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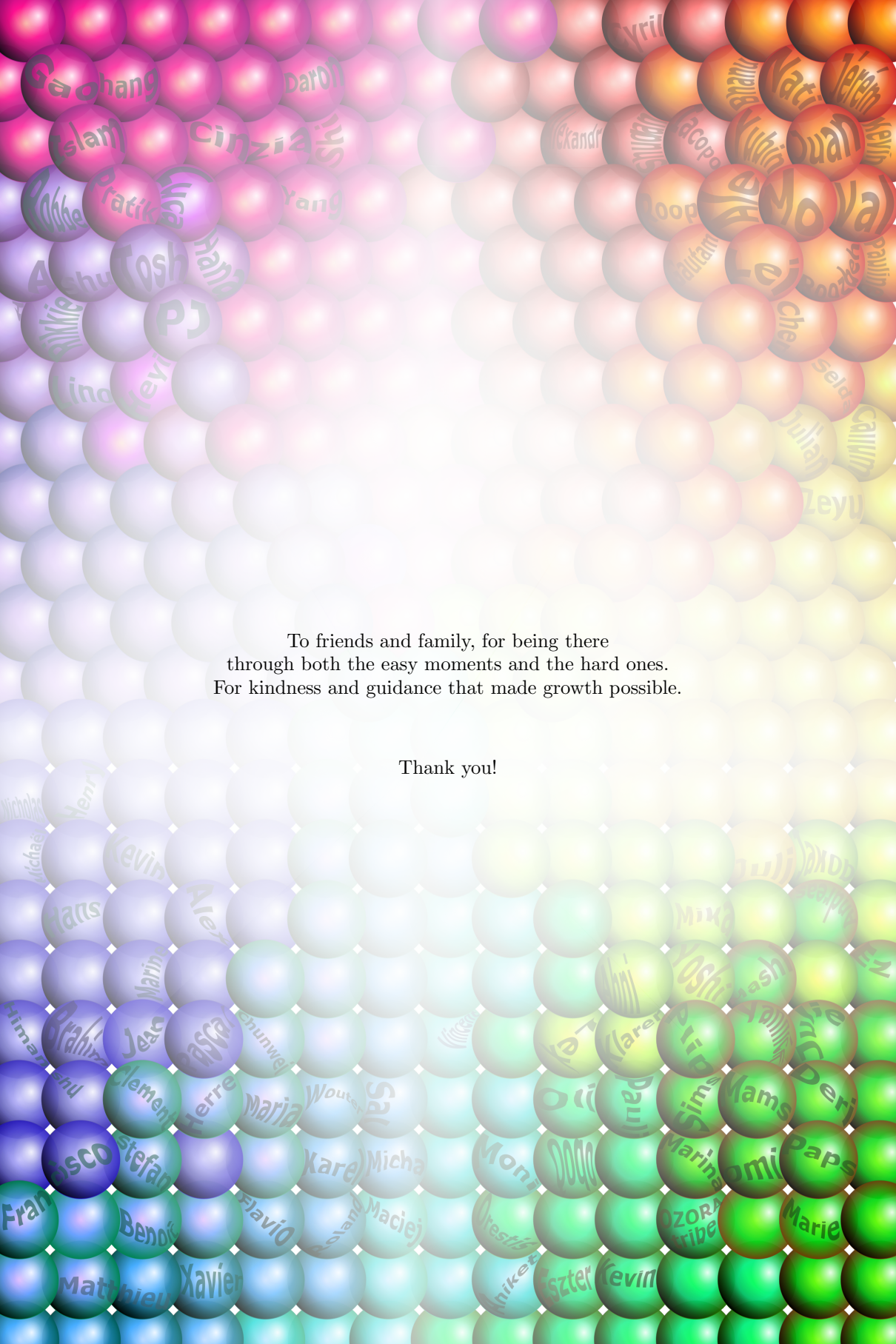
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PhD Thesis

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To friends and family, for being there
through both the easy moments and the hard ones.
For kindness and guidance that made growth possible.

Thank you!

Abstract

Material advances driven by the understanding and design of microscopic phenomena are a key enabler for next-generation energy management applications. Compounds formed by cobalt, tin, and sulfur are of particular interest in this context. Binary compounds within this system are relevant across multiple fields, including passive and active heat management, energy storage, and catalysis. The ternary compound $\text{Co}_3\text{Sn}_2\text{S}_2$ is a magnetic Weyl semimetal that exhibits record transverse thermoelectric benchmark values by harnessing both intrinsic magnetism and Berry curvature, making it a highly promising material for efficient active on-chip cooling.

Device-level integration relies on controlled synthesis at the nanoscale. Molecular beam epitaxy is well known for its high degree of control, enabling the growth of high-quality crystalline thin films, yet it has been only scarcely reported for these materials. This is largely due to the challenge of navigating the relatively complex phase diagram and, in particular for $\text{Co}_3\text{Sn}_2\text{S}_2$, achieving controlled sulfur incorporation.

In this thesis, we address the synthesis of binary and ternary compounds in the cobalt-tin-sulfur system using sulfur plasma-assisted molecular beam epitaxy. Highly crystalline, epitaxial binary thin films (≈ 20 nm range) are realized and characterized with respect to both their individual applications and their role as guiding references for ternary synthesis. Building on these insights, the growth mechanism leading to a mixed-phase $\text{Co}_3\text{Sn}_2\text{S}_2$ thin film is identified. This film exhibits signatures consistent with $\text{Co}_3\text{Sn}_2\text{S}_2$ in magnetometry and transport measurements, demonstrating the validity of this growth approach and paving the way for further thermoelectric characterization.

Résumé

Les avancées en science des matériaux, portées par la compréhension et la conception de phénomènes microscopiques, constituent un levier essentiel pour les applications de gestion de l'énergie de nouvelle génération. Les composés formés de cobalt, d'étain et de soufre présentent un intérêt particulier dans ce contexte. Les composés binaires de ce système sont pertinents dans de multiples domaines, notamment la gestion thermique passive et active, le stockage de l'énergie et la catalyse. Le composé ternaire $\text{Co}_3\text{Sn}_2\text{S}_2$ est un semi-métal de Weyl magnétique qui présente des valeurs record de coefficients thermoélectriques transverses en exploitant à la fois le magnétisme intrinsèque et la courbure de Berry, ce qui en fait un matériau très prometteur pour le refroidissement actif efficace à l'échelle de la puce.

L'intégration au niveau des dispositifs repose sur une synthèse contrôlée à l'échelle nanométrique. L'épitaxie par jets moléculaires est bien connue pour son haut degré de contrôle, permettant la croissance de couches minces cristallines de grande qualité, mais elle n'a été que rarement rapportée pour ces matériaux. Cela s'explique en grande partie par la difficulté à maîtriser un diagramme de phases relativement complexe et, en particulier pour $\text{Co}_3\text{Sn}_2\text{S}_2$, à contrôler l'incorporation du soufre.

Dans cette thèse, nous abordons la synthèse de composés binaires et ternaires dans le système cobalt–étain–soufre par épitaxie par jets moléculaires assistée par plasma de soufre. Des couches minces binaires épitaxiales hautement cristallines (≈ 20 nm) sont réalisées et caractérisées à la fois du point de vue de leurs applications propres et de leur rôle de références structurales pour la synthèse ternaire. Sur la base de ces résultats, le mécanisme de croissance conduisant à une couche mince de $\text{Co}_3\text{Sn}_2\text{S}_2$ à phases mixtes est identifié. Cette couche présente des signatures compatibles avec $\text{Co}_3\text{Sn}_2\text{S}_2$ en magnétométrie et en mesures de transport, démontrant la validité de cette approche de croissance et ouvrant la voie à une caractérisation thermoélectrique plus approfondie.

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List of Abbreviations

AFM	Atomic Force Microscopy
BP	Basal Plane
DFT	Density Functional Theory
DWM	Double Wave Measurement
EDS	Energy Dispersive Spectroscopy
FEM	Finite Element Modelling
FFT	Fast Fourier Transform
FWHM	Full Width Half Maximum
GCD	Galvanostatic Charge Discharge
(U)-HV	(Ultra) - High Vacuum
LTD	longitudinal thermoelectric devices
O/H-ER	Oxygen/Hydrogen - Evolution Reaction
OOP	Out Of Plane
(PA)-MBE	(Plasma Assisted) - Molecular Beam Epitaxy
PFM	Piezoresponse Force Microscopy
RBS	Rutherford Back-Scattering
RHEED	Reflection High Energy Electron Diffraction
RMS	Root Mean Square
RSM	Reciprocal Space Map
SQUID	Superconducting Quantum Interference Device
SThM	Scanning Thermal Microscopy
(S)-TEM	(Scanning) - Transmission Electron Microscopy
TE	Thermoelectric Effect
TFU	Thin Film Unit
ThC	Thermoelectric Cooling
TMD	Transition Metal Dichalcogenide
ToF-SIMS	Time of Flight Secondary Ion Mass Spectrometry
vdP	van der Pauw
vdW	van der Waals
VSM	Vibrating Sample Magnetometer
W-/DP	Weyl/Dirac-Point
WSM	Weyl Semi-Metal
XR-D/R	X Ray-Diffraction/Reflectivity
XPS	X-ray photoelectron spectroscopy
(Z)-FC	(Zero) - Field Cooling

List of re-occurring Symbols

Symbol	Property	SI Unit
T	Temperature	K
S	Seebeck coefficient	V/K
Π	Peltier coefficient	J/C
σ	Electric conductivity	S/m
κ or k	Thermal conductivity	W/(m·K)
zT	Thermoelectric figure of merit	unitless
α	Thermoelectric conductivity	A/(m·K)
N	Nernst coefficient	V/(K·T)
P	Ettingshausen coefficient	K·m/(A·T)
c_g	Gravimetric capacitance	Ah/g
R	Retention rate or (thermal-) resistance	unitless or (K/W) Ω
q	Elementary charge	C
I	Electrical current	A
J or j	Current density	A/m ²
V or U	Voltage	V
E	Electric field	V/m
B	Magnetic field	T
M	Magnetization	A/m
Ω	Berry curvature	m ²
ϵ	Energy	J = kg·m ² /s ²
$\hbar$	Planck's constant	kg·m ² /s
F	Mechanical force	N
v	Velocity	m/s
ρ	Mass density or Electrical resistivity	kg/m ³ or Ωm
d	Crystallographic spacing	$\text{\AA} = 10^{-10} \text{ m}$
a, b, c	Lattice parameters	$\text{\AA} = 10^{-10} \text{ m}$
x, y, z	Space directions	m
l, w, t, h	Length, width, thickness, height	m
a	Probe tip radius	m
W	Diffraction feature spacing	a.u.
θ	X-ray incidence or Anomalous Hall angle	° or unitless
ω, φ, χ	X-ray angles	°

Chapter 1

Introduction



1.1 Motivation

Challenges in energy management play a ubiquitous role in modern society and manifest across multiple fields and length scales. Heat distribution accounts for roughly 50 % of global energy consumption and 40 % of carbon emissions [1, 2], spanning scales from macroscopic everyday applications down to the nanoscale regimes of modern computing technologies. Energy storage through Li-ion batteries and fuel conversion continues to gain importance in the context of portable electronics and sustainable yet intermittent energy harvesting. At a fundamental level, microscopic phenomena govern material behaviour, which in turn determines the performance of functional building blocks. Consequently, advances at the material level - particularly at microscopic length scales - serve as a major driver of technological progress.

In this work, we explore the nanoscale synthesis and characterization of promising compounds formed by the elements Co, Sn, and S. Thin films (≈ 20 nm range) of binary crystals, including CoSn_2 , strained SnS , and mixed $\text{Co}_9\text{S}_8\text{-CoS}_2$, are synthesized and investigated within the context of their respective application fields. These materials are introduced in more detail in Chapter 4. Here, we focus on a specific material within the Co-Sn-S phase diagram: the ternary compound $\text{Co}_3\text{Sn}_2\text{S}_2$, which exhibits strong potential for temperature regulation applications.

In our every day experience, temperature regulation impacts the activity of biological matter from molecular building blocks to macroscopic lifeforms. In the nanoscopic world of condensed matter technology, thermal energy can be a major contributor to the energy balance of the system, impacting the dynamics of electrical charge carriers, atoms in crystal lattices and magnetic moments, among others. Every real system generates heat, often as a side product due to undesired energy losses. In many cases the proper continued function of electronics relies on adequate cooling in order to mitigate heat accumulation beyond a critical amount. If the conditions allow, sufficient cooling may be achieved through passive routes, for example heat conduction away from the functional element using a thermally conductive medium and releasing excess heat into the environment. However, when the functional element requires cooling far below the temperature of the environment or when the rate of passive cooling is too low to mitigate the build up of heat in the system, passive cooling alone becomes insufficient and active cooling becomes a necessity. Examples of the former include quantum systems where temperatures close to -273.15°C (or 0 K) are a common requirement for harnessing crucial low energy scale effects. Examples of the latter include computationally dense electronics (CPUs, GPUs etc.) where the high computational density comes at the cost of high

heat generation density.

To address the challenges of active cooling, a vast variety of cooling approaches have been developed. These can broadly be divided into 3 groups: air-based cooling (e.g. convection, evaporation), liquid cooling (e.g. single/two- phase immersion) and solid state cooling (thermoelectric and magnetocaloric devices). The strengths and weaknesses of each cooling approach are summarized in Fig. 1.1. On one hand, thermoelectric cooling (ThC) proffers some unique advantages compared to air and liquid cooling. It requires no moving parts, making it silent, vibration-free and easy to maintain. Also, it can be integrated into small devices down to the microchip level. Finally, ThC devices operate with superior precision and response time and, unlike two-phase liquid cooling systems, do not depend on gravity. On the other hand, ThC comes with a set of disadvantages: the cooling efficiency is generally much lower than for air and liquid cooling and ThC can only handle relatively small heat fluxes diminishing its appeal for large scale cooling and limiting its current use case to niche applications. However, there are ThC approaches that carry the potential of overcoming the current drawbacks of ThC. One of these approaches is the technique of transversal ThC (further explanation below). The broad aim of this thesis is to advance the field of transversal ThC by synthesising the appropriate material and demonstrating the working mechanism of transversal ThC at the micro-chip scale.

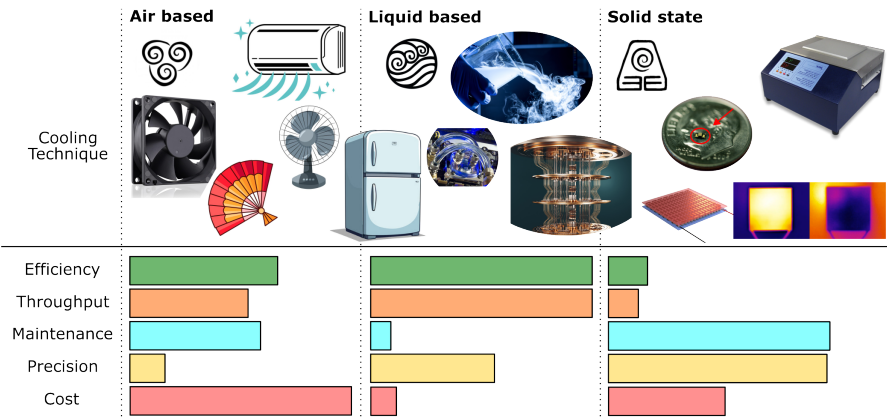


Figure 1.1: Strengths and weaknesses of major cooling approaches.

1.2 Background

1.2.1 Thermoelectric Cooling Mechanisms

The core mechanism of thermoelectric cooling devices is the thermoelectric effect (TE). One can categorize two kinds of TE, longitudinal TE and transverse TE (see Fig. 1.2). The terms “longitudinal” and “transverse” refer to the geometric arrangement of two key parameters: the electric field $\mathbf{E}$ and the temperature gradient ∇T . The former is directly linked to the dynamics of electrons, i.e. electric charges generate an electric field themselves and are at the same time influenced by the direction and magnitude of the surrounding electric field (which may for example power an electric circuit). The latter describes how strongly temperature varies along various directions (∇T itself points towards the largest change of absolute temperature T). Thermoelectric effects describe how both of these properties are linked. In other words, one can generate one of them by imposing the other on the system. When $\mathbf{E}$ and ∇T are aligned in the same direction, i.e. they are parallel, one refers to a longitudinal TE (l-TE). If they are perpendicular to each other one refers to transverse TE (t-TE). A further distinction is done based on whether E or ∇T takes the active role in the effect. The l-TE where ∇T is generated from an imposed E is called “Peltier” effect, the l-TE where $\mathbf{E}$ is generated from an imposed ∇T is called “Seebeck” effect. The t-TE where ∇T is generated from an imposed $\mathbf{E}$ is called “Ettingshausen” effect, the t-TE where E is generated from an imposed ∇T is called “Nernst” effect.

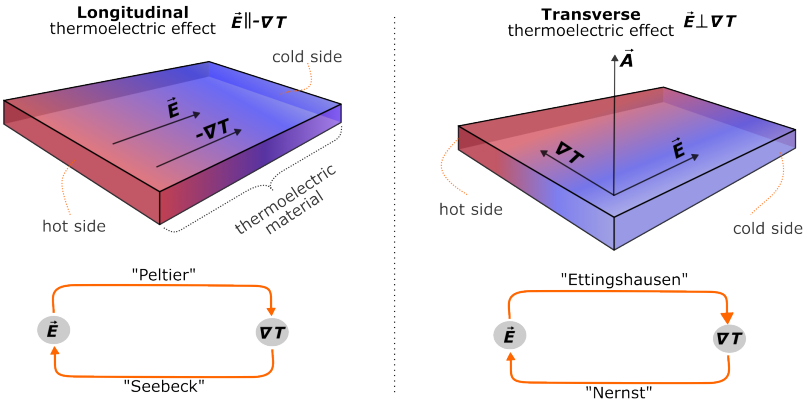


Figure 1.2: Geometry and terminology of thermoelectric effects.

As inconspicuous as it may seem at first glance, the geometric difference carries large potential to overcome shortcomings associated to thermoelectric

devices. This is due to two main reasons. The first reason is of practical nature: the transverse geometry substantially reduces the complexity of thermoelectric devices (i.e. the cost and scalability of fabrication). Instead of an intricate array of alternating longitudinal elements based on l-TE, the t-TE can be implemented with a single slab of material. The second reason is fundamental in nature. The ability to apply/generate ∇T in a different direction than $\mathbf{E}$ enables the potential to effectively decouple these two parameters. This decoupling overcomes a major efficiency bottleneck of conventional, longitudinal thermoelectric devices (LTD). The maximum efficiency of a LTD is directly linked to its figure of merit:

$$zT = \frac{S^2 \sigma T}{\kappa_{\text{tot}}} \quad \text{with} \quad \kappa_{\text{tot}} = \kappa_e + \kappa_l . \quad (1.1)$$

The zT value contains material specific parameters: the Seebeck coefficient S , the electric conductivity σ and the total thermal conductivity κ_{tot} (κ_e and κ_l are electronic and lattice contributions, respectively). Increasing this value thus demands an increase of S and σ and/or decrease of κ_{tot} . The bottleneck is that in regular metals σ and κ_e are directly linked following the Wiedemann-Franz law

$$\frac{\kappa_e}{\sigma} = L T , \quad (1.2)$$

where $L \approx 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. In the t-TE however, σ and κ_e are measured in different directions (σ in the direction of $\mathbf{E}$ and κ_e in the direction of ∇T) and thus higher zT and thermoelectric efficiencies become accessible. The new challenge becomes to actually realize a pronounced t-TE. The crucial point is hinted at in Fig. 1.2 where the t-TE is depicted to involve an additional out-of-plane (OOP) field $\mathbf{A}$. The role of $\mathbf{A}$ can be taken by an external magnetic field $\mathbf{B}$ [3]. This $\mathbf{B}$ field achieves a transverse contribution to the electron motion through the cross product in the Lorentz force

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B}) , \quad (1.3)$$

where $\mathbf{F}$ is the force acting on the object (e.g. an electron), q is its electrical charge, and v is its velocity. Unfortunately, the zT values achieved this way comes at the cost of having to generate a $\mathbf{B}$ field. This cost generally outweighs the gain in efficiency of such devices. To overcome this predicament, one can consider different fields replacing or enhancing the $\mathbf{B}$ field in its role as $\mathbf{A}$. A promising approach is to integrate an effective magnetic field into the material's structure, i.e. use materials with intrinsic magnetization $\mathbf{M}$ such as ferromagnets or anti-ferromagnets. More recently, an additional transverse contribution coming from another intrinsic property of the material has been identified: its

Berry curvature $\mathbf{\Omega}$. Somewhat similarly to a magnetic field, $\mathbf{\Omega}$ introduces a transverse component to the electron motion through a cross product

$$\mathbf{v}(\mathbf{k}) = \mathbf{v}^e(\mathbf{k}) - \frac{e}{\hbar} \mathbf{E} \times \mathbf{\Omega}(\mathbf{k}) , \quad (1.4)$$

where the electrons velocity $\mathbf{v}$, the electrons energy ϵ and $\mathbf{\Omega}$ are specific to the electron's wave vector $\mathbf{k}$, $\mathbf{v}^e(\mathbf{k}) = \frac{\partial \epsilon(\mathbf{k})}{\hbar \partial \mathbf{k}}$ is the well known contribution from the electronic band structure of the crystal and e and $\hbar$ are constants ($-e = -1.60217663 \times 10^{-19}$ C is the charge of an electron or minus one “elementary charge” and $\hbar = 1.05457182 \times 10^{-34}$ m²kg s⁻¹ is the reduced Planck's constant)[4]. Due to the similarity to the effect of $\mathbf{B}$, $\mathbf{\Omega}$ is often described as “magnetic field in k -space”. Both, $\mathbf{M}$ and $\mathbf{\Omega}$ can introduce a transverse thermoelectric effect without necessarily requiring the application of an external field. Thus, the search for an efficient thermoelectric device becomes the search for a material with large $\mathbf{M}$ and $\mathbf{\Omega}$ (or ideally, both). One class of materials satisfies those requirements particularly well by combining both intrinsic transverse contributions: magnetic Weyl-semimetals.

In Weyl-semimetals (WSM), the Berry curvature is particularly pronounced near specific points in their band structure called Weyl points (WP), named after Herman Weyl who developed Weyl-fermions as a solution to the Dirac equation in particle physics. These WP have a lot in common with the well known Dirac points (DP). They are crossings of linear electronic bands, a special condition that is at the root of extraordinary properties (exceptional mobility, high conductivity and exotic transport phenomena) of materials such as Graphene. Both WP and DP carry a property called “chirality” or handedness. This chirality is inherited by electrons moving at momenta and energies corresponding to that WP or DP, influencing their dynamics.

In DP, points of two opposite chirality overlap in both energy and momentum; the electronic state is said to be degenerate. The defining feature of WP is that those chiral points are instead separated. This can occur by breaking the inversion symmetry or the time reversal symmetry (or both) in the underlying crystal leading to a separation into WP in terms of momentum or energy, respectively (illustrated in Fig.1.3a)). While in DP the net chiral charge is zero, individual WP carry a net chiral charge of ± 1 , creating an environment with pronounced Berry curvature $\mathbf{\Omega}$. Fig.1.3 a) shows a property called Berry flux which is directly linked to $\mathbf{\Omega}$.

Few examples of magnetic WSM are reported: Co₃Sn₂S₂[6], Co₂MnGa[7], Fe₃Sn₂[8], MnSn₃[9], and MnGe₃[10, 11]. Additionally, WSM phases can occur with field-induced ferromagnetic ordering in MnBi₂Te₄[12]. Among these, Co₃Sn₂S₂ (see Fig. 1.3b for its crystal structure) stands out due to the large body of evidence supporting its magnetic Weyl semimetal character, as well

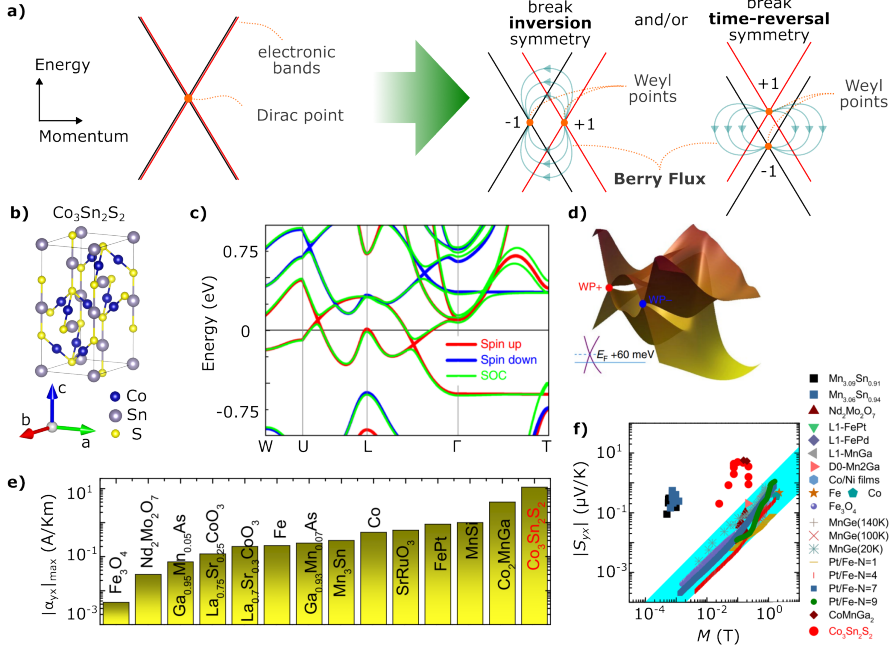


Figure 1.3: a) DP vs WP. b) Crystal structure of trigonal $\text{Co}_3\text{Sn}_2\text{S}_2$. Lattice parameters are $a = b = 5.36 \text{ \AA}$ and $c = 13.02 \text{ \AA}$. c) Electronic band structure of $\text{Co}_3\text{Sn}_2\text{S}_2$. Zero on the y-axis refers to the fermi energy E_F . d) Illustration of band crossing at WPs near E_F . e) Transverse thermoelectric conductivity of known ferromagnets. f) Magnetization dependence of Nernst signal in ferromagnets. Blue shaded area represents expectations from magnetization alone. c)-f) have been adopted from literature[5, 6].

as its transverse thermoelectric response, which is the highest reported to date among magnetic Weyl semimetals (Fig. 1.3 e))[5], as measured by the transverse thermoelectric conductivity α_{yx} in:

$$J_y = \alpha_{yx}(-\nabla_x T), \quad (1.5)$$

where J_y is the transverse electric current density (measured along direction labelled “y” in units of A/m^2) and $-\nabla_x T$ is the applied temperature gradient (measured along a perpendicular direction labelled “x” in units of K/m). This exceptionally high value can be understood as a result of strong transport contributions from Ω in $\text{Co}_3\text{Sn}_2\text{S}_2$ from WPs very near fermi energy (Fig.1.3c) and d)). In addition, with *magnetic* WSM it is useful to look at the

transverse thermoelectric response in relation to the material's magnetization $\mathbf{M}$ (Fig. 1.3 f)). In $\text{Co}_3\text{Sn}_2\text{S}_2$, the value of the experimental Nernst signal S_{yx} (which is linked to α_{yx}) far surpasses expectations based on its $\mathbf{M}$ alone ($S_{yx}/M \lesssim 1 \mu\text{V K}^{-1} \text{T}^{-1}$ in common ferromagnets)[13], further supporting the enhancing role of Ω in this compound.

The Nernst signal alone is not direct proof for the cooling performance of the material because it describes the electric response to a temperature gradient, not vice versa. Onsanger relations are a general framework for describing flux-force relationships (such as this one). For l-TE these relationships link the Seebeck and Peltier effect by $\Pi = ST$, where Π is the Peltier coefficient. The t-TE analogous to this relationship is given by $N = LP$, where N is the Nernst coefficient, P is the Ettingshausen coefficient and L is the Lorentz number from the Wiedeman Franz law.

	Longitudinal	Transverse
Thermal $\leftrightarrow$ Electrical	Seebeck (S)	Nernst (N)
Electrical $\leftrightarrow$ Thermal	Peltier (Π)	Ettingshausen (P)
Onsager reciprocity	$\Pi = ST$	$N = LP$

Table 1.1: Onsanger reciprocal relations for thermoelectric effects.

Thus, the record large value of Nernst coefficient already make $\text{Co}_3\text{Sn}_2\text{S}_2$ a very promising material for cooling applications based on t-TE. Nevertheless, these relations are based on the conventional t-TE effects. Whether these relations hold for the anomalous t-TE contributions related to magnetic WSM remains a critical point worth of scrutiny[14] and $\text{Co}_3\text{Sn}_2\text{S}_2$ - with its prominent occurrence of intrinsic WSM features - a prime candidate for probing these relations.

Unfortunately, the direct characterization of Ettingshausen-based micro-coolers is considerably more challenging than for the Nernst effect. This difficulty arises primarily from the need to measure local temperature gradients at the nanoscale, which is significantly more demanding than detecting the electronic counterpart, due to heat leakage, sensor sensitivity and noise, and Joule heating. To address this challenge, we employ scanning thermal microscopy (SThM) [15, 16] to detect the Ettingshausen effect in $\text{Co}_3\text{Sn}_2\text{S}_2$. SThM is capable of independently detecting thermal signals with nanometer spatial resolution and, under optimized conditions, millikelvin temperature sensitivity, making it far superior to on-chip heaters for mapping local thermal variations.

To fully exploit SThM, good thermal contact between the probe and the sample surface is essential, which in turn requires a homogeneous and smooth sample surface at the nanoscale. Achieving such surface quality depends primarily on the synthesis of the material, as epitaxial growth ensures both low

roughness and uniform microstructure necessary for reliable nanoscale thermal measurements.

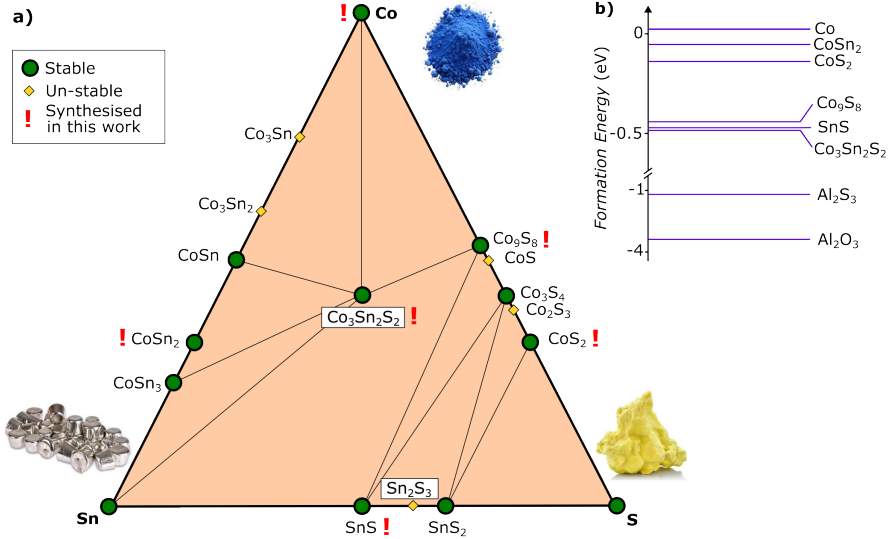


Figure 1.4: a) Phase diagram at 0 K of the ternary Co-Sn-S system. Phases observed in this work are highlighted by exclamation marks. b) Formation energies of phases observed in this work. (source: materials project)

1.2.2 Synthesis of $\text{Co}_3\text{Sn}_2\text{S}_2$

The phase diagram in Fig. 1.4 highlights the first challenge when it comes to the synthesis of $\text{Co}_3\text{Sn}_2\text{S}_2$: selectively growing just a single Co-Sn-S structure (phase) among a variety of possible phases. These include phases of different Co:Sn:S stoichiometry and also, occasionally, multiple possible structures within the same stoichiometry (polymorphs). Single crystals with controlled stoichiometry are commonly grown by what is known as the Bridgman method. The ingredients are sealed in a glass ampoule, placed in a temperature gradient (i.e. oven), and allowed to crystallize slowly (often aided with a seed crystal at one end of the ampoule). For $\text{Co}_3\text{Sn}_2\text{S}_2$, this method has repeatedly been reported to yield bulk crystals of the desired phase[17, 18, 19].

However, this method is only suitable for bulk material, not the thin crystal films targeted for this work. Thin films (where “thin” refers to few nm to few 10 nm thickness scale) not only address industrial concerns for chip integration

but also enable design capabilities (e.g. through strain, interfaces and gating) and nanoscale characterisation (e.g. SThM).

For $\text{Co}_3\text{Sn}_2\text{S}_2$, few thin films have been reported so far[20, 21, 22]. A common issue is the sufficient integration of sulfur: sulfur volatility and competing phase formation necessitate sulfur overpressure, or post-annealing to reach near-stoichiometric films. Addressing those issues motivates the use of another approach that has previously been demonstrated to achieve effective sulfur implementation in other compounds: sulfur plasma supply from cracking H_2S gas[23, 24, 25]. Here, this approach is integrated in a thin film deposition technique as further detailed in the following.

1.2.3 Thin Film Epitaxy by MBE

The term “Epitaxy” describes a mode of crystal growth hallmarked by a well-defined relationship between the orientations of the substrate and the layers of newly forming crystals. Thus, epitaxial growth implies a crucial role attributed to the crystalline substrate which can vary in terms of symmetry (cubic, orthorhombic, hexagonal etc.), lattice constant (matched or mismatched with growing crystal) and others (surface roughness, terraces, defects, contaminants, surface energy etc.). Controlling the set of variation in substrate surface parameters poses challenging demands on the experimental environment. Substrate induced strain or defects can generally relax as the distance to the initial substrate increases and new layers are formed on the already formed film. However, in the limit of ultra-thin films (order of $< \text{few } 10 \text{ nm}$), such relaxation has limited room to occur, making this type of growth particularly sensitive to the substrate surface and growth conditions. In previous studies, $\text{Co}_3\text{Sn}_2\text{S}_2(001)$ has been synthesised on two symmetry matched substrates with varying lattice mismatches, $\text{SrTiO}_3(111)$ by molecular beam epitaxy and on Al_2O_3 by co-sputtering [20, 21, 22]. $\text{SrTiO}_3(111)$ features a lattice spacing of $5.52 \text{ \AA}$, fairly close to $5.36 \text{ \AA}$ of $\text{Co}_3\text{Sn}_2\text{S}_2(001)$. Their epitaxial relation has not been reported in this study. $\text{Al}_2\text{O}_3(001)$ has a lattice spacing of $4.81 \text{ \AA}$ presenting a large mismatch with $\text{Co}_3\text{Sn}_2\text{S}_2(001)$. Their epitaxial relation has been reported as $\text{Co}_3\text{Sn}_2\text{S}_2[-1-10](001) \parallel \text{Al}_2\text{O}_3[110](001)$ with corresponding lattice spacings of $2.70 \text{ \AA}$ and $2.40 \text{ \AA}$ and possible in-plane grain rotations. These results indicate a relatively large tolerance of $\text{Co}_3\text{Sn}_2\text{S}_2(001)$ to lattice mismatches with the substrate and point out Al_2O_3 as a suitable choice.

On top of controlling the substrate properties, epitaxial growth also requires the control of conditions crucial for the formation of the desired crystal phase itself (both, qualitatively and quantitatively). To this end, deposition rates and substrate temperature are key parameters that influence the dynamics of atomic species on the surface by providing the time and energy conditions under which atoms can move and react (Fig.1.5).

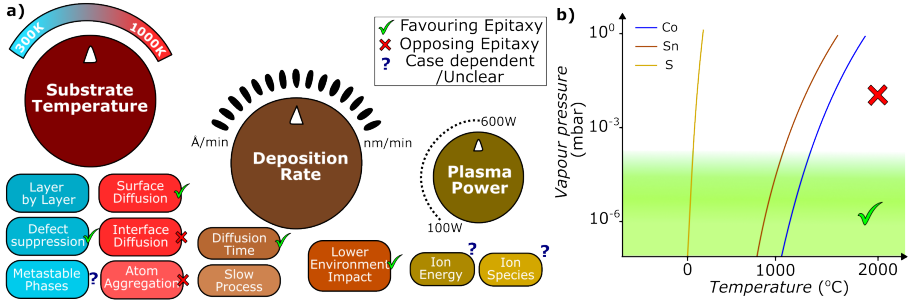


Figure 1.5: Considerations for the material synthesis by MBE. a) Main tuning parameters for the MBE growth process and their expected effect. c) Comparison of vapour pressures developed by Co, Sn and S depending on temperature.

Molecular Beam Epitaxy (MBE) is a thin-film growing technique that addresses these challenges by combining a high degree of control over both the growing environment and the depositing crystal constituents. Fig.1.6 shows the setup used in this work. The growth process is facilitated in a high vacuum (HV) environment (base pressure 10^{-9} Torr) by exposing the substrate (c-plane α - Al_2O_3 unless otherwise stated) to beams of vapor composed of ballistic atomic species. Depending on the element, different methods for vapor creation are used. A high temperature Knudsen cell electrically heating a Sn loaded “boat”, an e-gun heating a Co boat by electron bombardment and a capacitive plasma chamber for the creation of a S plasma from H_2S cracking. Due to the supply of S ions from plasma this technique is referred to as plasma assisted MBE (PA-MBE). It can be considered as a hybrid between physical and chemical deposition and has not been reported for $\text{Co}_3\text{Sn}_2\text{S}_2$ before. The high vapour pressure of thermally evaporated S (see Fig.1.5 b)) has two main implications in traditional MBE: 1) it requires high ambient pressures hindering the ballistic paths of other elemental species and 2) it implies rapid re-evaporation from the substrate before crystal formation. The use of S ions from H_2S plasma mitigates those issues. Lower S pressures are possible and S ions react more readily with the Co and Sn species on the substrate surface. The Co, Sn and S deposition rates can be controlled independently by calibrating and regulating the current/power supplied to the respective sources. Simultaneously, the temperature of the substrate is controlled by a heater mounted on the back-side of the substrate and monitored using a thermocouple. The H_2S and Sn sources were prepared prior to every deposition process. The H_2S plasma was

ignited (occasionally involving the addition of H_2 or H_2Se gas) and stabilized at target plasma power. The Sn (kept liquid by default) was outgassed at target temperature $+20^\circ\text{C}$ for 20 min.

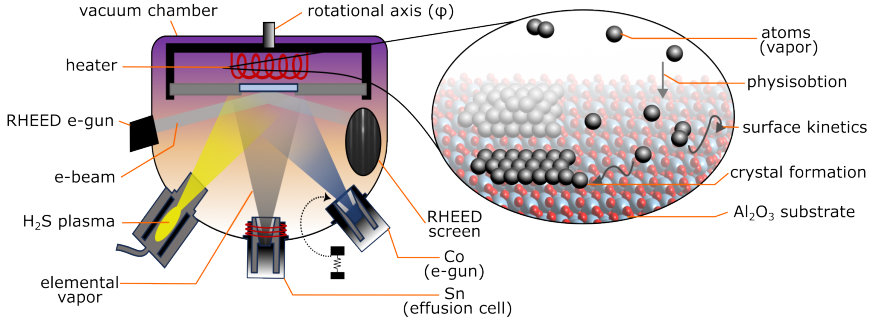


Figure 1.6: Plasma-assisted MBE setup used for all samples in this work.

1.2.4 Growth Strategy

The synthesis of the target ternary compound requires the determination of a suitable, potentially co-dependent parameter set including substrate temperature T , deposition rates of Co, Sn and S and pre-/post-treatments (Fig.1.5 a)). In order to systematically narrow down this parameter space, we first focused on the reduced problems of controlling the sources individually (Single compounds), then in combinations of two (Binary compounds) and finally, in combinations of three (ternary compound). A schematic of this strategy is shown in Fig.1.7. The tuning in all of these steps require effective feedback about deposition rate and crystal quality. These are discussed further in Chapter 3.

This concludes the introduction of basic principles and strategies relevant for this work. We are at this point ready to define the core goal and scope of the project.

1.3 Goal and Scope

The goal of this project is structured into three main objectives: O1) achieving the synthesis of thin films within the Co-Sn-S system including binary compounds and the ferromagnetic Weyl-semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$, O2) fabricating microscopic devices suitable for application oriented characterization and O3)

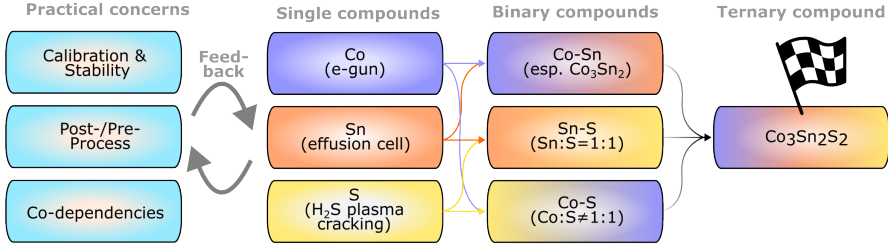


Figure 1.7: Practical concerns and growth strategy for synthesis of $\text{Co}_3\text{Sn}_2\text{S}_2$ building up from single and binary compounds.

measuring the Nernst effect and, for the first time, directly measuring the Ettingshausen effect in $\text{Co}_3\text{Sn}_2\text{S}_2$. These may be further subdivided into sub-objectives. O1 requires the choice of a suitable synthesis method (O1.0), the appropriate tuning of growth parameters using feedback from crystal characterization techniques (O1.1), and finally, the synthesis and assessment of films thin enough for later characterization in O3 (O1.2). O2 requires the development of a suitable device design (O2.1) and the transfer of that design into a fabrication process (O2.2). For $\text{Co}_3\text{Sn}_2\text{S}_2$ specifically, O3 requires the set up of a measurement apparatus designated to cryogenic characterization (O3.1) and in particular scanning capabilities (O3.2) and subsequently the implementation of the Nernst and Ettingshausen measurement (O3.3). The scope of this thesis focusses on the objectives related to O1.1-1.2. Furthermore, O2.1 has been realized on an optical lithography mask and O2.2 has been achieved using standard lithography processes combined with a dry etching step by ion milling. Realization of O3.1-3.3 remains in progress at the date of writing. Preliminary transport results on $\text{Co}_3\text{Sn}_2\text{S}_2$ are shown in Chapter 5.

1.4 Structure of this Work

The structure of this work is as follows. Following the growth strategy in **Section 1.2.4**, we first focus on the calibration and epitaxy of single and binary compounds within the Co-Sn-S system (**Chapter 3**). In **Chapter 4**, we study them in more detail in the framework of individual case studies, providing crucial references for $\text{Co}_3\text{Sn}_2\text{S}_2$ characterization. Building on the findings from these compounds, we present the epitaxy, characterization and preliminary transport characterization results on the ternary $\text{Co}_3\text{Sn}_2\text{S}_2$ in **Chapter 5**. Conclusive remarks and an outlook are presented in **Chapter 6**. A broad range of specialized but standard characterization techniques suitable for thin film

characterization has been used during the extent of this work. A breakdown of those techniques can be found in **Chapter 2** . Additional complementary data of the case studies from **Chapter 4** can be found in **Appendix A**.

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Chapter 2

Experimental Methods

For the comprehensive identification of materials grown in this work we adopted a multi-method approach spanning structural, chemical and electrical characterization methods. A particular focus was placed on structural characterization in parts due to its role as a feedback for the calibration of growth conditions (Chapter 3).

Structural

2.0.1 Scanning Probe Microscopy (AFM, PFM, SThM)

Scanning Probe Microscopy (SPM) is a class of non-invasive techniques for the characterization of the surface of a given material. All SPM techniques share a common concept depicted in Fig.2.1. A tip at the end of a cantilever ("the probe") is placed in contact with the sample and experiences an interaction with the surface. Depending on the strength of that interaction, the probe may experience a force which manifests in the deformation of the cantilever. This tiny deformation is measured, typically involving a type of amplification, and may serve as feedback for the movement of the cantilever holder. The controlled movement of the probe laterally across the sample thus allows mapping of the surface with a high degree of versatility. Under favorable conditions SPM allows imaging and manipulation at down to the atomic scale.

The type of probe, its interaction with the surface, and the way of handling the measured feedback are the main distinctors between different types and modes of SPM. A measurement mode where the probe is in direct contact with the samples surface is referred to as "contact mode". Alternatively, the probe may be moved vertically at a given frequency (typically close to its mechanical resonance frequency) at a given base-line distance to the sample surface. The frequency of that movement is then sensitive to the approach to the sample surface and can be used as probing feedback. This mode is referred to as "tapping mode". Relevant examples of SPM types in the context of this work are as follows. Atomic Force Microscopy (AFM) primarily probes van der Waals force between probe and sample surface and the resulting map represents the physical topography of the surface. AFM can be performed in both, contact and tapping mode. Piezo Response Microscopy (PFM) additionally probes the piezoelectric deformation in response to an applied electric field. This method is typically operated in contact mode and involves applying a modulation signal to disentangle signals from topography and piezo response. Scanning thermal microscopy (SThM) employs a microscopic thermal element at the apex of the tip. This allows for both, the sensing and application of heat at the sub 100 nm scale. This method is operated in contact mode.

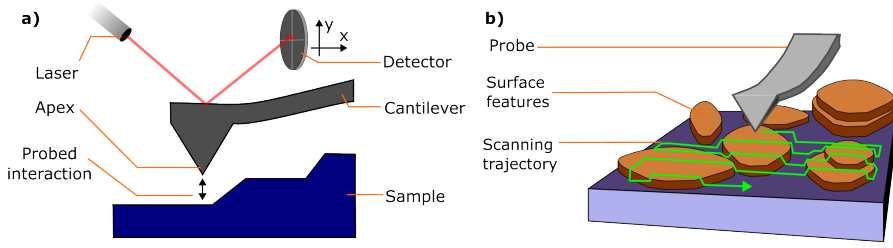


Figure 2.1: SPM concept. a) Example of traditional AFM: the small movement of the cantilever is caused by the apex-sample interaction and recorded by the reflecting laser hitting a 2x2 photo-sensor array. b) Example of AFM operated in constant height mode: Using the AFM signal as feedback to adjust the height of the cantilever while scanning the sample maps topographic data across the surface.

2.0.2 X-Ray Diffraction/Reflection Techniques (XRD, XRR)

An in-depth understanding of bulk structure can be obtained by probing the crystal with photons with wavelengths at the scale of atomic spacing (10^{-10} m). In X-Ray Diffraction (XRD), such photons are aimed at the sample at specific angles in order to measure diffraction following Bragg's law;

$$n\lambda = 2d \sin \theta \quad (2.1)$$

where n is the order of diffraction (here $n=1$), λ is the wavelength of the incident wave (here $\lambda=1.5046$ Å from Cu K- α line), d is the distance between crystal planes (inter-planar spacing), and θ is the angle between the incident wave and the crystal plane (see Fig.2.2a)). Using this simple relation provides a versatile way for non-intrusive crystal fingerprinting by scanning θ and measuring the intensity of diffracted X-rays (at 2θ relative to the incident beam) and relating the intensity peaks to lattice spacings in the material. Furthermore, detailed quality assessment and growth mode characterization can be achieved for highly oriented materials such as epitaxially grown thin films. Fig.2.2 b) shows a more complex schematic of angles involved in the XRD configuration necessary for detailed XRD measurement modes. Note that in the standard configuration for out-of-plane fingerprinting (as depicted in the schematic), ω and θ are equal.

Complementary to XRD, which works at the mid range of incident angles $10^\circ < \theta < 90^\circ$, X-Ray Reflectivity (XRR) utilizes small ("grazing") incidence angles $\theta_C < \theta < 10^\circ$, where θ_C is the critical angle for total reflection. In this

regime, the reflected intensity of a thin material layer shows multiple fringes ("Kiessing fringes") as a result of interference from multiple reflection processes (see Fig.2.2c)). Modeling the fringe oscillations, amplitude and amplitude decay returns information about the layer thickness, density and roughness, respectively.

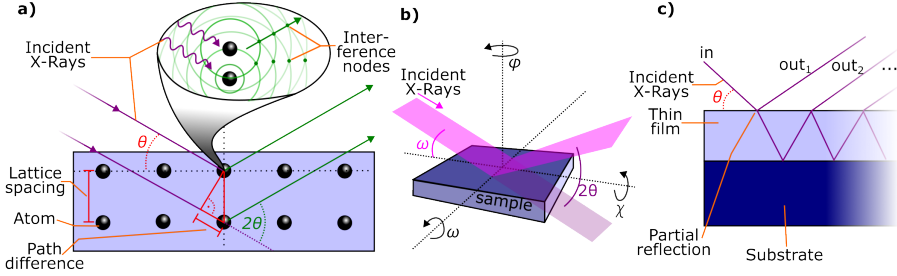


Figure 2.2: a) Bragg reflection as basic mechanism of XRD. The path difference for X-rays scattered at different atom sites results in constructive interference following Bragg's law. b) XRD configuration for detailed structural characterization. c) Schematic of XRR mechanism; X-rays pick up a optical phase during (multiple) partial reflection within the thin film leading to interference (e.g. between out_1 and out_2).

2.0.3 Electron Beam Techniques (RHEED, TEM, STEM)

Like photons, electrons exhibit wave-like behavior depending on their kinetic energy. By choosing a suitable energy and thus wavelength one can probe crystal structures by diffraction. Reflective High Energy Electron Diffraction (RHEED) uses electrons accelerated to a suitable kinetic energy (here acceleration voltage 15 kV) targeted at the sample surface at a grazing incidence angle (few $^\circ$). The reflected/diffracted electrons then form distinctive patterns on a phosphorous screen depending qualitatively and quantitatively on the present crystal structure (see Fig.2.3a)). Due to the incident mounting angle and in-situ feedback this technique is particularly compatible with the MBE setup. Beyond qualitatively assessing the growing material and its symmetries, RHEED offers quantitative in-situ insight into the in-plane lattice. In the kinematic approximation [1], the spacing W of diffraction streaks in the RHEED pattern is directly linked to the reciprocal lattice spacing of the crystal by

$$\frac{1}{d} \propto W, \quad (2.2)$$

where d is the real space lattice spacing within the targeted sample. Thus, by comparing to a reference with known lattice spacings values for d in the growing material can be collected and used for fingerprinting.

Transmission Electron Microscopy (TEM) likewise utilizes high energy electrons to characterize a thin (few 100 nm) slice ("lamella") of material. Unlike RHEED, this technique is operated in through-plane configuration (see Fig. 2.3b)) and probes the sample lattice more locally. The resulting information is a characteristic diffraction pattern collected from the exposed area of the sample that can be converted to a real space image. In Scanning TEM (STEM) the exposed area is reduced significantly (down to atomic scale under favorable conditions) by focusing the electron beam with magnetic lenses. This probing window is then scanned across the sample to obtain even more localized information within the area of interest. Multiple modes of STEM are common, depending on the detectors used and their position and angle relative to the incident beam; dark field (DF), annular bright field (ABF) and high angle annular dark field (HAADF), among others.

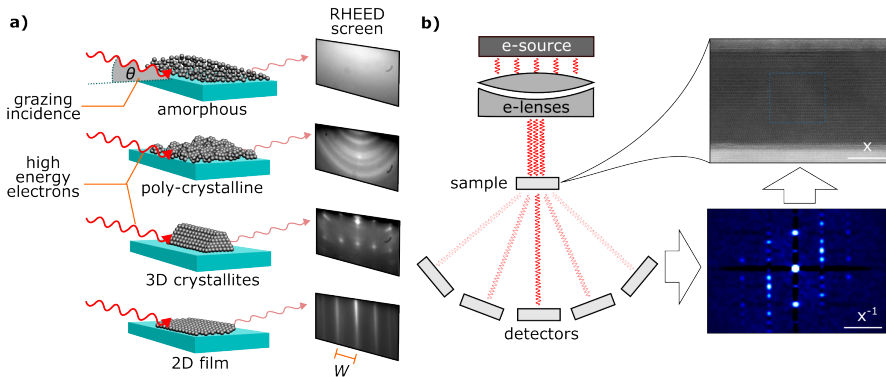


Figure 2.3: a) Representative RHEED patterns of thin films with various types of crystallographic order. b) Simplified schematic of the TEM setup. The diffraction pattern picked up by the detectors can be transformed into a real space image at nanoscopic scale.

Chemical

While the central aim of structural characterization is to determine the position and symmetries of the contributing atomic species and their lattice, chemical characterization aims at determining the atomic species and their close range

relation (chemical bonds) to each other. Atomic species are distinct by their mass and the number of electric charges Z within their nuclei ($Z= 50, 27$ and 16 for Sn, Co and S, respectively). Chemical bonds have characteristic energy scales corresponding to the energy of photons in visible and infra red (IR) range. A schematic of all chemical methods used in this work is shown in Fig.2.4.

2.0.4 Probing by Ions (RBS, ToF-SIMS)

Rutherford Back-scattering Spectrometry (RBS) uses a non-destructive process of collision between a target nuclei and a projectile beam of ions accelerated to a suitable energy. The energy E_0 of the incident projectile is slightly decreased after the collision event

$$E_{after} = E_0 \times k, \quad (2.3)$$

where the kinematic factor k at a given scattering angle θ depends on the involved masses m_{proj} and m_{targ} of the projectile and target nucleus, respectively;

$$k = \left(\frac{m_{proj} \cos \theta \pm \sqrt{m_{targ}^2 - m_{proj}^2 (\sin \theta)^2}}{m_{proj} + m_{targ}} \right)^2.$$

thus allowing for the distinction of different atomic species by measuring the energy of scattered projectiles. RBS spectra in this work were recorded using He⁺ ions accelerated to 1.523 MeV. Thus the method quantifies the elemental contributions to a film (typically measured in TFU=10¹⁵atoms/cm²).

Time of Flight Secondary Ion Spectrometry (ToF-SIMS) measures the mass of molecules removed from a sample's surface by a pulsed ion beam. The typical lateral resolution of the technique is 1 μ m but can reach below 100 nm. With a mass detection limit $\ll 1$ amu = 1.66×10^{-27} kg, its mass distinction capabilities are exceptional at high trace element detection capabilities in the part per million (ppm) range.

2.0.5 Probing by Electrons (EDS)

Energy Dispersive X-Ray Spectroscopy (EDS) detects X-rays emitted by electronic transitions in the inner shells of atoms ionized by high energy electrons. The energies of those electronic transitions are related to the atomic number of the targeted atomic species ($\propto Z^2$) which allows the identification of elements by measuring the characteristic emitted X-ray spectrum. The technique is compatible with TEM and STEM and can be performed at comparable spatial resolution.

2.0.6 Probing by Photons (Raman)

Raman Spectroscopy probes the spectrum of inter-atomic, vibrational states, such as are present in molecules or between atoms in a crystal. The physical process involves the excitation into a short lived vibrational state by visible light. In the majority of cases the state will relax back into the initial state and the same light will be emitted (Rayleigh scattering). However, if permitted in the probed material, alternative routes are possible and the emitted light may be shifted by a small amount of wavelength corresponding to the energy level difference between initial and final state (see for example state A and B in Fig.2.4d)). The shifts are commonly measured in cm^{-1} ($1 \text{ cm}^{-1} \approx 1.24 \times 10^{-4} \text{ eV}$) and characteristic for the given material, depending on composition, bond strength, optical selection rules and photo-absorption properties.

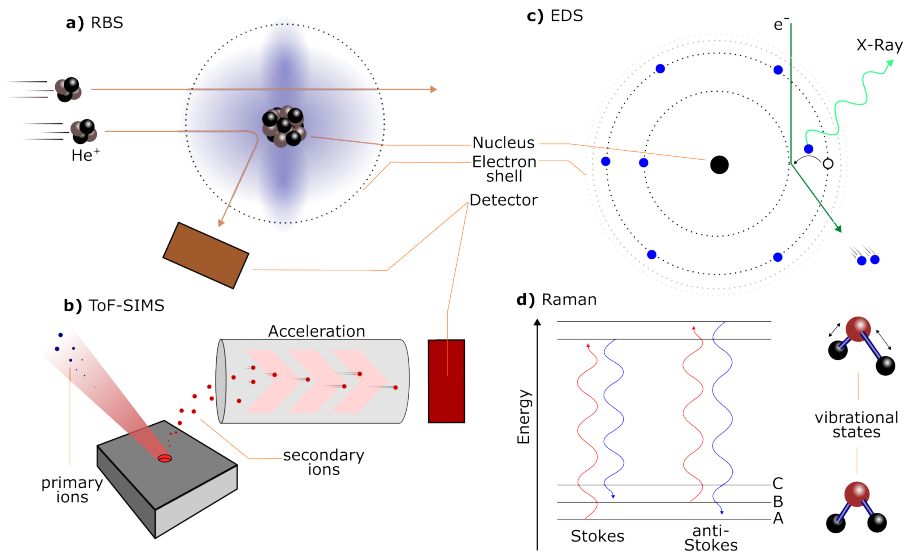


Figure 2.4: Schematic representations of a) RBS, b) ToF-SIMS, c) EDS and d) Raman.

Magnetometry (VSM)

In a vibrating sample magnetometer (VSM), the sample is placed in a uniform magnetic field (often generated using electro magnets) and moved vertically

with a given frequency (i.e. vibration). Depending on the magnetization of the sample, the movement of the sample induces a current in nearby conductors following Faraday's law of induction. By measuring the current induced in closely placed pick-up coils, VSM probes the magnetic properties of the sample along the direction of the applied external field. For particularly high sensitivity demands the pick-up coils may be replaced with a superconducting quantum interference device (SQUID). A schematic is shown in Fig.2.5a).

Electro-Chemical (GCD)

Electrochemical probing by Galvanostatic Charge / Discharge testing (GCD) characterizes the materials electro-chemical energy storage performance by measuring key parameters such as electro-chemical capacity, efficiency and cyclability. It involves the application of a constant charge/discharge current to a test half-cell (see Fig.2.5b)) while measuring the resulting electric potential based on the underlying redox mechanism. The half cells in this work were composed as follows: CR2032-type coin cells were assembled with a Li metal foil as counter and pseudo-reference electrode, one sheet of glass fiber separator soaked with 30-50 μL 1 M LiPF₆-EC/DMC + 5% FEC (battery grade, DoDochem, China) electrolyte, and one CoSn₂ chip wrapped in Cu mesh as the working positive electrode.

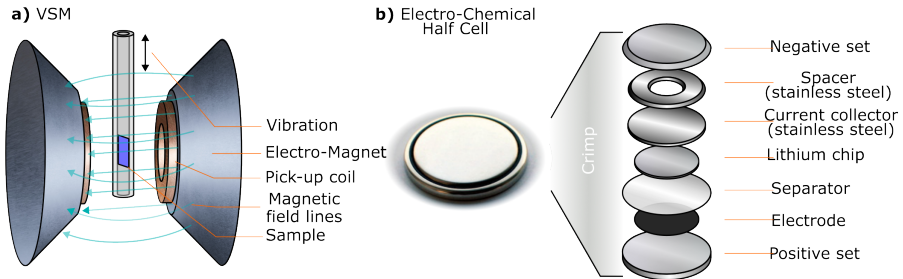


Figure 2.5: a) Schematic of VSM method. b) Electro-chemical half-cell for GCD.

Device Fabrication

A multitude of characterization methods benefit from or even require the fabrication of testing structures (devices) such as transport channels, hall bars or

micro-heaters. To this end, devices have been fabricated from thin films grown by MBE on cleaved pieces (dice) of the original wafers. Here, we broadly categorize the multitude of steps into two parts; the transfer of a predetermined pattern onto the dice by lithography and the selective removal of material by etching.

2.0.7 Lithography

Lithography refers to the transfer of a pattern or image from an original onto a variety of suitable materials. The process generally involves a selective modification of the surface of the target material. In this work we focus on a standard type of optical lithography, where this modification is achieved by exposing parts of a layer of polymer (resist) to ultra-violet (UV) light. The general process is outlined in Fig.2.6a); (i) A thin layer of resist is deposited on the target material, (ii) desired parts of the resist are exposed to UV light while other parts are protected by a mask, (iii) parts of the resist, depending on the polarity of the resist (positive/negative), are removed by "developer" solution. (iv) The remaining resist is then removed by a "lift-off" process, leaving the patterned surface.

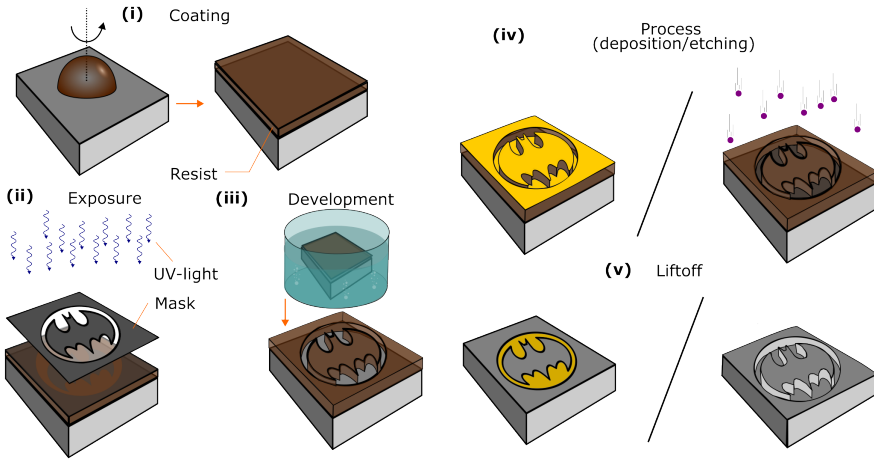


Figure 2.6: Steps of the optical lithography process. (Schematic showcases use of positive resist.)

The maximum resolution and quality of a device fabricated by a lithography process depends on a range of parameters: choice of resist/developer, resist thickness, baking conditions, mask to film distance and alignment during exposure, exposure dose, development time and lift-off conditions. The specifics of the processes used in this work are displayed in 2.7.

Time ↓	Facility	Winfab, UCLouvain		imec, Leuven	
	Resist	AZMIR701 (positive)	AZ5510 (negative)	(LOR-1A optional) + IX845G (positive)	AZ5214 (negative)
	Spinning	4000 RPM, 60s (~1µm)	3000 RPM, 60s	(4000RPM, 30s) 2000RPM, 30s	3000RPM, 30s
	Pre-bake	90°C, 90s+	90°C, 60s+	(190°C, 5min) 120°C, 60s	90°C, 50s
	Exposure	170mJ/cm ² hard contact	120mJ/cm ² hard contact	?? hard contact	?? hard contact
	Post-bake	110°C, 90s+	105°C, 60s+	na	120°C, 50s +second exposure (flood)
	Development	70s in AZ726MIF -> 30s water rinse	70s in AZ726MIF -> 30s water rinse	OPD5262, 90s, DIW rinse	200/50 H ₂ O/dev351 60s DIW rinse
	Process	Ion milling (Co compounds) or Deposition (Metal evaporation, ALD) or Plasma etching (SnS) (~10s Ar+@200W, 20°C)			
	Cleaning/Liftoff	acetone or microstrip or@50°C + (optional) sonication or pipet flushing ,IPA rinse, N2 dry			

Figure 2.7: Lithography parameters used in this work depending on location and used resist type.

2.0.8 Etching Methods

To remove undesired material from the dice, two methods of dry etching were employed; ion milling for all compounds containing Co and plasma etching else. Ion milling is a highly directional method that removes material by bombarding the surface with high energy ions. Plasma etching relies on the reaction of reactive gas with the material forming compounds that either disperse on their own or can be selectively removed in a succeeding step. These methods can be considered complementary and differ in their removal mechanism, directionality and impact on resist.

Electrical Transport

Transport measurements play a crucial part in the characterization of fundamental material properties (e.g. electronic band gap, conductivity and mobility, topology) and their interplay with diverse means of electron manipulation (e.g. B-field, temperature, light), particularly in the context of on chip integration. Often this involves the fabrication of dedicated test structures which can be fabricated using the procedure described in the previous section. Device structures used in this work are summarized in Fig.2.8.

2.0.9 Two-Probe VS Four-Probe

Two-probe measurements apply a electric potential difference (source voltage V_S) across two contacts connected to the sample and measures the resulting electric current I . The resulting circuit can be considered as a series of resistances leading up to and away from the probed material. Contributions of metallic wires and macroscopic metallic interfaces are typically of the order 0.1Ω and can often be neglected. This leaves the interface resistance with the sample R_C and the resistance of the sample itself R . These can be at a similar scale when dealing with nanoscopically thin materials as in this work.

A four-probe measurement disentangles R_C from the sample contribution by decoupling the application of driving current (by V_S) and voltage probing (V_M in Fig.2.8b)). This way the extra voltage needed to overcome R_C will contribute only to V_S , not V_M and thus

$$R = V_M / I. \quad (2.4)$$

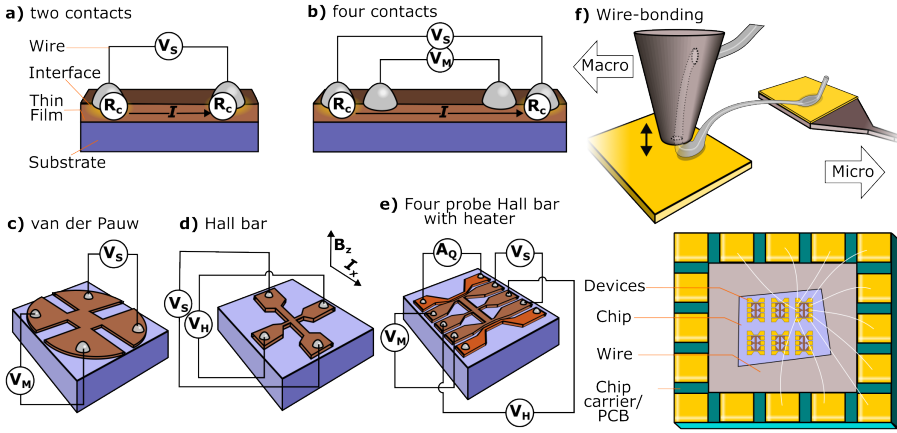


Figure 2.8: Device schematics for transport measurements. a) Two-probe contact, b) Four-probe contact, c) optimal vdP device, d) one armed, two-probe Hall bar and e) one-armed, four-probe, heated hall bar. f) Process for connecting microscopic devices to macroscopic measurement apparatus.

2.0.10 Probe Configurations (vdP, Hall, MR)

The an der Pauw (vdP) method is a type of four probe technique commonly used to probe the sheet resistance R_S and is highly independent on variations

of contact geometry and contact resistance (although certain device geometries such as the clover shape are preferable to minimize experimental error). The method involves recording V_S and I on parallel contacts in a (more or less) square shaped contact array resulting in a vertical and a horizontal resistance value $R_{vdP,V}$ and $R_{vdP,H}$, respectively. Further averaging can be done by switching contacts for V_S and I and by switching the polarity V_S (i.e. up to 8 measurements). R_S can then be obtained by numerically solving

$$e^{-\pi R_{vdP,V}/R_S} + e^{-\pi R_{vdP,H}/R_S} = 1. \quad (2.5)$$

Given the thickness t of the sample, R_S directly relates to the material resistivity ρ by

$$\rho = R_S \times t. \quad (2.6)$$

Hall bars have a more clearly defined geometry specifically designed to measure the Hall voltage V_H with minimal geometric inaccuracies and current spread to the probes. As a result of Lorentzian force, the trajectory of charge carriers is changed in a magnetic field B_z perpendicular to the current I_x which results in the buildup of transversal voltage

$$V_H = \frac{I_x B_z}{nte}, \quad (2.7)$$

where n is the carrier charge density and $e=1.60217663 \times 10^{-19}$ C is the elemental charge and the sign of V_H depends on carrier type (electron or hole). The hall coefficient R_H is defined as

$$R_H = \frac{1}{ne} = V_H \times \frac{t}{I_x B_z} = \mu \times \rho, \quad (2.8)$$

where μ is the mobility of charge carriers. Thus, given B_z , t and ρ , one can derive n , μ and dominant charge carrier type from a hall measurement. In a hall measurement, V_H can be measured simultaneously to the transversal resistivity ρ , i.e. one can simultaneously probe hall effect and $\rho(B_z)$ for magneto-resistance (MR) measurements. Magneto-resistance is defined as

$$\frac{\Delta \rho}{\rho(B_z = 0)} = \frac{\rho(B_z) - \rho(B_z = 0)}{\rho(B_z = 0)} = \frac{R(B_z) - R(B_z = 0)}{R(B_z = 0)} \quad (2.9)$$

Probing the thermoelectric properties of the sample requires the application of a temperature T gradient. To this end, devices may feature an on chip heater that creates a localized source of heat from joule heating

$$p = j^2 \times \rho, \quad (2.10)$$

where p is the heat-power volume-density and j is the current density of the heating current A_Q . j can be controlled geometrically (e.g. by creating constrictions).

Fig.2.8e) shows a device that combines four probes, hall-bar and on-chip heater.

2.0.11 Macro contacts (Wire-bonding, In-needles)

As sample size approaches the nanoscale, transport measurements require smaller devices as resistance rises with decreasing material thickness, material synthesis becomes limited by cost or directly by scale and spacial limitations may be imposed by characterization methods. A common approach for connecting microscopic devices to the macroscopic measurement apparatus is connecting the measurement platform (e.g. chip carrier or printed circuit board (PCB)), to a conductive contact layer overlapping with the sample (e.g. by evaporation or In needle deposition), by a type of welding called wire bonding. Devices in this work were wire bonded by aluminum wedge bonding which applies pressure and ultrasonic vibration for the welding process.

Chapter 3

Deposition of Single and Binary Compounds of Co, Sn and S

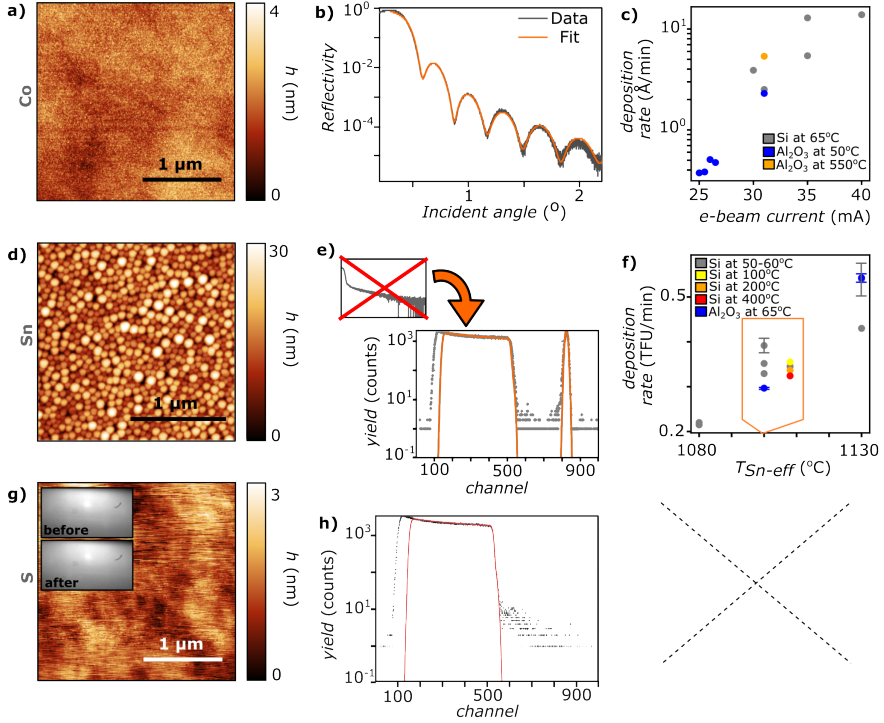
Material synthesis (MBE), processing (dicing, packaging, device fabrication) and structural characterization (RHEED, AFM, XRD) was performed, analysed and interpreted by Michael Rohde with major contributions by Dr. Gaohang He and under the supervision of Prof. Clement Merckling at Interuniversity Microelectronics Centre (IMEC) in Leuven. RBS measurements were performed by Johan Desmet and Johan Meersschaut. We express our appreciation for the training provided by Dr. Himanshu Sharma and technical support by Kevin Dubois, Hans Costermans, Kim Baumanns, among others.

Single Co, Sn and S

The works of Shuhui Li et al. [1] and Junya Ikeda et al. [2] have been chosen as a starting point. We targeted deposition rates and growth temperatures close to the reported values[1] and selected $\text{Al}_2\text{O}_3(001)$ as our primary substrate due to its previously demonstrated compatibility with $\text{Co}_3\text{Sn}_2\text{S}_2$ epitaxy and a wide range of advantages such as chemical stability, electrically insulating, thermal stability, commercial availability, and surface smoothness. By default, substrates have been outgassed in the vacuum environment of the MBE chamber for 10 min at 400°C (450°C for targetted growth temperatures $>400^\circ\text{C}$). Here, we first focus on the calibration of deposition rates for each element individually. The employed calibration methods are summarized in Fig.3.1 and described in the following sections. We then gradually increase material complexity by combining into binary compounds (Section 3.0.3) and, finally, ternary compounds (Chapter 5).

3.0.1 Single Co

Co deposits in a smooth polycrystalline film (see for example Fig.3.1a)) which makes it compatible with the X-Ray reflection (XRR) method. This method is non-intrusive and quick (around 1 h) and requires only relatively common equipment. In Fig.3.1b) a model has been fitted to a XRR spectrum of a Co thin film deposited on a Si wafer. Here we assumed the formation of a thin native Co-oxide top layer and a disordered substrate interface resulting in a $\text{CoO}/\text{Co}/\text{SiO}_x(\text{amorphous})/\text{Si}(\text{crystalline})$ material stack (Al_2O_3 substrate has been used in the models of other samples where applicable). Including the CoO layer has been found to significantly improve the quality of the fit. Using such fits allows to determine the deposition rate of Co depending on the e-beam current of the Co source as shown in Fig.3.1c). Due to the roughly twice lower density of Co in CoO compared to pure Co, this layer has been weighed by a factor 0.5. We observe a clear trend consistent with the expected



vapour pressure to Co temperature relationship (see also Fig.1.5). We observe a trend for increased deposition rate on Al_2O_3 compared to Si substrate and at 550°C compared to 50°C on Al_2O_3 . This could be due to substrate- and temperature-dependent Co sticking and incorporation kinetics, with the polished Al_2O_3 surface providing a higher density of favorable adsorption sites and a larger effective sticking coefficient than native SiO_x , while elevated substrate temperature enhances adatom mobility and incorporation into stable Co nuclei. Notably, this observation is based on only few points and more measurements would be required to confirm this trend.

3.0.2 Single Sn

A typical AFM image of Sn deposited on Si is shown in Fig.3.1d). The Sn shows a surface roughness of 5.6 nm, more than 10 times larger than the aforementioned Co films. The inset of Fig.3.1e) shows a XRR spectrum of that same film. Clearly, the spectrum does not show the reflectivity fringes necessary for extracting layer thickness, making this approach unsuitable for use as calibration feedback. Instead, we employed Rutherford back-scattering (RBS) to determine the deposited amount of Sn in thin film units (TFU = 10^{15} atoms/cm²). A typical spectrum is shown in Fig.3.1e)).

This method requires more demanding equipment, extending the time scale (days-weeks) and complexity for the calibration feedback loop. The conversion between TFU and film thickness requires a value for material density. This density can vary depending on the nano structure of the Sn atoms: 7.3 g/cm^3 (β -Sn or "white tin", body centered tetragonal), 5.8 g/cm^3 (α -Sn or "gray tin", diamond cubic), $5.5\text{-}6.5 \text{ g/cm}^3$ (amorphous) and $2.0\text{-}5.0 \text{ g/cm}^3$ (porous). Estimating from the volume in the AFM image (average thickness 15 nm) and the RBS results (41.37 TFU) we obtain 5.4 g/cm^3 which is in reasonable agreement with the amorphous phase. Thus, assuming this Sn density across samples of amorphous Sn, 1 TFU/min of Sn corresponds to roughly $3.6 \text{ \AA/min}$. In Fig.3.1f) we plot the deposition rate in TFU of Sn per minute as a function of the set evaporation temperature of the effusion cell $T_{\text{Sn-eff}}$ (three values were used: $T_{\text{Sn-eff}}=1080^\circ\text{C}$, 1100°C and 1130°C). We observe an overall consistent upwards trend with increased $T_{\text{Sn-eff}}$ albeit with significant variations even at constant $T_{\text{Sn-eff}}$. This is exemplified by the spread at $T_{\text{Sn-eff}}=1100^\circ\text{C}$. Moreover, elevated substrate temperature appears to affect the deposition rate negatively. This effect is consistent with re-evaporation of volatile Sn surface atoms but is smaller than the variation within the calibration process itself (7.5% for samples grown at $T_{\text{Sn-eff}}=1100^\circ\text{C}$). The statistical uncertainty and systematic error from the RBS measurement are each $<2\%$ and thus too small to account for this variation. Error bars in Fig.3.1 represent variation from thin film inhomogeneity. Here both the centre and edge of the film were

probed by RBS to exclude variation from the variation of probed area on the wafer (RBS probes an area much smaller than the full deposition area: $300\text{ }\mu\text{m}$ - few mm vs $\approx 5\text{ cm}$). From these cases, film inhomogeneity seems to produce a significant amount of variation but is still insufficient to fully explain the spread in Sn deposition rate. Further sources of deposition rate spread could be flux variations created due to small differences in effusion cell temperature, an effect particularly pronounced for volatile elements as Sn in effusion cells operated at high temperatures.

3.0.3 Single S

Finally, we tested the deposition of elemental S by exposing Si and Al_2O_3 substrates to H_2S plasma. Fig.3.1 a)-c) show RHEED, AFM and RBS characterization of a Si wafer kept at $50\text{ }^\circ\text{C}$ and exposed for 20 min to H_2S plasma generated at 600 W. We detected no trace of S deposited following this process.

Key Takeaways

1. Easy Co calibration: Co deposits smoothly on Si and Al_2O_3 - XRR compatible.
2. Difficult Sn calibration: Sn deposits in rough agglomerates on both Si and Al_2O_3 - not XRR compatible, need of RBS.
3. No S calibration feasible.: S does not deposit on Si exposed to H_2S plasma only.

Binary Systems

As demonstrated in Section 3.0.2, achieving the Co:Sn:S=3:2:2 stoichiometry in the target material by single element calibration in our PA-MBE approach is primarily limited due to two factors: A) the tendency of Sn to deposit with varying deposition rates even at constant source control parameters, resulting in rough films unsuitable for XRR, and B) the tendency of S to not deposit at all on substrates exposed to the H_2S plasma alone. The epitaxy study of binary compounds (Co-Sn, Sn-S, and Co-S) serves a triple purpose: it advances the broader understanding of the Co-Sn-S system across multiple fields (heat management, low-energy electronics, energy storage and catalysis), addresses the aforementioned issues in Sn and S source calibration by incorporating these elements into more stable compounds and finally, provides a valuable set of reference data crucial for identifying quality characteristics in the target ternary compound $\text{Co}_3\text{Sn}_2\text{S}_2$. To this end, a substantial body of characterization data

has been collected, including RHEED, AFM, XRD/XRR and RBS for almost all samples. In this section we focus on stoichiometric data provided by RBS. For a select few crystalline samples, more detailed characterization - including RHEED, AFM, XRD, Raman, TEM/EDS analysis and, where relevant, electrochemical, electrical, or thermal measurements - is presented as case studies in Chapter 4.

3.0.4 Binary Co-Sn System

Fig.3.2a) shows a simplified phase diagram of the Co-Sn binary system (for full temperature-phase diagram, see Ref[3, 4, 5]). Neither of the stable Co-Sn phases in Fig.3.2a) correspond to the target Co:Sn ratio of 3:2. However, the target stoichiometry can be present in a metastable Co_3Sn_2 phase at finite T as depicted by the inset. Fig.3.2b) shows an overview of all Co-Sn samples obtained in this work including a range of samples with a stoichiometry close to 3:2. All samples close to this ratio have shown signs of crystallization in RHEED, XRD and AFM with high resemblance to epitaxial Co (see Appendix, Fig.A.1) and are thus likely a result of Co crystallization ignorant of the co-deposited Sn fraction. We observed the same trend among two samples with Sn fraction close to 30 % grown at high temperature (700 °C). At a higher Sn fraction around 70 % however, we observed the crystallization of a CoSn_2 phase which is particularly interesting in the context of Li-storage. Further investigation on this phase has led to a draft for a publication detailed in Section 4.1.

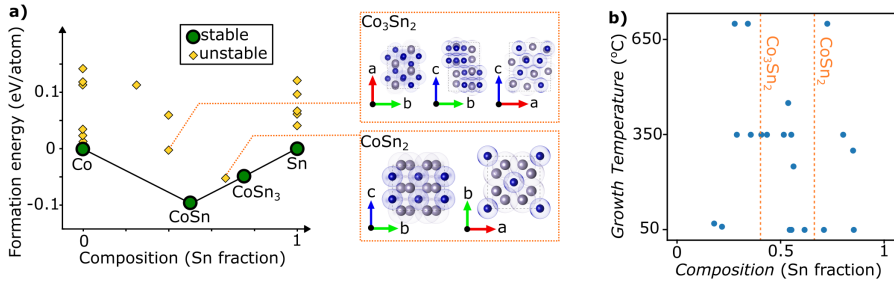


Figure 3.2: a) Simplified phase diagram of the Co-Sn binary system (source: materials project, computed by density functional theory (DFT) at 0 K). The insets show the crystal structures of two Co-Sn phases: Co_3Sn_2 with the target Co:Sn=3:2 ratio and CoSn_2 , the crystalline phase which has been synthesized and further studied in this work. b) Overview of all binary Co-Sn samples with full range of achievable elemental Co:Sn ratios.

Key Takeaways: Co-Sn system

1. Co:Sn ratio can be effectively controlled in binary system.
2. Co:Sn=3:2 is achieved at medium temperature showing signs of Co crystallization.
3. High temperature synthesis of highly crystalline CoSn_2 phase. First reported epitaxial thin film of this phase (see case study in Chapter 4).

3.0.5 Binary Sn-S System

Fig.3.3a) shows a simplified phase diagram of the Sn-S binary system (for a discussion of a full temperature-phase diagram, see Ref.[6, 7]). Multiple stable phases exist at similar formation energies within the $S \geq 50\%$ regime splitting up further into multiple metastable polymorphs at a S fraction of 50 % (SnS). Notable SnS polymorphs include the low temperature orthorhombic SnS phase (Pnma, AB stacked, depicted in the inset), a transitional phase (similar to first but AA stacked), and the high symmetry, high temperature phase (critical temperature $T_c=878$ K, Cmcn, AA stacked)[8]. Fig.3.3b) shows Sn-S films deposited at various deposition conditions. Despite the availability of high S fraction phases, all of the observed samples range close to a Sn:S ratio of 1:1, independent on total deposition rate within the explored range (differing by up to factor 3, controlled by Sn cell temperature), H_2S power within the technical limits (100 W and 600 W) and the addition of Co-traces ($\leq 9\%$). There are two exceptions where Sn:S deviates significantly from 1:1: the sample at zero S fraction has been grown with plasma generated from H_2S diluted with H_2 and the sample with exceptionally high S has been grown without pre-treatment (details below) or addition of Co. All samples have been grown at 350-370 °C. All samples with Sn:S = 1:1 share common features in RHEED, and XRD (see for example Fig.A.6b)). In particular, we discovered the high impact of a high temperature H_2S pre-treatment on the growth of SnS (see Chapter 4.2). This has not been reported thus far in literature and is of direct interest for the synthesis and application of SnS in electronics and thermal management. Further investigation on the samples produced with this pretreatment has led to publications detailed in 4.2 and 4.3 (both are centred around the same sample marked by exclamation mark in Fig.3.3b)).

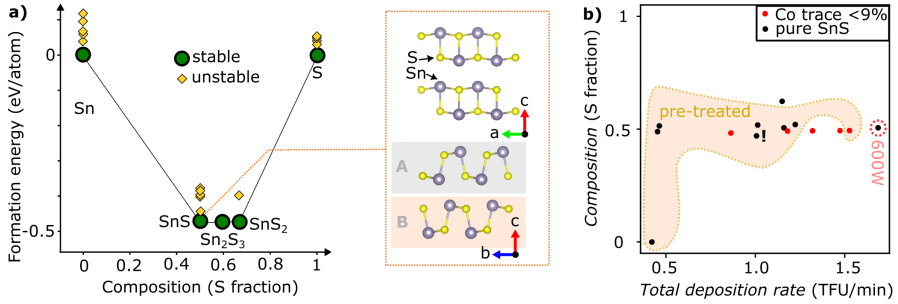


Figure 3.3: a) Simplified phase diagram of the Sn-S binary system (source: materials project, DFT at 0 K). The inset shows the crystal structure of stable SnS. b) Overview of RBS data on Sn-S films. All samples grown at 100 W unless stated otherwise.

Key Takeaways: Sn-S system

1. S saturation within explored parameter range (deposition rate variation by 300 %): Sn:S remains close to 1:1.
2. Signs of orthorhombic SnS remain prominent in this deposition rate range, even with the addition of Co traces.
3. Pre-treatment determines morphology of crystal; standing poly-crystals vs basal plane grains (see case study in Chapter 4)

3.0.6 Binary Co-S System

Fig.3.4a) shows a simplified phase diagram of the Co-S binary system based on data from materials project (phase diagrams are discussed further in Ref.[9, 10]). The binary system features three main stable compounds with Co_9S_8 closest to the Co:S=1:1 ratio and no stable phase at Co:S=3:2 (as it occurs in the target ternary). Nevertheless, it is instructive to consider the ability to tune the Co:S ratio. Here, we explored the feasibility of controlling this ratio via growth parameters of Co-deposition rates, H_2S plasma power and substrate temperature. Fig.3.4b) shows the Co fraction of all Co-S samples grown within this work as a function of total deposition rate (including S atoms) over a range of 0.2-3.8 TFU/min. Along the full range, we observe the Co ratio remaining at around 50%. This trend remains also within varying H_2S plasma power (100 W-600 W) and substrate temperature (300 °C - 450 °C). The displayed values for Co fraction can be understood as an upper limit for the real as grown Co fraction as oxidation from ambient effectively decreases the sulfur fraction.

Interestingly, these trends appear to remain even with the addition of Sn (more on that in Chapter 5). Out of these samples two comprised highly crystalline features: one formed a discontinuous film of island-type grains and the other formed a continuous and homogeneous epitaxial thin film. A detailed investigation on the latter has led the discovery of record high quality Co_9S_8 (lowest FWHM in rocking curve) mixed with a so far unreported CoS_2 phase, making this material a high interest case for catalysis applications. These findings lead to a draft that is currently in review for publication (see 4.4).

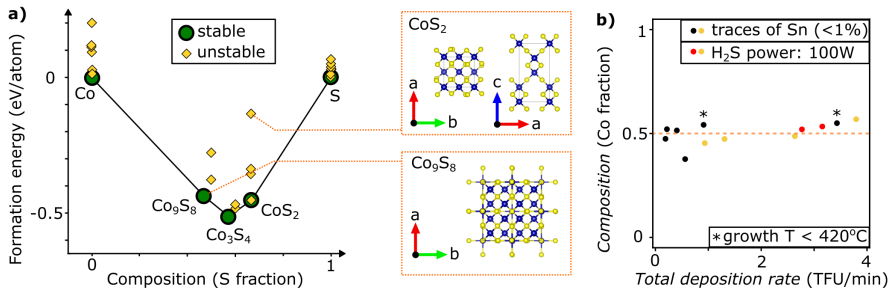


Figure 3.4: a) Simplified phase diagram of the Co-S binary system (source: materials project, DFT at 0 K). The inset shows the crystal structure of synthesized crystals from this work. b) Overview of RBS data on Co-S films. H_2S plasma power was 400 W and 600 W for samples marked black.

Key Takeaways: Co-S system

1. S saturation within explored parameter range (deposition rates variation by $>$ factor 10): Combination of Co and S from H_2S produces compounds with Co:S ratio close to 1:1.
2. The addition of Sn retains the ratio of $(\text{Co}+\text{Sn}):S=1:1$ with minimal impact from Co deposition rates.
3. Achieved first synthesis of tetragonal CoS_2 phase in mixed phase Co_9S_8 - CoS_2 epitaxial thin film (see case study in Chapter 4).

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Chapter 4

Case Studies on Binary Compounds

Material synthesis (MBE), processing (dicing, packaging, device fabrication) and structural characterization (RHEED, AFM, XRD) was conducted, analysed and interpreted by Michael Rohde with major contributions by Dr. Gaohang He and under the supervision of Prof. Clement Merckling at Interuniversity Microelectronics Centre (IMEC) in Leuven. TEM specimen preparation and imaging were performed by Chris Drijbooms, Han Han, Laura Nelissen and Olivier Richard at IMEC. All case studies were conceptualized, managed and revised by Michael Rohde under supervision of Prof. Pascal Gehring (UC Louvain) and Prof. Francisco Molina-Lopez (KU Leuven). Additional, case-specific contributions are stated at the beginnings of the respective studies.

In this chapter, published and ready-to-publish works of binary compounds from the Co-Sn-S system are presented. These studies serve as crucial references for the synthesis of $\text{Co}_3\text{Sn}_2\text{S}_2$ but also comprise interesting stand alone cases due to the overlap of nano-material growth and a variety of research fields: energy storage and conversion (Section 4.1)¹, neuromorphic computation (Section 4.2)², thermal characterization and management (Section 4.3)³ and chemical catalysis (Section 4.4)⁴.

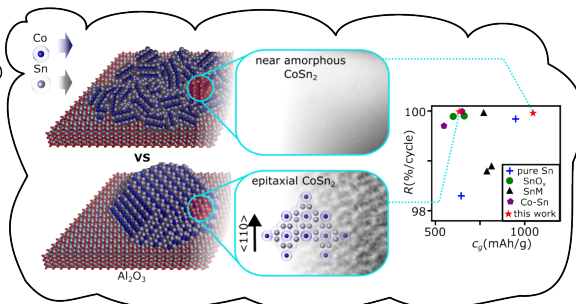
¹This section corresponds to a publication draft currently under editorial review in *Applied Materials & Interfaces*.

²The contents of this section have been published in *Advanced Functional Materials*, <https://doi.org/10.1002/adfm.202508196>.

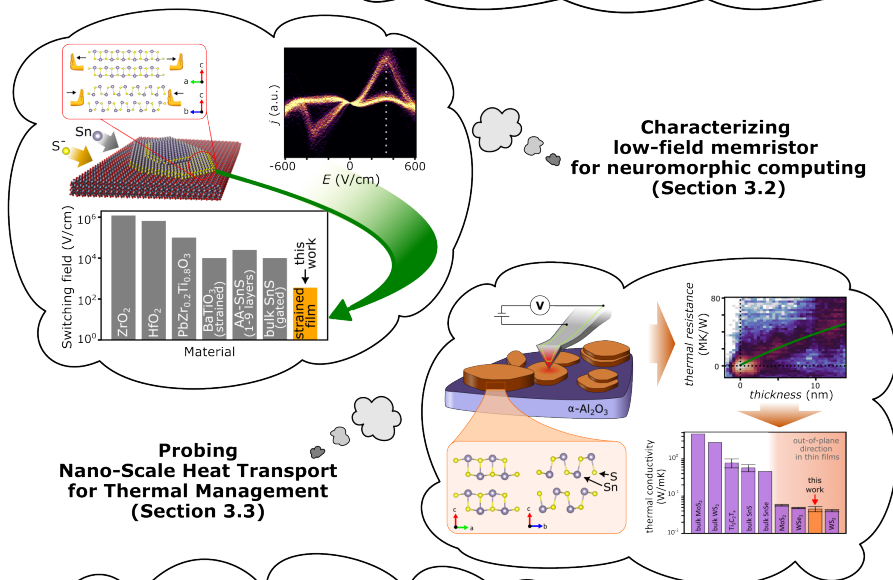
³The contents of this section have been published in *Applied Physics Letters*, <https://doi.org/10.1063/5.0293148>.

⁴This section corresponds to an article published in *Crystal Growth & Design*, <https://doi.org/10.1021/acs.cgd.5c01203>.

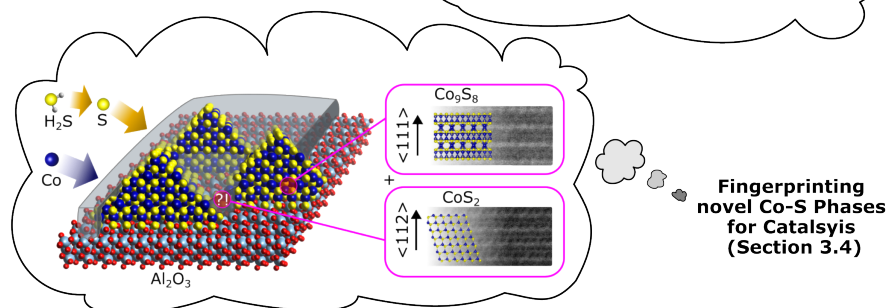
Exploring structure - Li storage link for energy storage (Section 3.1)



Characterizing low-field memristor for neuromorphic computing (Section 3.2)



Probing Nano-Scale Heat Transport for Thermal Management (Section 3.3)



Fingerprinting novel Co-S Phases for Catalysis (Section 3.4)

4.1 CoSn₂ as Thin Film Anode: "Epitaxial and Near-Amorphous CoSn₂ Thin Films: Crystallinity as a Lever for Li-Storage"

We thank Dr. Xiaodong Lin for carrying out the electro-chemical measurements, and Dr. Gaohang He[‡] for the material synthesis and structural characterization. We are grateful to Dr. Alessandra Canetta* for the Raman measurements and data analysis. We also acknowledge Prof. Alexandru Vlad*,[§] for conceptual input, provision of resources, and manuscript revision, as well as Prof. Clement Merckling^{†,‡}, Prof. Francisco Molina-Lopez[†], and Prof. Pascal Gehring*,[§] for their guidance, support, and supervision throughout the project.*

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Abstract

We use crystallinity as a controlled nanoscale parameter to reveal distinct Li-storage mechanisms in ultra-thin intermetallic films. Epitaxial CoSn₂ thin films are synthesized by molecular beam epitaxy and directly contrasted with chemically equivalent, near-amorphous CoSn₂ networks composed of sub-3 nm grains. Structural characterization (RHEED, AFM, XRD, TEM) confirms well-defined long-range order in the epitaxial films and its deliberate suppression in the near-amorphous analogue, while preserving near-ideal Co:Sn stoichiometry. Despite comparable chemistry, the two structures exhibit fundamentally different electrochemical responses: Li storage in the near-amorphous film is strongly enhanced and exceptionally stable, consistent with interfacial Li accommodation at grain boundaries rather than bulk alloying or conversion processes. By establishing epitaxial CoSn₂ as a crystalline reference and near amorphous CoSn₂ as a disorder-engineered counterpart, this work isolates the role of crystallinity in intermetallic Li storage and identifies grain boundaries as active, designable Li-hosting interfaces. These findings highlight a general strategy for probing and engineering ion–solid interactions in nanoscale intermetallic systems.

4.1.1 Introduction

The transition toward sustainable yet intermittent energy harvesting, together with the growing demand for portable and rechargeable devices, continues to

drive the search for reliable, high-density energy storage. In Li-ion batteries, the choice of anode material is critical, as it governs ion uptake and storage efficiency. Owing to its low cost and toxicity, low (de-)lithiation potential, acceptable electronic conductivity, and high theoretical capacity, Sn has emerged as a promising alternative anode material[1, 2, 3]. Through reversible alloying reactions up to $\text{Li}_{4.4}\text{Sn}$ [4, 5], Sn can deliver a gravimetric capacity of up to 993 mAh/g - more than twice that of commercial graphite - and, due to its relatively high density (7.3 g/cm^3), an exceptionally high volumetric capacity of 7,200 mAh/cm³[6, 1]. However, the relatively low melting point of Sn results in high atomic mobility compared to other high-capacity anode materials such as Si and Ge, promoting crystallization, fracture, and diffusion during cycling, and ultimately compromising long-term electrochemical stability.

Previous efforts to mitigate the mechanical and structural instability of Sn anodes have largely focused on embedding Sn into composite architectures, including carbon matrices, oxides, and multi-component nanostructures[7, 8, 9]. While these approaches can improve cycling stability, the coexistence of multiple phases and interfaces often obscures the respective roles of chemistry, microstructure, and mechanics. An alternative and comparatively underexplored strategy is the use of intermetallic compounds, in which Sn is constrained within a chemically well-defined, Li-inactive host lattice.

In this context, CoSn_2 (Khatyrkite structure, space group $I4/mcm$) has emerged as a promising candidate, offering a non-oxide route to Sn stabilization. Electrochemical studies on CoSn_2 -based powders and thin films have reported improved performance relative to elemental Sn, with reversible capacities approaching 650 mAh/g and good capacity retention over thousands of cycles[10, 11, 12]. These improvements are commonly attributed to nanoscaling and structural confinement of Sn within the intermetallic framework. However, existing CoSn_2 reports predominantly rely on disordered, amorphous, or nanocrystalline morphologies, limiting the ability to disentangle intrinsic crystallographic effects from microstructural or chemical disorder. As a result, the fundamental role of crystallinity in governing Li-storage behavior in CoSn_2 remains unresolved. In this regard, epitaxial thin films provide a uniquely well-defined platform, enabling precise control over crystallinity while eliminating extrinsic contributions from secondary phases.

Here, we report the synthesis of two ultra-thin CoSn_2 films grown on $\alpha\text{-Al}_2\text{O}_3$ by molecular beam epitaxy (MBE): a nearly amorphous film with sub-3 nm grains (B1) and a highly crystalline, epitaxial film (B2) (Fig. 4.1a)); see Methods for details). To our knowledge, B2 represents the first epitaxial CoSn_2 thin film realized by MBE. The promotion of epitaxial CoSn_2 is confirmed by comprehensive structural characterization, including reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). Rutherford

backscattering spectrometry (RBS) establishes a composition close to $\text{Co:Sn} = 1:2$ for both films, while Raman spectroscopy reveals the characteristic vibrational fingerprint of CoSn_2 , independent of long-range order. By correlating these controlled structural differences with electrochemical measurements in galvanostatic half cells, we show that the nanocrystalline film delivers high gravimetric capacity with exceptionally stable cycling ($>99.99\%$ retention per cycle). Together, these results identify nanocrystalline CoSn_2 as a promising route to overcoming intrinsic limitations of Sn-based anodes and establish epitaxial CoSn_2 as a model system for disentangling structural and chemical effects in metal-anode materials.

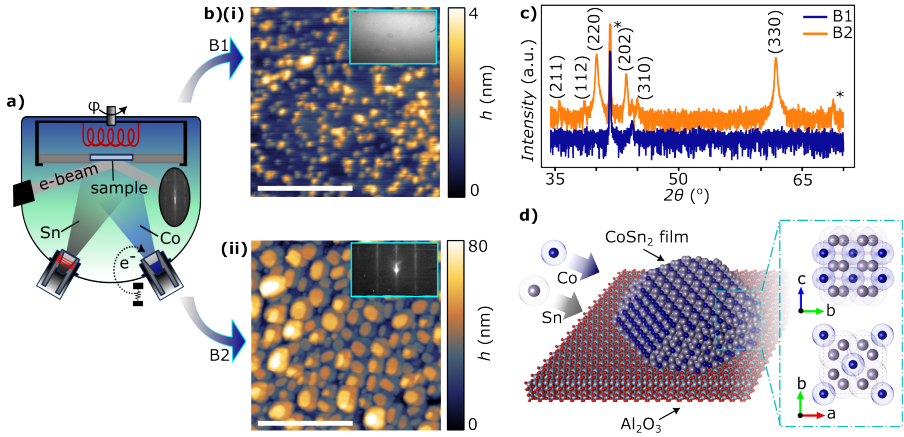


Figure 4.1: Synthesis of CoSn_2 films. a) Schematic of the growth setup featuring a Sn effusion cell and Co e-gun. b) Topographic AFM images of film surfaces of B1 and B2 (scale bar is $1\mu\text{m}$). Insets show corresponding RHEED images recorded in-situ after completed growth. c) XRD spectra taken on B1 and B2. The spectrum of B1 is offset for clarity, value scale is logarithmic. The (006) peak of the $\alpha\text{-Al}_2\text{O}_3$ is marked by *. d) Atomic models of thin film and crystal structure of CoSn_2 , respectively. Lattice parameters of CoSn_2 are $a = b = 6.30 \text{ \AA}$ and $c = 5.45 \text{ \AA}$.

4.1.2 Results

We begin by establishing the structural and chemical differences between the two CoSn_2 films, which form the basis for interpreting their electrochemical behavior. Topographic images and their corresponding in-situ RHEED images in Fig.4.1b) (i) and (ii) give first insight into the large difference in crystallinity

between B1 and B2. On B1, we find a smooth surface with RMS roughness of 511 pm. The corresponding RHEED image merely shows an amorphous background. In contrast, on B2, we find large (200 nm x 200 nm x 40 nm) crystalline grains resulting in a rough discontinuous film (RMS=14.5 nm). The corresponding RHEED image shows clear signs of a textured, epitaxial layer with lattice spacings matching two main growth directions of the CoSn_2 phase (see Supporting Info, Fig.A.3 for more details). In Fig.4.1c), these findings are verified by XRD (recorded ex-situ). B1 shows little signal in the XRD spectrum beyond the calibration substrate peak at $2\theta = 41.65^\circ$ in coherence with its near amorphous structure. The small peak at $2\theta = 44.3^\circ$ can be attributed to $\text{Co}(111)$ from a minor phase of crystallized cubic Co. The spectrum of B2 shows major diffraction peaks at $\theta = 40.1^\circ$, 43.6° and 61.8° (full width half maximum (FWHM) = 0.19° , 0.23° and 0.19° , respectively, see Supporting Info, Fig.A.4) atop a background of minor peaks at $\theta = 35.5^\circ$, 38.6° and 45.0° . All these peaks can be indexed with a single phase of CoSn_2 (see Fig.4.1d) with two preferred growth directions G1 (out of plane direction $\langle 110 \rangle$) and G2 (out of plane direction $\langle 101 \rangle$). Among these, G1 outweighs G2 by roughly 25:1 (estimated from diffraction Intensities in out-of-plane vs polar scans). The epitaxial relations found from pole figures are $\text{CoSn}_2 \langle 1-10 \rangle \parallel \text{Al}_2\text{O}_3 \langle 110 \rangle$ and $\text{CoSn}_2 \langle -332 \rangle \parallel \text{Al}_2\text{O}_3 \langle 110 \rangle$, resulting in strains of 7.3 % ($d_{1-10}^{\text{CoSn}_2} = 4.46 \text{ \AA}$ vs $2 \times d_{110}^{\text{Al}_2\text{O}_3} = 4.81 \text{ \AA}$) and 18.7 % ($3 \times d_{-332}^{\text{CoSn}_2} = 3.91 \text{ \AA}$ vs $2 \times d_{110}^{\text{Al}_2\text{O}_3} = 4.81 \text{ \AA}$) for G1 and G2, respectively (see Supporting Info, Fig.4.2).

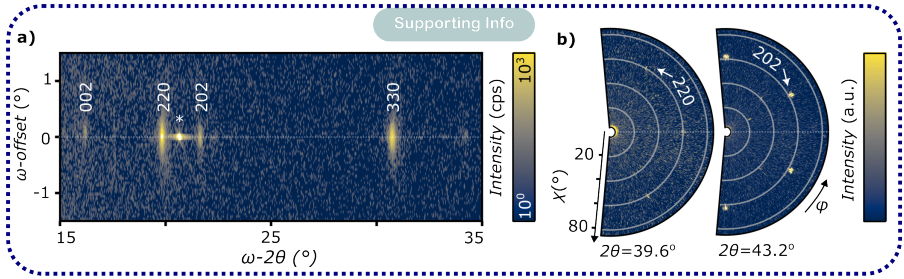


Figure 4.2: Structural details characterized by XRD. a) XRD reciprocal space map (RSM) with logarithmic colour scale. Characteristic $\text{CoSn}_2(002), (220), (202)$ and (330) diffraction peaks along the $\omega\text{-offset}=0^\circ$ axis are located at 16.2° , 19.8° , 21.7° and 30.7° , respectively. The (006) peak of the Al_2O_3 substrate is marked by (*). b) Half pole figures at two different incident angles $2\theta=39.6^\circ$ and 43.2° , corresponding to $\text{CoSn}_2(220)$ and (202) , respectively. The epitaxial relation between film and substrate can be extracted using the horizontal calibration line which was aligned with $\text{Al}_2\text{O}_3(012)$.

Note that $\langle -332 \rangle$ and $\langle 101 \rangle$ are slightly of perpendicular by 2.5° . Thus, we attribute the growth direction selectivity and lower FWHM towards G1 to lower interfacial strain imposed on G1 as compared to G2 and the lack of planes perfectly perpendicular to $\langle 101 \rangle$ in G2. Fig.4.3a) and b) show a high-angle annular dark-field (HAADF) STEM image and EDS map of a grain grown in direction G1. The match with atomic models of the CoSn_2 consistent with the XRD results, the sub-nm interface with the substrate and the consistent elemental composition are further proof of the epitaxial nature of growth in B2. Note that even after months of exposure to ambient conditions the To probe the forming surface oxide is contained within 4-6 nm and we observe no notable film-substrate inter-diffusion.

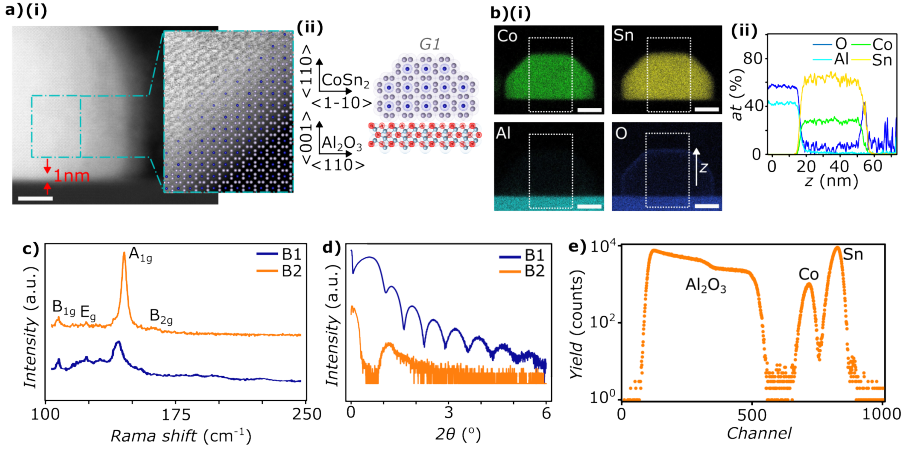


Figure 4.3: Chemical and structural characterisation of B1 and B2. a)(i) HAADF-STEM image showing the sub-nm film-substrate interface and a match with G1 (scale bar is 5 nm). (ii) shows the most common growth direction, G1, and its epitaxial relation to the substrate. b)(i) EDS maps and (ii) averaged elemental profiles (scale bars are 20 nm). c) Raman spectrum of B1 and B2. d) XRR spectra of B1 and B2. Intensity is plotted in logarithmic scale. e) RBS spectrum of film B2 showing two clear peaks for Co and Sn.

The Raman scan of B2 in Fig.4.3c) shows peaks at 107.3 cm^{-1} , 122.1 cm^{-1} , 144.9 cm^{-1} and 161.5 cm^{-1} which can be attributed to B_{1g} , E_g , A_{1g} and E_g in a phase pure CoSn_2 film, respectively[13]. Notably even the scan of XRD-amorphous B1 shows intensity peaks at 107.3 cm^{-1} , 121.4 cm^{-1} and 141.8 cm^{-1} which can be attributed to B_{1g} , E_g and a shifted A_{1g} , respectively. The occurrence of these Raman peaks suggests the presence of short range order even in B1. We attribute the shift and broadening of the fully symmetric A_{1g}

mode to phonon confinement and uniform volumetric distortions of crystallites due to the nano scale disorder in the film[14, 15]. This is consistent with our observation XRD-amorphism which sets an upper limit on the crystallite size in B1 of about 2-3 nm[16]. We employed two complementary methods for determining the volume and mass loading of B1 and B2: thickness measurement by X-ray reflection (XRR) and mass estimate by RBS. Fig.4.3d) shows XRR spectra of both materials, B1 and B2. The spectrum of B1 shows clear reflection fringes. From these we extract a thickness of 12.7 nm. On B2 however, no clear fringes appear due to the large surface roughness of the film (see Fig.4.1b)). Thus, we used RBS to determine the mass loading of B2 (Fig.4.3e). We find an areal loading of 30.4×10^{15} Co atoms/cm² and 79.1×10^{15} Sn atoms/cm² on B2. For B1 we find 17.1×10^{15} Co atoms/cm² and 41.1×10^{15} Sn atoms/cm². These results correspond to a density of 7.69 g/cm³ which is about 15% lower than the literature value of 9.09 g/cm³. We attribute this difference to the lack of long range packing efficiency and the partial formation of amorphous surface SnO_x.

To probe the electrochemical performance, we assembled a half-cell using the CoSn₂ films as anode material (see the "Methods" section for details). Fig.4.4a) shows the charge/discharge profiles of individual cycles during the long cycling tests for both B1 and B2, respectively. After initial capacity decrease from cycle 1 to 500, both anodes remain strikingly stable. Fig.4.4b) further highlight this effect. In region I the capacity degrades relatively quickly with retention rates $R=99.76$ %/cycle (B1) and 99.93 %/cycle (B2). This is accompanied by charging efficiencies (CE) of 98.0 - 98.5 %. First cycle CE were 93.3 % and 90.1 % for B1 and B2, respectively. We attribute this initially rapid decay to high capacitance contributions from irreversible conversion of surface SnO_x similar to previous reports[7, 17] as well as small contributions from agglomerates of pure Sn. In region II retention rates stabilize to 99.96 %/cycle and 99.97 %/cycle and CE increases for both. Finally, in region III, retention rates stabilize further to >99.99 %/cycle for both samples and CE reaches 98.8 % and 99.3 % for B1 and B2, respectively.

Combining RBS and galvanostatic cycling results, we calculate the gravimetric capacitances. We find average values of 1048 mAh/g and 634 mAh/g (see also discussion below) and stable (region III in Fig.4.4b)) values of 576 mAh/g and 902 mAh/g for B1 and B2, respectively. In the inset of Fig.4.4b) we compare the average retention rate and gravimetric capacitance c_g of B1 and B2 to typical values of Sn-bases anodes in literature.

4.1.3 Discussion

In this study we compared the electrochemical performance of epitaxial, 200 nm (lateral) x 40 nm (vertical) scale CoSn₂ grains (B2) and their near amorphous

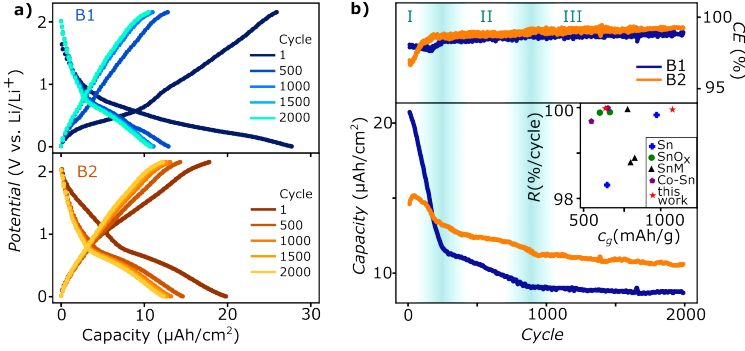


Figure 4.4: Electro-chemical characterization of CoSn_2 films. a) Galvanostatic charge/discharge profile at different cycle numbers up to 2000 recorded at room temperature. Charge/discharge current was around $16.7 \mu\text{A}/\text{cm}^2$ (small difference due to variation in sample size, see Supporting Info, Fig.A.5). b) Capacity and charging efficiency vs cycle number showing excellent cycling stability of the thin film anodes. The inset shows a comparison of average capacity and retention rate per cycle r with typical literature values of Sn [10, 18], SnO_x [7, 17], Sn-M ($\text{M}=\text{Cu, Fe, Ni}$)[5] and Co-Sn compounds[5, 10].

(sub 3 nm grains) analogue (B1). The performance of B2 matches well previous reports on CoSn_2 anodes showing gravimetric capacitance in the 600 mAh/g range at high R [5, 10]. B1 on the other hand exceeds the performance of these reports even within its fully stabilized state at $R > 99.99\%$ and $c_g = 902 \text{ mAh/g}$ in region III in Fig.4.4b). The theoretical c_g limit of Sn lithiation ($\text{SnLi}_{4.4}$) lies at 993 mAh/g ($1991 \text{ mAh}/\text{cm}^3$) for pure Sn and 787 mAh/g for pure CoSn_2 . Some of the excess capacitance in B1 may stem from an excess of Sn in ($\text{Co}:\text{Sn}=1:2.4$) and SnO_x conversion in early cycles as hinted at by the low initial CE. However, this seems unlikely to contribute at later stages of the cycling given the relatively low retention rate found for pure Sn and SnO_x in previous studies[7, 17] and the absence of significant capacitance excess in B2. Interfacial Li storage at grain boundaries is well discussed for transition-metal oxides[19], explicitly demonstrated for $\text{Fe}/\text{Li}_3\text{PO}_4$ [20] and has been evoked previously to explain beyond-alloy capacitance in CoSn_2 nano structures[21]. Using a typical surface charge density of $50\text{--}200 \mu\text{C}/\text{cm}^2$ [22, 23] and the expression for the specific surface area of spherical grains, $S=3/(\rho r)$, where ρ is the density and r the grain radius, we estimate the grain size required to account for a capacitive contribution of 100 mAh/g. For CoSn_2 with $\rho=7.7 \text{ g}/\text{cm}^3$, this corresponds to grain radii of approximately 0.5–2 nm, i.e. grain diameters of

1–4 nm, in good agreement with the short-range order inferred from Raman spectroscopy combined with RHEED and XRD amorphism. Thus, we attribute the excess capacitance in B1 to interfacial Li storage at nano-grain boundaries. Considering the large crystallite size in B2, surface charges 50-200 $\mu\text{C}/\text{cm}^2$ contribute an estimated negligible <1 mAh/g to the total capacitance, coherent with our observation of a below CoSn_2 -limit capacitance. Finally, we highlight the potential of ultra-thin film CoSn_2 in full cell batteries by estimating power- and energy density. We did not find clear charge/discharge plateaus and thus we resort to the average potential (about 1 V) for an estimate of the lithiation potential. Charging/discharging rate was 0.02 mA. Accordingly, our estimates of stable power- and energy density in (B1/B2) are (1.68/0.93) W/g and (576/902) mWh/g, higher than in previous studies on CoSn_2 prepared by reduction, ball milling or electroplating[10, 12, 24] and with superior cycling stability. These results highlight the exceptional potential of Sn lithiation in this nano-crystalline network.

4.1.4 Conclusion

We report a direct comparison between two ultra-thin CoSn_2 films: a nearly amorphous, nano-crystalline film with sub-3 nm grains and an epitaxial film with large, well-defined grains. Structural characterization using RHEED, XRD, TEM, pole figures, and reciprocal space mapping confirms the long-range order and epitaxial nature of the latter, while Raman spectroscopy reveals a common CoSn_2 vibrational fingerprint in both systems. To our knowledge, this constitutes the first realization of an epitaxial CoSn_2 thin film. Despite comparable stoichiometry and local bonding, the nanocrystalline film exhibits markedly enhanced and exceptionally stable Li storage (902 mAh/g with $>99.99\%$ capacity retention per cycle), which we attribute to the high density of interfacial sites associated with its ultra-small grains. These results identify crystallinity as a decisive lever in Li-storage behavior and establish epitaxial CoSn_2 as a model platform for disentangling structural and chemical effects in Sn-based anodes, pointing toward a materials-driven route to durable, high-performance Li-ion storage.

4.1.5 Methods

Thin Film Growth

Films were grown on commercial 2" c-plane $\alpha\text{-Al}_2\text{O}_3$ wafers by MBE. The base pressure of the growth chamber was 10^{-9} Torr. B1 and B2 differed in growth conditions; B1 was grown at a substrate temperature of 50 °C for 120 min with Co e-gun and Sn evaporator set to 21 mA and 1100 °C, respectively. B2

was grown at 700 °C for 30 min with Co and Sn sources set to 23.5 mA and 1190 °C, respectively. Both samples were left to cool passively after growth.

Half Cell Assembly

CR2032-type coin cells were assembled with a Li metal foil as counter and pseudo-reference electrode, one sheet of glass fiber separator soaked with 30-50 μ L 1 M LiPF₆-EC/DMC + 5% FEC (battery grade, DoDochem, China) electrolyte, and the sample chip wrapped in Cu mesh as the working positive electrode.

Structural, Chemical and Electro-chemical Characterization

RHEED electrons with 15 kV acceleration voltage where directed at the sample surface at an incident angle of 2-3°. The pixel axis was converted to 1/d using the Al₂O₃ substrate for calibration. AFM images where recorded with a Dimension Edge tool (Bruker) operated in tapping mode. XRD and XRR scans were performed with XRD diffractometer X'pert (Malvern Panalytical) operated at 45kV/40mA acceleration/filament current. Calibration was done on the Al₂O₃(006) peak of the substrate. Incident X-rays had Cu-K α energy of 8keV and spectra where recorded with a PIXcel as point detector. Peak positions were compared to spectra based on data from materials project (CoSn₂-mp20155). TEM samples were prepared by covering the sample with spin on carbon by drop casting followed by Pt deposition (5 kV, then 30 kV) and side thinning lift out (Helios, TFS). The lamella was cut along the Al₂O₃ <110> direction of the substrate. TEM, STEM and EDS maps were recorded using a Thermo Fisher G2 60-300 Titan³ operated at 200 kV. The galvanostatic charge-discharge tests were conducted on a Neware battery testing system (Shenzhen Neware Electron. Co. Ltd., China) at room temperature. Current was 20 μ A.

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4.2 SnS as Memristor: "Low-Field Memristive Switching in Epitaxially Strained SnS Thin Film"

We gratefully acknowledge Mohammadali Razeghi for device fabrication and transport measurements, and Dr. Jean Spiece* for performing PFM studies. Special thanks to Dr. Gaohang He† for material synthesis and characterization, and to Dr. Alessandra Canetta* for Raman measurements and data interpretation. We also thank Valentin Fonck* for transport measurements, with overarching guidance, resources, and manuscript revision provided by Prof. Francisco Molina-Lopez‡, Prof. Clement Merckling†,‡, and Prof. Pascal Gehring*,§.*

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Abstract

The quasi van der Waals (vdW) polarizable semiconductor, tin monosulfide (SnS), holds exceptional potential as a memristor in neuromorphic architectures as well as for sustainable, mechanically flexible and biocompatible photovoltaic and piezoelectric applications. So far, the synthesis of SnS remained limited to flake scale growth or subject to a compromise between substrate interaction and crystal order. In this work, we overcome this limitation by introducing a substrate pre-treatment with reactive sulfur to a hybrid chemical/physical growth method. Our approach achieves the sharply interfaced growth of a textured epitaxial SnS thin film directly on α -Al₂O₃ introducing in-plane strain and centrosymmetry breaking. These films possess stable and programmable memristive switching behaviour with a switching field of 360 V/cm, orders of magnitude lower than in previous studies on SnS. We thus demonstrate the interplay of epitaxially induced strain and symmetry breaking in SnS, paving the way for its thin film scale integration in the next generation of energy efficient and material-level adaptive electronics.

4.2.1 Introduction

In a polarizable material, electric dipoles form domains that can be manipulated and stabilized by means of an electric field. By combining information storage and computation in a single device, these materials are of high interest for

energy cost efficient switches in non-volatile memory applications or memristors for analog neuromorphic architectures [1, 2].

Meanwhile, research on layered vdW materials has pushed the layer thickness scale down to the 2D limit allowing the exploration of unique physical properties and fabrication prospects [3]. The overlap of these two fields, namely ultra-thin, polarizable and layered materials, holds great promise for multi-functional nano devices as the low dimensionality can introduce inter-coupling of photoelectricity, piezoelectricity, spin polarization and electric polarization[4].

Among the few examples[5, 6, 7], the group-IV monochalcogenide and semiconductor SnS stands out thanks to its high electric response to force, light and temperature [8, 9, 10], as well as its relatively abundant and non-toxic constituents. However, mechanical exfoliation is particularly challenging for SnS due to relatively strong inter-layer coupling sometimes referred to as "weak covalent bonding"[11], hence the term "quasi" vdW. This has motivated the exploration of engineering its thin film properties by bottom-up synthesis routes.

In its most stable form at room temperature, basal plane SnS adopts a layered orthorhombic structure (space group Pnma) with vdW layers parallel to the surface. Traditionally, SnS with an even number of AB-stacked layers (see Supporting Info, Figure.A.7) is centrosymmetric and spontaneous polarization can occur only in the mono- and odd- layered system where centrosymmetry breaking is guaranteed, leading to ferroelectricity[12, 13, 14]. The search to overcome this limitation has led to the discovery of systems where centrosymmetry is instead broken either by an external electric field or by modifications of the SnS structure into AA-type stacking[15, 16]. In principle, such structural alterations can be controlled during epitaxial growth which is sensitive to stress initiated at the substrate interface. So far however, the synthesis on strongly interacting substrates typically yielded relatively disordered films or was accompanied by the formation of an amorphous SnS buffer layer[17, 18, 19].

In this work, we demonstrate centrosymmetry breaking and memristive switching behaviour in ultra thin (18 nm) basal plane textured SnS films grown by a plasma assisted molecular beam epitaxy (PA-MBE) method directly on α -Al₂O₃. This was achieved by adding a reactive sulfur pre-treatment to a hybrid physical/chemical deposition method which has previously been effective for MoS₂ synthesis [20]. We find high crystal quality and strain evidenced by electron diffraction (RHEED), atomic force microscopy (AFM), Raman spectroscopy (Raman), scanning transmission electron microscopy (STEM) and X-ray diffraction (XRD). Using piezoresponse force microscopy (PFM) we show local centro-symmetry breaking and demonstrate in transport measurements, that our films can be switched in a cyclic and memristive manner, exhibiting the lowest switching field for SnS reported to date.

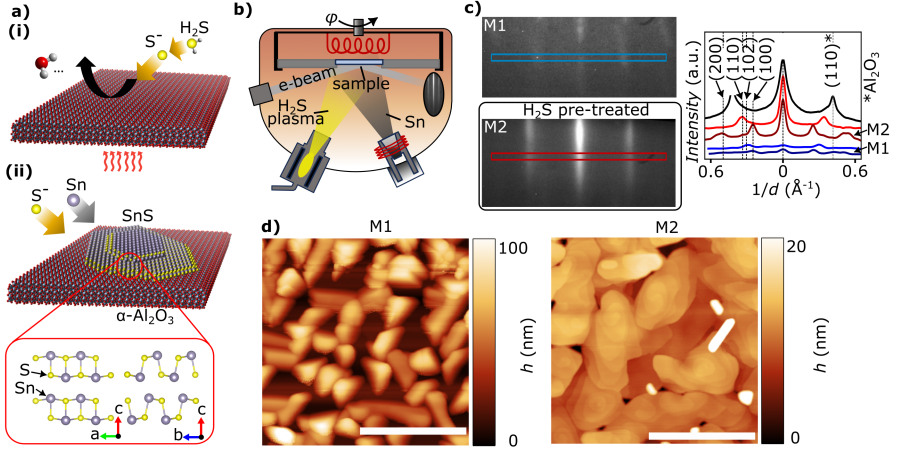


Figure 4.5: SnS growth process. a) Growth strategy involving high temperature H_2S plasma pre-treatment (i) followed by H_2S plasma assisted deposition (ii) resulting in basal plane SnS. b) Schematic of the growth chamber for PA-MBE. c) RHEED images of M2 vs M1. Taking the pattern of the $\alpha\text{-Al}_2\text{O}_3$ substrate for calibration allows quantification of reciprocal lattice spacing $1/d$ observed in M1 and M2 at different azimuth angles (see Supporting Info, Fig. 4.6). The intensity plot shows cuts of frames at two different azimuth angle for each, M1 and M2. Expected reciprocal lattice spacings are indicated with dashed lines. d) Surface morphology of M1 (RMS=18.9 nm) vs M2 (RMS=3.6 nm) measured by AFM. Grains in M1 grow in distinct angles consistent with RHEED data (see Supporting Info, Fig. A.8). Scale bar is 500 nm.

4.2.2 Results

Two films (M1 and M2) with different growth strategies are presented in the main text (see Supporting Info, Figure A.6 for other films M3 - M6). Schematics of the growth method for M2, which involves a H_2S plasma pretreatment, are shown in **Figure 4.5** a) and b) (for more detail see "Experimental Section").

The effect of the pre-treatment is apparent in Figure 4.5 c) and d). Figure 4.5 c) shows in-situ RHEED images of M1 and M2 along with intensity profiles extracted horizontally across the pattern. In the kinematic approximation [21], the spacing W of diffraction streaks in the RHEED pattern is directly linked to the reciprocal lattice spacing of the crystal by $1/d \propto W$. Taking the known pattern of the Al_2O_3 substrate for in-plane lattice calibration we quantify the streak/spot distance of the SnS patterns and compare

with expected values of the SnS lattice parameters. On M1, transmission-like RHEED spots indicate the growth of 3D islands with crystal spacings matching SnS(100) and SnS(102) planes. In contrast, on M2, we obtain intense diffraction streaks showing the growth of 2D layers with spacings matching vertical planes SnS(200) and SnS(110) (see dashed lines in Figure 4.5 c)).

The difference of growth mode between M1 and M2 is further highlighted by the contrast of surface morphology in AFM images shown in Figure 4.5 d). On M1, standing grains grow at distinct angles (see Supporting Info, Figure A.8) that match the RHEED observations and form a discontinuous 3D film. On M2, a distinctly more continuous thin film of flat grains is formed. On some grains we find spiralling terraces (28 spirals/ $2\mu\text{m} \times 2\mu\text{m}$), a feature stemming from screw dislocations that has been linked to inversion symmetry breaking in other layered structures [22].

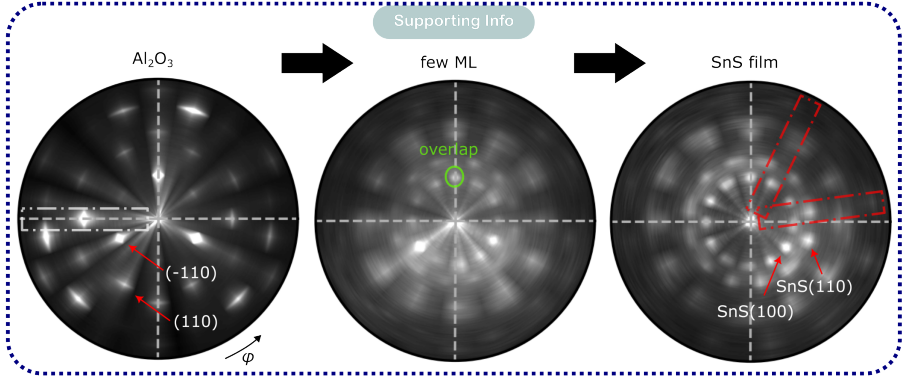


Figure 4.6: Polar RHEED scans of M2 showing in-situ the transition from substrate to film pattern. Grazing incidence RHEED polar figures are plotted by extracting line cuts for each frame during an azimuth rotation. Using this method to probe vertical planes allows to characterise the film texture in-situ. We observe a 12-fold symmetry corresponding to a 6-fold texture. By observing the transitional pattern at a few mono-layers (ML) we can estimate the epitaxial relation of the film with the substrate within resolution limited by the frame rate. In this case we get $\text{Al}_2\text{O}_3(1-10) \parallel \text{SnS}(100)$ at $360^\circ/40$ frames which agrees with the TEM data shown in the main text. Marked areas correspond to line profiles shown in main text.

For chemical and structural characterization we probed M2 by Raman, XRD and STEM. The results are displayed in **Figure 4.7**. We fit the Raman spectrum (raw data: solid blue line, fit: dotted black line in Figure 4.7 a)) with 10 Lorentzian peaks. Four of the most prominent modes at 95.4 cm^{-1} , 185.4 cm^{-1} ,

220.8 cm^{-1} and 156.4 cm^{-1} can be attributed to the $A_{g(1-3)}$ and a B_g mode, respectively [14]. The additional peak at 133.6 cm^{-1} (marked by *) can be attributed to an infra red active (but Raman forbidden) B_u mode hinting at centro-symmetry breaking. The Raman spectrum of M1 shows similar characteristics (see Supporting Info, Figure A.9) highlighting that their difference is predominantly structural and excluding significant amounts of further Sn-S phases. The observed Raman shift differences of M1 and M2 can be attributed to anisotropic strain differences between the samples (see Supplementary Info, Figure A.13 c) for more detail). The additional strain on M2 may be a result of increased interface area with the lattice mismatched substrate or lower grain thickness compared to M1. For further chemical characterization, Figure 4.7 f) shows EDS maps along with elemental profiles taken across the z direction. Oxidation is confined to a few nm at the surface after months of storage in ambient conditions and only a small amount of S replacement occurred during lamella extraction and transfer, confirming the excellent chemical stability of the film.

In Figure 4.7 b)-e) we study the structure in more detail by out-of-plane (OOP) XRD scans and cross sectional STEM. OOP ω - 2θ scans reveal SnS(004) and SnS(008) peaks in M1 and M2 showing the presence of basal plane-SnS in both samples. The intensity of the SnS(004) diffraction peak is about 25 times higher in the H_2S pretreated M2, confirming the significant increase in crystallographic order compared to the non-pretreated M1. In our ω -scan (rocking curve) at the SnS(004) angle (ω - $2\theta = 15.68^\circ$), we find an additional superposed peak with low full width half maximum (FWHM) of 0.15° showing a high degree of crystallographic order. This peak is associated with $c/4$ lattice spacing in the crystal, i.e. the vertical spacing of Sn atoms in basal plane SnS layers. Mapping out diffraction in a reciprocal space map (RSM), we find faint peaks at (p_1 at (ω -offset, 2θ) = (2.2° , 34.7°) and p_2 (1.5° , 45.5°)) on both M1 and M2 (see Supporting Info, Figure A.9), possibly due to minor amounts of non-basal plane SnS or SnS_2 . In Figure 4.7 c), we characterize off axis planes SnS(102) and SnS(111) by varying the polar angle χ . Fixing $2\theta = 25.4^\circ$ simultaneously probes SnS(012) and $\text{Al}_2\text{O}_3(012)$ (marked with *) showing the presence of a defined epitaxial relationship. We observe a small splitting of the SnS(111) diffraction peaks due to the multi-domain nature of the film in combination with the inequality between lattice parameters a and b . The $\Delta\phi_1$ of this splitting as well as $\Delta\phi_2$ between SnS(012) and SnS(111) provide a measure of the ratio a/b according to a simple geometrical consideration (see Supporting Info, Figure 4.8 for more detail).

We find $\Delta\phi_1 = 3.2(4)^\circ$ and $\Delta\phi_2 = 16.7(2)^\circ$ and thus $a/b = 0.942(6)$ and $0.946(6)$, respectively. Compared to common a/b ratios in literature this value is surprisingly high (Figure 4.7 d)). In fact, we obtain the best match for SnS at 700 K, close to the growth temperature used for M2 (650 K). Hence,

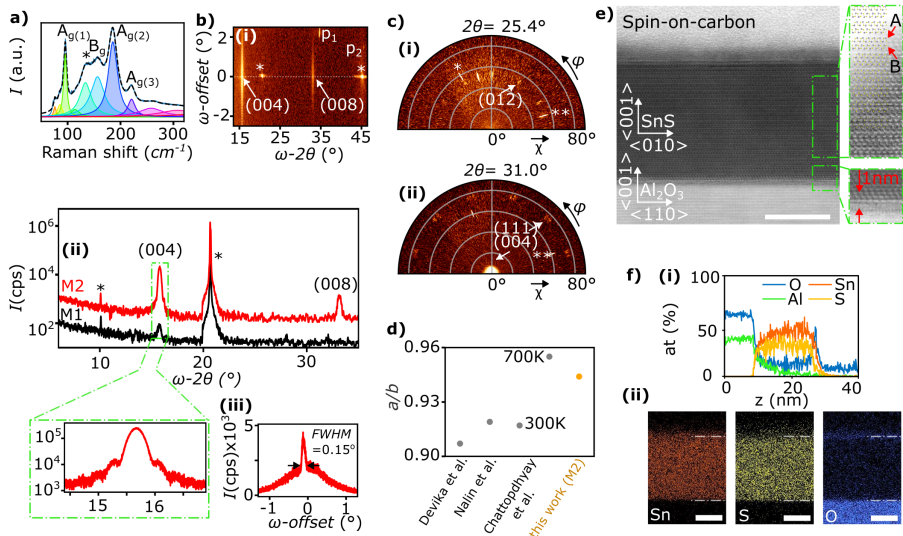


Figure 4.7: Structural characterization M2. a) Raman spectrum showing signature SnS peaks and an additional peak marked by * as discussed in the main text. b) (i) RSM of M2. The OOP scan (ii) and rocking curve (iii) correspond to cuts along the ω -offset = 0° and ω - $2\theta = 15.68^\circ$ lines, respectively. The plotted intensity of M2 in (ii) is offset by a factor of 100 for clarity and substrate peaks are marked by *. c) Pole figures probing (i) SnS(102) and (ii) SnS(111) planes. d) comparison of a/b ratio with literature[18, 23, 24]. a/b of this work matches best with a high T value. Signal from the substrate and Si carrier wafer are marked with * and **, respectively. e) Cross section ABF-STEM image displaying the dislocation free, sharp interface of the AB stacked film with the substrate. f) (i) Elemental percentage profile and (ii) corresponding EDS maps across the film showing a homogeneous elemental distribution of Sn, S and O. All scale bars in f) and e) are 10 nm.

we attribute the a/b ratio to a high temperature variant of SnS intermediate between Pnma and Cmc $\bar{m}$ formed at growth temperature and remaining stable during cool down.

Here, we study the epitaxial relation and strain in more detail. The annular bright-field (ABF)-STEM image in Figure 4.7 e) reveals an intimate contact between the AB stacked SnS film and the substrate featuring a dislocation-free, sub-nm interface with a defined epitaxial relation. Notably, this interface is virtually free of an amorphous buffer in contrast to previous SnS films grown

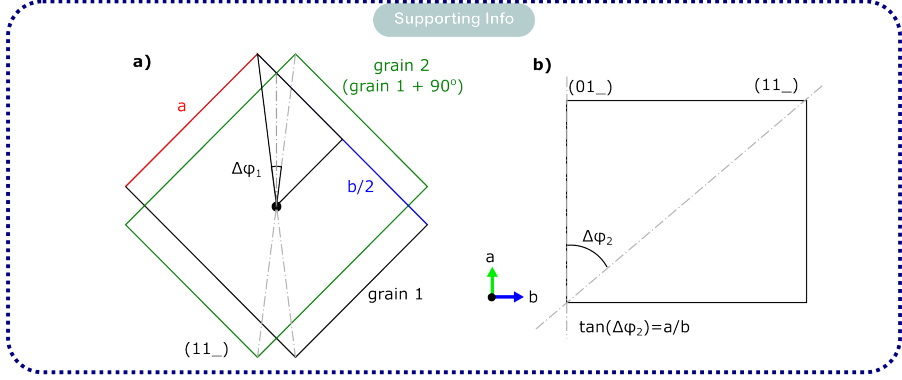


Figure 4.8: Geometry considerations relating XRD data to ratio a/b . a) $\Delta\phi_1$ between two perpendicular grains as measured in pole figures in the main text. c) $\Delta\phi_1$ is linked to a/b by $b/a = \tan(45^\circ + \Delta\phi_1/2)$. b) $\Delta\phi_2$ between SnS(012) and SnS(111) planes which is directly related to a/b . The third index of (hkl) is accounted for by inclination around the polar angle χ and can be ignored in these considerations.

on non-vdW substrates [18, 19]. We find $a = 4.045 \text{ \AA}$, $b = 4.300 \text{ \AA}$ and $c = 11.290 \text{ \AA}$ (see Supporting Info, Figure A.10), corresponding to a considerable mismatch of a and b relative to $2 \times d_{110}^{Al_2O_3} = 4.82 \text{ \AA}$ of the substrate by -19.1 % and -12.1 %, respectively.

To study the effect of strain on the materials properties we performed electrical testing on the as-grown films contacted in van der Pauw geometry using Indium spheres (see schematic in **Figure 4.9 a**). We find a sheet resistivity of $1.97 \text{ } \Omega\text{cm}$ at room temperature. This value is comparable but lower than $5.18 \text{ } \Omega\text{cm}$ measured parallel to layers in single crystal SnS[25].

Figure 4.9 a) shows the temperature dependence of the sheet conductivity σ of the basal plane SnS films. Using an Arrhenius model $\sigma(T) = \sigma_0 \exp(-E_a/k_B T)$, where k_B is the Boltzmann constant and where the activation energy is $E_a = E_g/2$ for intrinsic semiconductors, we can estimate a band gap of $E_g = 0.38 \text{ eV}$. This value is lower than 1 eV previously found for SnS films [26]. As discussed above (see Figure 4.5 d)), the present SnS film appears to be an epitaxially stabilized intermediate between its low temperature Pnma and high temperature Cmcm phase. Recent studies have found that the transition between these two phases corresponds to a significant and monotonous reduction of optical band gap as the crystal approaches the SnS Cmcm phase at high pressures[27]. This sizeable effect further begs the question whether the amount of stabilized structural distortion is sufficient to affect the centro-symmetry and polarization of

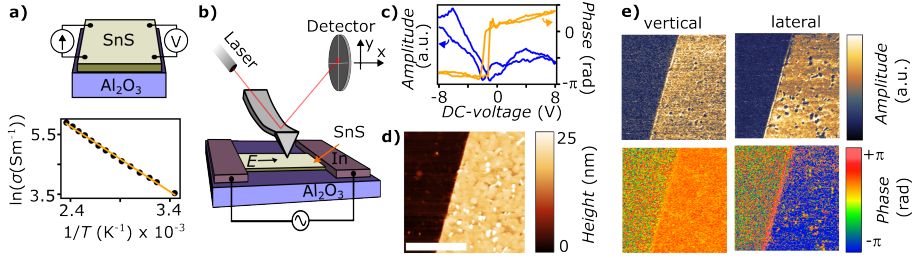


Figure 4.9: Sheet resistance and PFM in M2. a) σ as a function of $1/T$. A schematic of the used vdp geometry is shown above. b) Schematic of the in-plane PFM configuration. c) Sweep of the DC voltage offset applied to the In contacts and resulting vertical PFM amplitude and phase showing a small hysteresis. d) topographic map (scale bar is $2 \mu\text{m}$). e) PFM amplitude and phase of the vertical and lateral deflection mapped over the edge of the film.

the SnS crystal. Such an effect has been predicted for related chalcogenides[28]. An indication of such an effect in the present film has been found in Raman as mentined above (see Figure4.7 a)). Furthermore, centro-symmetry breaking is a necessary condition for the piezoelectric effect and can thus be measured by PFM. In conventional PFM, an electric field perpendicular to the film is applied between a back electrode and a conductive AFM tip (out-of-plane configuration) and the piezoelectric response is measured by the deflection of that same AFM tip. Here, to stimulate the in-plane polarization of SnS, we apply the electric field laterally (in-plane configuration in Figure 4.9 b)) using manually placed In contacts. This method comes with the added benefit of decoupling the AFM probe from the applied electric field and has previously been adopted to probe the piezoelectric response of MoS_2 [29].

In Figure 4.9 c), we show the PFM amplitude and phase signal recorded in the center of the film as a function of the DC voltage (added to an AC voltage used for lock-in demodulation, see Methods) applied to the device. We observe hysteric behavior in both, the amplitude and phase signal, and a maximum PFM response at -7 V . We then scan across the edge of the patterned film as shown in the topographic image in Figure 4.9 d) which enables a direct comparison with the non-piezoelectric substrate. In Figure 4.9 e) we show the resulting maps of the vertical and lateral PFM amplitude and phase recorded at -7 V DC bias. We find strong PFM signal on the entire SnS film and no signal beyond lockin noise on the substrate. Here, "vertical" and "lateral" refer to the y and x deflection recorded on the laser detector. We attribute the higher signal-to-noise ratio of the lateral image to the lower stiffness associ-

ated to the lateral movement of the probe. The average phase on the film is $56(20)^\circ$ and $-80(130)^\circ$ for the vertical and lateral measurement, respectively (standard deviation across full area is noted in brackets). This difference contains contributions from probing orthogonal directions of deformation as well as contributions from differing probe-surface interactions associated to the x and y deflection.

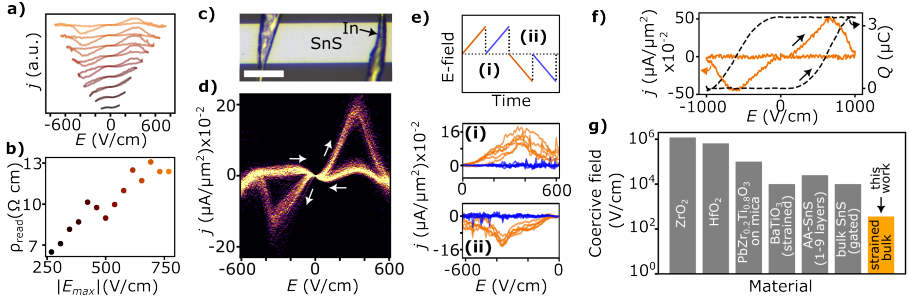


Figure 4.10: Memristive switching in thin film M2. a) IV curves recorded at incrementally increased applied electric field. b) Backtrace resistivity (measured at $E_{read}=270$ V/cm) in function of max field range in IV sweeps from a). c) Microscope image of the device. Scale bar is $50 \mu\text{m}$. d) Overlay of 100 traces showing highly reproducible behaviour and switching fields of 360 V/cm. e) Repeated DWM by applying voltage according to the schematic on top (schematic shows one DWM cycle). The primary (orange) is clearly distinct from the secondary (blue) sweep by a high conductance peak. f) Simultaneous measurement of current and charge. The arrows indicate the direction of the voltage bias sweep. g) Comparison of switching fields of various material systems.

These results prove local non-centrosymmetry and open up the potential for the appearance of polarization and memristive behaviour in M2[12]. **Figure 4.10** shows transport data recorded on the same device as in Figure 4.9 a)-d). We observed a sizeable impact of microscope illumination in favour of both, overall conductance and the switching behaviour in M2 (see Supporting Info, Figure 4.11). All transport measurements presented in Figure 4.10 have been recorded under that same illumination. In Figure 4.10 a) we show the current density of the SnS device as a function of increasing electric field range E_{max} . A linear background was fitted to the highest range sweeps and subtracted from the raw data for clarity (see Supporting Information, Figure 4.11 for more details). We observe loops opening up as E_{max} is incrementally increased up to 770 V/cm. We observe partial loops varying continuously as a function of the applied field range. The overall resistance ρ also varies continuously with E_{max} .

until saturation is reached at $E_{max} = 600$ V/cm.

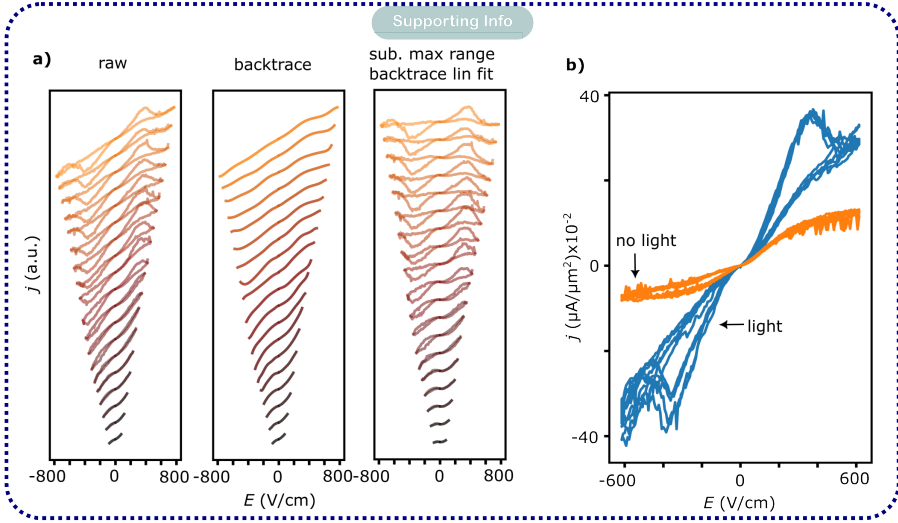


Figure 4.11: Background subtraction for IV curves recorded on the 2 terminal device shown in the main text. a) Exemplarily shows the processing steps applied to the transport data. We extract a linear background from the back-trace of curves recorded in the saturated switching regime, i.e. with a measurement range of 10V/130 μm . This linear background is subsequently extracted from curves of all ranges. The sample was exposed to the light of the microscope for all curves. b) We found a significant dependence of switching amplitude and overall current on light exposure. Here, we compare two loops with the microscope light turned on and off.

We quantified the variation of ρ in Figure 4.10 a) by extracting current values from IV back traces at a fixed reading voltage E_{read} , a process akin to memristor writing and reading cycles. Figure 4.10 b) shows the variation of this reading resistivity ρ_{read} in function of the IV sweep range E_{max} (i.e. writing fields). ρ_{read} is smallest at the minimum writing field, $\rho_{read,min} = 6.5 \Omega\text{cm}$ at $E_{max} = 270$ V/cm, and reaches up to $\rho_{read,max} = 12.4 \Omega\text{cm}$ at $E_{max} = 770$ V/cm, a programmable variation of 91 %. Values for ρ_{read} include the linear background that has been subtracted in Figure 4.10 a). In Figure 4.10 d) we recorded 100 consecutive traces within the saturated range ($E_{max} > 600$ V/cm) and consistently reproduce the same current peak amplitude and field corresponding to a switching field of 360 V/cm. Following the measurement scheme in Figure 4.10 e) we conducted repeated double wave measurements (DWM)

[30]. This method probes non-volatile contributions by subtracting (possibly non-linear) dielectric contributions measured by a follow up secondary sweep. Accordingly, in Figure 4.10 e)(i-ii) we plot both, primary and secondary sweeps for both polarities, where a polynomial fit to the secondary waves (i.e. dielectric background) have been subtracted. The primary sweep (orange) is clearly distinguished from the secondary sweep (blue) by a pronounced current peak for both electric field polarities. The amplitude in the DWM is consistent with the amplitude observed in Figure 4.10 d) showing the non-volatility of the memristive state[15, 30]. In Figure 4.10 f), we show a simultaneous measurement of current and accumulated charge Q (conductive background contributions have been subtracted, see Supporting Info Figure A.11). The hysteresis is a result of the conductance switching during the voltage sweep.

4.2.3 Discussion

Growth facilitated strain engineering of vdW thin films poses the challenge of manipulating epitaxial stress while maintaining crystal order. The desired stress can be induced by reactive conditions, such as the choice of a reactive substrate or the involvement of reactive gases, but these may also result in disordered films. Especially for vdW materials, growth mechanisms are favoured at the edges of layers which can lead to standing grain type growth on reactive substrates[17]. Our results on M1 confirm this trend for SnS. However, we demonstrate that this hurdle can be overcome with the pre-treatment on M2 and the resulting strained film has a defined epitaxial relation and a sharp interface with the substrate. The exact mechanism of the pre-treatment remains open for further investigation. We compared AFM images of a pristine and pre-treated α -Al₂O₃(001) substrate (see Supplementary Info, Figure A.12) which shows the appearance of smooth but amorphous features on the substrate surface. This could be due to the formation of Al-S phases at high temperatures[31]. We found that even sub-nm resolution characterization by STEM was unable to identify such phases, perhaps due to re-oxidization of Al, making the characterization of such a mechanism highly challenging. The red shift for $A_{g(2)}$ and B_g in our Raman spectrum has previously been linked to increased lattice parameters a and c and decreased b which matches our observations in XRD and STEM in M2[32]. Based on lattice constants reported in literature[23, 24] ($a = 3.98 \text{ \AA}$, $b = 4.33 \text{ \AA}$ and $c = 11.20 \text{ \AA}$) and our STEM measurements ($a = 4.045 \text{ \AA}$, $b = 4.300 \text{ \AA}$ and $c = 11.290 \text{ \AA}$), we obtain tensile strain of 1.6% and 0.8% for a and c , respectively, and compressive strain of 0.7% for b . A high temperature SnS structure appears to have formed during the high temperature growth and been supported by the substrate during cool down to room temperature, explaining the present a/b ratio. This hypothesis is further supported by a/b ratios found from XRD pole figures, the observation of

a reduced band gap[27], our findings of a mismatched but sharp film-substrate interface, the strong inter-layer coupling unique to SnS and previous observations of strain stabilization in SnS on Sn-buffered MgO [33]. Comparable deformations of the lattice are associated to the difference between AB- and AA stacked SnS in previous studies (0.3%, 0.3% and 1.3% for a , b and c , respectively)[23], where the largest strain lies in the c direction as opposed to the a direction in the present study. Interestingly, we found that anisotropic strain in a direction can be maintained over >15 nm, the critical thickness found for the c direction. This likewise appears to lead to centro-symmetry breaking and memristive behavior.

We found a switching field of 360 V/cm, orders of magnitude below the previously reported 25 kV/cm in up to 9 layer, AA-stacked SnS, 10.7 kV/cm for bulk SnS with gate induced non-centrosymmetry[15, 16] and reported values of coercive fields in ferroelectric materials (see Fig.4.10g))[34, 35, 36].

In parts this can be attributed to the larger thickness d which scales down the switching field by $E_c \propto d^{-2/3}$ according to the Janovec-Kay Dunn model and by lowering the depolarization field and contributions from non-switchable interfaces which become most pronounced in the few nm regime[36, 34]. Strain can have the additional effect of lowering E_c which has previously lead to low-voltage-switching in BaTiO₃ and can tune ferroelectric behaviour in TMDs[37, 12]. Furthermore, our findings attribute a key role to the exposure to light (see Supplementary Info, Figure 4.11) which might drive phase instability and mobility of ferroelectric domains. Another clue is given by the observation of a lack of macroscopic ferroelectric domains within the resolution in our PFM maps (Figure 4.9). The formation of nano-domains due to the strain in the present SnS thin film is consistent with the significantly decreased switching fields observed in this study. This effect is analogous to lower coercive fields in disordered ferromagnets and has recently been discussed for ferroelectrics[38]. We show that under these conditions the conductivity of the SnS film is both programmable by applied electric field and stable once the field is removed. The link between partial ferroelectric switching and bulk conductivity in the strained SnS system may be caused by the interaction between polarization and Schottky barriers, band structure, defects or counter-polarized domains and would be an interesting aspect in further studies.

As previously demonstrated for polycrystalline SnS films [39], E-field induced partial resistance switching of SnS as shown in Figure 4.10 a) and b) offers a way for neuromorphic programming in synaptic devices. Furthermore, due to the particularly low switching field, SnS has high potential in low energy cost applications. Finally, due to the photosensitivity of SnS, light exposure could provide an additional tuning parameter for the development of remote, optically controlled switching applications[40].

4.2.4 Conclusion

In summary, we explored a physical/chemical hybrid synthesis method for growing epitaxial SnS under high stress conditions. We identified H₂S plasma pre-treatment as an effective and crucial step for the basal plane growth on the lattice mismatched α -Al₂O₃ substrate demonstrating its key role for epitaxial strain induced tuning of the SnS structure. The resulting strained thin film shows multiple signs of centro-symmetry breaking together with reproducible and programmable resistance switching at an ultra-low switching field of 360 V/cm under illumination, making it a readily applicable quasi vdW polarizable material with great potential for scalable and energy-efficient memristor applications.

4.2.5 Experimental Section

Film Growth

Growth strategies with different pre-treatment have been adopted for M1 and M2. The pre-treatment of M1 involved outgassing at 400 °C for 10 min. The pre-treatment of M2 involved 10 min of exposure to H₂S plasma (radio frequency power of 600 W) at elevated substrate temperature (T set point of 750 °C) which resulted in a chamber pressure of 10^{-5} Torr. We find that the film's growth mode sensitively depends on T during this step, where executing the pre-treatment with a substrate temperature of $T = 600$ °C reduces the basal plane growth of the grains significantly (see sample M4 in Supporting Info, Figure A.6). After their respective pre-treatments, both samples were left to cool to growth temperature (370 °C for M1 and 350 °C for M2). Both films were grown on commercial 2" c-plane α -Al₂O₃ wafers by simultaneous exposure to 100 W H₂S plasma and Sn vapor from an effusion cell kept at 1130 °C. The base pressure of the growth chamber was 10^{-9} Torr. Chemical uniformity of M2 was confirmed by comparing Raman and X-ray photoelectron spectroscopy (XPS) spectra in the central region and edge region of the wafer (see Figure A.13).

Device Fabrication

The device for transport and PFM was prepared by standard optical lithography including a Ar plasma dry etch step for removing the SnS film. The needle contacts were manually placed using In melt.

Structural Characterization and Transport

RHEED electrons with 15 kV acceleration voltage were directed at the sample surface at an incident angle of $2-3^\circ$. AFM images were recorded with a Dimension Edge tool (Bruker) operated in tapping mode. Raman spectra were recorded with LabRAM HR system (Horiba Scientific), a excitation wavelength of 633nm and a 600 grating. XRD scans were performed with XRD diffractometer X'pert (Malvern Panalytical) operated at 45 kV/40 mA acceleration/filament current. Calibration was done on the $\text{Al}_2\text{O}_3(006)$ peak of the substrate. Incident X-rays had $\text{Cu-K}\alpha$ energy of 8 keV and spectra were recorded with a PIXcel as point detector. TEM samples were prepared by covering the sample with Spin-on-Carbon by drop casting followed by Pt deposition (5 kV, then 30 kV) and side thinning lift out (Helios, TFS). TEM, STEM and EDS maps were recorded using a Thermo Fisher G2 60-300 Titan³ operated at 200 kV. PFM signal was recorded by lockin technique using HF2LI (Zurich Instruments). We applied a modulated voltage ($-7 \text{ V DC} + 6 \text{ V AC}$) in an in-plane configuration, fully polarizing the film. Joule heating can be estimated as $P = V^2/R$, with $R = 1.97 \text{ } \Omega\text{cm} \times 130 \text{ } \mu\text{m}/(50 \text{ } \mu\text{m} \times 18 \text{ nm}) = 36 \text{ } \mu\text{W}$. To estimate the resulting temperature rise within the film we consider dominant heat conduction through the substrate across the contact area $A_{int} = 50 \text{ } \mu\text{m} \times 130 \mu\text{m}$. Assuming typical thermal boundary conductivities at the film-substrate interface ($G_{int} = 10 - 100 \text{ MWcm}^{-2}\text{K}^{-1}$) we obtain $\Delta T \approx P/(G_{int}A_{int}) = 0.055 - 0.55 \text{ K}$. Vertical and lateral deformations were measured using the lock-in technique on the x and y deflection of an electrically floating AFM probe operated in contact mode. The driving frequency was 1 kHz which is off resonance for the used probe. Transport measurements were performed with an externally controlled Keithley 2450 sourcemeter and a Keithley 6514 electrometer. Voltages V and currents I were converted to electric field E and current density j using the dimensions of the device $l \times w \times t = 130 \text{ } \mu\text{m} \times 50 \text{ } \mu\text{m} \times 18 \text{ nm}$ and $E=V/l$, $j=I/A$, $A=w \times t$. This should slightly overestimate the field acting on the SnS film due to the voltage drop at the contact interfaces.

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4.3 SnS as Thermal Insulator: "Ultra-Low Thermal Conductivity in Nanoscale, Epitaxial SnS Grains"

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Abstract

Thermally insulating nanoscale building blocks enable efficient routes to both passive and active heat management in miniaturized architectures. However, identifying suitable nano materials by computational and experimental means is difficult as critical dimensions reach the scale of thermal carriers and thermal interfaces become dominant. In this work, we propose epitaxially grown layered SnS as an outstanding thermal insulator at the thin film limit. The challenge of measuring heat transport at the nanoscale was tackled by locally probing out-of-plane thermal transport on grains of varying thickness utilizing scanning thermal microscopy. We consistently find an ultra-low thermal conductivity value of $45 \text{ mWm}^{-1}\text{K}^{-1}$ which is among the lowest reported for dense solids to date. This finding challenges previous predictions of the SnS system and opens up promising prospects for its integration into heat management components.

4.3.1 Introduction

The ongoing increase in computational density and energy consumption is accompanied by an increasing demand for efficient heat management at the nanoscale either by passive routes such as thermal insulation/channelling and waste heat recycling or by active routes such as thermoelectric cooling. Passive

approaches critically depend on the availability of materials with low thermal conductivity k . Also active approaches benefit from low k as the thermoelectric figure of merit $zT = \sigma TS^2/k$ (where T is temperature, σ is the electrical conductivity and S is the Seebeck coefficient) inversely scales with k , making decreasing k a cornerstone for both passive and active thermal management technologies.

Tin mono sulfide (SnS) has attracted interest in the fields of ferroelectrics, photoabsorbers and thermoelectrics. [1, 2, 3, 4]. SnS grows in an orthorhombic crystal structure analogous to phosphorene, featuring a combination of high S (400-700 $\mu\text{V/K}$), moderate electrical conductivity (0.1-1 S/m, depending on structure and doping), a low k (0.45-0.7 $\text{Wm}^{-1}\text{K}^{-1}$ at room temperature) and a high degree of anisotropy with out-of-plane (OOP) stacked quasi van der Waals (vdW) layers and two anisotropic in-plane directions (see Fig.4.12 a))[5, 6, 2, 7, 8]. As a consequence of this anisotropy, thermal conductivity k is expected to differ significantly along the diverse crystallographic directions in SnS and especially between the in-plane and OOP directions[9].

Nevertheless, as with other anisotropic materials, SnS is often characterized globally as accessing the transport along different crystal axes is complicated, especially at the nanoscale. In this regime, critical dimensions reach the scale of the mean-free-path of thermal carriers (electrons and phonons) and thermal interfaces become dominant[10]. Additionally, approaching the nanoscale raises challenges in (at relevant scale) uniform material synthesis and ambient stability. Hence, overcoming these challenges in thermal characterization of nanoscale, anisotropic systems requires ideally local, non-invasive and consistent methods.

The Scanning Thermal Microscopy (SThM) method meets the demands for non-invasive nanoscale characterization, offering high spatial resolution and thermal sensitivity but suffering somewhat from a set of tip-sample interactions which complicate quantitative interpretations. The feasibility of SThM for characterizing thermal transport in 2D materials and the closely related SnSe system has previously been reported[11, 12, 13, 14]. On SnS, however, such studies have been absent in the literature.

In this work, we demonstrate nanoscale characterization of thermal transport in ultra-thin, highly crystalline SnS grains epitaxially grown on c-plane $\alpha\text{-Al}_2\text{O}_3$. We use SThM to locally measure the thermal resistance of crystallographically aligned SnS grains, revealing an ultra low effective thermal conductivity, one order of magnitude lower than in bulk SnS. We attribute this finding to strain induced inter-planar disorder of AB stacked SnS layers which can suppress thermal transport as previously reported in other vdW materials[15, 16]. Our findings are consolidated by using multiple calibration method approaches for the thermal probes, ensuring statistically significant results. With its ultra-low thermal conductivity, SnS shows great potential for heat

management applications, paving the way for boosted efficiency by integrating thin SnS films into thermal devices.

4.3.2 Results

SnS thin films were grown on commercial 2" c-plane α -Al₂O₃ wafers by plasma-assisted molecular beam epitaxy. The base pressure of the growth chamber was 10^{-9} Torr. The as-delivered wafer was pretreated by heating from the back of the substrate up to a T set point of 750 °C and exposure to H₂S plasma from a radio frequency (RF) source with a power of 600 W and resulting in a temporary chamber pressure of 10^{-5} Torr. After 10 minutes pre-treatment, the sample was left to cool to growth temperature (set point 350 °C). The film was grown by simultaneous exposure to 100 W RF H₂S plasma and Sn vapor from an effusion cell kept at 1130 °C. For the reference sample, 300 nm of SiO₂ were thermally grown on bulk Si. The variation of SiO₂ thickness was achieved through an inclined cut by a focused ion beam.

To determine the crystal structure of the SnS thin film, we performed high-angle annular dark field scanning transmission microscopy (HAADF-STEM) and X-ray diffraction (XRD). A good match between the characteristic stacking of the SnS layers (a-face) with the HAADF-STEM image of a 18 nm thick grain is shown in Fig.4.12 b). The XRD spectrum in Fig.4.12 c) shows exclusively two peaks matching to OOP directions SnS(004) and SnS(008) which confirms the global alignment of SnS grains. We observe small deviations from theoretical 2θ values, which we attribute to crystallographic strain. An additional confirmation of the SnS phase is provided by the Raman spectrum shown in Fig.4.12 d)(i). Five of the most prominent modes at 95.0 cm⁻¹, 187.4 cm⁻¹, 220.0 cm⁻¹, 158.7 cm⁻¹ and 135.1 cm⁻¹ can be attributed to the $A_{g(1-3)}$ and a double set of B_g modes, respectively [17]. Next, we consider the edge of the as-grown SnS thin film, where average grain thickness is gradually decreased and the amount of exposed substrate gradually increases. Fig.4.12 d)(ii) shows Raman spectra recorded along a 40 μ m long line across this transitional area (marked green in the optical image).

We find a transition between saturated signal at $x=0$ μ m to completely vanished signal at $x=40$ μ m. Notably, the major Raman peaks from Fig.4.12 d)(i) decrease equally across the full 40 μ m until vanishing (see Supporting Info, Fig. 4.13) and without the appearance of any further Raman peaks. Hence, we conclude that the SnS phase remains pure across the edge transition.

To characterize the thermal conductivity, we recorded SThM data within the transitional area of the SnS film edge, making use of the gradual variation

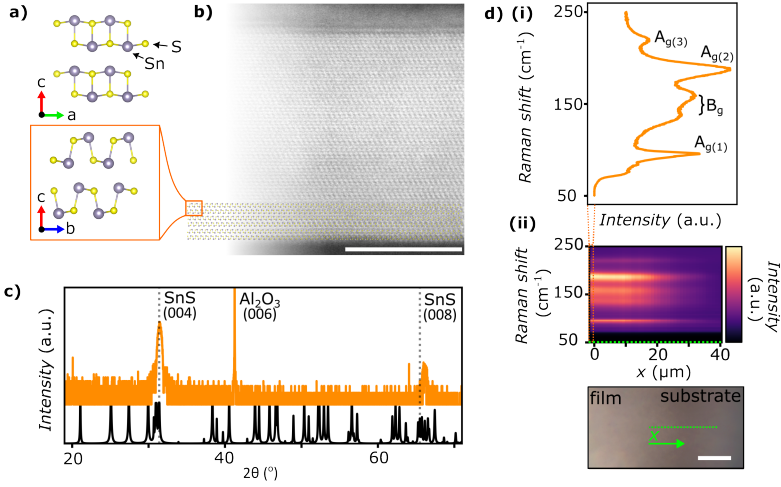


Figure 4.12: a) b-face and a-face of SnS. b) Overlay of a-face SnS model with HAADF-STEM image of a SnS grain. Scale bar is 10 nm. c) Out-of-plane XRD scan of SnS thin film (orange) and theoretical XRD spectrum (black, computed using VESTA software). d) (i) Raman spectrum on the SnS thin film and (ii) across the transition at the edge of the film. The substrate is Raman silent in the displayed range (first peak at 417 cm^{-1}). The scale bar in the image is $20 \mu\text{m}$.

of material thickness. Fig.4.14 a) shows a topographic map of the SnS films edge region (see also Fig.4.14 b)), transitioning from an almost continuous coverage with roughly 20 nm high SnS grains on the left to a region with sparse coverage with only few nm high, dendritic SnS shreds and a high amount of substrate exposure. Subsections of this map contain a varying distribution of grain thickness while the lateral scale of the grains remains similar. In Fig.4.14 c), we show a schematic of the thermal transport measurement which allows simultaneous recording of topography and thermal voltage U_{SThM} . U_{SThM} is a measure of the cool-down of the heated probe caused by varying thermal conductance through the tip-sample interface which depends on both, interface and material properties. Maps of topography and U_{SThM} are shown in Fig.4.14 d). The topographic and thermal voltage maps were recorded using a Bruker Icon Dimension scanning probe platform with a commercially available SThM probe (KNT-SThM-2an, Kelvin Nanotechnology) under an ambient environment. The thermal voltage signal was amplified and read out by the lock-in technique (operated at 91 kHz) coupled to a Wheatstone bridge as reported elsewhere[18, 12]. Due to the thermalization time of the probe ($\approx 1 \text{ ms}$),

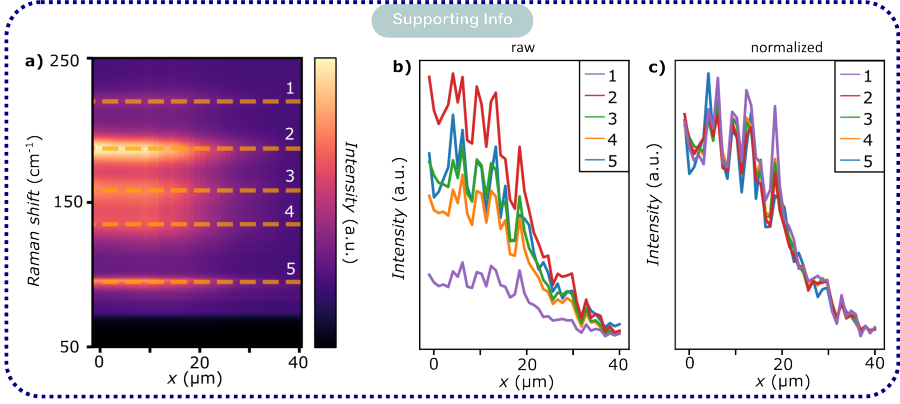


Figure 4.13: Further Raman analysis. a) Shows Raman spectra mapped across the edge of the SnS film. Major peak positions are marked and labeled 1-5. b) Peak intensities along lines marked in a). c) Normalized peak intensities showing equal behavior of all major peaks.

the heating remains effectively constant at this frequency, depending only on the DC part of the applied current. The thermal response (i.e. $R_{el}(T)$, where R_{el} is the electrical probe resistance and T is temperature) was calibrated prior to measurements as explained elsewhere[12].

To obtain the thermal resistance R_{th} from U_{SThM} , we calibrated the probe by recording point traces (Fig.4.14 e)) on the α -Al₂O₃ substrate (thermal conductivity of α -Al₂O₃[19]: $k_{Al_2O_3}=35 \text{ Wm}^{-1}\text{K}^{-1}$). In such a point trace, the change in U_{SThM} is measured while the distance between probe and surface is gradually decreased beyond contact. Using this calibration effectively compares the recorded U_{SThM} signal to ΔU_{SThM} from when the tip is in full thermal contact with the substrate and when the tip is thermally out of contact. This ΔU_{SThM} depends on the specifics of the probe and the thermal conductivity of the substrate (see also Supporting Info, Fig. A.14). The thermal resistance R_{th} measured by the SThM method comprises several components in series[18, 13]: the tip thermal resistance R_{tip} , the tip-sample interface resistance R_{int} and the heat spreading resistance R_S . For a given material, R_{tip} and R_{int} can be considered constant, leaving only R_S to vary with sample thickness h . Fig.4.14 f) shows a histogram representation of all values computed from the images in Fig.4.14 d). Here, constant contributions have been subtracted in $\Delta R_{th} = R_S(h) - R_{S,0}$, where $R_{S,0}$ is the thermal resistance measured at $h = 0 \text{ nm}$. Thus, the variation in ΔR_{th} in Fig.4.14 f) arises only from the thickness variation of the SnS grains. We fit $\Delta R_{th}(h)$ with $R_S(h)$ (green line

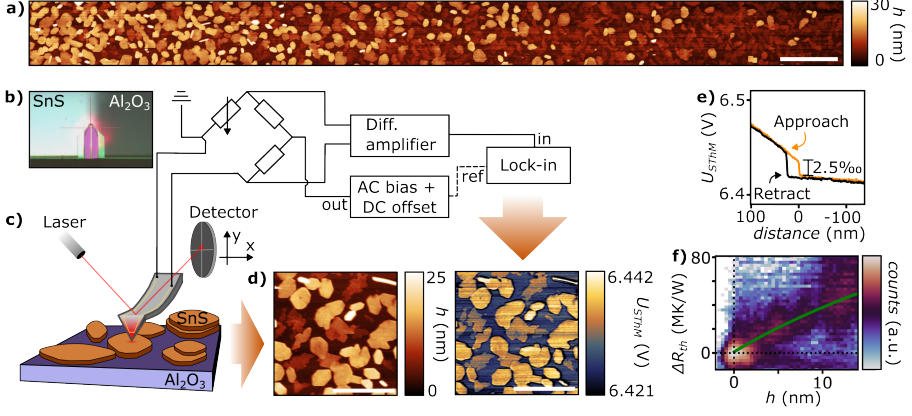


Figure 4.14: SThM across the edge of a SnS thin film on α -Al₂O₃. a) Topographic map of the transition from continuous SnS film to isolated SnS grains. Scale bar is 2 μ m. b) Optical image of the SThM probe scanning the edge of the SnS film. c) Schematic of SThM measurement as detailed in the main text. d) Topographic and SThM signal U_{STHM} map of SnS grains in an area with balanced thickness h distribution. Scale bars are 1 μ m. e) Approach curve taken on the α -Al₂O₃ substrate. The distance on the x-axis is defined as the tip-substrate separation. f) Histogram of ΔR_{th} VS grain thickness h of SnS. Data outside dotted lines are due to a small variation of measured substrate signal (at $h < 0$ nm) and artifacts from short loss of thermal contact (visible as shadow in U_{STHM} map in d) leading to data at $\Delta R_{\text{th}} < 0$ MK/W) and have been excluded from the fit (green line).

in Fig.4.14 f)) using a model developed in previous works[20, 18];

$$R_S(h) = \frac{1}{\pi k_1 a_{\text{eff}}} \int_0^\infty \left[\frac{1 + K \exp\left(-\frac{2\xi h_{\text{eff}}}{a_{\text{eff}}}\right)}{1 - K \exp\left(-\frac{2\xi h_{\text{eff}}}{a_{\text{eff}}}\right)} \right] J_1(\xi) \sin(\xi) \frac{d\xi}{\xi^2} \quad (4.1)$$

, where a_{eff} is the radius of the effective thermal contact area, $h_{\text{eff}} = h + r_{\text{int}} \times k_1$ is an effective thickness including the layer-substrate interfacial resistance (r_{int}) and effective thermal conductivity of the material layer (k_1), J_1 is the first-order Bessel function of the first kind and the K parameter is defined as

$$K = \frac{1 - \frac{k_s}{k_1}}{1 + \frac{k_s}{k_1}} \quad (4.2)$$

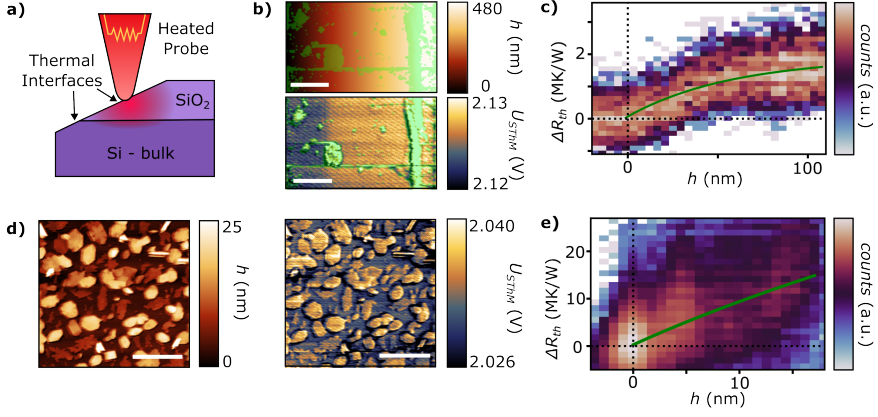


Figure 4.15: SThM dataset B including a SiO_2/Si reference. a) Schematic of reference measurement. b) Topographic and U_{STHM} maps of the SiO_2/Si reference. Contamination on the sample surface are marked in green and excluded from analysis. c) Histogram of ΔR_{th} VS grain thickness h of SiO_2/Si . Dotted lines indicate the data thresholds for the fit. d) Topography and U_{STHM} maps of SnS grains. e) Histogram of ΔR_{th} VS grain thickness h of SnS. As before, dotted lines indicate the thresholds of data inclusion for the fit (green line). All scale bars in the maps are $1 \mu\text{m}$.

where k_S is the thermal conductivity of the substrate. We obtain ultra-low values of order $k_1 \approx 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ for the thin SnS grains (more details below, see Fig.4.16 a)). Here, the effective contact area has been approximated based on line traces in the topographic map (see Supporting Info, Fig. A.15 and A.16).

To substantiate our finding of ultra-low thermal conductivity further, we performed a complementary approach (dataset B) for the approximation of the effective tip radius. In Fig.4.15, we present dataset B recorded using another SThM probe and a SiO_2/Si reference sample. Fig.4.15 a) shows a schematic of the reference measurement; thermal resistance variation is achieved through thickness variation by an inclined cut through a 300 nm SiO_2 layer as reported elsewhere[18]. Fig.4.15 b) shows topographic and U_{STHM} maps recorded on the reference sample represented by a ΔR_{th} vs thickness h histogram in Fig.4.15 c). Using the known thermal conductivity of SiO_2 , $k_{\text{SiO}_2} = 1.3 - 1.4 \text{ W m}^{-1} \text{ K}^{-1}$, we fit R_S and extract $a_{\text{eff}} = 74.1 - 88.5 \text{ nm}$. In analogy to Fig.4.14 d) and f), Fig.4.15 d) and e) show topographic and U_{STHM} maps of an area semi-populated by SnS grains of various heights and a histogram of ΔR_{th} VS SnS thickness

tainty about the exact SiO_2 thermal conductivity, and the possible formation of a water meniscus between tip and thin film, which can contribute an estimated 6% to the flow of heat[23]. Dataset A and B are consistent within error estimates. At the same time, these findings highlight the need and challenge to accurately estimate a_{eff} . We find that the use of a calibration sample (dataset B) is providing a significantly improved accuracy compared to the common method of estimating a_{eff} by topographic line-traces (dataset A), which is particularly prone to variation of topographic line traces and edge-sharpness related overestimates of the effective thermal contact radius (see Supporting Info, Fig. A.16). Further sources of error that may lead to an underestimate in our analysis such as the effect of lateral thermal penetration depth and additional thermal interfaces due to grain overlap have been excluded in our analysis (see Supporting Info, Fig. 4.17 for more detail).

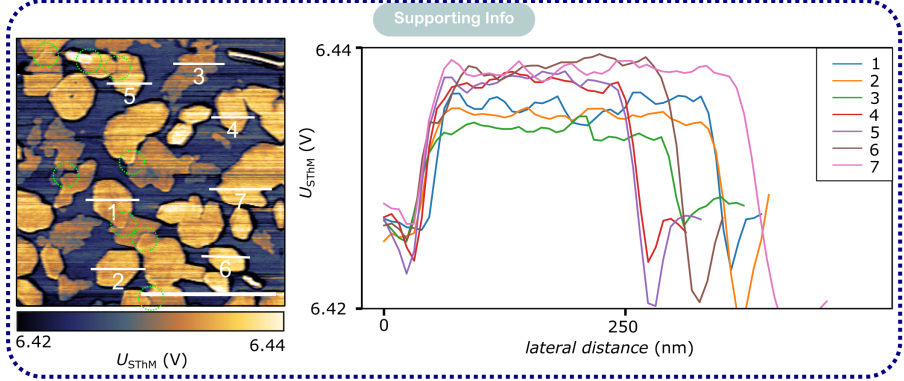


Figure 4.17: Closer inspection of individual grains on the U_{STHM} map from Fig.4.14 d) for assessing artificial contributions to k_{SnS} . Line profiles are flat along lateral dimension of 7 assessed grains. We find no significant difference between central and edge regions of SnS grains. Additionally, interfaces formed between overlapping SnS grains may locally decrease U_{STHM} decreasing the value of k_{SnS} . However, we find no significant impact of this effect in such regions (highlighted by green dotted circles). Scale bar is 1 μm .

Concerning the ultra-low value of thermal conductivity, three key factors contributing to low thermal conductivity in SnS have been identified in previous studies: low intrinsic thermal conductivity (low phonon velocity, high phonon scattering probability), SnS phase ($k_{\text{cubic}} < k_{\text{orthorhombic}}$) and transport direction (c-axis is the hard axis, i.e. has lowest thermal conductivity)[24, 25, 26]. Indeed, vdW materials naturally host the potential for large thermal anisotropy[16, 25]. We note that our measurement geometry applies a temper-

ature gradient along the OOP axis (i.e., c-axis) and the film thickness is small compared to the thermal contact radius (i.e. $h / a_{\text{eff}} \ll 1$). Thus, the measured thermal resistance predominately reflects the OOP thermal transport in the grains. This assessment is further supported by finite element modelling (see Supporting Info, Fig. A.17). Nevertheless, a thermal conductivity as low as in the present study occurs rarely in dense solids. Ultra-low cross-plane thermal conductivities, especially compared to their bulk counterparts, have been measured by time-domain thermoreflectance on WSe_2 , WS_2 and MoS_2 thin films with interlayer disorder [15, 16]. In analogy to the materials in these studies, the observed strain in our SnS film (Fig.4.12 c)) likely promotes the ultra-low thermal conductivity in multiple ways: by altering phonon transport intrinsically as previously reported in other thin film materials [27, 28] and with dopant induced strain in SnS [29], and by inducing inter-planar stacking variation leading to impeded inter-layer phonon transport.

The potential of simultaneously tuning electrical conductivity and, via the hypothetical link with strain, the thermal conductivity by doping, points out the significant prospects for the design of thermoelectrics and thermal rectifiers or resonators based on thin film SnS. At present, the already ultra-low thermal conductivity observed in this study makes this material a high potential ingredient in components for multiple applications such as photo absorber layers, thermal insulators and active thermoelectric materials, all of which benefit from the spatial retention of heat flows.

4.3.4 Conclusion

In summary, we measured the out-of-plane thermal conductivity of SnS by a local probing method that utilizes thickness variation of grains at a film transition area. We report two datasets, each with a different approach for determining the effective thermal contact area between the SThM probe and the material, a parameter that crucially impacts the modelling of the thin film thermal conductivity. The two approaches vary in accuracy but consistently yield an ultra-low thermal conductivity value $k_{\text{SnS}} = 45 \pm 7 \text{ mWm}^{-1}\text{K}^{-1}$ which is among the lowest reported for dense solids to date. This finding highlights the exceptional potential of SnS based building blocks for heat management and outlines the progression of nanoscale thermal insulation based on vdW layered materials.

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4.4 Additional Fingerprinting of CoS₂: ”Synthesis and Fingerprint of a Fully Coalescent, High Quality Epitaxial Co₉S₈-CoS₂ Thin Film”

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Abstract

Cobalt sulfide (Co-S) phases are of significant interest for energy conversion and sensing technologies due to their combined catalytic activity and electronic conductivity. In particular, Co₉S₈ is a promising pre-catalyst for oxygen evolution reaction, but its synthesis as high-quality thin films has been scarcely reported. Here, we demonstrate the synthesis of highly crystalline, coalescent, mixed-phase Co-S thin films using plasma-assisted molecular beam epitaxy (PA-MBE). The epitaxial film exhibits substantially improved crystallinity of Co₉S₈ compared to conventional deposition techniques and reveals the formation of epitaxial, non-magnetic, tetragonal CoS₂, which has not been previously observed in its non-magnetic form. Thus, this work provides crucial diagnostic tools supporting the fabrication of phase-pure, single-crystal Co-S thin films and, with the discovery of the non-magnetic CoS₂ phase, a new platform for investigating Co-S catalysts in energy and sensing applications.

4.4.1 Introduction

The Co-S binary system combines the high catalytic activity of elemental Co with contributions from elemental S favourable for electronic conduction. Ac-

cordingly, various Cobalt sulfide phases (e.g. CoS, CoS₂, Co₃S₄ and Co₉S₈) have been regarded as promising catalysts in the context of Pt-free dye sensitized solar cells[1, 2], supercapacitors[3], H₂S/NO_x/H₂ gas sensors[4, 5, 6] and filters for pollution control[7]. Specifically, Co₉S₈ has shown high stability and performance in hydrogen-/oxygen evolution reaction (HER/OER). Here it acts as a pre-catalyst in OER while its role remains under debate in HER [8, 9, 10].

Despite the potential of Co₉S₈ and, in particular (111) plane Co₉S₈ due to it's optimal OER capability, few studies have thus far reported on its synthesis[5, 11, 12] and thin uniform films[9, 8]. Thus, in prospect of the full realization of Co₉S₈'s potential, achieving a controlled, scalable and cost effective synthesis route and identification protocol for high quality epitaxial thin film Co₉S₈(111) crystals remains in demand.

In this work, we present an epitaxial Co₉S₈(111)-CoS₂ thin film (hereafter referred to as Co-S film) on α -Al₂O₃(0001), achieved by PAMBE (see Fig.4.19a)). This method shows improved Co₉S₈(111) thin film crystal quality on this substrate evidenced by low X-ray diffraction (XRD) full width half maximum (FWHM) Bragg reflection, and results in the first report of the epitaxy of a metastable non-magnetic CoS₂ phase with ultra-high crystal quality. By systematically studying the ultra-thin (28 nm) film using a combination of structural and chemical characterization: in-situ reflective high energy electron diffraction (RHEED), atomic force microscopy (AFM), out-of-plane XRD, Raman spectroscopy, scanning tunnelling electron microscopy (STEM) and energy dispersive spectroscopy (EDS), we identify the contributing Co-S phases, thus providing unambiguous fingerprinting of the Co₉S₈ and CoS₂ contributions.

4.4.2 Results

Films were grown on commercial 2" c-plane α -Al₂O₃ wafers by MBE. The base pressure of the growth chamber was 10⁻⁹ Torr. Prior to growth, the substrate was outgassed for 10 min at 450 °C. For growth, the sample was exposed to Co from an e-gun and reactive S from H₂S fuelled plasma at 100 W power for 60 min (resulting chamber pressure was 5 x 10⁻⁶ Torr. Growth temperature was 420 °C. Estimating the resulting growth rate is challenging due to the formation of surface oxide discussed below. Using the remaining crystal film thickness after oxidation we can set a lower limit for the growth rate of 4.6 Å/min. After growth, the sample was left to cool passively. Wafer scale homogeneity of the film was confirmed using XRD and X-ray reflectivity (XRR) spectroscopy, (see Supporting Info, Fig. 4.18).

Fig.4.19b) shows a schematic of the present thin-film crystal. In Fig.4.19c), we probe the surface morphology by AFM and find a macroscopically continuous film with relatively low surface RMS roughness of 2 nm. The high degree of crystallinity and anisotropy is shown by the ubiquitously ordered orientation

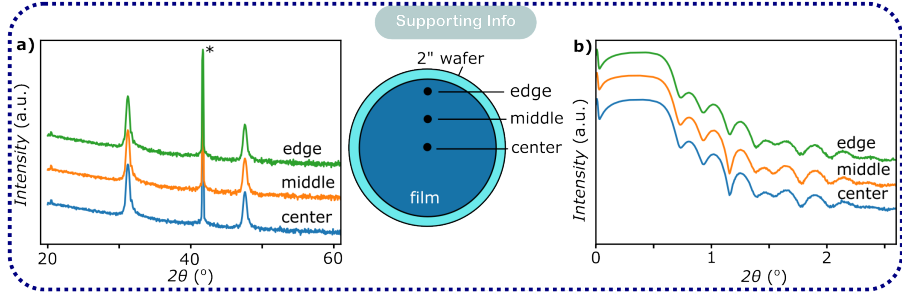


Figure 4.18: Confirmation of wafer scale uniformity of the thin film. a) XRD spectra recorded on different areas on the wafer (center, middle and edge according to schematic). b) XRR spectra recorded on the same positions as in a). The independence of spectra features on wafer position confirms the film homogeneity. Intensity scales are plotted in log scale, spectra are offset for visibility, astrix marks the peak position of the substrate (α - $\text{Al}_2\text{O}_3(006)$).

of triangular features. These qualitatively match expectations for a Co_9S_8 film grown in the out-of-plane (OOP) (111) direction.

Further insight is provided by the analysis of in situ RHEED data in Fig. 4.19d-f). In Fig.4.19d) we plot polar RHEED figures obtained from RHEED frames recorded at progressing azimuth angle φ . For a given radial position (e.g. in between marked circles in Fig.4.19d)), we observe six intensity spots on the substrate, as expected from the hexagonal structure of the c-plane of α - Al_2O_3 . Likewise, on the Co-S film, we also observe six intensity spots per revolution indicating a six-fold rotation symmetric structure of the film surface around the out of plane axis. This matches qualitatively with the observation of triangles in Fig.4.19c) and OOP $\text{Co}_9\text{S}_8(111)$. The single frames f1 and f2 in Fig.4.19e) show intensity streaks showing the epitaxial 2D nature of the film. In the kinematic approximation[13], the spacing of planes d is directly linked to the spacing W of corresponding intensity streaks $1/d \propto W$. By taking the substrate for calibration, we extract lattice spacings of vertical planes in the Co-S film (see Fig.4.19f)): 1.52 Å, 2.03 Å, 3.02 Å, 6.04 Å in frame f1 and 1.73 Å, 3.46 Å in f2, respectively. In Co_9S_8 , Co atoms are arranged in planes every 0.992 Å along the $\langle -12-1 \rangle$ direction which is perpendicular to $\text{Co}_9\text{S}_8(111)$. Thus, all but the first lattice spacing extracted from f1 can be associated to the atomic spacing in Co_9S_8 within an accuracy of $< 3\%$. Likewise the lattice spacings in f2 can be associated to atomic spacing in Co_9S_8 along the $\langle -110 \rangle$ direction: 1.72 Å and 3.44 Å. Notably, CoS_2 (materials project, mp-1042106) also features similar atomic spacings in planes nearly

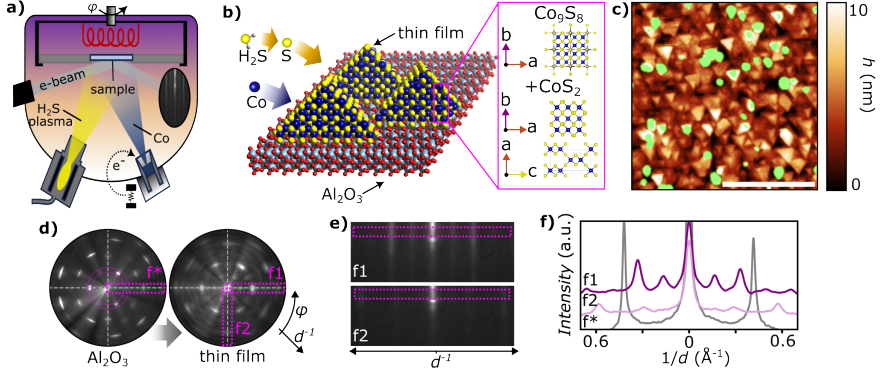


Figure 4.19: Synthesis of epitaxial thin film. a) Setup of the growth chamber featuring a reactive S source from H_2S plasma and a Co e-gun. b) Schematic of the growth process along with unit cell atomic models of the involved Co-S phases: $\text{Co}_9\text{S}_8(111)$ and $\text{CoS}_2(112)$. c) AFM image of the epitaxial thin film reflecting the underlying Co_9S_8 structure (scale bar is $1\ \mu\text{m}$). RMS roughness of the surface (excluding particles marked in green) is 2.0 nm. d) in-situ RHEED recordings with azimuthal rotation before and after growth showing 6-fold symmetry in the film. e) Single frames f1 and f2 of RHEED recordings as indicated in d). f) Intensity profiles of RHEED cuts indicated in e) allowing for in situ lattice constant estimates. Pixel scale has been converted to $1/d$ scale using a RHEED frame from the substrate indicated as f^* in d) and f).

perpendicular to its $\langle 112 \rangle$ axis: the $\text{CoS}_2\langle 10\text{-}2 \rangle$ and $\text{CoS}_2\langle \text{-}1\text{-}14 \rangle$ directions are off perpendicular from the $\text{CoS}_2\langle 112 \rangle$ axis by 2.2° and 2.5° and feature multiples of $1.76\ \text{\AA}$ and $1.01\ \text{\AA}$, respectively. Thus, this phase can hardly be excluded based on RHEED analysis alone.

In Fig.4.20, we further study the thin films structure using XRD and Raman spectroscopy. Fig.4.20a) shows an OOP XRD scan, i.e. the OOP axis is aligned by calibration with the out of plane axis ($\alpha\text{-Al}_2\text{O}_3(0006)$ at $2\theta=41.26^\circ$, marked by *) of the substrate. Thus, this scan probes lattice planes parallel to the substrate. In total we observe four intensity peaks, three pronounced ones at $2\theta=15.1^\circ$, 30.9° , 47.3° and one weak peak at 64.8° . We compared these peak positions to powder diffraction patterns of known Co-S phases. Fig.4.20a) shows three plausible phases based on the absence of magnetic order as measured by volumetric magnetometry (see Supporting Info, Fig.A.18), lattice spacing, and elemental composition. All of these phases have peaks close to the observed $2\theta=30.9^\circ$ but only Co_9S_8 has a close match with $2\theta=15.1^\circ$ for its (111) planes. The $\{111\}$ peaks of Co_9S_8 are all at a lower angle than ex-

pected which we attribute to OOP tensile strain imposed by the heteroepitaxy (+2.3, % computed from (222) peak). Other Co-S phases share lattice spacings with Co_9S_8 , i.e. their XRD peak could overlap with the one for Co_9S_8 at $2\theta=30.9^\circ$. Indeed, considering $2\theta=30.9^\circ$ alone, a better match is obtained with $\text{CoS}(100)$ and $\text{CoS}_2(112)$. Fig.4.20b) shows rocking curves recorded at OOP XRD peak positions $2\theta=15.1^\circ$, 30.9° , and 47.3° . We find a shared FWHM slightly below 1° in all of the rocking curves, significantly lower than previously reported in Co_9S_8 films grown on GaN (FWHM= 1.5°) and $\alpha\text{-Al}_2\text{O}_3(0006)$ by atomic layer deposition [8]. In the rocking curve at $2\theta=30.9^\circ$ we find two additional sharp, superimposed peaks with FWHM= 0.074° and 0.036° , respectively, indicating additional highly crystalline Co-S domains. Only the weak superimposed peak is reproduced in rocking curves at $2\theta=15.1^\circ$. Thus, we attribute the weaker of the sharp peaks to a highly ordered $\text{Co}_9\text{S}_8(111)$ phase. The other sharp peak can be attributed to the presence of an additional, highly crystalline Co-S phase warranting further characterization.

In Fig.4.20c) we probe the film by Raman spectroscopy. The spectrum (raw data: purple-solid, fit: dotted-black) shows four major peaks at 280.5 cm^{-1} (light yellow), 337.5 cm^{-1} (brown), 394.9 cm^{-1} (pink) and 401.7 cm^{-1} (purple), and another three minor peaks at 195.5 cm^{-1} (ochre), 226.1 cm^{-1} (light blue) and 360.1 cm^{-1} (blue). The small sharp peak at 418.0 cm^{-1} (dark blue) can be attributed to the substrate showing that both, the entire thickness of the film and some amount of the substrate contribute to the signal. No further peaks are detected up to 1500 cm^{-1} (see Supporting Info, Fig.A.18). In Fig.4.20d) we compare these Raman shifts to literature values for the plausible phases discussed for XRD above. The modes at 195.9 cm^{-1} and 360.1 cm^{-1} can be attributed to CoO_x [14, 15]. The minor broad peak at 226.1 cm^{-1} can be attributed to elemental S[16, 17], possibly from remnants of surface Co oxidation. The assignment of the major modes is more obscured due to the large variety of experimental modes and a lack of computational validation of Co_9S_8 and tetragonal CoS_2 modes reported in literature. Thus, here we include Raman modes of non-magnetic CoS_2 computed by density functional theory (DFT) (see "Methods" section for details) along with references of its magnetic polymorph (pyrite structure)[18, 19, 20]. The major peaks at 337.5 cm^{-1} , 394.9 cm^{-1} and 401.7 cm^{-1} are in reasonable agreement with most of the literature values of Co_9S_8 [18, 21, 22, 23, 24]. Only one literature value of pyrite type CoS_2 matches the major peak at 280.5 cm^{-1} [20]. This phase can however be excluded due to the lack of magnetism in our film, leaving this mode unaccounted for. We attribute this peak to the appearance of tetragonal CoS_2 in our film. This surmise is supported by a close match with the A_1 mode in our DFT validation of this phase. We note that Raman modes of CoS are reported at $>450\text{ cm}^{-1}$ [4, 25] and thus this phase can be excluded from contributing significantly to the film (see Supporting Info, Fig.A.18).

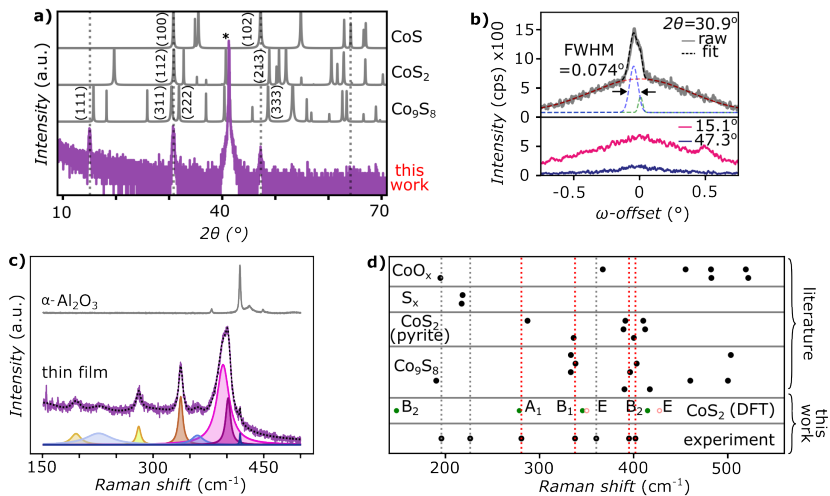


Figure 4.20: Structural and chemical analysis. a) XRD out-of plane scan probing planes parallel to the c-surface of the $\alpha\text{-Al}_2\text{O}_3$ substrate ((006) marked by *) are compared to models of Co-S phases. The intensity scale is logarithmic. b) Rocking curves at 2θ positions of peaks in a). The rocking curve at $2\theta=30.9^\circ$ shows superimposed peaks with FWHM extracted from fits (dotted lines) of 0.887° (red), 0.074° (blue), and 0.036° (green). c) Raman spectra taken on the Co-S film and substrate for reference. d) Comparison of Raman shifts from c) with literature values of CoO_x , elemental S, pyrite type CoS_2 other magnetic Co-S phases are excluded from comparison, see Supporting Info, Fig.A.18), Co_9S_8 and computed modes of tetragonal CoS_2 (structure of mp-1042106 as retrieved and relaxed). The dashed lines for major peaks from c) are highlighted in red.

For a final confirmation of the phase and to elucidate the interplay of the two Co-S phases we show nano-structural characterization by cross sectional annular bright field (ABF)-STEM and EDS in Fig.4.21. Fig.4.21a) shows a large area scan of a full film cross section. The thickness of the film is 28 nm which agrees with our findings from XRR measurements (see Supporting Info, Fig.A.19). Layers of alternating contrast parallel to the substrate can be made out through the majority of the film. In Fig.4.21b) we imaged a transitional area between two of these layered areas. A consistent OOP spacing is observed in both of the sections marked (i) and (ii), consistent with the XRD observations. By overlaying the atomic structures of Co_9S_8 to (i) and CoS_2 to (ii) we indeed identify both phases. In particular, the Co_9S_8 matches with the layering

observed also in Fig.4.21a). To determine the in-plane (IP) lattice spacing, we performed FFT analysis on these images (Supporting Info, Fig.A.20) obtaining $d_{\text{Co}_9\text{S}_8}^{\text{observed}}=3.66 \text{ \AA}$ from (i) and $d_{\text{CoS}_2}^{\text{observed}}=3.06 \text{ \AA}$ from (ii). Expected values for $\text{Co}_9\text{S}_8(101)$ and CoS_2 IP lattice spacing are $0.5 \times d_{\text{Co}_9\text{S}_8(101)}^{\text{theoretical}}=3.44 \text{ \AA}$ and $d_{\text{CoS}_2}^{\text{theoretical}}=3.08 \text{ \AA}$. We attribute the +6 % deviation to large tensile strain imposed through the substrate and the intimate, sub-nm interface. This strain reduces the lattice mismatch of the predominant Co_9S_8 from +4.7%(theoretical) to -1.6%(observed) (values computed by comparing $3 \times d_{\text{Al}_2\text{O}_3(110)}$ to $2 \times d_{\text{Co}_9\text{S}_8(101)}$). The CoS_2 phase on the other hand appears to be not significantly affected by the expected mismatch with the substrate (15% using the same comparison). The deviation of $d_{\text{CoS}_2}^{\text{observed}}$ from the theoretical value is only 0.6 %. Taking a closer look at the interface between CoS_2 and the substrate we can recognize a mono/double layer of Co_9S_8 acting as a buffer which can explain the low strain imposed on the CoS_2 phase. In Fig.4.21c) we present EDS maps and elemental profiles taken across a film area with the Co_9S_8 phase. The Co:S ratio deviates from that of Co_9S_8 due to significant replacement of S atoms by O atoms (20% out of 47%). Our EDS data confirms the diffusion free, sharp interface with the substrate and excludes the formation of CoO_x at the interface. An amorphous layer of CoO_x has formed on the top of the film, in this case spanning roughly 20 nm. The range of CoO_x elsewhere within the TEM lamella is 5 nm-50 nm at constant Co-S film thickness of 28 nm, consistent with XRR. Notably, the lateral scale of oxide thickness variation (100 nm) is far greater than the typical scale of grain transitions between the observed Co-S phases (5 nm) and no third Co-S phase has been observed in RHEED, XRD and TEM, excluding the effect of selective oxidation. The oxidation appears to stagnate after <4 days (time between growth and XRR characterization), leaves no clear trace in the XRR spectrum and multiple Co_9S_8 grains appear to protrude beyond the oxidation layer without significant oxidation (see AFM in Fig.4.19c) and Supporting Info, Fig.A.19). The exact mechanism of the present oxidation remains inconclusive in this study and could be an interesting and relevant subject of further studies. Lastly, to confirm the metallic character of the film, we conducted IP transport and hall measurements in van der Pauw (vdP) geometry of a roughly 1 cm^2 sized area to characterize the sheet resistance R_S , film resistivity ρ , carrier density n and mobility μ . This method measures bulk resistivity excluding contact resistance. We found room temperature values of $R_S=850 \text{ \Omega/sq}$, $\rho=2.38 \text{ m}\Omega \text{ cm}$, $n=8.8 \times 10^{21} \text{ cm}^{-3}$ and $\mu=0.3 \text{ cm}^2/\text{Vs}$, respectively. Note that resistivity values of amorphous CoO_x films range in the order of $100 \text{ \Omega cm}$, increasing with elevated amounts of oxygen[26]. The oxide in this work is composed of a Co:O ratio close to 1:2 (see Fig.4.21c)). Thus, we expect the CoO_x contributes negligibly to the overall transport in the present measurement. A resistivity value of $70 \text{ }\mu\Omega\text{cm}$ has been

reported for textured Co_9S_8 films deposited on $\alpha\text{-Al}_2\text{O}_3$, roughly 30 times lower than in this work despite the improvement in Co_9S_8 crystal quality[8]. We attribute the relatively low mobility and high resistivity to the textured nature of the Co_9S_8 grains and the occurrence of the co-existing CoS_2 phase, leading to phase boundaries that hinder the in-plane electronic transport.

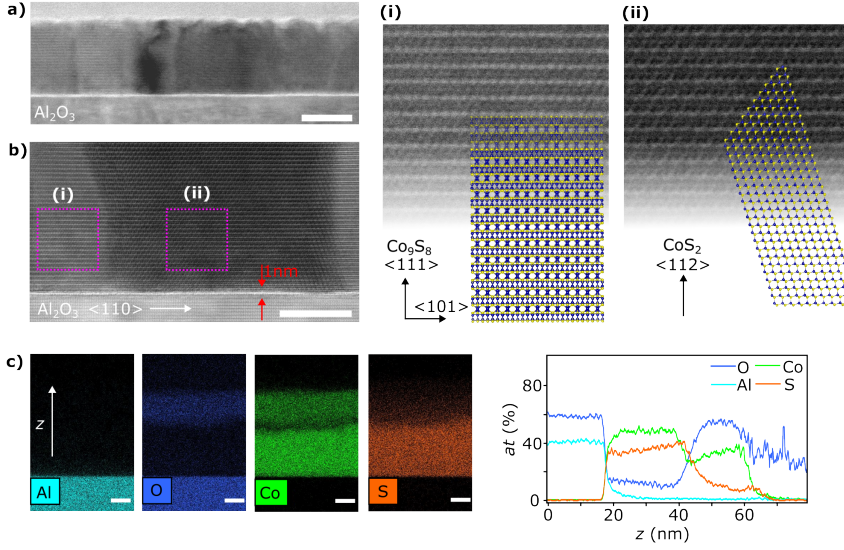


Figure 4.21: Nano structural characterization by ABF-STEM and EDS. a) large range STEM image across the film (scale bar is 20 nm). b) Cross section of Co_9S_8 grains (i) bridged by in-plane aligned CoS_2 (ii). Scale bar is 10 nm. Overlays with the respective atomic models are shown in (i) and (ii). c) EDS maps and averaged elemental profiles showing the distribution of Al, O, Co and S across a Co_9S_8 grain. Scale bar is 10 nm.

4.4.3 Discussion

Our thin film shows high OOP crystalline quality with unprecedented rocking curve FWHM on $\alpha\text{-Al}_2\text{O}_3$ substrate but relatively high IP resistance. The resistivity could be significantly lowered by removal of the $\text{Co}_9\text{S}_8(111)$ bridging CoS_2 phase. These appear to be facilitated by mono/dual buffer layers of $\text{Co}_9\text{S}_8(111)$. This can be readily rationalized from the reduction of nucleation energy associated to the lower nucleation barrier and increased wetting factor due to the chemical similarity between the Co-S phases (as compared to between Co-S and Al_2O_3). Our nano structural characterization demonstrates

the high structural interphase compatibility of Co_9S_8 and CoS_2 which could enable templated growth strategies but also makes selective growth of a single phase more difficult. The CoS_2 found in this study can easily be overlooked and its synthesis and potential has not been reported in literature so far. We highlight the challenge of excluding its contribution in common fingerprinting (OOP-XRD and in-situ RHEED) alone and point out Raman spectroscopy and nano structural imaging as necessary approaches. We expect our finding of the synthesis and fingerprint of non-magnetic CoS_2 will motivate further studies on its potential as a catalyst and contribute favourably to the development of single phase Co_9S_8 crystals.

Furthermore, addressing cost and scalability aspects for Co_9S_8 synthesis, we have demonstrated the feasibility of high quality $\text{Co}_9\text{S}_8(111)\text{-CoS}_2$ thin films on cost effective $\alpha\text{-Al}_2\text{O}_3$ substrates using scalable PA-MBE. This enables further progress towards single crystal $\text{Co}_9\text{S}_8(111)$ thin films and supports its utilisation as thin film catalyst in OER.

4.4.4 Conclusion

For the first time, we used the scalable PA-MBE method for the synthesis of a fully coalescent $\text{Co}_9\text{S}_8\text{-CoS}_2$ on $\alpha\text{-Al}_2\text{O}_3$. Our systematic characterization revealed textured $\text{Co}_9\text{S}_8(111)$ grains strained by epitaxial stress through the sharp substrate-film interface. For the first time, we observe the epitaxy of a highly lattice mismatched, non-magnetic $\text{CoS}_2(112)$ minority phase. The CoS_2 grains coalesce with the $\text{Co}_9\text{S}_8(111)$ phase while maintaining OOP lattice spacing rendering both phases indistinguishable by structural characterization methods that depend on the out of plane axis alone. The single crystal growth of Co-S phases demands effective methods for quantifying and excluding co-existing phases such as CoS_2 , making this first fingerprint of metastable CoS_2 essential for further progress in Co-S based catalysts. Thus, our findings contribute to the optimized utilization of Co_9S_8 and other phases of the Co-S system as catalytic thin films applicable to a broad range of research fields.

4.4.5 Methods

Experimental Characterisation

RHEED electrons with 15 kV acceleration voltage were directed at the sample surface at an incident angle of $2\text{-}3^\circ$. AFM images were recorded with a Dimension Edge tool (Bruker) operated in tapping mode. XRD and XRR scans were performed with XRD diffractometer X'pert (Malvern Panalytical) operated at 45 kV/40 mA acceleration voltage/filament current. Calibration was done on the $\alpha\text{-Al}_2\text{O}_3(006)$ peak of the substrate. Incident X-rays had $\text{Cu-K}\alpha$

energy of 8 keV and spectra where recorded with a PIXcel as point detector. TEM samples were prepared by covering the sample with spin on carbon by drop casting followed by Pt deposition (5 kV, then 30 kV) and side thinning lift out (Helios, TFS). TEM, STEM and EDS maps were recorded using a Thermo Fisher G2 60 -300 Titan³ operated at 200 kV. Atomic models and XRD powder diffraction patterns have been generated using open source data from materials project and VESTA software (Co₉S₈:mp-1513, CoS₂:mp-1042106).

Computational Details

The phonon frequencies were calculated with the ABINIT package[27] using standard Density Functional Theory (DFT)[28] and Perturbation theory (DFPT)[29]. The exchange correlation energy was approximated using the Perdew Burke Ernzerhoff Generalized Gradient Approximation (PBE GGA [30]). ABINIT employs a plane wave basis set (limited to 40 Hartree of kinetic energy, converged to within 16 meV per atom), and a reciprocal space (k-point) sampling which was set to 16x16x16 (unshifted) for all systems, which is converged to within 0.03 meV per atom for the smallest volume case. The core electrons are replaced with non-relativistic norm conserving pseudopotentials of the ONCVSP type[31] from the pseudo-dojo web site[32] (v0.4). Zone center phonon frequencies are calculated and their eigenvectors used to identify Raman active modes using the `anaddbirrep` script https://github.com/maillhexu/anaddb_irreps and the phonopy library[33]. The structure was recovered from the Materials Project[mp] database (id number 1042106 for CoS₂), and the residual stress and force were relaxed to below 2×10^{-8} Ha/bohr³ and 10^{-5} Ha/bohr resp. The resulting lattice constants are $a=2.69$ Å $c=5.14$ Å for body centered tetragonal mp-1042106 (space group 122).

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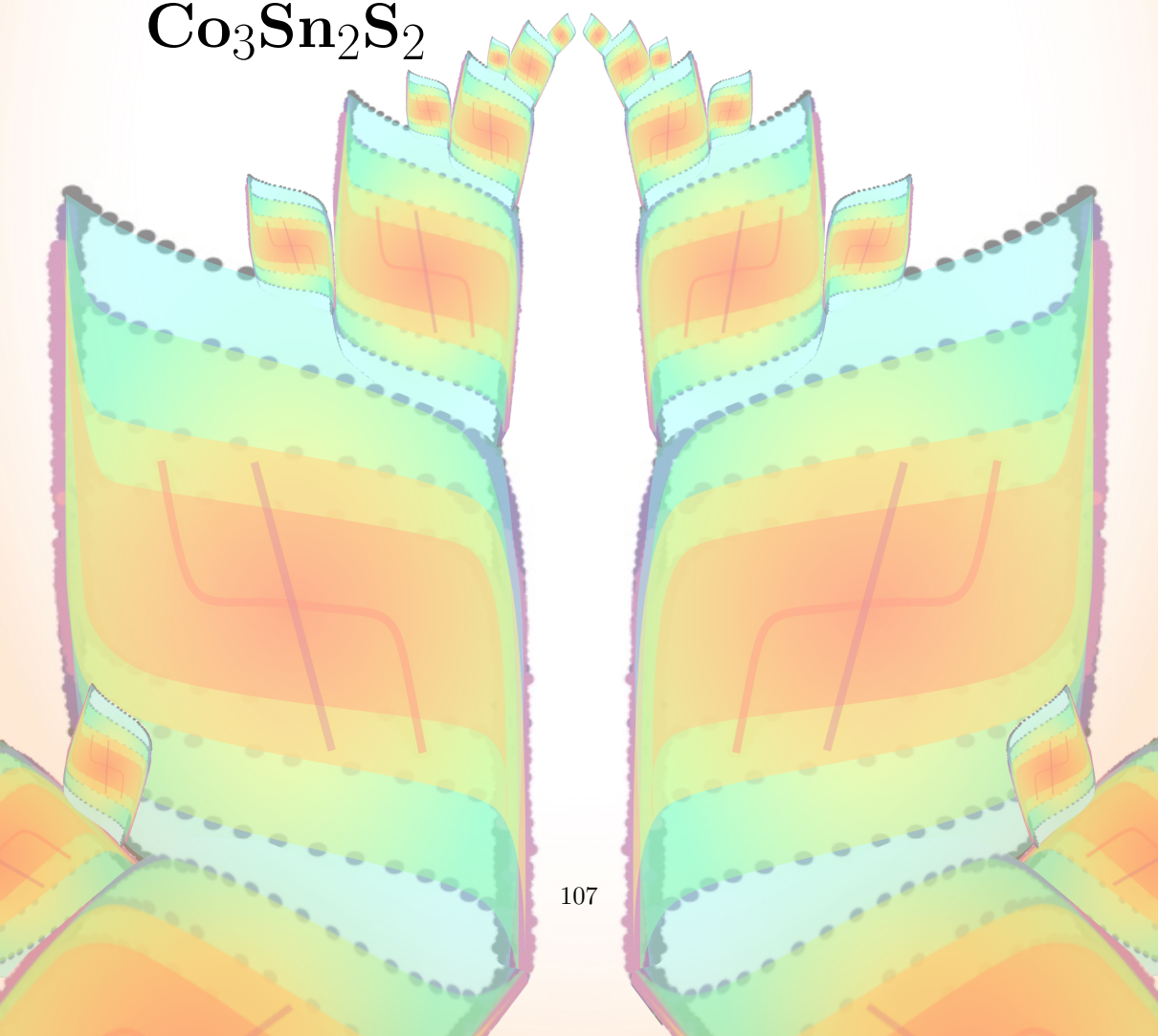
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Chapter 5

Epitaxy and First Characterization of Ternary $\text{Co}_3\text{Sn}_2\text{S}_2$



Material synthesis (MBE), processing (dicing, packaging, device fabrication) and structural characterization (RHEED, AFM, XRD) was conducted, managed, analysed and interpreted by Michael Rohde with major contributions by Dr. Gaohang He and under the supervision of Prof. Clement Merckling at Interuniversity Microelectronics Centre (IMEC) in Leuven. We express our appreciation for the training provided by Dr. Himanshu Sharma and technical support by Kevin Dubois, Hans Costermans, Kim Baumans, among others. We thank Johan Desmet and Johan Meersschaut for performing the RBS measurement and analysis.

TEM characterisation was carried out by Heyi Xia at KU Leuven and under supervision of Prof. Maria Seo and Prof. Francisco Molina-Lopez. Magnetometry measurements were performed by Rikkie Joris at KU Leuven under supervision of Prof. Lino da Costa Pereira.

Device fabrication was performed at both, IMEC and UC Louvain with the support of Michaël Coloumbier, Nicolas André, Luca Ceccon and Mohammadali Razeghi.

Raman spectra were recorded by Dr. Alessandra Canetta at UCLouvain. Transport measurements were - and still are - lead by Valentin Fonck under the supervision of Prof. Pascal Gehring.

Building up on the key observations obtained from binary compound synthesis (Section 3.0.3), we approached the synthesis of the ternary compound by simultaneous exposure of the substrate to all three elemental sources. In Section 5.1 we present an overview of all samples and highlight main observations concerning the challenge of elemental stoichiometry control using PA-MBE. In Section 5.2, we characterize a film showing clear signs of the ternary compound $\text{Co}_3\text{Sn}_2\text{S}_2$.

5.1 Growth

In most cases, excepting only 3 out of 79 characterized samples, the S fraction was found well above the target of 2/7, ranging around 50% as was already observed with binary compounds in the previous chapter. The two exceptions that show near 0% S content are SnS grown with H_2 diluted H_2S plasma (about 1/3 H_2S in the pre-plasma gas mix) and an attempted ternary sample at 0 W plasma power respectively. The remaining exception showed polycrystalline film character in RHEED and AFM but lacked any XRD signal and its stoichiometry could not be reproduced with similar growth conditions. As shown in previous chapters, multiple binary compounds can in principle form along the target $\text{Co}_3\text{Sn}_2\text{S}_2$ within the current range of growth rate, plasma power and substrate temperature.

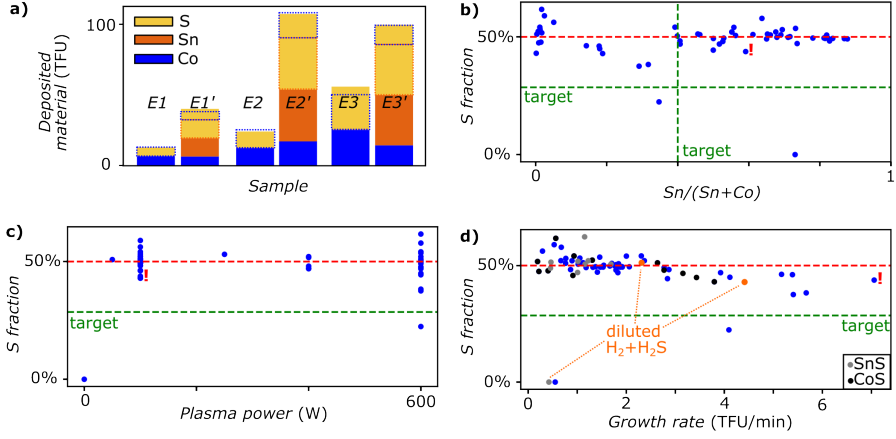


Figure 5.1: S incorporation measured by RBS, depending on various parameters. a) Set of three sample pairs illustrating the co-incorporation of S with added Sn content. Un-primed and primed sample labels correspond to equivalent growth conditions except for their growth temperature; $E1 - 3$ are grown at ≥ 420 °C and $E'1 - 3$ at ≤ 370 °C. Dashed outlines correspond to the corresponding amount of Sn (orange) and Co (blue) of each sample. b)-d) S fraction depending on $\text{Sn}/(\text{Co}+\text{Sn})$ ratio, H_2S plasma power and total growth rate, respectively. The exclamation mark marks the sample "F1" used for further characterization below. Samples already discussed in section 3.0.3 are marked by grey (SnS) and black (CoS) in d).

Fig.5.1a) shows a set of three sample pairs. Within each, the two sample's growth conditions differ only by substrate temperature. Samples $E1'-E3'$ (grown at ≤ 370 °C) show the common S fraction $\approx 50\%$ while simultaneously incorporating significant amounts of Sn and Co. In contrast, $E1-E3$ (grown at ≥ 420 °C) show similar S fractions but with the almost full absence of Sn and a matching reduction of absolute amount of S. We detected the XRD signature of SnS in $E2'$ and $E3'$ and no XRD signature in $E1-E3$. This strongly indicates that Sn incorporation was dominated by the formation of binary SnS. This SnS appears to either fail to form or evaporate within the temperature T range 370 °C $\leq T \leq 420$ °C. For the synthesis of $\text{Co}_3\text{Sn}_2\text{S}_2$, such integration by formation of 1:1 binary compounds is rather undesirable as it introduces competing phases that may dominate the thin film. The S fraction and the occurrence of binary phase characteristics can be understood as diagnostic indicators corresponding to such binary phase formation. Thus, we focused on the objective of the controlled reduction of the S content. Based on initial ob-

servations, the impact on S fraction of three growth parameters were further investigated: Sn/(Sn+Co) ratio, plasma power and total growth rate (shown in Fig.5.1b),c) and d), respectively). One possible mechanism by which the target stoichiometry may be achieved is through self limiting S incorporation. Fig.5.1b) shows the S fraction as a function of Sn/(Sn+Co). Looking at only the region of $\text{Sn}/(\text{Sn}+\text{Co}) \leq 0.4$ one might indeed interpret the data as a type of reduction in S fraction setting in when Sn/(Sn+Co) approaches the target 40 %. However, we observe S fractions of close to 50% for samples very close to $\text{Sn}/(\text{Sn}+\text{Co})=40$ %, as well as no clear trend for S fractions in the $\text{Sn}/(\text{Sn}+\text{Co}) \geq 40$ % region. This rather contradicts the occurrence of a self limiting S integration mechanism. Decreasing plasma power can be expected to lower both, the H₂S cracking efficiency and the kinetic energy of arriving S ions of the resulting plasma. Both may result in significant variation of S incorporation. Fig.5.1c) shows the S fraction as a function of plasma power. We observe a wide spread of values for the main powers used (100 W and 600 W) which may be due to experimental variation or the dominance of the impact of other growth parameters. Beyond this variation, the only clear decrease in S fraction occurs between 50 W, the lower limit for stabilizing the plasma, and 0 W, where no plasma is formed and S incorporation is below the detection limit of 0.01×10^{15} TFU. Another approach is the increase of Sn and Co growth rate, reducing the time available for reaction with S into binary compounds. Fig.5.1d) shows a weak trend of decreasing S fraction with total growth rate of roughly $-2.3 \text{ \%}(\text{TFU}/\text{min})^{-1}$. Following this trend and assuming S fraction = 50% at low growth rates, a growth rate of 9.3 TFU/min would be required to achieve the target 2/7 S fraction. Epitaxial thin films of Co₃Sn₂S₂ have previously been achieved by co-sputtering using growth rates around 6-7 nm/min (i.e. 13-15 TFU/min), significantly higher than the present projected requirement[2]. Therefore, achieving improved stoichiometry by increasing growth rate further, and without compromising significantly on crystal quality, appears to be a viable prospect.

Finally, we note that, in contrast to the case for binary SnS (1/3 H₂S in the pre-plasma gas mix), plasma dilution (in this case, 1/2 H₂S in the pre-plasma gas mix) with H₂ did not totally remove the S content in two samples that also contained Co. With the limited amount of samples generated using this approach, these findings should be considered preliminary but appear to offer another (in principle continuous) growth parameter with an impact on the S fraction. Thus further attempts using plasma dilution may yet turn out a promising approach.

The sample grown at highest growth rate ("F1" marked by exclamation marks in Fig.5.1b)-d)) showed signs of Co₃Sn₂S₂ crystallization and was further investigated below.

5.2 Structural Characterization

In this section we analyze sample F1 in more detail using the same methods applied above for binary compounds: RHEED, AFM, XRD, VSM, Raman, STEM and EDS. Fig.5.2 a) shows the RHEED pattern recorded in situ directly after growth. The image shows a mix of patterns indicating the co-occurrence of amorphous (diffuse background), polycrystalline (rings) and epitaxial (weak streaks) phases. The AFM image in Fig.5.2b) qualitatively agrees with those observations showing large roughness (RMS=9.6 nm) with 100 nm scale grains protruding a background layer of relatively flat grains. The low degree of order is reflected also in the signal to noise ratio of film peaks in the XRD spectrum in Fig.5.2c). Apart from substrate signal, the spectrum shows two intensity peaks at $2\theta = 31.50^\circ$ and 40.65° . The former fits well with SnS(004) and the latter is within 0.1° of the $\text{Co}_3\text{Sn}_2\text{S}_2$ (006) peak reported on a 5 nm thin film in previous synthesis studies[3]. Further evidence for the presence of $\text{Co}_3\text{Sn}_2\text{S}_2$ (006) by SQUID-VSM (zero-) field cooling ((Z-)FC) and volumetric magnetometry is presented in Fig.5.2d). Indeed the ZFC and FC curves match closely previous reports for $\text{Co}_3\text{Sn}_2\text{S}_2$ with a curie temperature of 170 K [4]. In Fig.5.2 e) we provide further fingerprinting of F1 by Raman. A comparison with Raman signatures found in binary compounds in the previous chapters shows the coexistence of multiple phases in the film. We clearly identify features similar to spectra taken on fully identified and characterized Co-S films and SnS films. This suggests a significant amount of admixed binary phases. Notably, we do not identify contributions from crystalline CoSn_2 . Expected peaks for the ternary phase lie at 289 cm^{-1} and 386 cm^{-1} according to previous reports [5]. These peaks are not prominent in our spectrum of F1 compared to the signal generated from SnS. Signal around 289 cm^{-1} may stem from $\text{Co}_3\text{Sn}_2\text{S}_2$ but might as well come from Co-S phases. The shoulder at 387.4 cm^{-1} however, does not overlap with any peaks found in the binary compounds and thus plausibly comes from the ternary phase.

Next, to gather insight into the nature of the mixture in F1, we move on to nanoscopic characterization. Fig.5.3 shows STEM based images of F1. EDS maps in Fig.5.3a) show the elemental distribution of the participating elements over a cross section cleaved along $\alpha\text{-Al}_2\text{O}_3\langle 011 \rangle$. Co, Sn and S appear in continuous film across the entire image albeit with strongly varying thickness (17-38 nm for Co). The distribution of Sn and S match qualitatively with each other but not with Co which is occasionally absent in areas where Sn and S are present. We observed no significant substrate-film inter-diffusion. The high resolution HAADF-STEM image in Fig.5.3 shows a highly crystalline grain that contains contributions of all three elements, Co, Sn and S and features a sharp, 1 nm substrate interface. On closer examination, the lattice spacings of this grain match precisely with the unit cell of $\text{Co}_3\text{Sn}_2\text{S}_2$ viewed along the

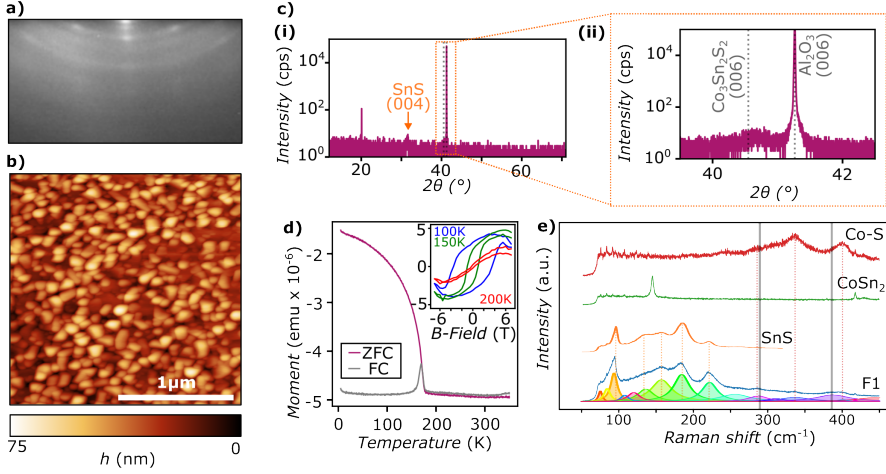


Figure 5.2: Further characterization of F1 by a) RHEED, b) AFM (RMS roughness 9.6 nm), c) XRD and d) out-of-plane SQUID-VSM (y-axis is shared with inset, B field was applied in the OOP direction). e) Raman spectrum of F1 compared to other spectra obtained in this work. Vertical grey lines represent expected peak positions of $\text{Co}_3\text{Sn}_2\text{S}_2$.

$\langle -114 \rangle$ direction. With this alignment, this grain can be expected to have contributed negligibly to the $\text{Co}_3\text{Sn}_2\text{S}_2(006)$ peak observed in XRD but could have contributed to out-of-plane VSM signal. A different type of grain is depicted in Fig.5.3c). Here, the $\text{Co}_3\text{Sn}_2\text{S}_2\langle 006 \rangle$ axis is aligned with the $\langle 006 \rangle$ of the substrate in agreement with the OOP XRD and VSM signal. All observed $\text{Co}_3\text{Sn}_2\text{S}_2$ grains have been located exclusively at the interface with the substrate in coherence with the Co distribution described above. Interestingly, the latter $\text{Co}_3\text{Sn}_2\text{S}_2$ grain is surrounded by a SnS crystal with a sharp boundary in the OOP direction but less defined in-plane boundary. This agrees with the observation of SnS(004) signal in XRD and Raman. EDS analysis of this region in Fig.5.3d)+e) substantiates this finding. The mechanism by which the admixture of binary phases occurs on the ternary compound remains inconclusive but these findings suggest the potential of obtaining single phase $\text{Co}_3\text{Sn}_2\text{S}_2$ films with shorter growth processes.

At this point we have gathered high confidence in the presence of $\text{Co}_3\text{Sn}_2\text{S}_2$ in F1 but it remains to probe whether this film produces desired effects in transport. We fabricated hall bar devices from F1 according to optical lithography described in 2.7. Two device designs were employed: simple hall bars for first transport characterization (Fig. 5.4 a)) and hall bars with joule heaters placed

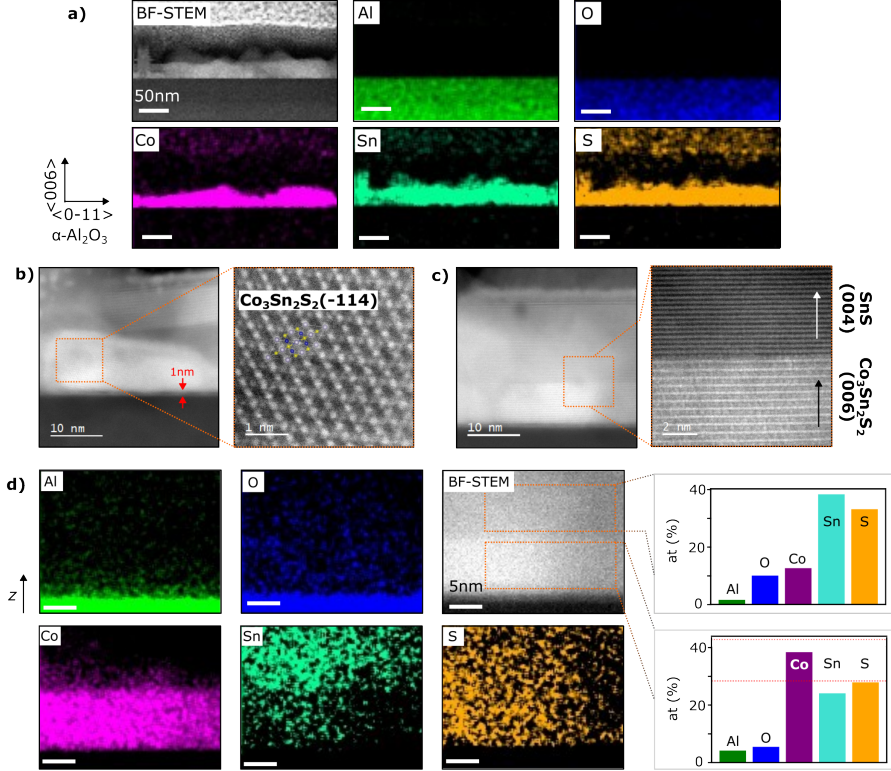


Figure 5.3: Nanoscopic characterization of F1 using STEM. a) and c) show HAADF-STEM images of crystalline grains of $\text{Co}_3\text{Sn}_2\text{S}_2$ bordering to additional crystal phases. b) and d) show EDS maps. The EDS map in b) shows a continuous film of Co, Sn and S along the entire sample. The EDS map in d) corresponds to the phase interface in c) showing an elemental interface separating a Co rich and Co deficient area. The results of a quantitative analysis of elemental composition in these areas are shown on the right.

in proximity to the source and drain electrodes (Fig. 5.4 c)). Fig. 5.4 b)(i) shows IV traces obtained on $\text{Co}_3\text{Sn}_2\text{S}_2$ hall bars with contacts wirebonded directly on the film. These appear to form Ohmic contacts as evidenced by the linear quality of the IV traces. Fig. 5.4 b)(ii) shows magneto transport results obtained from the same device. The peaks in longitudinal magneto resistivity ρ_{xx} coincide with the switching of anomalous hall conductivity σ_{xy} . Such behaviour is common in magnetic materials where σ_{xy} follows the magnetization of the film and ρ_{xx} peaks during magnetization reversal where electron scattering is enhanced due to spin and domain disorder. In a Weyl semimetal, transport is affected due to intrinsic changes in band topology (Weyl nodes move, Berry curvature redistributes). Combining both magnetism and Weyl features, in magnetic Weyl semimetals such as $\text{Co}_3\text{Sn}_2\text{S}_2$ the anomalous Hall behaviour from Fig. 5.4 b)(ii) is expected to be particularly pronounced ("giant" even) as quantified by the anomalous hall angle

$$\theta_{\text{H}}^{\text{AHE}} = \frac{\sigma_{xy}}{\sigma_{xx}} \quad (5.1)$$

Here we find $\theta_{\text{H}}^{\text{AHE}} = 8.1\%$ which is unusually large for a conventional magnets and comparable with other Weyl magnets (e.g. Fe_3GeTe_2 (7-9%), Co_2MnGa (13 %) [6, 7, 8] and previously reported values for $\text{Co}_3\text{Sn}_2\text{S}_2$ (5-20 %) [9]. While a large Hall angle alone does not prove Weyl physics, it strongly suggests a significant intrinsic Berry-curvature contribution. Further distinction between purely magnetic and Weyl phenomena could be done by examining in more detail the $M(T)$ dependence of σ_{xy} and studying the surface band structure by angle-resolved photoemission spectroscopy (if the surface of the active material can be exposed). Here however, we aim to focus on thermal characterization.

Fig. 5.4 c) shows a completed device for thermoelectric characterization employing side heaters. This design is relatively easy to implement since it requires only two lithography steps and does not involve the necessity of electrically separating heaters and electrodes. However, it has the disadvantage of significant heat loss to the substrate (in particular for thermally conductive substrates such as Al_2O_3). A design with top-heaters has been drafted but its implementation currently remains an open issue for future work. A continuation of this work - encompassing thermoelectric transport measurements and a more comprehensive magnetotransport data set - is currently being pursued in the laboratory of Prof. Pascal Gehring and will form the basis of upcoming studies.

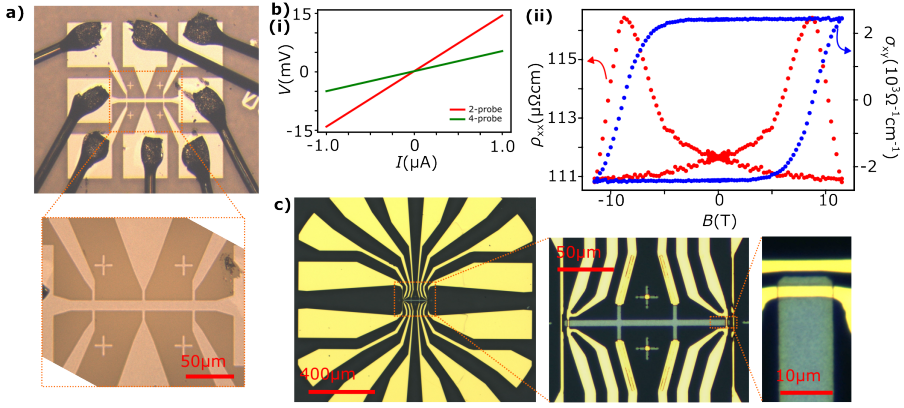


Figure 5.4: First transport on F1. a) shows hall bars made from wafer F1 using a one step lithography procedure. Pads have been wirebonded directly on the film. b) IV traces recorded at RT (i) and magneto resistivity vs hall conductivity measurements at 1.3 K showing a clear anomalous hall effect. Data has been symmetrized linear hall contributions have been subtracted. The B field was aligned with the OOP direction of the device. c) Devices fabricated for thermoelectric characterization. Heaters are placed closely on the side of the contacts to induce a temperature gradient.

Key Takeaways: Co-Sn-S system

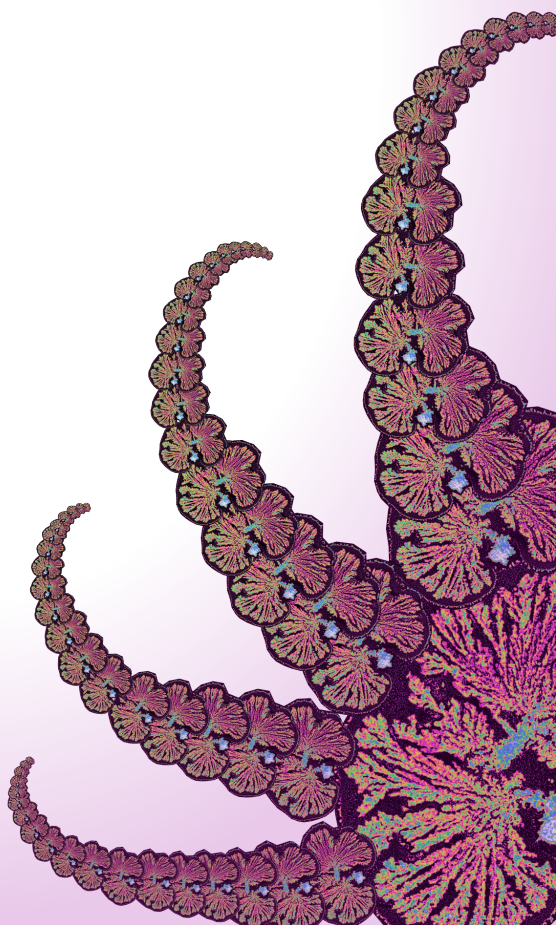
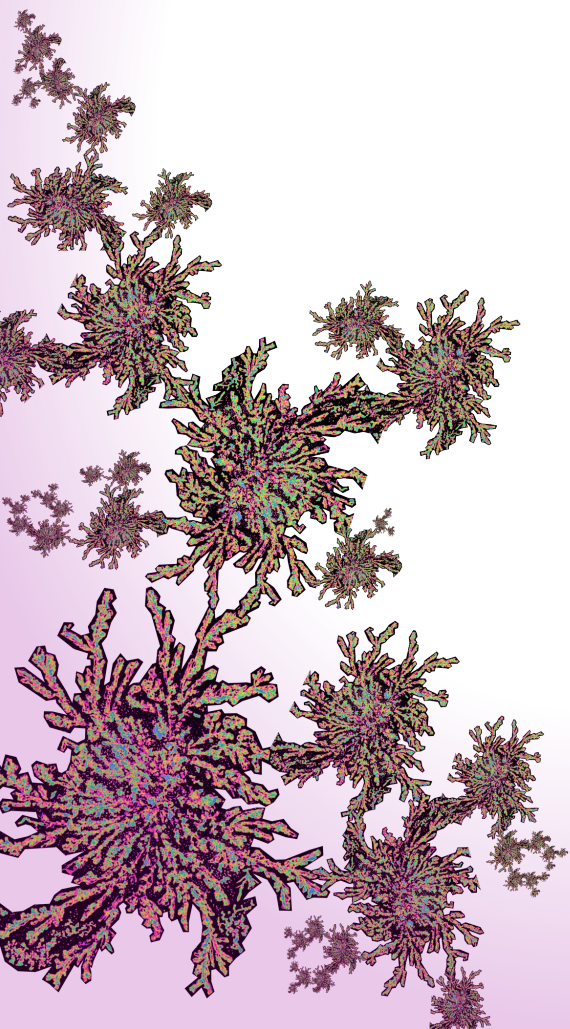
1. S fraction close to 50% for most samples, likely due to binary Sn-S and Co-S compounds with elemental ratio 1:1 each.
2. No observed impact of Sn/(Sn+Co) ratio within 0-100 % and H_2 plasma power within 50-600 W but trend of S fraction reduction by $-2.3 \text{ } (\text{TFU}/\text{min})^{-1}$ with total growth rate.
3. High growth rate sample F1 shows XRD, VSM, STEM and transport signature of roughly aligned $\text{Co}_3\text{Sn}_2\text{S}_2(006)$ grains with average thickness of few nm and covered by SnS and Co-S phases.

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Chapter 6

Conclusion and Outlook



This thesis has explored the synthesis of epitaxial thin-film materials within the Co-Sn-S phase diagram, with a particular focus on the growth and characterization of the magnetic Weyl semimetal $\text{Co}_3\text{Sn}_2\text{S}_2$ due to its exceptional potential for transverse thermoelectric (t-TE) applications.

The introduction summarized the fundamental motivation of addressing key challenges in modern energy management. The exploration of binary Co-Sn, Sn-S, and Co-S compounds serves a dual purpose: they provide a crucial foundation for identifying synthesis routes and quality assessment tools for the ternary compound, while also being of individual interest in the fields of Li-storage, memristive computing, heat management, and catalysis, where their synthesis in thin-film form has remained comparatively underexplored. In this work, multiple epitaxial binary compounds were synthesised on $\alpha\text{-Al}_2\text{O}_3$, characterized in detail, and investigated in light of their respective applications: CoSn_2 as a model platform for studying the impact of grain size on Li-storage, and epitaxially strained SnS as a candidate memristor and thermal insulator. A previously overlooked, non-magnetic CoS_2 phase coexisting with highly crystalline Co_9S_8 was identified. Insights gained from the investigation of these binary sub-systems are expected to positively impact multiple research areas by providing a deeper understanding of phase stability, composition control, and structure-property relationships. Further exploration of the proposed mechanisms, as well as steps toward device integration, represent promising directions for future studies.

As a magnetic Weyl semimetal, the ternary compound $\text{Co}_3\text{Sn}_2\text{S}_2$ combines intrinsic magnetization M and Berry curvature Ω , offering a natural platform for enhanced transverse thermoelectric responses. However, its synthesis by conventional methods suffers from insufficient sulfur incorporation.

A key achievement of this work is the successful incorporation of sulfur using plasma-assisted molecular beam epitaxy (PA-MBE) for the growth of $\text{Co}_3\text{Sn}_2\text{S}_2$ thin films. While this method ensures sufficient sulfur incorporation, it also revealed a tendency toward over-incorporation, approaching an atomic ratio of $\text{S}/(\text{Sn}+\text{Co})=1:1$. This occurred through the formation of binary Co-S and Sn-S compounds - as confirmed by comparison with crystalline binary references - and led to global deviations from the ideal $\text{Co}_3\text{Sn}_2\text{S}_2$ stoichiometry. Addressing this issue will require refined growth strategies aimed at reducing sulfur abundance. Several approaches were tested, including enhanced total growth rates, partial plasma passivation through dilution, and lower-power H_2S plasma formation. Among these, only increased growth rates proved effective within the explored parameter ranges.

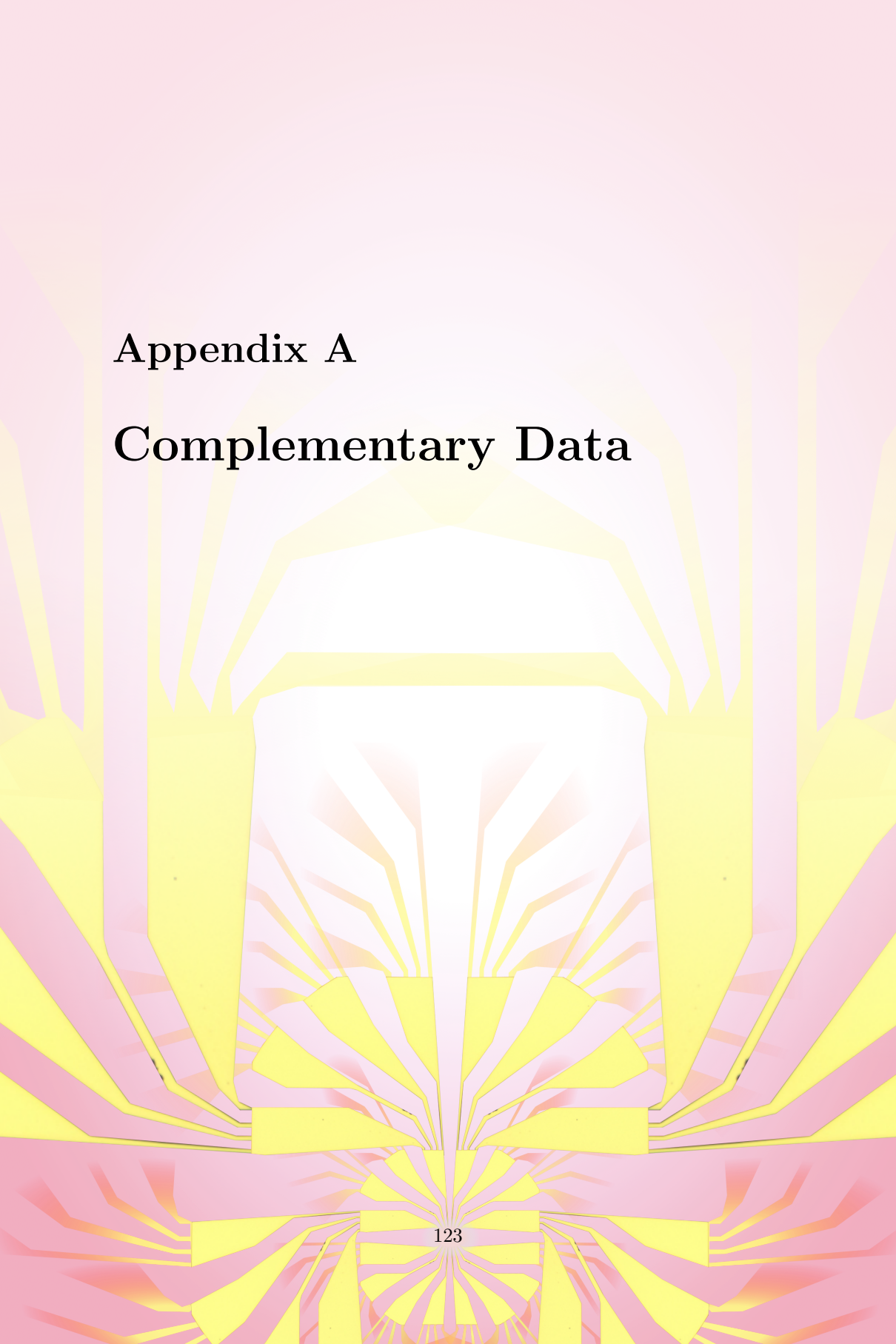
A thin film containing the target $\text{Co}_3\text{Sn}_2\text{S}_2$ phase was successfully synthesized, resulting in a mixed ternary/binary thin film composed predominantly of disordered microcrystallites. In this structure, $\text{Co}_3\text{Sn}_2\text{S}_2$ was found exclusively

at the interface with the substrate, as confirmed by structural and compositional analysis. These grains did not extend throughout the entire film thickness, suggesting that shorter deposition bursts may provide an effective strategy for promoting this phase. Preliminary transport measurements showed signatures of transverse transport phenomena consistent with expectations based on the material's intrinsic M and Ω . This demonstrates that PA-MBE is a viable route for producing thin films suitable for nanoscale transport studies.

Looking forward, several avenues for further investigation emerge. First, detailed Nernst and Ettingshausen measurements will enable quantitative assessment of t-TE performance, while device-level gating studies could probe the tunability of transverse transport in these ultra-thin films. Second, mitigating sulfur over-incorporation will be critical for achieving reproducible, stoichiometric films with improved structural quality.

In summary, this work establishes a foundation for the controlled synthesis of binary Co-Sn-S compounds and $\text{Co}_3\text{Sn}_2\text{S}_2$ thin films, and opens pathways for future experimental and device-oriented exploration of materials relevant to advanced energy management technologies.

* * *



Appendix A

Complementary Data

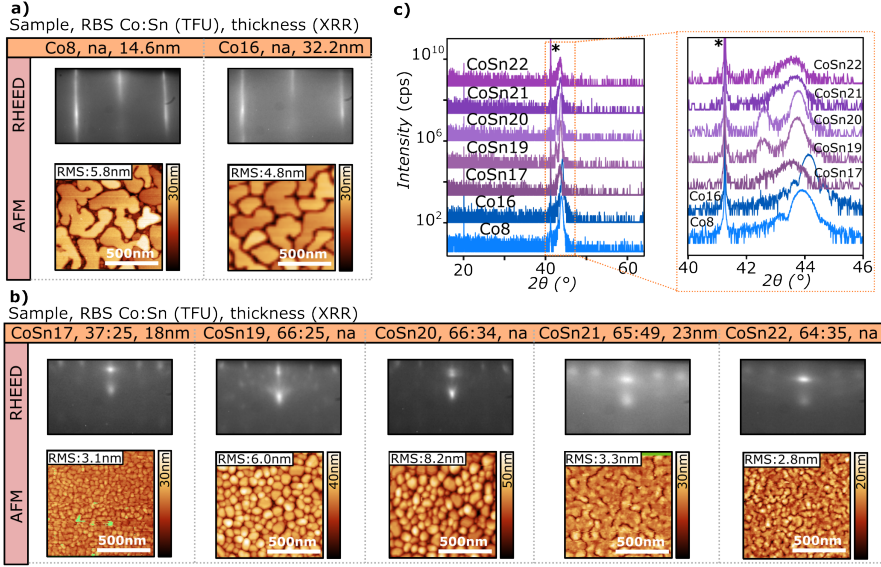


Figure A.1: Comparison of CoSn samples (close to Co:Sn=3:2) with crystalline Co samples. a) and b) show RHEED, AFM and RBS. RHEED of all samples shows similar spacing but differ in showing streaks (Co samples) and spots (CoSn samples) indicating 2D and 3D type growth, respectively. Samples grown at 400 °C (Co8 at 450 °C, Co16 at 550 °C, CoSn19 at 700 °C and CoSn20 at 700 °C) show similar morphology in AFM. We found a morphology transition in pure Co around 300-500 °C, see Fig.A.2 which might be related to this observation. All other CoSn samples shown here have been grown at 350 °C. c) XRD scans calibrated using the $\text{Al}_2\text{O}_3(006)$ marked with *. Plots are offset for visibility. The high temperature CoSn samples show an additional peak at 42.6°.

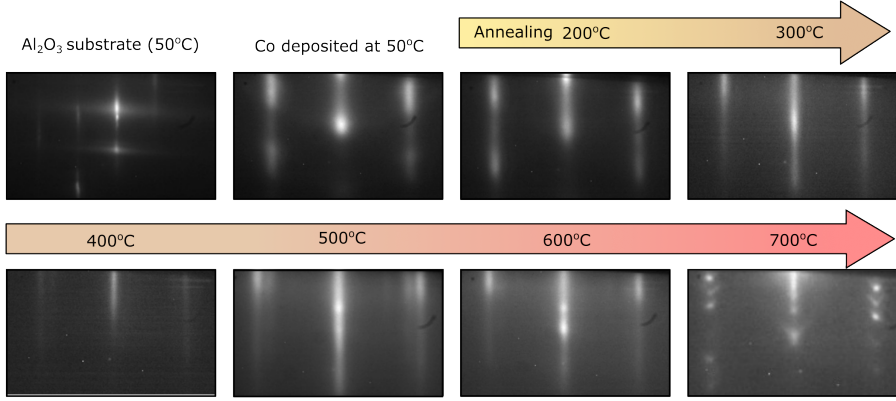


Figure A.2: RHEED recordings of a morphological transition of Co thin film. Streaks become more pronounced at 300-500 °C reminiscent of Co8 and Co16 in Fig.A.1 and turn into a spotty pattern at 600-700 °C.

A.0.1 Additional Supporting Info: CoSn_2 as Thin Film Anode

RHEED provides an in-situ recording of the growth process giving first insights into the structure of the growing film. As expected for the hexagonal substrate surface lattice we observe 6 spots/revolution for a given d^{-1} (measured by the position on the radial axis). On the finished film we observe 12 spots/revolution, i.e. a 3-fold texture assuming the 4-fold symmetric associated CoSn_2 lattice. Looking at single frames reveals a transitional 3D type growth mode indicated by the spot-like RHEED pattern. Eventually, this pattern turns into streaks showing the emergent film character with off-streak features that can be associated to facets of grains. The kinematic approximation directly relates the spacing of RHEED features W to the lattice spacing of the crystal d through $1/d \propto W$. The detected peaks of the final film overall agree with those of the intermediate film but with less signal to noise ratio. The peaks in the intermediate film correspond to crystal spacing estimates of 1.513 Å, 2.261 Å, 4.525 Å and 1.705 Å, 2.488 Å, 4.058 Å for the two distinct frames, respectively. The former three can be associated with CoSn_2 planes (330), (220) and (110), respectively, matching the dominant growth direction G1. The latter can be associated to $c/3$, $c/2$ and $\sqrt{a^2 + c^2}/2$ crystal spacings matching the second most dominant growth direction G2.

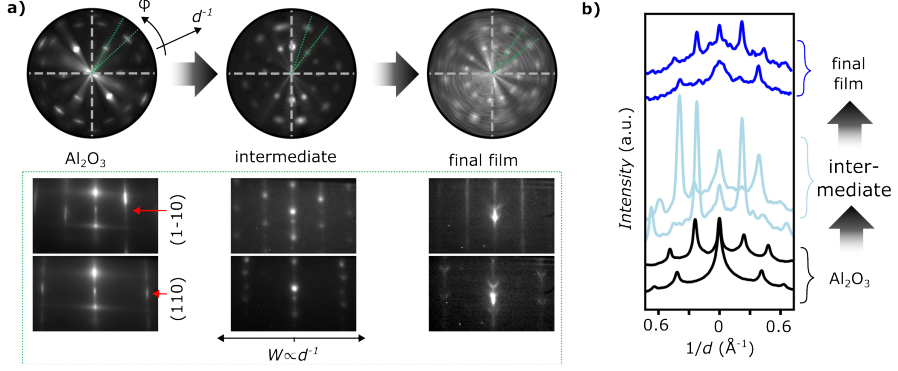


Figure A.3: Further characterization by RHEED. a) RHEED pole figures with azimuth (ϕ) rotation and single frames showing intermediate 3D mode growth. b) Intensity profiles along horizontal cuts of single RHEED frames in a). (Further discussion below).

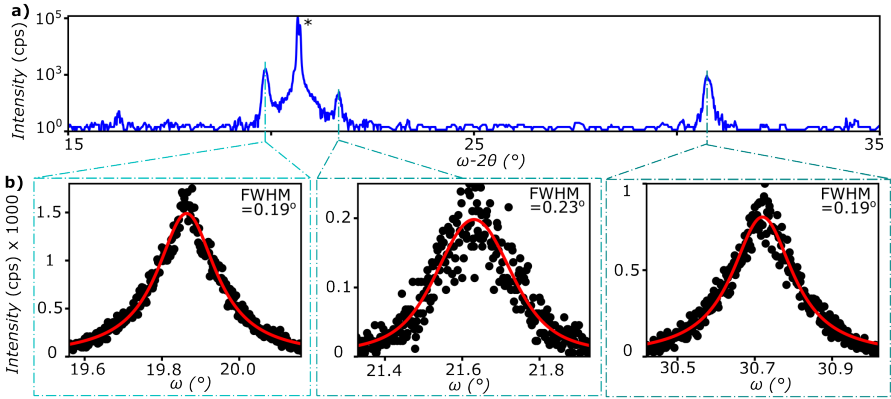


Figure A.4: Rocking curves of XRD peaks from Fig.4.3 in the main text. a) $\omega-2\theta$ scan equivalent to the ω -offset= 0° line in Fig.4.3a). b) Rocking curves of the $\text{CoSn}_2(220)$, (202) and (330) with FWHM of 0.19° , 0.23° and 0.19° , respectively. The plot shows data (black points) and Voigt function fits (red line).

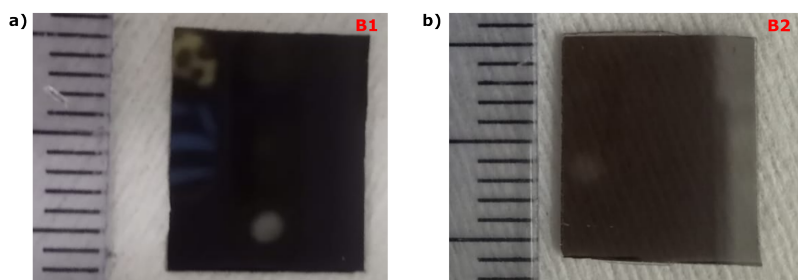


Figure A.5: Determination of sample area. We find 1.16 cm^2 and 1.22 cm^2 for B1 and B2, respectively. Increments on the ruler are mm.

A.0.2 Additional Supporting Info: SnS as Memristor

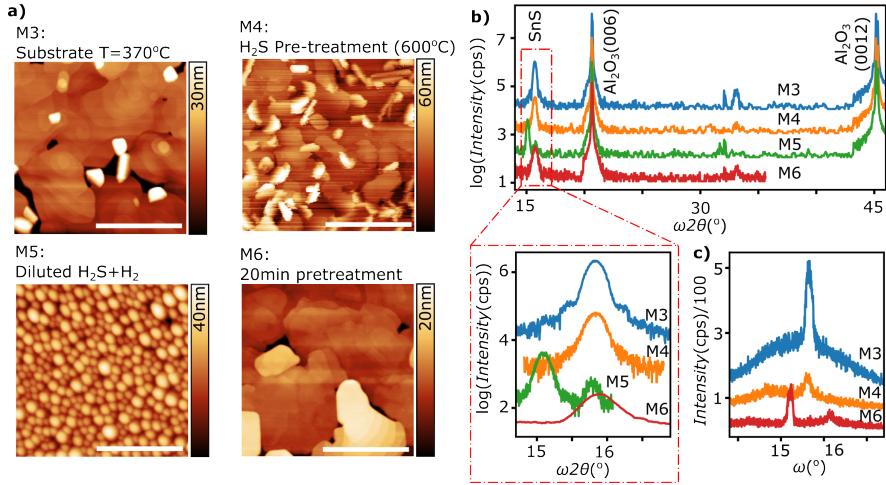


Figure A.6: Comparison of various growth strategies for M3-M6 by AFM in a) and XRD in b). M3 was grown with an additional 20°C relative to M2. M4 shows a high impact of executing the H₂S pre-treatment at 600°C, 150°C lower than for M2. M5 demonstrates a large morphology change when using H₂S diluted with H₂ for the pre-treatment. M6 shows increased grain size with adding 10min to the H₂S pre-treatment time. XRD scans on M3 are consistent with M2. Two peaks in M5 at $\omega 2\theta=15.1^{\circ}$ and 15.8° can be assigned to SnS(111) and SnS(004), respectively. c) XRD rocking curves on M3,4 and 6. The superposed sharp peak on M4 is significantly reduced compared to M2. On M6, it forms at a different ω angle. Scale bars in AFM images are 500 nm.

System	SnS unit cell (AB)	single layer	multiple layers (AB, even)	multiple layers (AB, odd)	multiple layers (AA)
Centro-symmetry	yes	no	yes	no	no

Figure A.7: Schematics of different stacking orders in SnS.

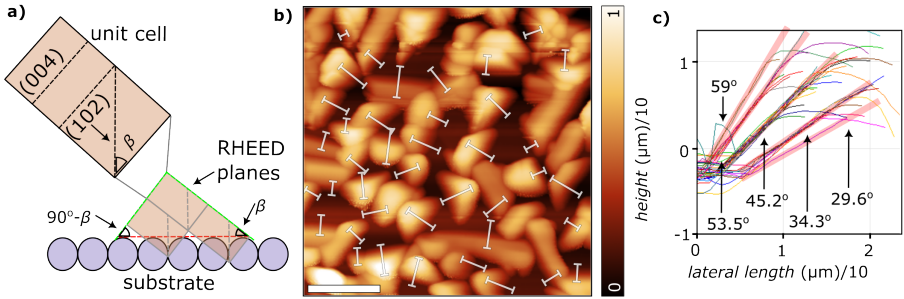


Figure A.8: Grain angles measured on M1. a) Schematic of the relationship between planes measured by RHEED and angles observed in AFM. SnS(004) and SnS(102) are used as example. b) Topographic AFM image from main text overlaid with profile lines taken perpendicular to grain gradients. Scale bar is 250 nm. c) Collection of line profiles that align with five angles; 59.0° , 53.5° , 45.2° , 34.3° and 29.6° . Red areas represent average angles $\pm 2^\circ$ giving an error estimate of this method. SnS(004) and SnS(114) form an angle of 43.8° ($90^\circ - 43.8^\circ = 46.2^\circ$) matching the most common angle. SnS(004) and SnS(102) form an angle of 54.9° and $90^\circ - 54.9^\circ = 35.1^\circ$ matching well two of the most common observed angles consistent with RHEED data shown in the main text. SnS(004) and SnS(023) form 59.8° and 30.02° matching well with the two less common angles.

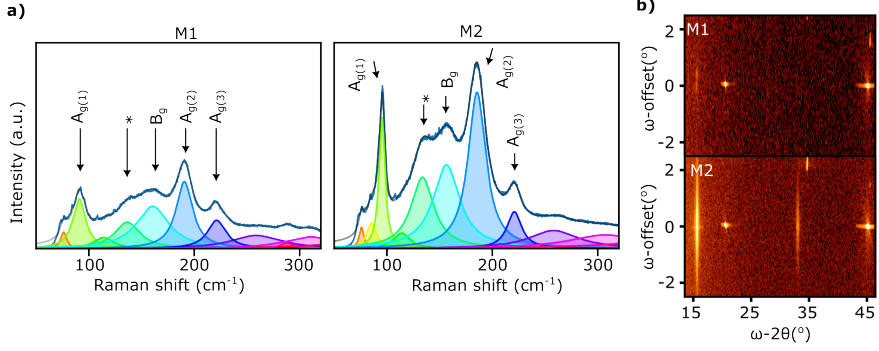


Figure A.9: Comparison of M1 and M2 in Raman and XRD maps. a) Peak positions are ($A_{g(1)}$, *, B_g , $A_{g(2)}$, $A_{g(3)}$) = (90.9, 136.4, 160.5, 190.6, 221.2) cm^{-1} and (95.4, 133.6, 156.4, 185.4, 220.8) cm^{-1} for M1 and M2, respectively. Qualitatively, M1 and M2 produce the same Raman profile confirming that their difference is predominantly structural. Despite featuring a roughly equal amount of material, the general intensity is roughly 3 times larger in M2 confirming the superior crystallographic order. The peaks in M2 are diversely shifted in respect to M1 by a few cm^{-1} ; red for $A_{g(1)}$ and blue for all others. This could be attributed to stress stemming from the differing growth mode and larger substrate interface. b) The off-axis peaks RSM are present in both samples but at different positions and intensities.

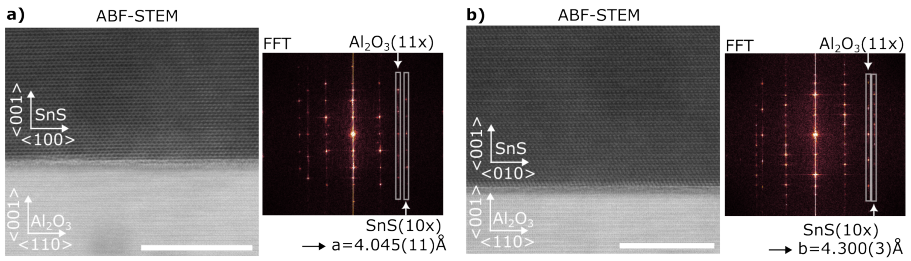


Figure A.10: Cross sectional ABF-STEM images of the two main crystallographic in-plane directions in BP-SnS recorded from the same lamella of textured film M2. Lattice constants were extracted from the FFT images using the known lattice spacing of $\alpha\text{-Al}_2\text{O}_3(110)$, $d_{110}^{\text{Al}_2\text{O}_3} = 2.41 \text{ \AA}$, yielding $a^{\text{SnS}} = 4.051 \text{ \AA}$ in a) and $b^{\text{SnS}} = 4.319 \text{ \AA}$ in b). Scale bars are 10 nm.

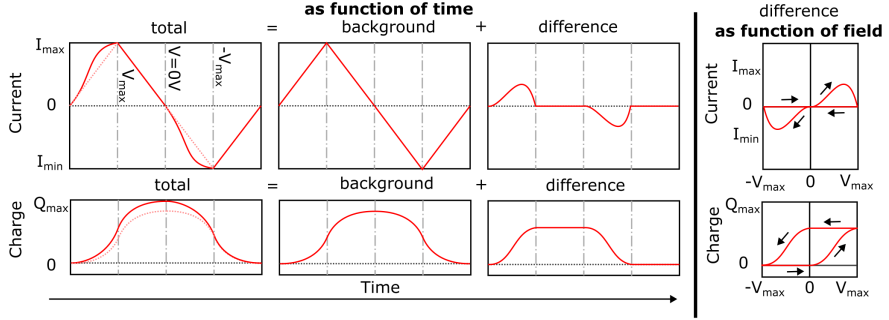


Figure A.11: Background subtraction for the charge measurement. The schematic illustrates the process for a ohmic background which results in quadratic charge contributions. In the present analysis, non-linear background contributions have been accounted for by fitting a 4th order polynomial to the background.

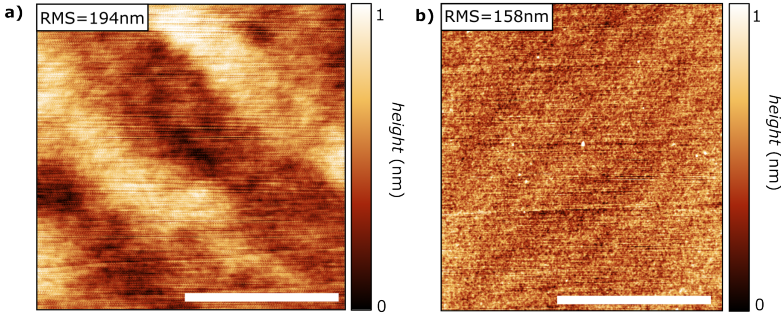


Figure A.12: Comparison of a) pristine $\alpha\text{-Al}_2\text{O}_3(001)$ (RMS=194 nm) and b) $\alpha\text{-Al}_2\text{O}_3$ pretreated by exposure to 500 W H_2S plasma for 10 min at substrate temperature of 600°C (RMS=158 nm). Scale bars are $1\ \mu\text{m}$.

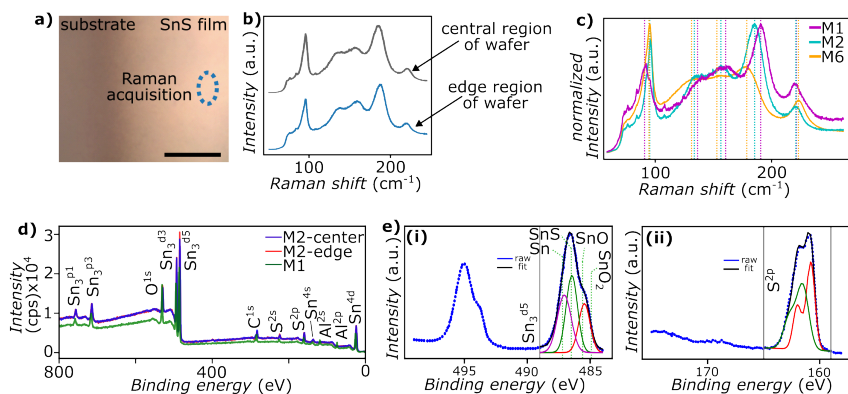


Figure A.13: Confirmation of chemical uniformity of the SnS thin film and Raman comparison of M1, M2 and M6. a) Microscope image of the edge region of the wafer. Scale bar is $20\text{ }\mu\text{m}$. b) Comparison of Raman spectra obtained at the central region of the film (shown in main text) and the edge region (highlighted in a)). c) The Ag(1) mode is blue shifted in M2–M6 compared to M1. Ag(2) and Bg modes are red shifted in M2–M6 compared to M1 (more for M6 which has roughly half of M2’s film thickness). These observations are coherent with strain as the primary cause for inter-sample Raman shift differences. Intensities have been normalized to aid visual comparison. d) large range XPS survey scan comparing M1 and edge/center of the wafer in M2. e) detailed XPS scans of (i) Sn3d5 and (ii) S2p signal on M2. We attribute the three Sn3d5 peaks to SnS, SnO and SnO₂ at the surface of the film (see also Figure 4.7 f). The dotted lines in (i) indicate values from literature (M. Fondell, M. Gorgoi, M. Boman, A. Lindblad, Journal of Electron Spectroscopy and Related Phenomena 2014, 195–195). The two doublets observed in the S2p spectrum in (ii) are separated by 0.93 eV. This can be attributed to bulk/surface coordination differences (G. Von Oertzen, S. Harmer, W. Skinner, Molecular Simulation 2006, 32, 15–1207). XPS spectra were recorded using a monochromatized photon beam with 1486.6 eV and spot size of $100\text{ }\mu\text{m}$.

A.0.3 Additional Supporting Info: SnS as Thermal Insulator

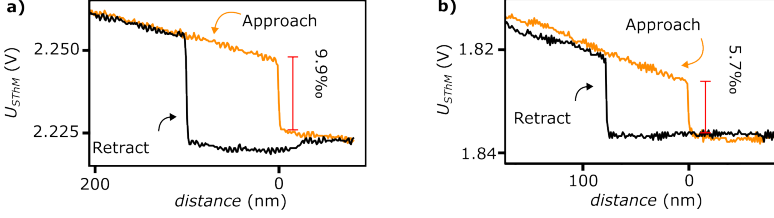


Figure A.14: Approach curves recorded on a) Si and b) Al_2O_3 for dataset B in main text. The same probe yields more variation on the Si substrate due to its higher thermal conductivity.

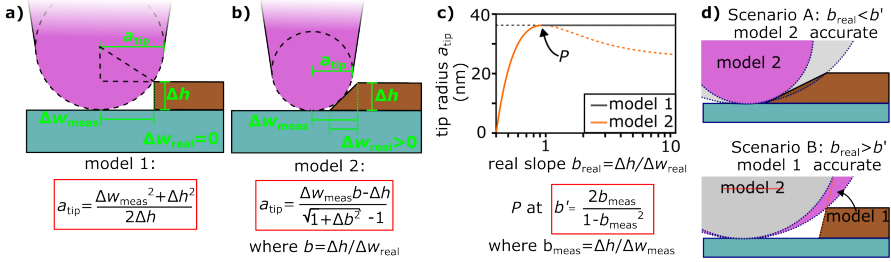


Figure A.15: Illustration of edge slope impact on tip radius a_{tip} estimate. a) and b) show idealized cases for when the grain's slope may or may not be omitted (model 1 and model 2, respectively). c) demonstrates the error for a given scenario with $b_{\text{meas}}=0.4$; for $b_{\text{real}} < b'_{\text{real}}$ model 1 overestimates a_{tip} and model 2 is accurate and vice versa. d) shows both scenarios for this exemplary case.

As discussed in the main text, the effective radius a_{eff} of the thermal contact area plays a crucial role in the analysis of scanning thermal microscopy (SThM) data. Here, we discuss two potential sources of error on a_{eff} in more detail: omitting the finite slope of grain edges (here modeled as straight slopes) and the overestimate of the contribution of the physical tip radius a_{tip} to the effective

radius for thermal transport a_{eff} . Fig.A.15 illustrates the former potential source of error coming into play when

$$b_{\text{real}} < b' = \frac{2b_{\text{meas}}}{1 - b_{\text{meas}}^2}, \quad (\text{A.1})$$

where $b_{\text{real}} = \Delta h / \Delta w_{\text{real}}$, $b_{\text{meas}} = \Delta h / \Delta w_{\text{meas}}$ are the real and measured slope of the grain edges, respectively.

Given b_{real} , this relation provides a quantifiable threshold useful for assessing whether the grain edge slope can be neglected. In Fig.A.16 a) and b) we estimate a lower limit for b_{real} from a high resolution tapping-mode AFM image taken on the more continuous part of the film.

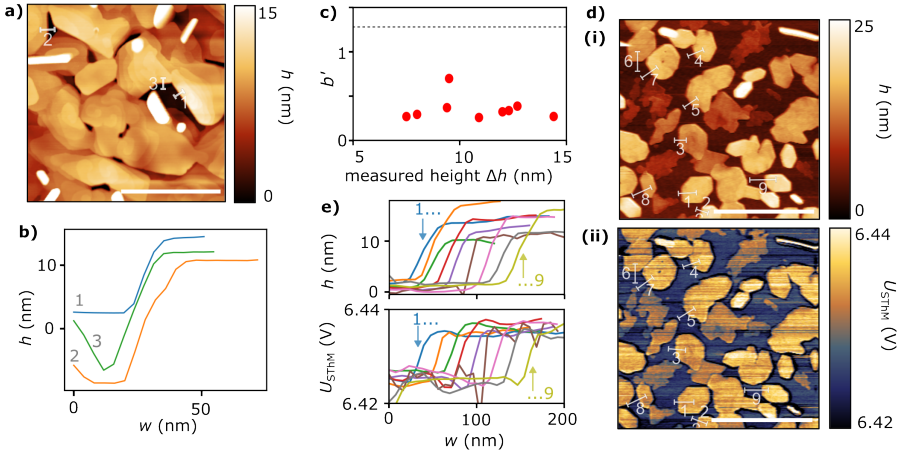


Figure A.16: Topographic and SThM data for the estimate of a_{eff} . a) High resolution tapping-mode AFM of semi-continuous part of SnS film. b) Profiles extracted from edges in a). c) b' extracted from topographic profiles in d)(i). The dotted line represents the lower limit estimate of b_{real} extracted from b). d) Topographic and SThM signal maps. Indicated profile lines correspond to profiles in e) (labelled 1-9 from left to right). Scale bars in all images are $1 \mu\text{m}$.

We obtain $b_{\text{real}} \geq 1.28$. In Fig.A.16c), we compare b' in Eqn.A.1 (computed for profiles 1-9 across grain edges in topographic data in Fig.A.16 d)(i)) to this lower limit. We find the condition is not met for any of the measured grain edges. Consequently, using model 1, we obtain $a_{\text{tip}} = (58.2 \pm 24.8) \text{ nm}$. To estimate the contribution of the physical tip radius a_{tip} to the effective thermal contact radius a_{eff} , we compare the aforementioned topographic profiles 1-9 to

their corresponding counterparts in the SThM signal (Fig.A.16 d)(i) and (ii) and e)). The widths of the SThM profile steps are consistently smaller than the width of the corresponding topographic steps by an average factor $c = 0.72$. Factoring in this correction into our measurement of topographic width w in our estimate from model 1 finally yields $a_{\text{eff}} = (32.7 \pm 13.9) \text{ nm}$.

We performed finite element modeling to assess the impact of the lateral boundaries on the thermal spreading resistance. We model the grain with a fixed thickness of 20 nm, resting on an alumina substrate and vary the grain radius. The substrate is a square of 10 μm lateral size. The SThM tip is modeled as a circular heat source on the grain surface. To determine the thermal spreading resistance, we compute the average temperature rise in the circle and normalize to the power injected, as $R_{\text{th}} = dT/Q$. We performed the simulations for the two tip contact radii used in the experiments (32 nm and 74 nm). The results are shown in Fig. A.17 a). It can be observed that the grain radius only has a marginal effect on thermal resistance.

Next, by systematically changing the in-plane and out-of-plane thermal conductivity of the grain, we obtained a thermal resistance heatmap to study the impact of the anisotropy. For both, a 10 nm (Fig. A.17 b)(i)) and a 20 nm (Fig. A.17 b)(ii)) thick grain, it can be observed that the in-plane thermal conductivity (horizontal axis) has less impact on the measured thermal resistance than the out-of-plane thermal conductivity (vertical axis).

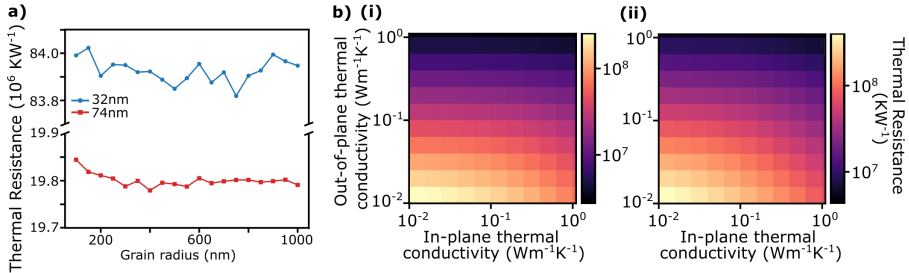


Figure A.17: Finite element modeling of the grain radius impact a) and thermal conductivity anisotropy b) on the thermal spreading resistance. In a), two contact radii are used, as in the experiment. In b), the results are shown for a 10 nm (i) and a 20 nm (ii) thick grain.

A.0.4 Additional Supporting Info: Co-S Fingerprinting

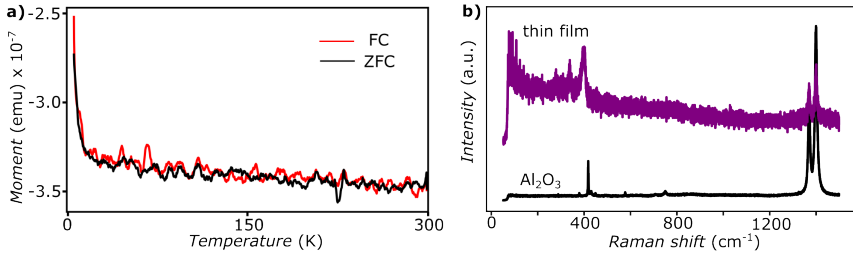


Figure A.18: a) In-plane magnetization measured as a function of temperature, under an applied field of 200 Oe, after zero-field cooling (ZFC) and after field cooling (FC). b) Raman spectra recorded at large range of the Al_2O_3 substrate and Co-S thin film. No additional peaks are observed on the Co-S film beyond 450 cm^{-1} .

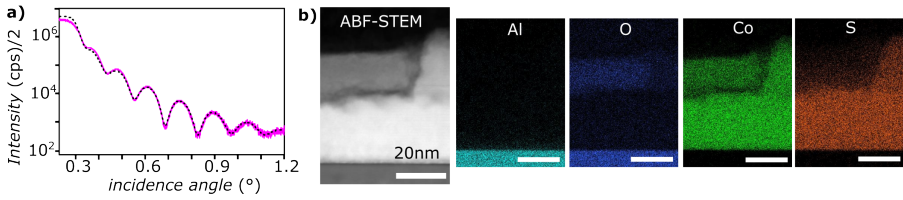


Figure A.19: a) XRR spectra and model fit (black, dotted) of a 28nm thick Co-S layer. This value matches ABF-STEM observations of large scans as presented in the main text. b) ABF-STEM and EDS maps of a protruding grain. The protruding grain shows a low degree of oxidation despite exposure to ambient conditions.

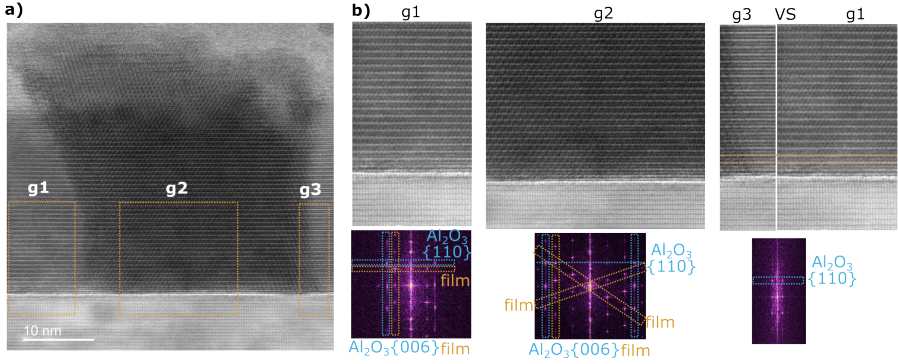


Figure A.20: Extraction of lattice spacings from ABF-STEM maps. a) Full ABF-STEM map of transitional area discussed in the main text. Areas g1-g3 used for lattice spacing extraction are highlighted. b) FFT analysis of g1 and g2. Parts of the pattern corresponding to the Al_2O_3 substrate are highlighted in blue. The overlapping point corresponds to $2.40 \text{ \AA}$ (in plane) and $4.37 \text{ \AA}$ (out of plane) of the $\{110\}$ and $\{006\}$ in Al_2O_3 , respectively. Consequently, we deduce lattice spacings of the film; $3.66 \text{ \AA}$ (in-plane), $5.72 \text{ \AA}$ (out-of-plane) in g1 and $3.06 \text{ \AA}$ (in-plane), $5.59 \text{ \AA}$ (out-of-plane) in g2, respectively. Atoms in area g3 are densely packed in the in-plane direction limiting the resolution in FFT. A direct comparison with g1 shows equivalent out-of-plane lattice spacing. Combined with the alternating contrast we surmise g3 to be a Co_9S_8 grain with a relative in-plane rotation compared to g1.

Growth Conditions

Sample Name	Substrate		Growth parameters				Analytics		
	Sub.	Sub. T [C]	Sn T [C]	Co-current [mA] (set/real)	H2S power [W]	time [min]	chamber pressure [torr]	H2S foreline pressure [Torr]	RBS obtained
CoSn1	Si	50	1100	31/27.8	na	30	1.20E-08	na	yes
CoSn2	Si	300	1100	31/27.8	na	30	2.50E-07	na	yes
CoSn3	Sa	50	1100	31/27.8	na	30	7.00E-09	na	no
CoSn4	Sa	450	1100	31/27.8	na	30	1.80E-08	na	no
CoSn5	Sa	450	1100	31/27.8	na	30	7.84E-09	na	no
CoSn6	Sa	300	1100	31/27.8	na	30	6.60E-09	na	no
CoSn7	Sa	50	1100	26	na	120	1.30E-07	na	yes
CoSn8	Sa	50	1100	26.5/23.3	na	120	9.50E-08	na	yes
CoSn9	Sa	50	1100	25.5/22.2	na	120	8.80E-08	na	yes
CoSn10	Sa	50	1100	24.5/21	na	120	3.40E-08	na	yes
CoSn11	Sa	350	1100	26.5/23.3	na	120	1.06E-08	na	yes
CoSn12	Sa	70	1130	31/27.8	na	30	1.30E-08	na	yes
CoSn13	Sa	60	1150	31/27.8	na	30	8.80E-08	na	yes
CoSn14	Sa	350	1130	27.5/23.9	na	30	2.80E-08	na	yes
CoSn15	Sa	450	1130	27.5/23.9	na	30	??	na	yes
CoSn16	Sa	250	1130	27.5/23.9	na	30	??	na	yes
CoSn17	Sa	350	1150	29/25.7	na	30	7.14E-09	na	yes
CoSn18	Sa	700	1130	30/26.9	na	30	4.36E-08	na	no
CoSn19	Sa	700	1150	30/26.9	na	30	3.83E-08	na	yes
CoSn20	Sa	700	1170	30/26.9	na	30	??	na	yes
CoSn21	Sa	350	1190	30/26.9	na	30	9.00E-09	na	yes
CoSn22	Sa	350	1170	30/26.9	na	30	8.80E-09	na	yes
CoSn23	Sa	350	1150	30/26.9	na	30	1.04E-08	na	yes
CoSn24	Sa	700	1190	27/23.5	na	30	6.25E-08	na	yes
CoSn25	Sa	700	1200	27/23.5	na	30	3.50E-08	na	yes
CoSn26	Sa	350	1170	30/26.9	na	30	2.00E-05	na	no
Explored range	Si, Sa	50	1100	21	na	30	7.00E-09	na	na
		-700	-1200	-27.8 (real)		-120	-2.00E-05		

Table A.1: All growth conditions explored in this work for binary Co-Sn system. Si refers to Silicon(001) wafers, Sa refers to α -Al₂O₃(006) wafers. A summary of the explored parameter range is given in the last row.

Sample Name	Substrate			Growth parameters				Analytics	
	Sub.	Sub. T [C]	pre-treatment	Sn T [C]	Co [mA] (set/real)	H2S power [W]	time [min]	chamber pressure [torr]	RBS obtained
sapp10/SnS1	Sa	350	na	1170	na	600	60	1.49E-05	yes
SnS2	Sa	370	10min 750C+H2S	1130	na	100	60	4.60E-06	yes
SnS3	Sa	370	10min 750C+H2S	1130	na	100	6	4.50E-06	yes
SnS4	Sa	370	10min 400C	1130	na	100	60	5.00E-06	yes
SnS5	Sa	350	10min 600C+H2S	1130	na	100	60	4.50E-06	yes
SnS6	Sa	350	10min 750C+H2S	1130	na	100	60	4.50E-06	yes
SnS7	Sa	350	10min 750C+dH2S	1130	na	100	60	1.49E-05	yes
SnS8	Sa	350	10min 750C+bake	1110	na	100	60	5.99E-06	yes
SnS9	Sa	350	10min 750C+bake	1150	na	100	60	5.80E-06	yes
SnS10	Sa	350	10min 750C+H2S	1130	na	100	60	5.70E-06	yes
SnS11	Sa	350	20min 750C+H2S	1130	na	100	60	5.60E-06	yes
SnS12	Sa	350	30min 750C+H2S	1130	na	100	60	5.50E-06	yes
SnS13set	various	350	30min 750C+H2S	1130	na	100	60	5.55E-06	yes
SnS14set	STO	350	30min 750C+H2S	1130	na	100	60	7.50E-06	yes
SnS15	STO	350	30min 750C	1130	na	100	60	7.30E-06	yes
CSS43	Sa	370	10min 750C	1130	27.5/23.9	100	60	5.4-5.5E-6	yes
CSS44	Sa	370	10min 400C	1130	27.5/23.9	100	60	5.4-5.8E-6	yes
CSS45	Sa	370	10min 750C+H2S	1130	27.5/23.9	100	60	5.2-5.5E-6	yes
CSS46	Sa	370	30min 750C+H2S	1130	27.5/23.9	100	60	5.4-E-6	yes
CSS47	Sa	370	10min 750C+H2S	1130	27.5/23.9	100	60	5.07-E-6	yes
Explored Range	Sa+, STO	350 -370	10-30min, 400-750C, vac/H2S/dH2S	1110 -1170	off/23.9(real)	100/600	6\60	5.0e-6 -1.5e-5	na

Table A.2: All growth conditions explored in this work for binary Sn-S system. Sa refers to α -Al₂O₃(006) wafers Sa+ refers to amorphous Al₂O₃ deposited on Si/Sa, STO refers to SrTiO₃. dH2S refers to plasma generated from H₂ gas diluted with H₂. A summary of the explored parameter range is given in the last row.

Sample Name	Substrate			Growth parameters				Analytics	
	Sub.	Sub. T [C]	pre-treatment	Sn T [C]	Co [mA] (set/real)	H2S power [W]	time [min]	chamber pressure [torr]	RBS obtained
CoS1	Sa	420	10min 450C	na	38.5/X	100	60	5.00E-06	yes
CoS2	Sa	420	10min 750+H2S	na	38.64/33.9-34.5	100	60	4.50E+06	yes
CSS2	Sa	300	10min 450C	1130	31	600	30	1.00E-05	yes
CSS4	Sa	350	10min 450C	1130	27	600	60	Around 9e-6	yes
CSS19	Sa	450	10min 500C	1160	28/24.5	600	60	1.28E-05	yes
CSS24	Sa	450	10min 500C	1130	27.5/23.9	600	60	1.33E-05	yes
CSS27	Sa	450	10min 450C	1130	27.5/23.9	400	60	1.02E-05	yes
CSS30	Sa	450	10min 450C	1190	29/25.7	600	60	1.22E-05	yes
CSS52	Sa	420	20min 450C	1130	29/25.7	100	60	5.9-5.3E-6	yes
CSS53	Sa	420	10min 450C	1130	30/26.9	100	60	5.7-5.1E-6	yes
CSS54	Sa	420	10min 450C	1130	31/27.8	100	60	5.3-5.1E-6	yes
CSS55	Sa	420	10min 450C	1130	32/28.1	100	60	5.8-5.1E-6	yes
Explored range	Sa	300-450	10/20min, 450/500C, vac/H2S	1130-1190	27.5-32	100-600	30-60	4.5e-6-1.3e-5	na

Table A.3: All growth conditions explored in this work for binary Co-S system. Sa refers to α -Al₂O₃(006) wafers. A summary of the explored parameter range is given in the last row.

Sample Name	Substrate			Growth parameters			chamber pressure [Torr]	Analytics		RBS obtained
	Sub.	Sub. T [C]	Sn T [C]	Co-current [mA] (set/real)	H2S power [W]	Growth time [min]		H2S foreline pressure [Torr]		
CSS1	Sa	300	1130	31	600	30	1.10E-05			yes
CSS2	Sa	300	1130	31	600	30	1.00E-05			yes
CSS3	Sa	400	1130	31	600	30	9.40E-06			yes
CSS4	Sa	350	1130	27	600	60	Around 9e-6			yes
CSS5	Sa	350	1130	25	600	60	8.70E-06			yes
CSS6	Sa	350	1180	30	600	30	8.30E-06			yes
CSS7	Sa	50	1190	30/26.3	600	30	1.50E-05	1.23E-05		yes
CSS8	Sa	350	1190	30/26.4	600	30	1.50E-05	1.14E-05		yes
CSS9	Sa	350	1130	27.5/23.9	600	60	1.52E-05	1.04E-05		yes
CSS10	Sa	50	1130	27.5/23.9	600	60	1.45E-05	1.05E-05		yes
CSS11	Sa	350	1130	27.5/23.9	600	60	1.40E-05	1.06E-05		yes
CSS12	Sa	350	1160	27.5/23.9	600	60	1.30E-05	1.02E-05		yes
CSS13	Sa	350	1190	27.5/23.9	600	60	1.30E-05	9.98E-06		yes
CSS14	Sa	350	1130	29/25.7	600	60	1.40E-05	1.09E-05		yes
CSS15	Sa	350	1190	29/25.7	600	60	1.30E-05	1.02E-05		yes
CSS16	Sa	350	1190	28/24.5	600	60	1.33E-05	1.02E-05		yes
CSS17	Sa	350	1160	28/24.5	600	60	1.33E-05	9.58E-06		yes
CSS18	Sa	250	1160	28/24.5	600	60	1.32E-05	9.98E-06		yes
CSS19	Sa	450	1160	28/24.5	600	60	1.28E-05	1.03E-05		yes
CSS20	Sa	400	1160	28/24.5	600	60	1.34E-05	9.57E-06		yes
CSS21	Sa	300	1160	28/24.5	600	60	1.30E-05	9.64E-06		yes
CSS22	Sa	350	1130	27.5/23.9	600	60	1.33E-05	1.02E-05		yes
CSS23	Sa	350	1130	27.5/23.9	600	60	1.22E-05	7.46E-06		yes
CSS24	Sa	450	1130	27.5/23.9	600	60	1.33E-05	8.30E-06		yes
CSS25	Sa	350	1130	27.5/23.9	250	60	7.41E-06	4.88E-06		yes
CSS26	Sa	350	1130	27.5/23.9	400	60	1.05E-05	7.27-7.52E-6		yes
CSS27	Sa	450	1130	27.5/23.9	400	60	1.02E-05	7.28-7.57E-6		yes
CSS28	Sa	350	1130	27.5/23.9	600	60	1.33E-05	1.04-1.08E-5		yes
CSS29	Sa	350	1190	29/25.7	600	60	1.20E-05	8.20E-06		yes
CSS30	Sa	450	1190	29/25.7	600	60	1.22E-05	8.46E-06		yes
CSS31	Sa	350	1190	29/25.7	400	60	9.45-9.35E-6	6.0-6.88E-6		yes
CSS32	Sa	350	1190	29/25.7	400	60	9.02E-06	6.8-7.6E-6		yes
CSS33	Sa	350	1190	29/25.7	400	20	9.32E-06	7.88-7.7E-6		yes
CSS34	Sa	350	1130	27.5/23.9	100	60	6.6-5.6E-6	6.8-7.0E-6		yes
CSS35	Sa	350	1110	27.5/23.9	100	60	6.0-5.9E-6	7.4-6.9E-6		yes
CSS36	Sa	350	1090	27.5/23.9	100	60	6.1-5.8E-6	7.5-7.0E-6		yes
CSS37	Sa	350	1090	27.5/23.9	0	60	1.73-E-5	1.16-E-5		yes
CSS38	Sa	350	1090	27.5/23.9	600	60	1.27-1.24E-5	1.6-1.1E-5		yes
CSS39	Sa	350	1090	27.5/23.9	50	60	6.35-6.1E-6	6.43-6.8E-6		yes
CSS40	Sa	350	1130	27.5/23.9	100	20	5.96-5.9E-6	6.96-6.8E-6		yes
CSS41	Sa	370	1130	27.5/23.9	100	60	5.53-5.5E-6	7.75-7.0E-6		yes
CSS42	Sa	390	1130	27.5/23.9	100	60	5.75-E-6	7.53-E-6		yes
CSS43	Sa	370	1130	27.5/23.9	100	60	5.4-5.5E-6	7.48-8E-6		yes
CSS44	Sa	370	1130	27.5/23.9	100	60	5.4-5.8E-6	7.41-8E-6		yes
CSS45	Sa	370	1130	27.5/23.9	100	60	5.2-5.5E-6	7.0-7.5E-6		yes
CSS46	Sa	370	1130	27.5/23.9	100	60	5.4-E-6	6.49-E-6		yes
CSS47	Sa	370	1130	27.5/23.9	100	60	5.07-E-6	8.0-E-6		yes
CSS48	Sa	370	1130	29/25.7	100	60	5.3-E-6	6.6-E-6		yes
CSS49	Sa	370	1130	30/26.9	100	60	5.90E-06	6.76E-06		yes
CSS50	Sa	410	1130	29/25.7	100	60	5.9-5.3E-6	6.8-7.3E-6		no
CSS51	Sa	410	1130	27.5/23.9	100	60	5.7-5.3E-6	7.7-7.3E-6		no
CSS52	Sa	420	1130	29/25.7	100	60	5.9-5.3E-6	7.6E-6.78		no
CSS53	Sa	420	1130	30/26.9	100	60	5.7-5.1E-6	7.8-E-6		yes
CSS54	Sa	420	1130	31/27.8	100	60	5.3-5.1E-6	7.7-E-6		yes
CSS55	Sa	420	1130	32/28.1	100	60	5.8-5.1E-6	7.1-7.3E-6		yes
CSS56	Sa	370	1130	29/25.7	100	60	5.14-5.1E-6	7.2-7.8E-6		yes
CSS57	Sa	420	1130	30/26.9	100	60	5.07-E-6	7.55-E-6		yes
CSS58	Sa	420	1130	30/26.9	100	60	5.53-E-6	7.03-E-6		yes
CSS59	Sa	420	1110	29/25.7	100	60	5.3-5.1E-6	7-6.5E-6		yes
CSS60	Sa	390	1110	29/25.7	100	60	5.1-E-6	7.1-E-6		yes
CSS61	Sa	370	1130	32/28.1	100	60	4.8-E-6	6.0-E-6		no
CSS62	Sa	370	1150	32/28.1	100	60	sameish	sameish		no
CSS63	Sa	370	1130	32/28.1	100	60	2.32E-05	1.68E-05		no
CSS64	Sa	370	1130	33/29.2	100	60	2.32E-05	1.77E-05		no
CSS65 aka F1	Sa	350	1225 -1216	40/35.2	100	20	5.98E-06	1.02E-05		yes
Explored Range	Sa	50-450	1030 -1250	27.5/23.9 -40/35.2	0-600	20-60	1 E-6 -2.3 E-5	5E-6 - 1.8E-5		no/yes xD

Table A.4: All growth conditions explored in this work for ternary Co-Sn-S system. Sa refers to α -Al₂O₃(006) wafers. H2S refers to plasma generated from H₂S gas. Sample F1 can be found in the second last row. A summary of the explored parameter range is given in the last row.