Silicon Etching Related to Fuel Cells

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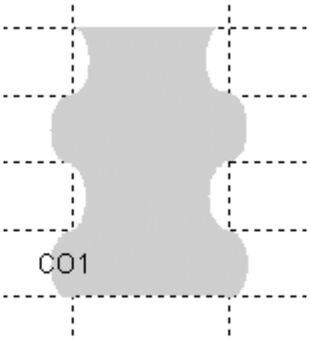
I. Introduction

The purpose of this research is to develop a feasible model to show the etching reaction which creates the porous silicon used in fuel cells. The actual etching process involves a treated silicon wafer that is mounted into an etching cell with a light source, applied potential, and strong acid pumped through the cell. The light source serves to enhance the replacement reaction between the silicon and the acid, therefore it will not be modeled directly in the file. Instead the Damkohler number was put sufficiently high to model an immediate reaction as soon as the two species interact. The main features that should be modeled are the fluid interaction and the applied potential.

The main phenomenon that I wanted to account for was the induced waviness in the walls of the pore. The sides of the pore are represented below. The waviness was initially described as symmetrical about the median y-axis (Figure 1). Additional research in the quality analysis department revealed that the waviness is not symmetrical, but somewhat offset. This is also shown in Figure 1 below.



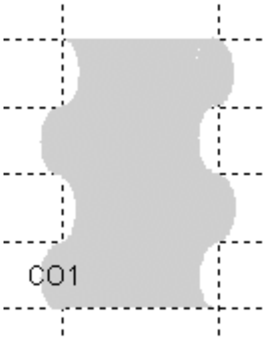


Figure 1a. Symmetric Pore Waviness. Figure 1b. More realistic representation of the uneven pore waviness.

In order to accomplish these tasks, the initial plan was to build a file to represent just the fluid flow portion of the dissolution reaction. The main objective was to manipulate the physical characteristics of the fluid in the well to simulate a solid rather than a liquid. The biggest concerns was accounting for the viscosity and diffusivity of the well. Initially a function was built so that the viscosity of the solid was dependent on concentration. The reasoning for this was to keep the material from flowing out of the well. The initial function was modeled as a Langmuir isotherm, and is shown in Figure 3. The diffusivity was adjusted so that the material would not diffuse down the well. The main feature of the diffusivity is that the diffusivity of the material in the well was two factors of ten different from the diffusivity of the material in the bulk. The fluid in the bulk was modeled as simple plug flow with a second concentration to model the acid.

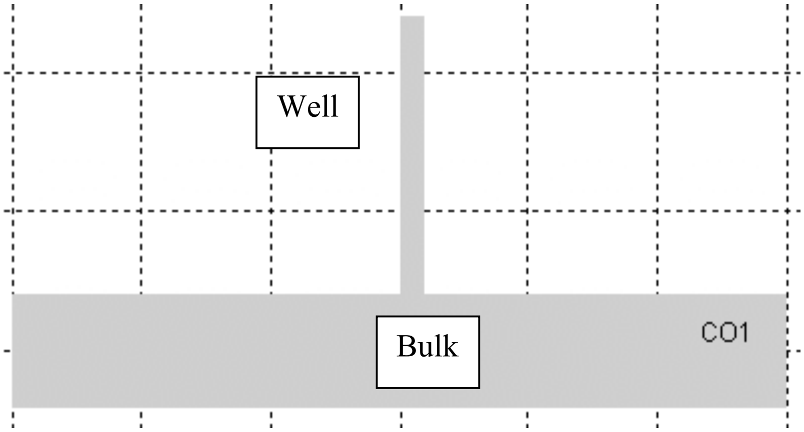


Figure 2: The basic etching Model. The pore is modeled as a well with an aspect ratio of 10:1 (length:width).

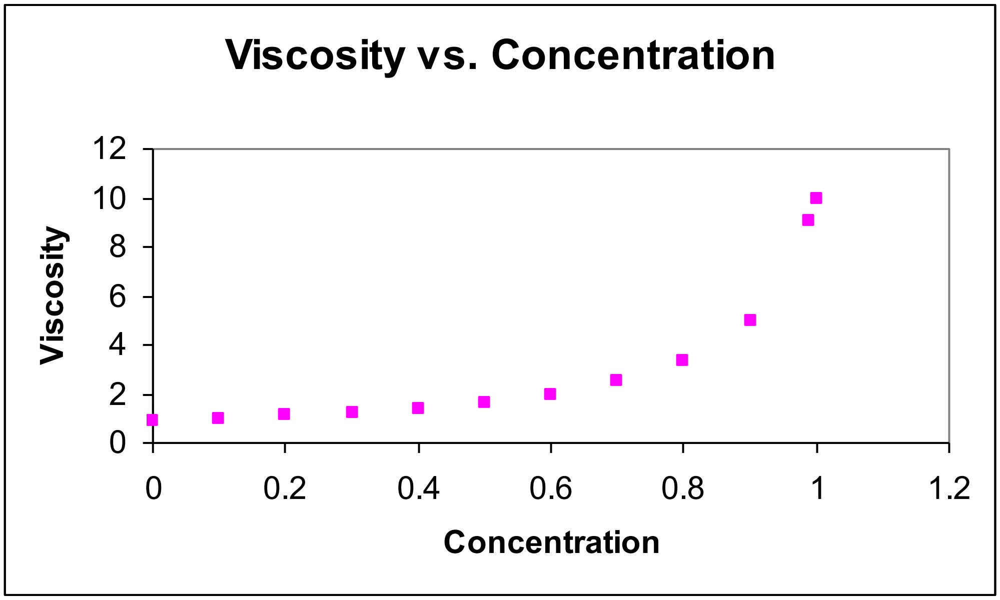


Figure 2: Proposed model for the Viscosity as function of Concentration for the solid in the well.

Once the initial model was built, then the file would be updated to account for the applied potential. The applied potential varies as a function of time, and is shown in Figure 3. The potential takes advantage of the mobility of the charged species in the bulk, and by varying the potential you can control the acid in the bulk. The application of the potential was supposed to be the most difficult part of the process.

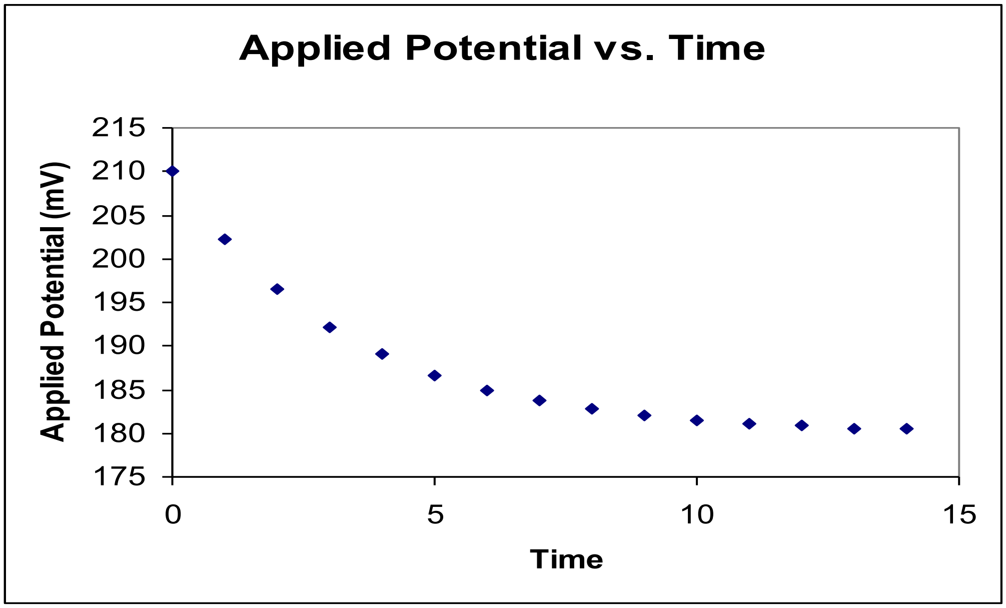


Figure 3: Applied potential versus time for the electrochemical portion of the dissolution reaction.

The initial hypothesis was that the combination of the fluid flow and effect of the electrochemical forces that resulted in the wavy borders. As the research progressed the scope of the project changed because of the possible connection between the wavy borders and recirculation zones in the well. A paper published by Dr. Finlayson showed a relationship between the aspect ratio of the well to the recirculation zones. Since there were many difficulties applying the electrochemical features, the scope of the research was changed to investigating the effect, if any, of these recirculation zones. The initial hypothesis was that the fluid recirculation was only two or three orders of magnitude lower than the velocity in the bulk and would account for the changes in the pore wall.

II. Results

The results section will be split into three different models that were built

1. Etching Reaction
2. Etching Diffusion
3. Etching Diffusion with a tighter range

1. Etching Reaction

The initial Etching Reaction file included the following features

1. Two different species: c (material in the well) and c2 (material in the bulk)
2. Plug flow in the bulk (v=1)
3. Langmuir Isotherm for the Viscosity
4. Change in the Diffusivity
5. Reaction in the well (Da*c*c2; Da=1000)

The model is shown below with the initialized mesh which consisted of 141 nodes and 70 elements. The mesh was kept very course because there were already so many calculations involving the concentration.

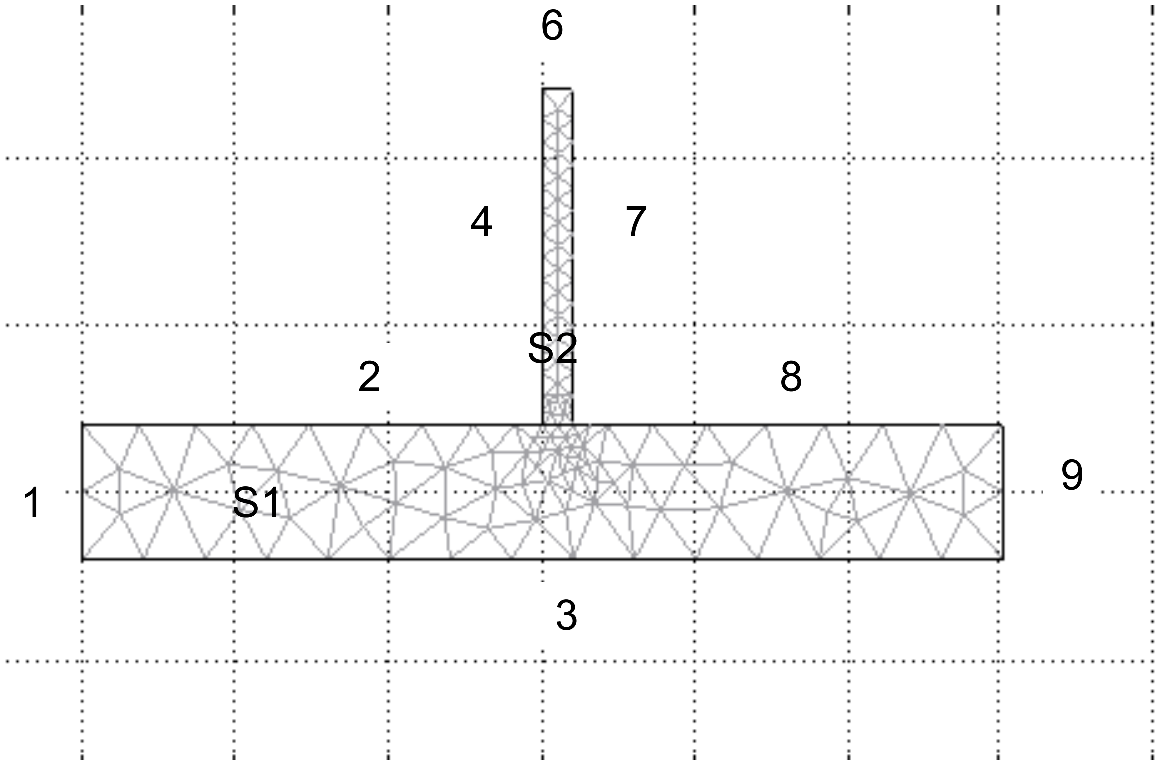


Figure 4: Mesh for the Etching Reaction file and the boundary/subdomain specifications. The mesh was refined only around the pore opening.

Table 1: Subdomain and Boundary Conditions for the Etching Reaction file.

Multiphysics	Subdomain 1	Subdomain 2	Boundary Conditions
Incompressible Navier-Stokes	$\rho = 1$ $\eta = 1$	$\rho = 10$ $\eta = 10*c$	1: u = 1 All other no-slip 9 is straight out
Convection and Diffusion (c) (Si)	$D_i = 1$ u = 0 v = 0	$D_i = 1e-2$ u = u v = v	1: c = 0 2,3,8: Insulation/Symmetry 4,6,7: c.*c2 9: Convection>>Diffusion
Convection and Diffusion (c2) (F$^-$)	$D_i = 1$ u = 0 v = 0	$D_i = 1e-2$ u = u v = v	1: c = 1 2,3,8: Insulation/Symmetry 4,6,7: c.*c2 9: Convection>>Diffusion

The file was run as a time-dependent file with the time steps of 1 from 0:10. The file would not run for a step size larger than 1, and for more than 10 steps. The file would slowly compile, but then would end in an error that said that the step size had been reduced to a bad preconditioner. Many different solutions were tried such as streamlining the diffusion and changing the iterative solver to GMRES. The results of the file that would run are shown in the mpeg file titled "Etching Rxn." Figure 5 shows the results for the concentration of c at time = 10.

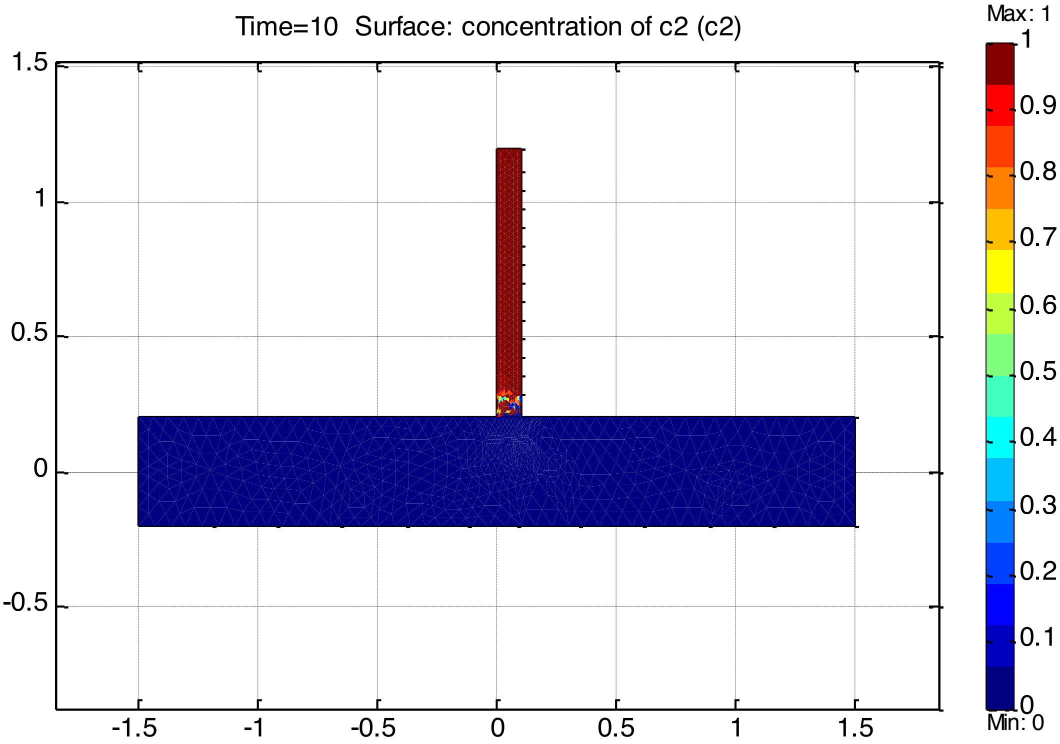


Figure 5: Etching Reaction results for t=10.

The results of the initial etching file did not give feasible results. The material in the well did not appear to react, or get swept into the well. The fluid flow around parts of the material did not seem likely. The probable cause of this was that the physical properties of the material in the well were creating unrealistic properties. The problem with making the viscosity a function of concentration was that it did not account for areas in the well where the concentration happened to accrue. Instead of taking that material into the bulk, it would clump up and form a viscous lump of material.

In order to try to get a more realistic physical description the viscosity terms were changed to just a constant (η=10). This gave better results but still showed some of the clumping of before, and again the file would not run beyond 10 time steps. There was a stretch of time where the entire file would not run. Eventually, I found that the problem was that I had overspecified the fluid velocities in the bulk. The first file that I built would show the material in the well leaving, but the concentration profile would remain at 1 for the entire well. Elena showed me that the problem was that in the Navier-Stokes system I did not allow for an x and y velocity in the pore. I changed this so that the x-velocity = u and the y-velocity =v. Somehow during all of the changes, those parameters got put into the bulk subdomain as well as the pore. Once that was taken out the file would run again, but still gave unrealistic answers.

2. Etching Diffusion

After the Etching Reaction file would not compile properly, I built another file that had less of the features that were probably interfering with the calculations. The Etching Diffusion file was initially discarded because I was having difficulties restricting the diffusion in the pore. As it turns out this may be a more realistic physical situation (see the Conclusion section for more information).

The initial Etching Diffusion file included the following features

1. One species: c (material in the well)
2. Plug flow in the bulk (v=1)
3. Viscosity as a linear function of Concentration ($\eta = 10*c$)
4. Change in the Diffusivity

The model is shown below with the initialized mesh which consisted of 180 nodes and 75 elements. The mesh was kept very course because there were already so many calculations involving the concentration.

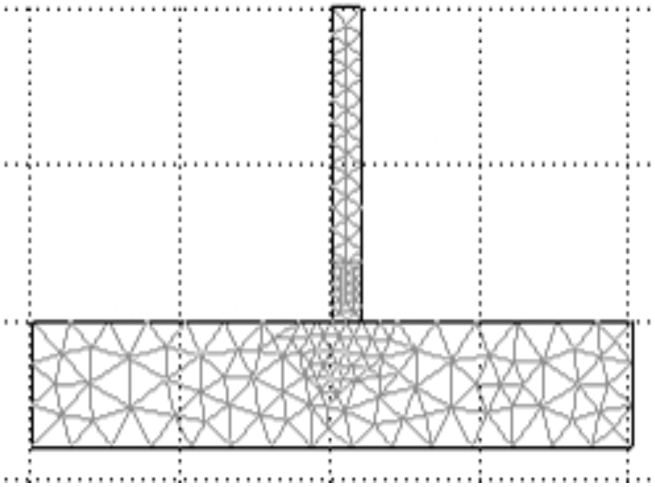


Figure 6: Mesh for the Etching Diffusion file. The boundaries and subdomain are the same as the previous file.

Table 2: Boundary and Subdomain conditions for the file.

Multiphysics	Subdomain 1	Subdomain 2	Boundary Conditions
Incompressible Navier-Stokes	$\rho = 1$ $\eta = 1$	$\rho = 10$ $\eta = 10$	1: u = 1 All other no-slip 9 is straight out
Convection and Diffusion (c) (Si)	$D_i = 1$ u = 0 v = 0	D_i = 1e-2 u = u v = v	1: c = 0 2,3,4,6,7,8: Insulation/Symmetry 9: Convection>>Diffusion

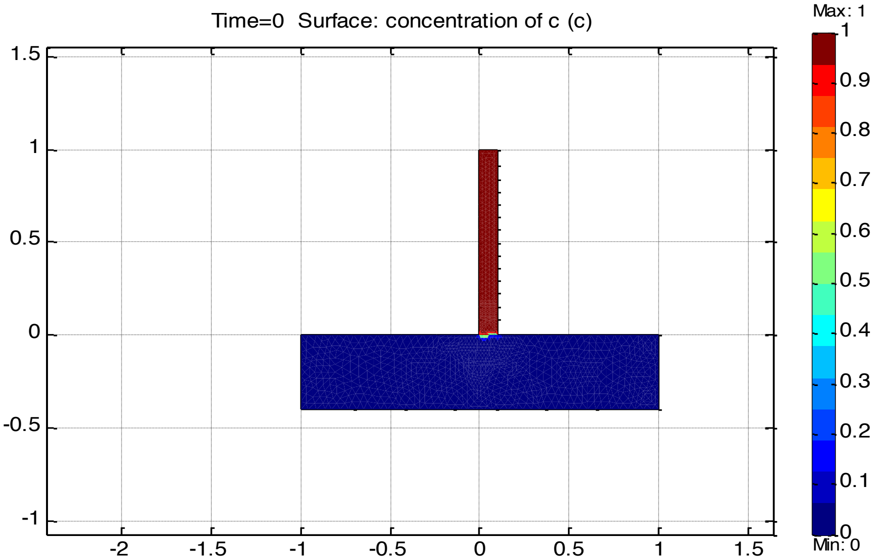


Figure 7: Surface Concentration of c at Time = 0

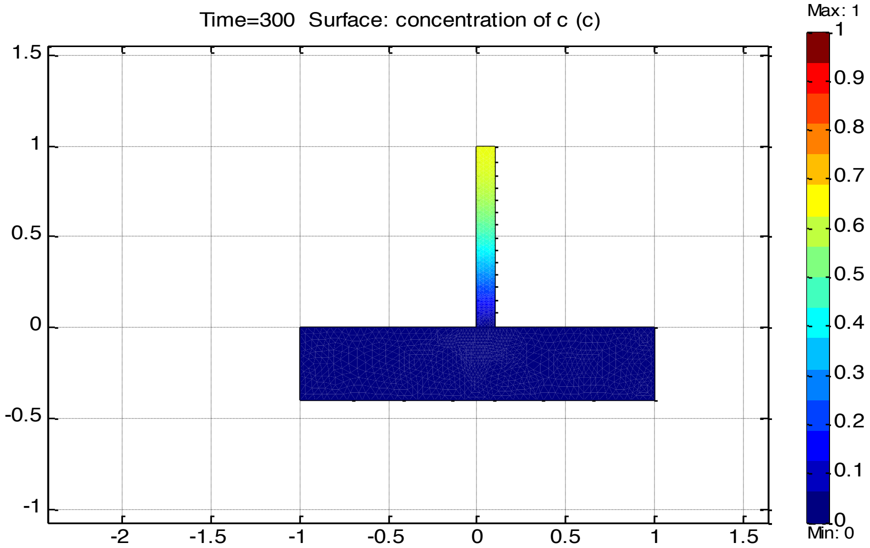


Figure 8: Surface Concentration of c at Time = 300

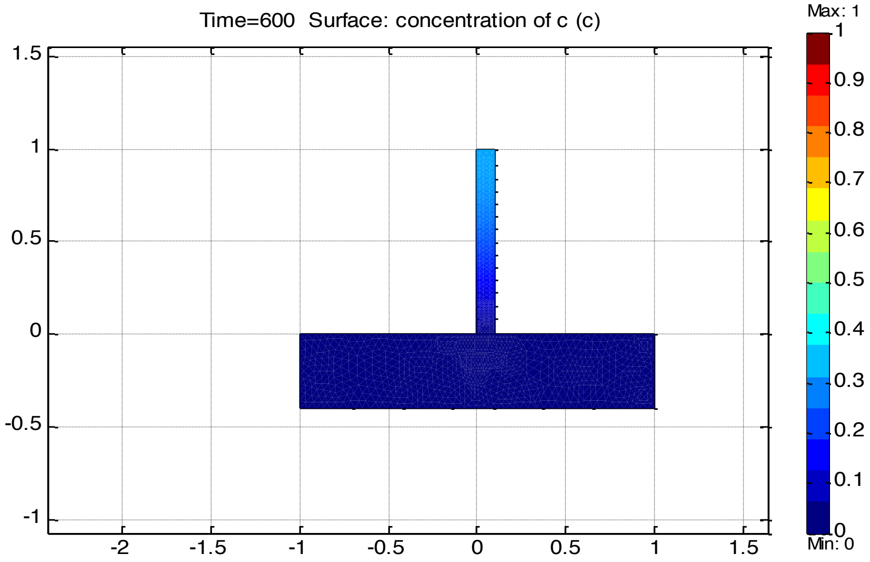


Figure 9: Surface Concentration of c at Time = 600

Although there was significant diffusion in the pore, this turns out to be closer to a reasonable model than initially expected. The diffusion in the pore is not quite accurate because the diffusion of the material out of the well would happen after the replacement reaction between the acid and the solid. So there should be a line where the concentration remains 1 until it diffuses out of the well, which would show a concentration gradient.

Even though the file was not entirely accurate, the affect of recirculation were investigated to see if it could possibly cause the waviness. The x and y velocities were plotted at t=600 to see the extent of circulation. As the range of the velocity plotted got smaller, there were areas that showed possible recirculation. At the pore opening the range was ±1e-2. In order to see the fluid flow in the entire pore, the range was reduced even more until it was ±1e-12. The final fluid flow figures are shown below. Although there is some degree of recirculation it is more than 12 magnitudes of order smaller than the fluid flow in the bulk.

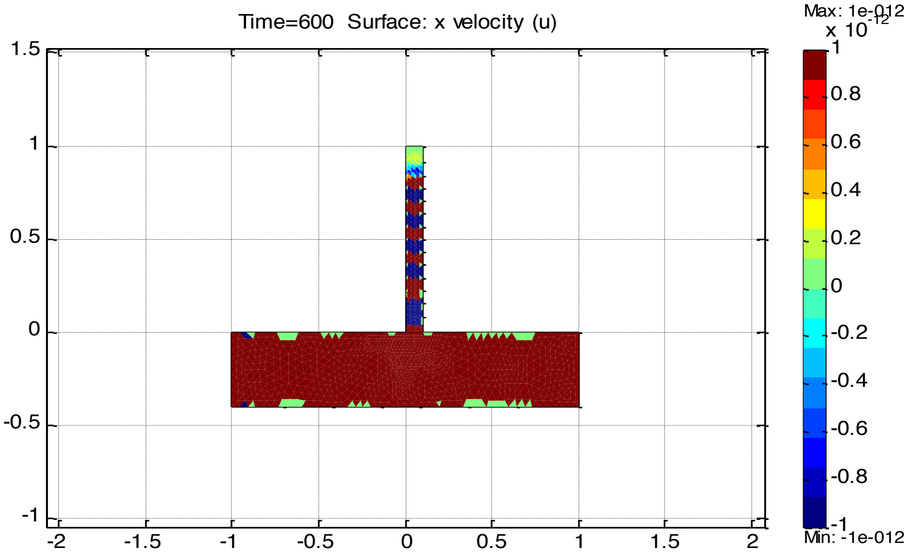


Figure 10: x-velocity in the pore at Time = 600

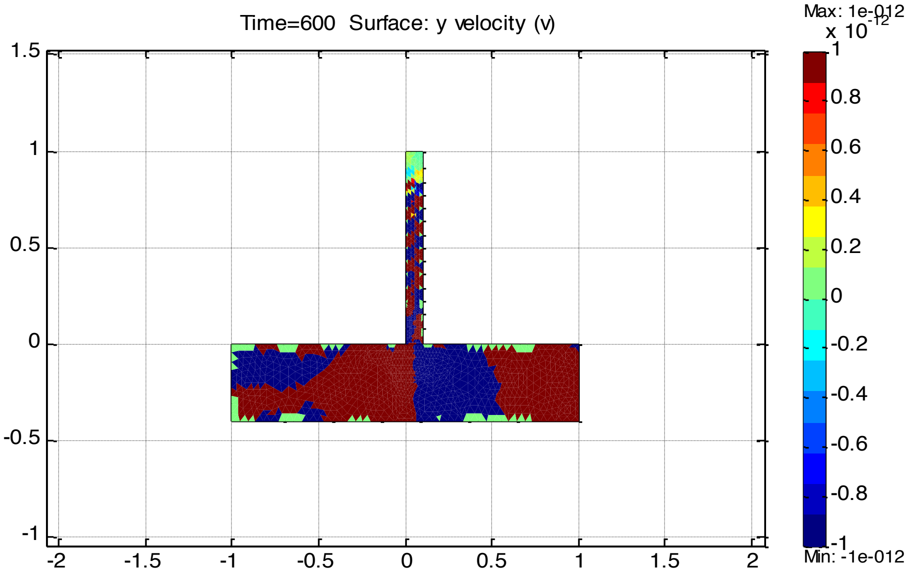


Figure 11: y-velocity in the pore at Time = 600

3. Etching Diffusion with a tighter range

Since I had an idea in my head regarding what the diffusion in the pore should look like, I began to work with the range of the concentration for the Etching Diffusion cell. Using the same mesh and conditions, I reduced the range of the concentrations until I could get a solid line that represented the unetched silicon. There was still diffusion of the released silicon down the pore and into the bulk, which was what I wanted to see. The final results are shown below with a concentration range from 0-0.1.

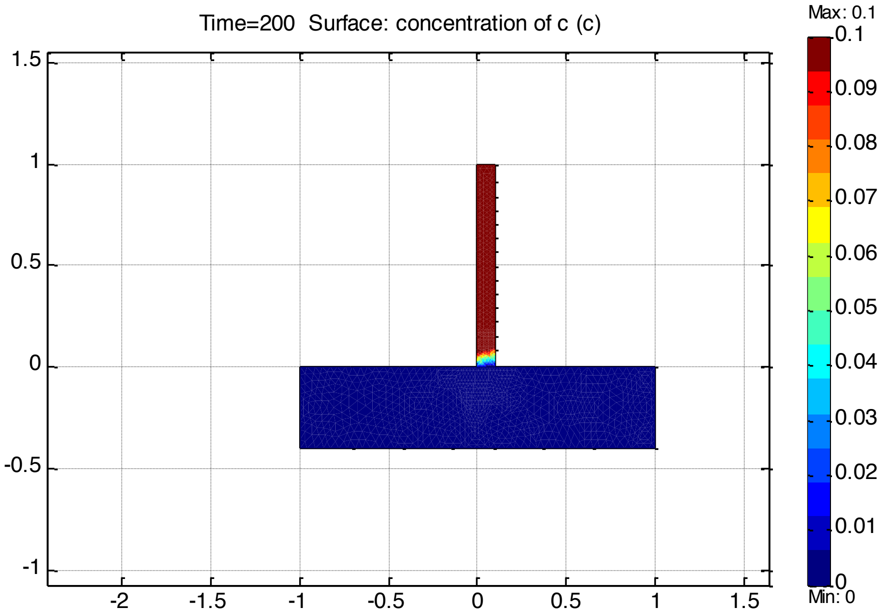


Figure 11: Reduced Range for the Concentration Profile of c at Time = 200

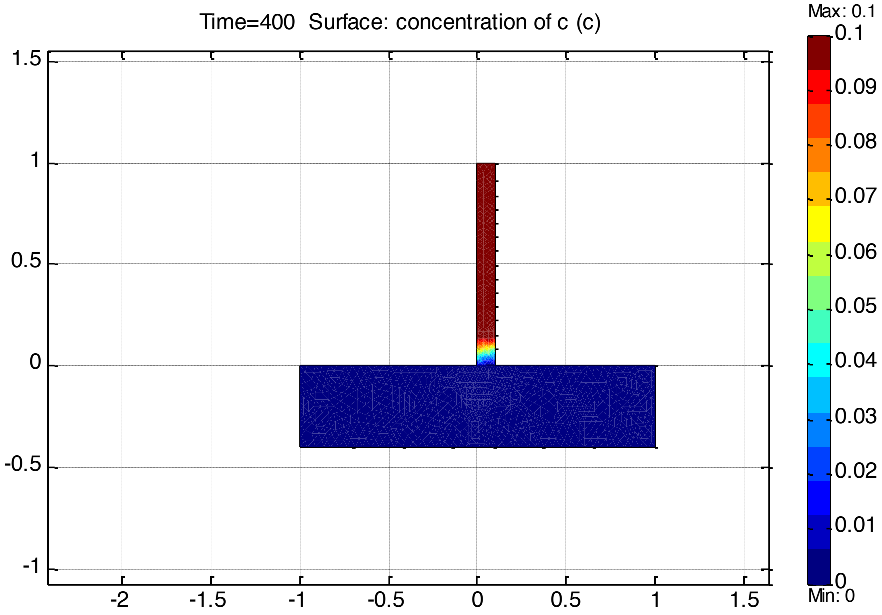


Figure 12: Reduced Range for the Concentration Profile of c at Time = 400

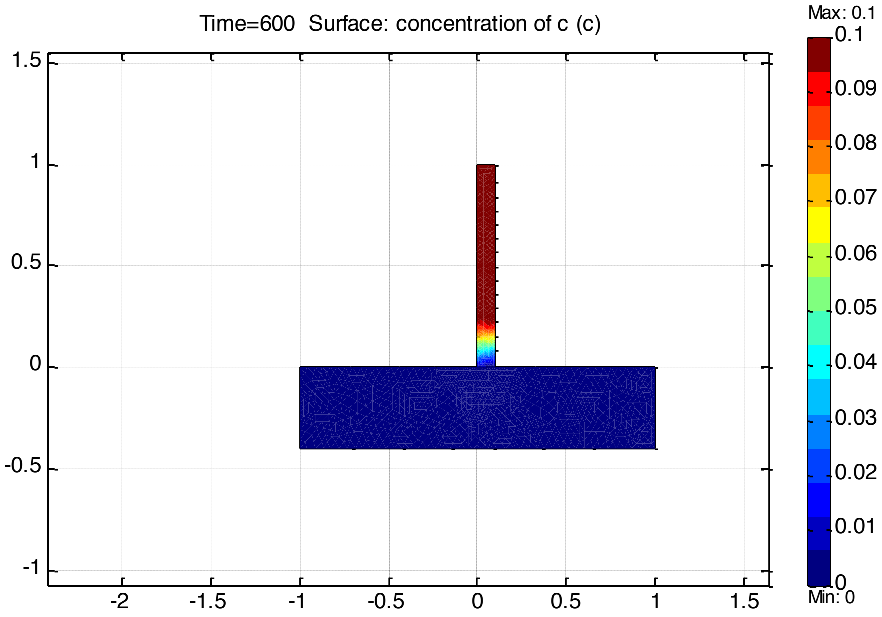


Figure 13: Reduced Range for the Concentration Profile of c at Time = 600

By changing the range of the surface concentration, I can force a semi-constant line that represents the solid surface during the etching process. The initial trend of the concentration shows that there is an initial difference between the two different sides of the pore. The material on the right hand side is initially etched faster than the material on the left hand side. This initial condition may be the justification for the nonsymmetrical waviness of the pore.

III. Conclusions

After trying to establish a connection between the recirculation and the etching walls, I approached the experts at Neah Power for their hypothesis regarding the waviness of the pore walls. We had been in contact during the quarter and they were aware of my hypothesis about the convective forces being the driving force for the waviness as opposed to either the applied potential or diffusion. As it turns out, the reason for the pore waviness is the applied potential. The main force within the pore is the diffusion of the acid up to the surface of the silicon, and then the immediate replacement reaction. After the silicon is removed from the solid it diffuses into the bulk and is swept away. The applied potential takes advantage of the mobility of the ions, and is the driving force for the waviness because it varies about the applied curve. Figure 3 in the Introduction shows the ideal condition for the applied voltage, but in actuality the voltage varies around the set point ±5mV. This oscillatory behavior results in the waviness.

The one thing that I may have accounted for is the offset nature of the waviness. The pore is not symmetrical about the y-axis. This may be due to that initial condition found in the Etching Diffusion file with the reduced concentration profile. The material on the right hand side is initially etched faster than the lefthand side. This could have a lasting effect on the overall shape of the pore.

Through many different trials and errors I discovered that modeling a solid in femlab is much more difficult than anticipated. The ability to set the parameters to have a solid edge was the main hold-up for doing more advanced calculations with the file. This is something that was discussed when I initially mentioned trying to model this physical problem.

Overall, I feel like I learned more about femlab and about using my intuition to either accept, reject, or manipulate a file. The three movies that I have built show the progression of a solution that could possibly be turned into something that can show the realistic etching process.

Attached Files:

- Etching3.mat – file for Etching Diffusion
- Etching_rxn.mat – file for Etching Reaction
- Etching_rxn.mpeg – Movie for Etching Reaction
- Etching_dif.mpeg – Movie for Etching Diffusion with range of 0-1
- Etching_dif_range.mpeg – Movie for Etching Diffusion with range of 1-0.1