

# SILYLATION OF POSITIVE PHOTORESIST

Donald R. Koszelak  
5th Year Microelectronic Engineering Student  
Rochester Institute of Technology

## ABSTRACT

The silylation of KTI Positive Resist 809 with hexamethyldisilazane (HMDS) was performed by liquid phase and vapor phase techniques. A vacuum chamber was designed and constructed for the vapor phase silylation. Process evaluation was performed by oxygen plasma etch rates of silylated exposed and unexposed resist which showed that the vapor phase technique did change etch rates while liquid phase did not.

## INTRODUCTION

The decreasing size of geometries in the fabrication of integrated circuits is stretching the limits of optical lithography and wet development of photoresist. In the past, multilayered resists extended optical lithography into the submicron range by decreasing such problems as standing waves and topography considerations. These multilayered systems are limited by the complexity of their processing. In order to obtain the desired resolution, each step of the multilayered process must stay under strict control. One way of obtaining a high resolution while minimizing the complexity of processing is to use a single or bilayer scheme in which the positive photoresist is silylated [1,2].

Silylation is the incorporation of silicon into the photoresist where the silicon reacts with the resin of novolac-based resists [3]. Conventional novolac based positive photoresist's with low glass transition temperatures,  $T_g$ , are ideal for silylation. KTI Positive Resist 809 is excellent example of such a resist, whose low  $T_g$  aids in the diffusion of silicon. Hexamethyldisilazane (HMDS) is a good silylation source for this process.

Selective incorporation of silicon into the exposed regions of the resist layer is the basis of image formation in the silylation process. The silicon containing material diffuses much easier in the exposed resist than the unexposed, since exposure changes the resist's chemical compound into a photoproduct acid [4]. This exposed area increase the incorporation of silicon, thus allowing selective diffusion to take place. Increasing temperature reduces the matrix of the exposed resist even more, again aiding the diffusion of silicon. However, the temperature must stay below  $T_g$  to prevent the resist from flowing.

The silicon that is in the top layer of the exposed resist reacts with oxygen to create a thin silicon dioxide layer during plasma ashing. It is this thin layer that acts as an etch mask when exposed to an oxygen plasma. This exposed resist etches slower than the unexposed, giving an image after dry development.

Positive or negative tone patterns can be obtained using a single or bilayered resist, respectively. For negative tone, a single layer resist is used. This occurs by exposing the resist, silylating, then dry etching. Figure 1 shows cross sections of this process. Positive tone can be obtained by using a bilayered system. This is done by first putting down a planarization layer that will not silylate, such as a hard baked positive photoresist with a high  $T_g$ . Next, a thin layer of the soft resist is exposed and wet developed to produce a positive image. This pattern is then flood exposed, silylated, and put in an oxygen plasma. This process is known as the SABRE process [2], which can be seen in Figure 2.

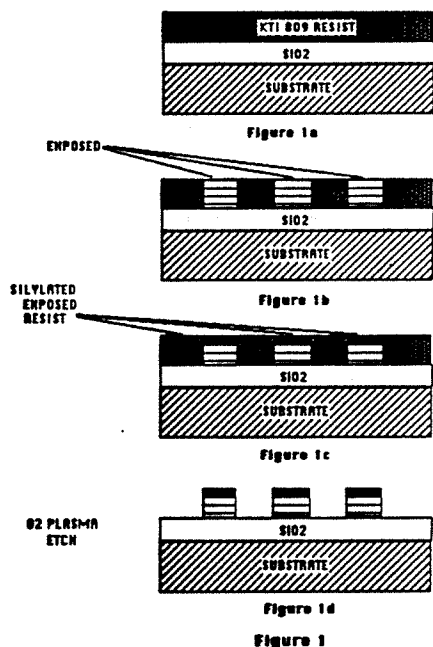


Figure 1  
Single layer negative silylated resist process

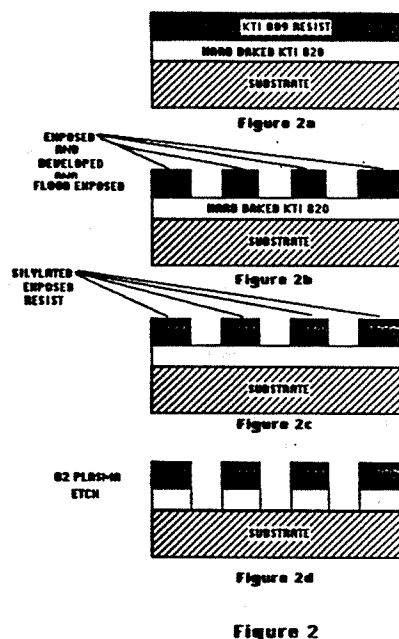


Figure 2  
Double layer negative silylated resist process

This project involved the design of a system to provide conditions so that vapor phase silylation could occur. The main concern of the vacuum chamber was to remove all oxygen out of the heated chamber before HMDS was introduced. This is a concern because HMDS may combust in an oxygen ambient at elevated temperatures.

## EXPERIMENT

Figure 3 shows the basic vacuum chamber that was built for the vapor phase silylation. The main components needed were a roughing pump, used to evacuate the oxygen from the chamber

before the HMDS was introduced, a hotplate, used to heat the surface of the wafer to the desired temperature, and an Omega "Type-J" thermocouple, used to measure the temperature.

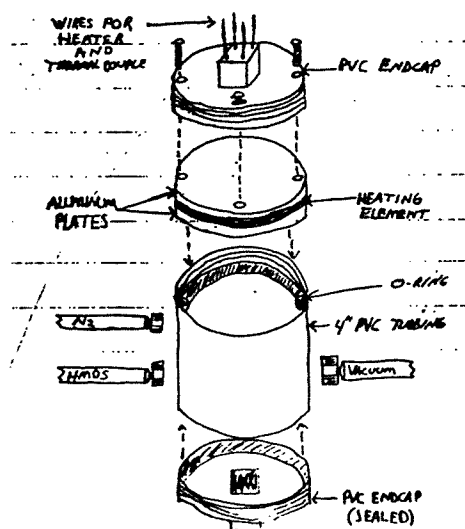


Figure 3  
VACUUM CHAMBER ASSEMBLY

The construction of the system was very important for this project. The chamber was made of 4" PVC tubing with two screw in endcaps so that it could be sealed. One endcap was cemented while the other had an O-ring to help seal the chamber. A nitrogen purge line and HMDS line were attached to the chamber along with the vacuum hose. Nitrogen was bubbled through the HMDS to allow HMDS vapors to enter the chamber. The tubing going from the chamber to the roughing pump was immersed in liquid nitrogen to act as a cold trap for the unused HMDS.

KTI Positive Resist 809 was the resist used for both liquid and vapor phase techniques. The resist was coated with the 809 resist on about 5000 angstroms of oxide for a thickness of about 1.0 microns. Table 1 shows the process conditions for the wafers used.

Table 1 : Processing Steps

Spin coat HMDS (33% in Freon)	5000 rpm	20 sec
Spin coat 809 (35% solids)	6000 rpm	30 sec
Hot plate bake	90 C	60 sec
Expose half the wafer	100mJ/cm <sup>2</sup>	
Silylate liquid or vapor phase		
Etch in oxygen plasma		

The liquid phase silylation was done by the steps followed in Table 2, With HMDS diluted in freon to give concentrations of HMDS of 33% and 3.3%.

Table 2 : Liquid Phase Silylation Process

Expose half the wafer	100mJ/cm2	
Heat wafer	70 C	
Heat HMDS	70 C	
Expose liquid HMDS to wafers	3 min	
Rinse in DI water		

The vapor phase was done for substrate temperatures of 75, 90, and 105 C. These process steps can be found in Table 3.

Table 3 : Vapor Phase Silylation Process

Expose half the wafer	100mJ/cm2	
Heat wafer to temperature		
Pump down to below 1000 microns		
N2 purge		
Pump down to below 1000 microns		
N2 purge		
Pump down to below 1000 microns		
Fill chamber with HMDS vapor	5 min	
pump down to below 1000 microns		
N2 purge		

The etch rates were studied for both the liquid and vapor phase techniques. This was done by measuring the exposed and unexposed regions prior to the etch. The etch was then done in the Tegal Plasmaline for 5 minutes. Again the exposed and unexposed regions were measured after the etch and etch rates for each were found.

## RESULTS/DISCUSSION

The number of results obtained in this experiment are limited because a large amount of time was spent in the design and construction of the vacuum chamber for the vapor phase silylation. Only the single layer reverse image was looked at through while the double layer positive image was ignored. The number of experiments done on the single layer for both techniques are small do to the lack of time.

The results obtained in the liquid phase silylation were not noticeable. For both the 33% and 3.3% HMDS in freon, no difference in etch rates in the oxygen plasma were found. The only evidence of silylation was a slight image seen on the wafer after silylation took place.

In using the vapor phase silylation method, results were obtained for three wafers which had different temperatures. After the silylation took place, a visible image was noted on the wafer. The wafers were then etched and the results from this part can be found in Table 4. These were all done for silylation times of 5 minutes.

Table 4 : Vapor Phase Silylation Etch Rate Results

TEMPERATURE DEGREES C	ETCH RATE UNEXPOSED ANGS/MIN	ETCH RATE EXPOSED ANGS/MIN	SELECTIVITY UNEXP/EXP
75 C	664	556	1.19
90 C	583	424	1.38
105 C	598	521	1.15

The results obtained in this experiment are not great, but they are a start for dry development at RIT. A few reasons that might explain the bad results obtained are given. First of all, the measurements taken of the resist after silylation may not be correct. This is because the small silicon dioxide layer on top of the resist changes the index of refraction and thus the true thickness. Another problem is that there may be a lack of HMDS vapors entering the chamber. Perhaps the design of a better bubbling system would help this problem.

#### SUMMARY

The effects of post exposure silylation on KTI Positive Photoresist 809 were studied for liquid and vapor phase techniques. It was found that the vapor phase does decrease the etch rate in an oxygen plasma of the exposed slightly, while the liquid phase had no apparent effect. For better results, adjusting the silylation time and temperature could be tried for a future project, since the vacuum chamber is already built. Also in the future, imaging of lines and spaces may be attempted and look how well the resist mask holds up under actual etch processes.

#### ACKNOWLEDGEMENTS

I would like to thank Scott Blondell, Mike Jackson, Dr. Daly and especially Gary Runkle, in assisting me in designing and building the vacuum chamber.

#### REFERENCES

- (1) Coopmans, Roland, and Lombaerts. "Effects of Silylation Parameters on the Lithographic Performance of the DESIRE System". Microelectronic Engineering 5. (1986) 291-297.
- (2) McColgin, Daly, Jech, and Burst. "Silicon-added bilayer resist (SABRE) system". SPIE Proceedings, 820, 1988.
- (3) Visser, Schellekens, Reuman-Huisken and van Ijzendoorn. "Mechanism and Kinetics of Silylation of Resist Layers from the Gas Phase". Proceedings of SPIE 1987.
- (4) Bailey, Daly, Brust, and Pearson. "Silicon Containing Polymers and Organo-Silicon Chemistries for Microelectronics". Polymers for Advanced Technologies, 1987.