POSITIVE PHOTORESIST HARDENING USING FORMALDEHYDE SOAK METHODS

Brian E. Stricker
5th Year Microelectronic Engineering Student
Rochester Institute of Technology

ABSTRACT

KTI-820, a positive photoresist, was hardened using a formaldehyde and hydrochloric acid solution consisting of five parts hydrochloric acid (HCl) and one part formaldehyde. The experiment involved varying the duration of the bath from three to ten minutes and varying the temperature of the bath from 70 to 100 degrees centigrade. The results of this process showed resist flow and thickness loss. The thickness loss was a result of the HCl attacking the resist during the soak in the HCl and formaldehyde solution.

INTRODUCTION

One problem with conventional positive photoresists is thermal stability. Thermal stability is the ability of a resist to maintain the image in the resist at elevated temperatures. A typical positive photoresist has a maximum usable temperature (thermal stability) of about 150 degrees centigrade [1]. This makes it unsuitable for masking high energy high dose ion implants, as these types of implants produce heat which can exceed the maximum usable temperature of the resist and cause the it to flow. Another problem with positive photoresist is plasma resistance. This is its ability to retain its thickness after being exposed to a plasma containing oxygen. Hardening, will reduce these two problems [2].

Photoresist hardening can be achieved using two methods. One method involves using deep UV radiation to crosslink the resist. The ultraviolet radiation is absorbed by the binder of the resist causing it to crosslink. The other method uses a formaldehyde soak to crosslink the resist. The addition of a formaldehyde soak after normal development introduces additional methylene bridges. These methylene bridges in the presence of heat (from a hotplate) and hydrochloric acid (HCL) will crosslink the novalak binder of the positive photoresist. This increases the average molecular weight of the binder, which translates to an increase the glass transition temperature of the resist. Finally this increase in the glass transition temperature results in increased thermal stability, and thus the resist has been hardened.

EXPERIMENT

A software package called RS1 was used to create a full factorial design with a response surface model (RSM) objective. The experiment consisted of nine runs with the variables being the temperature of the formaldehyde soak and the duration of the soak. The temperature of the bath was varied from 70 to 100 degrees centigrade and the duration of the soak was varied from three to ten minutes. The response of the experiment is the temperature at which the resist flowed. The response will be determined by using a scanning electron microscope (SEM) to determine the resist edge profile. The resist profile will show if the resist has flowed or not. In addition, a control wafer that was not exposed to the formaldehyde,but received standard processing, was used for comparison.

Nine three inch silicon wafers were obtained, scribed for identification purposes and cleaned using the standard RCA process. A wet oxide growth was performed and resulted in 5000 angstroms of oxide. The wafers were coated with 1.2 microns of KTI-820 positive photoresist on a GCA wafer track and were exposed at 45 mj/cm2 in a contact printer. The mask that was used contained lines and spaces of varying dimensions from one to ten microns to produce the image in the resist. The wafers were developed using ZX-934 developer for 30 seconds followed by a 140 degree centigrade post bake. The wafers then underwent the formaldehyde soak treatment, and the details of which are shown in Table 1.

Table 1 :Formaldehyde soak process parameters

SOAK TIME (min)	SOAK TEMPERATURE
3.0	70.0
6.5	70.0
10.0	70.0
3.0	85.0
6.5	85.0
10.0	85.0
3.0	100.0
6.5	100.0
10.0	100.0

NOTE: TEMPERATURES ARE IN DEGREES CELSIUS

After the formaldehyde treatment the wafers were broken into quarters and baked at 150, 200, 250, and 300 degrees centigrade with each quarter wafer seeing a different bake time on the hotplate. This bake is to determine the increased thermal stability of the resist. Following the bakes, samples were taken from each quarter wafer for SEM analysis. After the SEM analysis the results of the experiment were placed into the RS1 experiment worksheet to be analyzed. The analysis was to produce an RSM and optimization curves. These curves could then be interpreted to determine the optimum conditions for this experiment.

RESULTS/DISCUSSION

Scanning electron microscope analysis of the control wafer showed that the resist edge profiles were rounded. The standard RIT lithography process produces rounded resist profiles due to the 140 degree C bake on a hotplate for two minutes following development. A micrograph of the profiles is shown in Figure 1.

Figure 2 shows typical results from the formaldehyde soak. Notice that the profiles show drastic reduction in resist thickness and enhanced resist flow. A test bake of 150 degrees C was used to determine the increased thermal stability of the resist. This treatment was supposed to increase the thermal stability of the resist to 300 degrees C [1]. Obviously, there was a problem with the results.

It is speculated that the resist thickness loss was due to the HCl attacking the resist during the soak process. One reason may be that the HCl concentration, a 5:1 acid to formaldehyde volume ratio that was used, was too high. Another potential problem is that the bath was heated, and when acid is heated it reacts more readily. Also during the soak process the formaldehyde and acid bath was evaporating so it is possible that the bath ratios were changing. Further experimentation is needed to confirm if the acid was indeed attacking the resist and to refine this process to achieve a thermally stable image at 300 degrees C. Further experimentation could include varying the acid concentration, using lower soak times, and using a different resist.

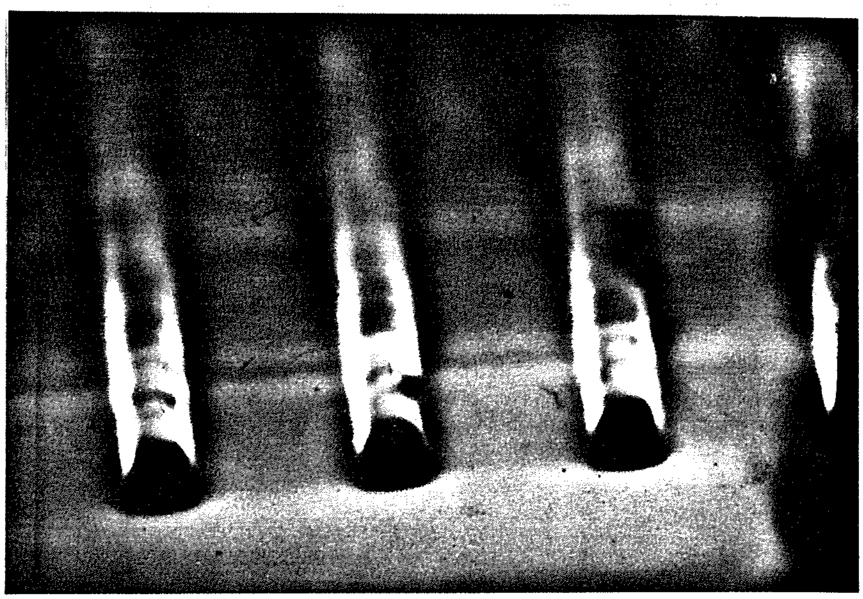

Figure 1 : Resist profiles from the control wafer

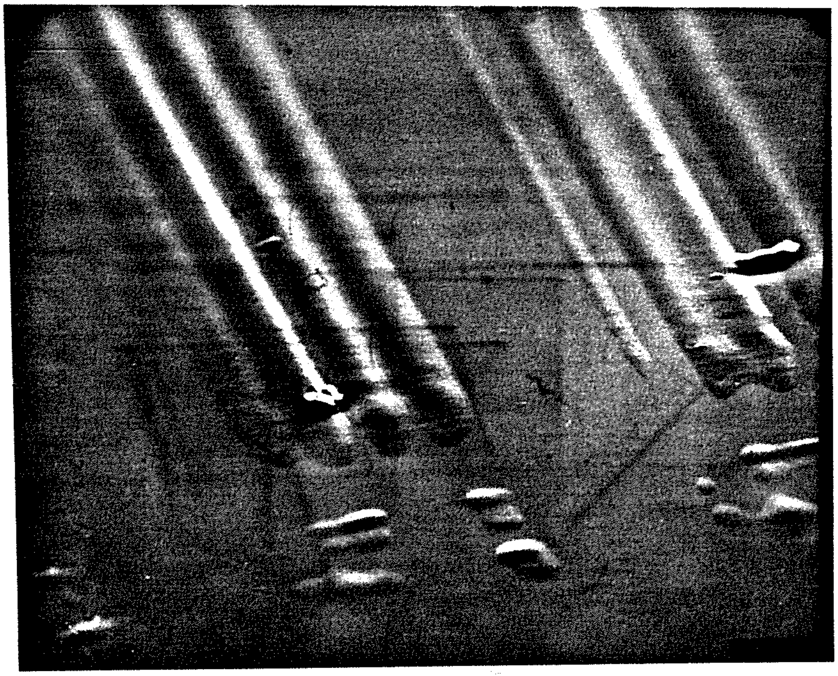

Figure 2 : Results of the formaldehyde soak

CONCLUSIONS

Positive photoresist hardening using formaldehyde soak methods can be used to increase the thermal stability of a positive resist to 300 degrees C, as seen in [1]. However in this experiment the SEM analysis showed that the resist had flowed at 150 degrees C for each of the nine trials and that there was also resist thickness loss. The resist thickness loss most likely due to a HCl concentration that was too high and that the HCl was heated, which increased the reactivity of the acid. This method of hardening can produce thermally stable resist images up to 300 degrees C [1]. With further experimentation, It is believed that these same results can be duplicated.

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REFERENCES

[1] KTI-820 positive photoresist data sheet.

[2] A. Gutman, A. Kleinhaus, W. Bade, Microelectronic Engineering #3 (1985),pp.329-337.