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Crystallization of Germanium for Use in Low-Cost Solar Cells

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Abstract

The technology for harnessing solar energy is a necessary one, but highly efficient cells are often expensive. The most commonly found solar cells on earth use silicon as a substrate. These cells at best are capable of transforming only one-fourth of the Sun's energy into electric energy, a record set in laboratory conditions, but silicon's economical price is what makes this type of solar cells attractive to the average consumer. Solar cells with a germanium substrate on the other hand can reach 40% efficiency on earth with the aid of solar concentrators. However, germanium tends to be an expensive element, meaning that these high-efficiency solar cells can only be funded for outer-orbit missions on satellites and spacecraft.

The purpose of this research is to determine if annealing germanium thin films may be a possible, low-cost alternative to slicing large, thick wafers of germanium for solar cells. To obtain this goal, samples of amorphous germanium were deposited on TEM grids through vacuum evaporation, annealed at various temperatures and lengths of time in a tube furnace, and then analyzed through the TEM.

It was found that the germanium crystallized at relatively cost-effective temperatures, specifically temperatures over 400 C with moderate grain sizes reaching 7 μ m. Further research needs to be done to determine if the grain size needs to be larger to support a photovoltaic layer.

1. Introduction

Thin-film solar cells are manufactured by depositing a layer of photovoltaic material onto a substrate. The substrate is usually a semiconductor, such as germanium or silicon, which can be amorphous, with no distinct structure, or crystallized. For this research we began with an amorphous thin film of germanium which we would crystallize. In order for it to become crystallized, the amorphous film must be annealed in a furnace or other heating apparatus. The extra energy provided by the heat facilitates the movement of atoms from the amorphous phase, which is metastable in nature to the crystalline phase.¹ This jump of atoms from one phase to another tends to happen in regions with some extra energy, or regions with impurities in the deposited substrate.² The goal of this research is to determine if germanium grains when grown in this method have the possibility of supporting a solar cell.

2. Broader Impact

The most efficient solar cells have a base of germanium. However, germanium is an expensive element, costing \$950 per kilogram.³ Silicon, a material used as a substitute for germanium substrates in solar cells, costs \$2.65 per kilogram.⁴ The tradeoff of using silicon rather than germanium is a decrease in efficiency since monocrystalline silicon solar cells have a maximum efficiency of 25% under laboratory conditions⁵ while germanium solar cells have 28% efficiency in space and over 40% efficiency with the use of solar concentrators while on earth⁶. In addition to the high cost of germanium, current production methods prevent the use of the

¹ Germain, Zellama, Squelard, Bourgoïn, & Gheorghiu, 1979

² Laine, Trapaga, Prokhorov, Morales-Sanchez, & Gonzalez-Hernandez, 2003

³ Guberman, 2010

⁴ Corathers, 2010

⁵ University of New South Wales, 2008

⁶ University of Utah, 2008

entire amount of germanium. In order to make wafers of germanium which serve as the base for solar cells, germanium ingots must be cut into wafers very slowly and carefully to prevent breaking the brittle metal. As with all cutting or sawing procedures, there will be some kerf, or wasted material similar to sawdust, once the slicing process is finished.⁷ The development of better, thinner, slicing techniques has reduced the waste material of germanium,⁸ but it may be possible to continue reducing the use of germanium further if grains of thin film germanium crystals can be used as the base of solar cells instead of wafers. The typical size of one of these germanium wafers could be as thick as 350 μm thick with a diameter of 66mm⁹, but in experiments with silicon-based solar cells, a thin-film 10-15 μm thick with grain size about 50 μm was large enough to support a solar cell which provided 18% efficiency¹⁰. When taking into account the total amount of germanium used to create a solar cell, including the loss of material during evaporation deposition and the sawing process, thin-films have the possibility to drastically reduce the amount of germanium used and hopefully bring the cost of efficient solar cells back down to earth.

This research hopes to aid in bringing more efficient solar cells into use on earth by showing that germanium crystals created through evaporation deposition and annealing will be theoretically large enough to support a solar cell.

⁷ Science2.0, 2008

⁸Rakwal, & Bamberg, 2009

⁹Rakwal, & Bamberg, 2009

¹⁰ Sopori, Chen, Madjdoour, & Symko, 1998

3. Experimental Procedure

3.1 Objectives

In order to see if thin-films of germanium crystals are large enough, they must first be crystallized. Once that occurs, the amount of crystallization and the size of the grains can be examined through analysis on a TEM. From that, the determination of whether or not this method of grain growth will work for the support of solar cells can be determined.

3.2 Equipment and Materials

- 1) JEE-4X/5B Vacuum Evaporator from Jeol Technics LTD.
- 2) TEM Grids: Silicon Monoxide substrate on 200 mesh Molybdenum grids obtained from Electron Microscopy Sciences
- 3) Carbolite tube furnace Type: MTF 12/38/250 with furnace controller 301. Voltage 120V 1-phase
- 4) Hitachi, Ltd. TEM (Transmission Electron Microscope), Model H-7110
- 5) Gatan Inc. Smart Set Hot Stage Controller, Model 901.60CK
- 6) Olympus SIS Veleta 14-bit, 4-megapixel CCD side-mount camera in the TEM
- 7) 99% Germanium

3.3 Sample Preparation

First, a thin layer of germanium was deposited on TEM grids through evaporation deposition as illustrated in Figure 1.

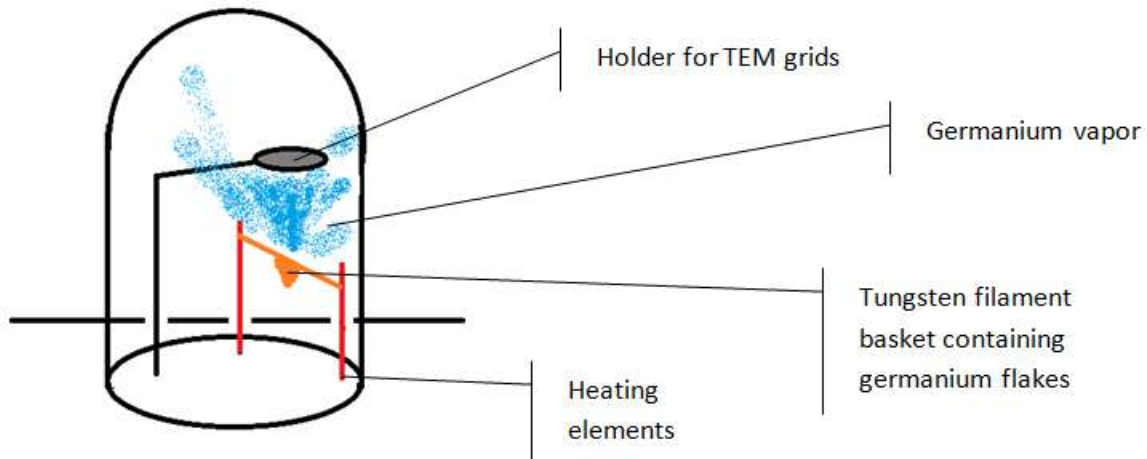


Figure 1: Image of evaporation deposition

To do this, the germanium sample was placed in a tungsten basket between two heating elements with three to five TEM grids per deposition in a holder. These sets of grids were grouped with a letter and each grid within that group was given a number for identification and later reference. The bell jar of the apparatus was then evacuated to near-zero pressure so that the temperature of evaporation is reduced to attainable temperatures. When heated, the germanium melts and then evaporates, sending particles in all directions and coating any available surface including the nearest face of the TEM grids. During this stage of research, a decent amount of deposited germanium is lost in this process since the source was not surrounded by usable surfaces and instead adhered to unusable surfaces such as the glass bell jar. Once the entirety of the germanium was deposited, the vacuum seal for the bell jar was broken, and the samples removed for the annealing stage of research.

The Carbolite tube furnace (Figure 2), or TEM hot stage was used to heat the samples to the point of full or partial crystallization. The tube furnace consists of a cylindrical heating element with openings along the axis which serve as entry points for the specimens. TEM grids were placed in a porcelain boat for safekeeping while being heated, as well as allowing for easier

removal. Once the samples were placed inside of the furnace, it was turned on and the temperature and time regulations were set so that once the furnace reached the desired temperature, the timer would start and maintain the desired temperature for only as long as set by the timer.

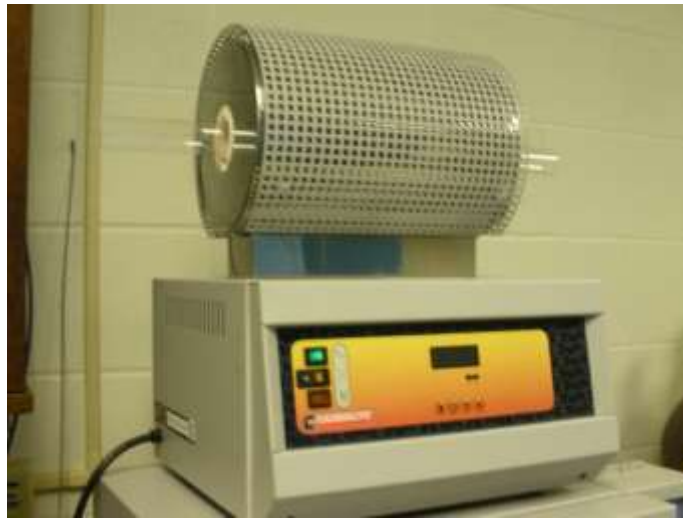


Figure 2: Carbolite tube furnace, Type: MTF 12/38/250 with furnace controller 301. Voltage 120V 1-phase

If the TEM grids were heated using the TEM hot stage instead of the furnace, the temperature would be set and monitored by a hot stage controller. The time would be monitored through image series, with each image set to be taken at a specified interval. This gives a more exact estimation of time when crystals begin to form, and after what amount of time the percent of crystallization.

3.4 Crystallization Verification and Analysis

X-ray diffraction (XRD) can be used to determine the crystallization to a certain degree if the film on the glass slide is thick enough. However, the thickness of the film needed for XRD analysis is much thicker than what is needed for use in the TEM, meaning that glass slides and TEM grids would have to be made separately. Because of this, comparisons between the slide

results and the grids may not be appropriate due to the differences in thickness. As a consequence, any results of XRD scans are not highlighted in this research.



Figure 3: Hitachi, Ltd. TEM, Model H-7110

With the TEM, a unique diffraction pattern off of the crystallized germanium grains as well as visual confirmation of crystallization can be observed and photographed. The change in the diffraction pattern alone can confirm that the sample is amorphous, partially crystallized, or fully crystallized.



Figure 4: Sample A2, amorphous diffraction pattern prior to heating

As seen in Figure 4, the amorphous diffraction pattern can be distinguished by the diffuse rings, as well as their relative evenness. At times, the rings are so diffuse that only the center point can be seen amongst a haze.



Figure 5: D2b, partially crystallized

The partially-crystallized diffraction pattern in Figure 5 is sometimes difficult to distinguish from the fully crystallized pattern, but the rings and distinct pattern are still not as distinct as in Figure 6. The pinpricks of light in the above image are specific grains of germanium, the first definite sign of crystallization.

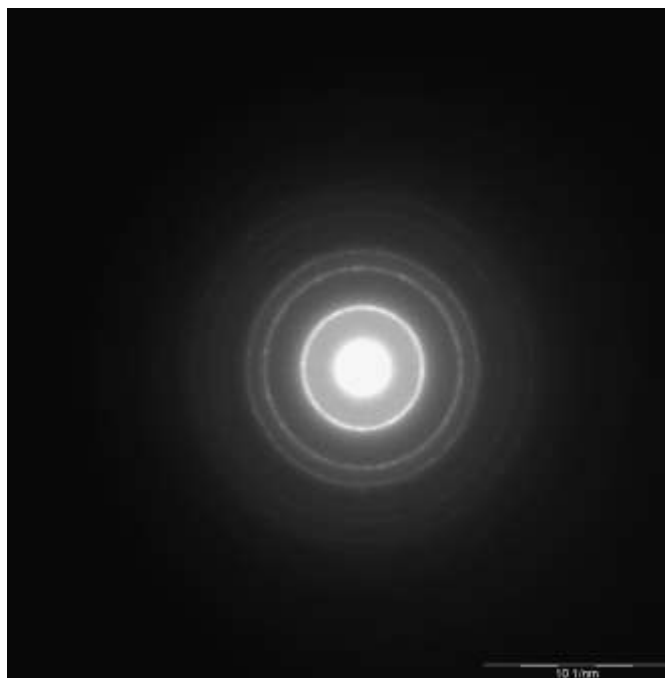


Figure 6: A2, fully crystallized with unique diffraction pattern.

Sample A2 only has smaller grains than sample D2b as indicated by the smaller individual pinpricks of light within the rings of Figure 6. The distinct ring pattern is clearly distinguishable from the rings in the amorphous pattern, characterized by pairs of rings.

4. Results and Discussion

4.1 Samples

Table 1: Summary of annealed Germanium Samples

Sample	Amount of Ge used for Deposition (mg)	Temperature Annealed (°C)	Time Annealed (minutes)	Average grain size (µm)	Estimated % crystallized	Notes
A1**	-	450	-	0.04	100%	
A2**	-	450	-	0.04	100%	Preliminary on copper grids Fig. 4, 6, 7
B1*	28.7	450	30	-	-	Fell apart on removal

						from furnace
B2*	28.7	450	60	-	-	Fell apart on removal from furnace
B3*		350	60	-	amorphous	
C1*	95.2	450	60	0.07	100%	Too thick for good analysis Fig. 8
D1*	51.9	400	60	-	amorphous	
D2a*		400	120	1.5	22%	Fig. 9, 16
D2b*		400	120 (240 total)	1.6	75%	No change in size from second heating Fig. 5, 10, 11
D3a*		375	300	-	amorphous	
D3b*		375	360 (660 total)	-	amorphous	
E1*	52.9	400	240	-	amorphous	Unusually amorphous Fig. 15
E2*		500	90	-	100%	Indistinguishable grain size
E3*		450	90	4	20%	Fig. 12, 13, 14
E4**		450	38	1.6	50%	100% after 60 min
E5**		450	18	1.6	50%	100% after 35 min

* Heated in tube furnace

** Heated in TEM hot stage

Sample set A was primarily used as a test run to determine the range of germanium crystallization as well as a way to become acquainted with the equipment. The heating process was done in the TEM up to 500°C, which crystallized the germanium very quickly and in very small grains. As seen in Figure 7, the largest grains which can be seen in black are only 40nm in size and many others seem to be much less than that. These preliminary findings were troublesome because a 40nm grain is in no way a reasonable size for supporting a photovoltaic cell.

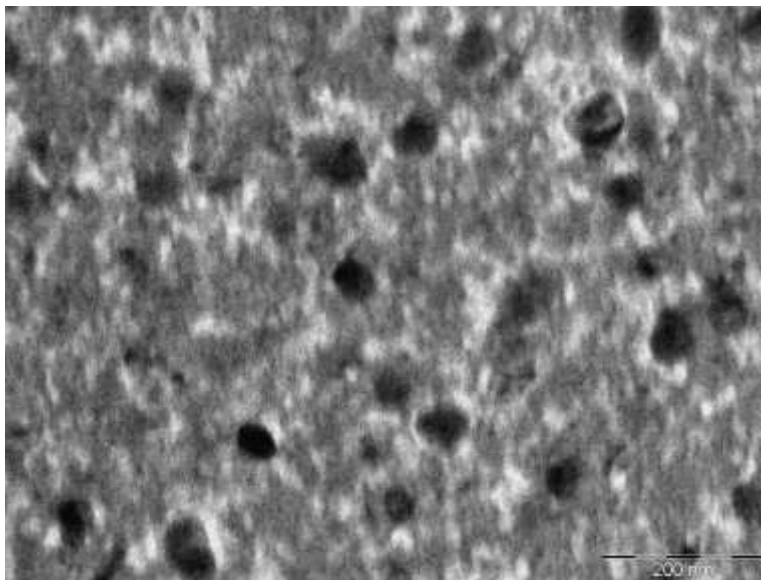


Figure 7: A2, above 400°C in TEM for an unknown time

For sample set B, 28.7 mg of germanium was used to create the thin film, but the layer created from this amount was too thin to be used. The film was able to withstand being moved to the tube furnace, but after the annealing process the film tended to disintegrate when lifted from the porcelain boat. The only sample that survived annealing was B3, which was heated at 350°C for an hour, and was amorphous when analyzed in the TEM.

Sample set C used 95.2 mg of germanium in the deposition. This amount made the film too thick to determine the amount of crystallization through TEM efficiently. Sample C1 was fully crystallized after an hour of annealing in the furnace. As can be seen in Figure 8, the individual grains were difficult to distinguish from one another, with the exception of the grain measured in the rightmost image of Figure 8, which was about 70nm in length.

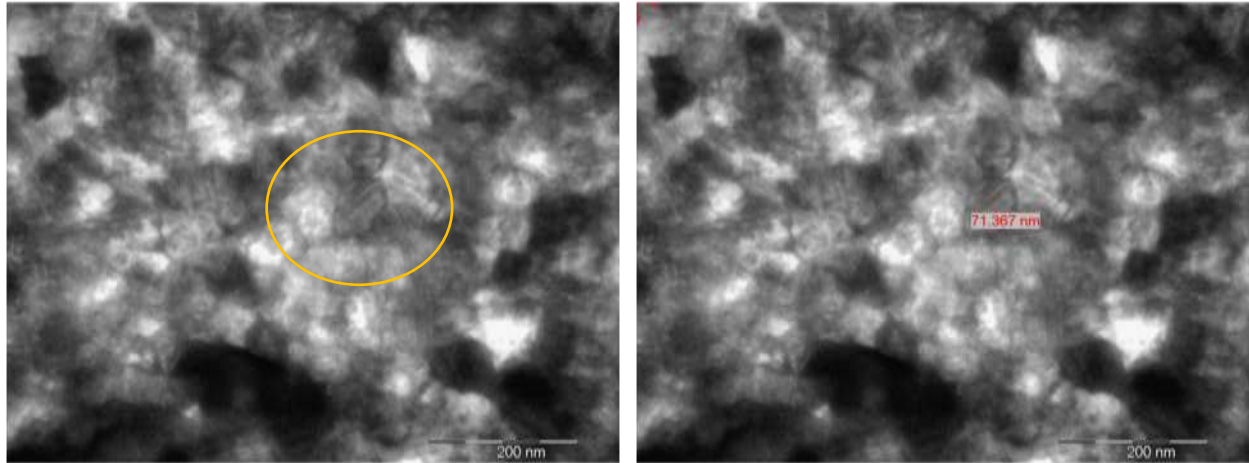


Figure 8: C1, 450°C for 1 hour, completely crystallized

Sample sets D and E had the best results and used about 50mg for each deposition. Set D used 51.9mg for the deposition. Samples D2 and D3 were annealed twice in the tube furnace (noted by an “a” or “b” following the sample name). This was to see if further annealing would grow the grains any larger. Interrupting the annealing process and then heating the samples a second time did increase the amount of crystallization from approximately 22% to 75%, which can easily be seen in Figure 9 and Figure 10.

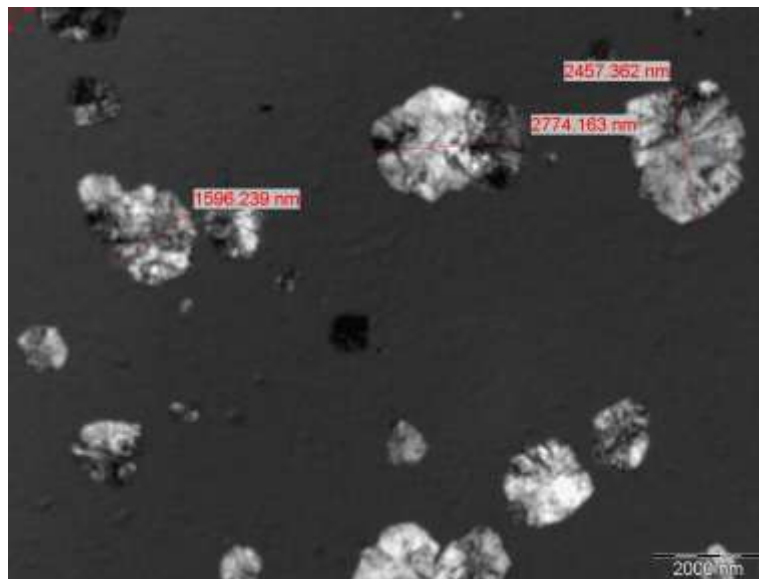


Figure 9: D2a, 400°C for 2 hours, sporadic crystallization, fairly large grains, the grain measuring 2774.163nm likely two, possibly three, grains

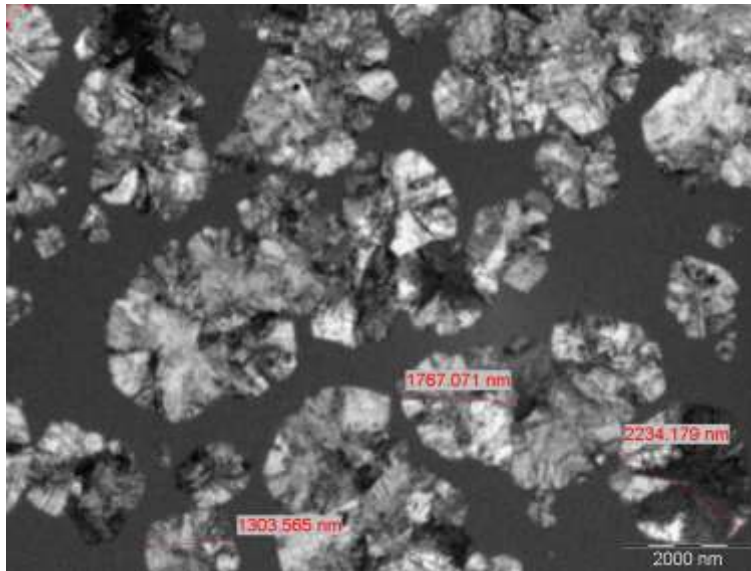


Figure 10: D2b, 400°C for an additional 2 hours –a total of 4 hours, over 50% crystallized

The grain size did not seem to be affected by the second annealing, though. Figure 10 is a little too crystallized to be able to accurately determine an average size for most of the grains. Judging by distinguishable grains in Figure 11 and Figure 12, there was no significant change in the size of the grains (from an average of 1.53 μ m to 1.58 μ m).

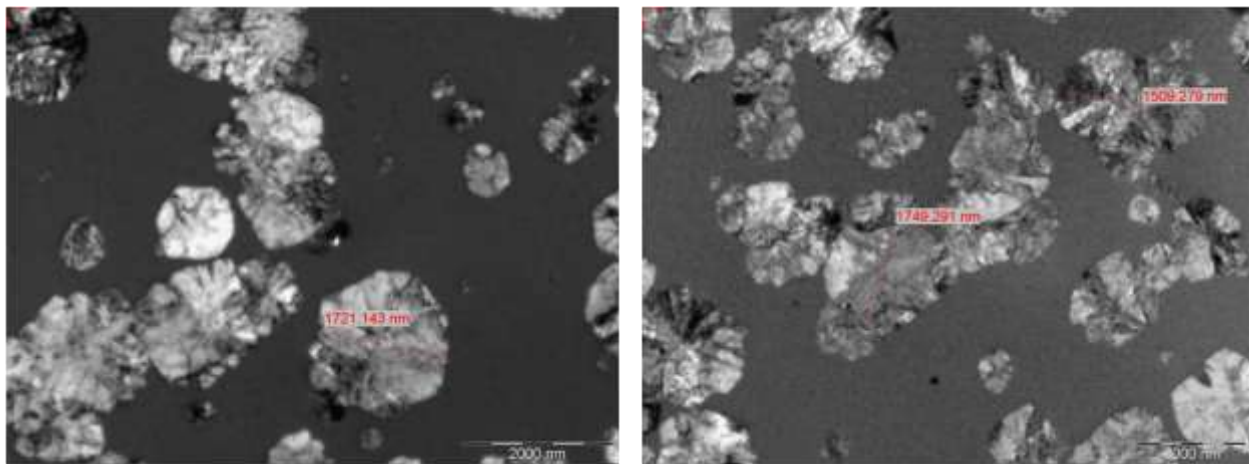


Figure 11: Sample D2b

Set E also had good results, and used 52.9mg of germanium for deposition. The average grain size was $4.15\mu\text{m}$, with the largest measuring nearly $7\mu\text{m}$. Figure 12 shows several of average size grains and the surrounding anomalies.

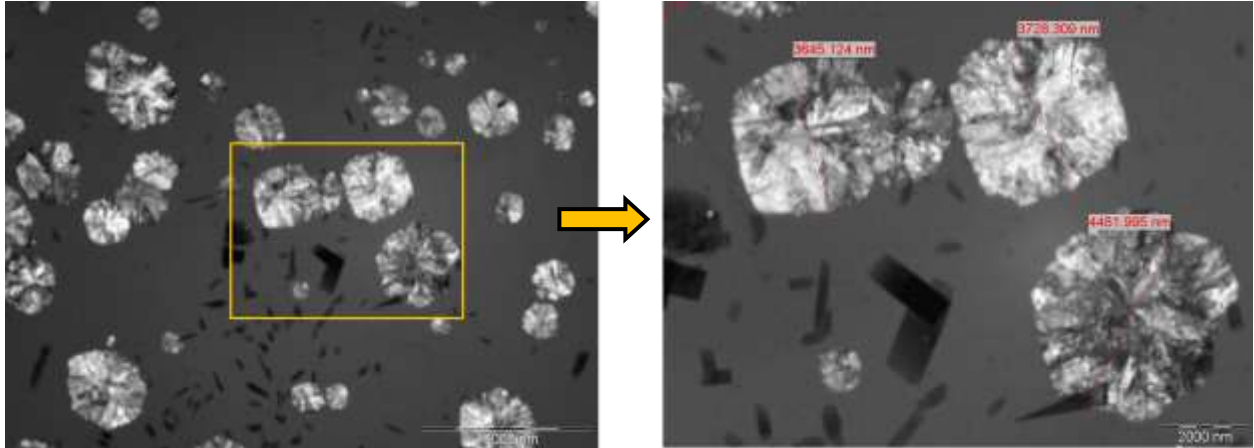


Figure 12: E3, 450°C for 1.5 hours, and its magnification

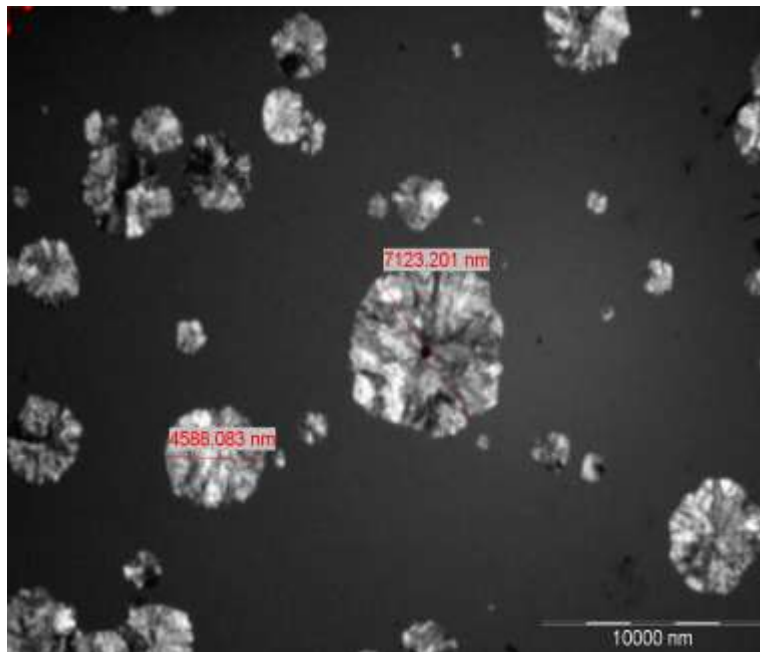


Figure 13: Sample E3 at a different location, showing the largest grain found, same magnification as Figure 12 to the left

The larger grains had a distinctive feature when compared to other samples since many of them had a dot near the center of each grain. The largest grain had one that measured $0.39\mu\text{m}$ in

diameter and was almost perfectly centered. At first it was thought that this could be an impurity in the germanium which acted as a nucleation site and contributed to the large amount of growth. Spectroscopy analysis was done to determine what type of impurity the dot could be, but the results found no other element except germanium in significant quantities.

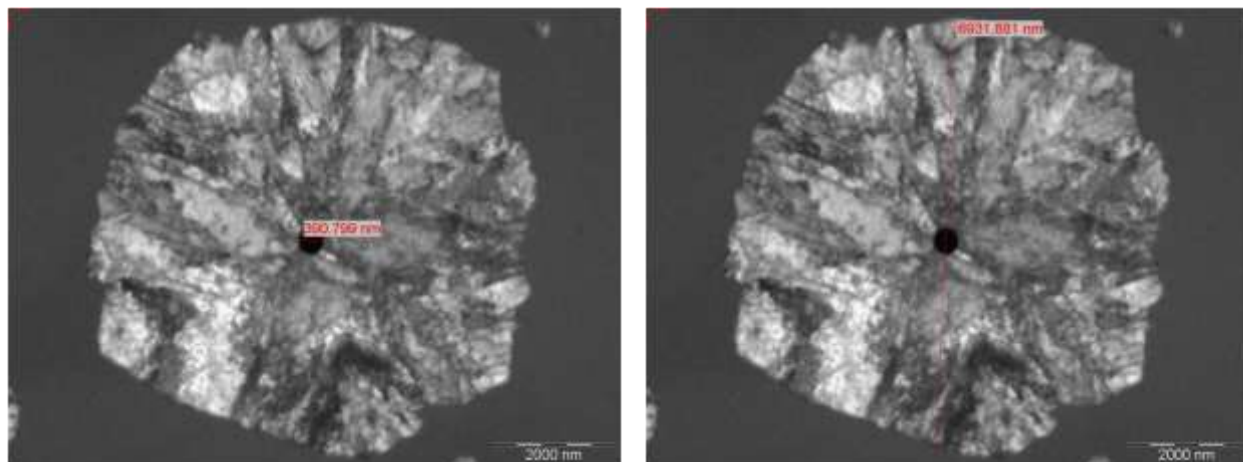


Figure 14: E3, the largest grain identified, also shown in Figure 13

Once the sample was analyzed in other areas of the film, other large grains with similar dots in the center were found. Not all of the other grains with dots were quite as centered as the grain in Figure 15, and none were quite as large.

Samples E4 and E5 were annealed in the TEM hot stage at 450°C. Both crystallized fully within an hour, sometimes faster, which is a different result from when samples were heated in the tube furnace for an hour. No other remarkable observations were made about these samples.

5.2 Troubles Encountered

Some temperature variations occurred between the TEM and the tube furnace. When annealing sample E4 and E5 in the TEM, crystallization seemed to occur at a higher rate than the same temperatures in the tube furnace. This could be because of the openings at both ends in the furnace. The openings allow for some amount of airflow through the tube where the sample was

heated, which could result in a lower temperature than what was displayed. The openings could also lead to excess debris on the films, similar to the rectangular impurities which can be seen in Figure 12.

The furnace, possibly as a result of a lower temperature than what was displayed, occasionally resulted in an amorphous sample after heating, even when other samples had shown that the given temperature and time would result in significant crystallization. The most characteristic sample of this sort was E1 which was heated for four hours at 400°C. The TEM analysis was amorphous (Figure 15), and the diffraction confirmed this on several occasions. These results make no sense since other similar samples, such as D2a, was heated in the furnace at the same temperature for only half of the time and still had about 22% crystallization. The furnace did not fully malfunction either since the porcelain boat used to hold the sample had to cool before being handled.

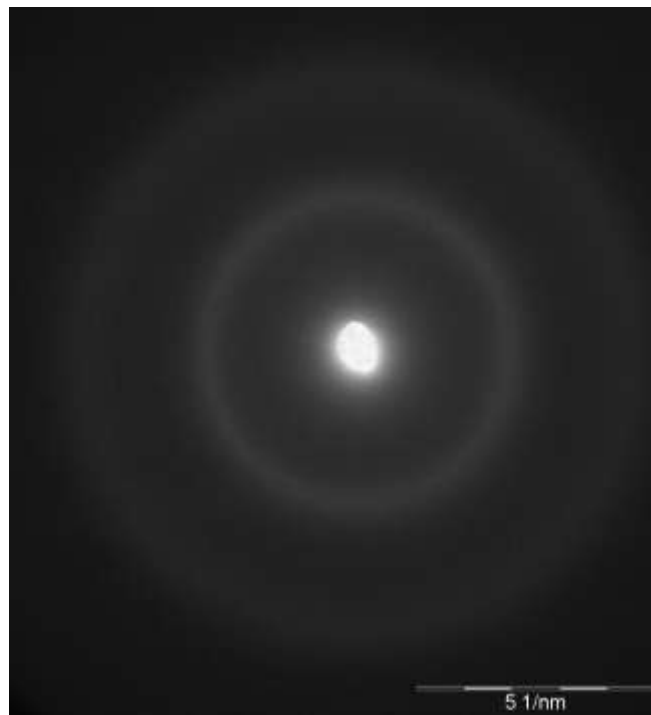


Figure 15: E1, 400°C for 4 hours, amorphous despite contradictory evidence for other samples

4.3 Germanium Characteristics

During the analysis of the samples, it was found that the germanium grains usually had a round shape with radial symmetry, sometimes shown distinctly as a split down the middle, such as in Figure 16. The implications of these findings remain to be seen, but may contribute to brittleness in the grains.

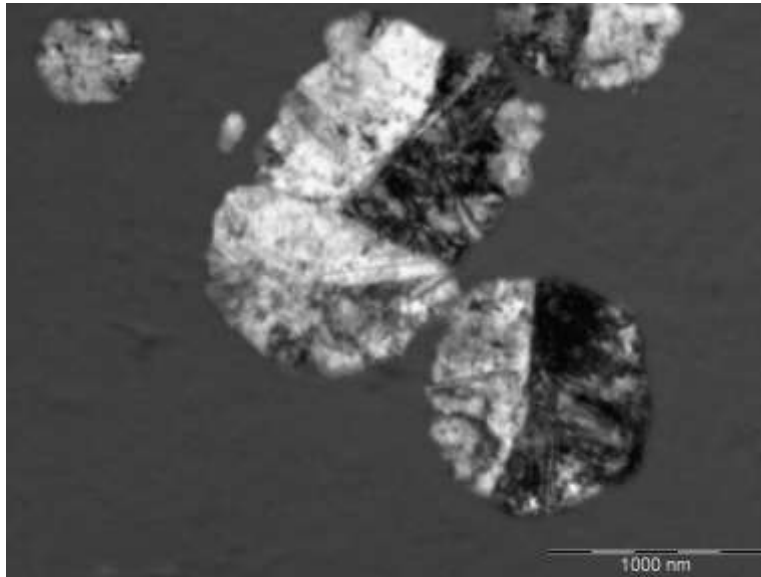


Figure 16: As seen by figure D2a, the grains seem to have a prominent “split” within a single grain

5. Conclusion

5.1 Summary

This research was quite successful. The range of temperatures which crystallized the germanium films was found to be from about 400-500°C. This range is very close to previously established temperatures 355-495°C.¹¹ Within this range, an optimal temperature of 450°C was found, due to the larger sized grains which were found when annealed at that temperature. This temperature is easily attainable in an academic or industrial setting, and would not contribute

¹¹ Germain, Zellama, Squelard, Bourgoin, & Gheorghiu, 1979

significantly to the cost of a thin-film germanium solar cell. The grain sizes did not reach the 50 μm diameter which was used in silicon solar cell testing, and without much else to go on, the max size of 7 μm seems small in comparison.

5.2 Future Research

The first process which needs to be further analyzed would be evaporation deposition. Estimates of how much germanium is lost, as well as designs to increase the efficiency of deposition, such as surrounding the source with more useable surface area, should be looked into. Without these increases in efficiency, more germanium would be lost than used and the cost of such waste could add up to be as much as when germanium wafers must be cut.

The ability of the grains to support a photovoltaic layer is very important research which needs to be done. This research did not determine any stability of the grains, so 4 μm grains could still be able to support the cell.

Hydrogen-passivation is another process which needs to be looked into. H-passivation has been used in silicon to maintain its electrical properties. Germanium will need a similar process, and the effects of this on the size and stability will need to be analyzed. In silicon, H-passivation has a tendency to increase the size of the grains, which may help increasing the size of the grains found in this research.

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