Pb etchant development towards Pb-based quantum device fabrication

Bachelor's thesis

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Abstract

Semiconductors-superconductors hybrid materials are mainly studied for their potential application for topological quantum computing. Majorana zero modes found in these heterostructure systems could be used to create more stable qubits, thus leading to scalable quantum computers. To realize these heterostructures, improvements to material quality and fabrication processes are needed. Samples of hybrids based on Pb as the superconductor and InAs and InSb as the semiconductor were etched with MF321. MF321 proved to be an effective etchant for Pb. The optimal etching time should at least be 60s. The best method to achieve an uniform etch was by shaking. AFM, SEM and EDS were used to characterize the etched samples. Atomic steps matching the lattice constant of InAs were found in AFM. SEM and EDS data showed no signals of Pb supporting the claim that MF321 could etch Pb.

Contents

1 Introduction

Semiconductor–superconductor hybrid materials can be used to design new quantum devices. These heterostructures combine the superconductivity of metals and large spin orbit coupling of semiconductors. They exhibit topological superconductivity, which are predicted to hold Majorana zero modes that can to be used in fault-tolerant quantum computing.[1] Hybrid materials are predominately studied using Al as the superconductor and InAs or InSb as the semiconductor.[2] There have not been many studies on Pb as the superconductor in hybrids compared to aluminum. Pb has the highest bulk critical temperature and critical magnetic field out of all the type I superconductors, which expands the parameter space where Majorana zero modes could reside. It has been shown that single crystal Pb thin films can be grown on InAs to create hybrid nanowires with no axial grain boundaries.[2] Pb could also be used in planer heterostructures, further increasing the interest for Pb based hybrid materials.

An important aspect for realizing these heterostructures is the removal of superconducting material. Therefore, there is an interest in finding suitable ways to remove superconducting material without harming the semiconductor. One way to do this is by etching. Wet etching has high selctivity, meaning that it will only target superconducting material and not the semiconducting material, if a suitable etchant is used. It is isotropic, meaning that it attacks surfaces from all directions and is hard to control. Several dimensions have effect on etching, these include type of etchant, etching time, etching method and amount of etchant.A slow etchant is preferred, because it is easier to control how much that is being etched away and to prevent damages to the substrate. Furthermore, how much surface contact an etchant has will influence the etching and this can be varied with different etching methods. The amount of etchant is also important, too little and the sample cannot be fully etched, too much and the sample might be over-etched. Washing with a neutral chemical can be used to remove left over etchant, albeit the etch rate should be small, it may lead to cause over-etching. The following etchants have been considered in this project. Milli-Q water (MQ) have been reported to etch pure Pb for Pb thin films grown on InAs nanowires.[2] A mixture of 1 part hydrogen peroxide and 3 part acetic acid will form acetic peroxide, which have been reported to etch Pb.[3] Tetramethylammonium hydroxide (MF321), which is a known etchant for Al. Since Al and Pb have similar properties, MF321 should also be able to etch Pb.

2 Methods

2.1 AFM analysis

Atomic Force Microscopy(AFM) was used to determine the results of the etchings by comparing surface roughness before and after etching. AFM functions by moving a cantilever with a sharp tip across a sample. A laser is pointed at the backside of the cantilever as seen in figure 1 and it is reflected into a photodiode. As the tip measure a surface, the position of the cantilever will alternate and so will the deflected laser signal. The photodiode translates the laser signals into heights based on the deflection.[4] By scanning the surface line by line, differences in heights can be obtained and the roughness can be calculated as seen in the next subsection.

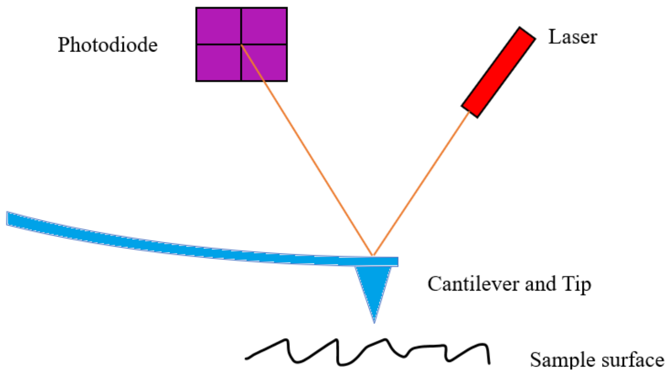


Figure 1: Schematic of AFM

2.2 Roughness: Ra and Rq

The roughness of the sample was qualified by the parameters: average roughness(Ra) and root mean square roughness(Rq). Ra is calculated by the following equation:

$$Ra = \frac{1}{l}\int_0^l |Z(x)|dx \tag{1}$$

Z(x) is the average height of the surface. Ra is therefore calculated by integrating for the average height and dividing that with the sample length. Rq represents the standard deviation of surface height and is given by the equation:

$$Rq = \sqrt{\frac{1}{l}\int_0^l |Z^2(x)|dx} \tag{2}$$

The semiconducting layer should be atomic flat and have a much smaller Ra and Rq than the Pb layer. This was used to determine if some Pb remained or fully etched away.

2.3 SEM and EDS analysis

Scanning Electron Microscope (SEM) is a useful tool to look at the surface of a sample. It sends out a beam of electrons that scans the surface. When the electron beam hits the sample, which is placed on a stage, three things happen. Firstly, the electrons can get absorbed by the atoms the sample consist of and emit electrons out again, these electrons are called secondary electrons and are very close to the surface. The secondary electrons are collected in a detector and rendered into an image by a computer. Secondly, they can get reflected at the surface or deeper down the sample, these electrons are called backscattered electrons. Lastly, backscattered electrons can get very deep inside the sample and be absorbed, giving off X-rays. These X-rays can be characterized by a Energy Dispersive X-ray spectrometer (EDS), since each element have their own unique X-ray spectra. This does not include elements lighter than Boron, since their energy levels are to closely spaced. EDS uses a semiconductor as the detector and it generates electrical current in form of electron-hole pairs by absorbing the X-rays. Measuring the electrical current enables you to obtain the values of X-ray energy.[5] SEM was used to take pictures of the surface of samples and EDS was used to detect the surface for Pb to see if Pb had been successfully etched away or not.

2.4 Assessment score

An assessment score will be given to each sample after etching. The assessment score will be based on the parameters Ra and Rq. Each parameter can give up to 5 points. How the points are distributed can be seen in table 1.

Points	0	1	2	3	4	5
Ra [nm]	4+	4-3	3-2	2-1	1-0.5	<0.5
Rq [nm]	5+	5-4	4-3	3-2	2-1	<1

Table 1: This table shows the how the assessment score will be given. A sample can get can get up to 5 points for Ra and Rq for a total of 10 points.

3 Results and discussion

The experimental results will be presented and discussed in this chapter. Two wafers were used in this project. One had a 20 nm Pb layer on top of InSb and the other had a 20 nm Pb layer on top of InAs. They were cleaved into smaller samples about 5mmx5mm in size. Some of the samples had defects from the cleaving, but it was determined for the scope of this project that those defected samples could still be used. AFM measurements of both wafers were taken before etching to be used as references. All AFM measurements of samples after etching were compared to their references. The AFM scans were all 5 μm^2 in size. The etching was done in small cups with 15 mL etchant, except when testing different etchant volumes.

3.1 Testing etchants

Etching with MQ showed no significant etch on the Pb layer. Table 2 shows that after etching a sample for 5min, the surface was more rough than the reference. This suggest MQ is not an effective etchant for Pb-oxide. Table 2 shows the initial

Material	Etching	Wash	Method	Ra [nm]	Rq [nm]	Assesment score
Pb/InSb Reference				4.16	5.46	
Pb/InSb	MQ 5min		dip	12.2	16.6	0
Pb/InSb	MF321 30s		dip	6.56	8.94	0
Pb/InSb	MF321 60s		dip	0.964	1.21	9
Pb/InSb	MF321 60s	MQ 60s	dip	1.84	3.32	5

Table 2: Etching test with MQ

experiments that tested if MF321 could etch Pb. The 60s etch was scanned by AFM and it showed significant lower roughness than the reference, which indicates that MF321 can be used to etch Pb, but it also leaves organic compound on the InSb layer, as seen in figure 2. An assessment score of 9 was given to the scan because of its low Ra and Rq values,

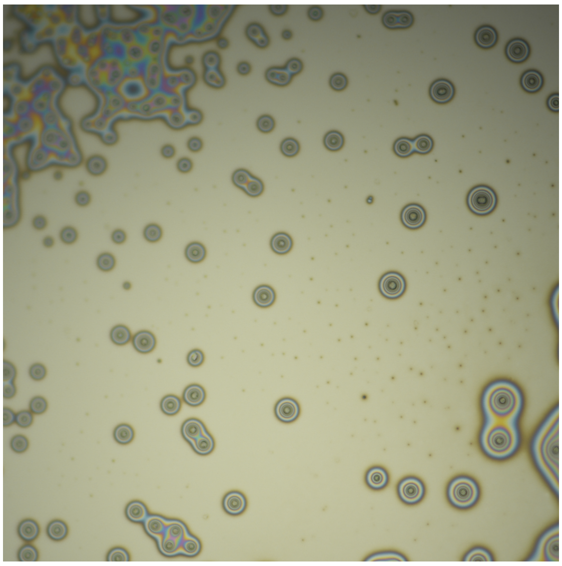


Figure 2: MF321 60s etch. Microscope 50x.

To remove the organic compound, washing with MQ was introduced to the process. The result can be seen in the last line of table 2. It showed lower roughness than the reference but was given a assessment score of 6, because it had large areas that were unetched like the left AFM scan in figure 3. Since MF321 could etch Pb, its etching process was tried to be further optimized.

3.2 Etching with MF321

This sections reports experimental data for tests varying different parameters. Different methods of etching were tested. These included dipping the sample in the etchant, continuously dipping the sample up and down without taking it up from the etchant and continously shaking the sample from side to side inside the etchant. The samples were washed with the same method as they were etched with MQ. Table 3 shows, that by shaking an assessment score of 10 was achieved. Shaking appeared to create a more uniform etch, thus it was used forward in the experiments.

Material	Etching	Wash	Method	Ra [nm]	Rq [nm]	Assesment score
Pb/InSb	MF321 60s	MQ 60s	dip	3.85	5.37	1
Pb/InSb	MF321 60s	MQ 60s	dip up and down	5.04	6.76	0
Pb/InSb	MF321 60s	MQ 60s	shaking	0.682	0.902	9

Table 3: This table shows the results of different etching methods

Different etching times were tested. The times 5, 15, 30, 45, 60, 75 and 90s were tested, as seen in table 4. The sample with etching time 60s were the same sample in table 3. It had the highest assesment score of 10 out of all the tests, therefore 60s of etching time was used for the rest of the experiments. This might not have been a good idea, because even though the assessment score was high, it might not have been fully etched. This is further discussed in the AFM section.

Material	Etching	Wash	Method	Ra [nm]	Rq [nm]	Assesment score
Pb/InSb Reference				4.16	5.46	
Pb/InSb	MF321 5s	MQ 60s	shaking	3.56	5.86	1
Pb/InSb	MF321 15s	MQ 60s	shaking	1.29	2.48	6
Pb/InSb	MF321 30s	MQ 60s	shaking	1.39	2.32	6
Pb/InSb	MF321 45s	MQ 60s	shaking	1.37	1.73	7
Pb/InSb	MF321 60s	MQ 60s	shaking	0.682	0.902	9
Pb/InSb	MF321 75s	MQ 60s	shaking	1.62	2.04	6
Pb/InSb	MF321 90s	MQ 60s	shaking	0.962	1.33	8

Table 4: This table shows the results of different etching times with MF321.

For table 5 and 6 the semiconductor was InAs. It had a much higher reference with Ra at 8.65 nm and Rq at 19.8 nm. This wafer is a lot more rough than the other wafer, which signals that there are impurities. In some cases this might have lead to many particles being left on the sample after etching, leading to worse assessment scores. Washing was also changed from MQ 60s to MQ 10s 60s. Now, the samples was being washed first for 10s in a cup with MQ and then in another cup with MQ for 60s. This was done to reduce the risk of carrying MF321 over to the cup with MQ.

Table 5 shows the results of samples being etched in different volumes of etchant. The washing volume was unchanged. The highest assesment score was giving to the 30 mL etch, but it is not conclusive to say that 30 mL is better than 15 mL or 50 mL. More test should ideally have been done and also testing for smaller volumes.

Material	Etching	Wash	Method	Volume [mL]	Ra [nm]	Rq [nm]	Assesment score
Pb/InAs Reference					8.65	19.8	
Pb/InAs	MF321 60s	MQ 10s MQ 60s	shaking	15	2.13	4.31	3
Pb/InAs	MF321 60s	MQ 10s MQ 60s	shaking	30	0.680	0.967	9
Pb/InAs	MF321 60s	MQ 10s MQ 60s	shaking	50	0.935	2.37	7

Table 5: This table shows etching with differet etchant volume.

Table 6 shows the results of different washing times that were tested for MQ: the times were 10s followed by 30, 60 and 90s. The sample washed with MQ 10s 60s can be seen in figure 4a and it got an assesment score of 10.

Material	Etching	Wash	Method	Ra [nm]	Rq [nm]	Assesment score
Pb/InAs Reference				8.65	19.8	
Pb/InAs	MF321 60s	MQ 10s MQ 30s	shaking	0.928	1.49	8
Pb/InAs	MF321 60s	MQ 10s MQ 60s	shaking	0.224	0.446	10
Pb/InAs	MF321 60s	MQ 10s MQ 90s	shaking	2.52	5.76	2

Table 6: This table shows test with different MQ washing times.

3.3 AFM

The left image of figure 3 shows a nonuniform scan of a sample, while the right image shows a uniform scan of a sample. The left image is nonuniform because it has clusters of what could be assumed to be Pb. Its z-range is a lot higher compared to the right image. By comparing the right AFM scan in figure 3 with the scan in figure 4b, it would suggest the first scan was not fully etched. There are no visible atomic steps and still some clusters left. The scan rate for the scan in figure 4a was 0.4 Hz, while the scan rate for the other samples were 1 Hz. Lowering the scan rate for other scans might have shown more cases of atomic steps.

Figure 4b shows a height profile over the green line. In the first 60 nm of the profile, the height of the sample is about 400 nm. From 200 to 250 nm the height is between 900 and 1000 nm. This is very close to the lattice constant of InAs that is 0.606 nm.[6]

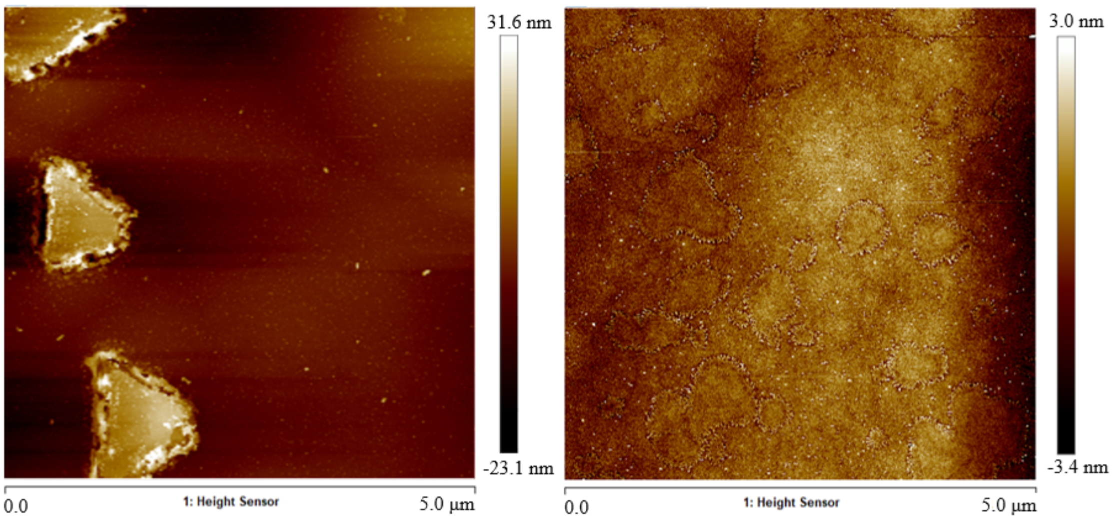
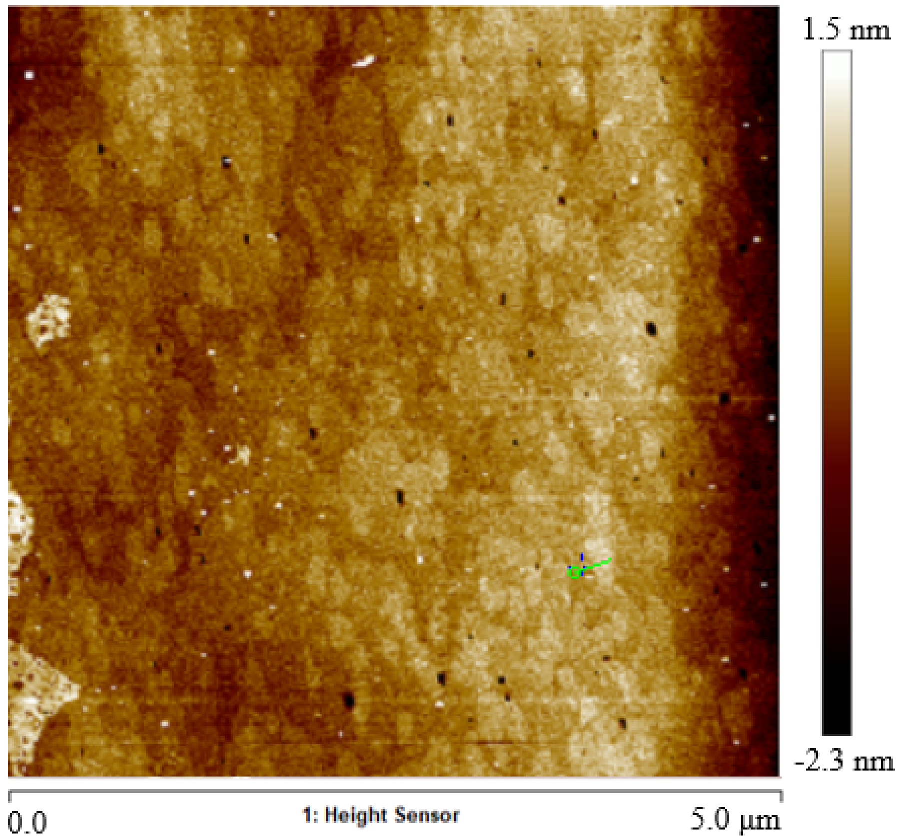
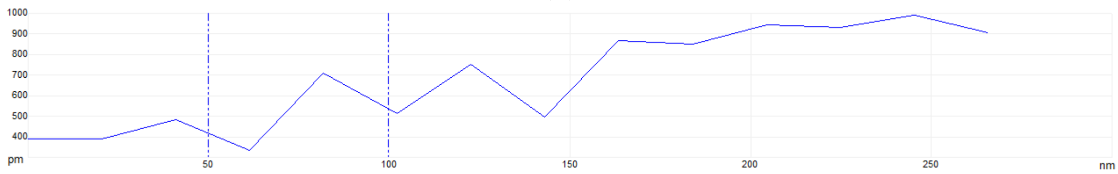


Figure 3: The left AFM scan is an example of a nonuniform etched sample. Method: MF321 5s MQ 60s shaking. The right AFM scan is an example of a uniform etched sample. Method: MF321 60s MQ 60s shaking.



(a)

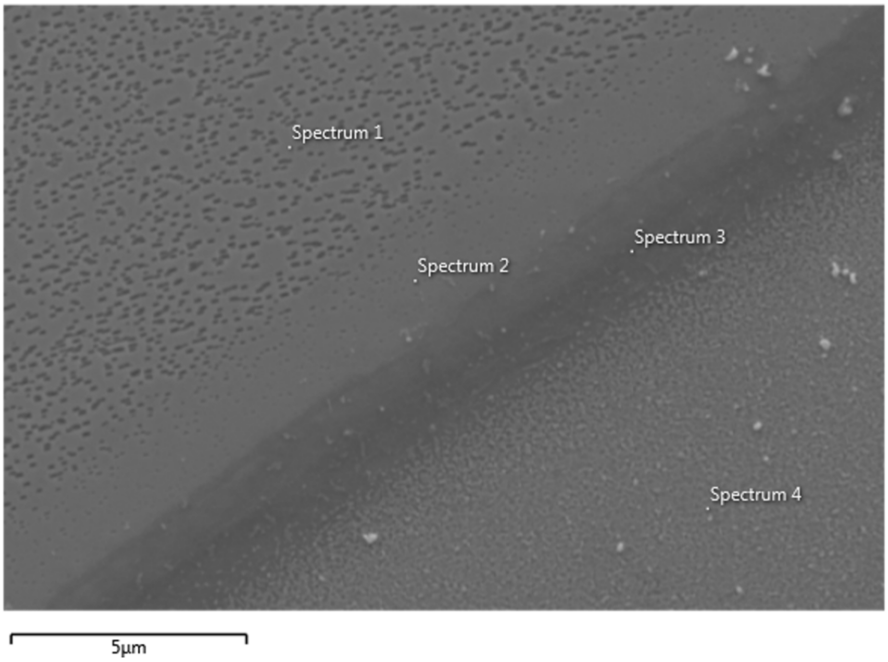


(b)

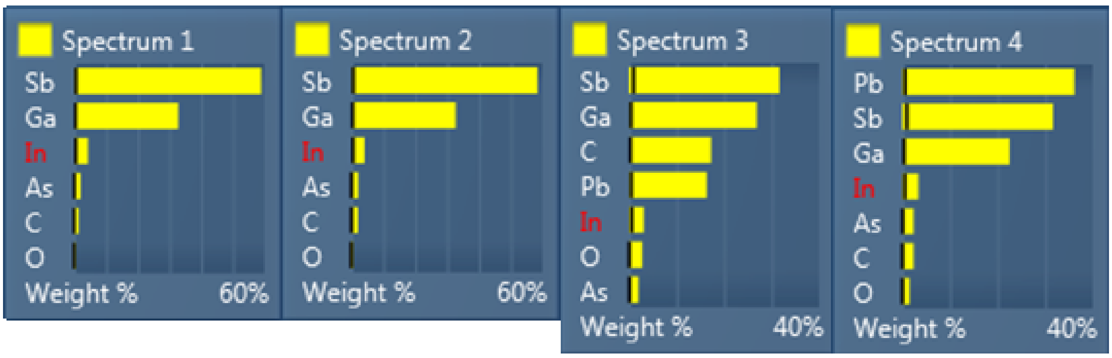
Figure 4: (a) The figure shows an AFM scan with atomic steps. Sample: InAs MF321 60s MQ 10s 60s shaking. (b) Height profile following the green line. The start of the profile is where the line has a circle.

3.4 SEM and EDS

This section will report the results from SEM and EDS. Figure 5a shows a SEM image of a sample coated with a resist before being etched with MF321. AZ 1505 was the used resist and it was removed with acetone by washing for 10s while shaking. After, the sample was with MQ for 10s. On the figure, 4 spectra are shown. The area around spectrum 1 and 2 were not coated with resist and should show no signals of Pb. The area around spectrum 3 is at the edge of the coating and spectrum 4 is inside the coating, both of these should have signals of Pb. As seen in figure 5b, spectra 3 and 4 does indeed have clear signals of Pb. In contrast, spectra 1 and 2 show no signals of Pb. Furthermore, figure 5b shows strong signals of Sb and Ga across all 4 spectra and traces of InAs, which indicates there is layers of GaSb on top of InAs. The lattice constant of GaSb is 0.6096 nm[6] and is similar to InAs. The carbon signal from spectrum 3 could be from the resist that had not been completely cleaned.



(a)



(b)

Figure 5: (a) SEM image of the edge of the resist. Method: MF321 60s MQ 10s 60s shaking. Coated with resist AZ 1505 and cleaned with acetone. (b) EDS data for each spectra.

4 Conclusion

Finding suitable etchants and etching processes can make a pathway to further studies on Pb based superconductor-semiconductor hybrid materials. These hybrid materials exhibit topological superconductivity, that could in the future lead to the findings of Majorana zero modes and take quantum computing to the next step. Out of the considered etchants, MQ and MF321 were tested. Since MF321 proved to be an effective etchant for Pb, acetic peroxide was not tested. Through experiments, it was found, that for etching a 20 nm layer of Pb a minimum of 60s was required. Shaking was the best method of etching in this case of planar structures. Atomic steps were observed in an AFM scan, which shows that MF321 had etched all the way down to the semiconductor layer. SEM and EDS also showed that MF321 was an effective etchant. It was also possible to coat a sample with resist and successfully protect the Pb layer under it, after etching.

5 Outlook

The effects of temperature on etching were not studied in this project. It is known that temperature affects chemicals solubility. This report only focused on etching on planar heterostructures, but this etching method could also be applied to nanowires. The next step would be to characterize the etching rate of MF321 or its effect on the semiconductor layer.

References

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