Three-Dimensional Defect Characterization: Focused Ion Beam Tomography Applied to Tin Sulfide Thin Films

by

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ABSTRACT

Porosity is postulated to be one of the reasons for the low efficiency of tin sulfide-based devices. This work is a preliminary investigation of the effects of two film growth parameters — deposition rate and substrate temperature — on porosity. We employ the focused ion beam tomography technique to characterize and quantify porosity in tin sulfide thin films. We then generate 3D reconstructions of pores inside milled volumes from the films and quantify pore volumes. To explain the results, we employ nucleation theory and develop two different models: (a) a thermodynamic model that assumes pores form primarily from an effect known as “self-shadowing,” whereby growth-rate anisotropy results in some grains that grow faster than their neighbors, and (b) a kinetic model that assumes a diffusion-driven process of void formation. We show that both models qualitatively support the experimental results, providing insight into process-structure relations that may improve film quality during growth.

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1.1 Solar Energy Overview

With the depletion of fossil fuel reserves in nature, the demand for renewable energy sources is increasing. The most abundant and environment friendly renewable energy source available on Earth is solar energy [1]. In fact, if the energy delivered by the sun to Earth in two hours can be completely harnessed, it will provide the total energy consumed by human activities throughout a year. The more efficiently solar energy can be converted into electricity, the less greenhouse gases may be emitted from using conventional energy sources [2]. Photovoltaic (PV) energy conversion has the potential to contribute significantly to the electrical energy generation [1]. In 2014, the production of solar cell module is expected to increase by 25% generating 49.7 GW compared to 39.7 GW in 2013. These figures take into account the improvements in the quality of wafers produced, which in turn increase the efficiency and reduce the cost per watt generated from multi-crystalline silicon modules [3].

Technologies in the solar industry are categorized into three different groups depending on their level of development: (1) first-generation PV that includes crystalline silicon technology, (2) second-generation PV that includes thin films such as amorphous silicon, copper indium gallium diselenide (CIGS), and cadmium telluride (CdTe), and (3) third-generation PV, which includes high-efficiency technologies still in the early stages of research [4].
Crystalline silicon currently dominates the solar industry with a market share of approximately 91% of all commercial production, while CIGS and CdTe comprise the most of the remainder [1, 4, 5]. This common utilization of silicon in the market is mainly due to the deep knowledge acquired throughout sixty years of research in this field, hence driving the cost of silicon based solar cells down compared to other technologies [5]. Lately, much effort has been channeled toward the thin-film PV industry, with particular interest in high-rate deposition techniques. The advantage that thin films have over crystalline silicon is that they are in principle much easier to manufacture and use less material because they are strong light absorbers that a thickness of one micron is enough to help reduce material cost [4]. Despite all this technological advancement, the cost of electricity produced by PV is still not competitive compared to conventional sources [1].

1.2 Tin Sulfide Thin Films

The two most prominent materials used as absorber layers in the thin film solar cells industry are cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) [6], which are direct bandgap materials having a high absorption coefficient of $10^4 - 10^5 \text{cm}^{-1}$ [7]. Both CdTe and CIGS yield cell efficiencies larger than 16% [7, 8]. Although major advancements have been made regarding these two materials, apprehension remains concerning the toxicity and environmental issues associated with the disposal of cadmium, indium [1, 6, 8, 9] and tellurium [9, 10]. Cadmium has an average crustal abundance of 0.1 parts per million (ppm), indium’s abundance is on the order of 0.1 ppm and tellurium exists in the Earth’s crust in 5 ppb while silicon makes up 28.15% of the crust making it the second most abundant element [11]. It would
be desirable to find an alternative thin-film semiconductor material that has the Earth-abundance of silicon, coupled to the performance of CIGS and CdTe. Tin sulfide, a IV-VI compound semiconductor, is a potential candidate absorber layer in thin film solar cells, given its near-optimal direct bandgap for sunlight photoconversion of 1.3 eV and indirect bandgap of 1.1 eV [9, 10, 12, 13, 14]. Figure 1.1 shows the range within which the bandgap of tin sulfide can be tuned; it clearly falls in the optimal spectral irradiance region. Also, tin and sulfur are environmentally benign, non-toxic and abundant in the Earth’s crust [10, 12, 13, 14], 2 and 260 ppm for tin and sulfur respectively [11], therefore enabling SnS solar cells to be scaled up to terawatt levels at low cost [9, 10, 12, 13, 14]. Besides all these advantages, tin sulfide has a low melting temperature allowing easily achievable film stoichiometry by thermal evaporation [15]. Nogushi et al. measured the resistivity, carrier density and Hall mobility of vacuum deposited p-type SnS thin films using the van der Pauw technique and reported values for resistivity of 13 – 20 Ω, a carrier concentration of $6.3 \times 10^{14} - 1.2 \times 10^{15}$ cm$^{-3}$ and a high Hall mobility of 400 – 500 cm$^2$/Vs [16]. Theoretically, tin sulfide based solar cell devices should be able to reach a solar conversion efficiency of 32%. In practice, the highest efficiency achieved so far doesn’t exceed 5%.

Therefore, it is necessary to characterize the material to investigate the reasons behind its low performance, and define areas of potential improvements [1, 9, 12]. Growing dense films of tin sulfide is a requirement for better efficiency because this will make use of its high optical absorption and reduce recombination at internal surfaces. One area that remains to be explored is bulk characterization of the absorber layer and the examination of its uniformity, porosity, and possible pinholes. In fact, the surface of thermal co-evaporated SnS thin films has been comprehensively imaged by scanning electron microscopy and it has been observed that these
polycrystalline films have both compact and porous regions at the surface. Thus, there is a need to investigate the bulk and identify whether the porous regions are confined to the surface, or they extend into the bulk of the film [17]. For this purpose, a 3D tomography technique is needed.

![Solar Spectra versus Wave Energy](image)

Figure 1.1: Solar spectra versus wave energy (dashed lines show tunable bandgap range of SnS).

### 1.3 Focused Ion Beam Tomography

With the development of nanotechnology, high resolution microscopy's importance is increasing, and several techniques such as scanning electron microscopy, transmission electron microscopy and atomic force microscopy have the ability of exposing nanometer scales. However, these methods are powerful for either two-dimensional or topological information [18].
Methods based on synchrotron and X-ray microscopy have been recently used for tomography of sequences of transmitted projections from a specimen. This volumetric information with tenths of a micron resolution is non-destructive and uses absorption contrast from various phases or pores in the sample to perform the reconstruction [19, 20]. However, the synchrotron is not easily accessible and the use of a technique with higher throughput and spatial resolution is desired.

Focused ion beam (FIB) tomography is a unique and powerful technique that covers the required range in resolution to investigate many microstructure effects with characteristic length on the order of 10 to 100 nm in modern semiconductor materials. Figure 1.2 shows an evolution of the technique toward larger volumes and higher resolution. The arrows show an expansion of the voxel matrix to the left and to the top, as the ion beam and detectors capacities are evolving, which increases the representativity of the data collected by FIB tomography. A larger voxel matrix means a larger volume examined and a smaller voxel size means better resolution. This improvement allows larger sample volumes (2000 μm³), containing larger number of particles while being able to examine particles as small as 5 nm in dimension, which is essential for any statistical analysis. The technique requires sequential FIB cross-sectioning and scanning electron microscopy imaging which allows the acquisition of a stack of micrographs used for volume rendering and reconstruction of the milled away volume based on contrast difference. The main limitations for the techniques are the slow data collection time, image quality and drift issues [21, 22].
One of the many applications of FIB tomography is in the field of energy technology. It is utilized to distinguish between internal surfaces and three phase boundaries as active or inactive electrochemical reactive sites. This helps understand the effect of microstructure on the performance of fuel cells and batteries and provides insights for improvements [23, 24]. Another application is investigating porous materials such as rocks, membranes, filters, and ceramics, to elucidate the relationship between the microstructure, pore homogeneity and mass transport processes [18, 25, 26].

![Figure 1.2: Resolution of FIB tomography compared to other 3D microscopy techniques, from Ref. [27]. The enlargement of the voxel matrix for FIB tomography up means larger volume of material capable of being analyzed, while the expansion to the left means higher spatial resolution with evolving technologies.](image-url)
In this work, our goal is to characterize the microstructure of tin sulfide thin films and quantify their porosity. Characterization of porosity is key as pores affect thin films performance adversely by lowering optical absorption because of the lower density, possible shunting of the devices if pores were large enough to act as pinholes in the absorber layer [28], being potential recombination active sites, reducing mechanical stability etc. Deposition rate and substrate temperature are two growth parameters that are known to affect the morphology of thermal evaporated SnS films via size of nuclei, nucleation site density and possible high diffusion rate at high enough substrate temperatures.

The main question to be addressed is: How is tin sulfide thin film porosity affected by deposition rate and substrate temperature?
2.1 Thermal Evaporation

Physical vapor deposition is employed in the large scale manufacturing of many electronic devices and thin film photovoltaics because of its ability to produce a high throughput while having a low cost. This technique encompasses three successive phases: vaporization, transport and deposition. Precursors of the desired elements to be deposited are heated to high temperatures in a crucible until they reach vapor phase [29]. The vapor precursors are transported by their kinetic energy of vaporization across the vacuum chamber from the heated source to the substrate and mixed right before condensing on the substrate and forming the desired crystal [29, 30].

Tin sulfide thin films have been grown using several different techniques so far, such as electro-deposition [31, 32], chemical bath deposition [33, 34], spray pyrolysis [35], plasma enhanced chemical vapor deposition [36, 37], sputtering [12, 14], atomic layer deposition [13, 38, 39] and thermal evaporation [1, 6, 16, 40, 41, 42].
Physical vapor deposition requires a high vacuum deposition chamber ($\sim 10^{-6}$ Torr) to reduce contamination of the deposit by controlling the amount of gas and vapor in the chamber. Also, high vacuum increases the length of the mean free path between the vaporization source and the substrate [44], reducing collisions of the source atoms with the background species [45].

The mean free path is the average distance traveled by a molecule before colliding with other molecules and it is proportional to $T/p$, where $T$ is the temperature and $P$ is the pressure [44]. Assuming the particle has a diameter $D$ and is moving at a speed $v$ with a number density of $n/V$, where $n$ is the total number of particles or molecules in a volume $V$, the collision cross-section area is $\pi D^2$. The collision volume swept during a period of time $dt$ is $\pi D^2 v dt$. The number of collisions during a time $dt$ is $\left(\frac{n}{V}\right)\pi D^2 v dt$. Finally, the mean free path is given by
\[ \lambda = \frac{v dt}{\text{number of collisions}} \]  
\hspace{1cm} \text{(Eq. 2.1)}

The derivation of Eq. 2.1 assumes that the background particles are at rest. This is an inaccurate assumption since the background particles actually have a high average velocity. Therefore, the average relative velocity should be used in the mean free path equation, which is given by

\[ v_{\text{rel}} = \sqrt{2}v \]  
\hspace{1cm} \text{(Eq. 2.2)}

Replacing Eq. 2.2 in Eq. 2.1 and using the ideal gas law such as \( PV = Nk_B T \), where \( k_B \) is the Boltzmann constant, we obtain the following result for the mean free path [45]

\[ \lambda = \frac{k_B T}{\sqrt{2\pi D^2 P}} \]  
\hspace{1cm} \text{(Eq. 2.3)}

---

**Figure 2.2:** Mean free path versus pressure for different chamber temperatures (log-log scale).
The pressure in the chamber during thermal evaporation of the studied samples was between $5 \times 10^{-7}$ Torr and $1 \times 10^{-6}$ Torr, which from the graph and assuming room temperature leads to a mean free path between 25.5 and 56 meters. With a chamber of side on the order of one meter, this mean free path is long enough for molecules to travel independently one of another. Therefore the atomic flux is directional, and self-shadowing occurs when atoms traveling perpendicular to the substrate plane land on elevated surfaces, growing faster than others, leaving voids between neighboring grains.

Figure 2.3 and Figure 2.4 are two scanning electron micrographs showing respectively a mechanically cleaved cross-section and the top surface of a thermal evaporated tin sulfide film grown on borosilicate glass. Thermally annealed commercial tin sulfide powder is used as the precursor that is going to be sublimed in the thermal evaporator and deposited on the glass. The crystallites are plate-shaped growing in random orientation to one another, having visible voids in between each crystallite and its neighboring ones.

![Figure 2.3: Scanning electron micrograph of thermal evaporated SnS film (Side view), courtesy of K. Hartman.](image)
2.2 Control Parameters

The necessary control parameters to be measured and controlled in a thermal evaporation process are: the deposition rate, the substrate and source temperature, the distance between the source and the substrate surface [16, 46]. The substrate temperature affects the crystallinity of the film and its preferential crystal plane such that, below 200°C, the (111) crystal plane is the preferential plane orientation, whereas above 280°C the (040) plane becomes the most prominent crystal orientation to grow parallel to the substrate plane [1, 16]. Beside crystal structure, substrate temperature and source temperature affect the stoichiometric composition of the grown film [17]. Hence, we should inspect the $P, T, x$ (composition percent) phase diagram of tin sulfide to grow thin films under controlled stoichiometric conditions [47]. It has been shown that, for substrate temperatures between 300°C and 400°C, the vapor pressure of sulfur increases at a faster rate than the vapor pressure of tin causing sulfur to re-evaporate from the film. As a result,
films grown at increasingly higher substrate temperature are increasingly tin-rich [6, 35, 38, 41, 42], whereas increasing the source temperature yields more tin-rich films [42] and hence temperature and pressure influence the phases present in the film (Figures 2.5 and 2.6). Non-stoichiometric evaporation affects the bandgap of the absorber layer moving it away from the optimal bandgap of around 1.3 eV [6, 42]. Previous XRD measurements showed that the films grown by thermal co-evaporation at a substrate temperature around 300°C revealed a dominant SnS phase compared to other SnSx phases [17] (Figure 2.5).

![Figure 2.5: Sn-S Phase Diagram between 45 and 75 at. % S, from Ref. [48].](image-url)
Nonetheless, annealing sulfur rich films showed useful in reducing the sulfur content by re-evaporating some of the excess sulfur during the annealing process [50]. Also, it has been extensively tested experimentally that grain size increases with increasing substrate temperature [35] by scanning electron micrographs. This is believed to be caused by the increased surface diffusion of adatoms at higher temperatures, resulting in larger grains in the aim of reducing surface energy by reducing grain boundary areas [41]. Deposition rate is a measure of the thickness which affects the refractive index [51] along with the substrate temperature that also shows influence on the refractive index and the optical conductivity [52]. A substrate temperature of 300°C has proven to produce nearly stoichiometric tin sulfide films with a ratio Sn-to-S of 1.009 with a higher surface roughness compared to tin sulfide films grown by other
techniques. Nucleation process, growth and adatoms diffusion affect the roughness of the films. Also, the coalescence process of the nuclei is responsible for dislocations, the most likely defect that is encountered in thermally evaporated films. Due to relatively small grain sizes in vacuum evaporated films, low mobility is measured compared to other material since the carriers have to travel across multiple grain boundaries [1]. It has also been found that optical properties of SnS thin films are function of the thickness of thermally evaporated films [40]. In addition, the nature of the substrate can also affect the crystallinity, roughness, electrical resistivity [36, 53] and density of the films. For instance, measured films grown on molybdenum coated glass substrate are significantly denser than films grown directly on glass with similar growth parameters.

Besides previously discussed control parameters, the distance between the source and the substrate in a thermal evaporator affects the properties of the films such as the thickness, the roughness, the grain size, as well as the tin-to-sulfur atomic percent ratio which proved to decrease with increasing the distance. In fact, with a higher vapor pressure, sulfur atoms have a higher kinetic energy and thus scatter, more likely than tin atoms, away from the hot substrate at lower source-to-substrate distances. Due to the composition variation at different source-substrate distances, films grown at a distance lower than 15 cm have p-type conduction, while evaporation at a distance larger than 15 cm yield a n-type SnS films [46].

Regarding the porosity of the films, scanning electron micrographs revealed uniform thickness across the film with some pores on the surface in all the studies [50], however investigating the bulk of the film probing pores is still an area to be explored.
2.3 In-Situ Measurement Methods

In situ measurement of the mass of the film is required to calculate the deposition rate, which is a growth parameter that influences the properties of SnS films [13]. A quartz crystal microbalance (QCM) is used for this purpose based upon the piezoelectric effect [54]. This measurement is based on the frequency of the oscillations of a crystal which changes in a well understood fashion with the increase of the mass of the substrate. The oscillation frequency of the QCM is monitored by an external circuit. The frequency is converted to mass, which is then converted to thickness, and knowing the deposition period, the deposition rate can be then calculated. QCM can be applied to any film deposition and the measurement sensitivity is very high, which gives very accurate results [45]. This technique has a large detection range and can detect subtle changes such as monolayer addition coverage [54]. The characteristic mechanical oscillation frequency is produced in the crystal by applying an alternating electric field across the quartz crystal through the two metal electrodes sandwiching the quartz surface.

2.4 Samples Studied

<table>
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<td>150°C</td>
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<tr>
<td>Deposition rate</td>
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<td>4 Å/s</td>
</tr>
<tr>
<td>Film Thickness</td>
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<td>1 μm</td>
<td>1 μm</td>
<td>1 μm</td>
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</table>

Table 2.1: Growth parameters of the 4 studied samples.
From all the control parameters, only two growth parameters are changed: the deposition rate and the substrate temperature, and the effect of these two parameters on porosity in the films is investigated. Four samples are considered. For the first two samples, the substrate temperature is kept constant at 240°C while the deposition rate is varied in one sample it is 1 Å/s and this sample will be referred to as the low deposition rate sample, and 10 Å/s in the second sample which will be named high deposition rate sample. For the third and fourth samples, the deposition rate is kept constant, at a value between 1 and 10 Å/s which is 4 Å/s, while the substrate temperature is 150°C for the third sample which will be referred to as the low temperature sample and 300°C for the fourth sample which will be referred to as the high temperature sample. At the end of the deposition, we measure the film thickness to (1) validate the deposition rate measured from the quartz crystal microbalance, and (2) calculate the total volume of the milled region, which is an input to quantifying porosity.
FOCUSED ION BEAM TOMOGRAPHY

3.1 The Focused Ion Beam

The focused ion beam (FIB) system has analogous abilities to a scanning electron microscope (SEM) with an advantage of including a precision machining tool in the system capable of milling or depositing material from a gas layer above the sample on a nanometer scale. The FIB system has advantages over other systems such as photolithography for having better resolution, electron beam lithography for being faster and having higher momentum ions more effective in etching or milling a sample while imaging the sample simultaneously. Given its ability to sputter material off the sample while imaging, a dual beam system having a FIB column combined with an SEM column helps reduce the damage that may be caused by a long exposure time of the sample to the ion beam by using the SEM for imaging purposes [55].

3.1.1 Working Principle

A FIB requires a vacuum on the order of $1 \times 10^8$ Torr to avoid source contamination and electrical discharges in the ion column. As the pressure increases, the mean free path of the ions decreases and chances of interactions with the gas molecules increase [55, 56]. With a pressure of $P = 1 \times 10^8$ Torr the mean free path would be:

$$\lambda = \frac{k_B T}{\pi \sqrt{2PD^2}} = 542 \text{ m}$$  \hspace{1cm} (Eq. 3.1)
Where $k_B$ is the Boltzmann constant $1.38 \times 10^{-23} \text{ m}^2 \text{kg.s}^{-2} \text{K}^{-1}$, $D$ is the diameter of gallium which is $1.3 \, \text{Å}$ and $T$ is the temperature taken to be $295 \, \text{K}$.

The FIB system used is the Carl Zeiss NVision 40 dual beam system in which the FIB column provides a beam of gallium from a liquid metal ion source (LMIS) which allows an ion beam of diameter as small as $5 \, \text{nm}$ when operated at $30 \, \text{kV}$. Gallium is used for its many advantages promoting it for this application among which:

- Gallium has a melting temperature of $29.8^\circ \text{C}$, which reduces the heating requires to form a tip out of it and thus reducing inter-diffusion between the gallium and the tungsten needle that is wetted by the gallium, as shown in Figure 3.1.
- Gallium has a low volatility at $29.8^\circ \text{C}$ and a low vapor pressure which gives the source a longer lifetime.

![Figure 3.1: Liquid Metal Ion Source schematic, from Ref. [56].](image)
An electric field on the order of $1 \times 10^8$ V/cm is applied at the tip of the tungsten needle causing the formation of a conical source point of 2–5 nm. The extractor voltage ionizes the gallium by field evaporation which is constantly replaced by the liquid gallium flow. The extracted Ga$^+$ ions are accelerated through the column. The objective lens will focus the beam onto the sample. Apertures define the beam current reaching the sample by changing its size. As it hits the sample surface, atoms sputtered and electrons are ejected away in the form of secondary ions and secondary electrons which can be used to image the surface of the sample by means of appropriate detectors. Typically small currents (around 80 pA) are used to image in FIB mode in order not to damage the sample significantly while doing so [55].

Figure 3.2: Dual beam (FIB/SEM) schematic, reproduced from Ref. [57].
3.1.2 Interaction of ions/electrons with matter

The ions effect on the sample is qualitatively different than that of electrons. A focused beam of gallium ions colliding with the sample can knock off the sample atoms sputtering them away.

<table>
<thead>
<tr>
<th>Particles</th>
<th>FIB</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Ga⁺</td>
<td>Electron</td>
</tr>
<tr>
<td>Particle Size (nm)</td>
<td>0.2</td>
<td>1.0×10⁻⁵</td>
</tr>
<tr>
<td>Particle Mass (Kg)</td>
<td>1.16×10⁻²⁵</td>
<td>9.1×10⁻³¹</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of FIB ions and SEM electrons.

The energy of an accelerated particle is given by:

\[ E = \frac{1}{2} mV^2 \]  (Eq. 3.2)

The momentum of the particle is the product of its mass and velocity. Both an electron and a gallium ion are accelerated with the same energy in the FIB system and is this case the energy was equal to 30 kV. Calculating the ratio of a gallium ion momentum to an electron momentum:

\[ \frac{p_{Ga}}{p_{e^-}} = \frac{m_{Ga}}{m_{e^-}} \sqrt{\frac{2E}{m_{Ga}}} = \sqrt{\frac{m_{Ga}}{m_{e^-}}} = 357 \]  (Eq. 3.3)

It is important to mention that the momentum ratio is not a function of the velocities of the particles which is a function of the voltage applied. Gallium ions being 20,000 times larger than electrons penetrate to a lower depth than the latter. Given that the scattering cross-section is proportional to the product of the atomic masses of the incident and the target particles, the
Implantation range of a gallium ion beam interacting with the sample’s lattice is higher than that of an electron beam, because of the large atomic mass of a gallium ion compared to the mass of an electron.

![Ion Ranges Diagram](image)

**Figure 3.3:** TRIM Simulation of the Ion implantation distribution in a layer of tin sulfide for a Ga ion beam at zero angle of incidence.

The total distance traveled by the gallium ions into the material is the “ion range.” The statistical nature of the atomic collisions gives the Gaussian distribution shown above (Figure 3.3) by running a Monte Carlo simulation using SRIM (SRIM 2008.04) [55, 58]. The target depth is the region that will develop defects due to ion implantation. Having the thickness of each milled slice close to the target depth ensures removing the implanted region and imaging a cross-section with minimal Ga⁺ implantation and thus minimal defects. Figure 3.3 shows that Ga⁺ implantation depth into tin sulfide is on the order of 25 nm which is roughly the thickness of one slice in this current experiment which is about 23 nm. This is important, because it shows whether the beam is damaging the sample, by ion implantation, further away from the milled slice, which is not the case here.
3.2 Focused Ion Beam (FIB) Tomography

One of many applications of the dual beam (FIB and SEM) system is three-dimensional characterization by FIB tomography [56]. It is a destructive technique consisting of serial cross-sectioning of a selected volume of the sample by milling away slices tens of nanometers thick. After each milling step, the ion beam is blanked and a high-resolution image is recorded [59]. Imaging is made using the SEM and the blanking of each beam between each milling/imaging step is automated by a built-in script in the software. The resolution depends on both the SEM resolution which can reach 10 nanometers and the thickness of each slice. The collection of all SEM micrograph is subsequently used to reconstruct 3D images using contrast mechanism and employing a tomography software [56].

3.2.1 Obstacles and limits of the Technique

**Charging and Image Quality:**

When imaging insulting materials, such as glass, charging occurs. It is the building up of electrons on the imaged surface causing undesired deflections in the detected secondary electrons. The contrast will be affected by charging, in which bright and dark areas of contrast will form that do not represent underlying sample morphology. This is caused by the fact that these charges implanted in an insulating material are stuck and cannot flow elsewhere. Coating the sample with a conductor or using conducting tape such as gold and carbon tape help solve this problem [55, 58]. Another way to avoid charging will be making sure during the milling process not to directly image the glass substrate of the sample- achieved by avoiding over-
milling of the cross-section and keeping the glass substrate away from scanned area which also
requires avoiding drift.

During the sequential milling process, the focal depth has to be corrected especially when
looking at a relatively large volume. This is done by adjusting the focus of the SEM manually as
the working distance increases while more material is being milled away [18].

**Drift:**

Several causes can be behind drifting effects, primarily caused by charging and thus the
deflection of the electron or ion beam. Charging is one main reason, while sample deformation
and mechanical and electromagnetic instabilities play an additional role in drift. X-and Y-drift
should be compensated to reduce subsequent analysis problems in cropping and aligning slices.
This can be done by applying a routine on the software prior to milling step [60]. Sometimes,
even with applying drift correction, charging caused by the glass substrate as the volume is
milled away still induce some drift. This can be corrected for by slice alignment in X and Y
manually after image acquisition or using software routines that can translate the image by as
many pixels as required [22].

**Heating due to the Ion Beam:**

Heating the sample due to the applied beam onto it is an important aspect one needs to
consider. It is possible to neglect any heat loss from the sample by radiation, and model the point
under the beam as a semi-infinite body in spherical coordinates hit by a uniform beam of radius
$R$. The input power from the beam is given by $P = \pi \rho^2 V J$ where $V$ is the voltage and $J$ the
current density of the beam [61]. Thus the heat flow out of a hemisphere of radius $\rho$ into a semi-infinite body is:

\[
Q = -2\pi k \rho^2 \frac{d\theta}{d\rho}
\]  
(Eq. 3.4)

The temperature distribution for this system becomes:

\[
T(\rho) - T(\infty) = \left(\frac{V}{2nkR^2}\right) \left(\frac{R^2}{\rho}\right) \text{ for } \rho \geq R
\]  
(Eq. 3.5)

The highest temperature would be at $\rho = R$, and so for a voltage of $V = 30$ kV, $I = 150$ pA, $R = 60$ $\mu$m and taking the thermal conductivity of tin sulfide to be $k = 66$ W/m.K

Finally, the maximum change in temperature is: $\Delta T_{\text{max}} = 0.05^\circ C$ which is a very small variation to affect grains of any microstructure of the material.

### 3.3 Experimental Setup

Figure 3.4 depicts the schematic of the experimental process tilted $54^\circ$ from the horizontal. The sample holder is tilted perpendicular to the ion beam. The FIB column is tilted $54^\circ$ from the horizontal plane. The process starts by milling away three trenches around the volume that will later be investigated. These trenches are milled for two main reasons: avoid redeposition of sputtered material onto the volume of interest and make the sharp edge of the cross-section to be imaged clearly visible (Figures 3.4 and 3.5)
After the trenches are created and the volume of the sample to be studied is well defined, an ion beam of 30 kV and 150 pA is used to sequentially mill away slices 23 nm thick. How thick a slice is, represents a compromise between the duration of the experiment and high thickness resolution. A low depth resolution is dominated by the aliasing effect wherein a thick slice hides depth information by either milling away pores, and thus underestimating the number of pores in the sample, or milling away a part of a pore that is larger than the slice thickness, and thus either underestimating or overestimating the volume of the pores depending on their shape and the interpolation made by the 3D reconstruction software during the analysis step. Reducing the slice thickness is done by reducing the beam current, this leads to less information getting lost by milling away material; however more time is required to sequentially mill and image the practically measurable volume of the sample. The beam current also affects the smoothness of the milled surface, re-deposition, and curtaining effects. The latter is a consequence of the multi-
crystalline nature of the tin sulfide thin films and the plate-shaped grains grown in different directions. While it can be reduced by coating the top surface of the sample in-situ with platinum before starting the milling steps, however many pores start from the top of the sample, depositing platinum would fill them and they won’t be detected anymore by contrast mechanism.

Figure 3.5: SEM micrograph of milled volume showing re-deposition on the outer side of the trenches.

Simultaneously, for each milling step, a high resolution SEM micrograph is recorded, as shown in Figure 3.6, of the new cross-sectional surface using a 36° tilt correction since the SEM beam is not looking straight at the cross-section (Figure 3.4).

Figure 3.6: Representative SEM micrograph of a single cross-section.
3D images are produced in the tomography software (AVIZO Fire) from the SEM micrographs which are turned into binary images and thresholded based on contrast mechanism. Darker regions show the pores in the films whereas brighter regions are regions filled with tin sulfide material. Three-dimensional reconstructions of the pores inside the volume milled from the collected SEM micrographs are shown in Chapter 4.
CHAPTER

4

EXPERIMENTAL RESULTS

4.1 General Results

We converted the collected images to binary images. These images are loaded as 3D images into the software AVIZO FIRE. A threshold is set based on the contrast gradient differentiating the pores from the rest of the material. The pores are then reconstructed for the 4 different samples at 4 different set of parameters. For all 4 samples, 220 images are recorded to reconstruct the volume milled; therefore the thickness of each slice is around 23 nm. To unify the computations on the nanometer scale, pixels need to be converted into nanometers while retaining the scale in all directions.

We then compute the surface area and volume of each pore using the number of voxels that constitute the pore. Figures 4.1 and 4.2 show pore 3D reconstructions for the sample grown at 1 Å/s and the sample grown at 10 Å/s deposition rates respectively. We note that, both samples had the same substrate temperature of 240°C with a milled surface area of 5×5 μm². The samples however had different thicknesses: the sample in Figure 4.1 is 0.6 μm and the sample in Figure 4.2 is 1 μm thick.
Inspecting the 3D reconstructions qualitatively, we observe the sample grown at a higher deposition rate contains few large pores. Moreover, the sample grown at a lower deposition rate shows larger and more numerous pores inside the film, compared to the sample grown at a higher deposition rate. We note that the few large pores in the sample evaporated with a higher deposition rate start from the substrate and end at the surface of the sample, the reason could be just because the low deposition rate sample is thinner than the high deposition rate sample. This may cause problems in the device fabrication phase, in particular in the metallization step, since these pores may shunt the device, resulting in a resistor rather than a diode.

Figure 4.1: Pore 3D reconstruction of the sample grown at a deposition rate of 1 Å/s and a substrate temperature of 240°C (sample dimensions are 5×5×0.6 μm³).
Figure 4.2: Pore 3D reconstruction of the sample grown at a deposition rate of 10 Å/s and a substrate temperature of 240°C (sample dimensions are 5×5×1 μm³).

Figures 4.3 and 4.4 are pore 3D reconstructions of the sample grown at a substrate temperature of 150°C and the one grown at a substrate temperature of 300°C respectively. Both samples were grown at a deposition rate of 4 Å/s. Both milled samples have the same dimensions with a surface area of 5×5 μm² and a thickness of 1 μm.

By examining the 3D images, we observe that the sample grown at a lower substrate temperature has more pores than the one grown at a higher substrate temperature. Also, the pores in the sample shown in Figure 4.3 are smaller on average than those shown in the sample of Figure 4.4.
Figure 4.3: Pore 3D reconstruction of the sample grown at a substrate temperature of 150°C and a deposition rate of 4 Å/s (sample dimensions are 5×5×1 µm³).

Figure 4.4: Pore 3D reconstruction of the sample grown at a substrate temperature of 300°C and a deposition rate of 4 Å/s (sample dimensions are 5×5×1 µm³).
4.2 Quantitative Results

Figure 4.5 shows the total pore count as function of the pore volume for the sample grown at 1 Å/s and 240°C (low deposition rate sample) and the sample grown at 10 Å/s and 240°C (high deposition rate sample). For a pore volume of $2.2 \times 10^{-4} \ \mu m^3$ and below, the high deposition rate sample contains almost twice as many pores as the low deposition rate sample with 151 and 80 pores, respectively. The high deposition rate sample maintains its high porosity compared to the low deposition rate sample until a pore volume of $1.2 \times 10^{-3} \ \mu m^3$. For larger pore volumes, the low deposition rate sample shows a larger number of pores than the high deposition rate sample. In particular, for a pore volume larger than $2.4 \times 10^{-3} \ \mu m^3$, the low deposition rate sample contains 7 more pores than the high deposition rate sample.

Figure 4.5: Pore Volume distribution for the two samples grown at 1 Å/s and 10 Å/s with a constant substrate temperature of 240°C.
Figure 4.6: Pore Volume distribution for the two samples grown at 150°C and 300°C with a constant deposition rate of 4 Å/s.

Figure 4.6 depicts the total pore count as function of the pore volume for the sample grown at 4 Å/s and 150°C (low substrate temperature sample) and the sample grown at 4 Å/s and 300°C (high substrate temperature sample). At any pore volume ranging from $2.2 \times 10^{-4}$ μm$^3$ to $2 \times 10^{-2}$ μm$^3$, the sample grown at a substrate temperature of 150°C contains more absolute number of pores than the sample grown at a substrate temperature of 300°C.

Figure 4.7 graphs the average porosity by volume for all four samples. The low deposition rate sample is approximately twice as porous as the high deposition rate sample with 6.08% and 3.32%, respectively. The low temperature sample is the most porous of all samples.
with a porosity of 10.23%, whereas the high temperature sample is the less porous of all with a porosity of 3.16%.

---

![Average Porosity (by Volume)](image)

**Figure 4.7:** Average porosity by volume for the 4 different samples.

By inspecting Figure 4.5, we expect the sample grown at a higher deposition rate to be more porous than the sample grown at a lower deposition rate. However, this is not the case when looking at the average porosity by volume. Therefore, we need to normalize the graphs in Figures 4.5 and 4.6 to extract further information.
Figure 4.8 shows the pore volume distribution normalized by the total number of pores inside the volume of interest in each sample. We observe that 95% of the total pores in the high deposition rate sample have a volume smaller or equal to $7 \times 10^{-5} \text{ m}^3$, compared to 85.6% for the low deposition rate sample. Figure 4.9 provides the same information as Figure 4.8, zooming in to larger pore volumes. We observe that, for pores larger than $2.2 \times 10^{-4} \text{ m}^3$, the low deposition rate sample has a consistently higher per volume percentage. Having a higher pore volume percent at larger pore size explains why the low deposition rate is twice as porous as the high deposition rate sample as seen in Figure 4.7.

For the sake of direct comparison, the pore volume distributions for the samples grown at different substrate temperatures are also normalized by the total number of pores in the whole milled volume of each sample. Figures 4.10 and 4.11 show a similar trend to the one depicted in Figures 4.8 and 4.9. The high substrate temperature sample has 90.2% of its pores with a volume smaller or equal to $7 \times 10^{-5} \text{ m}^3$, while 95.5% of the total pores of the low substrate temperature sample fall within this volume range. As the pore volumes become larger or equal to $2.2 \times 10^{-4} \text{ m}^3$, the high substrate temperature sample has consistently more pores than the low substrate temperature sample. This suggests the higher average porosity observed in the low substrate temperature samples, as indicated in Figure 4.7, is mainly caused by the much larger number of pores with volume below $2.2 \times 10^{-4} \text{ m}^3$.

To explain this experimental data, we develop two nucleation models that support the results: a thermodynamic and a kinetic model. The two models are developed in the following chapter.
Figure 4.8: Normalized pore volume distribution by the total number of pores for the two samples grown at 1 Å/s and 10 Å/s with a constant substrate temperature of 240°C.

Figure 4.9: Normalized pore volume distribution by the total number of pores for the two samples grown at 1 Å/s and 10 Å/s with a constant substrate temperature of 240°C (zoomed in).
Figure 4.10: Normalized pore volume distribution by total number of pores for the two samples grown at 150°C and 300°C with a constant deposition rate of 4 Å/s.

Figure 4.11: Normalized pore volume distribution by total number of pores for the two samples grown at 150°C and 300°C with a constant deposition rate of 4 Å/s (zoomed in).
5.1 Thin Film Nucleation: An Introduction

To understand the nucleation and grain formation in the films, it is necessary to study the thermodynamics and kinetics of the system. For nucleation (phase change) to happen, the partial pressure of the gaseous tin sulfide should be greater or equal than its vapor pressure in the solid phase at a given temperature [30, 62]. Nucleation is a key process in thin film formation because it influences the structure of the developing grains. Assuming a uniform distribution of potential adsorption sites, atoms are adsorbed as they impinge on the surface of the substrate from the vapor phase and are accommodated. The adsorbed adatoms may desorb or diffuse to combine with other adatoms or clusters of atoms. By applying a free energy argument, there will be a critical size beyond which the likelihood of a cluster to grow is higher than that of decay: the cluster's growth is a nucleation phenomenon. Stable clusters eventually keep growing by capturing atoms either directly impinging on them or diffusing towards them, until several clusters are large enough to coalesce with each other and form the films [63]. Frequently, both nucleation and growth happen simultaneously as the film is formed [62]. Nucleation rate and growth are both affected by the grain structure of the growing stable nuclei, the deposition rate and the substrate temperature [64].
5.2 Gibbs-Thomson Equation and Supersaturation Ratio

The Gibbs-Thomson formula relates the vapor pressure at equilibrium for a spherical island to its curvature and size. In the nucleation framework, the influence of interface curvature on equilibrium should be taken into account in the solubility limits [65]. Therefore, it is useful to look at “classical” Gibbs-Thomson equation which governs the formation of nuclei in a supersaturated gas limited by the free energy barrier. A supersaturated system’s free Gibbs energy is decreased as islands nucleate. The classical Gibbs-Thomson equation which assumes that the surrounding gas is an ideal gas is given by:

\[
\ln \left( \frac{p_f}{p_\infty} \right) = \frac{\gamma}{r p_s k_B T} + \frac{p_f - p_\infty}{p_s}, \tag{Eq. 5.1}
\]

where \( p_f \) is the number density of the vapor, \( p_\infty \) the number density of the gas in equilibrium with a straight interface, \( p_s \) the number density of the condensed solid, \( \gamma \) the surface energy, \( r \) the radius of the nucleus, \( k_B \) the Boltzmann constant, and \( T \) the absolute temperature.

The second right hand side term is usually very small and thus can be neglected, which yields:

\[
p(r) = p_\infty e^{\frac{\gamma}{r p_s k_B T}}. \tag{Eq. 5.2}
\]

The expression in Eq. 5.2 shows that, keeping all other parameters constant, smaller particles have higher vapor pressures than the bulk [62, 66]. Therefore, for nucleation to occur, the ratio of the partial pressure of the vapor to the vapor pressure at equilibrium of the bulk, known as the supersaturation ratio, should be greater than unity. As this ratio increases, the nucleation rate increases quickly [67, 68]. The supersaturation ratio influences how large and how many crystals grow and the rate at which they grow [69].
5.3 Nucleation Theory: Thermodynamic Approach - Capillarity Model

When an atom impinges on the substrate, it is either adsorbed onto the substrate, or diffuses on the surface for a while before re-evaporating again, or desorbs instantly [71]. The energy of the atoms hitting the substrate is larger than \( k_B T \), where \( T \) denotes the temperature of the substrate. The atom gets adsorbed if it equilibrates quickly with the substrate, otherwise, it will have enough energy to jump off the substrate. Under the assumptions of an instantaneous adsorption, nucleation models assume a steady state in which monomers diffuse and collide together and with other clusters during the mean residence time \( \tau_a \) expressed as:

\[
\tau_a = \frac{1}{v_0} e^{\left(\frac{\Delta G_{\text{des}}}{k_B T}\right)}, \tag{Eq. 5.3}
\]

where \( v_0 \) is the vibrational frequency of the vapor atom, \( \Delta G_{\text{des}} \) the free activation energy for desorption, \( k_B \) the Boltzmann constant and \( T \) the substrate temperature [62].

---

Figure 5.1: Change in critical nucleus radius with degree of supersaturation, adapted from Ref. [70].
The capillarity theory assumes positive free energy variation in order to form stable islands from the vapor phase. For this to occur, the activation barrier, also called nucleation barrier, must be overcome. The concept of the nucleation barrier explains why the supersaturation ratio needs to be greater than one for nucleation to take place because as the supersaturation ratio increases much larger than unity, the barrier to nucleation decreases, hence increasing the nucleation rate (Figure 5.1) [62, 72]. The model should be analyzed for the heterogeneous nucleation on a substrate in which nuclei appear at preferential sites, such as grain boundaries, impurities etc. [73]. Although this model yields simple qualitative insight, it might return inaccurate quantitative results since it lacks a kinetics argument from the atomistic point of view. Nonetheless, this model is comprehensive and provides a useful approach to describe the relationship between the parameters studied in our experiment: (1) the substrate temperature and the deposition rate, and (2) the nucleus critical size and the nucleation size density [30].

Assuming that a formed nucleus has a spherical cap shape as shown in Figure 5.2, the change of the Gibbs free energy of the system is given by:

\[ \Delta G = a_3 r^3 \Delta G_v + a_1 r^2 \gamma_{lv} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv}. \]  
(Eq. 5.4)

Here, \( \Delta G_v \) is the free energy of condensation from vapor to solid phase per unit volume in the bulk under the same conditions of supersaturation. We note that, for a constant temperature and pressure, this term should be negative for the reaction to occur spontaneously, as stated by the second law of thermodynamics. This is described by the fact that a system tends to minimize its available free energy in order to reach thermodynamic equilibrium.

For a condensation reaction from vapor to solid, the chemical free energy is given by:

\[ \Delta G_v = -\frac{k_B T}{\alpha} \ln \left( \frac{p_v}{p_s} \right) = -\frac{k_B T}{\alpha} \ln(1 + S), \]  
(Eq. 5.5)
where $p_v$ is the supersaturated vapor pressure, $p_s$ the vapor pressure right above the solid, $\Omega$ the atomic volume. $S$ is the vapor supersaturation defined as:

$$S = \frac{p_v - p_s}{p_s} \quad \text{(Eq. 5.6)}$$

If $S$ is zero, nucleation is unlikely to occur, however when $S$ is greater than one, the change in chemical free energy is then negative and nucleation can occur [29, 30].

In Eq. 5.4, the subscripts $s$, $v$ and $f$ refer respectively to substrate, vapor and film. $\gamma_{fv}$ is the surface energy at the interface film-vapor, $\gamma_{fs}$ is the surface energy at the interface film-substrate and $\gamma_{sv}$ is the surface energy at the interface substrate-vapor. The term $a_1r^2$ is the curved surface area of the spherical cap shape of the nucleus (Figure 5.2), $a_2r^2$ is the projected circular area of the cap and $a_3r^3$ is the volume of the nucleus. The geometric constants are defined as follows:

$$a_1 = 2\pi(1 - \cos\theta) \quad \text{(Eq. 5.7)}$$

$$a_2 = \pi\sin^2\theta \quad \text{(Eq. 5.8)}$$

$$a_3 = \frac{\pi}{3}(2 - 3\cos\theta + \cos^3\theta) \quad \text{(Eq. 5.9)}$$

The negative sign in front of the term related to the surface energy of the substrate-vapor interface relates to the fact that, as the cap of the nucleus increases, the substrate-vapor interface is lost, which implies a reduction in the system’s free energy change [30].
Applying a force balance in the horizontal direction (Figure 5.2) yields Young’s equation:

\[ \gamma_{sv} = \gamma_{fs} + \gamma_{fv} \cos \theta \]  
\text{(Eq. 5.10)}

Taking the derivative of the system's change in Gibbs free energy with respect to the radius of the nucleus yields:

\[ \frac{d\Delta G}{dr} = 3a_3 r^2 \Delta G_v + 2a_1 r \gamma_{fv} + 2a_2 r \gamma_{fs} - 2a_2 r \gamma_{sv} \]  
\text{(Eq. 5.11)}

This assumes that the shape of a nucleus does not change as its size increases, and that the change in chemical free energy and the surface energies stay constant with changing size [62].

The system's change in Gibb's free energy is maximized when:

\[ \frac{d\Delta G}{dr} = 0 \]

And the critical nucleus radius at which thermodynamic equilibrium is reached is then:

\[ r^* = \frac{-2(a_1 \gamma_{fv} + a_2 \gamma_{fs} - a_2 \gamma_{sv})}{3a_3 \Delta G_v} \]  
\text{(Eq. 5.12)}
Re-evaluating Gibb's free energy's equation at the critical nucleus radius $r^*$ gives:

$$\Delta G^* = \frac{4(a_1Y_{tv} + a_2Y_{fs} - a_2Y_{sv})^3}{27a_f^2\Delta G_f^*} \quad (\text{Eq. 5.13})$$

Now replacing the geometric constants from Eq. 5.7 to 5.9 into Eq. 5.13, the nucleation barrier looks as follows:

$$\Delta G^* = \frac{16\pi(Y_{tv})^3}{3(\Delta G_v)^2} \left( \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \right) \quad (\text{Eq. 5.14})$$

The first term in the right hand side is common to the homogeneous nucleation barrier; the second term is dependent on the wetting angle and is heterogeneous nucleation specific. If $\theta = 0^\circ$, the term in the brackets is zero and there is no barrier to nucleation, on the other hand when $\theta = 180^\circ$, the term in the brackets is equal to one and the barrier is maximum and equal to the homogeneous nucleation barrier [30]. The wetting factor is always less than one, hence reducing the height of the nucleation barrier. Therefore, the nucleation barrier for a heterogeneous nucleation is always less than the nucleation barrier in a homogeneous nucleation, which leads to more nuclei at the surface in heterogeneous than in homogeneous nucleation.

![Figure 5.3: Free energy of formation as a function of the nucleus radius, adapted from Ref. [30].](image)
Figure 5.3 shows that a cluster smaller than the critical radius $r^*$ tends to reduce its free energy. Thus, such cluster shrinks and disappears or diffuses on the surface and attaches to a larger nucleus. As more atoms are being deposited onto the substrate, nuclei that grow to supercritical size will tend to grow even bigger, lowering their free energy. The nucleation barrier, on the other hand, influences the number of nuclei formed. The larger the barrier, the harder it is for nucleation to occur, and thus fewer nuclei will appear. If the nucleation barrier is smaller, then more nuclei are able to overcome it and grow bigger.
5.3.1 Deposition Rate and Substrate Temperature Effect on Nucleation

Assuming the deposition rate $\dot{R}$ is proportional to the vapor pressure, Eq. 5.5 can be written as follows:

$$\Delta G_v = -\frac{k_BT}{n} \ln \left( \frac{\dot{R}}{\dot{R}_e} \right),$$

(Eq. 5.15)

where $\dot{R}_e$ is the equilibrium evaporation rate from the nucleus at the given substrate temperature. Assuming that the glass substrate is inert, $\gamma_{fv} = \gamma_{fs}$ and differentiating Eq. 5.12 with respect to the substrate temperature, keeping the deposition rate constant gives:

$$\left( \frac{\partial r^*}{\partial T} \right)_R = \frac{2}{3} \left[ \frac{\gamma_{fv} \left( \frac{\partial \Delta G_v}{\partial T} \right) - (a_1 + a_2) \Delta G_v \left( \frac{\partial \gamma_{fv}}{\partial T} \right)}{a_3 (\Delta G_v)^2} \right]$$

(Eq. 5.16)

To reduce the above equation, it is necessary to assume typical values for $\gamma_{fv} = 1$ J/m$^2$ and $\partial \gamma_{fv}/\partial T = -0.05$ mJ/m$^2$K. Given these assumptions, as long as $|\Delta G_v| < 1.6 \times 10^{10}$ J/m$^3$ and $\partial \Delta G_v/\partial T$ is roughly around $8 \times 10^6$ J/m$^3$K, the following analysis is valid [30].

Therefore, it is important to check these values for tin sulfide. The following are properties of tin sulfide needed to calculate the entropy change of vaporization $\frac{\partial G_v}{\partial T}$:

$$\Delta H_{vap}(SnS) = 220 \text{ kJ/mol}$$

$$M(SnS) = 150 \text{ g/mol}$$

$$\rho(SnS) = 5.22 \text{ g/cm}^3$$

$$\frac{\partial G_v}{\partial T} = \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = 5 \times 10^6 \text{ J/m}^3\text{K}$$

$$|\Delta G_v| = 2.865 \times 10^9 \text{ J/m}^3 < 1.6 \times 10^{10} \text{ J/m}^3$$
We note that the highest temperature in our study is 300°C for the thermal evaporation of tin sulfide. At this temperature, the change in chemical free energy is less than $1.6 \times 10^{10}$ J/m$^3$, implying that we can carry our analysis using this theory [30, 51].

Looking at the sign of Eq. 5.16 after reducing it using the assumptions explained above yields $\left( \frac{\partial r^*}{\partial T} \right)_R > 0$. This means that, as the substrate temperature increases, the critical nucleus radius increases as well at a constant deposition rate.

Similarly for the nucleation barrier, we have $\left( \frac{\partial \Delta G^*}{\partial T} \right)_R > 0$, which implies that the substrate temperature increases, the nucleation barrier also increases at a constant deposition rate.

Now differentiating the solution for the critical nucleus radius while keeping the substrate temperature constant, using the chain rule yields:

$$\left( \frac{\partial r^*}{\partial \tilde{R}} \right)_T = \left( \frac{\partial r^*}{\partial \Delta G_v} \right) \left( \frac{\partial \Delta G_v}{\partial \tilde{R}} \right) = \left( -\frac{r^*}{\Delta G_v} \right) \left( -\frac{k_B T}{\Omega \tilde{R}} \right)$$

Recall that $\Delta G_v$ is negative, as a result, the sign of the above is also negative:

$$\left( \frac{\partial r^*}{\partial \tilde{R}} \right)_T < 0$$

hence suggesting that, as the deposition rate increases, the critical nucleus radius decreases at a constant substrate temperature.

Similarly, the analysis for the nucleation barrier yields:

$$\left( \frac{\partial \Delta G^*}{\partial \tilde{R}} \right)_T < 0$$

And thus as the deposition rate increases, the nucleation barrier becomes smaller at a constant substrate temperature [30, 62].
Anisotropic crystallographic growth is the result of different free energies at the different interfaces, surface diffusion, substrate temperature, pressure, substrate roughness and rotation or tilting of the substrate. This leads to pore formation resulting from the self-shadowing effect. Note that self-shadowing is the outcome of varying in-plane growth rates due to atoms reaching the substrate at an angle or to preferential deposition. This is based on the probability that an atom gets attached to a cluster of atoms on the surface of the substrate and leads to a rough and porous microstructure [74, 75]. The thermodynamic model assumes a limit in which surface diffusion is not dominant: substrate temperature being well below the melting temperature of the evaporated material. In this regime, the atoms growing on the grains diffuse slower to redistribute themselves on the film surface than in a higher substrate temperature regime. The microstructure is therefore governed only by the geometric distribution of the grains characterized by the self-shadowing phenomenon [74]. Self-shadowing takes place in a regime where the substrate temperature is high enough for anisotropic crystal growth to occur, but low enough so that surface diffusion does not overcome self-shadowing effects, otherwise kinetics will need to be taken into account [76].

However, at higher temperatures, surface diffusion becomes significant and hence competes with self-shadowing effects. In fact, while self-shadowing results in porous films, diffusion reduces porosity by smoothing the film surface as atoms diffuse to fill the voids [74, 75]. Therefore, considering a kinetic model that takes diffusion into account helps give a complete understanding of the system.
5.4 Nucleation Theory: Kinetic Approach – Atomistic Model

Although the statistical macroscopic model gives a simple general approach to the nucleation phenomenon, the kinetic microscopic approach gives a better understanding of the comparison between the theory and the experimental results [30, 63]. As nucleation becomes possible to occur, we are interested in identifying the nucleation rate $\dot{N}$, which defines the number of stable nucleation sites per unit volume per unit time [30]. The nucleation rate and the in-plane growth dominated by surface diffusion are influenced by the substrate temperature and the deposition rate. This will dictate the average size of the crystallites. Films deposited at lower temperatures which result in lower adatoms mobility usually have smaller grain sizes [64].

![Diagram](image)

Figure 5.4: a) top view b) side view of a spherical cap shaped nucleus, adapted from Ref. [64].
Considering again an island growing with a spherical cap shape, if an atom is deposited within the annular region of width $\delta$ around the nucleus, it will diffuse towards that nucleus and attach to it, instead of starting a new nucleus or desorbing off the substrate surface.

This approach assumes that the flux of the atoms hits the substrate normally to its surface with a constant flux over time i.e. steady state conditions. The atoms directly impinging on the nucleus are added to the substrate, while the atoms impinging within a distance $\delta$ from the island diffuse towards it and then become attached to the nucleus. It also assumes that no stable nucleus can grow inside the diffusion zone $\delta$ because it will have to dissolve and join the neighboring stable nucleus instead, which makes the diffusion zone a region in which nucleation prohibited [64]. The diffusion zone width depends on the surface diffusivity and the desorption rate and is approximated by:

$$\delta = \sqrt{2D_{SD}\tau},$$  \hspace{1cm} (Eq. 5.17)

where $\tau$ is the mean time between adsorption and desorption of an atom and $D_{SD}$ is the surface diffusivity [30, 64], which is dependent on the substrate temperature in the following form:

$$D_{SD} = D_{SD,0} e^{\left(\frac{-E_{SD}}{k_B T}\right)},$$  \hspace{1cm} (Eq. 5.18)

where $E_{SD}$ is the activation energy for surface diffusion, $k_B$ is the Boltzmann constant, $D_{SD,0}$ is a temperature independent constant defined as the exponential of the y-intercept of the Arrhenius plot of the diffusion coefficient.

The mean adatom residence time $\tau$ also has substrate temperature dependence at low deposition limits as follows:

$$\tau = \tau_0 e^{\left(\frac{E_D}{k_B T}\right)},$$  \hspace{1cm} (Eq. 5.19)

where $E_D$ is the desorption energy.
The mean residence time is to the first order independent of the deposition rate, but is influenced by the energy and the flux of the atoms impinging on the substrate as shown in the following equation combining Eq. 5.18 and Eq. 5.19:

\[ \delta = \sqrt{2\tau_0 D_{SD,0}} e^{\left(\frac{E_D - E_{SD}}{2k_B T}\right)} \]  

(Eq. 5.20)

Now an equation of the nucleation rate needs to be derived [30, 64]. The critical density of clusters per unit area is given by:

\[ \frac{N_i^*}{n_0} = \left(\frac{N_i}{n_0}\right) \left(\frac{E_i^*}{k_B T}\right) \]  

(Eq. 5.21)

In the previous equation, \( E_i^* \) is the critical dissociation energy, \( n_0 \) is the total density of adsorption sites and \( N_i \) is the monomer density given by:

\[ N_1 = \dot{R} \tau, \]  

(Eq. 5.22)

where \( \dot{R} \) is the deposition rate.

Combining Eq. 5.19 and Eq. 5.22 one gets:

\[ N_1 = \dot{R} \tau_0 e^{\left(\frac{E_D}{k_B T}\right)} \]  

(Eq. 5.23)

The critical monomer flux is a function of the diffusion region and the deposition rate:

\[ \dot{R}\delta^2 = 2\dot{R} \tau_0 D_{SD,0} e^{\left(\frac{E_D - E_{SD}}{k_B T}\right)} \]  

(Eq. 5.24)

The general form of the nucleation rate \( \dot{N} \) in terms of the deposition rate and the temperature is given by combining Eq. 5.21, 5.23 and 5.24 [30]:

\[ \dot{N}_i = 2\dot{R} \tau_0 D_{SD,0} n_0 \left(\frac{\dot{R} \tau_0}{n_0}\right) \left(\frac{\tau^*}{k_B T}\right) e^{\left(\frac{(\tau^*+1)E_D - E_{SD} + E_i^*}{k_B T}\right)} \]  

(Eq. 5.25)

The numerator in the exponential term \( \Delta E_i = (\tau^* + 1)E_D - E_{SD} + E_i^* \) is experimentally proved to take a positive value and to discontinuously increase with increasing substrate temperature \( T \) as atoms are added to the nucleus [63, 64, 71, 29]. This suggests that, for a constant deposition
rate, as temperature increases, the nucleation rate decreases. A lower nucleation rate means fewer grains will be forming at the substrate surface. On the other hand, for a constant substrate temperature, as the deposition rate increases, the nucleation rate increases even faster especially if the critical size of the nucleus is larger.

As for the grain size and its dependence on the two parameters substrate temperature and deposition rate, the relationship can be explained as follows. For a spherical cap shaped grain, assuming the islands on the substrates are immobile, the diameter is given as a function of the average grain area $A$ by:

$$d = \sqrt{\frac{4A}{\pi}} \quad (\text{Eq. 5.26})$$

And the growth of an island is given by:

$$G = \frac{dr}{dt} = G_0 \left(1 + \frac{\delta}{r_s}\right) \quad (\text{Eq. 5.27})$$

$$G_0 = \frac{\dot{r}}{4} \Omega \frac{\sin^3 \theta}{S(\theta)} \quad (\text{Eq. 5.28})$$

where $\theta$ is the angle the nucleus makes with the substrate surface, $\Omega$ is the atomic volume, $r_s$ is the radius of the nucleus and $S(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2/4$.

From previous nucleation and growth simulations, the grain area $A$ versus $\frac{G_0}{N_{i^*}}$ shows two different regimes (Figure 5.6). The first regime corresponds to smaller values of $\frac{G_0}{N_{i^*}}$ and suggests that the average grain size is a function of the diffusion region width $\delta$ but is independent on $\frac{G_0}{N_{i^*}}$. As $\frac{G_0}{N_{i^*}}$ increases, the average grain area becomes strictly a function of $\frac{G_0}{N_{i^*}}$.

Curve fittings (Figure 5.6) give the following dependences of $A$ for the first and the second regimes respectively:

$$A = \frac{\pi}{4} (1.3516)^2 \quad (\text{Eq. 5.29})$$
Figure 5.5: Average grain size resulting from a nucleation rate and growth rate for different diffusion region widths, adapted from Ref. [64].

Using Eq. 5.26, the average grain diameter becomes for the first and the second regimes respectively:

\[ d = 1.351\delta \quad \text{for } \delta \ll \left( \frac{G_o}{N_1} \right)^{1/3} \]  
\[ d = 1.203 \left( \frac{G_o}{N_1} \right)^{1/3} \quad \text{for } \delta \gg \left( \frac{G_o}{N_1} \right)^{1/3} \]

The combined average grain diameter for any \( \delta \) and \( \frac{G_o}{N_1} \) can be approximated to:

\[ d = 1.351\delta + 1.203 \left( \frac{G_o}{N_1} \right)^{1/3} \]

Considering the average grain size dependence on the deposition rate, Eq. 5.20 shows no dependence of the diffusion zone width on the deposition rate. The term \( G_o \) is directly proportional to \( \hat{R} \) from Eq. 5.28. At relatively low constant temperatures, the critical size is estimated to be 1, therefore \( \hat{N}_1 \) is also proportional to \( \hat{R} \) which makes the ratio \( \frac{G_o}{\hat{N}_1} \) independent.
of $\dot{R}$. For relatively higher substrate temperatures, the critical cluster size is expected to increase, hence the proportionality which is now defined as $\frac{G_0}{N_{1^*}} \sim \dot{R}^{1-i^*}$ infers that $\frac{G_0}{N_{1^*}}$ decreases with increasing $\dot{R}$. Therefore, for substrate temperatures at which $i^* \geq 2$, the average grain size decreases with increasing deposition rate [30, 64, 77], until $\frac{G_0}{N_{1^*}}$ is small enough for Eq. 5.31 to become dominant, and then the average grain size stays constant with increasing $\dot{R}$ [64].

Now considering the average grain size dependency on the substrate temperature, Eq. 5.20 shows that the diffusion zone width increases with increasing substrate temperature. The term $G_0$ is independent of the substrate temperature. Thus, $\frac{G_0}{N_{1^*}}$ will increase as the substrate temperature increases since $\Delta E_{1^*}$ is experimentally proven to be positive. Hence, the average grain size at impingement is always increasing with substrate temperature [30, 64].

Thin film porosity is governed by two main processes competing with each other during thermal evaporation: surface diffusion and self-shadowing. Reducing surface diffusion by lowering the substrate temperature theoretically leads to higher film porosity, where self-shadowing is dominant. In the self-shadowing dominant regime, evaporated atoms from the source land on elevated surfaces on the substrate and do not reach depressed regions, growing the elevated regions even more and rendering the depressed regions even more depressed. As surface diffusion becomes more significant, some atoms become able to fill the depressed regions, thus lowering the film porosity [78]. Relating to these two processes, the thermodynamic model, assumes equilibrium conditions whereby self-shadowing is dominant,
while the kinetic model assumes a diffusion-driven nucleation process and pore formation under steady state conditions.
6.1 Thermodynamic Model

The results of the thermodynamic model described in Chapter 5 are shown in Figure 6.1.

![Table](image)

<table>
<thead>
<tr>
<th>Constant Substrate Temperature</th>
<th>Constant Deposition Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \left( \frac{\partial r^*}{\partial \dot{R}} \right)_T &lt; 0 )</td>
<td>( \left( \frac{\partial \Delta G^*}{\partial \dot{R}} \right)_T &lt; 0 )</td>
</tr>
<tr>
<td>As ( \dot{R} ) increases, ( r^* ) decreases</td>
<td>As ( \dot{R} ) increases, ( \Delta G^* ) decreases</td>
</tr>
<tr>
<td>( \left( \frac{\partial r^*}{\partial T} \right)_{\dot{R}} &gt; 0 )</td>
<td>( \left( \frac{\partial \Delta G^*}{\partial T} \right)_{\dot{R}} &gt; 0 )</td>
</tr>
<tr>
<td>As ( T ) increases, ( r^* ) increases</td>
<td>As ( T ) increases, ( \Delta G^* ) increases</td>
</tr>
</tbody>
</table>

**Figure 6.1: Thermodynamic Model Summary.**

The thermodynamic model assumes self-shadowing is the dominant mechanism affecting grain nucleation and growth, rather than diffusion. Thus, we use a geometric argument to relate the size and density of crystallites to the size and density of pores between the randomly oriented plate-shaped grains.

At a constant substrate temperature, a higher deposition rate leads to (1) a lower nucleus critical size, yielding smaller crystallites, and (2) a lower nucleation barrier yielding a larger
average grain density. By applying a geometric argument, and given randomly oriented grains
with respect to each other with a limited diffusion rate, the voids between them will follow the
same trend. This is what the experimental data support, wherein the higher deposition rate
sample showed 95% of the total pores in the milled volume falling below the $7 \times 10^{-5} \mu m^3$ range
compared to 85.6% for the low deposition rate sample, yet the low deposition rate sample
exhibits more pores in the larger range. As for the average pore density, the low deposition rate
sample has 161 pores/$\mu m^3$ compared to 239 pores/$\mu m^3$ in the high deposition rate sample (Please
refer to Table 6.1).

At a constant deposition rate, a higher substrate temperature leads to (1) a larger nucleus
critical size, yielding fewer and larger crystallites, and (2) a larger nucleation barrier yielding a
lower average grain density. By a geometric argument, films grown at a higher substrate
temperature have larger but fewer pores than films grown at lower substrate temperature. This is
validated by the experimental results. Figure 4.3 displays smaller pores in the film grown at
150°C compared to the pores in the film grown at 300°C depicted in Figure 4.4. Table 6.1 further
shows that the average pore density in the low temperature sample is twice as large as the
average pore density for the high temperature sample.
<table>
<thead>
<tr>
<th>Theory</th>
<th>Low Dep. Rate</th>
<th>High Dep. Rate</th>
<th>Low Temp</th>
<th>High Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nuclei Size</td>
<td>Larger</td>
<td>Smaller</td>
<td>Smaller</td>
<td>Larger</td>
</tr>
<tr>
<td>Nucleation site density</td>
<td>Smaller</td>
<td>Larger</td>
<td>Larger</td>
<td>Smaller</td>
</tr>
<tr>
<td>Data</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average Pore Size</td>
<td>$2.59 \times 10^{-4}$</td>
<td>$5.43 \times 10^{-5}$</td>
<td>$8.56 \times 10^{-5}$</td>
<td>$9.87 \times 10^{-5}$</td>
</tr>
<tr>
<td>Pores/µm$^3$</td>
<td>161</td>
<td>239</td>
<td>428</td>
<td>215</td>
</tr>
</tbody>
</table>

Table 6.1: Comparing thermodynamic model to experimental results.
6.2 Kinetic Model

The temperatures in the studied samples reach relatively high values; it is therefore essential to compare the results against a kinetic model that assumes diffusion dominates pore growth. We perform a qualitative validation, given that many of the measurable parameters in the kinetic model are not known for tin sulfide, hence requiring the design of a different set of experiments to determine them. Nevertheless, if the qualitative assessment determines that the trend is also satisfied by the kinetic model, it is then possible to interpret the effect of deposition rate and substrate temperature on the porosity of the films and optimize in view of obtaining the best output.

<table>
<thead>
<tr>
<th>Constant Substrate Temperature</th>
<th>Constant Deposition Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ \frac{G_0}{N_{i^<em>}} \sim \dot{R}^{1-i^</em>} ]</td>
<td>[ \delta^2 \sim e^{\left( \frac{E_D-E_{SD}}{k_B T} \right)} ]</td>
</tr>
<tr>
<td>As ( \dot{R} ) increases, ( \frac{G_0}{N_{i^*}} ) decreases</td>
<td>As ( T ) increases, ( E_D &lt; E_{SD} )</td>
</tr>
<tr>
<td>( d \sim \left( \frac{G_0}{N_{i^*}} \right)^{1/3} )</td>
<td>( N_{i^<em>} \sim e^{\left( \frac{\Delta E_{i^</em>}}{k_B T} \right)} )</td>
</tr>
<tr>
<td>As ( \frac{G_0}{N_{i^*}} ) decreases, ( d ) decreases</td>
<td>As ( T ) increases, ( N_{i^*} ) decreases</td>
</tr>
</tbody>
</table>

Smaller Crystallites (smaller pores) / more of them

Larger Crystallites (larger pores) / fewer of them

Figure 6.2: Kinetic Model Summary.

In the case of a constant substrate temperature, the diffusion zone width \( \delta \) is not affected by the deposition rate. However, at a relatively high temperature, an increase in the deposition rate yields an increasing nucleation rate and a decreasing critical gain area. With smaller nuclei but with no change of the diffusion zone width, more grains can nucleate in a given area.
Therefore at a higher deposition rate, smaller grains and higher grain density leads to smaller pores with higher average pore density.

In the case of a constant deposition rate, and assuming a desorption energy lower than the activation energy, an increase in the substrate temperature yields an increasing diffusion zone and a decreasing nucleation rate, given that $\Delta E_i^*$ is experimentally demonstrated to be positive. With a lower nucleation rate, the ratio $G_0/\dot{N}_i$ is higher, given that $G_0$ is independent of the substrate temperature. This results in an increasing average grain area, which coupled with a larger diffusion zone, yields films with larger crystallites and a lower grain density. Therefore, at higher substrate temperatures, thin films display larger pores with a lower average pore density. These results are again compatible with the experimental data and can be compared to the summary depicted in Table 6.1.

In the statistical thermodynamic model, equilibrium is presumed such that opposite-direction mechanisms, such as desorption and deposition, occur at the same rate (Figure 5.2). Therefore, there is no net growth of the cluster from the macroscopic point of view. However, at the microscopic scale, the system is experiencing changes due to these surface mechanisms. On the contrary, crystal growth is a kinetic process that is not under equilibrium but under steady-state conditions [79].

Also, in the thermodynamic nucleation theory, islands must maintain their shape unchanged for the equilibrium assumption to hold, by minimizing surface energy terms. Nevertheless, this assumption is not maintained in many situations, particularly in the case of anisotropy due to slower growth of atomically flat facets than of the atomically coarse parts or
lower index facets [76, 79]. Consequently, surface diffusion rate is important compared to other nucleation and growth kinetic mechanisms in deciding whether the equilibrium form is retained.

Hence, the kinetic model is a better approach for this analysis since it (1) assumes steady-state condition which is the case during the deposition period by constantly evaporating atoms onto the substrate and (2) assumes that surface diffusion is important and thus its effects are not omitted compared to the thermodynamic model that discounts surface diffusion and assumes equilibrium. The thermodynamic model would be more appropriate in an annealing process. An equilibrium condition can be more suitable for the interface between SnS film and the glass substrate during a long period of annealing.

The thermodynamic model is useful for drawing interpretations as to what is the influence of variables such as deposition rate, substrate temperature and critical nucleus size on evaporated films' microstructure. However, the description of these effects remains qualitative because of the lack of thorough atomistic assumptions. On the other hand, the kinetic approach can be treated quantitatively because it presents the advantage of expressing the nucleation rate and diffusion region width in terms of measurable parameters ($E_{SD}, E_D, \Delta E_I$) [30, 79]. For example, the activation energy is the slope calculated from an Arrhenius plot of diffusivity, graphed using fitted data acquired from a set of diffusion experiments conducted at different temperatures [80].
CHAPTER 7

CONCLUSION AND FUTURE WORK

7.1 Conclusion

Firstly, this work demonstrated that focused ion beam tomography is capable of characterizing and quantifying pores inside thin-film solar cell materials, in this case tin sulfide absorber layers. Pores are believed to be detrimental to thin-film solar cell absorbers, because these defects can lower the optical absorptance and create pinholes that shunt devices, both mechanisms reducing device efficiency.

Secondly, a comparison of different growth conditions suggests that average pore size and density is affected by substrate temperature and growth rate. Four samples were investigated, were two growth parameters were changed: deposition rate and substrate temperature. In two samples, the deposition rate was kept constant, while the substrate temperature was varied from a low 150°C to a high 300°C. In the two other samples, the substrate temperature was kept constant, while the deposition rate was 1 Å/s in one sample and 10 Å/s in the other sample. Results showed agreement with both thermodynamic and kinetic models of nucleation: At a higher substrate temperature, the films exhibited larger pores but lower pore density compared to lower substrate temperature. On the other hand, at lower deposition rate, films revealed larger pores with a lower pore density compared to higher deposition rate. The most porous sample was the one grown at a substrate temperature of 150°C and a deposition rate of 4 Å/s. These findings
allow one to relate the effect of growth parameters to the microstructure of tin sulfide thin films, providing plausible path toward absorber layer improvement.
7.2 Future Work

To apply these models quantitatively to tin sulfide, some parameters that are material dependent should be measured. Ripple features observed at the surface of the larger pores need to be understood by comparing these measurements to those obtained by atomic force microscopy. Another way to investigate these ripples is by deposition of a few nanometers of platinum inside the focused ion beam, which reduces curtaining effects that may be the reason behind the ripples features.

Further studies may entail studying the crystallographic effects on porosity by combining this experiment with X-ray diffraction measurements. This could be coupled to a study of grain orientation, modified by substrate material.

Lastly, greatly enhanced statistics (greater number of samples analyzed) may enable one to more conclusively decouple the different physical mechanisms that define film structure during crystal growth.


