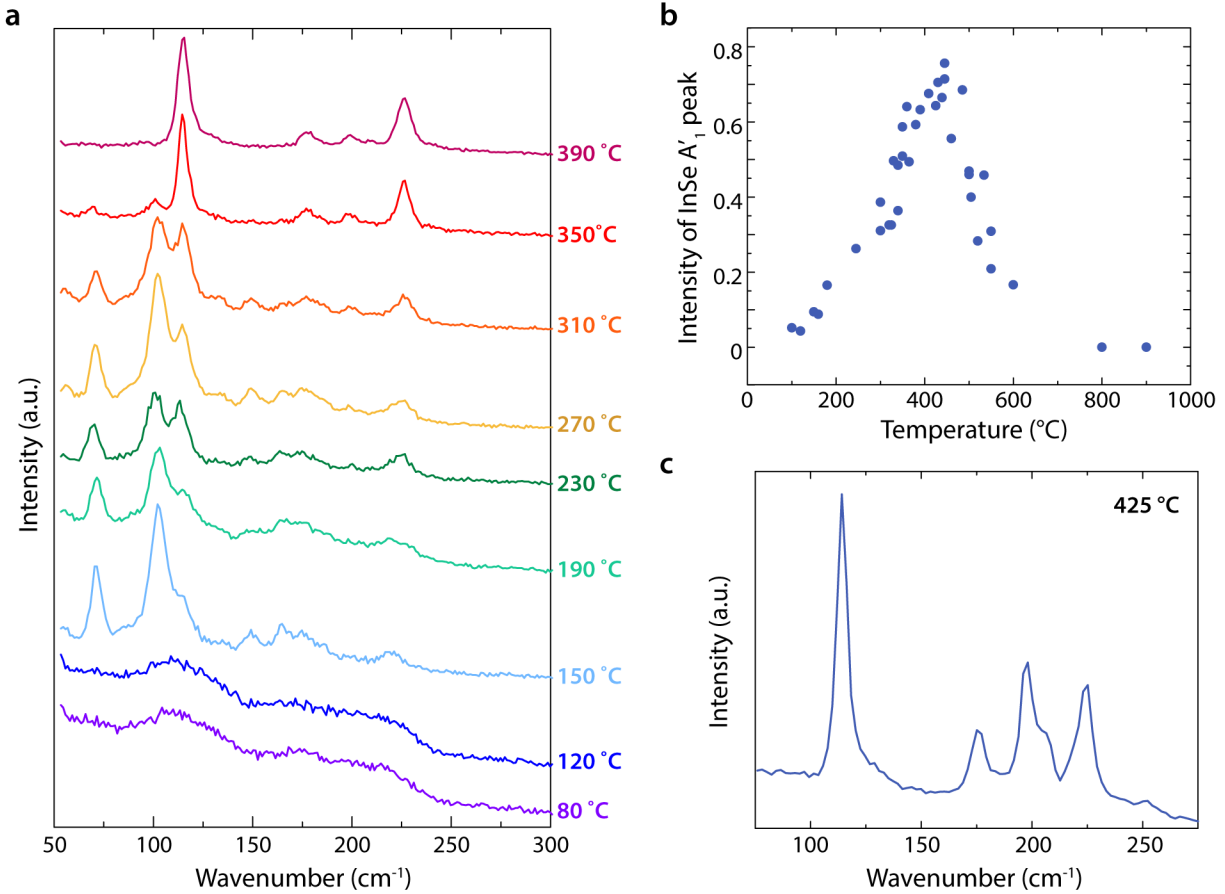


Figure 10.5: Generizability of the InSe post-annealing procedure to an alternative (a) substrate and (b-c) annealing method. (a) Raman spectra from 8-nm-thick InSe films deposited on *c*-plane sapphire and post-annealed in the PLD chamber. The optimal annealing temperature is comparable to InSe films on 300-nm-thick SiO₂/Si (~400 °C). (b) Laser annealing of 8-nm-thick InSe on Si micro-pillars studied using *in situ* Raman spectroscopy. The plot shows the ratio of the intensity of the InSe A₁' Raman peak at ~116 cm⁻¹ to the intensity of the Si substrate Raman mode at ~520 cm⁻¹ as a function of annealing temperature. The intensity of the InSe A₁' Raman peak is maximized at ~400 °C. (c) *Ex situ* Raman spectrum from an 8-nm-thick PLD InSe film on an Si-micropillar annealed at 425 °C for 90 s using laser irradiation. A signature InSe spectrum is observed and is free from impurity phases.

Chapter 11

Synthesis of InSe Films

11.1 Determination of optimal InSe synthesis conditions

11.1.1 Post-annealing temperature

Despite the unchanging initial composition of the film, this material has a very dynamic nature. From the study on the structural and compositional evolution of PLD InSe films processed using vacuum thermal annealing, it is clear that temperature is a principal parameter in the phase control of InSe films. We used this insight to rationally determine synthesis conditions for pure InSe ultrathin films. Both the *in situ* XRD experiment and *ex situ* characterization of InSe films annealed in the PLD chamber indicated that there was a specific temperature window in which pure InSe could be formed, and both studies suggested that this window is 325-425 °C. For post-annealing in the PLD chamber, a temperature around 400 °C yielded pure InSe.

11.1.2 Co-deposition scheme using both InSe and In₂Se₃ targets

In addition to the determination of optimal annealing temperatures, the compositional study revealed a process of mass loss to achieve the targeted stoichiometry of 1:1 In:Se. While the mass loss mediates a transition to structurally and compositionally pure InSe, we also suspect that it is detrimental to the quality of the InSe film. As discussed later, reducing the stoichiometric mismatch between the starting amorphous film and the targeted 1:1 In:Se composition resulted in improved morphology and electronic properties of the annealed InSe films. Consequently, we developed a co-deposition scheme using both an InSe and In₂Se₃ PLD target to enrich the initial RT deposition with Se. In principle, this scheme should reduce the loss of material due to the mismatch between the starting and targeted stoichiometry. Several ratios of the number of pulses from the InSe target to the In₂Se₃ target were tested, resulting in the film stoichiometries presented in Table 11.1 and Figure 11.1. The totality of the film is composed of repeated cycles of a particular InSe:In₂Se₃ unit. In addition to the pulse ratio, the absolute number of pulses in a cycle was considered. In particular, the total number of InSe and In₂Se₃ pulses per cycle was chosen to remain well below the InSe monolayer to ensure mixing of the InSe and In₂Se₃ deposition. Since a monolayer of InSe corresponds to ~ 40 pulses, a basis of a total of 20 pulses was chosen. Hence, based on the composition and total number of pulses, an optimal co-deposition scheme of 16:4 InSe:In₂Se₃ was determined. As shown in Table 11.1 and Figure 11.1, the 16:4 InSe:In₂Se₃ co-deposition scheme resulted in an as-deposited Se:In ratio of 1.0 as measured by XPS.

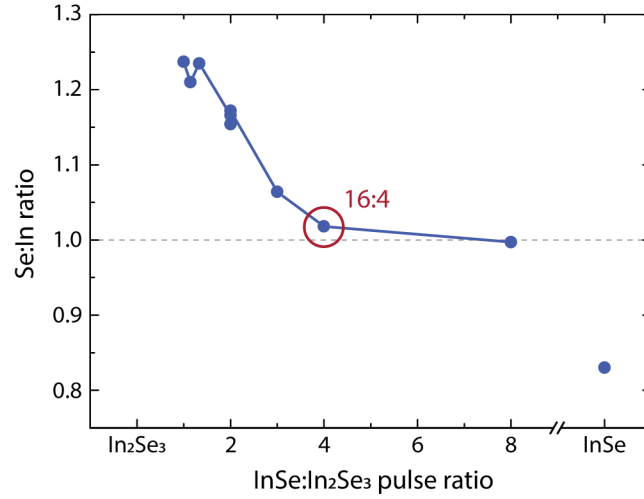


Figure 11.1: Stoichiometry of films deposited using various ratios of InSe:In₂Se₃ pulses. The Se:In ratio, as determined by XPS, of as-deposited ~ 8 -nm-thick InSe films as a function of the ratio of the number of pulses from the InSe target to the In₂Se₃ target. The 16:4 InSe:In₂Se₃ ratio was chosen as the optimal co-deposition scheme.

# of InSe pulses:# of In ₂ Se ₃ pulses	InSe:In ₂ Se ₃ ratio	Se:In ratio of film
8:8	1	1.24
8:7	1.14	1.21
8:6	1.33	1.24
8:4	2	1.17
16:8	2	1.15
24:12	2	1.17
12:4	3	1.06
16:4	4	1.02
32:4	8	1.00
1:0	∞	0.83

Table 11.1: Stoichiometry of ~ 8 -nm-thick films obtained from PLD using various ratios of InSe:In₂Se₃ pulses

11.2 Characterization of optimized InSe films

11.2.1 Thickness tunability

Using a co-deposition scheme of 16:4 InSe:In₂Se₃ pulses and *in situ* vacuum post-annealing at ~ 400 °C, pure InSe films of various thicknesses were synthesized on 300 nm SiO₂/Si substrates. The film thickness, as determined using XRR, can be controlled by the number of total PLD laser pulses, as shown in Figure 11.2a. Furthermore, the thickness was compared with the vertical domain size of the films calculated using the Scherrer equation and the FWHM of the InSe (004) XRD peak. The XRR and XRD data and fits are presented in Figure 14.1. The vertical domains sizes were found to be 4.3 nm, 7.4 nm, 15.8 nm, and 22.1 nm which match the 4.5 nm, 7.5 nm, 15.3 nm, and 23.4 nm thicknesses of the samples, respectively. Hence, the synthesis technique presented here yields highly (00*l*)-textured InSe films where the vertical domain size corresponds to the film thickness. A linear fit of the thickness of the crystallized films as a function of the number of deposition laser pulses yields an overall growth rate of 0.2 Å/pulse. The normalized Raman spectra and optical images obtained from films of various thickness are presented in Figure 11.2b and Figure 11.2c, respectively, showing uniform, continuous, and large-area (1 cm $\times$ 1 cm) films of pure InSe.

11.2.2 Composition and morphology

Further characterization of optimized InSe films was performed to evaluate their quality. The micron-scale homogeneity was assessed using Raman spectroscopy mapping over a 30 $\mu\text{m} \times 30 \mu\text{m}$ region of a 15-nm-thick crystalline InSe film. The position and intensity of the InSe A'₁ Raman mode over the mapped area is plotted in Figure 11.3a,b, showing the homogeneous location of the peak at $\sim 116 \text{ cm}^{-1}$. The InSe Raman spectra were normalized to the intensity and location of the Si Raman mode at $\sim 520 \text{ cm}^{-1}$. No extraneous peaks

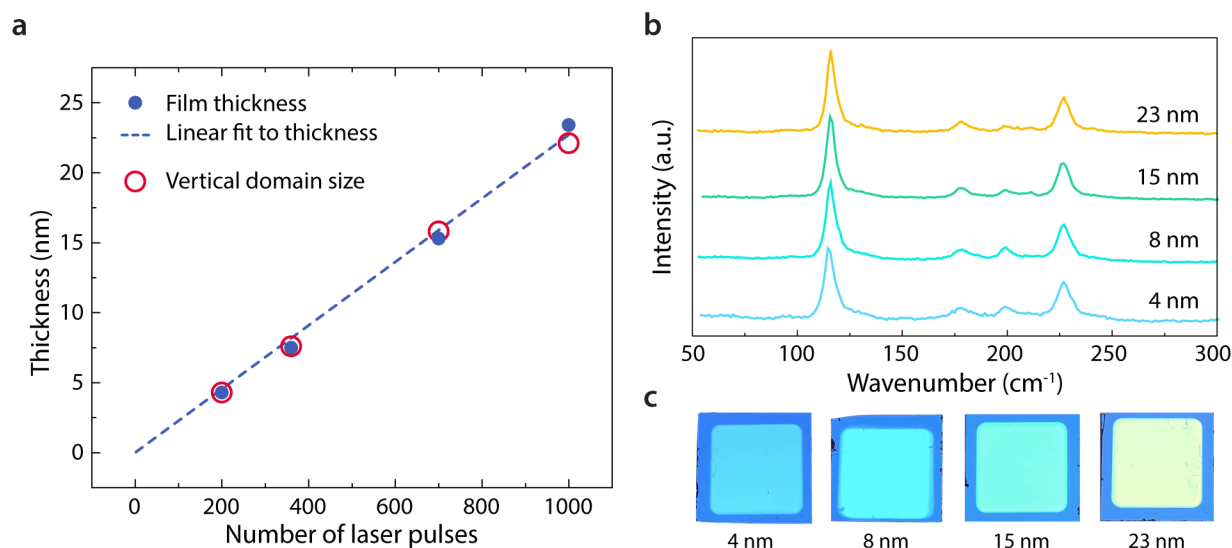


Figure 11.2: Thickness tunability of the optimized PLD InSe films. The films were deposited using the 16:4 InSe:In₂Se₃ co-deposition scheme on 300-nm-thick SiO₂/Si substrates and post-annealed *in situ* at ~ 400 °C. **(a)** XRR determined thickness and XRD determined out-of-plane single crystal domain size of optimized InSe films as a function of the total number of laser pulses. A linear fit to the film thickness with a fixed intercept at 0 yields a slope of 0.2 Å/pulse. **(b)** Normalized Raman spectra of films of various thicknesses showing modes corresponding to InSe with no impurity phases. **(c)** Optical images of the optimized InSe films of various thicknesses. The substrates are approximately 1 cm $\times$ 1 cm in dimension.

were observed, as attested to by the plot of all the acquired spectra in Figure 11.3c. The AFM height image (Figure 11.4a) and corresponding phase image (Figure 11.4b) of a 5 μm $\times$ 5 μm area of a 15-nm-thick crystalline InSe film show a continuous film. The root mean square (RMS) roughness of the film was 1.0 nm. In contrast, AFM of crystalline InSe films which did not employ the InSe:In₂Se₃ co-deposition scheme (Figure 11.4c,d) exhibited an RMS roughness of 2.0 nm. Thereby, we observed an improvement in the morphology of the films when using the co-deposition scheme, presumably from a reduction in mass loss by counteracting the initial stoichiometric mismatch.

The XPS spectra of the In 3d, Se 3d, and O1s core levels of a 15-nm-thick InSe film are shown in Figure 11.5a-c. The peak positions of the In 3d_{5/2} and In 3d_{3/2} are 445.3 eV and

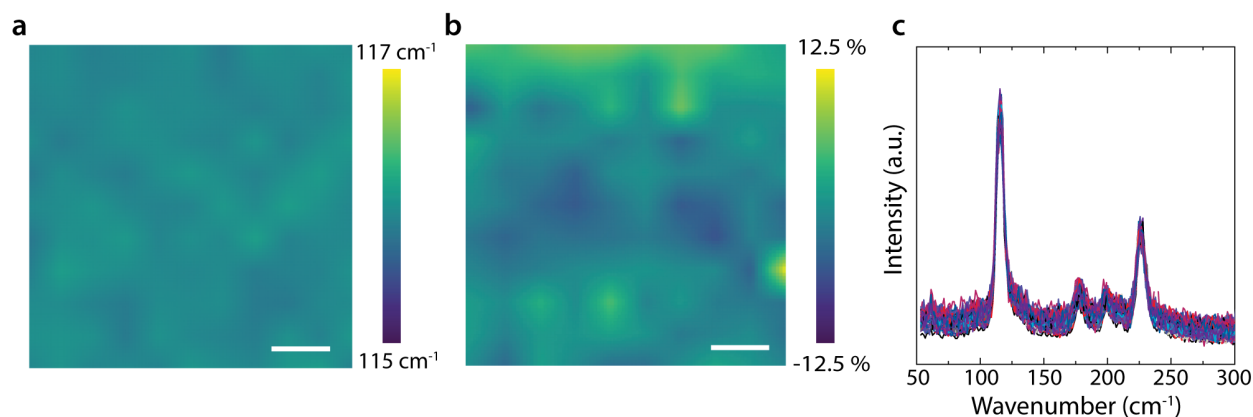


Figure 11.3: Raman spectroscopy map of an optimized InSe film. The 15-nm-thick InSe film was synthesized using the 16:4 InSe:In₂Se₃ co-deposition scheme and *in situ* post-annealing at 410 °C. 2D Raman spectroscopy map of the InSe A'1 Raman mode (a) peak position and (b) peak intensity normalized to the Si Raman peak intensity. The uniformity of the map shows the homogeneity of the position of the A'1 Raman mode around 116 cm⁻¹ and little variation in its intensity. The scale bar is 5 μm. (c) All 121 of the acquired Raman spectra.

452.8 eV respectively, which match well with those of pristine exfoliated InSe in literature,³³² as well as those of the measured bulk InSe crystal (445.3 eV and 452.9 eV). Similarly, the Se 3d_{5/2} and Se 3d_{3/2} peak positions at 54.6 eV and 55.4 eV also matched the values of pristine exfoliated InSe in literature and the bulk InSe crystal (54.7 eV and 55.5 eV). The lack of an O 1s peak signifies that there is no detectable oxidation of the films.

11.2.3 Crystallinity and polytype identification

The crystallinity of an optimized 15-nm-thick InSe film was investigated with transmission electron microscopy (TEM), STEM, SAED, and HAADF-STEM imaging. The sample was prepared by the direct synthesis of a 15-nm-thick InSe film on an 8-nm-thick amorphous SiO₂ support membrane for TEM and was oriented perpendicular to the [001] zone axis. Figure 11.6a shows a TEM image of the InSe film wherein the polycrystallinity of the film is apparent. From this data, we estimate lateral crystal domain sizes of 50-150 nm. The

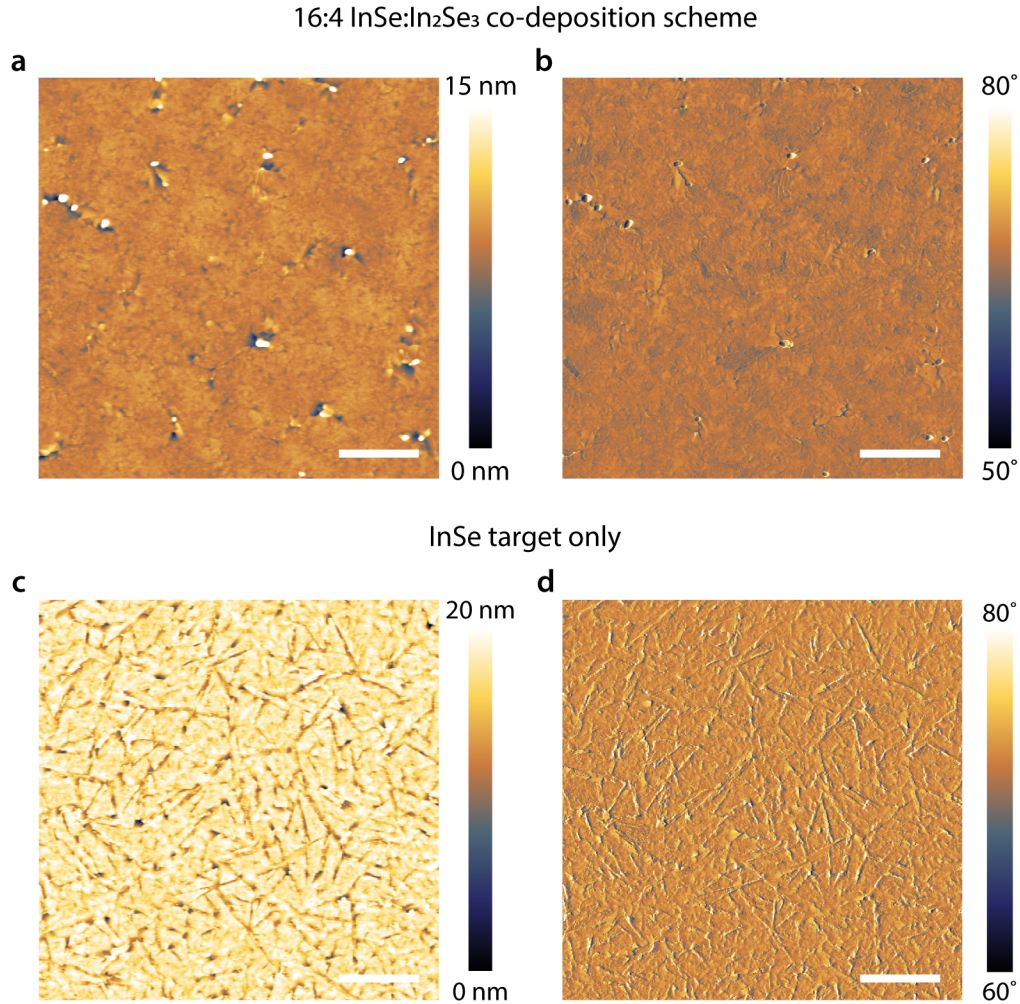


Figure 11.4: AFM of InSe films synthesized (a,b) with and (c,d) without the InSe:In₂Se₃ co-deposition scheme. (a) AFM height and (b) phase image of a 15-nm-thick InSe film synthesized using the 16:4 InSe:In₂Se₃ co-deposition scheme and *in situ* post-annealing at 410 °C. The scale bar is 1 μ m. (c) AFM height and (d) phase image of a 15-nm-thick InSe film synthesized using only the InSe PLD target and *in situ* post-annealing at 410 °C. The scale bar is 2 μ m.

high-resolution TEM image (Figure 11.6b) shows a hexagonal lattice structure with d -spacing of 0.20 nm between $\{110\}$ planes (denoted by the yellow lines) and 120° angle between the (100) and $(1\bar{2}0)$ lattice planes (denoted by the white arc), consistent with InSe. The SAED pattern along the $[001]$ zone axis with an aperture of ~ 110 nm (Figure 11.6c) shows a single-crystal domain. The diffraction spots can be indexed to the ϵ -InSe structure, as

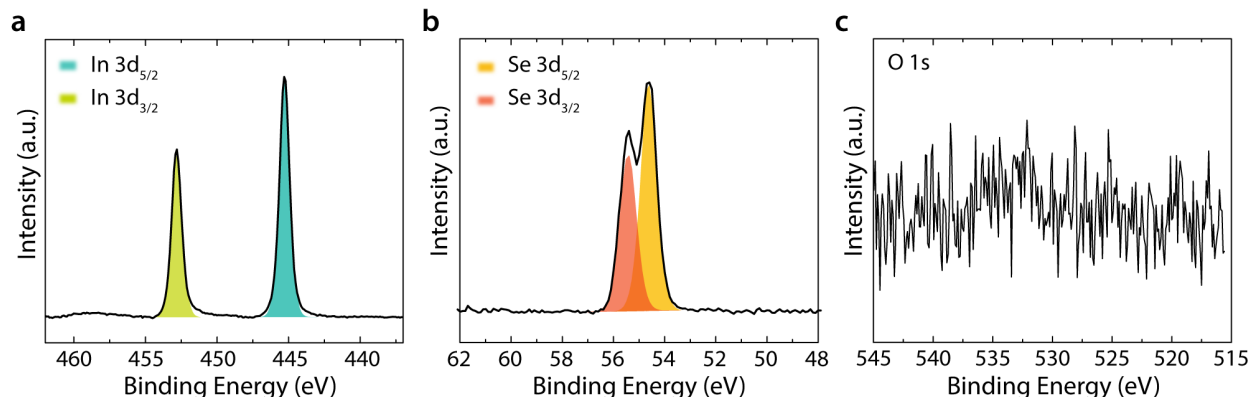


Figure 11.5: XPS of an optimized InSe film. The 15-nm-thick InSe films was synthesized using the 16:4 InSe:In₂Se₃ co-deposition scheme and *in situ* post-annealing at 410 °C. (a) In 3d, (b) Se 3d, and (c) O 1s core-level XPS spectra of an InSe film.

marked in the figure. The SAED pattern with a larger aperture of ~ 900 nm (Figure 11.6d) demonstrates the polycrystallinity of the sample with all the diffraction rings accountable to the InSe structure and supports that they are free from impurity phases.

Due to similar in-plane structures, discerning the exact polytype of synthesized InSe films can prove difficult with most characterization techniques. However, HAADF-STEM paired with imaging simulations has been shown with exfoliated InSe to successfully identify the polytype.⁶⁹ We used the technique here to identify our ultrathin InSe films as ϵ -InSe (2H_b stacking). The experimental HAADF-STEM image obtained from the 15-nm-thick InSe film is shown in Figure 11.6e. Since contrast in HAADF strongly depends on the atomic number, the differences in intensity of the atomic columns can be used to distinguish polytypes. As illustrated in the top view of the structural diagrams in Figure 9.1b, the presence of atoms at the center of the hexagonal ring of atoms rules out β -InSe and the contrast between the intensities of the center and ring atoms suggest that the structure corresponds to ϵ -InSe rather than γ -InSe. These differences in contrast are clear in the simulated HAADF images (Figure 11.6f): no atom column is present at the center of the hexagonal rings for β -InSe, an atom column of equal intensity is present at the center of the hexagonal ring atoms for γ -InSe,

and an atom column of significantly lesser intensity is present at the center of the hexagonal ring atoms for ϵ -InSe. The experimental HAADF image of the synthesized 15-nm-thick InSe film most closely matches the contrast of the ϵ -InSe polytype simulated image and matches very well with a previously reported HAADF-STEM image obtained from multilayer exfoliated ϵ -InSe.⁶⁹ The identification of the films as ϵ -InSe polytype is commensurate with the observations of (1) the InSe A_2'' Raman mode at 200 cm^{-1} only exhibited by ϵ -InSe and γ -InSe and (2) the first reflections in SAED belonging to the InSe (100) and (010) spots which are forbidden in γ -InSe, but allowed in ϵ -InSe and β -InSe. Overall, the preceding analysis agrees with previous reports of exfoliated 2D ϵ -InSe.^{69,350}

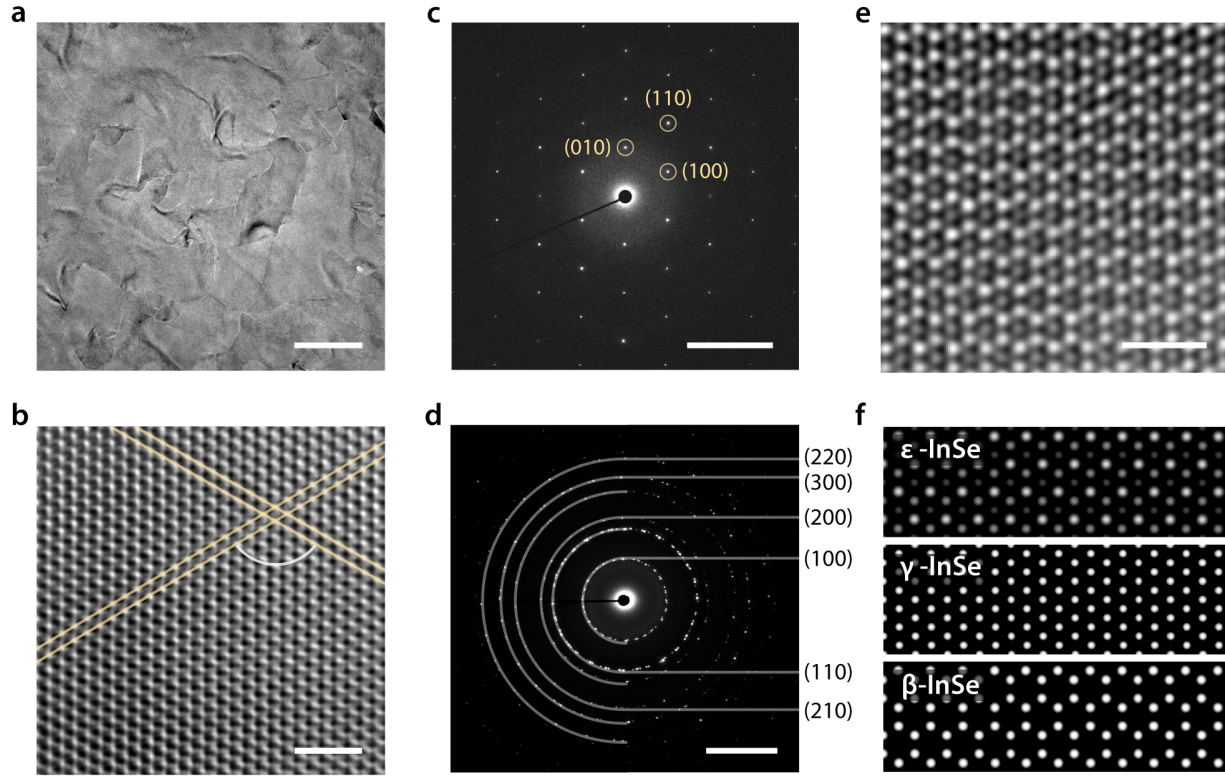


Figure 11.6: TEM, SAED, and HAADF-STEM of an optimized InSe film. The 15-nm-thick InSe film was synthesized using the 16:4 InSe:In₂Se₃ co-deposition scheme and *in situ* post-annealing at 410 °C. **(a)** TEM image of the InSe film showing lateral grain sizes from 50-150 nm. The scale bar is 100 nm. **(b)** High-resolution TEM image of the InSe film along the [001] zone axis. The yellow lines denote a ~0.20 nm lattice spacing, and the white arc denotes a 120° angle between the (110) and (1̄20) axes consistent with crystalline InSe. The scale bar is 2 nm. **(c)** SAED pattern along the [001] zone axis with a ~110 nm aperture showing a single crystal domain with six-fold symmetry consistent with InSe. The scale bar is 5 nm⁻¹. **(d)** SAED pattern with a ~900 nm aperture showing polycrystalline InSe with a consistent structure. The scale bar is 5 nm⁻¹. **(e)** HAADF image of the InSe film along the [001] zone axis. The scale bar is 1 nm. Upon comparison to **(f)** the simulated HAADF images for the polytypes of InSe, the observed contrast in **(e)** best corresponds to ε-InSe.

Chapter 12

Optoelectronic and Electronic Performance of Synthesized InSe Films

12.1 Bottom-gated InSe phototransistors

Utilizing our optimized co-deposition scheme, we demonstrated the high-performance optoelectronic response of the InSe ultrathin films. The phototransistors were fabricated by depositing 15-nm-thick InSe on 300 nm SiO₂/Si substrates. The source-drain metal contacts (10 nm In and 50 nm Au) were deposited using thermal evaporation through shadow masks in a solvent-free fabrication process. The doped Si substrate served as a bottom-gate. To achieve high photodetector performance, the channel length (L) and channel width (W) of the phototransistors were chosen to be 7 μm and 30 μm , respectively, since the net photocarrier gain in phototransistors scales as L^{-2} .^{351–353} All photocurrent measurements were conducted in vacuum ($< 10^{-5}$ Torr) using a laser diode emitting at 515.6 nm (additional details can be found in chapter 14). The transfer characteristics at a drain bias of $V_D = 10$ V (Figure 12.1a) reveal that the photocurrent (I_{pc}) increased with the bottom-gate bias. The drain current under illumination (I_{light}) decreased the V_{TH} by ~ 10 V such that the I_{pc} exceeded the drain current in the dark (I_{dark}) by ten-fold in the off state ($V_{BG} = -60$ V), indicating an extrinsic

gain mechanism of the photovoltaic effect arising from trapped charges in the channel.^{352,354} The temporal photoresponse at $V_{BG} = 80$ V and $V_D = 10$ V was probed by a modulating laser, resulting in rise and fall times of 1 ms and 2.5 ms, respectively (Figure 12.1b). The photoconductivity mechanism was further probed by varying the illumination power (P). The I_{pc} measured at $V_{BG} = 80$ V and $V_{BG} = 10$ V in three devices was found to increase with P as $P^{0.43 \pm 0.03}$, $P^{0.47 \pm 0.02}$, and $P^{0.47 \pm 0.01}$ (Figure 12.1c). The resulting responsivity (R), defined as $R = I_{pc}/P$, varied approximately as $R \sim P^{-0.5}$ (Figure 12.1d). This power law behavior suggests the dominance of bimolecular recombination, similar to what has been previously observed in exfoliated InSe phototransistors in accumulation.^{326,351,355} The maximum value of R obtained at low power intensity ($0.1 \mu\text{W}/\text{cm}^2$) approached $\sim 10^3$ A/W, which exceeds previously reported values for phototransistors fabricated from scalable ultrathin InSe films,^{70,235} as well as thicker films of solution-processed InSe nanoflakes.^{355,356}

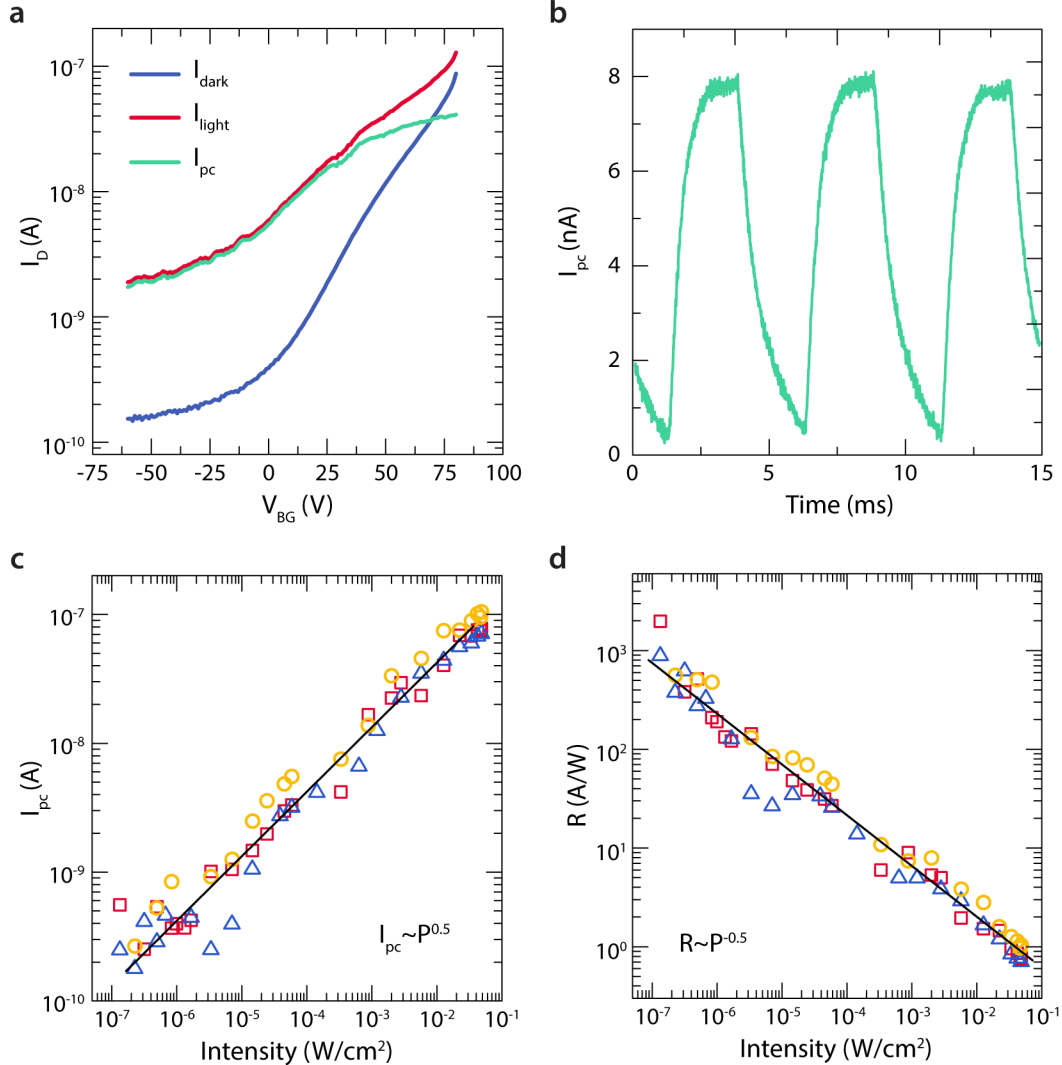


Figure 12.1: Bottom-gated InSe phototransistor characteristics. The FETs were made from 15-nm-thick InSe grown using the co-deposition scheme and post-annealed at $\sim 400^\circ\text{C}$. **(a)** Transfer characteristics of an InSe phototransistor at an illumination wavelength and intensity of 515.6 nm and 2 mW/cm^2 , respectively. V_{BG} was swept from 80 V to -60 V at a sweep rate of 10 V/s and V_D was fixed at 10 V. **(b)** Temporal response of the InSe phototransistor obtained by switching the laser on and off at a frequency of 200 Hz while the device was biased at $V_{BG} = 80$ V and $V_D = 10$ V. The rise time of ~ 1 ms and fall time of ~ 2.5 ms was extracted from 90% of the maximum and minimum values, respectively. **(c)** Photocurrent versus illumination intensity for three devices (yellow circles, red squares, and blue triangles) at $V_{BG} = 80$ V and $V_D = 10$ V. The black line indicates the $I_{\text{pc}} \sim P^{0.5}$ behavior. **(d)** Responsivity versus illumination intensity for the three devices, showing a maximum $R \sim 10^3$ A/W at $0.1 \mu\text{W}/\text{cm}^2$. The black line indicates the $R \sim P^{-0.5}$ behavior.

12.2 Top-gated InSe FET array over large areas

12.2.1 Top-gated FET fabrication

We further leveraged this synthesis technique for the fabrication of homogeneous enhancement-mode top-gated ultrathin InSe FETs over large areas. The fabrication procedure is depicted in Figure 12.2. Following the InSe:In₂Se₃ co-deposition with a shadow mask (step 1), the patterned films were directly annealed at ~ 400 °C in the PLD instrument to prevent ambient exposure between the co-deposition and annealing steps (step 2). If amorphous InSe films were exposed to ambient conditions prior to annealing, we observed significant degradation of the electronic properties of the film (see subsection 12.2.3). The FET contacts (10 nm In and 70 nm Au) were patterned using shadow mask for a solvent-free fabrication process (step 3). The channel length and width were 100 μm and 150 μm , respectively. Following the InSe and electrode contact depositions, an encapsulation layer of 3 nm alumina and 20 nm hafnia was deposited using ALD to prevent ambient degradation of the InSe (step 4).^{326,357} This dielectric stack was also used as the top-gate dielectric with a measured capacitance of 437.5 nF/cm². Lastly, the top-gate contact (10 nm Cr and 70 nm Au) was deposited with a shadow mask (step 5). An optical image of patterned 15 nm InSe films with source-drain contacts (prior to top-gate fabrication for clarity) is shown in Figure 12.3a. The FETs were measured under ambient conditions. Additional details are provided in chapter 14.

12.2.2 Top-gated FET performance

The presented synthesis method enabled the realization of 118 functioning top-gated InSe FETs on a 1 cm $\times$ 1 cm substrate, which corresponds to a 91% yield. The yield was calculated excluding fabrication errors and is detailed in chapter 14. The output characteristics of a single top-gated FET at various top-gate voltages (V_{TG}) are shown in Figure 12.3b. At low

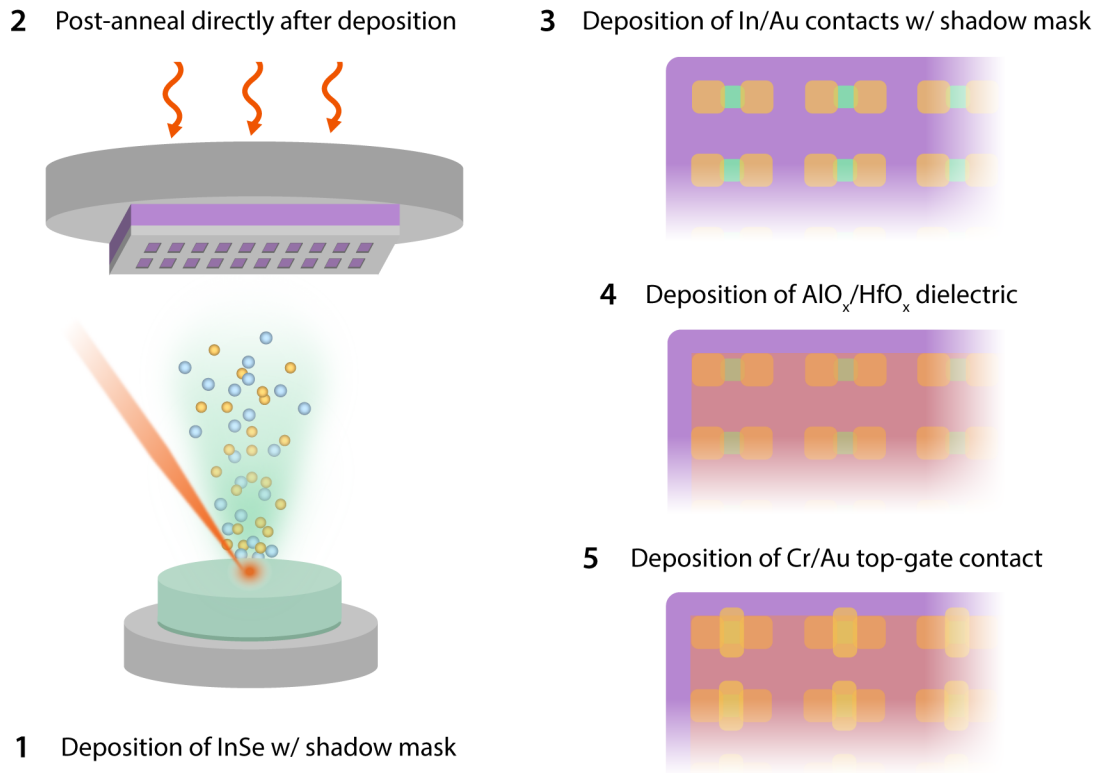


Figure 12.2: Top-gated InSe FET array fabrication procedure. The FETs were made from 15-nm-thick InSe grown using the 16:4 InSe:In₂Se₃ co-deposition scheme and post-annealed at $\sim 400^\circ\text{C}$. The deposition of the metal contacts were performed using thermal evaporation and the dielectric was deposited using ALD.

biases, the output demonstrated linear behavior and began to saturate past $V_D = 1\text{ V}$. The transfer characteristics of the same FET showed a low V_{TH} of 7 V, a high $I_{\text{on}}/I_{\text{off}}$ ratio greater than 10^4 , and a field-effect mobility (μ_{FE}) of $0.55\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at $V_D = 1\text{ V}$ (Figure 12.3c). The hysteresis observed is consistent with previous studies of exfoliated InSe on SiO_2 .^{157,313} A maximum $I_{\text{on}}/I_{\text{off}}$ ratio of $\sim 10^5$ was achieved when using a source-drain bias of $V_D = 5\text{ V}$ (Figure 12.3d), which is 1-2 orders of magnitude greater than previously reported FETs from 2D InSe films synthesized using scalable methods.^{70,235,325,356,358}

The FETs demonstrated here using the InSe:In₂Se₃ co-deposition scheme showed significantly better transport properties than FETs fabricated from films using the InSe PLD target

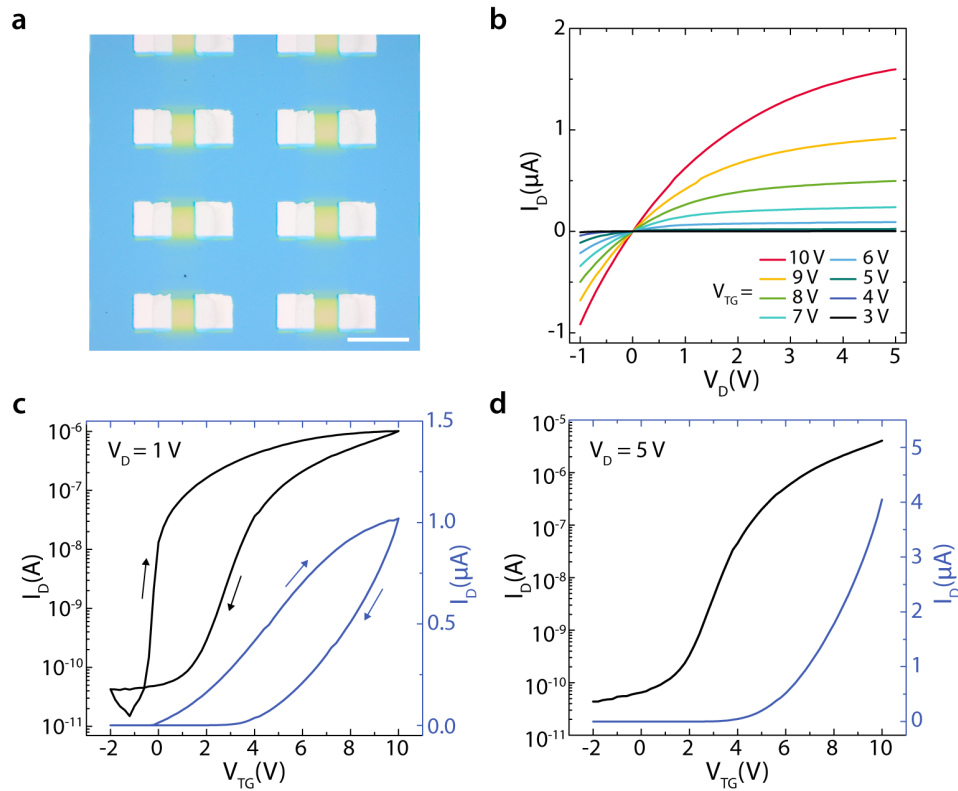


Figure 12.3: Top-gated InSe FET characteristics. The FETs were made from 15-nm-thick InSe grown using the co-deposition scheme and post-annealed at $\sim 400^\circ\text{C}$. **(a)** Optical micrograph of patterned InSe channels with shadow-masked In/Au contacts prior to top-gate fabrication. The scale bar is 300 μm . **(b)** Output characteristics of an InSe FET at various top-gate voltages. **(c)** Transfer characteristics of the InSe FET in **(b)** at a source-drain bias of 1 V. The sweep directions are indicated by the arrows. **(d)** Transfer characteristics of a high-performance InSe FET at a source-drain bias of 5 V, demonstrating an I_{on}/I_{off} of $\sim 10^5$.

alone. Presented in Figure 12.4a are the transfer characteristics from the 118 top-gated FETs from InSe films made using the InSe:In₂Se₃ co-deposition scheme. All the FETs were off at $V_{TG} = 0$ V and turned on past $V_{TH} \approx 7$ V. As a result, the FETs operated in enhancement-mode, which is necessary for low power consumption. On the other hand, top-gated FETs made using the InSe PLD target alone exhibited poorer electronic performance. As shown in Figure 12.4b, the FETs required an order of magnitude increase in source-drain voltage (10 V instead of 1 V) to attain the same I_{on}/I_{off} ratio of $\sim 10^4$. Furthermore, there is a significant current flow at $V_{TG} = 0$ V. As a result, the FETs made without the InSe:In₂Se₃ co-deposition

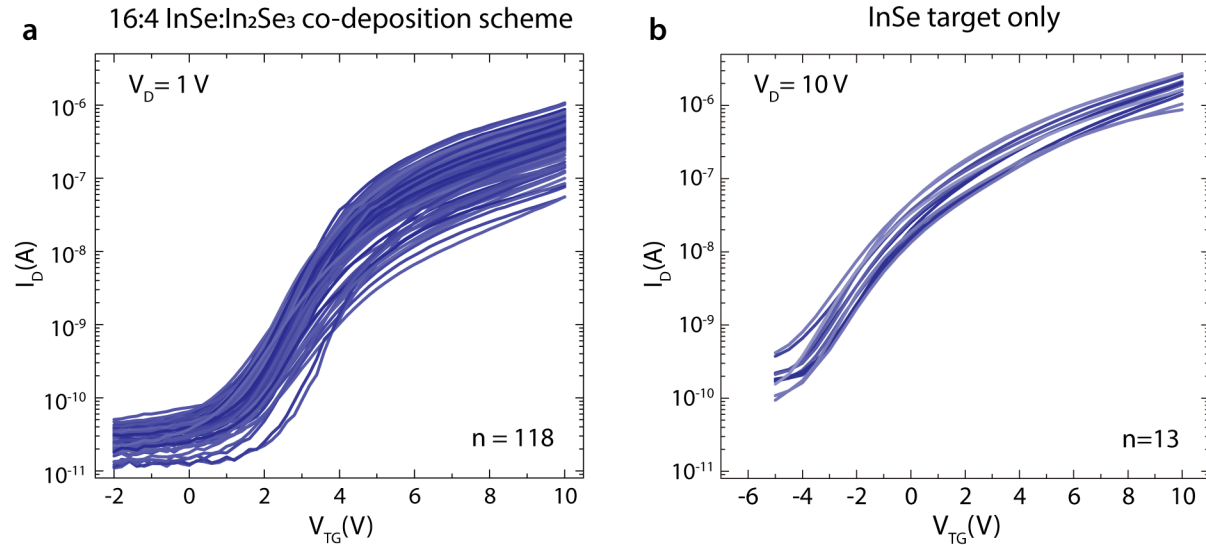


Figure 12.4: Transfer characteristics of top-gated FETs made from InSe films synthesized (a) with and (b) without the InSe:In₂Se₃ co-deposition scheme. The FETs were made from 15-nm-thick InSe post-annealed at ~ 400 °C. **(a)** Transfer curves for 118 top-gated InSe FETs on a single chip, including the devices in Figure 12.3. The patterned InSe is grown using the InSe:In₂Se₃ co-deposition scheme. The source-drain bias is 1 V. **(b)** Transfer curves for 13 top-gated InSe FETs on a single chip. The patterned InSe is grown using only the InSe PLD target. The source-drain bias is 10 V. The geometry of the FETs are the same as those in **(a)**, same except for a 50 μm channel length instead of 100 μm .

scheme were not enhancement-mode. Instead, their state at $V_{TG} = 0$ V was ill-defined. The calculated field-effect mobility for the films deposited from the InSe target only was $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, which is about an order of magnitude less than the films deposited with both the InSe and In₂Se₃ targets. Hence, the co-deposition scheme improved both the film morphology (Figure 11.4) and electronic properties.

The distributions of the threshold voltage, $I_{\text{on}}/I_{\text{off}}$ ratio, and field-effect mobility from all 118 FETs are plotted in Figure 12.5. The means of the threshold voltage, $I_{\text{on}}/I_{\text{off}}$ ratio, and field-effect mobility are given by $V_{\text{TH}} = 6.8 \pm 0.2$, $I_{\text{on}}/I_{\text{off}} = (1.6 \pm 0.6) \times 10^4$, and $\mu_{\text{FE}} = 0.2 \pm 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The distributions indicate consistent device behavior and support the presented synthesis method in providing a scalable pathway to ultrathin InSe films for electronic applications. Moreover, FETs from ultrathin InSe films grown using scalable

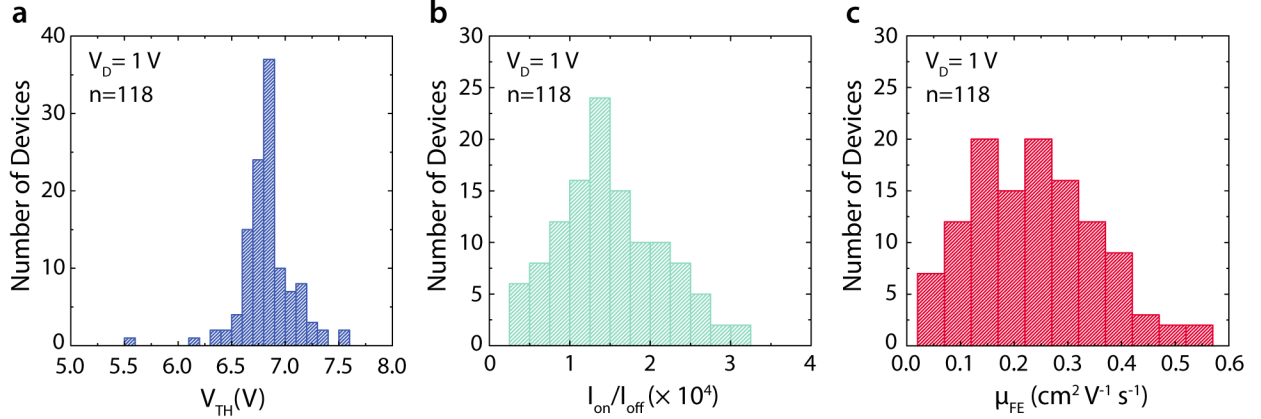


Figure 12.5: Histograms of the metrics extracted from 118 top-gated InSe FETs. Histogram of the (a) threshold voltage (V_{TH}), (b) I_{on}/I_{off} ratio, and (c) field-effect mobility (μ_{FE}) of 118 FETs fabricated from the patterned 15-nm-thick InSe on a single substrate with a source-drain bias of 1 V and top-gate voltage of 10 V. The bin sizes are 0.1 V, 2500, and $0.05 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for the threshold voltage, I_{on}/I_{off} ratio, and field-effect mobility, respectively. The FETs were made from InSe grown using the InSe:In₂Se₃ co-deposition scheme and post-annealing at $\sim 400^\circ \text{C}$.

vapor-phase techniques do not consistently operate in enhancement-mode. Many require an applied gate voltage to turn the FET off in addition to establishing operating current levels,^{70,235} as was the case with the InSe films prepared from the InSe target alone. Notably, the FETs fabricated using the optimized scheme showed enhancement-mode behavior with high CMOS I_{on}/I_{off} ratios of $\sim 10^4$, where I_{off} is measured at a gate voltage of 0 V. In tandem with a tight threshold voltage distribution of $V_{TH} = 6.8 \pm 0.2$ and source-drain bias of 1 V, these InSe FETs thus demonstrate significant potential for low-power electronic devices.

Further improvements in the electronic performance of the synthesized InSe films could be achieved by pursuing (1) tighter I_{on}/I_{off} and field-effect mobility distributions and (2) increasing the mean of the field-effect mobility. Specifically, the development of a more reliable shadow mask alignment method for the InSe channel and corresponding In/Au contacts could eliminate the contribution of spreads in alignment to the variance of the metrics' distributions. Additionally, better contact between the mask and substrate during InSe deposition could

improve the homogeneity of the channel dimensions as well. As pictured in Figure 12.3a, there is an ill-defined shadow around the bulk of the InSe channels which could be minimized by better masking during deposition. To increase the film mobility, the crystallinity could be improved, as discussed further in section 15.2. Additionally, the mobility could also be improved by utilizing the schemes previously shown to attain the high values reported for InSe. These include deposition of an ultrathin indium layer,^{312,313} dry oxidation,³³² encapsulation with hBN,^{310,314} or growth on substrate other than amorphous SiO₂.^{157,158}

12.2.3 Effect of ambient exposure on the electronic performance of InSe films

As detailed in previous studies, exfoliated InSe is sensitive to ambient exposure. Wells *et al.* investigated the effect of exposing exfoliated InSe flakes to ambient conditions on the electronic properties of InSe FETs.³²⁶ Specifically, it was determined that prolonged ambient exposure (> 6 hours) reduced the field-effect mobility by about two orders of magnitude and the $I_{\text{on}}/I_{\text{off}}$ by an order of magnitude. This occurred *via* an increase in the off current and decrease in the on current. To prevent degradation, the authors developed a low-temperature ALD process to encapsulate InSe flakes encapsulated with a 30-nm-thick AlO_x layer. As a result, the high performance of the InSe flakes were preserved even after 6 months of ambient exposure. However, authors had to coat the InSe flakes with *n*-methyl-2-pyrrolidone (NMP) to seed the ALD of AlO_x for proper conformal growth.

In our PLD InSe films, we also observed a sensitivity of the electronic properties to ambient conditions. If the as-deposited amorphous films were exposed to ambient conditions prior to the annealing step in the PLD chamber, significant degradation of the electronic properties was observed. A control measurement is shown in Figure 12.6a and corresponds to the transfer characteristics from 140 bottom-gated FETs where the annealing occurred

immediately following deposition in the PLD chamber. The FETs were made from 8-nm-thick patterned InSe films deposited on 300-nm-thick SiO₂/Si using the InSe target alone and post-annealed at $\sim 400^\circ\text{C}$. The FETs were then encapsulated with 3 nm AlO_x and 20 nm HfO_x using ALD, and measured in ambient conditions. For comparison, the exact same procedure was followed to obtain the FET transfer characteristics shown in Figure 12.6b, except that the films suffered 15 minutes of exposure to ambient conditions between the deposition and annealing steps. The most notable differences are the increase in the off current by about 2 orders of magnitude and increase in the spread of the transfer curves, especially in the magnitude of the off current. The on current also increased significantly, such that there was an overall increase in the calculated mobility, but the $I_{\text{on}}/I_{\text{off}}$ ratio was decreased to a value of ~ 10 . Overall, the films became more inhomogeneous and lost gate-tunability.

While the increase in off current is consistent with the study on exfoliated InSe flakes by Wells *et al.*, the increase in the on current is contradictory to their observations. However, it is not surprising that the degradation behavior may differ since the synthesized polycrystalline films are qualitatively different from exfoliated single crystals. Furthermore, instead of exposing crystalline material to ambient conditions, the procedure described exposes amorphous films to ambient conditions followed by post-annealing for crystallization. The post-annealing step could also contribute to a different effect of ambient exposure. Presumably, both exfoliated and PLD InSe films experience electronic degradation through oxidation. Based on the discussion in section 10.1, the amorphous InSe films are quickly oxidized to form an In₂O₃ layer. This is consistent with previous studies on the formation of In₂O₃ from InSe, which can occur in ambient conditions over time³³² or can be accelerated *via* thermal or photonic annealing.^{359,360} The oxidation process is mediated by selenium vacancies,³²⁷ and as a result, the formation of In₂O₃ would be aggravated in amorphous PLD InSe films in comparison to exfoliated single crystals. Thus, the amorphous PLD InSe films could form a significant In₂O₃ layer after 15 minutes of exposure to ambient conditions, and the In₂O₃ would crystallize

along with the InSe in the post-annealing step.³⁶¹ The In_2O_3 layer could act as a highly doped conducting layer on top of the InSe film, resulting in poor gate-tunability but improved mobility (since PLD In_2O_3 films show Hall mobilities between $20\text{-}70\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).³⁶¹ This explanation is thus consistent with the results presented in Figure 12.6a,b. Therefore, to avoid electronic degradation of the InSe films and maintain phase purity, post-annealing of the PLD InSe films must be performed directly in the PLD chamber following deposition. Furthermore, annealing of PLD InSe films in environments with poor oxygen control (*e.g.*, in tube furnace without H_2) should also be avoided.

Following post-annealing, the electronic performance of the synthesized InSe films can be preserved using an encapsulation scheme similar to that used by Wells. *et al.*³²⁶ As shown in Figure 12.6c, an encapsulated top-gated InSe FET showed ambient stability with no change in behavior following 218 hours in ambient conditions. The transfer curve shown in Figure 12.6c was obtained from the same chip as the FETs shown in Figure 12.3. Furthermore, the ALD growth of the $\text{AlO}_x/\text{HfO}_x$ overlayer did not require seeding using NMP, presumably due to the $\sim 1\text{ nm}$ RMS roughness of the films being sufficient to nucleate the growth.

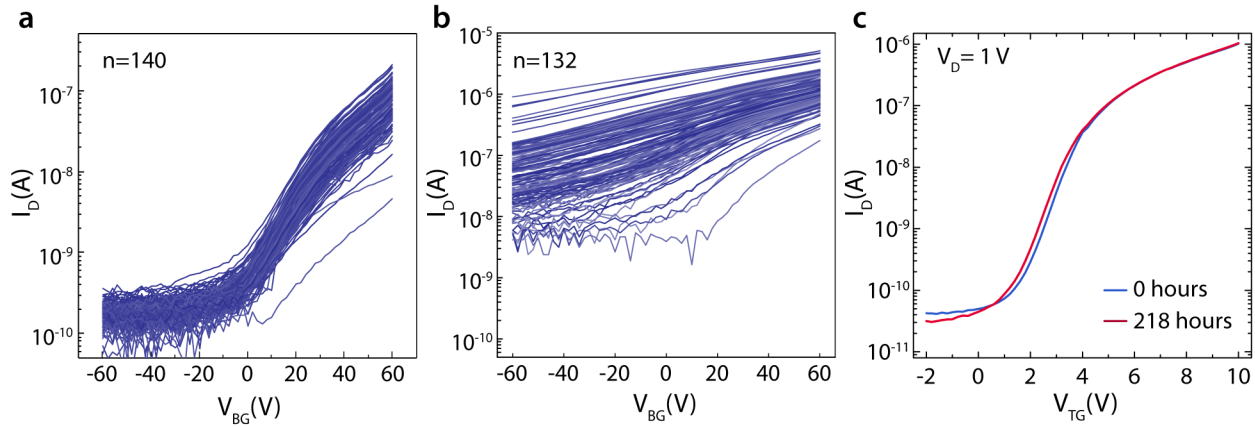


Figure 12.6: Effect of ambient exposure on InSe FET transfer characteristics. (a) Transfer characteristics from 140 bottom-gated FETs made from a patterned 8-nm-thick InSe film on 300-nm-thick SiO_2/Si . The InSe was deposited using only the InSe target and was annealed directly following deposition in the PLD chamber. (b) Transfer curves from 132 bottom-gated FETs made from an InSe film which suffered from 15 minutes of ambient exposure prior to annealing in the PLD chamber. The 8-nm-thick InSe film were patterned onto 300-nm-thick SiO_2/Si using only the InSe target. Due to the ambient exposure, there was a significant increase in the off current. The source-drain voltage was 20 V for both (a) and (b). (c) Encapsulation of InSe films with 3 nm AlO_x /20 nm HfO_x after post-annealing prevents electronic degradation, as shown by the similar transfer characteristics of the same FET following fabrication (0 hours) and after 218 hours in ambient conditions. The FET was made from 8-nm-thick InSe patterned onto 300-nm-thick SiO_2/Si using the InSe: In_2Se_3 co-deposition scheme and belongs to the array presented in Figure 12.3.

Chapter 13

Conclusions and Future Work

Comprehensively, the presented suite of characterization elucidates the structural and compositional evolution of ultrathin PLD InSe films through several phases of the indium–selenium material system as a function of annealing temperature. In particular, *in situ* XRD of the PLD InSe films showed the progression of an amorphous film to crystalline InSe, passing through a partial In_4Se_3 crystallization and degrading into In_2Se_3 at higher temperatures. This pathway is corroborated by Raman spectroscopy and XPS measurements. Consequently, we efficiently determined that ultrathin InSe films with no detectable impurity phases can be achieved at post-deposition annealing temperatures between 325 °C and 425 °C. Furthermore, the study informed the development of a co-deposition scheme using both an InSe and In_2Se_3 PLD target in a 16:4 laser pulse ratio to improve the material quality by reducing stoichiometric mismatch between the starting and crystallized films.

The synthesized ultrathin ϵ -InSe films are tunable in thickness and highly uniform over large areas (1 cm²), with crystal domains well-oriented along the substrate. As a result, we realized phototransistors with a responsivity of 10³ A/W and top-gated enhancement-mode FET arrays with 91% yield and consistent device performance. The FETs demonstrated high $I_{\text{on}}/I_{\text{off}}$ ratios >10⁴ with a level of uniformity yet to be established for the synthesis of ultrathin InSe. The uniformity was afforded by the PLD technique which provides

homogenous deposition and stoichiometric tuning of the starting material. Together with *in situ* post-annealing, the method presented here enables the controllable navigation of the complex phase space of the indium-selenium material system and is generalizable to a wide range of substrates suitable for nanoelectronic applications. Moreover, we hope this study may serve as a roadmap to guide future efforts in the synthesis of ultrathin InSe and other post-transition metal chalcogenides.

As gleaned from this study, ultrathin InSe films are difficult to synthesize due to a low and narrow temperature range which limits the crystallinity and phase purity, respectively. Furthermore, the sensitivity of InSe to ambient conditions threatens the phase purity of InSe films (*via* formation of In_2O_3) and the preservation of its attractive electronic performance. Hence, the fabrication methods applied to other 2D materials like the TMDs will be more difficult for 2D InSe. As demonstrated by the InSe patterning scheme developed in this study, innovation is required for *in situ* device fabrication if exposure of the InSe films to ambient conditions is to be avoided. For example, the PLD chamber holds several different targets, including metals and Al_2O_3 , which could enable the deposition of many layers of material without ever breaking vacuum. This idea is discussed further in section 15.3. More importantly, future studies into the synthesis of InSe should focus on improving InSe crystallinity at lower temperatures. In particular, the lateral sizes of the InSe crystalline domains, here restricted to sub-micron dimensions, should be increased to improve the mobility of the InSe films, which is currently significantly lower than exfoliated InSe on SiO_2 ($50\text{-}200\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). It is possible to achieve this by performing heated PLD instead of a post-annealing technique. However, as demonstrated by this study, the PLD process results in Se-deficient deposition even at room temperature. It would be necessary to introduce an independent source of selenium for a reactive PLD process. A less flexible solution would be a co-deposition scheme. However, in this case, an In_2Se_3 target may not be rich enough in Se to counteract the poor chalcogen sticking coefficient at high temperatures. The use

of a suitable substrate to template the heated PLD of ultrathin InSe would also be highly beneficial for increasing the crystallinity of the film, as further discussed in section 15.2.

Chapter 14

Experimental Methods

PLD of amorphous InSe films

The pulsed laser depositions were performed in a PVD Nano PLD 1000 using a 248 nm KrF excimer laser and at a base pressure of $\sim 2 \times 10^{-7}$ Torr. A repetition rate of 1 Hz was used with a laser energy of 200 mJ. The laser spot size of $\sim 7 \text{ mm}^2$ is rastered upon the target over a radius of 1.5 cm. The targets are rotated at 15 rpm while the substrates are rotated at 10 rpm. The substrates are at RT. The InSe (99.99%) and In₂Se₃ (99.99%) targets are 1" in diameter and $\frac{1}{4}$ " thick and purchased from Stanford Advanced Materials.

For the InSe/In₂Se₃ co-deposition scheme, the deposition alternates between 16 pulses from the InSe target and 4 pulses from the In₂Se₃ target, which is sub-monolayer in coverage to obtain better mixing. The total film is formed by cycles of the 16:4 units. For example, the 15-nm-thick film corresponds to 700 total pulses constituted from 35 cycles of 16:4 units.

In situ annealing of InSe films in the PLD instrument

The InSe films are annealed directly following deposition in the PLD chamber with a ramp rate of 30 °C/min and dwell time of 15 minutes, and cooling rate of 30°C/min or less

using natural cooling. The heating is performed with an IR lamp with feedback from a thermocouple near the lamp. Consequently, the temperature setpoint is nominal and a calibration to the substrate identity was performed to obtain the actual temperature. The calibration is performed using a pyrometer to read the temperature of blank silicon substrates as they are heated. The temperature for sapphire substrates was estimated using an offset of -100 °C from the silicon calibration curve. As a result, the accuracy of the reported sapphire substrate temperature is than that of silicon.

***in situ* X-ray diffraction of InSe films being annealed**

The *in situ* XRD is performed in a Rigaku Smartlab 9kW Gen3 instrument with a Cu rotating anode and equipped with an Anton Paar HTK 12000N high temperature furnace chamber. Prior to annealing, the chamber is evacuated to a vacuum level of 0.1 mTorr. The diffraction patterns were acquired with a Cu K α radiation ($\lambda = 1.5418$ Å) in the Bragg-Brentano geometry with a linear detector, an incident slit of 0.2 mm, and a receiving slit of 0.5 mm. The samples were heated at a rate of 30 °C/min and cooled at a rate of 30 °C/min or less using natural cooling.

Laser annealing of InSe films

The *in situ* laser annealing experiments were conducted in ARES (Autonomous Research System),^{348,349} a cold-wall reactor installed on a 2-axis motion stage above an inverted Raman microscope (Nikon Ti-E). The substrate consisted of 5×5 arrays of silicon micropillars (10 μm tall and 10 μm in diameter) spaced 50 μm apart on a thermally insulating SiO₂ sublayer. Each pillar was therefore thermally isolated and experiments were conducted by focusing a 6 W 532 nm laser (Spectra Physics Verdi V6) through a 50 $\times$ objective lens; the laser served as

the heat source as well as the Raman excitation source. The small thermal mass of the pillar enabled heating to high temperatures within a fraction of a second when the laser power was varied in the 0 – 1 W range. The temperature-induced shift of the Si stokes and anti-stokes Raman bands ($\pm 520 \text{ cm}^{-1}$) was used to calculate the growth temperature with an accuracy of approximately $\pm 15 \text{ }^\circ\text{C}$.

For the annealing experiments, amorphous InSe films ($\sim 8 \text{ nm}$ thick) were first deposited by PLD on to the ARES micro-pillars. The substrate was loaded into the chamber and evacuated down to a base pressure of $\sim 1 \times 10^{-4} \text{ Torr}$. Thermal annealing was performed by varying the laser power to heat the micropillars to a range of temperatures ($100\text{-}900 \text{ }^\circ\text{C}$) and by holding the temperature for 90 seconds. *Ex situ* Raman spectroscopy characterization was performed with a Raman microscope (Renishaw inVia, 514.5 nm excitation). 2D Raman maps were collected from the micropillars, and the average intensity of the A'_1 peak at $\sim 114 \text{ cm}^{-1}$, normalized to the Raman peak from the Si substrate, was used as a measure of crystalline quality of the InSe films.

X-ray diffraction and X-ray reflectivity of InSe films

XRR/XRD measurements of annealed InSe samples were carried out using a Rigaku ATXG diffractometer equipped with an 18 kW Cu rotating anode ($\lambda = 1.5418 \text{ \AA}$). XRR and XRD measurements were done using a collimated beam of $0.1 \times 2 \text{ mm}^2$ and $0.5 \times 2 \text{ mm}^2$, respectively. All measurements were normalized to the measured incident beam intensity and the results are plotted in terms of the scattering vector $q = 4\pi \sin(\theta)/\lambda$. In the XRD measurements, the Scherrer equation was used to calculate the out-of-plane domain size of the film:

$$L_z = 2\pi(0.94)/(\Delta q^2 - \Delta q_{\text{inst}}^2)^{1/2} \quad (14.1)$$

where Δq is the FWHM obtained by a Gaussian fit to the InSe (004) diffraction peak and Δq_{inst} is the FWHM of the substrate Si (004) peak, which determines the resolution of the equipment. In the XRR measurements the data were corrected for footprint and background. The analysis was done using Motofit.³⁰⁹ The XRR and XRD fits are presented in Figure 14.1 and the fitting parameters are presented in Table 14.1. An electron density (ρ_{InSe}) of 1.18-1.23 $\text{e}^- \text{\AA}^{-3}$ was obtained for the InSe films which is approximately 88% of the expected electron density of 1.38 $\text{e}^- \text{\AA}^{-3}$ corresponding to ϵ -InSe (ICSD ID 640503).³⁶² The film thickness (t_{InSe}) and the roughness (σ_{InSe}) are also shown in the fitting parameters. In addition, a surface layer was included to improve the fitting in the $q > 0.15 - 0.20 \text{ \AA}^{-1}$ region. This layer is most likely formed due to oxidation from prolonged exposure to air/moisture following several preceding rounds of characterization.

Pulses	t_{InSe} ($\text{\AA}$)	σ_{InSe}	ρ_{InSe}	t_{surf}	ρ_{InSe}	FWHM ($\text{\AA}^{-1}$)
1000	236.6	18.6	1.23	78.2	0.52	0.0267
700	152.9	13.8	1.21	14.6	0.37	0.0374
350	75.1	8.3	1.18	4.7	0.52	0.0797
200	42.7	5.4	1.21	2.5	0.20	0.1361

Table 14.1: XRR and XRD fitting parameters for InSe films

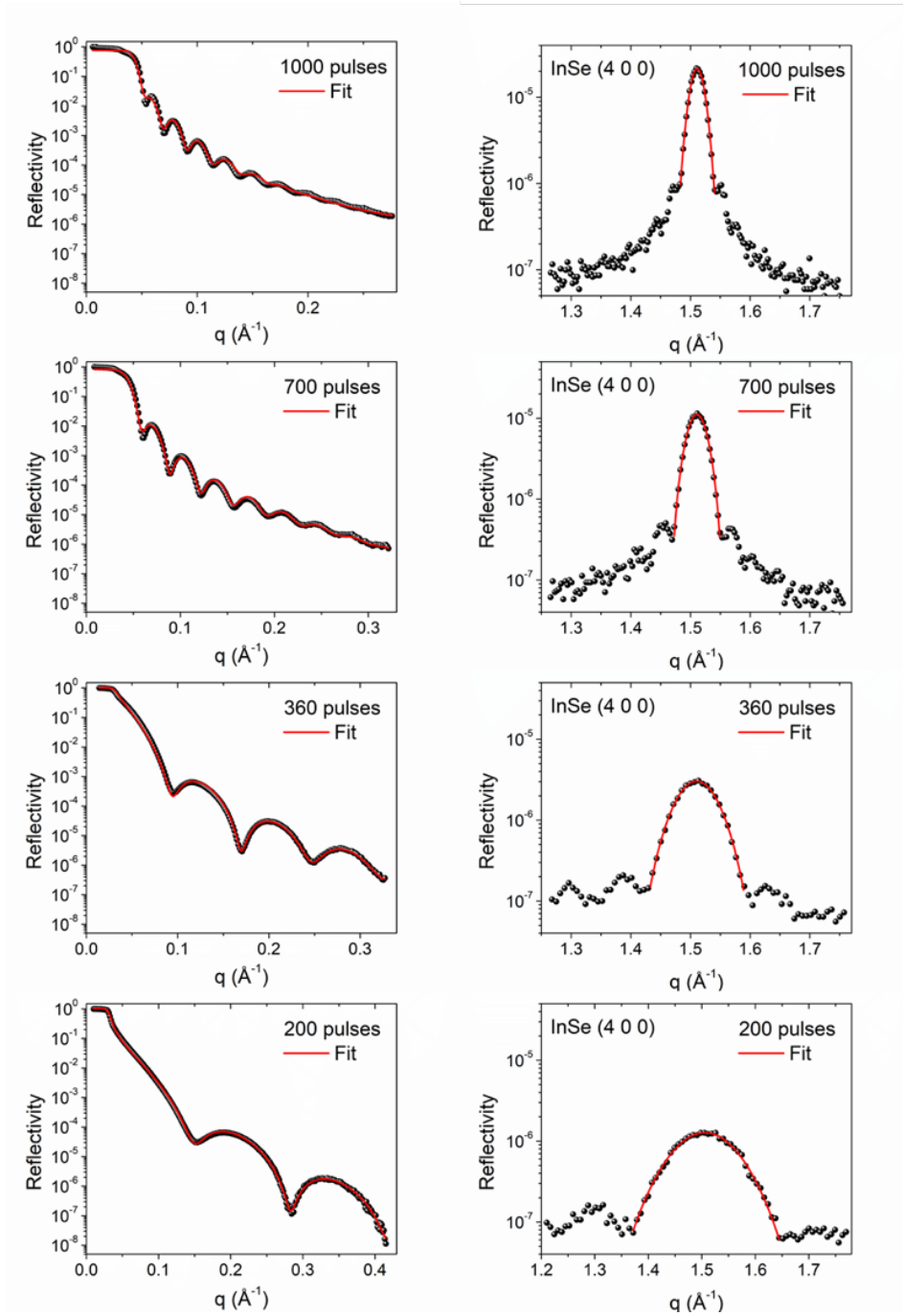


Figure 14.1: XRR and XRD of optimized InSe films with model fits. The films were deposited using the 16:4 InSe:In₂Se₃ co-deposition scheme on 300-nm-thick SiO₂/Si substrates and post-annealed *in situ* at ~400 °C. XRR of the various InSe samples is on the left and the corresponding XRD is on the right.

Raman spectroscopy of InSe films

Raman spectroscopy was performed with a Horiba Scientific XploRA PLUS Raman microscope with a 532 nm laser. The spectra were acquired in ambient conditions with a 100 $\times$ Olympus objective (NA = 0.9), an incident laser power of ~ 1 mW, spot size of $\sim 1 \mu\text{m}^2$, and 2400 grooves/mm grating for a spectral resolution of 1.1 cm^{-1} . Each spectrum is an average of two spectra acquired for 60 seconds. The positions of the peaks were calibrated by shifting the Si peak to 520.7 cm^{-1} . The Raman map was performed over an area of $30 \mu\text{m} \times 30 \mu\text{m}$ with a step size of $3 \mu\text{m}$. Each spectrum was acquired for 60 seconds with the parameters described previously. The spectral intensities were normalized to the Si peak intensity. The image in Figure 5a was smoothed using interpolation.

X-ray photoelectron spectroscopy of InSe films

The XPS spectra were acquired using a Thermo Scientific ESCA Lab 250Xi scanning XPS equipped with a monochromated Al K α source ($E = 1486.6 \text{ eV}$), a spot size of $\sim 500 \mu\text{m}$, and a flood gun for charge compensation. Each spectrum is an average of five spectra with a pass energy of 15 eV and dwell time of 100 s. Analysis was performed using the Advantage (Thermo Scientific) software in which the core level sub-peaks were fit with a modified Shirley background and charge corrected with the adventitious carbon peak at 284.8 eV. The stoichiometry was extracted from the In $3d_{5/2}$ and Se $3d_{5/2}$ peaks in the Advantage software. This method yielded an inflated Se:In ratio by ~ 0.2 . The Se:In ratios obtained from the XPS study were systematically corrected using values obtained from energy-dispersive X-ray spectroscopy (EDS) analyzed with AZtec LayerProbe on samples of amorphous and crystalline PLD InSe, as well as mechanically exfoliated InSe from a bulk crystal purchased from American Elements.

Atomic force microscopy of InSe films

Tapping mode AFM was performed using an Asylum Cypher AFM and a 320 kHz NanoWorld NCHR-W Si cantilever. The images were acquired at a scanning rate of 1 Hz with pixel resolution of 512×512 .

Scanning and transmission electron microscopy of InSe films

The InSe films were directly deposited onto 8-nm-thick amorphous SiO₂ membranes supported by a Si₃N₄ grid and post-annealed at 410 °C. The TEM grids are by Pelco and sold by Ted Pella Inc. Conventional TEM images, high-resolution TEM images, SAED patterns were obtained using a JEOL ARM300 operated at 300 kV. Atomic-resolution HAADF (90-200 mrad of collection angle) STEM images were acquired using a Cs-corrected JEOL ARM 200CF. The multislice simulation was conducted with software Dr. Probe³⁶³ under 200 kV, a convergence angle of 24 mrad, a defocus of 0 nm, and using frozen lattice configurations.

Top-gated FET fabrication and electrical characterization

Top-gated InSe FETs were fabricated on undoped Si with 300 nm of thermally grown SiO₂ to provide optical contrast. First, the InSe was deposited at RT *via* PLD through a shadow mask to define 250 μm by 150 μm InSe channels in an 18×11 array over 1 cm². The deposited InSe and attached shadow mask were annealed at $\sim 400^\circ\text{C}$ in the PLD chamber immediately following deposition and prior to any ambient exposure. After annealing, the substrates were removed from the PLD chamber, and an additional shadow mask of 200 μm

by 200 μm windows with 100 μm gaps was aligned with the patterned InSe channels to define electrode contacts. Thus, the channel length of the devices was defined as 100 μm . Thermal evaporation was used to deposit 10 nm In and 70 nm Au as the contact material.

ALD of an encapsulation layer and top gate dielectric was performed using a Cambridge Nanotech ALD S100. The encapsulation layer from 5 pulses of TMA followed by 30 full cycles of TMA and H_2O at 55 $^\circ\text{C}$ resulted in a 3 nm film of AlO_x previously shown to preserve the properties of ambient reactive materials.^{326,357} The top-gate dielectric (20 nm of HfO_x) was then deposited at 100 $^\circ\text{C}$ from 200 cycles of tetrakis(ethylmethylamino)hafnium (TMDAH) and H_2O . The capacitance of the full dielectric stack was 437.5 nF/cm² as obtained from C-V measurements. After encapsulation, a third shadow mask of 120 μm wide by 350 μm long regions was aligned with the devices for the thermally evaporated top-gate metal of 10 nm Cr and 70 nm Au. The top-gate regions were slightly wider (120 μm) than the channel length of the devices (100 μm) to ensure complete coverage of the semiconductor channel by the top-gate. During this solvent free fabrication process, the crystalline InSe samples experienced less than 10 minutes of ambient exposure prior to encapsulation.

All electrical measurements were performed in ambient on a Cascade MicroTech semi-automated probe system using a Keithley 4200 semiconductor analyzer. The device yield was determined as follows. Of the 162 devices that were fabricated, 135 were measured by the auto-prober. For the other 27 devices, the probes did not scratch through the dielectric layer to the source-drain contacts for proper current flow due to misalignment between the probes and electrode contacts during the automated measurement process. Of the 135 devices measured, 6 had hard shorts due to mishandling or a fabrication issue. Of the 129 devices that did not encounter any physical damage or fabrication issues, 118 showed consistent behavior, resulting in a $118/129 = 91.4\%$ yield.

The $I_{\text{on}}/I_{\text{off}}$ ratio was calculated from the magnitude of the current at $V_{\text{TG}} = 10 \text{ V}$ (I_{on}) and -2 V (I_{off}). The threshold voltage was given as the V_{TG} -intercept of the extrapolation

from the linear fit to the transfer curve between $V_{TG} = 9$ V and 10 V. The field-effect mobility μ_{FE} was calculated from the following equation:

$$\mu_{FE} = \left(\frac{L}{WC} \right) \left(\frac{1}{V_D} \right) \left(\frac{\Delta I_{DS}}{\Delta V_{TG}} \right) \quad (14.2)$$

where $L = 100$ μm and $W = 150$ μm , C is the capacitance of the dielectric (437.5 nF/cm²), and $\frac{\Delta I_{DS}}{\Delta V_{TG}}$ is the slope of the linear region of the transfer curve (between $V_{TG} = 9$ V and 10 V). All of the metrics were calculated at $V_D = 1$ V.

Phototransistor fabrication and characterization

InSe phototransistors were fabricated following a similar protocol as the FETs. A 15-nm-thick InSe film was first deposited on doped Si substrates capped by 300-nm-thick thermal oxide using the optimized 16:4 InSe:In₂Se₃ co-deposition scheme. Exposure to ambient conditions was minimized by keeping the samples under an N₂ environment during all handling and transportation between growth chambers and glove boxes. Phototransistors were fabricated by evaporating a 10 nm indium film followed by a 50 nm gold film through a shadow mask to define source and drain electrodes using a thermal evaporator inside an N₂ glove box. The channel length and width were 7 μm and 30 μm , respectively, while the InSe film between neighboring phototransistors was not patterned. The devices were measured in vacuum ($<10^{-5}$ Torr) using a LakeShore CRX 4K probe station and home-built LabVIEW programs. The details of the photocurrent measurement setup are described in previous reports.^{326,353,355} Briefly, a fiber-coupled laser diode with excitation wavelength of 515.6 nm (LP520MF100, Thor Labs) was operated in constant-current mode while the temperature (25 °C) was controlled by a TEC controller (ITC4001, Thor Labs). The illumination intensity was varied by controlling the laser diode current, and the intensity at the center of the spot

(2 mm in diameter) was calibrated by using an aperture of known area ($2200 \mu\text{m}^2$) and a Si detector (PM100D, Thor Labs). The responsivity was calculated by normalizing the input intensity with total channel area ($210 \mu\text{m}^2$) and using the photocurrent measured at $V_{\text{BG}} = 80 \text{ V}$ and $V_{\text{D}} = 10 \text{ V}$. The dark current was measured after each illuminated current measurement to account for irreversible changes in the device during illumination. For temporal measurements, a $1 \text{ M}\Omega$ resistor was connected in series with source electrodes and the voltage waveform was captured with an oscilloscope (MDO4000C Tektronix Inc.). The intrinsic rise time of the laser diode is expected to be less than $1 \mu\text{s}$. Thus, the time constants on the order of milliseconds are governed by the InSe phototransistors.

Part IV

Outlook

Chapter 15

Future directions for 2D metal chalcogenide synthesis

15.1 Substrate engineering for the self-limited growth of monolayer MoS₂

Since MoS₂ and several other TMDs exhibit direct bandgaps exclusively in the monolayer limit, the controlled growth of exclusively monolayer MoS₂ is highly desirable. This discussion will focus on MoS₂, but presumably the methods would be translatable to other isostructural semiconducting TMDs. Currently, continuous monolayer growth of MoS₂ is achieved through careful tuning of the growth parameters. For solid precursor CVD, the lack of control is compensated by the placement of substrates along the precursor concentration gradient, such that a small region will contain monolayer growth. Using MOCVD, the homogeneity is better and consequently the parameters require more careful optimization. To suppress multilayer MoS₂ formation, the growth must be performed in a diffusion-controlled regime to promote edge attachment instead of nucleation between on top of existing TMD domains.¹⁴⁵ To achieve this, the rate of precursor in-flow has to be reduced, reducing the overall growth rate. The process of depositing continuous monolayers then becomes lengthy, expensive, and

very reliant on the growth time. Hence, a method for the self-limited growth of exclusively monolayer MoS_2 would improve the yield and industrial feasibility of CVD growth in the synthesis of MoS_2 .

Substrate engineering is a promising avenue for self-limited vapor-phase growth of monolayer MoS_2 . Previously, substrate engineering has proven to be a fruitful method to obtain single-layer graphene. Firstly, the use of metal (*e.g.*, Cu(111)) in graphene synthesis provides a catalytic function. The temperature for decomposition of the CH_4 precursor, diffusion barrier of carbon atoms on Cu (111), and barrier for carbon edge attachment to graphene islands are all significantly lowered.³⁶⁵ The result is substrate-driven growth of graphene which favors single-layer graphene, though multilayers can still form for high CH_4 to H_2 ratios.³⁶⁶ The use of a catalytic substrate is one strategy for self-limited growth of 2D materials and corresponds to the general tactic of filtering the adsorption of reactants onto the substrate

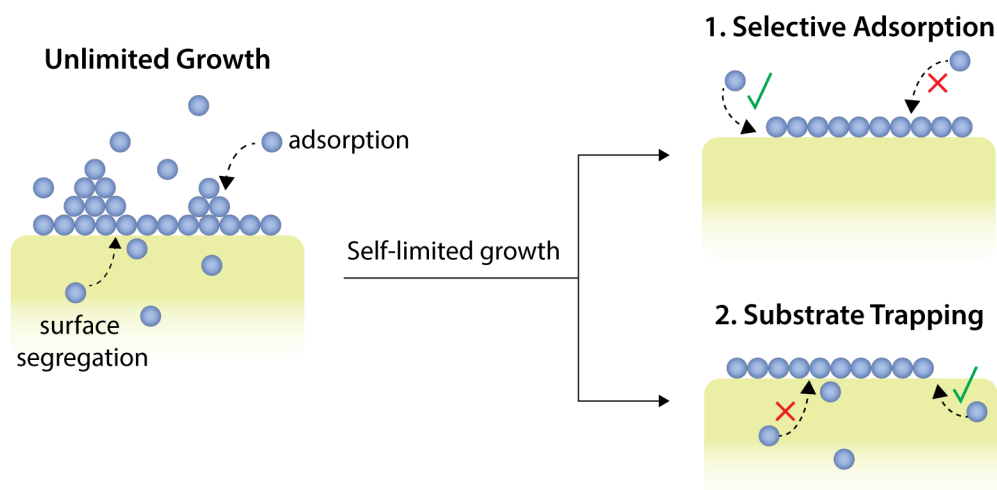


Figure 15.1: Substrate-driven self-limited growth strategies for 2D materials. Left: without control measures, the vapor-phase growth of 2D materials is not self-limited. Unlimited growth can result from both/either unlimited surface adsorption of reactants and/or unlimited surface segregation of reactants dissolved into the bulk of the substrate. Right: substrates can be engineered to promote self-limited monolayer growth of *via* two strategies: (1) a catalytic surface for selective adsorption of reactants and (2) substrate trapping of excess reactants into the bulk upon cooling. Adapted with permission from [364].

(Figure 15.1). Further improvements in the self-limited CVD of graphene were made using liquid-metal substrates, which yielded strictly single-layer graphene with lower grain-boundary density. Using liquid metals, the growth of monolayer graphene was observed for a wide range of processing parameters, making it a robust synthesis method.³⁶⁷ Interestingly, the mechanism behind the self-limited growth of graphene on liquid metals is the trapping of excess carbon into the bulk metal during cooling (i.e., the substrate trapping strategy), rather than selective adsorption (Figure 15.1). Inspired by the success of liquid metals, Zhongfan Liu’s research group grew graphene on molten soda-lime glass,³⁶⁸ but the carrier mobilities ($127\text{--}426\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) were far below those of liquid-metal grown CVD graphene (up to $7400\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). However, their use of molten glass for the CVD of monolayer MoS_2 seems more promising.¹⁷⁵

In the last few years, there has been significant effort towards the catalyzed growth of 2D MoS_2 , especially through the use of additives such as alkali metal halides or salts (see subsection 2.4.1). However, a reproducible method for the high-quality self-limited growth of monolayer TMDs is still lacking. Attempts at both selective adsorption and substrate trapping design strategies have been made; many research groups have used alkali metal-containing compounds to catalyze the growth of TMDs^{124,369,370} and others have also used molten glass to trap excess MoO_x reactants.^{371,372} However, the latter attempts were not able to show continuous coverage. Additionally, Yang *et al.* reported the self-limited growth of monolayer MoS_2 on molten glass due to catalysis from the sodium contained in the substrate. However, our attempts at reproducing these results have not succeeded so further work is required.

15.1.1 Selective adsorption

For the filtered adsorption strategy, the identity and delivery of the catalyst must be carefully chosen. While several compounds (mostly salts) have been identified as potential MoS_2 growth catalysts, their delivery remains highly uncontrolled. As illustrated in Figure 15.2,

salt is usually introduced in the following ways: placement of a salt into or near the precursor, use of salt as a precursor (e.g., Na_2WO_4), or placement of the salt onto or into the substrate.¹⁷³ Researchers have also directly grown TMDs onto salt substrates, but the results are inhomogeneous.^{373,374} To incorporate the salt onto or into the substrate, it is spin-coated from a solution or incorporated from the soda-lime glass fabrication process. However, there are large variations in the MoS_2 growth morphology and quality across different methods and reports of salt-assisted synthesis. Considering the various delivery methods, the pathway of directly incorporating the catalyst into the substrate seems the most promising. Instead of relying upon the serendipitous incorporation of sodium into soda-lime glass, the presence and concentration of the catalyst at the substrate should be precisely controlled and reproducible. This feat requires substrate engineering, such as developing a substrate where the catalyst identity and concentration can be customized. Ongoing work in our research group is currently investigating this avenue. Specifically, heterostructure substrates containing a bottom catalytic salt layer and capped with ALD Al_2O_3 can be used to explore various identities and concentrations of salts. The introduction of the catalyst to the substrate surface can be controlled by thermal annealing for diffusion of the salt species through the ALD Al_2O_3 layer. The work presented in Part II provides a starting point for the growth of MoS_2 on ALD Al_2O_3 . A well-chosen catalyst should enable lower temperature and self-limited growth of monolayer MoS_2 . Furthermore, once the deposition scheme is optimized, the heterostructure substrate could be further tailored for patterned growth of self-limited monolayer MoS_2 .

15.1.2 Substrate trapping

Molten soda-lime glass has also been reported to promote substrate trapping of reactive species in the solid-precursor CVD of 2D MoS_2 .^{371,372} Currently, molten glass is only reported to trap MoO_x and has not been demonstrated to yield continuous monolayers. For scalability,

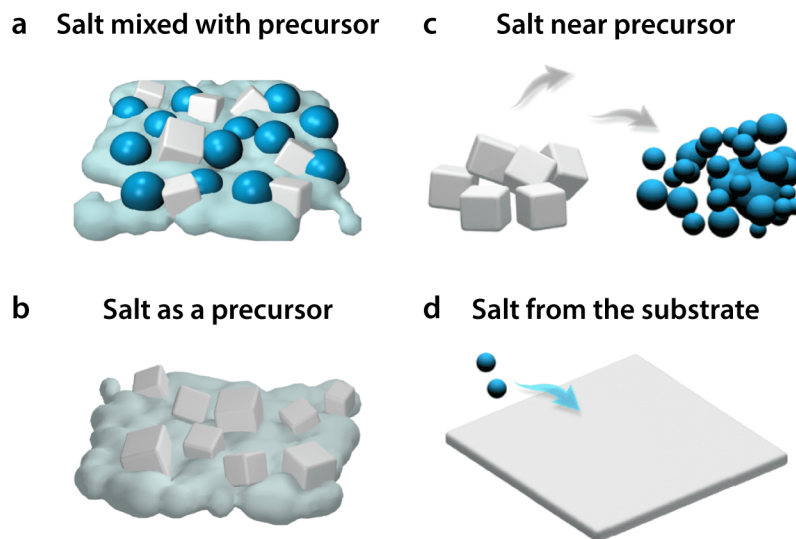


Figure 15.2: Methods for introducing catalytic salts into the vapor-phase synthesis of monolayer TMDs. (a) Mixing the salt into the transition metal precursor. (b) Using a salt as the transition metal precursors (*e.g.*, Na_2WO_4). (c) Placing the salt somewhere near the precursor. (d) Placement/incorporation of the salt onto/into the substrate. This is usually done by spin-coating the salt onto the substrate or incorporation of salt into the soda-lime glass production process. Adapted with permission from [173].

future work should explore alternative substrates applicable to MOCVD precursors, since MoO_x is not a reactant in the MOCVD of MoS_2 . Alternatively, a report by Lu *et al.* on the post-sulfurization of MoO_x -infused molten glass suggests that the substrate trapping of Mo precursors could be scalable, but the mobilities were discouragingly low ($< 0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$). The process could potentially be improved by using an alternative substrate, such as a metal, with high crystallinity and Mo solubility. In addition to graphene growth on molten Cu, a surface segregation mechanism is proposed for borophene growth on $\text{Au}(111)$ ³⁷⁵ and $\text{Cu}(111)$.³⁷⁶ The boron atoms are observed to segregate to the surface after high-temperature dissolution into the bulk of the metal substrate. By instead using Mo dissolution into a metal substrate, a post-sulfurization process could potentially yield monolayer MoS_2 . Ideally, both Mo and S reactants could be dissolved and segregated in direct analogy to graphene or borophene growth, but finding a suitable substrate may be impractical.

15.2 Substrates for templated 2D InSe growth

The crystallinity of the synthesized InSe films presented in Part III could be further improved by moving to PLD with a heated substrate. In this scheme, the substrate will be an important factor in controlling the crystallinity of the films. The difficulty in the synthesis of ultrathin InSe films was elucidated by the work presented in Part III. Essentially, there is a narrow window in which phase-pure InSe can form and the location of that window is fairly low in temperature. Based on the InSe phase evolution study, the window is between 325 °C and 425 °C. At temperatures below 425 °C, the mobility and diffusion of adatoms could be limited. The common tactic of increasing substrate temperature will not be available due to In_2Se_3 formation. Hence, the use of a templating substrate would be crucial to achieving high crystallinity with low substrate temperatures, as demonstrated in previous studies by Simpson *et al.*³⁷⁷ and Hilmi *et al.*³⁷⁸ In their work, the authors demonstrated significantly reduced crystallization temperatures when suitable substrates were chosen. Since InSe is a vdW material, the constraints of conventional epitaxy are relaxed, thus enabling many substrates to choose from. Growth on a vdW substrate should make transfer of the synthesized InSe films feasible. Suggested substrates include epitaxial graphene on SiC and TMDs with six-fold symmetry and similar lattice constants. Alternatively, remote epitaxy¹²⁹ through a graphene layer could also enable to use of better lattice-matched single-crystal non-vdW materials as a template. Even in the context of substrate templating, the temperature will be paramount since In_2Se_3 has very similar in-plane lattice parameters and symmetry to InSe (see Table 1.1 and Table 1.2), so relying on the templating of the substrate along is a poor phase-selection mechanism. In addition to the PLD technique proposed here, the MOCVD of InSe could also be considered. Previous attempts at the synthesis of micron-thick InSe films were made, but yielded poor results. Similarly, authors report difficulty with phase purity (favoring the formation of In_2Se_3), Se-deficiency, and poor morphology. In other words,

the same problems currently plaguing other methods of InSe synthesis.³⁷⁹ Therefore, future efforts should be invested in substrate engineering for enhanced InSe crystallization in the well-defined temperature range established in Part III, rather than optimization of synthesis conditions.

15.3 PLD for *in situ* 2D metal chalcogenide heterostructure and device fabrication

A significant advantage of PLD is its ability to deposit almost any solid material. The high-power laser ablation mechanism is applicable to many targets, though as discussed in Part III, the deposition is not always congruent. Consequently, the direct growth of heterostructures can easily be accomplished using different targets in the PLD process. The use of different targets was exploited to customize the stoichiometry of amorphous InSe films in Part III, but could be extended to completely different materials. The proposed concept could be especially useful for ambient-sensitive 2D materials such as InSe. In particular, the *in situ* encapsulation of 2D InSe could be achieved by the PLD of Al_2O_3 .^{380,381} Additionally, the passivation of InSe has also been demonstrated using dry oxygen exposure³³² and indium metal encapsulation,^{312,313} both of which could be performed in the PLD chamber directly following InSe synthesis using oxygen gas or an indium metal target, respectively. Going a step further, the deposition of contact electrodes for FET fabrication could also be performed *in situ* with PLD of contact metals, such as indium or gold. This scheme would require a dynamic shadow-masking system for accurate patterning of the InSe channels and contact electrodes. Dynamic masking has already been explored for combinatorial PLD studies,³⁸² and could be modified for device fabrication. Thus, one could imagine an all-in-one procedure with (1) the patterned PLD of the crystalline 2D InSe channels, (2) optional dry oxidation

or metallic indium encapsulation of the InSe (3) patterned and aligned PLD deposition of metallic contact electrodes, and (4) PLD of an amorphous Al_2O_3 encapsulation layer for long-term stability. The entire process would occur continuously in high vacuum, enabling the *in situ* fabrication of encapsulated FETs to probe the intrinsic properties of ambient-sensitive metal chalcogenides such as InSe. Such a fabrication scheme is not possible using CVD techniques and is a unique advantage of the PLD method and its ability to deposit a range of materials in a single setup.

15.4 Systematic exploration of 2D phase diagrams

While the phase diagrams and structures of bulk materials have been studied systematically and thoroughly, that understanding is not directly translatable to the 2D regime. As surface effects become more and more dominant toward the atomically thin limit, the balance of forces which dictates the stability of different structures may change. For example, several 2D materials go through thickness-driven structural transformations as they enter the 2D regime. These materials include GaTe,²⁵⁰ SnTe,^{383,384} bismuthene,³⁸⁵ and some vdW metal halides.^{386,387} Furthermore, several materials exhibit 2D polymorphs stable at standard temperature/pressure conditions that are only observed at high temperatures/pressures in the bulk or are altogether not observed in the bulk at all. This is the case for several monoelemental 2D materials (*e.g.*, borophene,³⁸⁸ antimonene,^{389,390} bismuthene³⁹¹) as well as In_2Se_3 . As discussed in section 10.2, the formation of the layered $\beta\text{-In}_2\text{Se}_3$ structure was observed upon over-annealing ultrathin InSe films (8-nm-thick) while thicker films (> 30 nm) resulted in non-layered $\gamma\text{-In}_2\text{Se}_3$. This observation is consistent with previous reports of $\beta\text{-In}_2\text{Se}_3$ being stable at room temperature in the 2D form while bulk $\beta\text{-In}_2\text{Se}_3$ is only observed at high temperatures.^{91,238} Thus, the established bulk phase diagrams are no longer accurate in the ultrathin regime. Therefore, a systematic exploration of the 2D phase diagram

of materials of interest is necessary. As demonstrated by the work presented in Part III, understanding the phase boundaries of a 2D material is directly applicable to the rational design of a synthesis method. The systematic exploration of 2D phase diagrams will not only promote synthetic phase control, but also enable the discovery of 2D polymorphs yet unknown.

To enable this exploration, computational methods should be employed alongside combinatorial experimental designs. Over the last 5 years, computational efforts have fruitfully predicted the 2D polymorphs of borophene,^{392,393} blue phosphorene,³⁹⁴ and selenium and tellurium.^{395–397} As machine learning and high-throughput screening methods have become more accessible, they should be leveraged for 2D polymorph discovery. Some initial work in this direction already exists.^{398–400} In parallel, experimental work in 2D material synthesis should be undertaken to map out the phase diagrams. This task is best tackled with combinatorial synthesis methods, ideally paired with *in situ* characterization techniques. An example of such a system is the ARES setup at the Airforce Research Laboratory (AFRL), which is equipped with an *in situ* Raman spectroscope and laser-annealing for localized micro-reactions. While combinatorial synthesis has been investigated in thin film communities,⁴⁰¹ it has yet to be applied to the 2D materials field.

A suggested technique for the combinatorial synthesis of 2D materials is PLD. Using PLD, a variety of parameters could be explored in a combinatorial fashion. As illustrated in Figure 15.3, PLD is compatible with the investigation of ultrathin film compositional gradients, substrate temperature gradients, and variations in substrate orientation (*i.e.*, combinatorial substrate epitaxy).⁴⁰⁶ Firstly, the composition of the film could be varied from one end of a binary phase diagram to another by using a multi-plume deposition or co-deposition method with a mask.⁴⁰⁷ This creates a library of compositions on a single substrate for subsequent characterization, enabling a finer and faster method for exploring the effect of composition on a binary (or even ternary) 2D material. For the synthesis of InSe discussed in

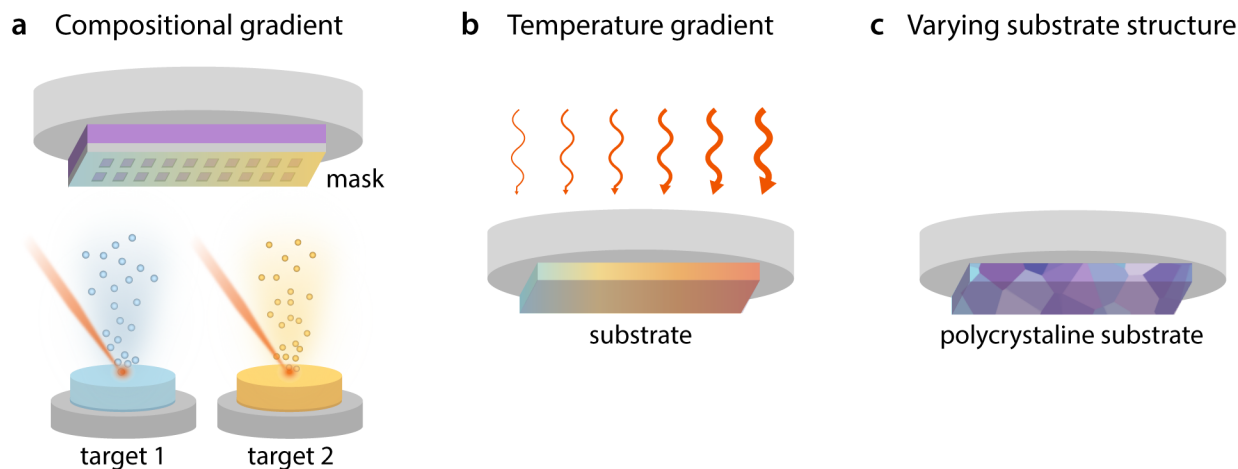


Figure 15.3: PLD-compatible combinatorial synthesis tactics for the exploration of 2D phase diagrams. (a) Combinatorial investigation of the composition of a binary 2D compound can be explored using a composition gradient. Depicted here is the use of multi-plume PLD using two separate targets (*e.g.*, In and Se) with a substrate mask to achieve an addressable compositional library from pure In to InSe, passing through InSe. (b) A well-defined substrate temperature gradient can be used to explore multiple deposition/post-annealing temperatures in a single experiment. This can be achieved using radiative heating⁴⁰² or a susceptor.^{403,404} (c) The use of a polycrystalline substrate can result in combinatorial substrate epitaxy, wherein multiple substrate crystalline orientations are explored in a single synthesis experiment to understand the templating of deposited structures.⁴⁰⁵

Part III, this process would have greatly accelerated the search for the optimal co-deposition ratio. Secondly, creating a well-defined temperature gradient across a substrate could enable high-throughput determination of the structural or compositional temperature dependence of a 2D material. Essentially, the InSe phase-evolution study performed in chapter 10 could be achieved in a single experiment. Demonstrations of combinatorial temperature-gradient vapor-phase synthesis of 3D thin films have recently been performed by Kim *et al.* for the ALD of ZnO⁴⁰³ and by Siol *et al.* for the reactive sputtering of In₂S₃.⁴⁰⁴ Temperature gradients can be established using radiative heating, susceptors, or laser irradiation.⁴⁰¹ Lastly, by using a bulk polycrystalline substrate, such that the surface embodies various structures, a variety of templates for the vapor-phase synthesis of 2D material can be explored. This is especially relevant to 2D materials which exhibit several polymorphs or for the discovery of

metastable/novel polymorphs that can be stabilized with the correct template. Wittkamper *et al.* recently demonstrated the significance of combinatorial substrate epitaxy by identifying the *c*-CoNb₂O₆ substrate grain orientations which were able to stabilize the metastable form of 3D *s*-SnO₂ versus the stable *r*-SnO₂ polymorph.⁴⁰⁵ This method has also been used to search for metastable structures of rare-earth compounds.⁴⁰⁸

Though PLD is not the optimal deposition method for all 2D materials, its niche may be in the exploration of 2D material phase space and discovery. Combinatorial studies performed with PLD would provide the basis for informed 2D material synthesis, which currently operates in a muddled trial-and-error method where negative results are rarely reported. Moreover, the insight from combinatorial synthesis would feed directly into computational materials design and discovery, which is hindered by a lack of reliable and high-volume experimental data. As set out by the Materials Genome Initiative, the way we design materials is overdue for a transformation, and the field of 2D materials would greatly benefit from such reformation.

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Vita

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Google Scholar: bit.ly/hadallia
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Education

Northwestern University, Evanston, IL

PhD Materials Science & Engineering | GPA: 3.72 Jun. 2020
Advisor: Prof. Mark C. Hersam

Management Certificate for Scientists & Engineers Aug. 2019
Kellogg School of Management

McGill University, Montréal, QC

BSc Physics, with distinction | GPA: 3.88 Dec. 2013
Advisors: Prof. Peter Grütter & Prof. Michael Hilke

Research Experience

Hersam Research Group | Northwestern University Sept. 2014 – Jun. 2020

Graduate Research Assistant

Established several scalable two-dimensional semiconductor crystal growth methods and managed semiconductor sample production for novel nanoelectronic heterostructures and devices.

Grütter Research Group | McGill University Sept. 2013 – May 2014

Undergraduate Research Assistant

Simplified the actuation and detection of atomic force microscope cantilever oscillation into a single optical fiber.

Laboratory for Optics and Biosciences | École Polytechnique, FR Jun. 2013 – Aug. 2013

Undergraduate Research Assistant

Investigated the efficacy of chemical methods for priming nanoparticles toward *in vivo* hydrogen peroxide detection.

Quantum Nanoelectronics Laboratory | McGill University Sept. 2012 – May 2013

Undergraduate Research Assistant

Optimized the synthesis of graphene, achieving the largest crystal domain size attained in the group.

Abbott Laboratories | North Chicago, IL Jun. 2011 – Aug. 2011

Junior Laboratory Technician

Established a procedure to ensure FDA-compliant functionality of sub-visible particle counting instruments for the drug Adalimumab (HUMIRA).

Teaching Experience

Science Club | Pedersen McCormick Boys & Girls Club Sept. 2016 – May 2019

Senior Mentor

Long-term, weekly mentoring of four middle-school students in an afterschool science program. Led team-based exploratory science experiments to communicate complex scientific concepts.

Graduate Solid-State Quantum Physics | Northwestern University Fall 2017, Fall 2018

Teaching Assistant

Led biweekly tutorial sessions and graded homework sets for a class of 50 students.

Leadership

Materials Science Alliance for Inclusive Community | Northwestern University 2017 – 2018

Co-Founder & Board Member

Created a graduate student group to improve inclusion in the Materials Science department.

Graduate Society of Women Engineers | Northwestern University 2017 – 2018

Social Chair

Strengthened the network of graduate women in STEM by hosting monthly meetups and quarterly socials (elected position).

Materials Science Graduate Curriculum Revision Committee | Northwestern University 2016

Student Chair

Assembled and led a group of 7 graduate students to work with faculty on the revision of the PhD curriculum.

Hierarchical Materials Cluster Fellowship | Northwestern University 2016

Seminar Chair

Organized a student seminar series in which graduate fellows presented their research and facilitated a proposal writing workshop for students applying to the fellowship.

Materials Science Student Association | Northwestern University 2015 – 2016

Volunteer & Outreach Chair

Coordinated outreach events for graduate students and fundraised several thousand dollars for science outreach.

Outreach

Letters to a Pre-Scientist 2014 – 2018

Scientist Pen Pal

Mentored 6th graders in under-resourced communities through letter correspondences over the school year.

Niles North High School & Mentor Matching Engine	2016, 2017
E-Mentor	
Guided high school students on their science fair projects <i>via</i> online correspondences.	
HerStory Museum of Science & Industry	2016, 2017
Organizer & Presenter	
Recruited attendees for an event for middle-school and high-school students featuring famous women in science and gave a presentation on the physicist Lene Hau.	
Materials Research Science and Engineering Center Northwestern University	2016
Exhibit Organizer	
Designed, organized, and presented materials science exhibits for children for STEM & Sports Day and Take Our Daughters and Sons to Work Day.	

Honors & Awards

Graduate Research Fellowship National Science Foundation	2016 – 2019
Post-graduate Scholarship – Doctoral Natural Science and Engineering Council	2016 – 2019
Nottingham Prize Finalist 79th Physical Electronics Conference	2019
First Place & Audience's Choice NU Materials Science Umbrella Society Poster Competition	2019
First Place in Graduate Research Competition Society of Women Engineers Midwest Conference	2018
Best Poster in Symposium Materials Research Society Fall Meeting	2017
Hierarchical Materials Cluster Fellowship Northwestern University	2015
International Research Experience for Undergraduates University of Michigan	2013
James McGill Entrance Scholarship McGill University	2010-2013
Undergraduate Scholarship Clara Abbott Foundation	2010-2012

Skills

Techniques	Solid precursor and metal-organic chemical vapor deposition, pulsed laser deposition, ultra-high vacuum, photolithography, field-effect transistor fabrication and electrical characterization, metal–insulator–semiconductor capacitance measurements
Instruments	Raman spectroscopy, photoluminescence spectroscopy, x-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy, x-ray diffraction, secondary ion mass spectrometry
Software	Matlab, Latex, Mathematica, Adobe Illustrator
Languages	Native English and French, intermediate Mandarin Chinese (verbal) and Spanish

Publications

1. M. E. Beck, A. Shylendra, V. K. Sangwan, S. Guo, W. A. Gaviria Rojas, H. Yoo, **H. Bergeron**, K. Su, A. R. Trivedi, and M. C. Hersam, "Spiking neurons from tunable Gaussian heterojunction transistors," *Nature Communications* 11, 1565 (2020).
2. Y. Miyahara, H. Griffin, A. Roy-Gobeil, R. Belyansky, **H. Bergeron**, J. Bustamante, and P. Grütter, "Optical excitation of atomic force microscopy cantilever for accurate spectroscopic measurements," *EPJ Techniques and Instrumentation* 7, 2 (2020).
3. S. Padgaonkar, S. H. Amsterdam, **H. Bergeron**, K. Su, T. J. Marks, M. C. Hersam, and E. A. Weiss, "Molecular-orientation-dependent interfacial charge transfer in phthalocyanine/MoS₂ mixed-dimensional heterojunctions," *The Journal of Physical Chemistry C* 123, 13337 (2019).
4. S. H. Amsterdam, T. K. Stanev, Q. Zhou, A. J.-T. Lou, **H. Bergeron**, P. Darancet, M. C. Hersam, N. P. Stern, and T. J. Marks, "Electronic coupling in metallophthalocyanine-transition metal dichalcogenide mixed-dimensional heterojunctions," *ACS Nano* 13, 4183 (2019).
5. J. Kang, I. Balla, X. Liu, **H. Bergeron**, S. Kim, C. Wolverton, and M. C. Hersam, "Selective transfer of rotationally commensurate MoS₂ from an epitaxially grown van der Waals heterostructure," *Chemistry of Materials* 30, 8495 (2018).
6. M. J. Moody, A. Henning, T. Jurca, J. Y. Shang, **H. Bergeron**, I. Balla, J. N. Olding, E. A. Weiss, M. C. Hersam, T. L. Lohr, T. J. Marks, and L. J. Lauhon, "Atomic layer deposition of molybdenum oxides with tunable stoichiometry enables controllable doping of MoS₂," *Chemistry of Materials* 30, 3628 (2018).
7. C. Zhong, V. K. Sangwan, C. Wang, **H. Bergeron**, M. C. Hersam, and E. A. Weiss, "Mechanisms of ultrafast charge separation in a PTB7/monolayer MoS₂ van der Waals heterojunction," *The Journal of Physical Chemistry Letters* 9, 2484 (2018).
8. A. Henning, V. K. Sangwan, **H. Bergeron**, I. Balla, Z. Sun, M. C. Hersam, and L. J. Lauhon, "Charge separation at mixed-dimensional single and multilayer MoS₂/Silicon Nanowire Heterojunctions," *ACS Applied Materials & Interfaces* 10, 16760 (2018).
9. V. K. Sangwan, M. E. Beck, A. Henning, J. Luo, **H. Bergeron**, J. Kang, I. Ball, H. Inbar, L. J. Lauhon, and M. C. Hersam, "Self-aligned van der Waals heterojunction diodes and transistors," *Nano Letters* 18, 1421 (2018).
10. V. K. Sangwan, H.-S. Lee, **H. Bergeron**, I. Balla, M. E. Beck, K.-S. Chen, and M. C. Hersam, "Multi-terminal memtransistors from polycrystalline monolayer MoS₂," *Nature* 554, 500 (2018). [Web of Science "highly cited paper in field"](#).
11. T. LaMountain, **H. Bergeron**, I. Balla, T. K. Stanev, M. C. Hersam, and N. P. Stern, "Valley-selective optical Stark effect probed by Kerr rotation," *Physical Review B* 97, 045307 (2018).
12. **H. Bergeron**, V. K. Sangwan, J. J. McMorro, G. P. Campbell, I. Balla, X. Liu, M. J. Bedzyk, T. J. Marks, and M. C. Hersam, "Chemical vapor deposition of monolayer MoS₂ directly on ultrathin Al₂O₃ for low-power electronics," *Applied Physics Letters* 11, 053101 (2017).
13. S. B. Homan, V. K. Sangwan, I. Balla, **H. Bergeron**, E. A. Weiss, and M. C. Hersam, "Ultrafast exciton dissociation and long-lived charge separation in a photovoltaic pentacene-MoS₂ van der Waals heterojunction," *Nano Letters* 17, 164 (2016).

14. T. A. Shastry, I. Balla, **H. Bergeron**, S. H. Amsterdam, T. J. Marks, and M. C. Hersam, "Mutual photoluminescence quenching and photovoltaic effect in large-area single-layer MoS₂-polymer heterojunctions," *ACS Nano* 11, 10573 (2016).
15. X. Liu, I. Balla, **H. Bergeron**, and M. C. Hersam. "Point defects and grain boundaries in rotationally commensurate MoS₂ on epitaxial graphene," *The Journal of Physical Chemistry C* 120, 20798 (2016).
16. X. Liu, I. Balla, **H. Bergeron**, G. P. Campbell, M. J. Bedzyk, and M. C. Hersam, "Rotationally commensurate growth of MoS₂ on epitaxial graphene," *ACS Nano* 10, 1067 (2016). **Web of Science "highly cited paper in field"**.

Manuscripts in Preparation

1. **H. Bergeron**, D. Lebedev, and M. C. Hersam, "Polymorphism in Post-Dichalcogenide 2D Materials," in preparation.
2. **H. Bergeron**, L. M. Guiney, M. E. Beck, C. Zhang, V. K. Sangwan, C. G. Torres-Castanedo, J. T. Gish, R. Rao, D. R. Austin, S. Guo, D. Lam, K. Su, P. T. Brown, N. R. Glavin, B. Maruyama, M. J. Bedzyk, V. P. Dravid, and M. C. Hersam, "Large-Area Optoelectronic-Grade InSe Films via Controlled Phase Evolution," in preparation.

Presentations

1. "Growth and characterization of large-area ultrathin InSe," Fall Materials Research Society Meeting, Boston, MA (December 2019).
2. "Vapor-phase synthesis of 2D semiconductors," SPIE-MRSEC Student Seminar Series, Northwestern University, Evanston, IL (June 2019).
3. "Growth and characterization of large-area ultrathin InSe," Nottingham Prize Competition at the 79th Physical Electronics Conference, Orlando, FL (June 2019).
4. "Low-power electronics in two dimensions: vapor-phase growth of ultrathin MoS₂/Al₂O₃ heterostructures" Hilliard Symposium, Northwestern University, Evanston, IL (May 2019).
5. "Low-power electronics in two dimensions: direct growth of monolayer MoS₂ on ultrathin Al₂O₃" Poster presentation, Northwestern University Materials Science Umbrella Society, Evanston, IL (February 2019).
6. "Preparing powerful application essays" Oral presentation, Society of Women Engineers National Conference, Minneapolis, MN (October 2018).
7. "Low-power electronics in two dimensions: direct growth of monolayer MoS₂ on ultrathin Al₂O₃" Oral and poster presentation, Society of Women Engineers Midwest Regional Conference, Milwaukee, WI (March 2018).
8. "Direct growth of monolayer MoS₂ on ultrathin Al₂O₃ for low-power electronic heterostructures" Poster presentation, 2017 Fall Materials Research Society Meeting, Boston, MA (November 2017).

9. "Controlling defects and doping in monolayer MoS₂ using low-dimensional nanoelectronic heterostructures." Poster presentation, CHiMaD Annual Meeting, Northwestern University, Evanston IL (March 2017).
10. "Rotationally commensurate growth of MoS₂ on epitaxial graphene." Poster presentation, Society of Women Engineers Region H Conference, University of Michigan, Ann Arbor, MI (March 2017).
11. "Engineering low-dimensional electronic materials via growth, doping, and heterostructures." Poster presentation, CHiMaD Summit on Data and Analytics for Materials Research, Northwestern University, Evanston, IL (November 2016).
12. "Engineering low-dimensional electronic materials via growth, defects, and heterostructures." Poster presentation, 2D Workshop – Beyond Graphene: Exploring the Heterostructures, Argonne National Laboratory, IL (May 2016).
13. "Engineering low-dimensional electronic materials via growth, doping, and heterostructures." Poster presentation, CHiMaD Annual Meeting, Northwestern University, Evanston IL (March 2016).
14. "Controlled doping of low-dimensional nanoelectronic materials via chemical functionalization." Poster presentation, CHiMaD Annual Meeting, Northwestern University, Evanston IL (May 2015).
15. "Single optical fiber AFM." Poster presentation, McGill University Center for the Physics of Materials Annual Meeting, Montreal QC (May 2014).
16. "Particle counting for HUMIRA using light-obscuring and micro-flow imaging technology." Poster presentation, Abbott Laboratories, North Chicago, IL (August 2011).