Surface Imaging Through Silylation

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Silylation is a surface imaging technique which allows silicon to absorb into photoresist in specified areas. Photoresist containing silicon creates a hard-mask which is resistant to oxygen plasma. This allows for the development process to occur strictly in dry etch systems. Surface imaging is a desirable technique because it removes the need to expose through the photoresist stack. Traditional lithography techniques require a high dose of ultra-violet (UV) light in order to penetrate to the bottom of a photoresist stack. It is critical, for quality imaging, that the photoresist not be over or under exposed. This creates a process window dependent on two main variables; the photoresist thickness and the dose needed to penetrate through the photoresist stack. Surface imaging allows for a larger process window because the dose is not depended on the thickness of the resist. In surface imaging, the UV light only exposes the top-most layer of the photoresist material. Surface imaging removes the resist thickness variable, this will allow for a wider process window. Variation in photoresist thickness is also important; traditional lithography requires a uniform photoresist thickness across the surface of the wafer in order to optimize depth of focus (DOF). Surface imaging tends to be less effected by photoresist variation due to short depth requirements of the exposure. This allows for a relaxed depth of focus (DOF) requirement, as well as a larger process window.[1]

Index Terms—**Silylation, Surface Imaging, Silicon Contrast**

I. Introduction

THIS PROJECT uses the Diffusion-Enhanced Silylating Resist (DESIRE) process[1] to incorporate silicon into OIR620-10 positive tone photoresist. During exposure, the ultra violet (UV) light causes carboxylic acid to form within the photoresist. A post-exposure bake (PEB) is performed in order to crosslink the unexposed photoresist. Crosslinking occurs when the sensitizer within the photoresist chemistry is raised to a temperature close to the glass transition temperature. The silylation step is preformed inside of a vacuum oven at the same temperature as the PEB. Hexamethyldisilazane (HMDS) is used as a silylation agent. This chemical was chosen because it has a high silicon content as well as the ability to form a gas at elevated temperatures. The silylation occurs when the silicon in the HMDS bonds with the carboxylic acid created in the exposed regions of the photoresist material. Silylation will not occur where crosslinking has taken place. The samples are placed in a dry etch tool (Drytek Quad, reactive ion etch system). An oxygen plasma is applied which selectively etches only the regions where silicon is not present. This project explores the application various power and oxygen settings within the etch chamber. Measurements to determine selectivity were conducted using an optical profilometer.

The metric used for determining the quality of the hard-mask created during silylation is silicon contrast. Silicon contrast is the ratio of silicon absorbed by the exposed photoresist as compared to the unexposed photoresist. An optimal silylation will have 100% silicon absorption in the exposed areas while still maintaining 0% silicon absorption in unexposed areas, see Fig 1.

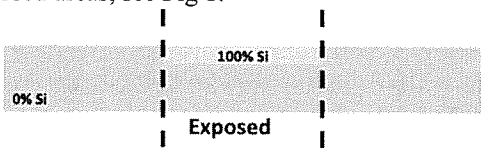

Fig. 1- Silicon Contrast

The ability to block an oxygen (O_2) plasma etch can be measured by monitoring the step height of the unexposed and exposed photoresist at various etch times. A designed experiment was conducted to reach the optimal silylation conditions. An optimal silylation condition of 30sec PEB with a 170C silylation temperature was chosen. A second designed experiment was conducted to optimized the dry etch conditions. Through this work it was clear that the silylation was able to block a portion of the dry etch but not the duration. This project was successful in showing that silylation can be achieved with the resources at RIT.

II. Theory of Surface Imaging and Silylation

The use of surface imaging through the technique of silylation has advantages in improving the depth of focus within a lithography process. This method removes the need to image to the bottom of the resist stack, in turn allowing for a greater depth of focus (DOF), see Fig 2.

Fig. 2- Methods of Lithography

The DOF is the range in which the image will be in focus. This means a larger depth of focus will produce a bigger process window. The use of surface imaging in the top most layer of resist will require a smaller DOF because the need to image though the entire photoresist stack is not necessary. This also allows topography to be less of an issue as well a reflectivity from the under laying films.

Coopmans and Roland[1] developed a silylation technique called the DESIRE process. Fig. 3 shows the process flow for the DESIRE process. The advantaged of the DESIRE process comes with the ability to change the silicon absorption rate of resist material after exposure to UV light. The best image is formed when the silicon absorption contrast between exposed and unexposed resist material is high. The unexposed areas will chemically crosslink during a PEB. The carboxylic acids hydroyl group will bond with the silicon in the HMDS. The areas absorbing silicon material will form a hard-mask at the top level of the resist, which can be used to with stand a dry etch process. This created the ability to selectively form lines and spaces without the development step.

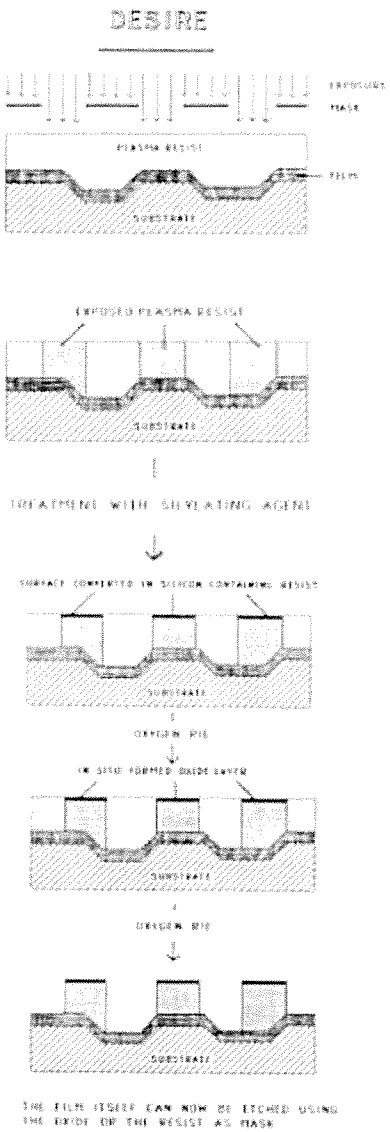

Fig. 3- DESIRE Process

Choosing a resist material, which will easily absorb silicon, is important. The optimal resist would be one, which will absorb silicon easily when exposed, but will also form strong chemical crosslinking when not exposed to UV light. The high level of selectivity will insure that residual formation of resist or surface attacks do not occur.

Research has shown that the pre-silyation bake time and temperature is important in the creation of a wide process window. The length of the bake is directly proportional to the temperature needed. Finding a balance between time and temperature is important. Also affecting these results are the use of sensitiser within the resist chemistry. The need for sensitisers is important because this ratio of sensitisers within the resist will affect the crosslinking of unexposed resist material. If not enough sensitisers are present in the resist material insufficient crosslinking in unexposed resist material will occur, thus allowing silyation to occur where it is unwanted. When sensitizers are in too high of a quantity then a larger exposure dose will be needed in order to rid the sensitizers from the chemistry. The PEB time and temperature will be affected by the

percentage of sensitizers present in the resist chemistry. It has been shown that a sensitiser concentration of 10% to 17% is an acceptable level.

Other chemical considerations in the resist material include the concentration of silicon in the resist material itself. The ability for the resist material to silyalate depends on the amount of free bonding sites in the resist between the OH and Si molecules. The number hydroxyl groups present in the carboxylic acid will allow the silyation material to bond. This means that the more silicon present in the resist the less opportunity for the silicon to incorporate with silyation. It has been shown that 7% to 10% silicon incorporation in the resist material produces the best image quality.

Finally the dry etch process required for the DESIRE process has been developed in a two step form[2]. The best profiles have been shown to occur in a two step dry etch process. This is necessary because of the inability to get perfect silicon contrast. The first step of the dry etch is to eliminate the slight widening in the image transfer, see Fig 4. The first step applies a fluorine and oxygen mixture. The fluorine allows for less selectivity than a pure oxygen plasma. The fluorine will remove both crosslinked and un-crosslinked material. The second dry etch step is an oxygen only chemistry. This will selectively etch only the areas that have not been crosslinked.

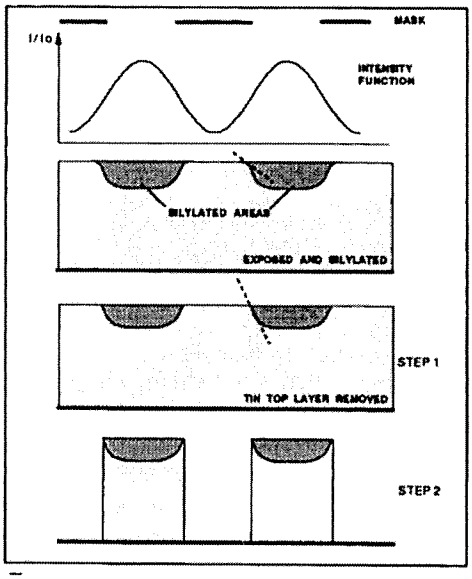

Fig. 4- Two Step Dry Etch Process

In order to choose the proper resist material a design experiment will be needed to determine the optimal pre-silyation time and temperature.

III. PROCEDURE

A. *Creation of Film Stack*

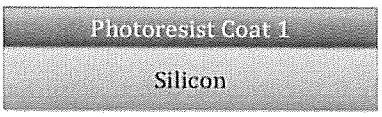

Fig. 5- Film Stack

The process begins with coating a silicon wafer with Oir620-10 photoresist. This application was completed using the SSI coat track. Each wafer was coated to a thickness of 1um.

B. *Expose Wafers to Ultra Violet Light*

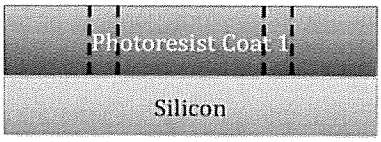

Fig. 6- Expose

Exposure to UV light is done on a contact aligner system with UV broadband light. The time of exposure varied but the dose remained the same in all cases. A dose of 175mJ/cm^2 was applied.

C. *Post Exposure Bake*

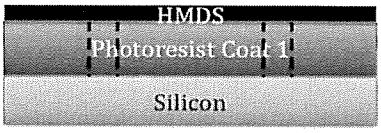

Fig. 7- PEB and Silylation

A PEB was applied in the silylation oven for a variety of times and temperatures. The PEB was completed in the silylation oven while the chamber was pumping down. All silylation times were held for 2 minutes. The silylation chemistry was HMDS.

D. *Dry Etch in O_2 Plasma*

Fig. 8- Dry Etch

Dry etch is completed in the Drytek Quad (reactive ion etch system). The etch is an O_2 plasma. The power and O_2 content were varied.

E. *Designed Experiments*

The project was broken into two sections; optimization of silylation conditions and optimization of dry etch conditions. The silylation designed experiment conditions can be seen in Fig 9. Two temperature and time settings were chosen for the PEB and silylation.

The second DOE was based around optimizing the dry etch conditions. The power, O_2 flow and silylation chemistry were varied. The conditions can be seen in Fig 10. In must be noted the the variation in power will change the level of physical etching while changing the O_2 flow will change the chemical etching properties in the dry etch system.

Fig.- 9-Silylation DOE

Fig. 10- Dry etch conditions

Condition Number	Silylation Temperature (C)		PEB Time (Sec)
Condition Number	Power (W)	O_2 Flow (cc)	Silylation Chemistry
2	150		30
1	80	200	1,2
4	80	166	1,2
3	80	133	1,2
4	120	200	1,2
5	120	166	1,2
6	120	133	1,2

IV. Results

The first major result was found through the metrology tool set traditionally used for thickness measurements. The results calculated were not consistent even with the same conditions applied to wafers. This lead to the conclusion that tools relying on the refractive index of a material would not produce reliable results do to variation in the refractive index which was a result of different amounts of silicon absorption. A new method of analysis of film thicknesses was needed; this lead to the use of the ellipsometer and optical profilometer for reliable results.

With the optical profilometer the best silylation conditions was concluded to be the 170C silylation temperature with a PEB time of 30 seconds. A summary table of the average step height for each condition can be seen in Fig. 11. This

These results may be explained by thinking about the glass transition temperature of the photoresist. The 170C temperature was closer to this value than the 150C value. The shorter PEB time means that the crosslinking of the resist was sufficient after 30sec and a 60sec PEB created too much crosslinking.

170C 30sec PEB	150C 30sec PEB	170C 60sec PEB	150C 60sec PEB
6.98nm	2.4nm	2.6nm	2.2nm

Fig. 11- Silylation DOE Results

The optical profilometer outputs an intensity plot as well as image plot. Fig 12 and Fig. 13 show the plots produced from the profilometer. The images show one of the measurements taken for the 170C silylation with 30sec PEB.

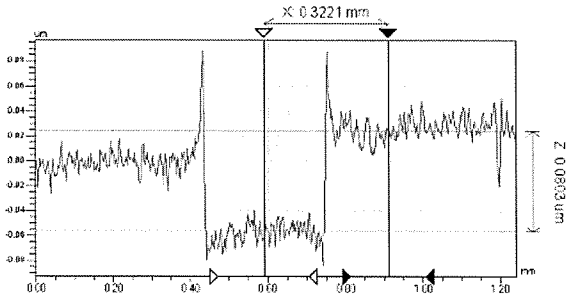

Fig. 12- Intensity plot taken from the optical profilometer

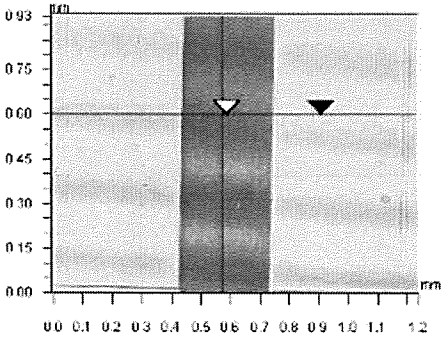

Fig. 13- Image taken from the optical profilometer

The next designed experiment gave insights into the dry etch process. From the silylation optimization it was concluded that the level of silylation was not dense enough to fully block the dry etch. The second experiment was analyzed at two etch times; 40sec and 80sec. The objective of the two etch times was to determine if the difference between the etch rates for the silylated and un-silylated photoresist materials changed during the second etch. This would indicate where the silylation layer was being etched away. Both etch times showed the same optimal dry conditions of 80W, 200sccm of O_2 and 2cc of silylation chemistry. The results of the 40sec etch can be seen in Fig 14 while the 80sec etch can be seen in Fig. 15.

80W, 200sccm	80W, 166sccm	80W, 133sccm	120W, 200sccm	120W, 166sccm	120W, 133sccm
49.5	46.9	22	16.5	33	37.3

Fig. 14- 40sec Etch Results

Fig. 15-80sec Etch Results

This data allowed for a statistic model to create models which predicts the step heights a various processing conditions. Leverage plots, showing the confidence intervals, for these models can be seen in Fig. 16 and Fig. 17.

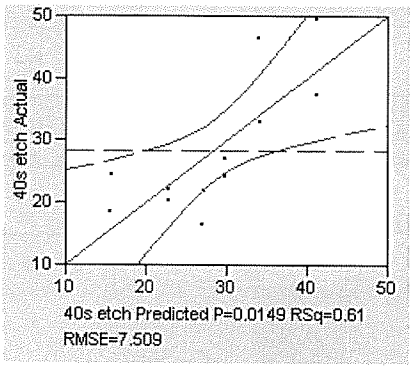

Fig. 16- 40sec Leverage Plot

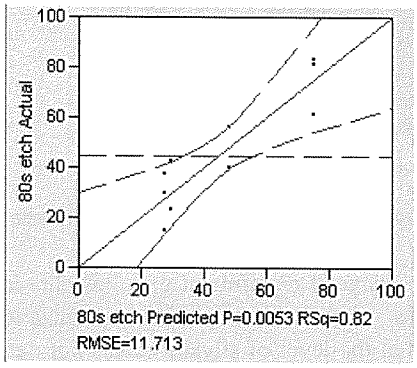

Fig. 17- 80sec Leverage Plot

Finally the models for the 40sec and 80sec etch can be seen in Fig. 18 and Fig 19. The 40sec etch time shows dependence on the amount of chemistry applied to the wafer as well as the cross between power and O_2 flow. The 80sec etch showed a dependence on silylation chemistry as well as power. This was a surprising result that the longer etch time showed a different statistical dependence. This gave more insight into the possibility that the silylation layer is being etched away.

80W, 200sccm	80W, 166sccm	80W, 133sccm	120W, 200sccm	120W, 166sccm	120W, 133sccm
83.1	81.1	61.3	14.8	29.8	37.7

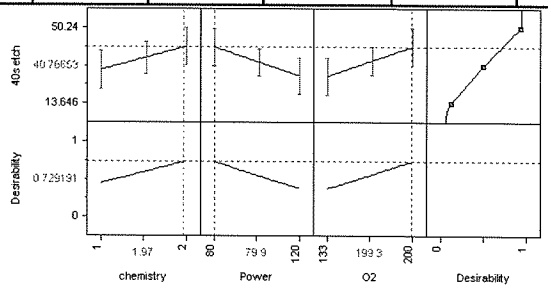

Fig. 18- 40sec Etch Model

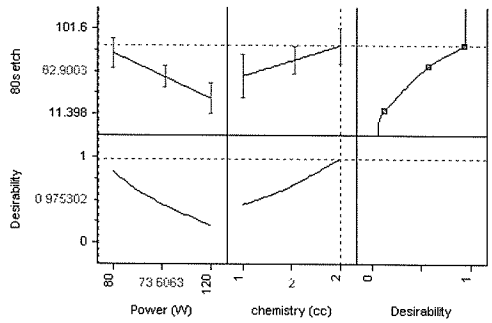

Fig. 19- 80sec Etch Model

V. Conclusions

It was concluded that silylation can be achieved with materials present at RIT. More research needs to be completed in order to have a silylation layer capable of blocking a full dry etch. This might be achieved by taking these results and further optimizing with iterative experiments.

The optimal silylation conditions were concluded to be 170C with 2cc of HMDS (1cc applied at the start of the silyation and 1cc half way through). The optimal dry etch conditions were concluded to be a lower power and a high O2 flow. The quantity applied in this case were 80W of power and 200sccm of O2. These values are at the low and high spectrum of what the drytek quad could produce.

Appendix

Operation of Silylation Oven at RIT:
Temperature and time settings were optimized using Oir620-10 positive tone photoresist.

1. Plug in heater.

2. Turn the heater on using the switch under the door, see Fig. 20. The red light above the control thermostat knob should light.

a. The oven is preset to reach 170C. This should take approximately 2 hour to reach temperature and stabilize.
b. The temperature control on the inside of the chamber will take longer to reach temperature.
c. The orange safety light may light at some points. This is normal.

3. Check pump pressure on gauge on the top of the over, see Fig. 20.

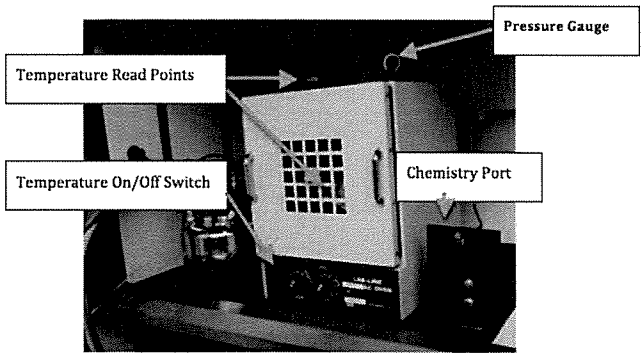

Fig. 20- Silyation Oven

4. If the pressure is at zero then the oven door can be opened. See step 5. If the chamber is pumped down the oven will need to be vented, see step 4a.

a. The door should never be opened unless you know that the previous user has properly vented the chamber. If this information is follow steps for venting the chamber safely.

b. Insure that the vacuum valve is closed, see Fig. 21. The valve is open when parallel to the vacuum line.

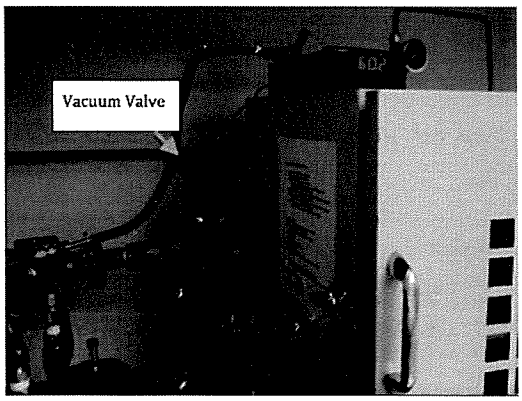

Fig. 21- Vacuum Value

c. Press the Nitrogen valve to release Nitrogen into the oven. This will allow the pressure in the chamber to drop. Hold the Nitrogen valve for about 20 to 25 seconds. The pressure should drop to somewhere between 10 to 15 inches.

d. Open vacuum valve on the side of the oven. This will pump the chamber back down to 29 inches.

e. Repeat steps 1b and 1c at least 3 times. This will insure no hazardous gases escape from the chamber.

f. Insure the vacuum valve is closed.

g. Fill the chamber with Nitrogen until the chamber pressure reaches zero. When the chamber pressure reaches zero turn off the Nitrogen.

5. Open the latch on the side of the oven by pushing the door in and up. The lever should move in the upward direction while the latch swings up.
6. Load your samples onto the plate inside the oven. Be careful!!! The oven will be hot!
7. Insure that the seal on the door is in place. Close and latch the door by pushing the door in and up.
8. Open the vacuum valve and allow the chamber to reach 29 inches. This should take about 1 minute. Once the chamber reaches 29 inches close the vacuum valve.
9. The time while the oven is stabilizing is used as a post exposure bake.

   a. While oven is stabilizing load the syringe with chemistry, typically 1cc of chemistry is used. A second application of 1cc can be applied mid way through the silylation.

   b. Inject the syringe into the inlet. Do not place your hands on the opposite site of the syringe needle.

   c. Allow the silyaltion to occur for 2 min.

Vent chamber as described previous.

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