Modeling Tin Sulfide Grain Growth during Post-Processing

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Abstract:

Tin sulfide (SnS) is a semiconductor material with both an indirect and direct bandgap at 1.1 eV and 1.3 eV respectively. Due to the availability of tin and sulfur, SnS is seen as a feasible alternative to the thin film CIGS and CdTe solar cells. With a direct bandgap of 1.1 eV and the ability to be produced as a thin film, the SnS solar cell should achieve high levels of efficiency of approximately 32% according to the Shockley-Queisser limit (Shockley, Queisser, 1961). However, the efficiency of most SnS systems is around 4% in low sun conditions (Hartman, 2011). To understand how to improve this efficiency, further research is being done on the grain structure and how grain growth occurs under different annealing conditions.

After thermal evaporation deposition, three different conditions were varied during annealing to affect grain growth: time, temperature, and annealing atmosphere. The samples were also deposited on two different substrates, glass and molybdenum. The samples were coated with Pt/Pd and characterized using SEM imaging. The SEM images were segmented to collect grain area information from each sample.

The characterization revealed that longer annealing times and higher annealing temperatures lead to faster and greater grain growth. The annealing atmosphere of the samples affected surface diffusion in that the greater the partial pressure of S₂ gas present in the environment the greater the facilitation of grain growth.

The key conclusion based on the experimental data was that the annealing grain growth mechanism for SnS films is secondary or abnormal grain growth. This was evidenced by the initial columnar structure, the bimodal grain area distribution, and the non-uniform grains present in the SEM images. Further research on grain boundary diffusion with respect to time and texture of the thin films is needed although they suggest secondary grain growth as well.
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Introduction:

Tin Sulfide Thin Films:

Solar cell research is crucial in the ongoing process to move away from fossil fuels as a primary global energy source. Currently, a great quantity of solar cell research works to optimize Si solar cells by changing factors such as thickness, adding different kinds of anti-reflective coating that decreases the amount of light reflected out of the solar cell, and the addition of p and n type dopants to make them more efficient (Zhao, Green, 1991). The key issue with Si solar cells is that they contain an indirect band gap which means that to transfer from valence to conduction bands a momentum term is also needed which requires the Si solar panels to be produced upwards of 100 μm thick. As an alternative, other semiconductors are used to make solar cells. This alternative list includes: GaAs (gallium arsenide), CIGS (copper indium gallium diselenide) and CdTe (cadmium tellurium) (Jaeger, 2002). However, the scarcity of metals like indium and tellurium in the earth’s crust would cause the solar cell market to be heavily dependent on the few sources of these metals.

An alternative material combination for solar cells is SnS (tin sulfide). The SnS semiconductor does not face the same problems as the rare earth semi-conductors because both tin and sulfur are relatively more abundant in the earth’s crust (Burton, Walsh, 2013). In addition, SnS has a direct band gap at 1.3 eV which is slightly larger than Si indirect band gap of 1.1 eV but the electrons do not require a momentum term to shift from the valence band into the conduction band because of the direct band gap structure (Burton, Walsh, 2013). SnS also has a direct band gap structure but its absorption coefficient is higher than that for Si at lower energy wavelengths so light does not have to penetrate as far into the material to excite an electron
SnS can be produced in thin film samples which enables continuous processing on the industrial scale. Continuous processing decreases solar cell cost and could make SnS an economically feasible solar cell material.

Annealing and Grain Growth

There are multiple methods for growing thin films of SnS such as: chemical vapor deposition, thermal evaporation, chemical solution deposition, and cathodic arc deposition (Sinsersmsaksakul, 2011). This thesis pertains to SnS films grown using thermal evaporation. The details of which will be discussed later in this section. During the growth of the thin film, the molecules of a material will organize themselves into a grain microstructure in an attempt to minimize the overall energy of the system but rarely actually achieves the low energy configuration.

The grain microstructure characteristics contribute to the film's properties: performance, and reliability in electronic, mechanical, and magnetic applications. The understanding of the grain structure is crucial in solar cell applications for determining things like diffusion rate, recombination rate, quantum efficiency, and electrical conductivity. The size and orientations of the grains are important for this as well as the grain boundaries and grain orientations.

During thermal evaporation, the steps for grain growth are: nucleation of the new grains on the substrate material, growth of the new grains over the substrate material which is heavily dependent on the surface energy values of the thin film-substrate interface, and coalescence of the grains into a continuous thin film (Jaeger, 2002). The grain boundaries can be mobile during this coalescence process. This leads to an evolving grain structure that continues to evolve during film thickening. Resulting in a more equiaxed structure in which the in-plane grain size tends to
be the same and scale with film thickness. This is not the case in tin sulfide structures where the grains are formed in columnar structures which suggest less mobile grain boundaries (Thompson, 2000).

Figure 1\textsuperscript{1}: The formation of grains due to the condensation of molecules on a substrate. The steps show the gradual condensation and the coalescence of the grains into a film layer.

\textsuperscript{1}Figure from C.V Thompson. "Structural Evolution during Processing of Polycrystalline Films."
The important microstructure characteristics include grain shapes, grain sizes, distribution of grain sizes, and distribution of grain orientations. The in-plane grain size can be determined by (assuming that the in-plane grains can be roughly modeled by a circle):

\[ D = \left( \frac{4A}{\pi} \right)^{\frac{1}{2}} \]

Where \( D \) is the diameter of the grain and \( A \) is the area. This equation and the enclosed object integration function of MATLAB are useful in determining the area of the SnS grains and finding the grain area distribution of various thin film samples (Thompson, 2000).

After the grains are initially grown on the film, they often undergo an annealing process to promote grain growth. The annealing process leads to a coarsening of the grains. With the additional energy being added to the system, the grain boundaries will move to a more energetically favorable position. Their motion will result in the shrinking and elimination of smaller grains which have a higher surface energy to volume ratio than the larger grains. This trend favors the development of low surface energy to volume ratio large grains which reduces the overall energy of the system. This results in an increase in average grain size in a phenomenon known as grain growth (Thompson, 1990).

In a defect-free material, normal grain growth is driven by the reduction in total grain boundary area which corresponds to a reduction in total grain boundary energy. The equation that models this defect-free growth is:

\[ \frac{d\bar{r}}{dt} = \bar{m} \bar{\gamma}_{gb} \bar{k} \]

Where \( \bar{r} \) is the average in-plane radius, \( \bar{\gamma}_{gb} \) is the average grain boundary energy, \( \bar{m} \) is the average grain boundary mobility, and \( \bar{k} \) is the average grain boundary curvature. From this
equation for normal grain growth it is expected that an average grain will grow at a rate of $t^{1/2}$ in
c accordance to the relationship between diffusion and time (Thompson, 1990).

There is a form of abnormal grain growth which is also known as secondary grain
growth. In this, energetically favorable grains grow rapidly within a matrix of finer less
ergetically favorable grains which leads to a bimodal grain size distribution. This bimodal
grain area distribution can be fitted with a lognormal function (Thompson, 1990).

Secondary grain growth can be caused by the interface energy between the film and the
substrate that minimizes the energy of a grain in precise orientations. The discrepancies between
the energies of specific orientations lead to the texturization of a film. When the majority of the
peaks are positioned in the same orientation then the film is considered textured (Thompson,
1990). If the sample is examined using x-ray diffraction then a textured sample will have a large
peak at the $2\theta$ position of the majority orientation. If the x-ray diffraction of a thin film sample
mimics the diffraction of a powder of the same material, in which there are many peaks at a
variety of angles, then the sample is considered randomly oriented. Annealing can enhance the
grain texture by adding excess energy to the system which allows the grain boundaries to shift
and change crystal orientation. Texturing is an indicator of secondary grain growth that shows
the energetically favored crystal orientations (Thompson, 1990).

Secondary grain growth can also be attributed to high intrinsic or extrinsic tensile stresses
in the film. The stresses affect growth because normal grain growth cannot occur until minimum
stress energy grain orientations are consumed during the coarsening process. This is because the
minimum stress energy grains encourage the grain boundaries to move in ways that facilitate
their shrinking, altering the grain growth process (Thompson, 1990).
Figure 2: Schematic microstructures and grain area distributions for a film undergoing secondary grain growth. The grains that are energetically favorable are growing at a faster rate than those which are not energetically favorable. Also, note the bimodal area distribution during step B which is indicative of secondary grain growth.

Annealing variable conditions

The SnS films were annealed in a variety of different ways to determine if their grains underwent abnormal secondary grain growth, and if so, how the growth varied based on the conditions. Initially the film samples were grown on either glass or molybdenum substrates. Each of the substrates has a distinct surface energy which affects the ease that molecules can diffuse across the film-substrate interface.

To determine the effect of the substrate, samples were grown on both molybdenum and glass and not annealed. These samples acted as a control to the annealed samples. There were three variables in the annealing phase: time, temperature, and gas conditions. Keeping the other

2 Figure from C.V Thompson, “Structural Evolution during Processing of Polycrystalline Films,” Annual Review in Material Science 2000, vol. 30, pp. 159-190.
two variables constant, the greater the annealing time, the more time is permitted for grain
growth and thus larger grains are expected to form. The same is true for temperature in which a
higher temperature would give the system more energy and allow greater grain mobility, leading
to grain coarsening. The grain mobility temperature dependence is:

\[ M = M_0 \exp \left( \frac{-Q_{gb}}{KT} \right) \]

Where \( M_0 \) is a temperature independent constant. \( Q_{gb} \) is the activation energy for the rate-
limiting atomic motion process in grain boundary mobility. \( K \) is Boltzmann’s constant and \( T \) is
temperature (Thompson, 1990).

The final condition is the annealing atmosphere. This can vary by having a high pressure
S\(_2\) gas present, a medium pressure S\(_2\) gas present, or a low pressure S\(_2\) gas present. This variable
will show how grain growth is affected by surface diffusion at the SnS-gas boundary.

<table>
<thead>
<tr>
<th>Variable Tested</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>at 300(^\circ)C or 400(^\circ)C</td>
</tr>
<tr>
<td>Time</td>
<td>for 6 minutes or 60 Minutes</td>
</tr>
<tr>
<td>Annealing Atmosphere</td>
<td>At Low, Medium, or High Partial Pressure of S(_2) gas</td>
</tr>
<tr>
<td>Substrate</td>
<td>On either Glass or Molybdenum</td>
</tr>
</tbody>
</table>

*Table 1:* Various conditions altered during annealing to test for secondary grain growth in SnS thin films.
Methods and Materials:

Thermal vapor deposition and imaging

Tin Sulfide thin films were deposited via thermal evaporation under high vacuum conditions on either glass or molybdenum substrates at a thickness of approximately 0.5 mm or 1 μm +/- 50 nm respectively (Hartman, 2011). The samples underwent annealing in an H₂S furnace under a variety of conditions as depicted by Table 1. After deposition, the grain structure of the thin films was characterized using SEM imaging. To facilitate this imaging and prevent charge buildup, the samples were first coated in platinum (Pt) and palladium (Pd) using the EMS 300 T Dual Head Sputter Coater at the Harvard Center for Nanoscale Systems (CNS). The thin films received a 5 nm PtPd coating.

The Zeiss FESEM Ultra 55 from the Harvard CNS facilities was used to characterize the samples’ grain structure. The images were taken at 50 kx (50,000 times) and 75 kx (75,000 times) magnification, at a voltage of 5 keV, and detected using an Inlens detector. For data processing purposes and to increase data sample size, the 50 kx images were primarily used.

The SEM images were processed with two different procedures. The first was using GIMP© to hand-trace the outline of the individual grains to segment them. ImageJ© was used to calculate the enclosed area of the traced outlines. Finally, the area information was graphically represented using MATLAB. The second method consisted of a MATLAB script that segmented the image around each grain and calculated grain area. This second set of information was graphically represented and compared to the hand-traced outline data.

The thin film data was represented in two different forms: histogram of grain size area and cumulative distribution function plots. The area distribution histograms showed the frequency of specific grain sizes appearing in the SEM images. The cumulative distribution
function displayed the probability of finding a specific grain size or smaller in the film in the material.
Results:

Figure 3: Example of MATLAB Image Tracing Compared to Hand-Traced Segmentation
Sample SnS131008D02-02AnOct25HiS2003, annealed in a High S₂ environment, 400°C for 1 hour. Figure 3 is an example of the image segmentation process from the MATLAB script compared to hand-traced grain segmentation compared to the non traced image. Note the large amount of noise present in darker regions of the MATLAB traced image compared to similar regions in the hand-traced image. This is due to the topography of the grains that are in different orientations. A grain that is relatively elevated in comparison to its neighbors can produce shadows and charging on the landscape. The MATLAB script has difficulty differentiating a grain boundary from a shadow which leads to noise.
An example of the grain area distribution generated using the MATLAB image segmentation of Figure 3. To reduce noise, grains smaller than 0.009 μm² were filtered out. 0.009 μm² was selected as the filtering threshold because 0.009 μm² was the size of the smallest grain present in the hand-traced image data. This figure suggests a bimodal distribution of grain sizes with one larger initial peak at a value of 0.01 μm² then a smaller peak at 0.21 μm². The grain area distribution appears to match a lognormal function. This means that a lognormal function could be used to fit this data.
An example of the grain area distribution produced by hand-tracing the grain segmentation. No noise threshold was applied to this distribution due to the inherently less noisy property of the hand-tracing method. The distribution suggests a bimodal distribution with the first peak at 0.04 μm² and a second peak at 0.38 μm². Similarly to Figure 4, the distribution appears to be compatible with a lognormal function for fitting.
Figure 6: Cumulative Distribution Function for MATLAB Data

Cumulative distribution function that represents the probability of finding a specific grain size or smaller in the sample image (on the y-axis) dependent on the grain size (x-axis). For example, at grain size 0.1 µm² there is a 78% chance of finding a 0.1 µm² grain or smaller within the sample image. This also means 22% of grains are larger than 0.1 µm². In general, the more curved inward (away from the y-axis) the CDF of a set of data is, the larger the average grain size of the sample that generated that data. Conversely, the more curved outward (closer to the y-axis) the CDF of a set of data is, the smaller the average grain size. This data compares the grain size for the MATLAB traced data to the hand-traced data. As seen in Figure 3, the hand-traced data is more accurate and has more accurate bounds around its grains. The MATLAB traced data has some grain boundaries missing and in some instances two or three grains are counted under a single grain area. As a result, the MATLAB traced data is shown to have a higher average grain area in this graph and with calculation it is revealed to be 0.0812 µm² compared to the hand-traced data average grain area of 0.0795 µm².
Cumulative distribution function for non-annealed samples on both molybdenum and glass. The data indicates that on average the SnS deposited on glass had larger average grain size than SnS deposited on molybdenum. The average grain sizes for the molybdenum substrate samples were 0.0442 and 0.0454 μm², while the average grain sizes for the glass substrate samples were 0.00491 and 0.00536 μm². The disparity is attributed to the difference in the surface energy between the substrate and thin film, and possible differences in substrate temperature during deposition.
This figure compares the effect of annealing time on grain growth for both glass and molybdenum substrates. The functions suggest that for both substrates the average grain size increased with a greater annealing time. However, the grains on molybdenum grew more quickly with respect to time than their glass analog. As a result the grains on molybdenum were much bigger on average shown by the more inward position of the CDF curves. The average grain area of the glass substrate samples increased from 0.0491 to 0.0504 to 0.0641 \( \mu m^2 \) while the average grain area of the molybdenum substrate samples increased from 0.0454 to 0.0760 to 0.1002 \( \mu m^2 \).
Figure 9 represents the cumulative distribution function that compared different annealing temperatures for molybdenum substrates at otherwise equal annealing conditions. The film as deposited had the smallest average grain size at 0.0454 μm² followed by the thin film annealed at 300°C at 0.0793 μm². The film with the largest average grain size was the one annealed at 400°C with an average grain size of 0.1002 μm². This relationship matches expectations since the higher the annealing temperature, the more energy the grain boundaries have to move into an energetically favorable position.
The cumulative distribution function for this data shows a correlation between annealing environment of S$_2$ gas and the average grain size after annealing. The medium partial pressure of S$_2$ yielded the largest grain size with an average grain area of 0.0998 $\mu$m$^2$ which is seen graphically since it is the innermost curve. The relative average grain area of the other three conditions of no annealing atmosphere, low S$_2$, and high S$_2$ are difficult to discern graphically. However the low S$_2$ annealing condition had the second highest average grain area at 0.0726 $\mu$m$^2$, followed by the high S$_2$ annealing condition at 0.0641 $\mu$m$^2$, and lastly the as deposited sample at 0.0491 $\mu$m$^2$.  

Figure 10: Cumulative Distribution Function for Different Annealing Atmospheres for Glass Substrate
The cumulative distribution function for this data shows a different relationship between the annealing atmosphere of S$_2$ gas and average grain size for the molybdenum rather than the glass substrate. There is a direct correlation between the average grain area and the partial pressure of S$_2$ present during annealing. On the molybdenum substrate, the grains in the high S$_2$ gas environment grew the largest after annealing while the grains in the medium S$_2$ gas atmosphere grew larger than in the low S$_2$ gas atmosphere. The average grain area for the high S$_2$ conditions was 0.1002 $\mu m^2$, while the average grain area for the medium S$_2$ and low S$_2$ conditions were 0.0724 $\mu m^2$ and 0.06581 $\mu m^2$ respectively. The as deposited sample had an average grain area of 0.0454 $\mu m^2$. Compared to the grains grown on the glass substrate, the grains grown on the molybdenum grew larger than their glass counterparts under the same annealing conditions.
These data points depict the relationship between annealing time and average grain radius. One of the conditions of normal grain growth is for the grain boundaries to shift proportionally with diffusion which is dependent on time$^{1/2}$. If the average grain radius did not grow proportionally to time$^{1/2}$ it would be an indicator that abnormal secondary grain growth has occurred. For the SnS deposited on glass, the grain radius changed at a rate proportional to time$^{0.37}$ which suggests abnormal secondary grain growth.
Similarly to Figure 13, the grain growth for SnS on molybdenum is proportional to time$^{0.57}$ which suggests abnormal secondary grain growth.
Figure 14 shows the profile image of a deposited thin film sample. The SnS grains are the uppermost layer while the second layer is the molybdenum this sample was deposited on. The SnS film is exhibiting what appears to be columnar structure with an elongation of the axis normal to the substrate surface. This columnar structure suggests abnormal grain growth.
Discussion:

Based upon the experimental data, the hand-traced data contained less noise and proved to be more consistent than the MATLAB segmented data. As a result, the hand-traced data was used for comparing the variables of film substrates, annealing time, temperature, and atmosphere to grain growth.

The grains deposited on the glass substrate appeared to be larger than those on molybdenum substrate after the samples that were produced and not annealed. This is related to the surface energy values between the SnS film and the substrate. In general, if there is a low surface energy at the interface the grain size during fabrication will be larger because the grain boundaries will move to minimize the overall energy of the system. This will result in large grains if the interface surface energy is low. If there is a high surface energy at the interface, the grain size during fabrication will be smaller because the grain boundaries will be stagnant in an effort to minimize overall energy of the system (Thompson, 2000). There may be variables other than surface energy that caused the grain size disparity between films on the glass substrate and films on molybdenum substrate. The fact that the samples grown on two different substrates but from the same B series are closer in comparison to films on the B series to the D series suggests that there may have been slight changes in conditions from one series to another when the samples were being thermally evaporated. More samples would need to be taken to check the validity of non-annealed glass substrate SnS having larger grains than non-annealed molybdenum substrate SnS.

The duration of annealing time was directly proportional to the amount of grain growth present in the film. This trend is present for samples grown on both glass and molybdenum substrates although the molybdenum substrate films experienced greater growth. This is due to
the fact that the longer annealing time provides the material with more energy over a greater period of time. This additional energy allows the grain boundaries to shift in a manner that coarsens the grains present in the thin film which is a more energetically favorable state for the film since it reduces total surface energy and thus the overall energy of the system.

The same trend was seen for increasing temperature, the higher the temperature of annealing, the greater the grain growth. With the temperature increase, there was a significant increase in grain size for the molybdenum substrate film. The same reasoning duration of annealing time applies. The higher the annealing temperature, the more energy the grains boundaries had to move into more energetically favorable state which correlates to a decrease of surface energy by coarsening the grains. The grain size dependence on temperature had a proportionality constant of $0.331$ where the relationship is grain size $\alpha$ Temperature$^{0.331}$ but more data would need to be taken to verify this.

The annealing atmosphere had two different effects on grain growth dependent on the partial pressure of S$_2$ gas and the film’s substrate. It was expected that samples that were annealed in high S$_2$ gas conditions would experience the greatest grain growth. This is because the S$_2$ gas would prevent the sulfur in SnS from diffusing out into the atmosphere in an effort to maintain equilibrium. The S$_2$-SnS interface would be a low energy interface that would facilitate the diffusion of grain boundaries and assist the coarsening the material.

For the glass substrate, it appeared that the medium pressure anneal had the highest grain growth and the highest pressure anneal having the lowest grain growth for an annealed sample. This occurred contrary to expectations. Further investigation is needed to compare the interface energy between SnS and glass versus the interface energy between SnS and H$_2$S gas. The results for the glass substrate may have come from an error in image processing which would be
The molybdenum substrate behaved in a manner that followed expectations. The high partial pressure S\textsubscript{2} anneal had the greatest grain growth followed by the medium and low partial pressure anneals which had roughly the same grain growth. Also, the average grain size after annealing was significantly larger for the molybdenum substrate samples than it was for the glass substrate samples. The molybdenum case illustrates that the greater the partial pressure of S\textsubscript{2} gas in the atmosphere, the more it facilitated the grain boundary diffusion during annealing. This matches the expectation of a low energy S\textsubscript{2}-SnS interface that aided the grain coarsening. Also at high partial pressures of S\textsubscript{2} gas the sulfur component of tin sulfide was not driven by equilibrium to move into the atmosphere.

The experimental data indicates that abnormal secondary grain growth is present in the SnS thin film. Secondary grain growth occurs when texture, initial columnar structure, and non-uniform grain size in imaging are present. Furthermore, normal grain growth is proportional to diffusion which is related to time\textsuperscript{1/2} (t\textsuperscript{1/2}) and bimodal distributions in grain areas should be observed (Thompson, 2000).

Some of these trends were present in the SnS samples. The samples had non-uniform grains that were accentuated post-annealing in the SEM images. The initial grain structure was also columnar. Further data would have to be taken to determine the texture of the material. It can only be assumed that a majority of the grains were in the same orientation, but further XRD analysis is needed to confirm this.

There was a consistent bimodal grain area distribution among the samples that were annealed. As seen in Figures 4 and 5, there was a first larger peak present at a smaller grain area and a second smaller peak of the less frequent and greater in size abnormal secondary grains.
This was the trend for a majority of the annealed samples, but not truly present in the histograms of the non-annealed samples. A reason for this is that the annealing process intensified secondary grain growth which is why the bimodal distribution was present for the annealed samples but was almost non-existent for the non-annealed samples.

Normal grain growth is dependent on grain boundary diffusion that moves with respect to \( t^{1/2} \). Abnormal grain growth does not strictly obey this relationship because select grains will coarsen at faster rates than other grains due to energetic favorability from orientation, composition, etc... The data from Figures 12 and 13 shows that the average grain radius with respect to time was not proportional to \( t^{1/2} \). A larger sample size with more time variations would need to be taken to determine the exact relationship between SnS grain growth and annealing time. However, the limited set of data suggests abnormal growth.
Conclusion:

Despite early efforts to contrast the methods of hand-tracing versus the method of using a MATLAB script for image segmentation, the MATLAB data was seen to be markedly unreliable due to noise that exaggerated the number of small particles and inexact borders being drawn on the SEM images. Therefore, the data for this lab is centered on using the hand-traced data. Further refinements to this MATLAB fitting routine may enable automation without sacrificing accuracy.

The general data trends indicate that the longer the duration of the anneal and the higher the temperature of the anneal, the greater the grain growth. Which matches expectations since a longer anneal time and higher anneal temperature introduce more energy into the system which allows the grain boundaries to move into a more energetically favorable state so the grains coarsen to reduce overall surface energy and the energy of the whole system which obeys the laws of thermodynamics.

Although the films on glass substrates had slightly larger average grain size than the films on molybdenum substrate after deposition, the secondary grain growth was more prevalent on the molybdenum substrate than the glass. A potential reason for this could be the interface energy between the substrate and the film.

The high partial pressure S\textsubscript{2} condition permitted the fastest grain growth when examining film deposited on molybdenum. This could be due to the idea that in high S\textsubscript{2} atmospheres the sulfur in the thin film does not diffuse into the atmosphere to maintain equilibrium conditions. Also, different gas environments can also affect surface diffusion which can aid in faster grain growth. The sulfur may have begun diffusing out of the samples annealed in medium and low partial pressures of S\textsubscript{2} which explains why the SEM images for these samples showed smaller
and degraded grain structure but more experimentation using chemical detection would be necessary. It is important to note that the samples deposited on glass do not follow these trends which may be due to differences in substrate-film interface energy.

The film grains behave in a way that Thompson describes as secondary grain growth. They have initial columnar structure, non-uniform grain size, bimodal grain area distribution, and would need further experimentation to prove that they are textured and do not obey the rule of average grain radii growth being proportional to $t^{1/2}$. This leads to the conclusion that SnS films experience secondary grain growth.
References:


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