

## Characteristics of silylation and wet develop in novolak/diazonaphthoquinone resist system

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New fine-patterning method named for silylation/wet develop process was introduced in order to improve resist profile and process latitude. When diazonaphthoquinone novolak(DQN) was silylated with gas phase hexamethyldisilazane (HMDS), resist profile was much steeper and exposure latitude was two times wider than those obtained in the conventional hot plat post exposure bake process due to the surface induction effect at surface area. The diffusion of gas phase HMDS into the exposed area and unexposed area showed Fickian and pseudo-fickian characteristics, respectively. The ratio of the degree of silylation between exposed and unexposed area at 140°C was 1.08, which gave the possibility for this method to be used in wet develop process in stead of dry develop process.

### 1. Introduction

As the density of VLSI (very large scale integrated circuit) increases, the sub-half micron photo lithography process is required. New fine-patterning methods to implement this requirement like surface hardening (1), multilayer (2), improved illuminator system(3), diffusion enhanced silylated resist (DESIRE) (4) are considered at device fabrication. Surface hardening method makes a surface of resist hard by ultraviolet light flood exposure or alkali soaking, which improve to the low develop rate at the surface. Multilayer uses bi or tri layers of resist in order to prevent a pattern degradation from the reflected u. v light at the topographical surface of a wafer. It is undesirable to use multilayer method at the mass production because of high cost, complicated process, defect generation and so on. Recently, DESIRE process was introduced to overcome these limits. But, it has still difficulties to optimize etch parameters, to control C. D and uniformity, to remove silylated resist. Silylation/wet develop process was studied and characterised to overcome disadvantages of DESIRE process and to improve process latitude. In stead of high selectivity of silylation between exposed and unexposed area, this study used the low selectivity of silylation at low temperature, which made the develop rate lower and improved resist profile

due to a surface induction effect. Conventional track system can be used by installation of a modified unit at the post exposure bake.

### 2. Experimental

Novolak/diazonaphthoquinone resist which is g-line sensitive was silylated with gas phase hexamethyldisilazane (HMDS) at low temperature. Silylation bake was performed with vacuum bake oven. Concentration of aqueous developer of tetra ammonium hydroxide(TMAH) was 0.255 normality. Canon stepper FPA MIII (N. A : 0.48,  $\sigma$ : 0.6) was used as an exposure tool.

### 3. Results and discussion

Figure 1 presents (SiO)-aryl absorbance with exposure energy. Silylation reaction at 140 C increased with exposure energy due to indenecarboxylic acid generation by u. v light which induced resist relaxation to be easy for diffusion of silylating agent. Silylation at unexposed area was shown that some extent of photo active compound reacted with H<sub>2</sub>O in the resist. Which resulted in the generation of indene carboxylic acid. The selectivity of silylation between exposed and unexposed area was 1.08. Which gave the good reason to use wet develop process. Figure 2 shows that

(SiO)<sub>2</sub> peak increases linearly with silylation time at higher exposure time. Fickian type diffusion behavior was shown at low exposure energy. Figure 3 shows resist retention with exposure energy. The retention of silylated resist was improved with silylation temperature and time. Especially, retention at low exposure time was elevated, which prevented loss of resist and pattern degradation. Other investigation was observed with many kind of process condition that is no bake, oven bake, hot plate bake, vacuum bake, and silylation bake were implemented whether the improved retention was derived from the silylation reaction. Figure 4 shows that retention against developer was much improved only with silylation. As a result, silylation of resist made develop rate slow and improved retention at the surface of resist. In order to compare the develop rate with each silylation condition and conventional hot plate post exposure bake condition. Develop rate monitoring system (DRM) was used. Develop rate after silylation at 125°C and 140°C was slower than developer rate without silylation by 1.8 and 2.9 times, respectively at figure 5,6. The time delaying at the surface of resist was explained that silylation was concentrated at the surface of 965 Å in depth. Develop rate changes very uniformly with silylation temperature which is expected to give clean side wall of resist pattern. From above results, it is obvious that the silylated resist at temperature of 140°C, 5 min shows good profile and clear side wall due to high retention and uniform develop rate change. Critical dimension size with exposure energy at various silylation conditions is shown at figure 7. Critical dimension change with high silylation temperature and long silylation time became insensitive to exposure energy. The exposure latitude at silylation temperature of 140°C, 5 min gave two time wider than those obtained at the conventional hot plate post exposure bake process. With this wide exposure latitude, it became much easier to control critical dimension with many lithographical parameter variations like light intensity of exposure tool, developer concentration and flow rate changes, and other factors of parameter. Figure 8 shows that profile of the silylated resist at higher temperature is steeper and clean side wall. When the silylation condition changed to improve resist profile, it gave very vertical profile which is shown at figure 8. In order to evaluate hard bake deformation temperature of silylated resist pattern profile, a silylated resist which size is more than

100 μm was baked at various temperature. The silylated resist pattern has the better resistance to higher temperature of 120°C at figure 9, 10. Also top surface of silylated resist has different shape at corner. This can be explained as silylation as silylation concentrated at the surface of the resist.

#### 4. Conclusions

When diazonaphthoquinone novolac resist (DQN) was silylated with hexamethyldisilazane, resist profile was much steeper and exposure latitude was much wider than those obtained in the conventional hot plate post exposure bake process due to surface induction effect by silylation. The ratio of the degree of silylation between exposed and unexposed area at 140°C was 1.08, which gave possibility for silylation to be used in wet develop process instead to the surface induction effect was 965 Å from the top surface of resist, which plays major roles to make steeper profile.

#### Acknowledgements

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#### References

1. Vollenbroek, H. Krook, J. Bartsen, and J. Dil, "Microcircuit Engineering" Academic Press edited by H. Beneking and H. Heuberger 555, (1985).
2. M. O' Tools, E. Liu, and M. Chang "Multilevel resist for Photolithography Utilizing an Absorbing Dye" proc, SPIE, VOL. 275, 128 (1981).
3. K. Kammon, T. Miyamoto, Y. Myoi, M. Fujinaga, H. Nagata and M. Tanaka, "Photolithography System Using Modified Illumination" Symposium on VLSI technology digest of technical paper, p 108, (1992).
4. M. op De Beek and L. Van Den hove "Silylation of novolac based Resist; Influence of Deep-U. V Induced Crosslinking" J. Vac. Sci. Technol., B 10(2), 701(1987).

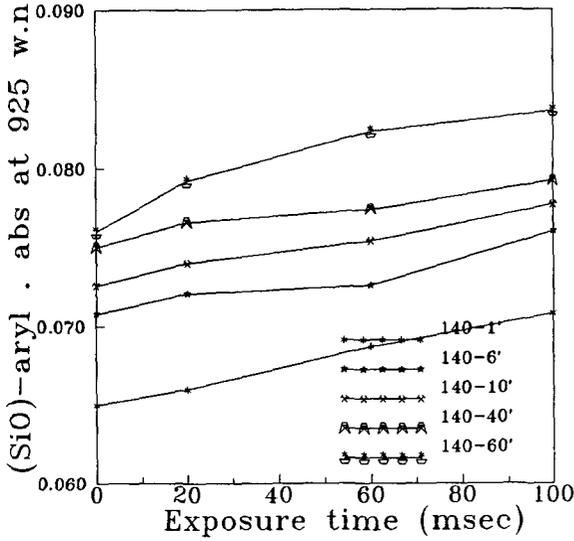


Figure 1. (SiO)-aryl absorbance vs. exposure time at soft bake temp. 118°C, 2'.presilylation and silylation temp. 140°C.

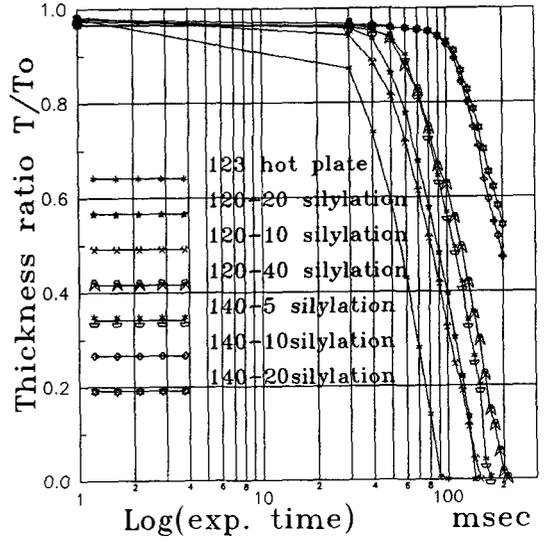


Figure 3. CMTF curve at various silylation time and temp.

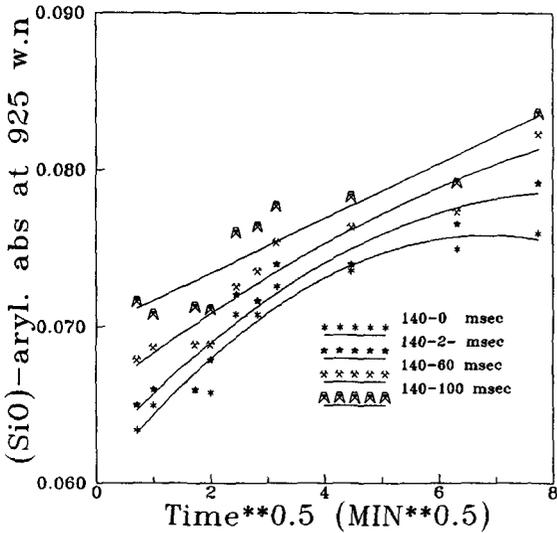


Figure 2. (SiO)-aryl absorbance vs. silylation  $\sqrt{\text{time}}$  at soft bake temp. 118°C, 2'.presilylation and silylation temp. 140°C.

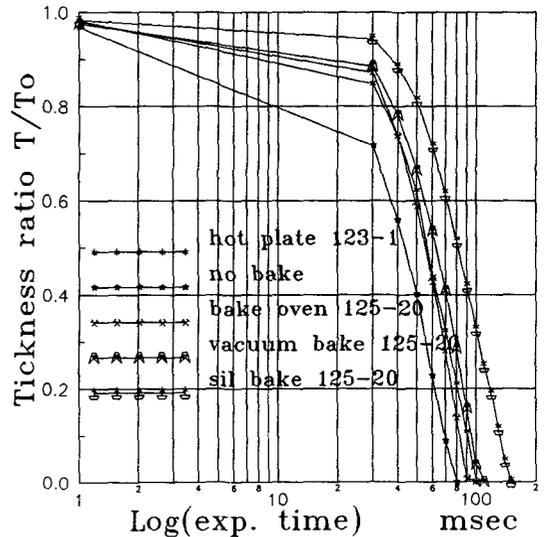


Figure 4. CMTF curve at various bake modes. no bake, oven bake, H.P bake, vacuum bake, silylation.

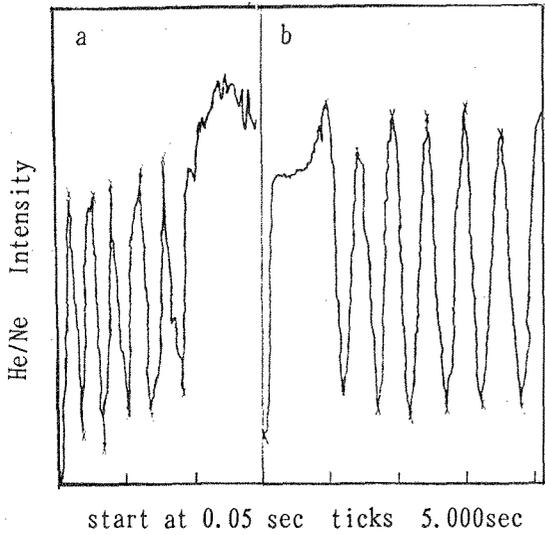


Figure 5. Develop rate measured by DRM at 123°C hot plate(a), at 125°C 20' silylation (b). 200msec exposure.

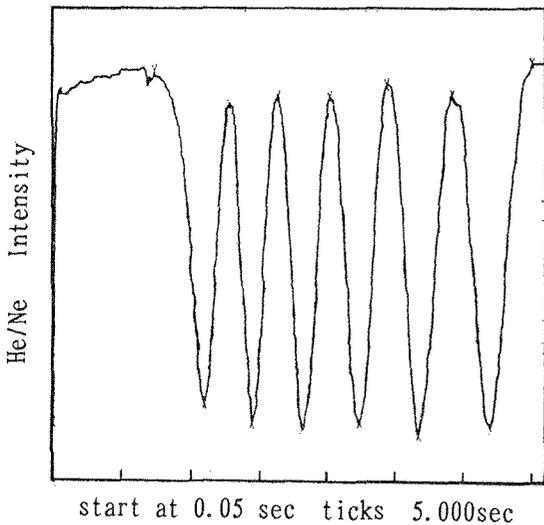


Figure 6. Develop rate measured by DRM at 140°C 5' silylation. 200msec exposure

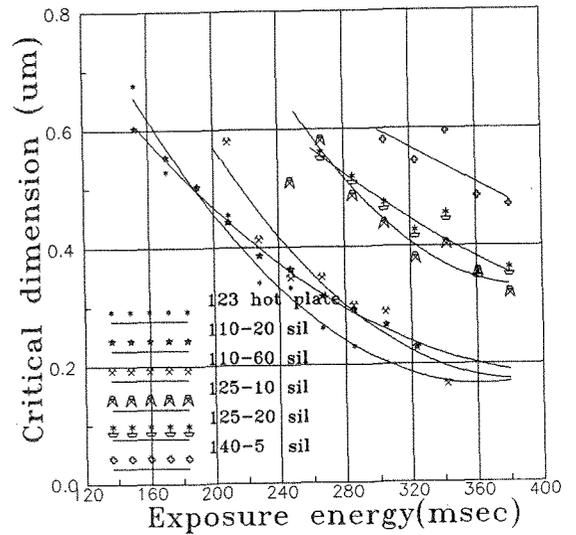


Figure 7. C.D changes vs. exposure time at various silylation conditions (0.6µm line/spcae - line measured).

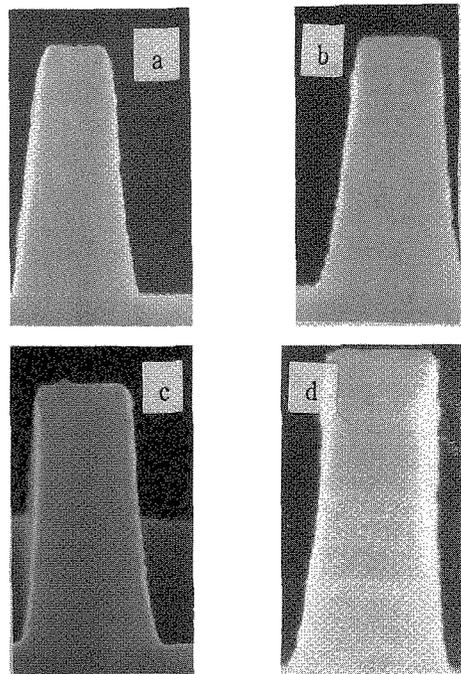


Figure 8. 0.6µm resist pattern profile obtained after 123 H.P (a), 125°C-20' (b), 140°C-5' (c), 125°C-20'-different press (d) silylation.

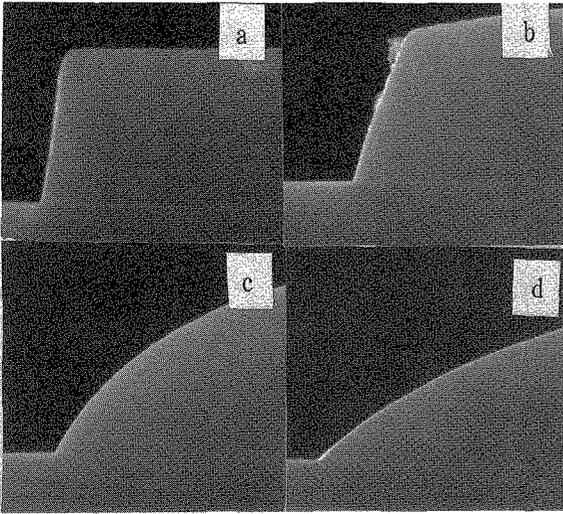


Figure 9. Resist profile deformation of 123 H.P conventional process at 110°C (a), 120°C (b), 130°C (c), 140°C (d) hard bake.

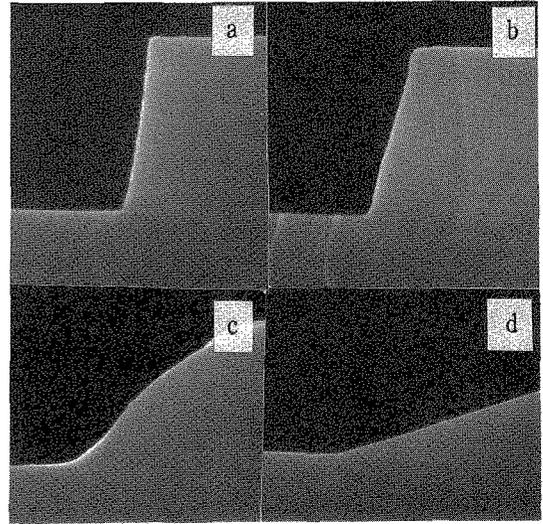


Figure 10. Resist profile deformation of silylation process at 110°C (a), 120°C (b), 130°C (c), 140°C (d) hard bake.