



LUND UNIVERSITY  
Faculty of Science

# Wet Etching of Silicon Germanium Nanowires

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## List of Acronyms

Si – Silicon

Ge – Germanium

SiGe – Silicon Germanium

TEM – Transmission Electron Microscope

NUS – National University of Singapore

## Abstract

The aim of this project is to understand the wet etching mechanism of SiGe at the nanoscale. We will use the etching of SiGe nanowires as a case study and we will optimize the etchant solution in order to achieve high selectivity over Si, preserve the shape of SiGe nanowire (isotropic etching) and control their diameter below the threshold of ten nanometers.

## Introduction

### Nanostructures and their unique properties

A nanostructure<sup>1</sup> is a structure which has at least one dimension of an order of  $10^{-8}$  m. The structures can be zero, one, two or three dimensional depending on how many dimensions are on the nanoscale. When compared to bulk materials, nanostructures have different properties as the quantum effects are pronounced at the nanoscale. One important effect is the quantum confinement<sup>2</sup> causing charge carriers to have discrete energy levels. It occurs in nanostructures because their size is of the same magnitude as the de Broglie wavelength of the electron wave function. Since the charge carriers have discrete energy levels, conductivity becomes quantized and depends on the number of energy levels which act as conducting channels.

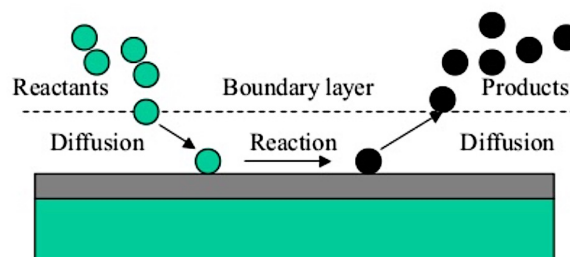
Nanowires<sup>3</sup> are wires with diameter of a few nanometers and therefore relate to 1 dimensional nanostructures. They have a few crucial advantages over the bulk materials. Firstly, one dimensional electronic pathways have reduced internal resistance which allows for efficient charge carrier transportation. Secondly, nanowires have high crystallinity which reduces scattering of the charge carriers. Finally, ballistic conduction is possible in the nanowires since the mean free path of the charge carriers becomes a lot longer due to reduced electron-phonon scattering. These

properties make nanowires attractive for various applications like vertical transistors, photodetectors, solar cells, etc.

SiGe nanowires which our research group worked on are to be used in vertical nanowire transistors since SiGe is highly conductive and quite cheap alloy. These transistors expand vertically while their width is only a few nanometers. This allows to place a lot more transistors on the chip and solve the problem of physical limitation for the size of the horizontal transistors. However to reduce the diameter of the SiGe nanowires, wet etching is required.

## Wet Etching

To reduce the size of the SiGe nanowires to the desired one, wet etching was used. Wet etching<sup>4</sup> is the process of removing a material using liquid reactants. It is an essential step in processing of any nanomaterial as it is used to create nanostructures of desired sizes and shapes. Furthermore, it is used to remove unwanted material and any defects present on the wafer. Unlike dry etching, wet etching does not introduce defects and preserves the crystallinity of the material which is why it is preferred for the etching of SiGe nanowire. The physical mechanism of wet etching is presented on the figure below.



**Figure 1:** Physical mechanism of wet etching

(Reproduced from: Ghanshyam Singh. "Wet and Dry Etching." *LinkedIn SlideShare*, Slide 11)

First, the reacting ions or molecules diffuse from the etchant solution towards the wafer surface.

Next, a controlled chemical reaction between the reactive ions or molecules and the exposed

material takes place. During this reaction, the bonds in the exposed material are broken and the byproducts containing the wafer material are formed. Then, the reaction byproducts diffuse from the wafer's surface towards the bulk of the etchant solution. This is how the surface layers of the exposed materials are removed.

## Background Information

### Oxidation and Etching of SiGe

In the following sections, the state of art of the SiGe etching is presented. From the literature, it was found that etching of SiGe occurs in two steps: oxidation of SiGe and dissolution of the oxide. Therefore, the background information for oxidation of SiGe and dissolution of SiGe oxide will be described individually. We begin with presenting the oxidation mechanism of pure Si due its simplicity and many similarities to that of SiGe.

#### Oxidation of Si

In 1965, Deal and Grove<sup>5</sup> proposed the theory on thermal oxidation of Si. Their theory is based on the various fluxes involved in the oxidation process. The first flux involved is the oxidant flow to the SiO<sub>2</sub> surface where it is absorbed. The second flux is the transportation of the oxidant through the existing SiO<sub>2</sub> layer to the Si-SiO<sub>2</sub> interface where it reacts with Si to form the oxide. These processes can be expressed mathematically using Fick's law<sup>6</sup> and Henry's law<sup>7</sup>, which form a system of equations with the following solution:

$$x^2 + Ax = B(t + \tau) \quad (1)$$

where  $t$  is the oxidation time,  $x$  is the oxide thickness, and  $A$  and  $B$  are experimentally determined constants.  $\tau$  is a variable to deal with initial oxide thickness.

Deal and Grove also discovered two limiting cases for the Si oxide growth. The first limiting case occurs when the oxide is very thin. Consequently,  $x^2$  is very small and can be neglected from the original equation. Then the equation is reduced to

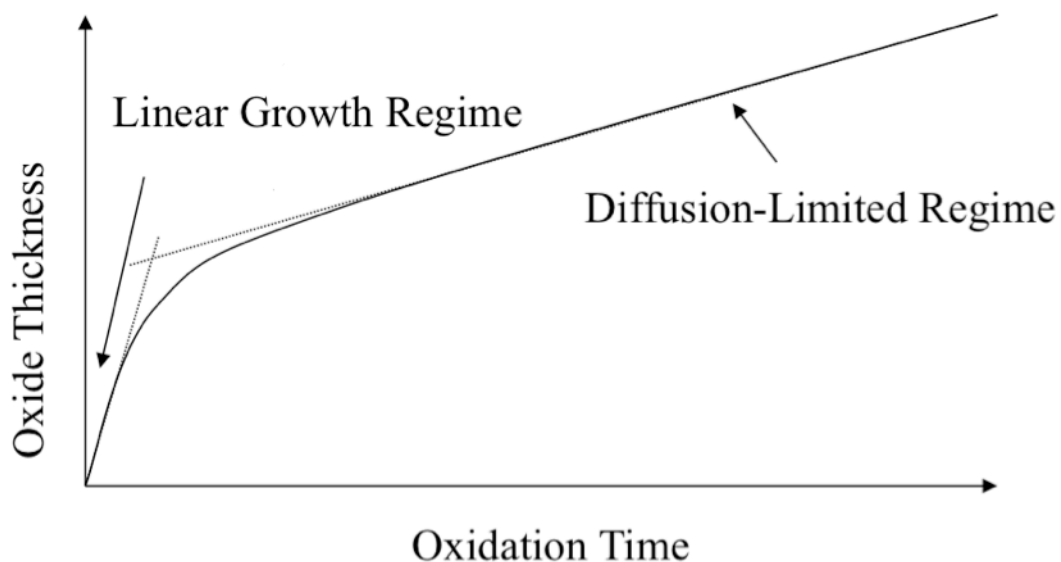
$$x = B/A(t + \tau) \quad (2)$$

For this limiting case, the oxide layer is thin and therefore oxidant quickly diffuses through the oxide layer. The rate of formation of  $\text{SiO}_2$  is limiting the oxidation rate.

The second limiting case is for thick oxides, causing  $x^2$  to be much larger than  $Ax$  term, so the equation is reduced to

$$x = \sqrt{B(t + \tau)} \quad (3)$$

In this case, the oxidant diffusion through the oxide layer is the rate limiting process.



**Figure 2:** According to the Deal-Grove model, oxidation of Si has two regimes: linear growth (reaction limited) and diffusion limited regimes  
(Reproduced from: Christopher Henderson. "Oxidation and Kinetics." *Semitracks, Inc.* | 2014 October Newsletter. Page 3, Web)

## Oxidation of SiGe

Oxidation of SiGe was found to be rather similar to that of Si, but with some differences as well. Overall the mechanism of SiGe oxidation is still not fully understood. We can identify 2 different regimes. Above 500°C, Si-Ge interdiffusion occurs, making the oxidation mechanism of SiGe quite different from that of pure Si as the interdiffusion greatly affects how uniformly Si and Ge will oxidize. Below 500°C, no Si-Ge interdiffusion occurs and the oxidation mechanism is very similar to that of pure Si. The regime closest to our conditions and in general relevant for wet etching is the second one and it has been investigated by Park et al.<sup>8</sup>.

In "*Kinetics and mechanism of wet oxidation of GeSi<sup>8n</sup>*", it was found that for wet oxidation of Si<sub>0.72</sub>Ge<sub>0.28</sub> at 500°C, both Si and Ge are fully oxidized and the Ge:Si ratio remains the same in the oxide layer as it is in the alloy. The oxidation was found to be processed via a diffusion limited regime. They have also discovered that for temperatures lower than 500°C, Ge does not diffuse into Si.

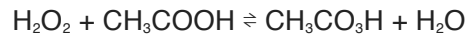
Park et al.<sup>7</sup> explanation was that Si and Ge in the alloy are virtually immobile compared to the oxidant which has a very high diffusion rate through the oxide. The oxidant reacts very fast with both Ge and Si when it reaches the SiGe and oxide interface, causing the rate of oxidation to be limited by the diffusion of the oxidant through the oxide. The Si<sub>0.72</sub>Ge<sub>0.28</sub> oxide layer growth rate was found to be around 5 nm/minute at 550°C.

Finally, Park et al.<sup>7</sup> noticed that the rate of SiGe oxide growth accelerated with Ge content in the alloy. They have also found that higher temperatures cause higher oxide growth rate.



## Etching of SiGe

Holländer et al.<sup>9</sup> have found that the etching process of SiGe consists of an oxidation and an oxide etch steps. They have performed SiGe etching using HF: H<sub>2</sub>O<sub>2</sub>: CH<sub>3</sub>COOH with volume ratio of 1:2:3. The etchant solution has been aged for at least 72 hours, as the H<sub>2</sub>O<sub>2</sub> needs time to reach the chemical equilibrium in the reaction with acetic acid CH<sub>3</sub>COOH to form peracetic acid:



Holländer et al.<sup>8</sup> then proposed a mechanism to explain the etching of SiGe. The etch depth increases linearly with time and that it depends significantly on the Ge content of the layers. The etching rate increases with the Ge content until it reaches about Si<sub>0.5</sub>Ge<sub>0.5</sub>. The etch rate increases from about 10 nm/min for pure Si to a maximum of 350 nm/min for Si<sub>0.5</sub>Ge<sub>0.5</sub>.

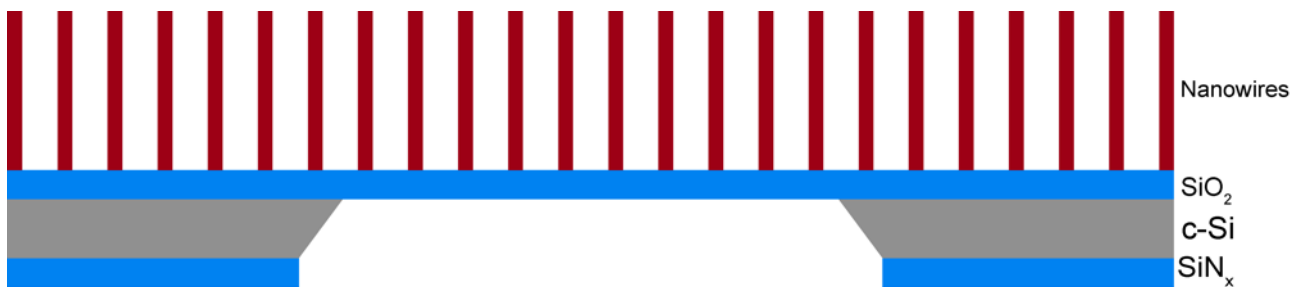
Holländer et al.<sup>8</sup> suggest that the etching process consists of two individual reactions: oxidation of SiGe by the mixture of hydrogen peroxide and acetic acid, and the oxide dissolution by HF. The etching rate is limited by the slowest of both processes.

Holländer et al.<sup>8</sup> also found that the selectivity of the solution over Si (defined as etch rate of SiGe over etch rate of Si) is higher for etching solutions containing a higher amount of HF.

It is worth mentioning that there are other common etchant solutions used for SiGe like HF and HNO<sub>3</sub> solution, NH<sub>4</sub>OH and H<sub>2</sub>O<sub>2</sub> solution, tetramethylammonium hydroxide (TMAH) solution<sup>10 11</sup>.

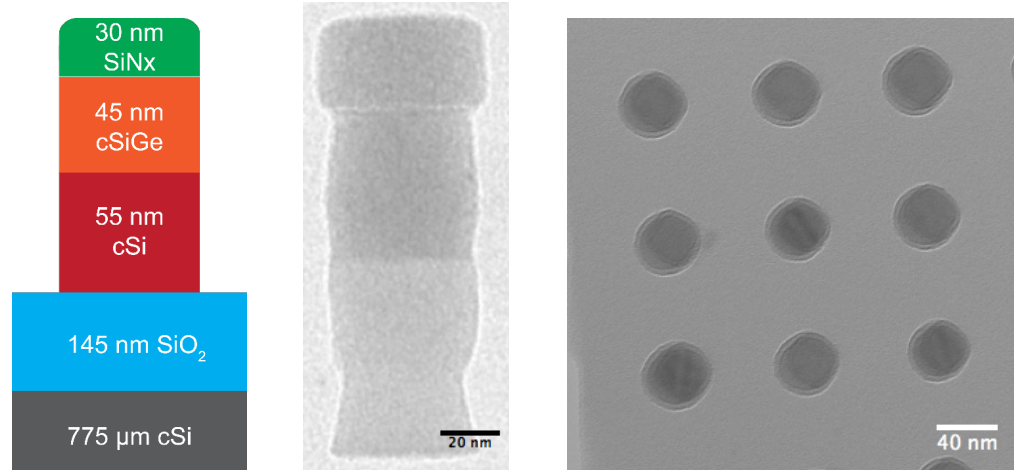
## Experimental Procedures and Details

First, the nanowires (a wire with diameter of an order of  $10^{-8}$  m) are created using electron beam lithography and dry etching by our research group's collaborators (Imec). The samples are then prepared in the clean room of NUS. First, the 300 mm wafers are diced into smaller pieces of approximately 75 mm by 75 mm. Next, conventional lithography, dry and wet etching are used to pattern the chips as displayed in figure 3. The silicon dioxide layer is 145 nm thin which makes it electron transparent and therefore transmission electron microscopy can be used to study the nanowires.



**Figure 3:** Schematic design of the chips used in the experiments

Figure 4 demonstrates the design of the nanowire. SiGe has the ratio of 75:25 of Si to Ge. The silicon part is added to test the etching selectivity of the solutions (defined as etching rate of SiGe divided by etching rate of Si). The silicon nitride ( $\text{Si}_3\text{N}_4$ ) cap provides the reference size as it is not etched by the used etchant solutions.



**Figure 4:** *On the left:* Schematic design of the nanowire used in experiments. *Middle:* Transmission electron microscope (TEM) photo of the side view of the nanowire. *On the right:* TEM photo of the top view of the nanowires

## Experimental Procedures

### Pre-etching treatment

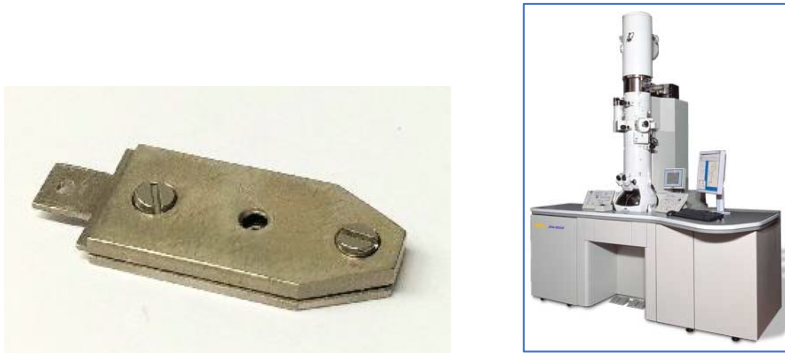
Before etching is done, the native oxide layer and organic contamination on the chip have to be removed. The oxide layer is removed by placing the nanowire in 0.25% hydrofluoric acid solution for 1 minute. To remove the organic contamination, the chip is plasma cleaned at low power for 45 seconds.

### Etching

Once the pre-etching treatment is done, the actual etching is carried out. In order to maximize the etching rate, the chip is moved around in the etchant solution to assure a constant flow of new solution to the nanowire. After the etching is finished, the nanowire is rinsed in de-ionized water to stop the etching.

## Imaging

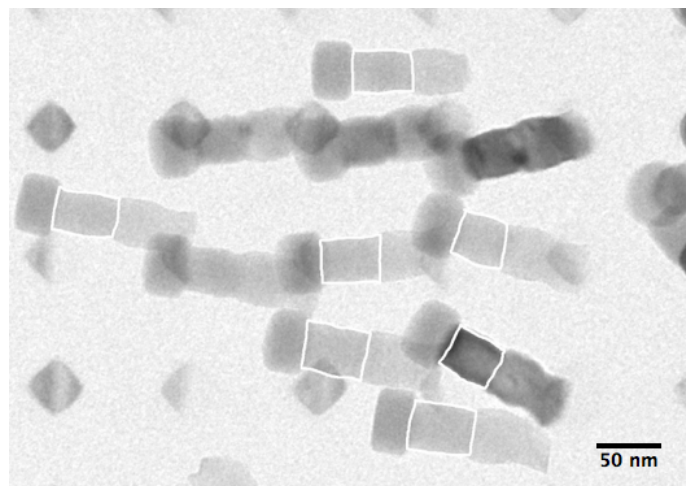
The imaging of the etched SiGe nanowire is done on the TEM microscope JEOL2100. Prior to placing the chip in the TEM, the chip is placed in the holder. The holder is then placed into the TEM.



**Figure 5:** *On the left:* Chip holder for the TEM. *On the right:* Transmission electron microscope JEOL2100

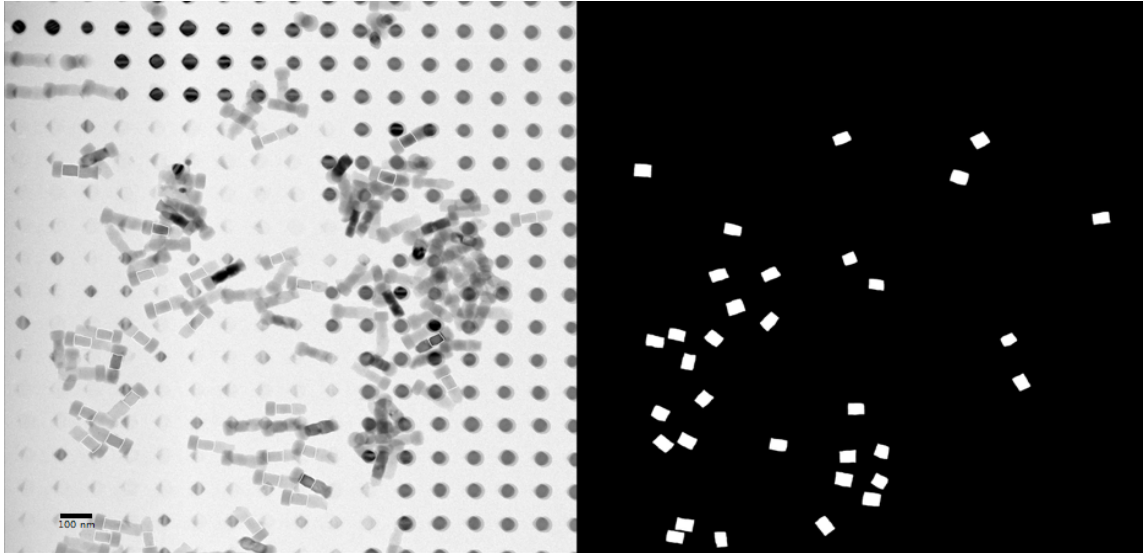
## Data Analysis

The first part of data analysis is the segmentation. The segmentation includes outlining the SiGe nanowires on the TEM images. On average, 100 nanowires are outlined for each sample to get a good statistical distribution of the diameter of the nanowire.



**Figure 6:** Example of segmentation of SiGe nanowire in the TEM image of the chip

Once the segmentation is finished, a program written in the programming language Python selects the segmented nanowires and calculates the diameter for each nanowire. After, the program plots the distribution of diameter of the nanowire.



**Figure 7:** *On the left:* Segmented TEM image. *On the right:* Segmented TEM image after Python program filters out everything but the SiGe nanowires

## Etchant Solutions

The experiments described in the background information section use HF, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>COOH etchant solutions in a volume ratio of 1:2:3. In our experiments, we selected very different concentrations, namely the two extreme cases. One etchant solution with a high concentration of H<sub>2</sub>O<sub>2</sub> (1:200:3) and the second one with a high concentration of CH<sub>3</sub>COOH (1:95:110). Using these solutions, we studied the different mechanisms involved in the etching of SiGe.

Since these pure solutions have too high of an etch rate for the nanoscale SiGe and cannot be used in the industry, we have also studied the dilution of these etchant solutions to reduce the etch rate in order to increase the etch time to a few minutes.

### PAA1 Etchant Solution

PAA1 is a solution containing HF, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>COOH in a volume ratio of 1:95:110. Etch rates for SiGe were tested for various dilutions of PAA1 and etch times. The dilutions with water of PAA1 and corresponding etch times are presented in table 1 below.

<b>Dilution\Solution</b>	<b>Etch Time</b>
Pure	0.33m, 0.67m, 1m
1.33x	0.5m, 1m, 1.5m, 2m
2x	1m, 2m, 3m
4x	3m, 5m, 8m
6x	3m, 7m, 11m, 15m

**Table 1:** Dilutions of PAA1 and etch times of SiGe using PAA1 solutions

### PAA2 Etchant Solution

PAA2 is a solution containing HF, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>COOH in a volume ratio of 1:200:3. Etch rates for SiGe were tested for various dilutions of PAA2 and etching times. The dilutions with water of PAA2 and corresponding etch times are presented in table 2 below.

<b>Dilution\Solution</b>	<b>Etch Times</b>
2x	0.17m, 0.5m, 0.83m, 1m, 1.17m
4x	0.5m, 1m, 1.5m, 2m
6x	1m, 2m, 3m, 4m, 5m
8x	3m, 5m, 8m, 11m

**Table 2:** Dilutions of PAA2 and etch times of SiGe using PAA2 solutions

### Other Etchant Solutions

Prior to PAA1 and PAA2, two other etchant solutions were tested:

1. H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O in a volume ratio of 4:1:5

2. HCl, H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O in a volume ratio of 36:1:364

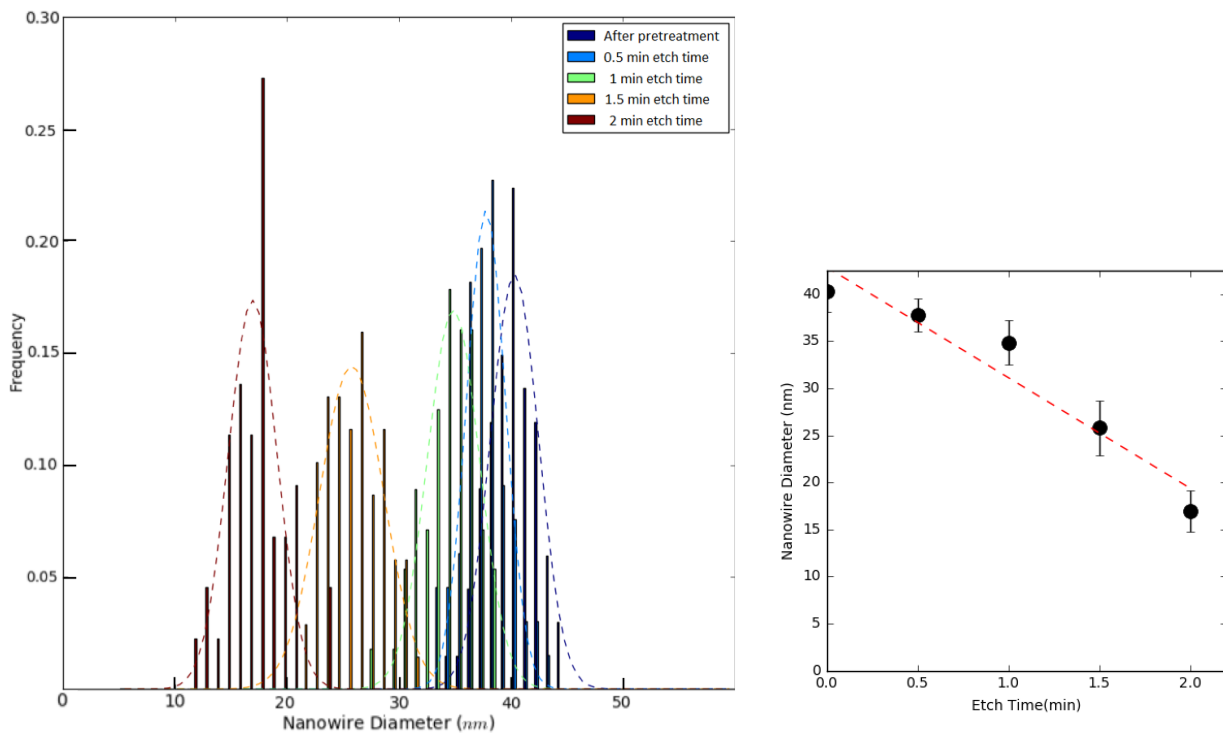
The reason for testing these etchant solutions was that they are known to etch Germanium (Ge).

The first solution has the etch rate of 10 nm/min for Ge and the second one's etch rate for Ge is 200 nm/min.

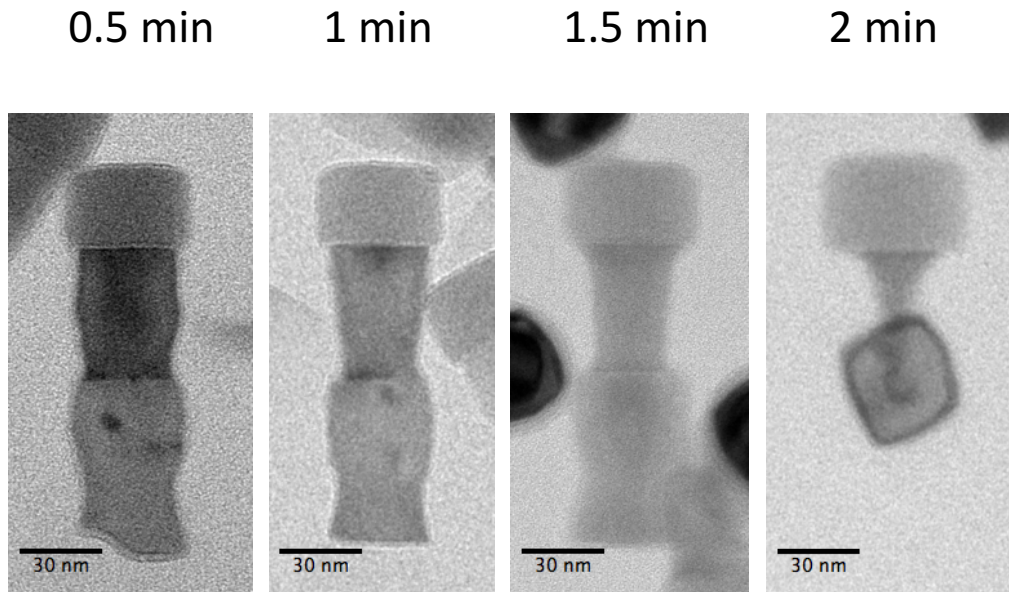
## Results

### PAA1 Etchant Solution

Below, a sample data is presented for 4 times diluted PAA1.



**Figure 8:** Data for 4 times diluted PAA1. *The left figure:* Distribution of SiGe nanowires' diameter after different etching times. *The right figure:* Displays the change of SiGe nanowires' diameter with etching time.



**Figure 9:** SiGe nanowires after 0.5, 1, 1.5 and 2 minutes of etching in 4 times diluted PAA1. It is worth noticing that after 1 minute etch time, the SiGe loses its original rectangular shape. After 2 minutes etch time, the SiGe has a cone-like shape.

In the table 3 below, the etch rates for PAA1 samples are shown:

Dilution\Solution	Etch rate, [nm/min]
2x	23.3
4x	11.8
6x	4.61
8x	2.55

**Table 3:** Etch rates of SiGe for various dilutions of PAA1

Selectivity over Si for PAA1 samples are presented in table 4 below.

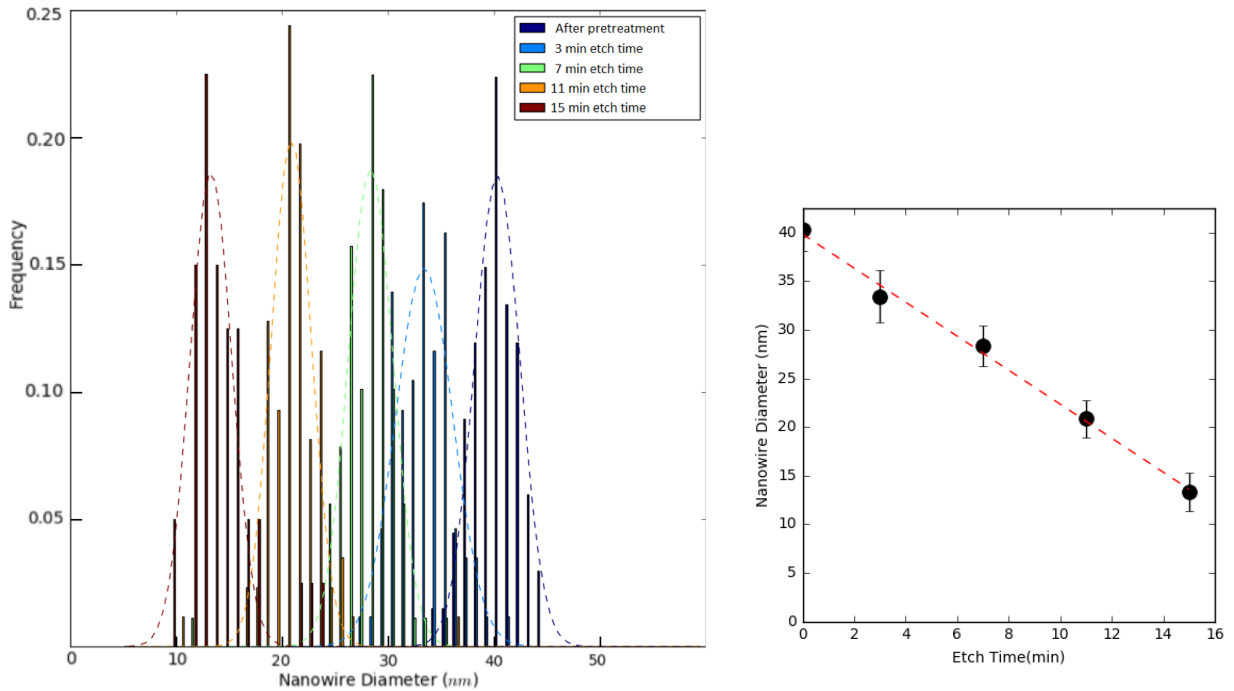
Dilution\Solution	Selectivity
2x	20.04
4x	8.78
6x	2.71
8x	1.58

**Table 4:** Selectivity over Si for various dilutions of PAA1

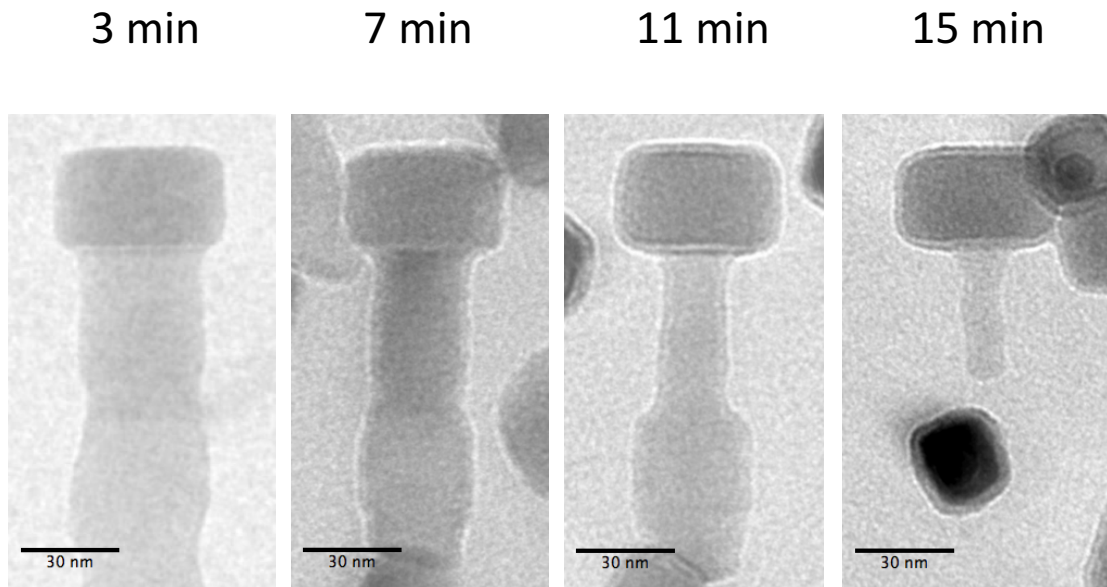


## PAA2 Etchant Solution

Below, a sample data is presented for 6 times diluted PAA2.



**Figure 10:** Data for 6 times diluted PAA2. *The left figure:* Distribution of SiGe nanowires' diameter after different etching times. *The right figure:* Displays the change of SiGe nanowires' diameter with etching time.



**Figure 11:** SiGe nanowires after 3, 7, 11 and 15 minutes of etching in 6 times diluted PAA2. Notice that the rectangular shape of SiGe nanowire is preserved

In the table 5 below, the etch rates for PAA2 are shown:

<b>Dilution\Solution</b>	<b>Etch rate, [nm/min]</b>
Pure	16.6
1.33x	12.0
2x	8.26
4x	3.41
6x	1.73

**Table 5:** Etch rates of SiGe for various dilutions of PAA2

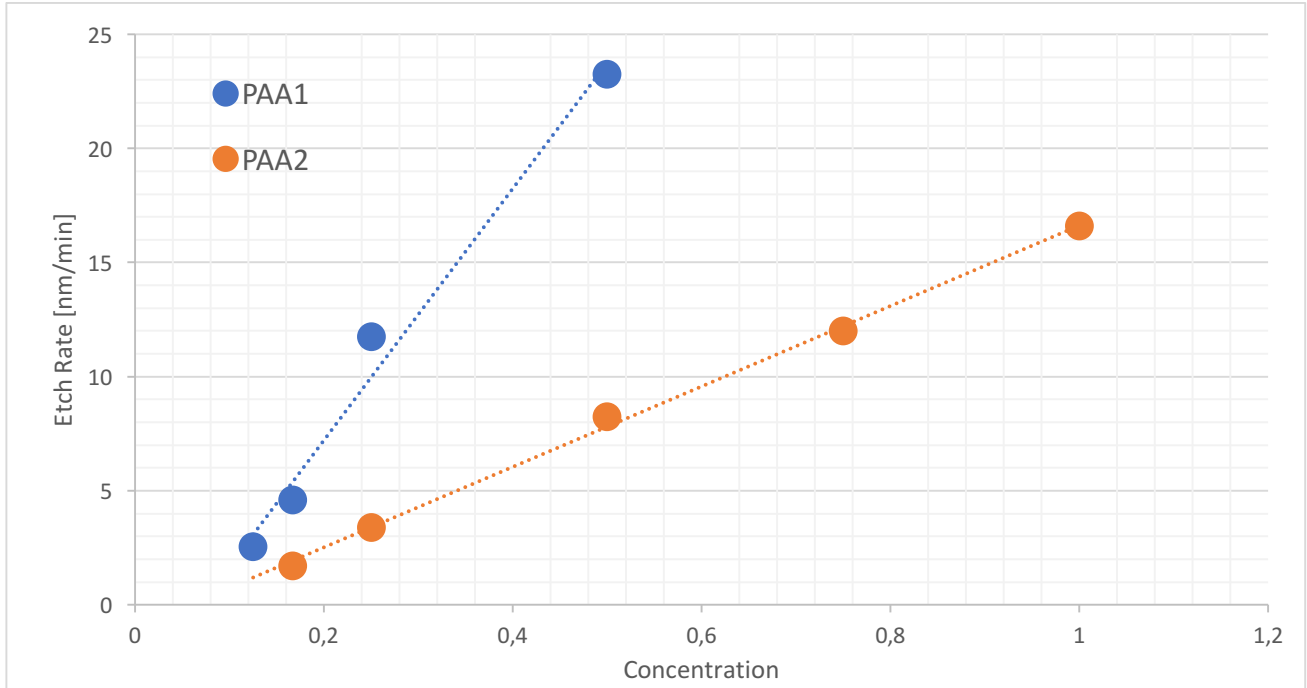
Selectivity over Si for PAA2 samples are presented in table 6 below:

<b>Dilution\Solution</b>	<b>Selectivity</b>
Pure	8.09
1.33x	5.86
2x	7.29
4x	3.86
6x	2.33

**Table 6:** Selectivity over Si for various dilutions of PAA2

### Comparison of PAA1 and PAA2 Etchant Solutions

In the figure 12 below, the etching rates for PAA1 and PAA2 as a function of concentration (defined by 1/dilution) were plotted together.



**Figure 12:** Etching rates for PAA1 and PAA2 as a function of concentration of these solutions. The etch rate has linear dependence on the solution concentration

Based on the linear regressions for etch rate of PAA1 and PAA2 from figure 12, the nanowire diameter ( $d$ ) can be predicted by a two-parameters linear equation:

$$d(t, c) = d^0 + \gamma^0 t + \rho c t \quad (4)$$

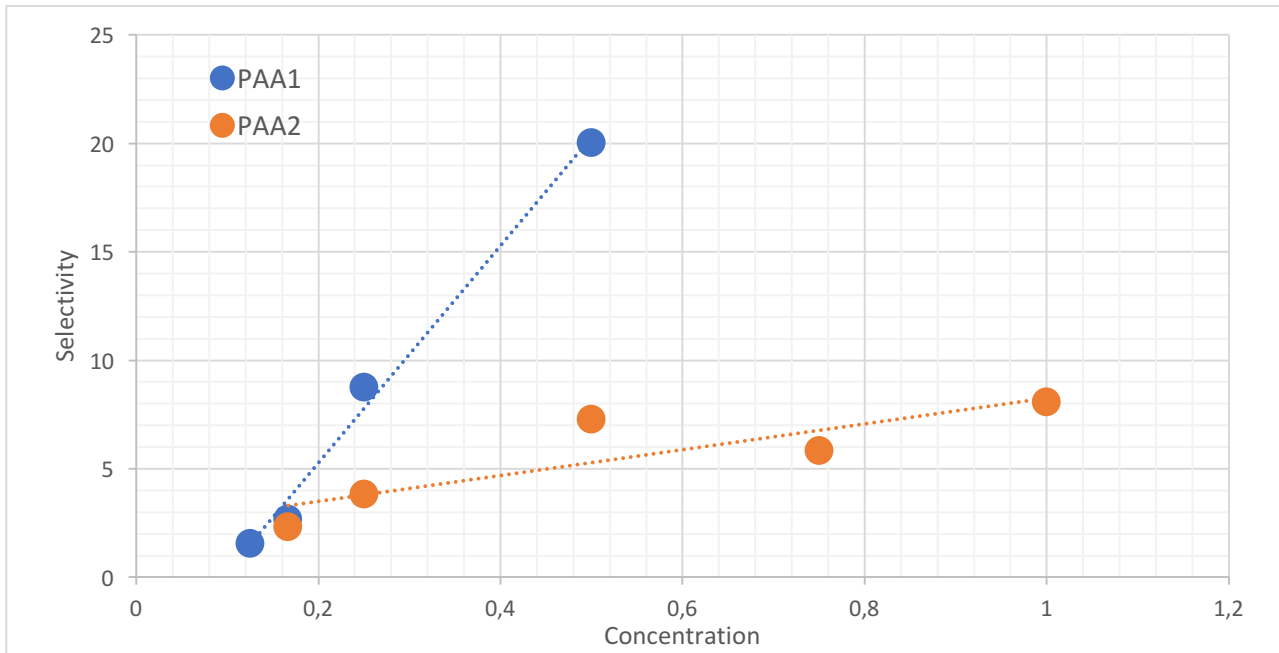
where  $d^0 = \text{initial diameter}$ ,  $c = \text{concentration [\%]}$ ,  $t = \text{time [min]}$

In the table 7 below, the relevant parameters for equation 4 are presented:

	<b>PAA1</b>	<b>PAA2</b>
$\gamma^0$ [nm/min]	3.83	1.00
$\rho$ [nm/min]	-55.2	-17.6

**Table 7:** Relevant parameters for equation 4 for PAA1 and PAA2

Selectivity of Si for PAA1 and PAA2 as a function of concentration (defined by 1/dilution) were plotted also plotted together. The results can be found in figure 13 below



**Figure 13:** Selectivity of Si for PAA1 and PAA2 as a function of concentration of these solutions. The selectivity also has linear dependence on the solution concentration.

Based on the linear regressions for selectivity of PAA1 and PAA2 from figure 13, the selectivity ( $S$ ) of the solution can be expressed in terms of concentration of the solution by the following linear equation:

$$S(c) = S^0 + Sc \quad (5)$$

where  $c = \text{concentration } [\%]$

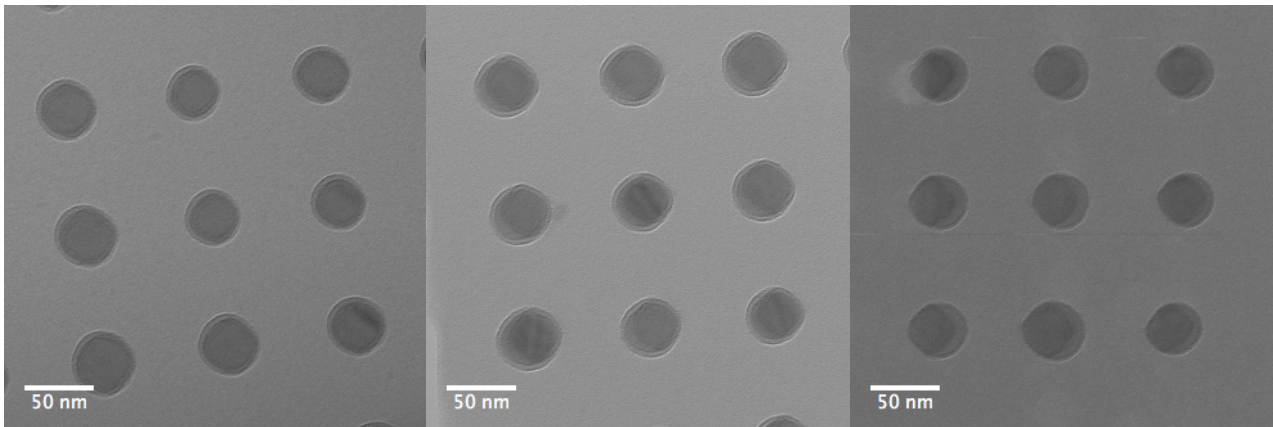
In the table 8 below, the relevant parameters for equation 5 are presented:

	<b>PAA1</b>	<b>PAA2</b>
$S^0$	-4.77	2.32
$S$	50.1	5.94

**Table 8:** Relevant parameters for equation 5 for PAA1 and PAA2

## Other etchant solutions

The first experiments that were carried out were 15 seconds etch time using  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  solution and 5 minutes etch time using  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  solution. However, neither of the solutions etched SiGe. Therefore, the etch time for  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  was increased to 1 minute and 20 minutes for  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$ . The results are presented in the figure 14 below:



**Figure 14:** *On the left:* SiGe nanowire before etching (top view). *Middle:* SiGe nanowire after 20 minutes of etching with  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  etchant solution (top view) Notice that barely any etching has occurred. *On the right:* SiGe nanowire after 1 minute of etching with  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  etchant solution (top view). Again, almost no SiGe has etched

As seen from the figure 13, it is clear that  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$ , and  $\text{HCl}$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  etchant solutions are not effective at etching SiGe. Therefore no further experiments were done using these etchant solutions.

## Discussion and Conclusion

### Etch rate

Based on the data from figure 12, it can be concluded that the etch rate has linear dependence on the solution concentration. It is also worth noticing that both PAA1 and PAA2 solutions linear

regressions intercept the x-axis at the solution concentration of 0.07. This seems to indicate that 0.07 is the threshold concentration, below which no etching happens for either solution.

As previously mentioned, Holländer et al.<sup>8</sup> found that the etching mechanism of SiGe is similar to that of Si and happens in two steps. The first step is oxidation of SiGe and the second step is the dissolution of SiGe oxide. Comparing the etch rates of PAA1 and PAA2 solutions, it was found that the PAA1 solution has higher etching rate than PAA2. One possible explanation for it is that PAA1 has about 100 times more acetic acid (AA). This causes faster dissolution of SiGe oxide layer and therefore faster etch rate. It is also possible that the oxide growth occurs only via reaction limited regime as it has no time to build up.

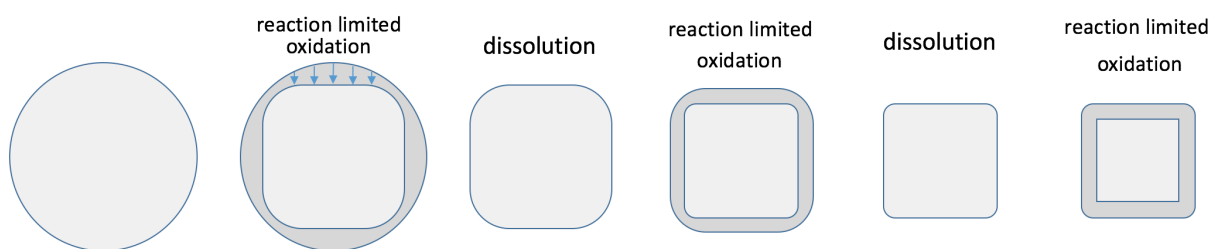
PAA2 solution on the other hand has a lot slower dissolution of oxide layer and therefore a slower etch rate. This could mean that the oxide growth regime switches from reaction to diffusion limited regime as the oxide is dissolved slowly and thus has the time to build up. Oxide growth rate is slower in the diffusion limited regime which consequently slows down the etch rate.

## Isotropy

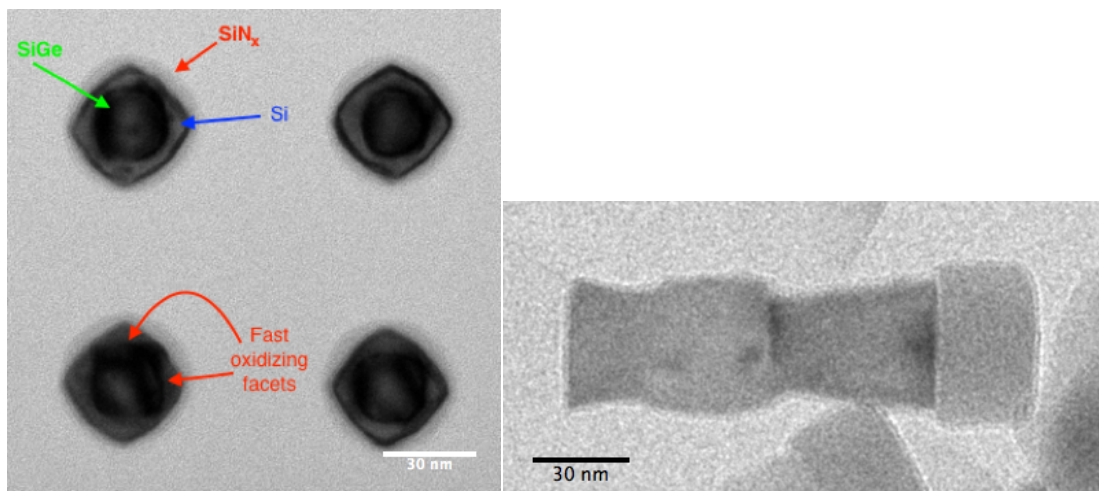
We observed that PAA2 caused isotropic etch of SiGe however PAA1 resulted in anisotropic etch. Thus, we tried to look for the steps involved in the etching of SiGe that are anisotropic. It is known that dissolution of oxide is isotropic since SiGe oxide is amorphous. Diffusion of the oxidant through the existing oxide layer is also isotropic. However oxidation of SiGe can be anisotropic since there are fast and slow oxidizing facets<sup>12</sup>.

Consequently, for the reaction limited etch regime, where oxidation of SiGe is the limiting step, anisotropy should be expected as fast oxidizing facets will be oxidized and etched faster. Since we are dealing with a convex structure, fast etched facets will be revealed causing the final shape of

SiGe nanowire to be composed of the fast etching facets<sup>13</sup>. This is indeed what was found for PAA1 solution which etches SiGe via reaction limited regime. The figure 15 below presents the schematics for the SiGe nanowire's etching to explain the steps that cause anisotropic etch of SiGe. It is important to note that the oxidation and oxide dissolution happen simultaneously however they are separated in figures 15 and 17 to make it easier to understand what happens at each step.

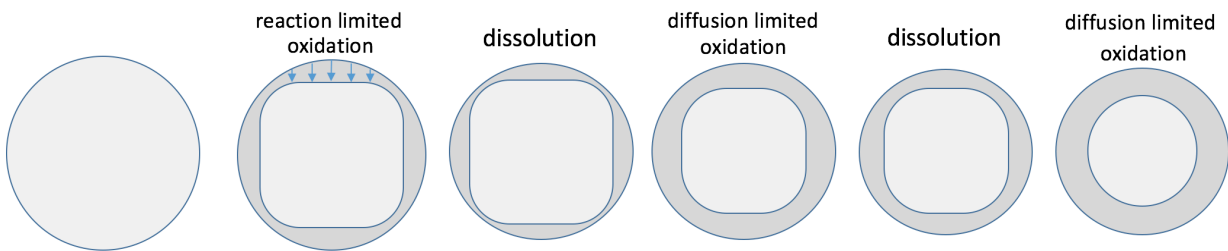


**Figure 15:** From left to right: Initial state of the SiGe nanowire. First, the reaction limited oxidation happens. Next, the formed oxide layer is dissolved. Since reaction limited oxidation is anisotropic, faster oxidizing facets will etch quicker causing anisotropy. Then, the reaction limited oxidation and dissolution of the oxide layer steps repeat.

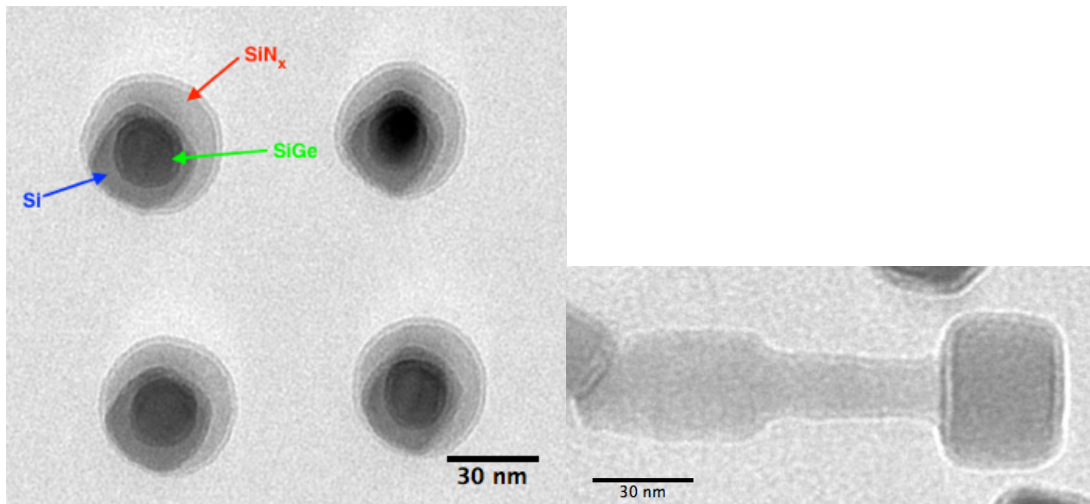


**Figure 16:** Nanowires after 4 minutes of etching with 4 times diluted PAA1 etching solution. *On the left:* Top view of the four nanowires. Notice the manifestation of the fast oxidizing facets due to anisotropic etching. *On the right:* Side view of the nanowire. SiGe loses its original rectangular shape due to anisotropic etching.

For diffusion limited etching regime, oxidant diffusion through the existing oxides is the limiting step. Therefore the oxidation of fast and slow facets happens at roughly the same rate causing isotropic oxidation of SiGe. Consequently, the diffusion limited etching regime should be isotropic. This is what was found for PAA2 solution, which etches SiGe mainly via diffusion limited regime. The figure 17 below presents the schematics for the SiGe nanowire's etching to explain the steps that cause isotropic etch of SiGe.



**Figure 17:** From left to right: Initial state of the SiGe nanowire. First, the reaction limited oxidation happens. Next, the formed oxide layer is dissolved. Since the oxide layer forms quicker than it is dissolved, the oxide builds up around the SiGe nanowire. Therefore, the oxidation shifts from reaction limited to diffusion limited regime. Diffusion limited oxidation is isotropic and consequently the SiGe etching becomes isotropic too.



**Figure 18:** Nanowires after 11 minutes of etching with 6 times diluted PAA2 etching solution. Both slow and fast oxidizing facets are oxidized at similar rates due to diffusion limited oxidation. *On the left:* Top view of the four nanowires. Notice that there is no manifestation of the fast oxidizing facet and the SiGe nanowire remains circular. *On the right:* Side view of the nanowire. SiGe preserves its original shape as the etching is isotropic



## Selectivity

It was found that the selectivity over Si is higher for the PAA1 solution. The reason why PAA1 solution has higher selectivity is because the etch rate of Si remained at around 1 nm/min and barely varied with concentration for both PAA1 and PAA2 solutions. Since the selectivity of the solution is defined as etching rate of SiGe divided by etching rate of Si, solution with higher etching rate of SiGe has higher selectivity which occurs for PAA1 solution. One possible explanation for why etch rate of Si varies so little with solution concentration is that oxidation of Si at room temperature is happening via diffusion limited regime so concentration of the etchant solution has little effect on the Si etch rate.

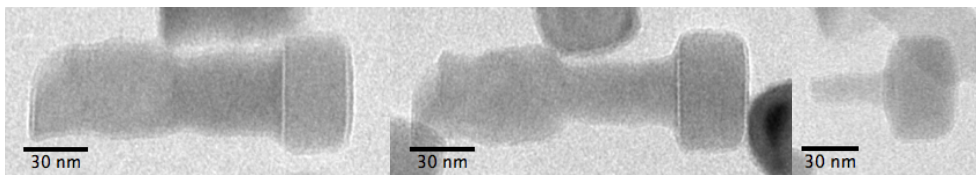
It is worth mentioning that the selectivity results do not agree with the findings of Holländer et al.<sup>8</sup> since PAA1 solution has less HF than PAA2 solution. One reason for that can be that Holländer et al.<sup>8</sup> used the HF, H<sub>2</sub>O<sub>2</sub>, and CH<sub>3</sub>COOH etchant solution in a volume ratio of 1:2:3. PAA1 and PAA2 etchant solutions have 1:95:110 and 2:200:3 volume ratios respectively. Since H<sub>2</sub>O<sub>2</sub> in the solution is the oxidizing agent, both PAA1 and PAA2 solutions have a lot more oxidizing agent. Thus, it is very likely that for Holländer et al.<sup>8</sup> solution, oxidation of Si has occurred via reaction limited regime while via diffusion limited for both PAA1 and PAA2 solutions. Therefore, the etch rate of Si varied with concentration of the solution for Holländer et al.<sup>8</sup> and more HF resulted in higher selectivity.

## Conclusion

To conclude, our research group studied two different etching regimes for the etching of SiGe: reaction and diffusion limited etching regimes. It has been observed that the reaction limited etching regime causes anisotropic etching of SiGe due to the anisotropic, reaction limited oxidation of SiGe. The diffusion limited etching regime caused isotropic etching of SiGe as the oxidation regime

quickly shifted from reaction limited to diffusion limited regimes. A new simple model has been proposed to explain under what conditions these etching regimes occur.

Finally, all the SiGe etchant solutions that were used throughout the project have been compared. It was concluded that the optimal solution is the PAA2 which is diluted two times.



**Figure 19:** *From left to right:* SiGe nanowire after 1,2 and 3 minutes of etching with 2 times diluted PAA2 etching solution

It has an etch rate of 8.26 nm/min for SiGe which is fast enough to etch the whole SiGe nanowire in about 5 and a half minutes. Therefore, it can be easily used to etch the SiGe nanowire to the desired size within 10 minutes. PAA2 diluted 2 times etchant solution has selectivity of 7.29 with respect to Si which is quite good. From figure 19, it can be seen that this etchant solution also etches SiGe quite isotropically.

## Outlook

For future research, it would be useful to consider different etchant solutions. In order to furthermore understand the etching mechanism, one should use the solutions with different volume ratios of only an oxidizer and the oxide dissolver:  $\text{H}_2\text{O}_2$  and HF respectively. This would allow to better understand how the competition between the oxidation and oxide dissolution steps takes place. Additionally, one can try to use a solution like PAA1 and PAA2 but with equal amounts of  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{COOH}$ .

Moreover, one should perform a campaign of in-situ experiments with PAA1 and PAA2 solutions. This would allow to observe the etching in real time and determine the exact diameter of the SiGe nanowire when the etching regime switches from reaction to diffusion limited.

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