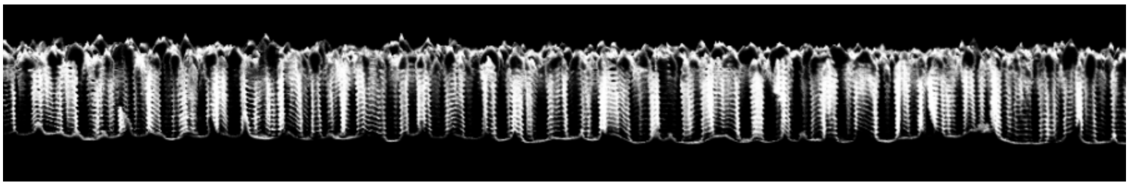
Using the Black Silicon Method to Monitor the Reproducibility of Plasma Etching Processes



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Contents

1 Motivation

This report will outline the robustness of using the black silicon method [Jansen et al., 1995] as a way to measure drift, in a 3-step Bosh process performed on the DRIE-Pegasus (SPTS) using a type of plasma etching called DRIE[1]. Countering drift is essential to ensure reproducible etching results.

We exploit that the parameter window of black silicon is small, which enables a user of Danchip's DRIE-Pegasus (and probably other etching techniques/machines) to be able to check the amount of parameter drift in the process and tune their recipes and control for drift in their experiments. The immediately recognisable visual characteristic of black silicon, makes it easy to identify for the user, and makes the use of SEM[2] or powerful optical microscopes superfluous when testing the behaviour of the etching process.

1.1 The Structure of the Report

The first part of the report will outline how black silicon can be manufactured, and the show the narrow parameter window that results in black silicon. It will illustrate how different parameters, change the outcome of the silicon etch process.

The second part will show how the etching profile obtained by traditional lithography mask etching, corresponds to different etching parameters and black silicon regimes. This will allow us to show how the black silicon method allows the user to monitor drift of the etching process.

2 Introduction to Black Silicon

Black silicon is a novel silicon based material, that consists of randomly distributed pillars on a silicon wafer, which gives it a very low reflectance which makes it appear dark(hence the name, black silicon). The nanograss has heights that are approximately the same size as the wavelength of visible light in silicon. This creates a graded refractive index layer [Stavroulakis et al., 2013, 1], which greatly reduces the Fresnel reflection, thus absorbing light in the wavelength range[3] of 200 to 1500 nm [Ravindra et al., 2016, 2]. The property of high reflectivity, means that black silicon is a good material to create highly light adsorbing solar cells that have shown an efficiency of up to 22.1% [Savin et al., 2015].

The structure of black silicon also makes it a highly effective substrate for SERS[4] [Seniutinas et al., 2015]. In addition to this, black silicon has been known to be hydrophobic which has opened up for applications in surface engineering, eg. [Kondrashov and Rhüe, 2014] or [Jokinen et al., 2008] where the former describes the creation of mechanically stable black silicon hydrophobic surfaces, and the later shows how to create interesting drop shapes with the use of black silicon.

3 Manufacturing Black Silicon

3.1 DRIE and the General 3-step Bosch-Process

The 3-step Bosch process is a form of DRIE process which relies on plasma etching. This process was used for our experiments. The process is outlined in figure 1 with the recipe outlined in section 3.1. It should be noted that figure 1 shows an etching using a mask, as was done later

[1] Deep Reactive Ion Etching
[2] Scanning Electron Microscope
[3] See our own measurements of this phenomena in figure 10, confirming the stated numbers
[4] Surface Enhanced Raman Scattering

on, however to create black silicon the photoresist and BARC[5] layers are not present; this is called maskless etching. Instead native silicon oxide, the initial deposition layer and dirt creates micromasks. If there is a large enough selectivity[6], nanograss is formed[Jansen et al., 1995, p. 119]. The Bosch Process can now be generally explained, and is the same for creating black silicon, barring the use of a mask

The process is fairly straightforward, with only 4 gases used and each serving a specific purpose. The gasses are ionized by a RF plasma generator to create plasma (this is where the name plasma etching comes from), and it is held by a coil in the top of the machine, to direct the plasma downwards onto the sample another coil called the platen is turned on and a bias is created between the two plates, which attracts the ions downward. The platen is only powered on for the 3rd step, which increases the ion-assisted etching on the wafer downstream.

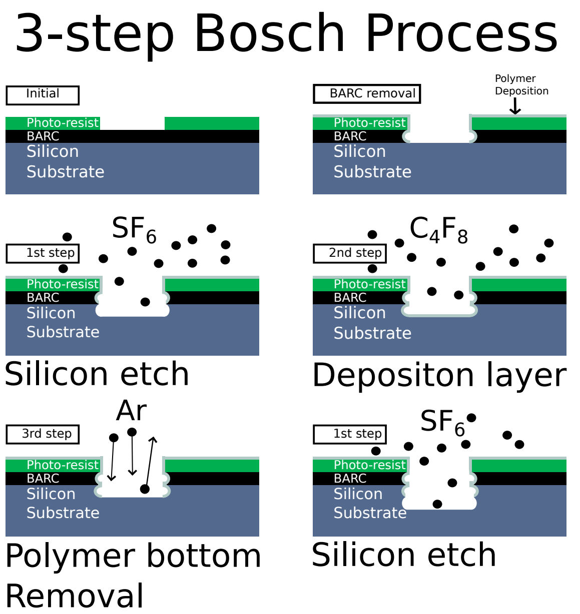


Figure 1: An illustration of the 3-step Bosch process, with BARC-removal.

First SF_6 is added to etch the wafer, next C_4F_8 is added to create a thin deposition layer of teflon^{TM} like polymer $(-CH_2-)_n$. This is needed since SF_6 etches isotropically, and if no deposition layer is made, it will just continue to etch outward. Argon is then added and a bias is applied, to direct the plasma down into the trenches to remove the layers of polymer in the bottom. The etch process is then repeated. Oxygen is also used [7], without a bias to remove some of the deposition from the sides to avoid a buildup of polymers that could close the trench[8]. Since the etching doesn't have the platen power on all the time, the process is slower but allows for smaller scallop sizes[9].

To remove the BARC layer, the same process was used, but with different parameters. The purpose of the BARC layer is to absorb the dUV light used for lithography. This prevents the dUV light from reflecting off the interface between resist and silicon, thus removing additional photoresist.

When creating black silicon, the time spent depositing needs to be balanced by the time spent etching and vice versa. If the deposition step is too long, the etching and bottom removal will fail and you will (in the extreme case) get a polymer coated wafer or very short pillars, this is seen when silicon is in the deposition regime. If on the other hand the deposition time is too short, the result will be large pillars with too much spacing to effectively absorb light. This is called the etching regime.

3.2 Black Silicon Parameter Space

To showcase the difference between silicon in etching, black or deposition regime. The samples are prepared in the DRIE-Pegasus with the recipe seen in appendix A. We cleave a silicon wafer

[5] Backside Anti Reflective Coating, used for silicone with masks.
[6] Silicon is etched more than the micromask
[7] Although not for the first run since 5 sccm (Standard Cubic Centimeter pr. Minute) O_2 corresponds to zero preasure change in the chamber, and thus no added oxygen.
[8] See figure 13(b) etch profile 1 for an example of a trench closing at low oxygen levels and high deposition.
[9] The scallops can be seen on figure 1 as the undulating features of the etch profile, caused by repeating the process.

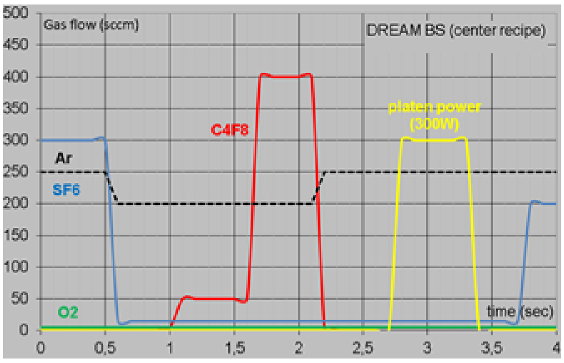


Figure 2: Schematic for the recipe for producing black silicon used in the experiments. For a more detailed look at the parameters used see figure 15, for the actual oscilloscope image of the process see appendix E

into small samples, sized 1x1 cm, and mount one of them on a 4 inch aluminiumoxide (Al_2O_3) coated wafer. Since Aluminium oxide has a bond energy of around 16 eV, while the silicon crystal has a bond energy of 3 eV, the etching process will mostly etch the silicon.

We start with creating 5 samples[10] with the three types (black silicon, etching and deposition) figure 3. By varying deposition time. but keeping a constant oxygen flow of 5 sccm. Notice that the initial deposition time is 2.0 s and that we vary in increments of 0.2 s. These 10 % changes however gives us a clearly different structures, as will be analysed further.

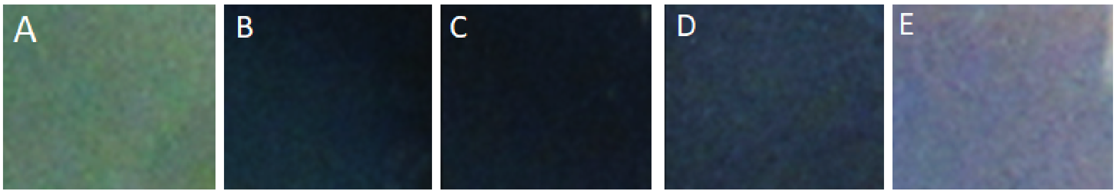


Figure 3: Images from experiment set 1 experiment 1-5. All with 5 sccm O_2, but varying deposition times **A** is 2.0 s and is in etching regime, **B** is 2.2 s and **C** is 2.4 s and both are black silicon and **D** is 2.6 s and **E** is 2.8 and both are deposition regime

3.2.1 The Structure of Etching, Black Silicon and Deposition Regime

To get an idea of the difference between the processing regimes we start by taking SEM images of the 5 samples (from figure 3).

As can be seen on figure 4 there is a clear difference of the spacing of the nanograss. There is a larger spacing in the etching regime, whereas there is a smaller spacing in the black silicon, this makes the surface of the processed wafer appear black (As described in section 2). In the deposition regime, the spacing is really small and in the last image figure 4 E where a layer of polymer is deposited on the wafer, no nanograss is formed. (See figure 5)

[10]We did initially also vary the Oxygen flow to 5 different levels (5, 15, 25, 50, 75 sccm) thus creating 25 samples but the rest of these will first be used in section 4. It is again noted that because of the way DRIE-Pegasus is set up, 5 sccm oxygen flow corresponds to 0 sccm oxygen, since there is no pressure difference in the chamber between the two setting

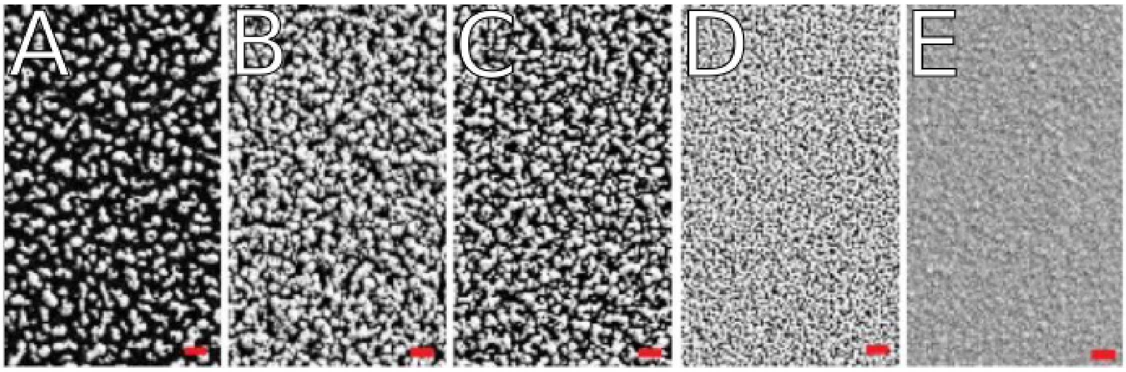


Figure 4: Topdown SEM images from experiment set 1, all with magnification of 10.000x, the bar is 1 µm. The density of nanograss is a function of the deposition time, a higher deposition time thus results in a larger density of nanograss, until no nanograss is formed (**D**). **A** is in etching regime, **B** and **C** is Black Silicon and **D** and **E** is deposition regime

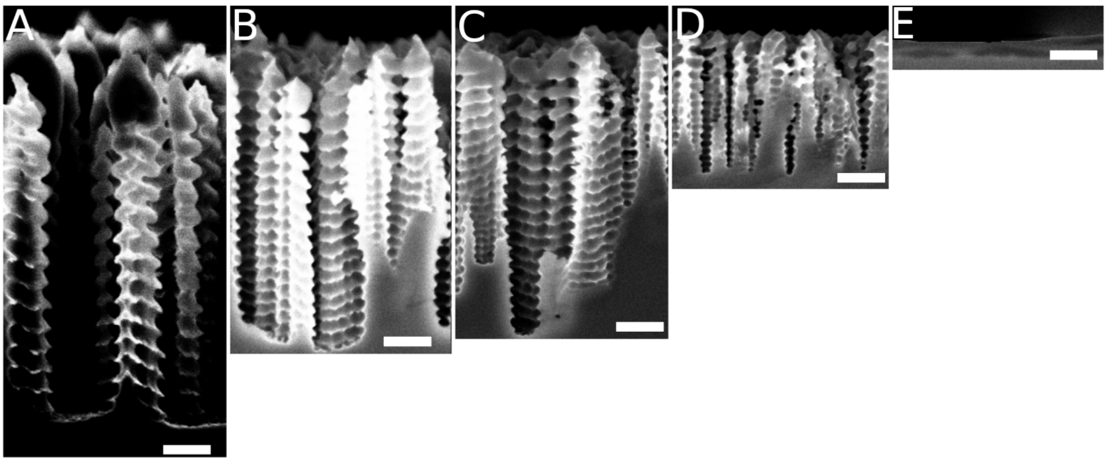


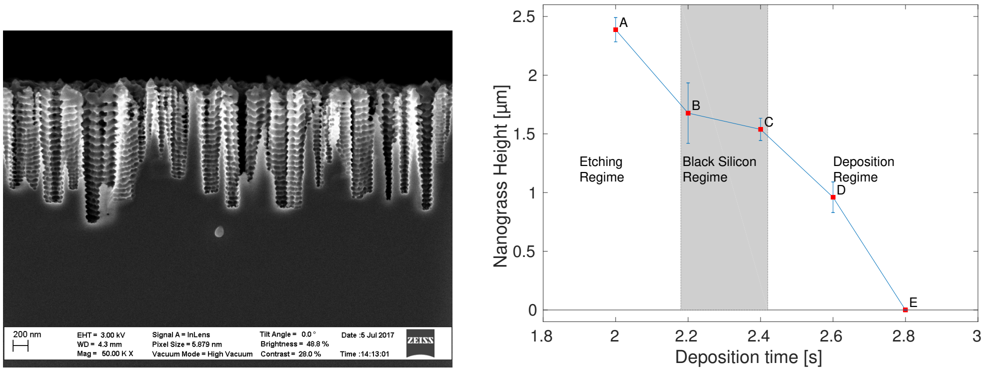
Figure 5: Cross-section SEM images from experiment set 1, O_2 gas flow in boost phase at 5 sccm, all with magnification of 50.000x, the scalebar on the images are all 0.3 µm. Figure **A** is in the etching regime, figures **B** and **C** are in the black silicon regime and figures **D** and **E** are in the deposition regime. It can be seen that as the deposition time is increased, the height of the nanograss becomes smaller and smaller, until no nanograss is formed (image **E**).

3.2.2 Measuring Atomic Composition

By analysing the five samples with an EDX[11] We can get an idea of the atomic composition of the different samples. The three main elements in all five samples are carbon, fluorine and silicon. A spectrum of the five samples can be seen in Figure 7. The amount of carbon and fluorine in the samples that are in the etching regime are generally higher but a better view will be given later in Section 3.2.2

In the spectrum (figure 7) the peak corresponding to fluorine appears to be much larger, than the peak for carbon, this indicates that the amount of fluorine in the sample is larger than the carbon. However in table 2 the amount of carbon is significantly higher. This is due to fact that the EDX requires a minimum of certain elements to be able to detect the element (This is called

[11] Energy-dispersive X-ray spectroscopy



(a) (b)

Figure 6: **Figure 6(a)**: A Cross section image of black silicon with a deposition time of 2.4 seconds and a O_2 gas flow in boost phase at 5 sccm. A magnification of 50.000 was used. The characteristic undulating form of the nanograss is caused by the Bosch process figure 2 **Figure 6(b)**: Plot of the etching depth as a function of the deposition time (with O_2 gas flow in boost phase at 5 sccm). 8 measurements of nanograss height were taken based on cross section images, the standard deviation was calculated. At a deposition time of 2.8 seconds no nanograss was produced, only a polymer coating, and thus no height was obtained. Letters correspond to the images in figure 5 and figure 4.

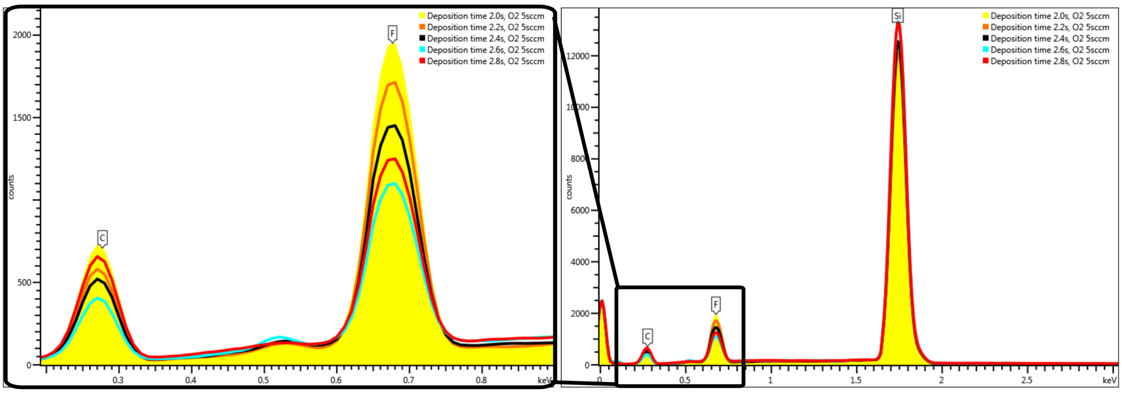
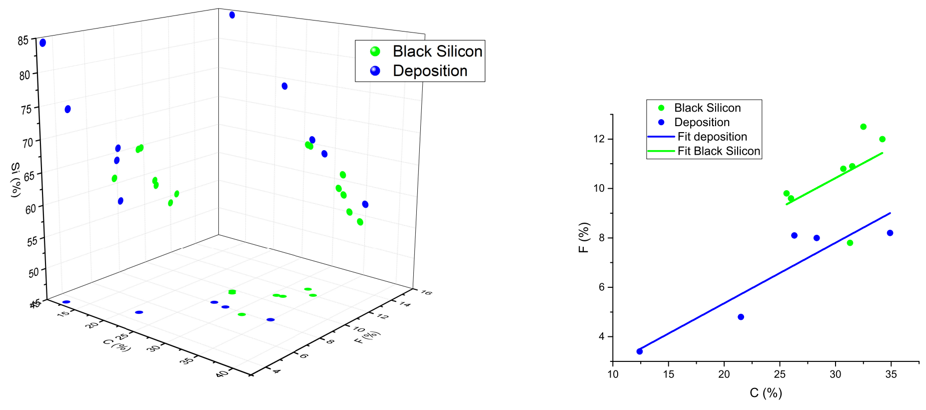


Figure 7: Spectrum of atomic composition of Silicon (Si), Fluorine (F) and Carbon (C) in the first experiment set. the five experiments all used an oxygen gas flow of 5 sccm (Squared Cubic cm) while the deposition time (from of C_4F_8 varied from 2.0 to 2.7 seconds in 0.2 s increments)

the sensitivity of an element) and this minimum varies from element to element. Carbon has a lower sensitivity and therefore the spectrum shows less carbon, but when calculating the atomic content the machine corrects for the sensitivity. [Shimadzu, 2017]

We can get a better idea of the atomic composition by performing EDX on even more samples. The data is compiled in table 2 and appendix D, it is also displayed in the 3D graph in figure 8.

Images of all the 25 samples can be seen in figure 13(b). The first 5 samples are the same as those seen in figure 3, and the rest are produced by increasing the oxygen flow. Since a lot of different parameters affect the creation of black silicon, a factorial experimental design was chosen, varying deposition time (as in figure 3) and varying the oxygen flow (see figure 13(b)). 5 different levels of oxygen flow were chosen: 5 sccm, 15 sccm, 25 sccm, 50 sccm and 75 sccm. The deposition time was increased from 2.0 s to 2.8 s in 0.2 s increments. This gives an idea of the relatively small



(a) (b)

Figure 8: **Figure 8(a)**: 3D plot of data from table 2, the colour of the dots indicates the regime of the samples. Black corresponds to samples with traces of black silicon, red dots are in the etching regime and blue dots are samples in the deposition regime. **Figure 8(b)**: Correlation between C and F atomic composition as it can be seen the trend is that Black silicon has a higher concentration of Fluorine than deposition regime with comparable Carbon levels.

parameter window that produces black silicon. As can be seen by figure 13(a) most rows only have 2 outcomes creating black silicon, making a change in 0.2 s of deposition time crucial.

3.2.3 Using OES to Monitor the Etching Process used to Make Black Silicon

By looking at the optical emission spectrum, using the optical end point detection of the Pegasus, it is possible to tell what regime a process produces.

The reason is that in the deposition regime, the polymer layer on top of the silicon wafer, will create interference between 2 light beams (one reflected off the surface of the polymer film and one reflected off the silicon in the interface between the polymer and wafer). This is called thin film interference and the following holds true [Lei, Tim C., 2005, 95]:

$$m\lambda = 2dn\cos(\theta) \tag{1}$$

Where n is the refractive index of the thin film, λ is the wavelength of the incoming light, d is the thickness of the film and θ is the angle of incidence, in our case this angle is 90° since the OES[12] is positioned straight above the sample. m must be an integer for constructive interference, analogous to Bragg's law.

The intensity between two light beams is given by the equation [Lei, Tim C., 2005, 88-89]:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos(\delta) \tag{2}$$

(Where I_1 and I_2 is the intensity of the two beams of incoming light and δ is the phase difference between the two)

In a thin film this phase lag is given by (with the use of equation (1)) [Lei, Tim C., 2005, 96]:

$$\delta = \frac{2\pi}{\lambda}(2nd\cos(\theta)) \tag{3}$$

Since the angle where the intensity is measured, is always 90° and the light source is the characteristic emissions of fluorine (in our case) with a wavelength of 685 nm, only the thickness of the

[12] Optical Emission Spectroscopy

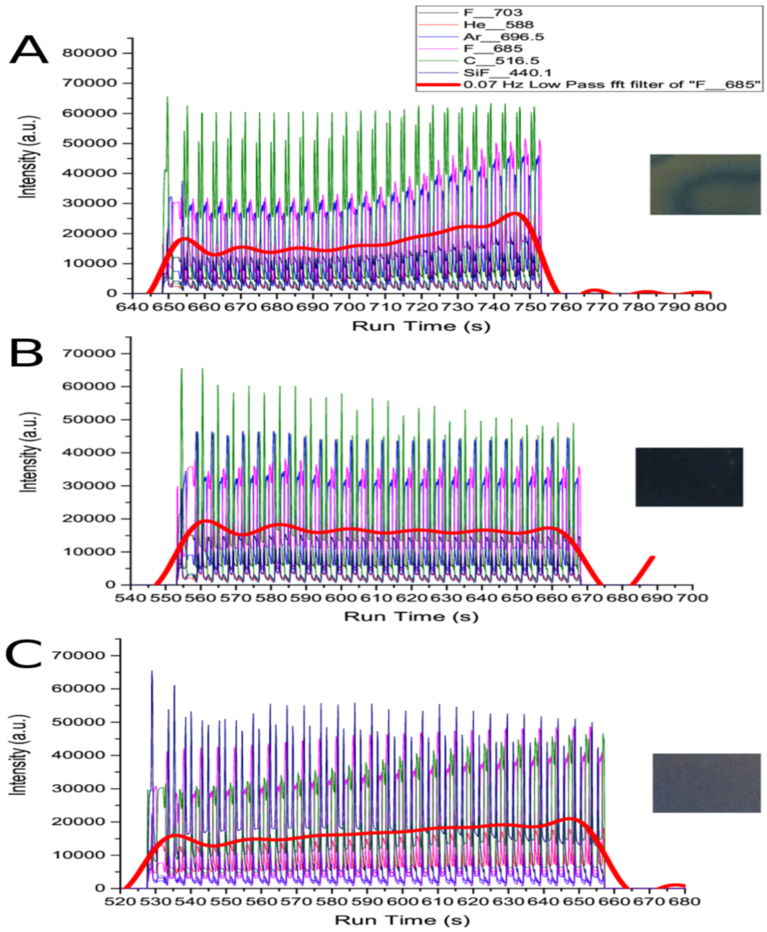


Figure 9: OES of etched silicon with FFT of the F 685 nm signal, to make the trend more visible. The important measurement is the F 685 nm (purple color). The deposition times are for **A** 2.0 s, for **B** 2.4 s and **C** 2.8 s. Gas flow (O_2): 15 sccm. Notice how as the deposition times changes, so does the total process time. To the right is a small picture of the sample for reference.

deposited layer varies as the process goes on. By combining equation (2) and equation (3). We get:

$$I = I_1 + I_2 + 2\sqrt{I_1 I_2}\cos(ad) \tag{4}$$

(Where a is a constant: $\frac{4\pi}{\lambda}n$,since $\cos(90°) = 1$)

We should therefore expect the intensity of the measured signal to follow a cosine wave, when the thickness of the film (d) increases. Which is also seen in the experiment (See figure 9 **C**).

By approximating that we have around 1/4 of the full cosine wave [13] we can estimate $m = \frac{1}{4}$ in equation (1) and measuring the refractive index on ellipsometer $n = 1.3$, this gives us:

$$\frac{1}{4}685\text{nm} = 2 \cdot 1.3d\cos(90°) \Rightarrow d = \frac{685\text{nm}}{8 \cdot 1.3} \approx 66\text{nm} \tag{5}$$

A measurement with the ellipsometer gives us 45 nm. Which is the same order of magnitude.

On the other hand the etching regime also has a characteristic shape. The fluorine levels are stable at the start of the process, but then steadily increase throughout, see the low pass FFT[14]

[13] This is a rough estimate and only serves to check if the thickness of the deposition film is in the same ballpark.
[14] Fast Fourier Transform, used as a low pass filter.

in figure 9 **A**. This is due to the roughness of the etched surface and not representative of the actual fluorine concentration. Using OES on a rough surface increases all signals and it is therefore relatively easy to distinguish etching regime from black silicon and deposition regime.

The OES signal from black silicon on the other hand is mostly constant when looking on the FFT, however there is a small increase in fluorine levels about a 1/4 into the process (see figure 9 **B**).

By looking at these characteristic shapes of the OES signals, it is possible to infer the outcome of the process, during the etching process.

3.2.4 Properties of Black Silicon

As referenced in the introduction (Section 2) two of the properties associated with black silicon is its low reflectivity and hydrophobic surface. We measured the reflectivity using an ellipsometer (Woolam M-2000) with wavelengths from around 200 nm to around 1700 nm. Reflectivity can be seen in Figure 10 the sample referred to as "Dark deposition" is a sample that we found too visually ambiguous to determine as either deposition or black silicon, but based on this reflection spectrum it looks to be black silicon. From the graph it can easily be seen that the deposition regime and untreated sample have a significantly higher reflectively compared to dark deposition and black silicon

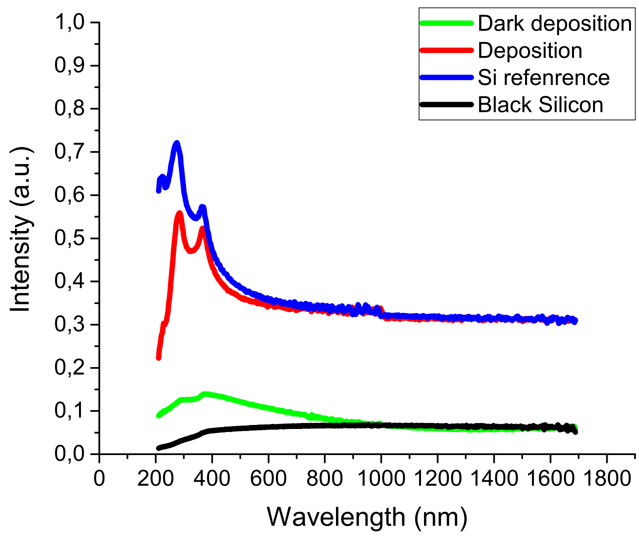


Figure 10: The reflection of wafers (including a reference silicon wafer), measured by an Ellipsometer (Woolam M-2000) with wavelengths from around 200 nm to around 1700 nm. It was not possible to measure reflectance of an Etched wafer due to roughness of surface. As can be seen in the figure the reflectance of the black silicon is significantly lower at all wave lengths (hence the black colour) while the wafer in deposition regime has reflectance comparable to the reference wafer

We also measured the contact angle of 1 µL water drops with a drop shape analyser[15]. By comparing water drops with a volume of 1, 2 and 5 µL, it was found that a drop size of 1 µL was the least affected by gravity, and the samples had a sufficient surface tension to avoid evaporation when using 1 µL. As can be seen on figure 12 all the processed surfaces have significantly higher contact angles, in the range of 120-140°, while the reference sample had around 40°. It can also be seen that even though the black silicon, etching and deposition regimes have comparable contact angles, the black silicon sample has a higher contact angle.

[15]Krüss DSA 100S Drop Shape Analyzer

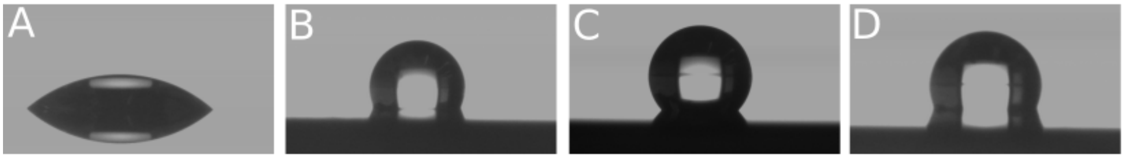


Figure 11: Images of the drops captured by the drop shape analyser. **A** is reference silicon, **B** is etching regime, **C** is black silicon and **D** is deposition regime as can be seen the 3 processed silicon wafers all have similar contact angles above 90° making them hydrophobic) while the reference sample is hydrophilic.

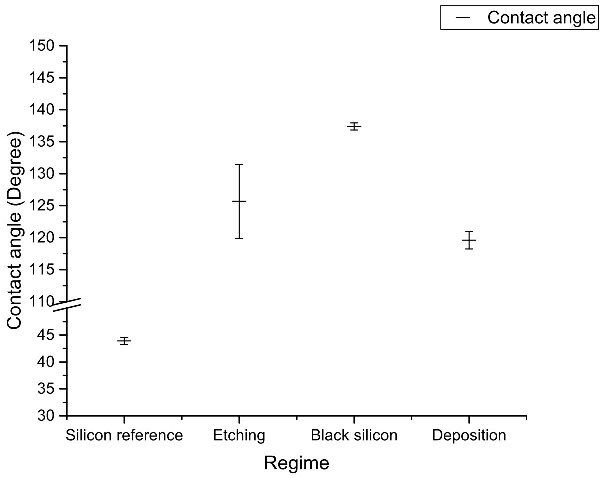


Figure 12: Contact angles measured by drop shape analyser with error bars, estimated based on several fits to the same image. Notice the break/discontinuity in the y-axis. The contact angle of water drops on silicon in etching regime is significantly higher compared to the other types, but black silicon still has a higher contact angle and therefore a more hydrophobic surface.

4 Black Silicon and Etching Profiles

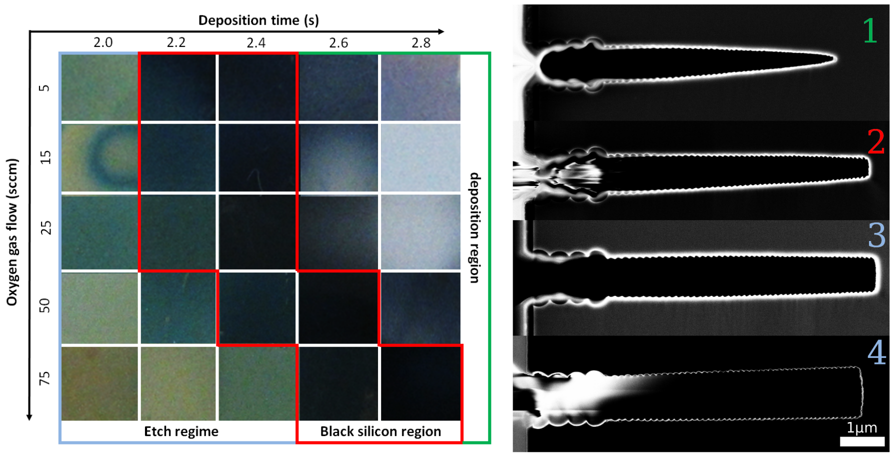
We repeat the process of producing black silicon with an oxygen flow of 5 sccm, but this time on a 1x1 cm wafer with an applied mask (not just the inherent micromask that are used in black silicon manufacturing). We also vary the deposition time more than previous experiments to get different etching profiles. The deposition times and measurements can be seen in table 1.

The DRIE-Pegasus machine had drifted since acquiring the other data set (from figure 3) which means that a deposition time of 2.4 s resulted in etching, and therefore we used 2.6 s as a center recipe to produce black silicon.

The results of the experiment can be seen in figure 13(b)

From the SEM images several important measurement can be made (Images with OM[16] can be seen in appendix in figure 17). An important measurement is selectivity, which is defined as the ratio of etched substrate over etched photoresist (the initial layer of photoresist is 300 nm ± 15 nm) a higher selectivity will allow deeper etching (and therefore a higher aspect ratio) since more substrate can be etched before etching the photoresist away. Another important measurement is the angle between the sidewalls, which gives an idea of how close the process is to vertical walls.

[16]Optical Microscope



(a) Pictures of the 1x1 cm silicon wafers at different deposition time and with different oxygen flow (see appendix A for the exact changes in the recipe). The brightness and contrast have been increased to allow for a easier comparison, but they are still fairly easy to distinguish in the lab. Three different regimes were identified; an etching, black silicon and deposition regime. Picture courtesy of Bingdong Chang

(b) SEM images of different etching profiles obtained with recipes corresponding to different regimes. Etching profile nr. **1** is in the deposition regime, **2** is in the black silicon regime and etching profiles **3** and **4** are in the etch regime.

Figure 13: A comparison of different etch profiles with the different regimes. This shows that different etching profiles corresponds to different regimes.

Both of these measurements can be seen in table 1[17].

It should be noted that the scallop sizes are measured as an average of the 5 top most scallops (after the BARC layer etch). The scallops further down the trench are a smaller size. This is due to fewer ions reaching the bottom of the trench, and thus less etching takes place the further down the trenches etching occur. This is commonly referred to as RIE[18] lag, and also causes narrow trenches to etch slower than wide trenches. [Franssila, 2010, 266-267]

No.	1	2	3	4
Deposition time	3.0 s	2.6 s	2.0 s	1.5 s
Regime	Deposition	Black silicon	Etch	Etch
Selectivity	∞	288 ± 14.4	99 ± 4.95	34 ± 1.7
Sidewall angle	3.9 °	2.25°	-0.9 °	-0.45 °
Scallop size (avg)	140 nm	161 nm	156 nm	140 nm

Table 1: Table of measurements for the different etching profiles.

The regime in which the unmasked wafer is in correlates to the etching profiles of the trenches as can be seen on figure 13. In the deposition regime we have a positive taper as more material is deposited than etched (which closes the trench). In the etching regime we get a more negatively tapered profile as more material is etched away. The sample in etching regime (1.5 s deposition time) has the least tapered profile with only a 0.45° angle. In production of structures vertical walls is wanted. [Jansen et al., 1995, 118].

[17] A negative angle indicates negatively tempered etch and a positive angle of positively tampered etch
[18] Reactive Ion Etching

5 Using Black Silicon Method to Monitor Drift

It is important to notice that the two parameters we changed in section 3.2.2 are only two of many parameters that have an effect on the creation of black silicon. In the addition to deposition time and oxygen flow, etching time (which we keep constant at 2.0 s), the temperature of the platen chiller (we maintained at 254 K), the power of the coil and platen (we maintained 3000 W and 300 W respectively), the overall pressure in the chamber, the gas flow of other reaction gasses (Ar, SF_6 and C_4F_8) as well as the time of gas flow of all four gasses. For the full recipe check appendix A and appendix C for a basic schematic of DRIE-Pegasus.

This means that we have, at least, 14 parameters that all effect the production of black silicon. Trying to map the full parameter space would be impossible, and the machine is known to drift, which can ruin the etching or comparative measurements, especially for high contrast etching.

The same problem applies to all etching, but is exacerbated when creating nano- or microstructures using masks. This is because it is (almost always) difficult to know how the process turned out, before checking the sample with a SEM. An optical microscope could be used, which is quicker than a SEM, but identifying the created etching profiles is trickier[19].

To check whether the machine behaves as expected, before performing high priority/time intensive experiments, one could use the black silicon method. Due to the small parameter space of black silicon, the relative ease with which it can be instantly distinguished[20] from etching or deposition regime and the short etching time for the samples. Testing the machine with a small sample of black silicon could save time and avoid ruined experiments.

We did see drift in the machine during the experiment in section 4, which illustrates that drift is a very real concern.

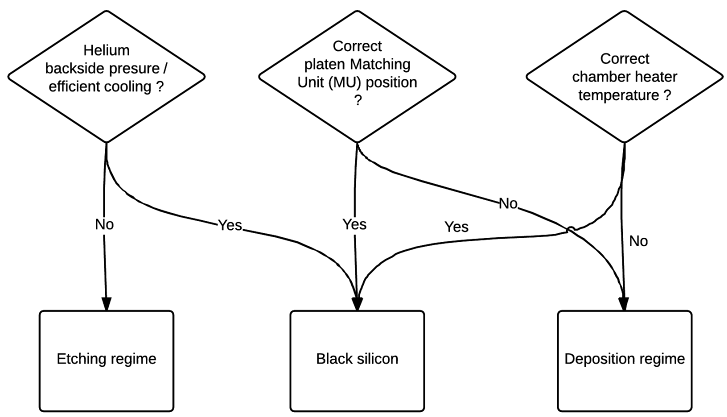


Figure 14: The expected influences of drift of the DRIE Pegasus machine. only if all three values have not drifted do we expect to see black silicon.

By changing the 3 parameters: Helium Backside cooling pressure, Platen Matching unit position[21] and chamber heater temperature. We can monitor which conditions the machine drifts. All tests were perfomed on a cut out piece of silicon, sized roughly 1 cm by 1 cm.

We perform a center recipe (appendix A) before and after changing each variable we can check if the machine has drifted. We expect the center recipe to give us black silicon.

[19]see image figure 17 in appendix

[20]Either visually or even before the process is finished using the OES signal section 3.2.3

[21]The platen matching unit is the position of the mechanical capacitor, which is used to match the coil and platens impedence, which ideally creates a constant bias between the platen power and the coil power. When the position of the two plates of the mechanical capicator are moved slightly out of alignment, it creates a reflective power and the bias won't be constant.

We start by lowering the Helium backside cooling pressure from the usual 20 Torr to 15 Torr and lastly 10 Torr[22]. We found that the backside pressure does not have a huge influence on the regime as all 3 samples turned out to be Black silicon.

Next we vary the platen matching unit position from 53 % (center recipe) which gave a reflective power of approximately 2 W, then 52.5 % (reflective power $\approx$ 18W) both of these gave black silicon. Lastly we tried 51 % (Reflective power $\approx$ 50W) which gave deposition.

Then we varied chamber heater temperature from 393 K (center recipe) to 398 K, both gave black silicon and afterwards 383 K and 403 K which were in the deposition regime (however with a temperature of 383 K a full size wafer became black silicon).

We did not get a sample in etching regime when lowering the Helium backside pressure so this would confirm that for normal etching processes a pressure of 10 Torr would be sufficient[23].

This should give an idea as to how the machine has drifted if the process has gone into deposition regime, the problem could be due to the heating not being sufficient or that the Matching Unit position is no longer correct. If the process on the other hand has gone into etching regime it could be due to improper cooling.

This could provide an easier fix to drifting since it is not normal to produce a matrix such as the one in figure 13(a)

6 Conclusion

It has been shown that by using the black silicon method, a user of the DRIE-Pegasus can monitor drift of the silicon etch. This has been shown to be possible because of the narrow parameter space of black silicon, which allows the user to run a quick black silicon recipe and monitor if the outcome is as expected.

It has been shown that the creation of black silicon, over-shooting (etch-regime) and under-shooting (deposition regime) corresponds to different etch profiles. This means that the user can use the result of the black silicon method to indicate what the etch-profile of their final etched wafer will be.

On a black silicon related note, a part of the infinite parameter space for creating black silicon has been investigated. Hydrophobic and reflective properties of black silicon have also been verified. The chemical composition showed that black silicon had a higher content of fluorine than the deposition regime.

The results gives the users of DRIE-Pegasus an easy way to validate their results by controlling for drift and gives them the opportunity to perhaps tweak the recipe or wait until the DRIE-Pegasus has returned to initial conditions, before wasting time doing experiments that will go wrong due to drift of the machine.

[22]20 Torr is maximum backside pressure as to not create a pressure under the wafer higher than the clamping holding the wafer in place.

[23]However for the aspect etching it could still be beneficial to have a higher cooling

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A Data log

Center recipe:							
Recipe: DREAM BS							
Substrate: cleaved small chips from silicon wafer (taken from new wafer box), size around 1cm*1cm. attached on carrier wafer by fomblin oil, carrier wafer is 100nm alumina coated silicon wafer (backside upwards to avoid high HeLUR problem)							
Parameter settings							
Step1. Homing matching unit position for both coil and platen							
Step2. Main etch							
		Deposition 2.0s			Etch 2.0s		
		Delay	Boost	Main	Delay	Boost	main
C4F8		1.0s / 5sccm	0.5s / 50sccm	0.5s / 400sccm	2.0s / 5sccm		
SF6		0.5s / 300sccm	0s / 0sccm	1.5s / 15sccm	1.6s / 15sccm	0.4s / 200sccm	
Ar		0.5s / 250sccm	1.5s / 200sccm		2.0s / 200sccm		
O2		0.5s / 5sccm	1.0s / 200sccm	1.3s / 5sccm	2.0s / 5sccm		
Throttle		4.3s / 100%					
Platen		2.8s / 1W			0.6s / 1W	0.5s / 300W	(1.4 -> 3.7) /1
ICP		4.3s / 3000W					
Coil (Automatic)	**L**	40%			40%		
	T	50%			50%		
Platen (Automatic)	**L**	38% (homing position 1)			38% (homing position 1)		
	T	53% (homing position 1)			53% (homing position 1)		
Other		Temperature -19C; S=D, E=E, He leak up around 13sccm (10Torr) / 35sccm (20Torr), which is normal. Total cycles 25, total etch time 1min40s					

-

Figure 15: Data log by Bingdong showing the parameters used in experiments creating black silicon, The yellow highlighted boxes show the parameters that were varied in experiment set 1

Center recipe:							
Recipe: DREAM BS							
Substrate: cleaved small chips from silicon wafer (taken from new wafer box), size around 1cm*1cm. attached on carrier wafer by fomblin oil, carrier wafer is 100nm alumina coated silicon wafer (backside upwards to avoid high HeLUR problem)							
Parameter settings							
Step1. Homing matching unit position for both coil and platen							
Step2. BARC etch (12 cycles)							
		Deposition 1.5s			Etch 3.5s		
		Delay	Boost	Main	Delay	Boost	main
C4F8		0.5s / 5sccm	0	1s / 300sccm	0		
SF6		0.5s / 300sccm	0	1.0s / 15sccm	1.6s / 15sccm	1.9s / 200sccm	
Ar		0.5s / 250sccm	1.5s / 200sccm		2.0s / 200sccm		
Throttle		5.0s / 100%					
Platen		1.5s / 1W			0.6s / 1W	1.0s / 200W	1.9s /1
ICP		5.0s / 3000W					
Coil (Automatic)	L	40%			40%		
	T	50%			50%		
Platen (Automatic)	L	38% (homing position 1)			38% (homing position 1)		
	T	53% (homing position 1)			53% (homing position 1)		
Other		Temperature -19C; Total cycles 12, total etch time 1min					
Step2. Main etch (50 cycles)							
		Deposition 2.0s			Etch 2.0s		
		Delay	Boost	Main	Delay	Boost	main
C4F8		1.0s / 5sccm	0.5s / 50sccm	0.5s / 400sccm	2.0s / 5sccm		
SF6		0.5s / 300sccm	0s / 0sccm	1.5s / 15sccm	1.6s / 15sccm	0.4s / 200sccm	
Ar		0.5s / 250sccm	1.5s / 200sccm		2.0s / 200sccm		
O2		0.5s / 5sccm	1.0s / 5sccm	1.3s / 5sccm	2.0s / 5sccm		
Throttle		4.0s / 100%					
Platen		2.8s / 1W			0.6s / 1W	0.5s / 300W	0.9s /1W
ICP		4.0s / 3000W					
Coil (Automatic)	L	40%			40%		
	T	50%			50%		
Platen (Automatic)	L	38% (homing position 1)			38% (homing position 1)		
	T	53% (homing position 1)			53% (homing position 1)		
Other		Temperature -19C; Total cycles 50, total etch time 3min20s					

Figure 16: Data log by Bingdong Chang showing the parameters used in etching experiments. Similar to recipe in figure 15 but with an initial BARC process for removing BARC-layer under photoresist

B OM Pictures of Etching Profiles

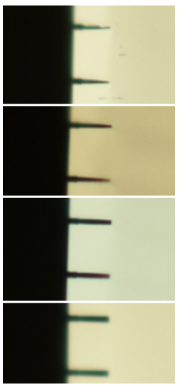

Figure 17: Comparison of etch profiles with OM, top to bottom is 3.0 s, 2.6 s, 2.0 s and 1,4 s deposition time with 5 SCCM Oxygen flow (Se recipe figure 15)

C Schematic of DRIE Pegasus

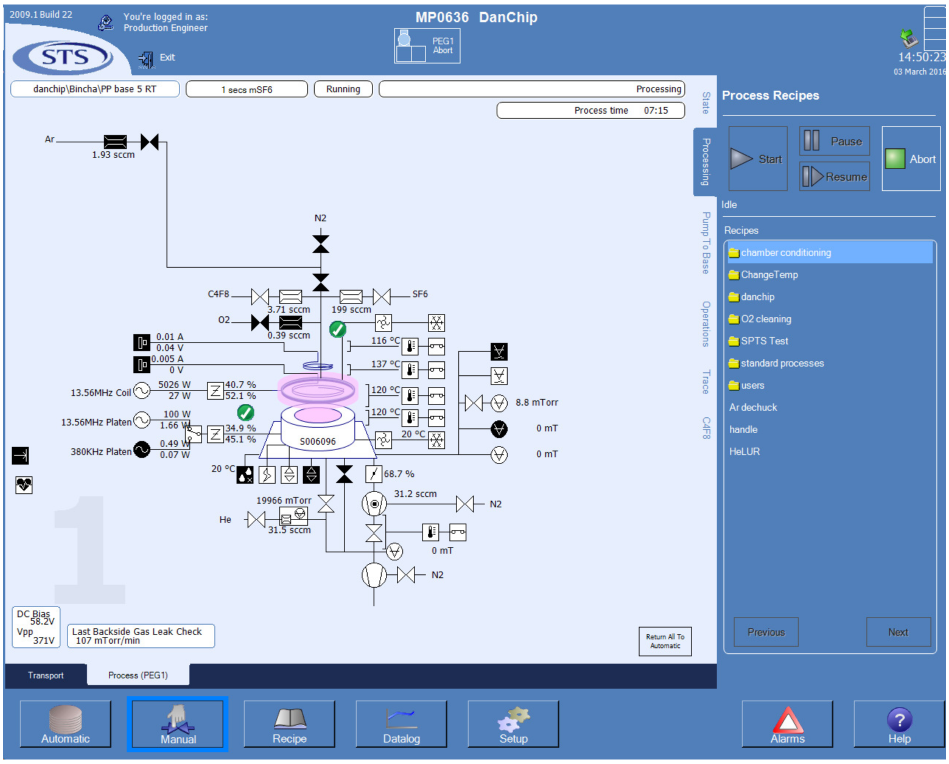

Figure 18: A schematic of the DRIE Pegasus, obtained from the STS DRIE Pegasus control software.

D EDX Table

No.	F	C	Si	Regime
1	13.5 %	35.8 %	50.7 %	Etch
2	12.5 %	32.5 %	55.0 %	Black Silicon
3	10.8 %	30.7 %	58.5 %	Black Silicon
4	8.1 %	26.3 %	65.6 %	Deposition
5	8.2 %	34.9 %	56.9 %	Deposition
6	3.4 %	12.4 %	84.2 %	Deposition
7	4.8 %	21.5 %	73.7 %	Deposition
8	8.0 %	28.3 %	63.7 %	Deposition
9	9.8 %	25.6 %	64.6 %	Black Silicon
10	10.9 %	31.5 %	57.6 %	Black Silicon
11	9.6 %	26.0 %	64.5 %	Black Silicon
12	12.0 %	34.2 %	53.8 %	Black Silicon
13	7.8 %	31.3 %	60.9 %	Black Silicon

Table 2: Table of atomic composition used to make figure 8(a)

E Oscilloscope

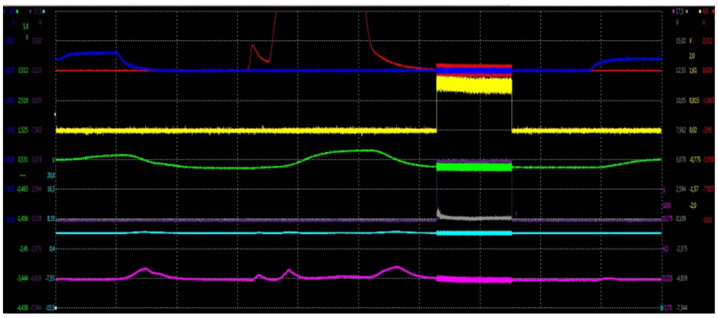

Figure 19: Oscilloscope image of a step in the production process