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Processing and Characterization of Spin-Coated As2S3 Films for Direct Laser Writing

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Abstract

Diffraction gratings, waveguides, and resonators are components of photonic devices that can be fabricated using chalcogenide glasses. These chalcogenide components can be made through a process of direct laser writing and etching to reveal targeted structures on the surface of the films. Thermal deposition in combination with targeted laser irradiation has been used on As_2S_3 films with excellent results , but spin-coating as a method of deposition has been less explored. Spin-Coating is a relatively inexpensive procedure where a bulk glass is dissolved into a solution using amines and spun onto a substrate. This is a low-cost alternative for film deposition that can be combined with lithography techniques for photonic device fabrication. This paper outlines spin coating and characterization of films on a substrate for the purpose of direct laser writing.

1 Introduction

Photonic devices are optical components that are used for manipulating or detecting light. Diffraction gratings, waveguides, and resonators are components that can be fabricated us-

ing chalcogenide glasses. These glasses are particularly useful because they have optically tunable properties [3].

1.1 Chalcogenide Glass

ChG's are functional for many infrared optical applications including IR photonics, laser power delivery, Raman gain amplification, and optical sensing devices, and the high photo-sensitivity makes them perfect for creating directly written waveguides, gratings, or microlenses.[1].

Chalcogenides (ChG's) are glasses that are composed of one of the elements S, Se, Te in some combination with the semi metals Ge, As, Ga, etc. These glasses can be crystalline or amorphous in form. What differentiates chalcogenides from oxides is that they posses large atoms with high atomic mass and similar electronic polarization[1]. This means they have low phonon energies and high refractive indices, leading to transparency from the visible to mid-IR region[3]. This high transparency makes ChG's ideal for IR photonic applications such as laser power delivery, Raman gain amplification, supercontinuum generation, and IR optical sensing [1]. ChG's also typically possess wide glass forming regions, which makes it easier to adhere to manufacturing constraints [1].

The low strength of the atoms' bonds makes chg's have low glass transition temperatures(T_g). With a low T_g, chalcogenides can be melt quenched at room temperature which leads to long term stability and makes the material sufficient for polishing and creating thin films, as well as the long-term stability needed for commercial devices [1].

ChG's also possess high photo-sensitivity. When these glasses are exposed to high intensity or short wavelength irradiation, the structural elements of the glasses can be rearranged. This can create permanent or reversible changes in the optical and physical properties of the glasses. Applications of this memory include inorganic photoresists, directly-written waveguides, gratings, and micro-lenses. To create these applications, the glass must be processed into thin films or fiber [1].

1.2 Thin film deposition

For optical device fabrication, the quality of the thin film is important. Their composition must be similar to that of the bulk glass, they must have low optical loss, and the refractive index should reproducible. It is also important that the films are homogeneous with a low surface roughness [2].

There are a few ways to create thin films. A traditional way has been using physical vapor deposition (PVD) methods including thermal evaporation, sputtering, or pulsed laser deposition. While these methods may have effective results, there are a few problems. These methods can be expensive and they limit the size and shape of the device being manufactured. In the case of thermal evaporation, which requires a large thermal deposition chamber, the film created often has a different stoichiometric composition than the bulk material as well as exhibits inhomogeneity across the film surface. To counter these problems, multi-source depositions are used, which complicate the overall process [1].

Another way to deposit is making solution derived films. Solution derived films are relatively inexpensive processes where a bulk glass is dissolved into a solution using amines and either spin coated or dip coated onto a substrate. This is a low-cost alternative for film deposition that can be combined with lithography techniques for photonic device fabrication [1]. In this method, a solution can be created with the right stoichiometric composition in a controlled way, and the solution will be transferred to the surface in a few different ways. This option also allows for the possibility of thin films on curved surfaces due to surface tension in the solution, which was not possible using PVD. This could also allow for larger surface areas to be covered as well as perhaps a more streamlined production process [1]. There are other possibilities, including the incorporation of other materials into the film, which makes solution based processes an exciting area of research [1].

Spin coating is a solution derived method that has proven to produce thin films with similar optical and physical properties. This method allows for homogeneous films with low

surface roughness and consistent composition. Through spin coating, Amorphous films that exhibit the optical properties of the bulk materials, can be layered on a surface [2]. During spin coating, a substrate is covered with excess solution. The substrate is then "spun" at high speeds which creates a homogeneous and uniform film. After this, there is usually an annealing step required. To spin coat, amines, bulk glass, as well, a spin-coater, and an oven are required. Multiple films may be made out of one solution. This makes spin-coating cost effective and time efficient, compared to PVD methods. The other advantage is that there are many parameters to adjust which allows for tun-able thickness and composition of the films.

1.3 Direct Laser Writing

The fabrication of these devices is often done through Direct Laser Writing or "multi-photon lithography" which is the process of changing the molecular structure of the film through laser exposure, so that the areas which were laser exposed are more or less resistant to amine-based solvents. When exposed to these solvents, the areas that have different molecular structures will "etch" at different rates (etching refers to the dissolving of the material by placing it in a solvent). This allows for the creating of nanostuctures on the surface of the material and is known as "selective etching." In the case of thermally deposited As_2S_3 films, the molecular structure after laser exposure is similar to the structure of bulk As_2S_3. It would take longer for bulk As_2S_3 films to dissolve in amine-based solution than thin film, which would be relatively quicker. When part of the film is laser-exposed, that part becomes more resistant to the solution, and therefore when etched, only the laser exposed areas remain. This allows for the fabrication of chalcogenide nanostructures. Figure 1 is an illustrative diagram showing this process. This process has been successfully used in device fabrication in thermally deposited As_2S_3 films, but relatively unexplored in solution derived films. This research is directed at creating films that would be suitable for laser exposure and selective

etching for device fabrication using spin-coating.

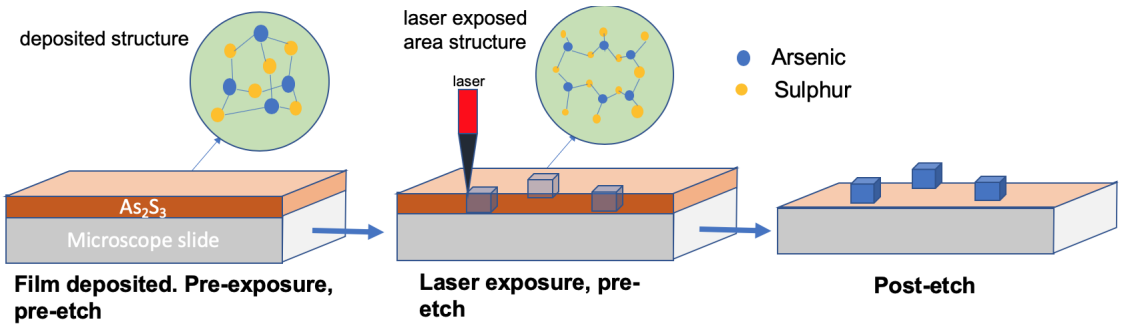

Figure 1: The process of a layer of thermally deposited As_2S_3 film going through the direct laser writing and etching process. First the layer is deposited and has the as-deposited structure. Then it undergoes targeted laser exposure in certain areas which changes those areas' molecular structure. The substrate and film is then etched, and only the laser-exposed areas remain.

2 Materials and Methods

2.1 Bulk Glass Preparation

The bulk arsenic sulfide that was used in this project was produced at UCF and shipped to Ursinus. The starting materials were weighed in a glove box in a nitrogen atmosphere. The glass was melted in a sealed ampoule and was placed in a rocking furnace for the purpose of creating a homogeneous glass. It was melt quenched by the removal of the glass from the furnace into the surrounding room temperature [1]. The bulk arsenic sulfide was delivered in thin rods. A thin piece was cut from the bulk material and polished for a transmission reference, the rest was also cut into smaller pieces. These pieces were ground into a powder using a mortle and pestle, and filtered through a sieve to result in a fine powder. The powder allows the glass to easily dissolve in the solution.

2.2 Solution and Substrate Preparation

5.988 grams of the powder were weighed into a vial and mixed with 10 mL of Ethylenediamine. The vial was left covered with a gauze with a hole poked in the middle and placed on a hot plate with a stir bar. It was left at 55° for 24 hours with a clamp to hold it in place. To ensure that the solution has dissolved completely, it was filtered through a 45 μm syringe.

Borosilicate glass slides were used as a substrate for the arsenic sulfide films. The slides were cut to be approximately 25 by 25 mm. Before spin coating, the slides were cleaned using acetone and wiped with a kim wipe.

2.3 Spin Coating Conditions

The glass slides were placed on the spin coater and around 30-40 drops of the solution were pipetted onto the substrate. It was important that the substrate was covered completely. The spin coater had different recipes that could be programmed. The spin coater was programmed so that the ramp up and ramp down speed was 5 seconds as well as the dwell time. This meant it was spinning for 15 seconds total. The speed was modified to experiment with how this affected the homogeneity, surface roughness, film thickness, and general composition. The films were spun at 1000, 1500, 2000, 2500, and 3000 rotations per minute (RPM).

2.4 Heat treatment

After spin coating, the substrates were heat treated to bake off the solution. They were moved to a hot plate at 90° where they were soft baked for 5 minutes. They were then transported to a furnace where they were hard baked at 220° for two hours. Afterwards, the films were placed on a hard surface to cool down, and then stored safely in a desiccator.

2.5 UV Exposure

After film deposition, some samples were UV exposed using a UV flood lamp. The UV-exposure was a close approximation of how the films would react under laser exposure conditions. The unexposed and exposed films could be compared to see how the molecular structure, transmission, and other characteristics would change under exposed conditions. In order for successful direct laser writing and selective etching, the molecular structure must change after laser exposure, so testing whether it changes after UV-exposure was relevant. It also should have the same transmission properties as the bulk material, in order for these properties to be used in device applications.

3 Results

Four total batches were made with different spin coating conditions. After the creation of each batch, the samples were characterized. The transmission was measured and etching tests were performed. The samples were also evaluated by looking at the surface composition. The samples with the best surface homogeneity were chosen to be shipped to UCF. These samples were also chosen so that there would be at least two samples from each RPM group: 1000, 1500, 2000, 2500, and 3000. The surface roughness, height profile, and molecular structure could be compared between the different RPM's to see how this may affect samples. 12 samples total were found to have acceptable surface homogeneity and were shipped to UCF for further characterization. At UCF the height profile, surface roughness, transmission, and Raman spectroscopy was measured for the 12 samples. 10 of the 12 samples had acceptable surface roughness and transmission and height were consistant and expected. The raman spectroscopy showed that the molecular structure in exposed films was indeed affected.

Table 1: Spin coated As_2S_3 films at different RPM

Number	Batch	Sample	RPM	UV	RMS Roughness	Height (μm)
1	3	9	1000	yes	.055 ± .01	5.90
2	3	7	1000	no	.081 ± .01	5.47
3	3	8	1000	no	.042 ± .01	5.37
4	1	3	1500	no	.014 ± .04	3.98
5	3	1	2000	no	.026 ± .01	4.08
6	3	2	2000	no	.008 ± .003	3.72
7	3	3	2000	yes	.055 ± .01	3.59
8	3	4	2500	no	.044 ± .04	2.83
9	3	5	2500	no	.044 ± .01	2.83
10	3	6	2500	yes	.051 ± .02	3.49
11	1	9	3000	yes	.046 ± .02	2.35
12	2	7	3000	no	.22 ± .06	2.63

3.1 Height Profile

A scratch was made on each sample so that the height profile could be measured. A height of 1 μm is desired for robust structure fabrication. The height for each sample ranged from 2.35-5.90 μms. There is a correspondence between thickness of the film and the spin coating speed. The films that were spun at higher RPM's were less thick (see Figure 2).

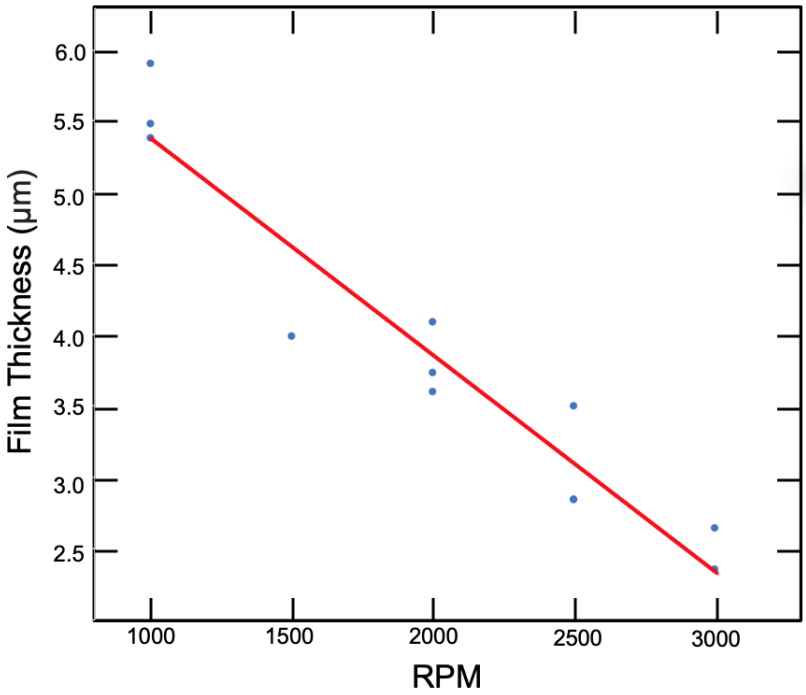

Figure 2: This figure shows a plot of RPM and corresponding height of the film. A best fit line shows a trend toward thinner films with higher RPM settings.

3.2 Surface Roughness

The surface roughness was measured as root mean square (RMS) roughness. The roughness was measured with a zygo white light interferometer. Three areas of each film were measured and the average roughness is listed in table 1. There was very little correspondence between surface roughness and RPM. The surface roughness was all acceptable, except two which were above 0.1 which would complicate laser exposure, and these samples would not be laser exposed.

3.3 Transmission

The transmission was measured for some of the samples before they were sent to UCF. Samples were measured before and after they underwent UV-exposure. The transmission

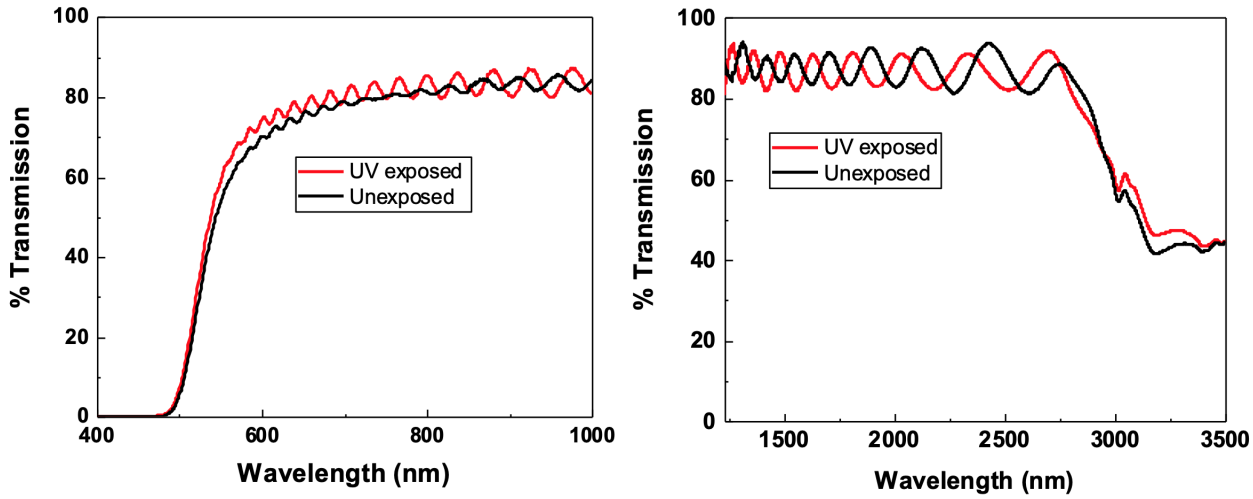

Figure 3: Average of three measurements for (left) UV-VIS and (right) FTIR measurements of a 2500 RPM sample before and after UV-exposure. There is a similar transmission range (450 nm-2750 nm) and the maximum transmission is also similar. A band edge is observed for the exposed and unexposed transmission. There is no significant change in transmission which indicates a robust film.

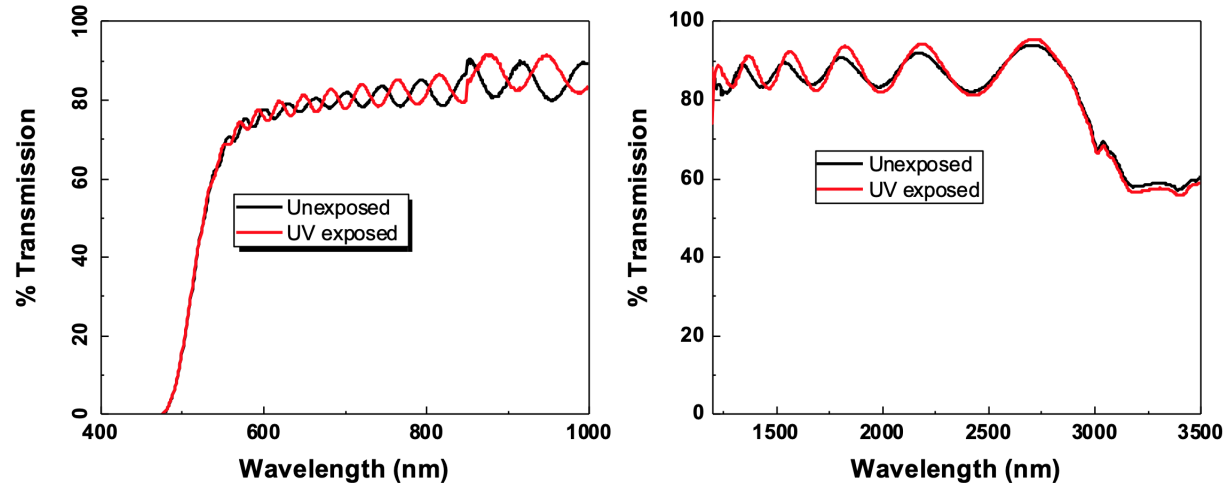

Figure 4: Average of three measurements for (left) UV-VIS and (right) FTIR measurements of a 3000 RPM sample before and after UV-exposure. As with the 2500 sample, there is a similar transmission range (450 nm-2750 nm) and the maximum transmission is also similar between the exposed and unexposed. A band edge is observed. There is no significant change in transmission.

of these samples are shown in figure 3 and figure 4. In these transmission spectrum, there is a similar transmission range and similar maximum transmission in both the exposed and unexposed. This indicates that the film transmission would not be greatly affected by laser

exposure. It is desired that the film transmission does not change greatly with exposure.

The 12 films that were sent to UCF were also measured for transmission. The FTIR transmission for the 12 films is shown in figure 5. The transmission spectrum and maximum transmission was similar for the films which had RPM's ranging from 1000-3000 and four of which were UV-exposed. This indicates consistency in the spin-coating process. In this as well, there was no significant change between the exposed and unexposed, which is desirable.

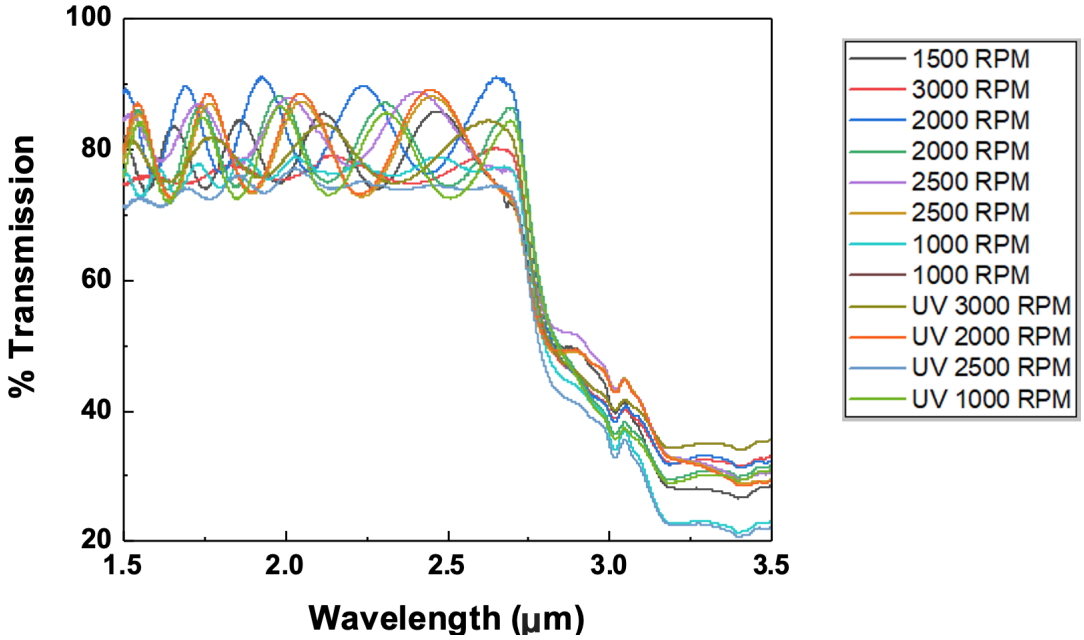

Figure 5: Transmission for 12 films sent to UCF. The RPM's ranged from 1000-3000.Each film was measured three times and averaged. Between the 12 films the transmission range (1.5 μm-2.7μm) and maximum transmission was consistent.

3.4 Raman Spectroscopy

Raman spectroscopy characterization was completed on the films to identify and compare molecular structure before and after UV exposure. Figure 6 shows the spectroscopy for three samples that were not UV exposed. When comparing to reference data, it looks similar to bulk and thin film spectra, and it seems to have a molecular structure resembling

a combination of the two. Broad peaks centered at 350 cm^{-1} indicate the presence of As_4S_6 bonds.

It is also important to compare the molecular structure before and after UV exposure. Figure 7 shows a comparison of the spectra from UV-exposed samples and the non-exposed samples for a 1000 RPM sample and a 3000 RPM sample. The most important thing to notice is that there is a change between the two, and that there are similar changes in both RPM sampels. After UV exposure, peaks emerge and intensify at lower wavenumbers, from 150-250 cm^{-1}, indicating the presence of As-As, S_8, and As_4S_4 bonds. After UV exposure, peaks emerge and intensify at 345 cm^{-1} indicating the presence of AsS_3. This indicates that before exposure, the molecular structure was more similar to the bulk material and after exposure it became more similar to the thin film structure. This is not expected, but as long as the molecular structure is affected by laser exposure, this can be used to create structures on the surface of the film through etching.

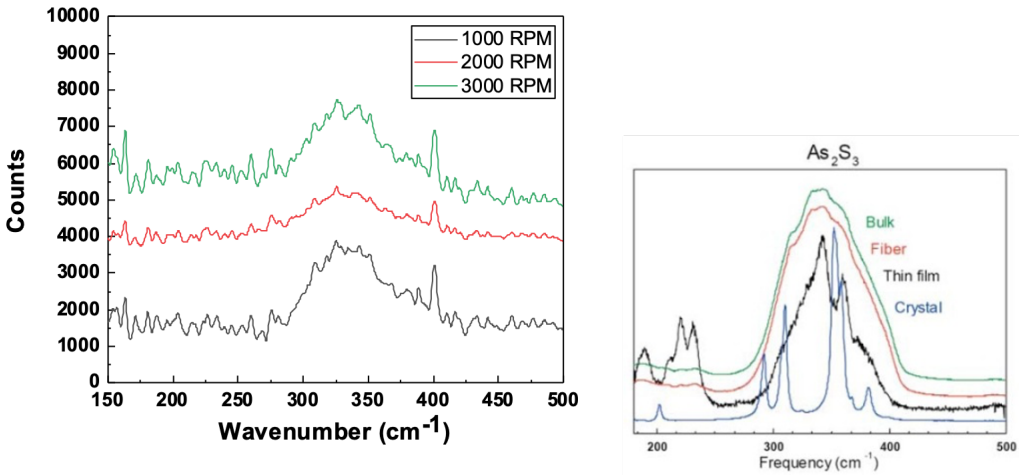

Figure 6: (left) spectra from three films with RPM's of 1000, 2000, and 3000 respectively. This spectra is separated for visual clarity on the y axis, and it is not normalized. (right) comparative data of As_2S_3 in different forms. Comparing this to the left data, it seems the films have a molecular structure similar to that of bulk and thin film.

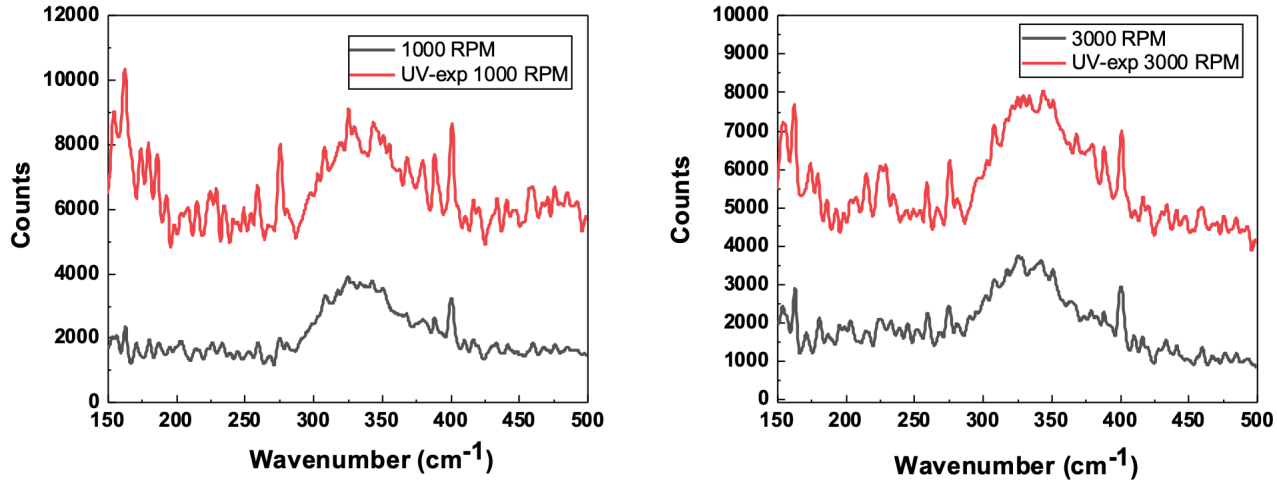

Figure 7: Comparison of unexposed and UV-exposed film Raman structure.After UV exposure, peaks emerge and intensify at lower wavenumbers, from 150-250 cm^{-1}, indicating the presence of As-As, S_8, and As_4S_4 bonds. After UV exposure, peaks emerge and intensify at 345 cm^{-1} indicating the presence of AsS_3.

4 Conclusions and Further Research

Although the films have not been laser processed at this moment, 10 films that were suitable for laser processing were produced. The next step for these films would be to laser pattern the films that had the lowest surface roughness and best homogeneity. After laser exposure the films could be selectively etched, and the resulting substrate could be characterized. From the Raman data it might be expected that the areas of laser exposure would be less resistant to amine-based etching solutions. This would result in the laser exposed areas being etched away while the unexposed areas would remain. Hopefully the remaining sections would have a thickness of around 1 μm. If structures could be successfully created through spin-coated As_2S_3 films, it would be an exciting development. Direct laser writing on deposited films has been highly successful, but DLW on spin-coated films has been relatively unexplored. This would open up options for a cheaper and more tunable process for creating these nanostructures which could be used in device fabrication for many optical components.

References

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