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Investigation of Spin and Dip-coating Phase Change Chalcogenide Materials as a Novel Technique for Coating and Functionalizing Conformal Optics

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Investigation of spin and dip-coating phase change chalcogenide materials as a novel technique for coating and functionalizing conformal optics

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Intro

Chalcogenides are bonded elements with bases of S, Se, and Te [1]. Chalcogens can be bonded with other elements such as Ge, As, Sb, and Ga to form Chalcogenide glasses (ChGs). These semiconducting materials have substantial use due to their high refractive indexes and wide IR transparency regions, high optical nonlinearities, photosensitivity, and photothermal quality [2]. ChGs low band gap also gives optical and electrical properties [2]. Common compositions of study usually involve Sulfides and Selenides, dissolved with propylamine, butylamine, or ethylenediaminie [2]. ChGs can be used in lenses, windows, and fibers, as well as an amorphous film to be deposited onto certain diffractive optical elements, waveguides, and high resolution photoresists [3]. All of these helpful properties make ChGs a perfect candidate for use in infrared (IR) technology and optics. However, the films are typically deposited onto glass slides using expensive physical vapor deposition techniques such as thermal evaporation, and laser ablation [3]. Thermal deposition uses a resistive heat source to heat up a solid to make it into a film in a vacuum environment [4]. Solution based techniques such as spin-coating and dip-coating offer a low cost alternative to create ChGs. Solution based techniques work because of the solubility of ChGs in volatile alkaline amines, but may be somewhat inefficient because of the techniques possible unwanted residuals on the slides [3].

IR imaging, sensing and detection have been advancing more and more, creating a more cost-efficient way to build these systems we use every day. ChGs are glassy substances that may be an alternative to past crystalline substances as ChGs are further studied [5]. Crystalline glass involves periodic ordered structure, while glassy refers to not being locked in a specific stoichiometry [5]. Due to the large wavelength spread of the IR region, it is broken down into subsections known as: near-IR (NIR), ranging from ~750nm to ~1500nm; shortwave IR (SWIR), ranging from ~1500nm to ~3000nm; the mid-wave IR (MWIR), ranging from ~3000nm to ~8000nm; the long-wave or thermal IR (LWIR / TIR), from ~6000nm to ~50µm; and the far infrared (FIR), for wavelengths larger than 50µm [5].

Chalcogenide fibers are useful for sensitive chemical structures, mainly because most molecular species vibrate in the IR region [4]. These fibers can be used in fiber-optic chemical sensing systems of all sorts both militaristic and civilian. For example, a fiber-optic chalcogenide dipstick that is in the gas or oil tank of a vehicle can more accurately detect how much oil or gas is left in the tank [4]. Another example is how IR can help distinguish tissue and organ samples using spectra [1].

The most important perk of dip-coating is its unique application for conformal lenses. Dip-coated optical windows, domes and other noncircular surfaces offer a valuable role in technology. Since spin coating a uniform film onto a conformal lens is impossible, other ways must be advanced. Spin-coating is effective, but limits the size and shape of the substrate.

Practical uses from ChGs are everywhere. The question is, which method is best for making the ChGs. Spin-coating and dip-coating can cause unwanted solvent residue, a disadvantage when making these films [1]. Heat treatment is key in removing residual solvents, and the annealing process must be done efficiently and properly [1]. Durations of heat, dipping time, and recipe spin process must be tested to properly dispose of any residual solvent and properly create an efficient and re-creatable sample [1]. Advantages of solution based techniques include covering a larger surface area with a thicker film while holding onto optical, physical and chemical properties compared to the more conventional thermal deposition techniques [1]. To validate this, spin-coating and dip-coating procedures must be studied to know all the specific durations and parameters for creating better and perfecting ChGs techniques.

Experimental Methods

The chalcogenide glasses studied in this research were As_2S_3 or As_2Se_3. Two solutions total were made. First, the mixture that is being deposited onto a glass slide must be made. The As_2S_3 and As_2Se_3 were ground up into a fine powder, so it would dissolve easier in a solvent. Ethylenediamine (EDA) was the chosen solvent for the two glass compounds. EDA was chosen because of its helpful properties that break Chalcogen bonds and it is also not very volatile. To make this, the powder was measured 4 grams in 10 milliliters each and poured in with EDA in a small glass container. The vials were left to mix using a

magnetic stirrer overnight, with a para-film covering the top of the containers with one hole in each of them for as little evaporation as possible. Both vials were left at an elevated temperature of 60°C for one hour. After heat treatment, the solutions were left to fully dissolve overnight once more. After the glass appeared to be fully dissolved, the two solutions were filtered using a glass pipette and a filter. The As_2Se_3 took the full two day process to fully dissolve, while the As_2S_3 dissolved after the first day. The As_2Se_3 mixture was a dark red and black color and the As_2S_3 was a bright yellow color after filtering both through (Fig. 1).
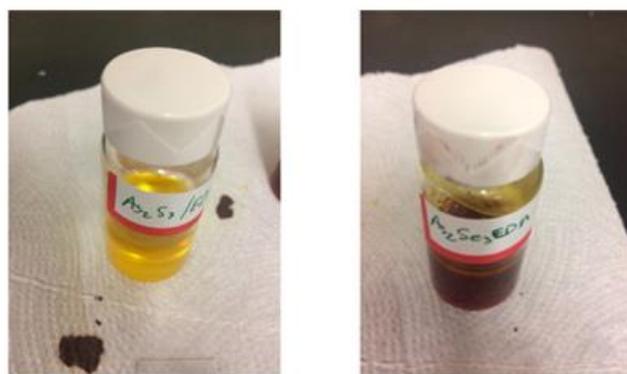

**(a)**   **(b)**

Fig. 1. (**a**) As_2Se_3 and (**b**) As_2S_3 mixed with EDA.

Glass rectangular slides were cut into squares to be used for spin-coating. When spin coating, there were many different viable recipes and ways to drop the solution onto the glass substrates. This experiment was conducted within a fume hood. Using a plastic pipette, the two solutions were each carefully dropped onto the slides while inside the spin-coating machine. The square slide was completely covered in a thin layer of solution for both As_2Se_3 and As_2S_3 separately (Fig. 2(a)). The slides were spun at 1000 RPM for 30 seconds. After letting the substrates were left to dwell, they were transferred from the spin-coater to a hot plate at 90°C for 5 minutes (Fig. 2(b)). Each slide was then transferred to an oven at 110-130°C for an hour while sitting upon an aluminum foil bench. This is all in an effort to reduce the amount of solvent left on the substrate.
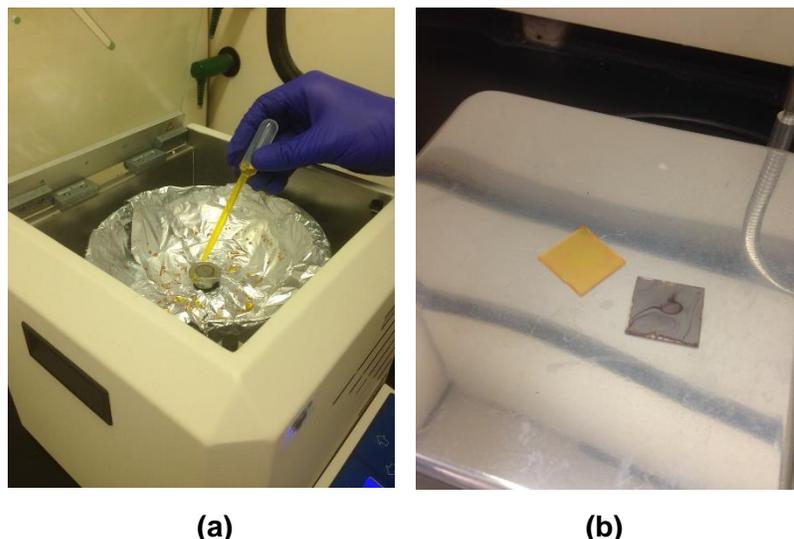
Fig. 2. (**a**) The spin-coating process completed with specific recipes, and then (**b**) heat treated on a hot plate.

Three different dip-coating techniques were used to get a plethora of different sample substrates with the film on it. First, a glass rectangular slide was cut in half vertically, so it could fit in the solution vial. A para film was wrapped above the vials of solution, and the long slide was put to soak in the each solution for 40 minutes (Fig. 3(a)). The half-slide was taken out of the vial, and set down on a hot plate at temperature 100°C to evaporate excess EDA. After 30 minutes, the temperature was changed to 150°C and let sit for 15 minutes. The hot plate was turned up again to 170°C and let sit again for 15 minutes. Another increase was made to the hot plate to 190°C after, and let sit for 15 minutes. Lastly, it was turned to 230°C and left to sit for 10 minutes (Fig. 3(b)). During all of this, note that the temperature was increased on the hot plate, but the slides were left to sit on the plate even while it was heating up. The recording time for each interval began as soon as the previous heat treatment interval was finished, meaning each of the substrates were heated for about a minute less than recorded due to the 30-45 second time period the hot plate was heating up. One sample was made for each solution of EDA/As_2S_3 and EDA/As_2S_3.
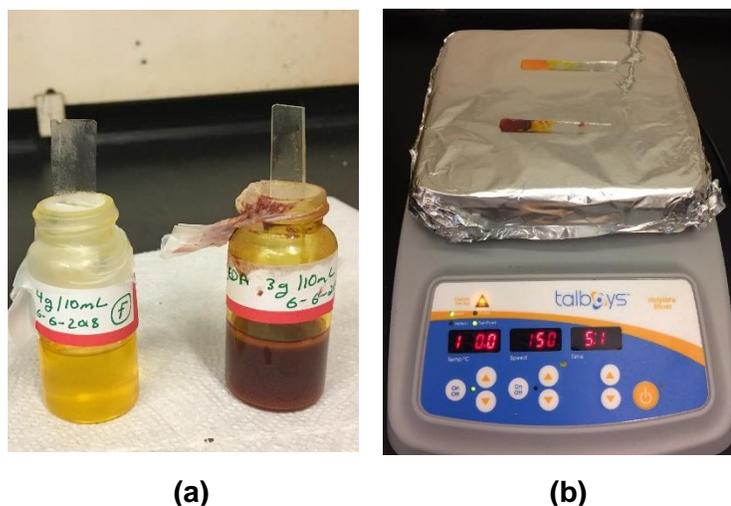
Fig. 3. (**a**) The dip-coating process for As_2S_3 and As_2Se_3. (**b**) Dipped for selected time frames then heated at various temperatures on a hot plate.

The second dip-coating technique was in a different fashion. The half-slides would be dipped in each of the solutions for 1 minute intervals, and manually lifted with a gloved hand for 10 seconds. After the 10 seconds, the slide would be put back into the solution to soak more. Each process was done for 20 minutes, including about 16-17 total minutes of the slide submerged in the solution. The dip coated substrate was placed on a hot plate set at 100°C for 30 minutes. Then, after taking 2 minutes to heat up from 100°C to 150°C (with the slide still on the plate), the substrate was left to sit on the plate for 15 more minutes.

The final trial of dip coating procedures is very similar to the last. The half-slide was left to sit in the solution for 1 minute intervals, and was taken out for 10 seconds, and put back in for a 10 minute length. Then the slide was transferred to a hot plate set at 100°C for 30 minutes.

Overall, there were many dip-coated slides of different varieties as well as the spin coated slides ready to be analyzed and examined. The UV/VIS Spectrometer was used to analyze these thin film substrates. This will give the transmission of each of the ChGs. Each sample was scanned 6 times in a light-free chamber inside the machine. After each scan, a slight shift of the slide was made to get more data to average for a more accurate result. The UV/VIS Spectrometer produced the graphs of each slide with %Transmission by the wavelength in nanometers. The UV/VIS band was set at 0.5nm and the NIR

bandwidth was set to 2.0 nm. The measurements were made on a scale of 1300-250nm with a data interval of 1.0nm, and a scan speed of 200nm/minute. The scanner also changed to the light scanner and is notable in the graphs as a steep drop off at 350nm, and the same change to the gratin scanner at 800nm. The filter exchange was set to step, and before each group of samples were taken, a baseline correction was measured using a piece of a plain glass slide. The sample holder used was a rectangular piece of plastic made using a 3-D printer with a shelf and small hole behind the shelf. This is to allow light to pass through the samples and get accurate data with as little exposure as possible.

The samples analyzed using the final dip-coating process were slightly adjusted to account for unreliable transmissions (Transmissions with 1000+%T or -1000+%T around the 290nm range). The new parameters included a scan speed of 2nm/min and only recorded the wavelength range of 300-1300nm for each sample.

Results and Discussion

Fig. 5. The %T graph of evaporated and dip-coated As_2S_3 spectra show the difference between a 10 and 20 minute dip-coat, as well as the wide range in the visible light spectrum and IR regions.
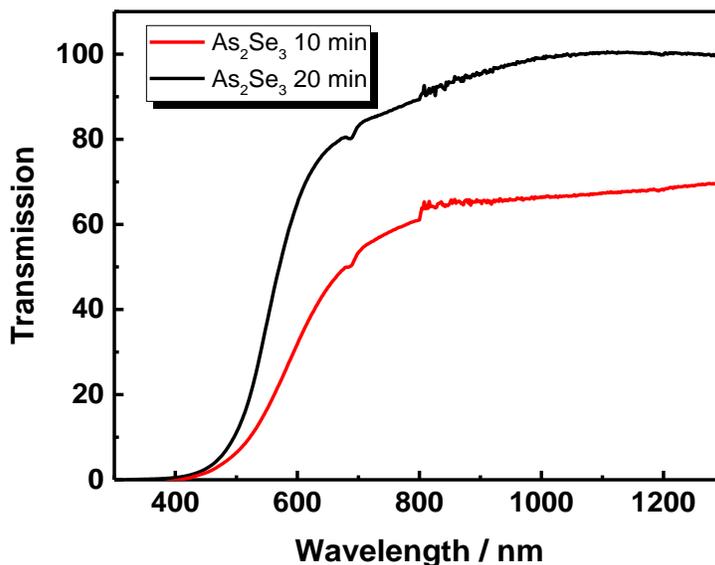
Fig. 6. The %T graph of evaporated and dip-coated As2Se3 spectra show the difference between 10 and 20 minute dip-coat, as well as the wide range in the visible light spectrum and IR regions.

Transmission was truly only accurately obtained from the evaporated regions of the dip coated film possibly due to lack of solvent evaporation in the thick regions. Transmission of the evaporated regions indicate nice cut off for As_2S_3 at 20 min but possible scattering tails for the others (Fig. 5). The spectra for the thick dip-coated regions were dropped. The small transmission percentage tells us it has little use in the visible light spectrum (Fig. 7, 8, 9, 10). It is also possible the films were scattered during the process at some point. It could be due to the heat treatment, or an inhomogeneous film that was deposited onto the substrate.

The graphs of the spin-coated data gave a great baseline for what the dip-coated data should look like if done correctly. The As_2Se_3 has doesn't reach into the visible light spectrum as much as the As_2S_3, but still shows significant use. The evaporated As_2S_3 and As_2Se_3 both show that a better transmission will occur if the dip-coating process is done in 20 minutes rather than 10 minutes. Transmission was better on the dip-coated sample of As_2Se_3 compared to the spin-coated sample (Fig. 6). All in all, the dip-coated data shows very similar results compared to the spin-coated data.

The amount of time dipped in the solution plays a major role in transmission as well. The 20 minute dip coating spectra for As_2Se_3 show a significantly lower transparency throughout the graph compared to the 10 minute dip-coated data. However, the transparency of the As_2S_3 10 minute dip levels off and catches up to and shows to be a better source of transparency than the 20 minute dip for As_2S_3. In the future we will develop a procedure for baking/annealing that will remove more solvent. On the other hand, the evaporated regions showed nice spectra with high %T and clear band edge. This evaporation method could be refined and used in future studies to apply thin films.

During experimentation, excessive heat treatment was used. Some samples began to crystalize as they were heated at too high a temperature for too long. That combination was slowly refined into the final product graphs that show successful dip-coating procedures can be done with a smaller amount of time, and a lower temperature if done correctly. Future work includes refining the dip coating & post-baking procedure in order to create thin films with better control over thickness, homogeneity, and surface quality. This would allow for the coating of conformal substrates and the use of other ChGs compositions.

Dip-coating is still an unknown process that has ample possibilities for use in optical technology. However, it was really a risky and experimental process to conduct. It was unknown whether the film would stick to the substrate, if a homogeneous film would be created, and if the EDA would be fully evaporated. It shows a cheap and simple way to accurately deposit thin films onto conformal lenses of any size, scale, and shape.

Conclusion

Many problems get in the way of making ideal thin film ChGs for conformal optics. In this research we compared the traditionally used spin-coating process to the novel process of dip-coating. Mainly, the biggest issue is evaporating all the EDA or any solvent used during dip-coating. Heat treatment is widely used to solve this issue, it is just necessary to experiment with different durations, temperatures, speeds, and quantities when working with these ChGs. The thick dip-coated spectra showed very inconclusive data, but taught a lesson that it's partially evaporated films were better tests than the thick coated films. Evaporation is an attractive alternative to dip-coating. Future procedures to correctly make dip-coated samples with high transmission and a better cutoff in the visible light spectrum are in the process with this new method. Dip-coating can work. We will refine our post baking procedure to better transmit data from thick regions, as the evaporated regions produced the best data. Dip-coating is a new, cost-efficient, and manual method for applying films on substrates.

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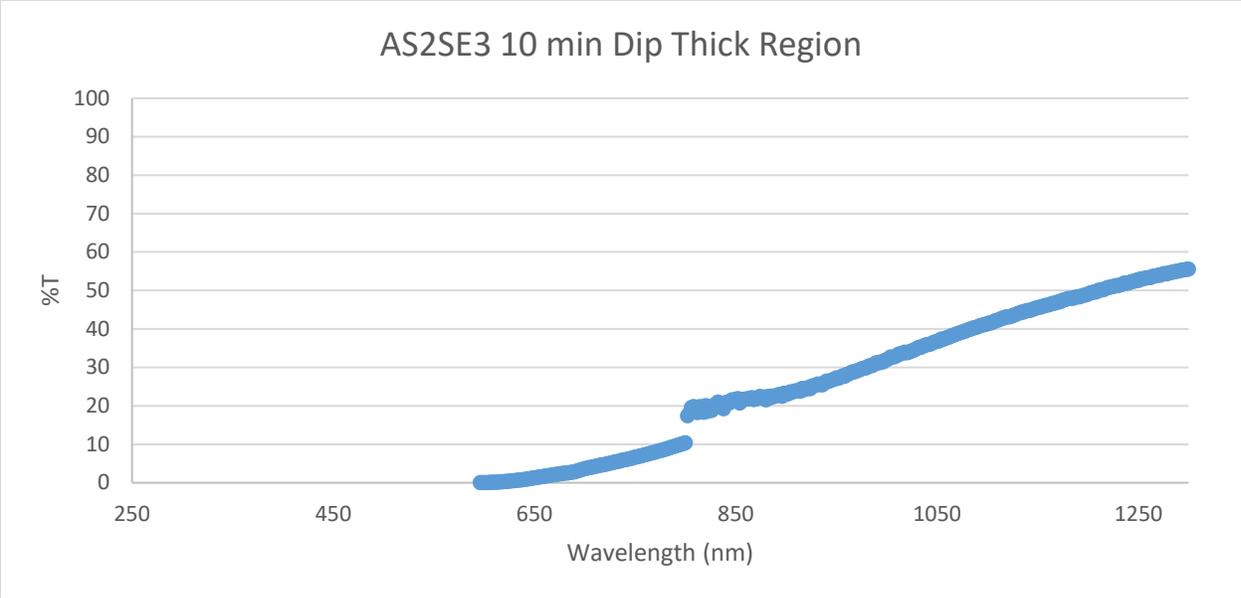
Appendix

Figure 7. The %T graph of As$_2$Se$_3$ after a 10 minute dip-coating process reveals very little transmission in the visible light spectrum.
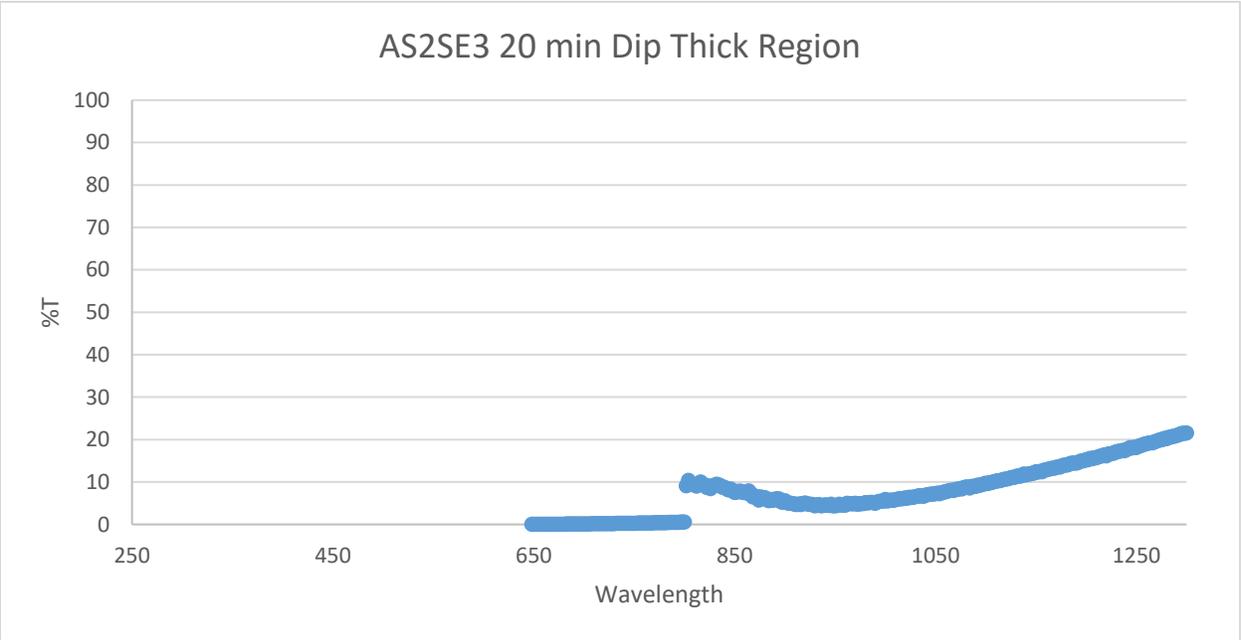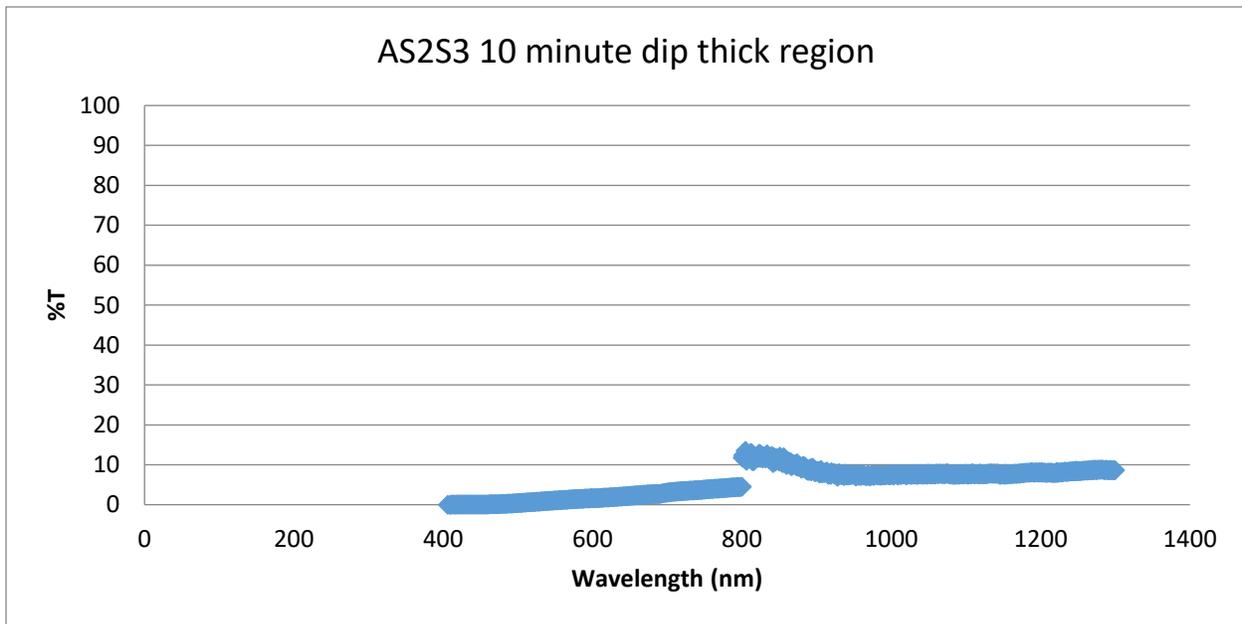

Figure 8. The %T graph of As$_2$Se$_3$ after a 20 minute dip-coating process shows similar data to the 10 minute dip, both showing little transmission.

Figure 9. The %T graph of As$_2$Se$_3$ after a 10 minute dip-coating process reveals very little transmission in the visible light spectrum.
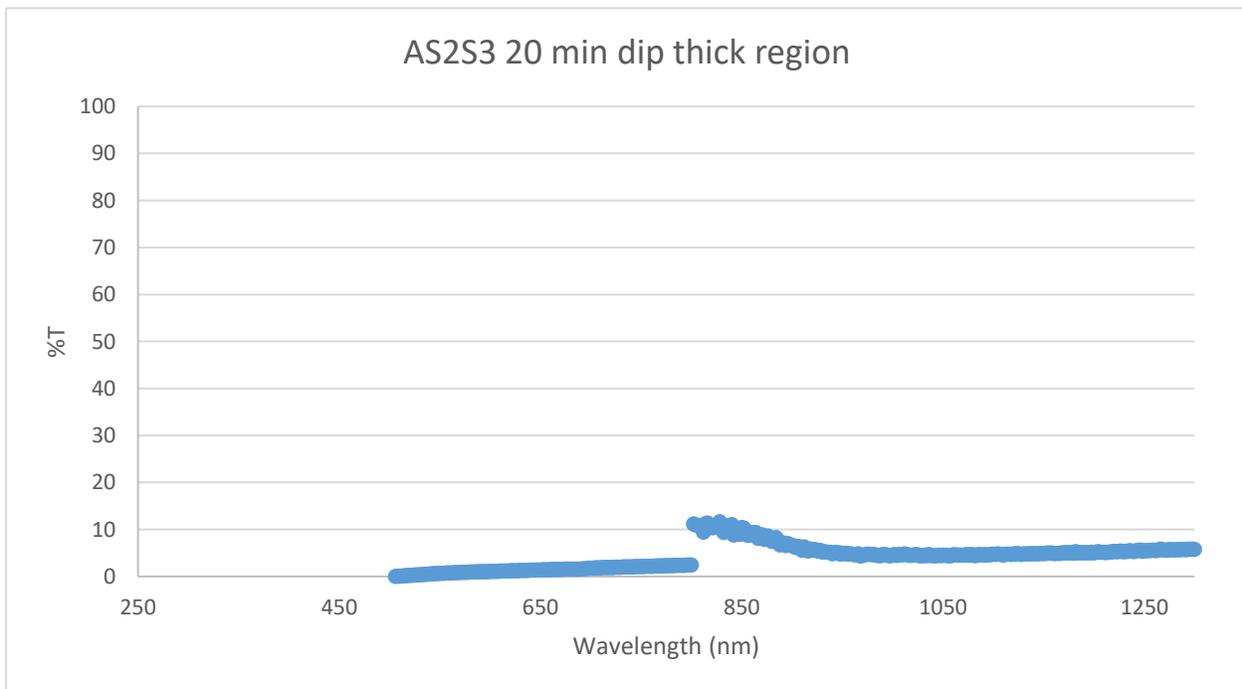

Figure 10. The %T graph of As$_2$S$_3$ after a 20 minute dip-coating process shows similar data to the 10 minute dip, both showing little transmission.
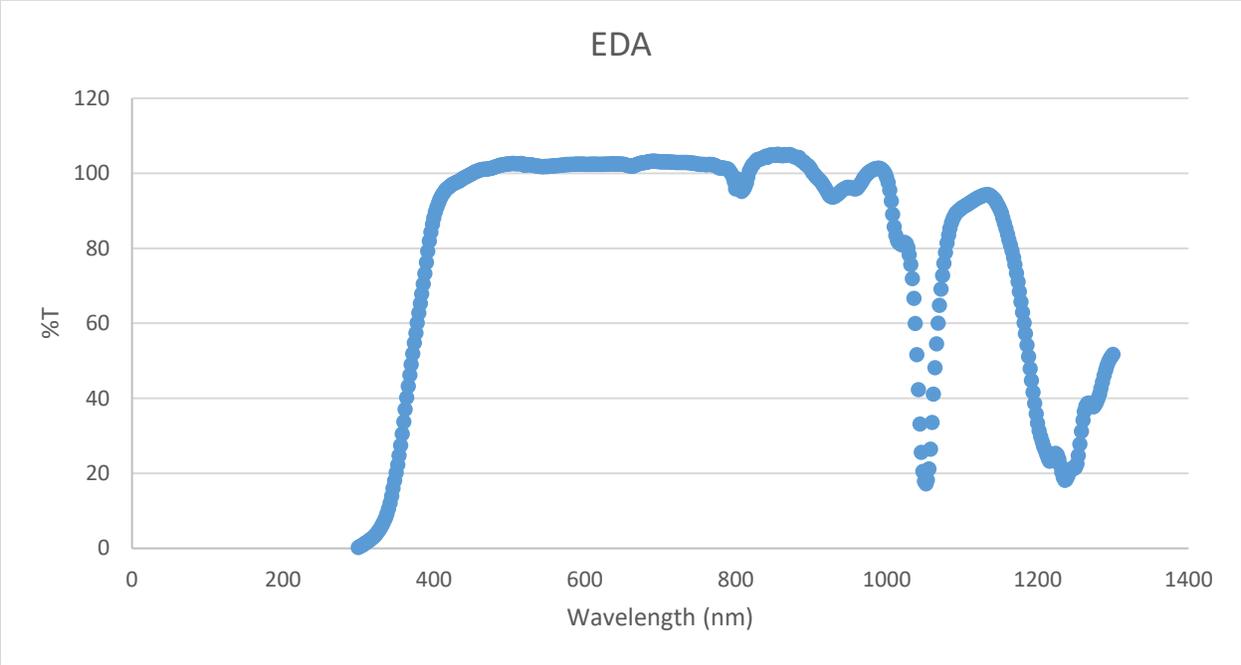
Figure 11. The %T graph of EDA shows there was not much EDA distinguishable in the spectra of the dip-coated films, both evaporated and thick.