POST EXPOSURE SILYLATION OF A POSITIVE PHOTORESIST

By

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ABSTRACT

A silylation process employing hexamethyldisilazane (HMDS) as a silylating agent was examined as a method of combining the high resolution capabilities of a multilevel resist and the process simplicity of a single layer resist scheme. Atmospheric pressure vapor phase silylation and liquid phase silylation were performed on Kodak 809 Micropositive resist. The vapor phase silylation did not result in significant alteration of the etch characteristics. The liquid phase silylation was performed for several HMDS concentrations in Freon. Liquid phase silylation was shown to provide significant etch selectivity upon exposure to an oxygen plasma.

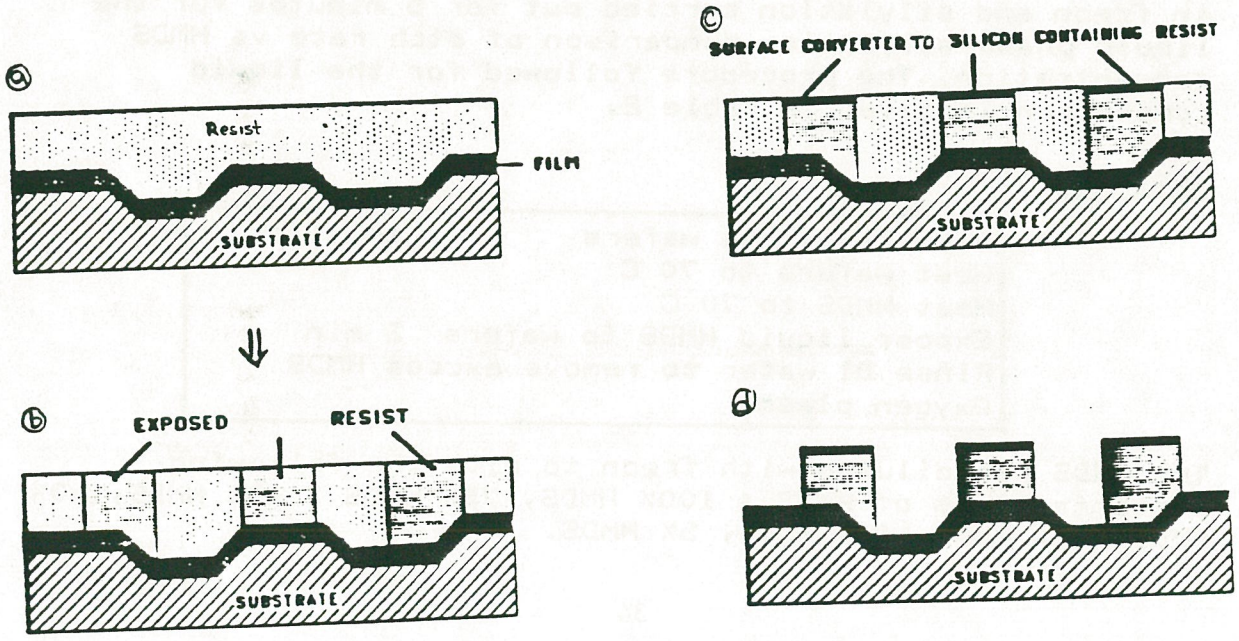
INTRODUCTION

Because of the difficulties encountered with e-beam, x-ray and other non-optical lithographic techniques such as low throughput, sensitivity of resist materials and difficulty in obtaining adequate masking materials, methods have been developed to extend optical lithography well beyond its perceived limits. By using multilayer technology, optical lithography has been extended into the submicron range. The problems associated with optical lithography such as standing waves, reflective notching, planarization, bulk effects and step coverage have been lessened by varying degrees through multilevel photoresist systems. In trilevel systems a spin on glass can be used between a thin imaging layer and a thick planarizing bottom layer. The spin on glass is used as a dry etch transfer mask using plasma anisotropic etch. While these trilayer systems are theoretically capable of extremely high resolution, there are significant processing problems that can be encountered due to the process complexity associated with three layers and multiple exposure and etch steps. Careful control of the etch steps is required to achieve the high resolution desired. The inorganic middle layer makes the possibility of successful reworks due to patterning problems very small.Bilevel systems offer a somewhat less complex processing schedule while still resulting in improvement over single layers. The added complexity of two photoresists and formation of interfacial layers however, still presents some added processing difficulties. The formation of interfacial layers between the

thin imaging resist and the thick planarizing layer can prove to be a significant problem in etching and stripping of the photoresist. There are several variations of the bilevel scheme available , each with its advantages over the traditional single level systems. Most bilevel systems consist of either a PCM (portable conformal mask) setup or employ the use of contrast enhancement or anti-reflection layers. All of these systems provide for increased resolution over single level resists. There is ,however, process difficulties associated with each system that has prevented them for the most part becoming standard procedures in manufacturing on a large scale. Control of the multiple etch and/or multiple exposure steps is required as in trilevel systems. The interfacial layers and poor thermal stability of contrast enhancement materials and some of the planarizing layers used further adds to complexities of bilevel systems.

The ideal system would combine the advantages of multilevel schemes with the simplicity of single layer systems. This combination can be achieved by using a silylation process. A photoresist is first exposed and then treated with a silicon containing vapor or liquid. There is a differential diffusion of the silicon containing material into exposed and unexposed regions of the resist. The resist is then exposed to an oxygen plasma causing the silicon to be converted into silicon dioxide. This silicon dioxide layer acts as an etch mask against dry development. The result is a negative tone resist pattern. Because only the upper part of the resist needs exposure, the problems associated with single level resists are nearly eliminated while the increased resolution of multilevel systems can be achieved.

Figure 1.



Outline of Silylation Process

EXPERIMENTAL

Hexamethyldisilazane (HMDS) was used as the silylating agent. Kodak 809 Micropositive was the resist chosen. Silylation was investigated using HMDS both as a liquid and a vapor. The substrate used was bare silicon. All wafers were coated with approximately 1.4 microns of resist and exposed with a high pressure mercury vapor source.The processing schedule is given in table 1.

Table 1.

Spin coat HMDS (33% in Freon)	5000 rpm	20 sec
Spin coat 809 (1:1 in 809 thinner)	6000 rpm	30 sec
Hot plate bake	90 C	1 min
Blanket exposed (high pressure Hg source)		
Silylated using liquid or vapor		
Exposed to oxygen plasma		

Several parameters were investigated, etch rate vs.silylation time, etch rate vs HMDS concentration, and the effect of different levels of exposure on the degree of silylation. To investigate the effect of exposure on silylation, the exposure dose was varied from 0 mj/cm2 to 270 mj/cm2 or from no exposure to maximum exposure to expose the entire thickness (approx. 1.4 microns).For the vapor phase silylation the substate was heated to a temperature of 70 C and HMDS vappr was introduced into the reaction chamber and allowed to diffuse for times ranging from 5 minutes to 30 minutes. For the liquid phase silylation both the substrate and the HMDS were heated to 70 C again by using a hot plate set up. The concentration of HMDS was varied from 100% to 5% in freon and silylation carried out for 5 minutes for the liquid phase silylation comparison of etch rate vs HMDS concentration. The procedure followed for the liquid comparison is given in table 2.

Table 2.

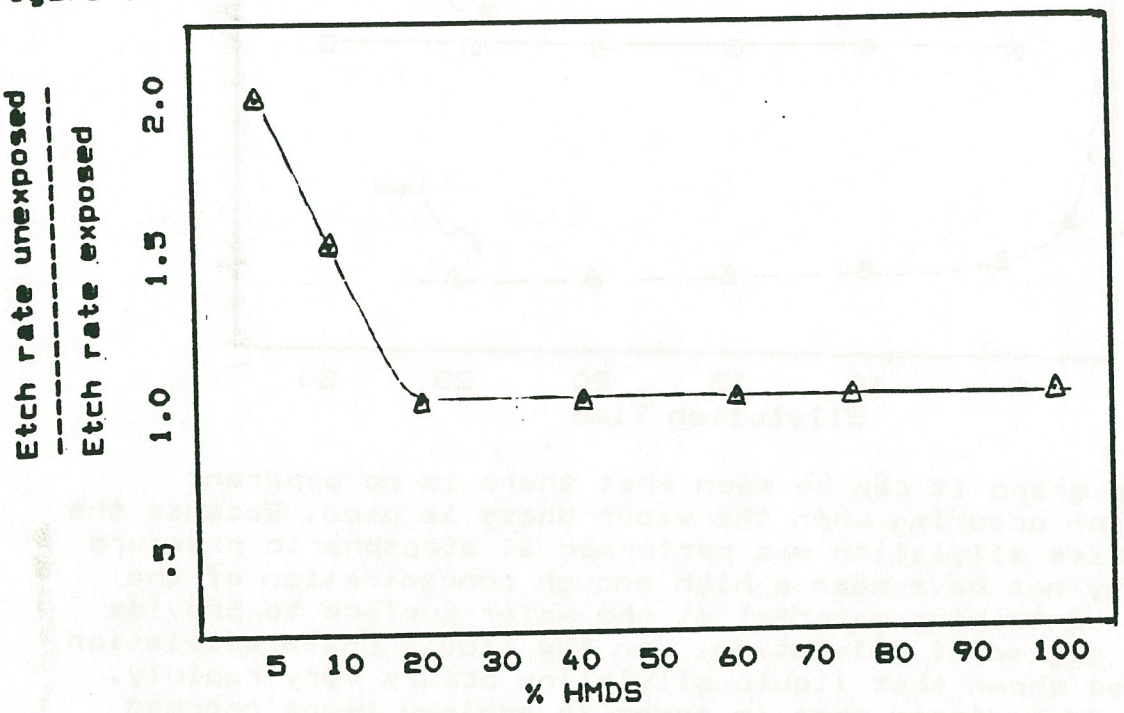
Blanket expose wafers	140mj/cm2
Heat wafers to 70 C	
Heat HMDS to 70 C	
Expose liquid HMDS to wafers	3 min
Rinse DI water to remove excess HMDS	
Oxygen plasma	

The HMDS was diluted with freon to give the following concentrations of HMDS ; 100% HMDS, 75% HMDS , 60% HMDS, 40% HMDS, 20% HMDS, 10% HMDS, 5% HMDS.

RESULTS/DISCUSSION

For the liquid phase silylation comparison of HMDS concentration vs etch rate discrimination the etch rate of exposed and unexposed silylated resist is compared for each HMDS concentration. The results are shown in figure 3.

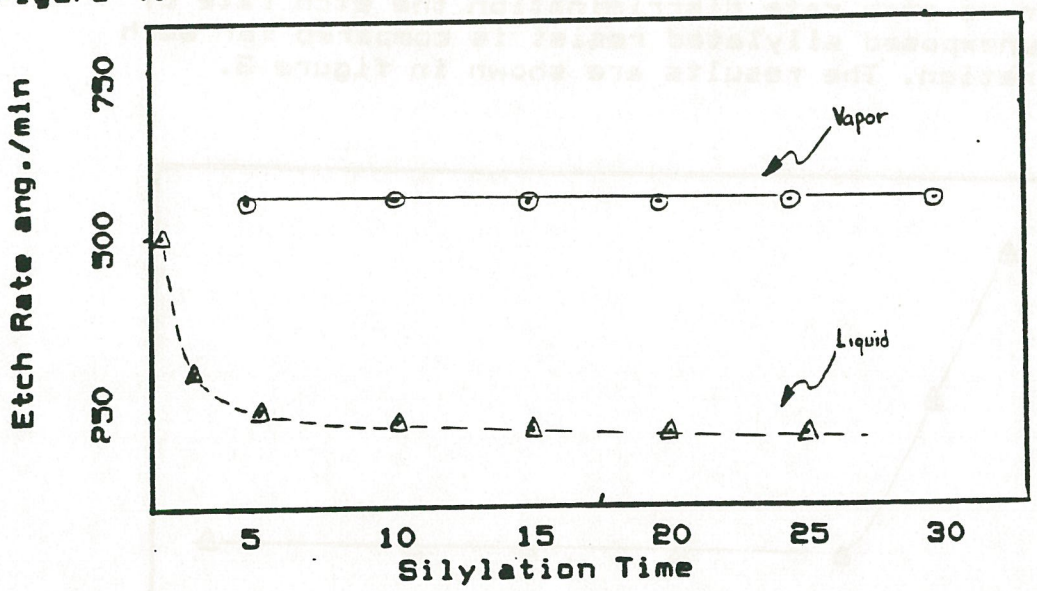
Figure 3.



From the graph it can be seen that while there is a decrease in etch rate for each concentration as compared to the values obtained for unexposed unsilylated resist, the difference between the etch rates of exposed silylated resist and unexposed silylated resist is very small for the higher concentrations of HMDS. This will not provide any discrimination between the two areas and thus yield no lithographic image after plasma development. When the concentration is reduced to 10% HMDS there begins to be a degree of discrimination. At this level the discrimination is close to 1.5:1 betweem unexposed and exposed resist. At 5% HMDS the discrimination rises to 2:1. While this is enough of a difference to provide an adequate lithographic pattern, the high film loss of the exposed region (50%) may require unreasonably thick resist coatings to achieve adequate masking during certain processing steps. A possible explaination for the lack of discrimination when using higher HMDS concentrations is that at these concentrations the diffusion of the silicon containing material is too aggressive to provide for any differential diffusion into either unexposed or exposed region.

For the comparison of etch rate vs silylation time, both liquid and vapor phase experiments were conducted. The results of silylation time vs etch rate are shown in figure 4.

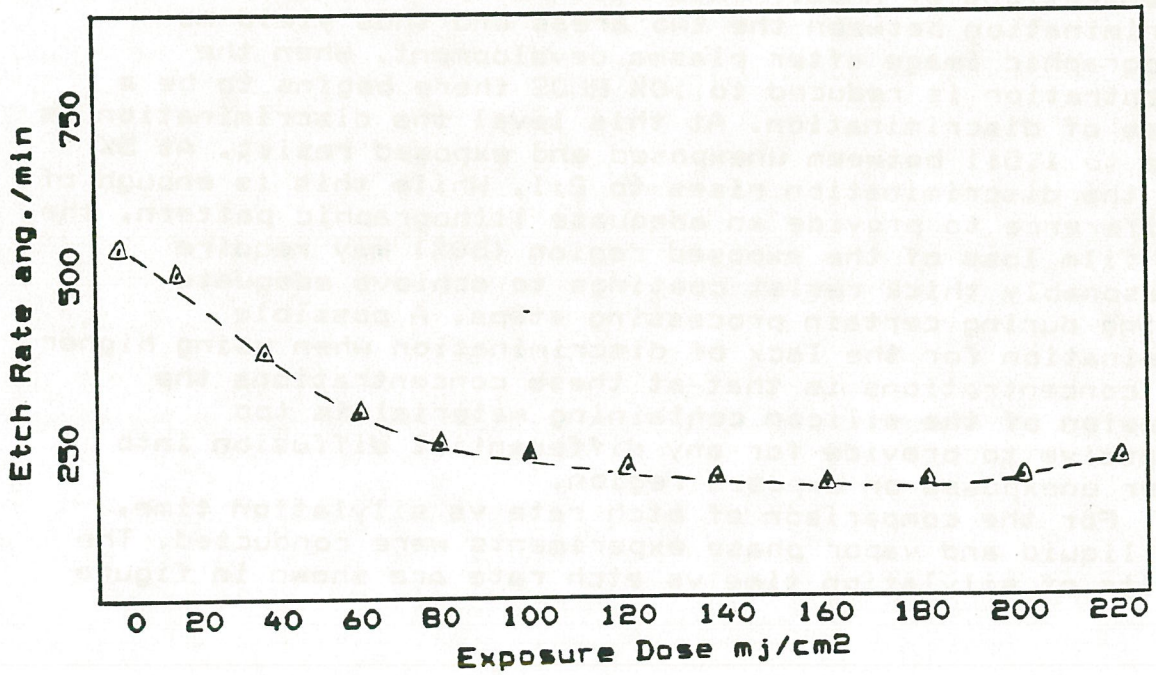
Figure 4.



From the graph it can be seen that there is no apparent silylation occuring when the vapor phase is used. Because the vapor phase silylation was performed at atmospheric pressure there may not have been a high enough concentration of the silicon containing material at the wafer surface to provide for any degree of silylation. For the liquid phase silylation it can be shown that liquid silylation occurs very rapidly. This would indicate that in order to achieve tight process control using this method careful monitoring and control of silylation times is essential.

Exposure vs etch rate is plotted in figure 5. to compare the effect of exposure on silylation.

Figure 5.



From this graph it can be shown that exposure dose is related to silylation degree. For very small exposure doses there is no apparent silylation. The etch rate decrease for increased exposure until an exposure of 140mj/cm2 is reached. After this the etch rate stays approximately the same. The reason for this result may be linked to the degree of photobleaching of the resist in the exposed areas. As the exposure is increased there is a higher percentage of the photoactive compound that is reacted. At 140mj/cm2 the increase in exposure has little effect on the etch rate. This may be accounted for due to the silylation only taking place in a thin surface layer rather than throughout the entire resist thickness. Because of this, the photoreaction in this surface area may be complete at or near 140mj/cm2

SUMMARY

Post exposure silylation was found to produce a reduction in etch rate of an exposed area of resist as compared to an unexposed region when exposed to an O2 plasma. It was shown that exposure, reagent concentration, and time are all important process variables. Because of its relative simplicity when compared to multilevel systems silylation processes could be advantageous to produce high resolution lithographic images as most of the deleterious optical effects can be eliminated with this approach. Low pressure vapor phase silylation may be shown to be the best method for achieving good process control and discrimination as liquid phase silylation is very aggressive. A possible problem is the difficulty in measuring the extent and uniformity of silylation prior to etching.

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REFERENCES

(1) Visser,Schellekens,Reuman-Huisken and van Ijzendoorn. "Mechanism and Kinetics of Silylation of Resist Layers from the Gas Phase". Proceedings of SPIE 1987

(2) Chiong, Yang, and Yang." Formation of Etch-resistant Resists Through Preferential Permeation". U.S. patent number 4,613,398. September 1986.

(3) Coopmans, Roland, and Lombaerts. "Effects of Silylation Parameters on the Lithographic Performance of the DESIRE System".Microelectronic Engineering 5. 1986 291-297.