

CHAPTER IV

RESULTS AND DISCUSSION

4.1 EG spirosilicate photoresist

4.1.1 Synthesis and characterization of EG spirosilicate monomer

EG spirosilicate monomer was synthesized by using 250 mmol of silica reacted with excess amount of EG, 125 mmol TETA and 0.2 mole % equivalent of NaOH to silica at 200°C for 6 hours under N₂ atmosphere, as studied by Chivin (Chivin, 1999). Figure 4.1 presents FTIR spectra of EG spirosilicate monomer along with all starting materials and catalyst. According to specific 886 wavenumber corresponding to Si-O-C bond as shown in table 4.1, all spectra do not contain this characteristic peak (Silverstein et.al., 1981). Moreover, it also showed that TETA was still left in the product solution, which would be used further as catalyst in the step of crosslinking EG spirosilicate.

To further confirm the structure of EG spirosilicate monomer both ¹H-NMR and ¹³C-NMR were also employed and resulted that the structure of EG spirosilicate monomer was definitely formed. Respectively, both ¹H-NMR and ¹³C-NMR (see appendix) result indicated at $\delta = 3.4$ ppm and $\delta = 40$ ppm which is consistent with the structure of EG spirosilicate, as shown in Fig. 4.2, whereas DMSO-d₆ used as reference peak was indicated at $\delta = 2.5$ ppm and $\delta = 63$ ppm (Silverstein et.al., 1991).

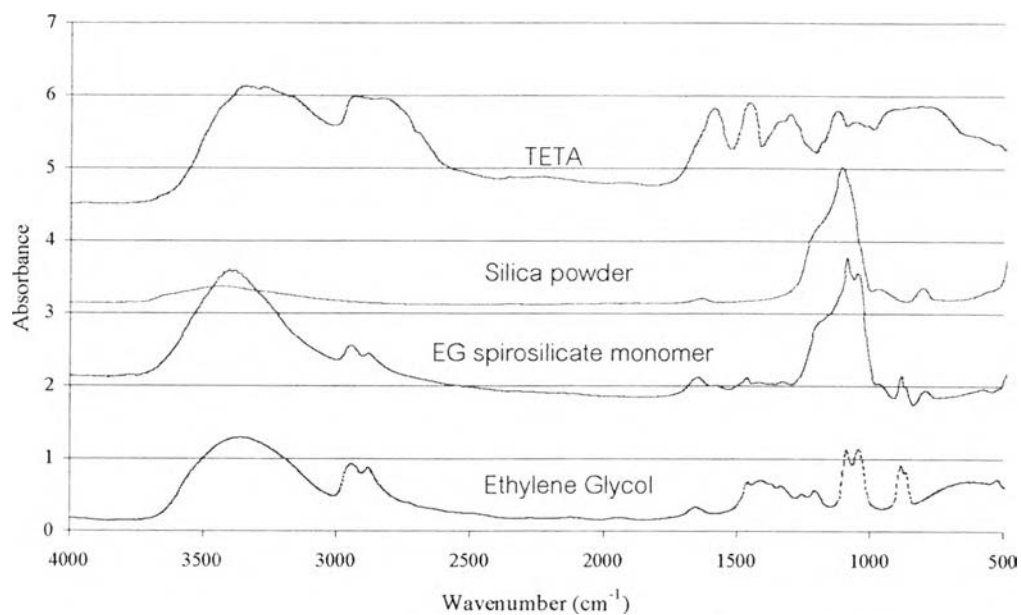


Figure 4.1 FTIR spectra of EG spirosilicate comparing with starting materials and catalyst.

Table 4.1 Assignment of FTIR spectrum.

Frequency (cm ⁻¹)	Functional group
3600	OH stretch : intermolecular H-bonding
2950	Saturated C-H stretching
1200	Saturated α -cyclic of alkanes
1100	Si-O-CH ₂
1000	Si-O-Si & Si-O-C
886	Si-O-C

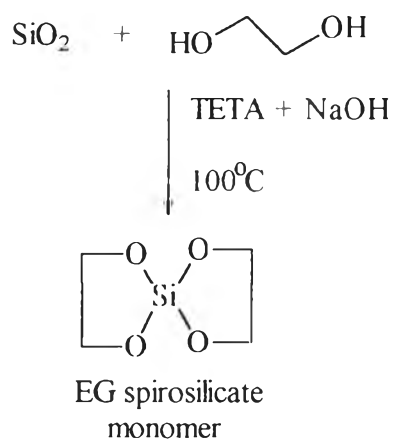


Figure 4.2 Synthesis of EG spiro silicate monomer.

In addition, % ceramic yield was used to determine the structure of product by comparing percent weight loss of experimental data with theoretical calculation. From the experimental data, it was found that % ceramic yield of EG spiro silicate monomer was 40.82%, which was presented quite close to the theoretical calculation, 40.54% as shown in Fig.4.3. For each decomposition step the product curve indicated oxidative decomposition to CO_2 and H_2O of cyclic ring of spiro silicate monomer, as shown in eq.(4.1), and the silica was the product after decomposition, as shown in Fig. 4.4.

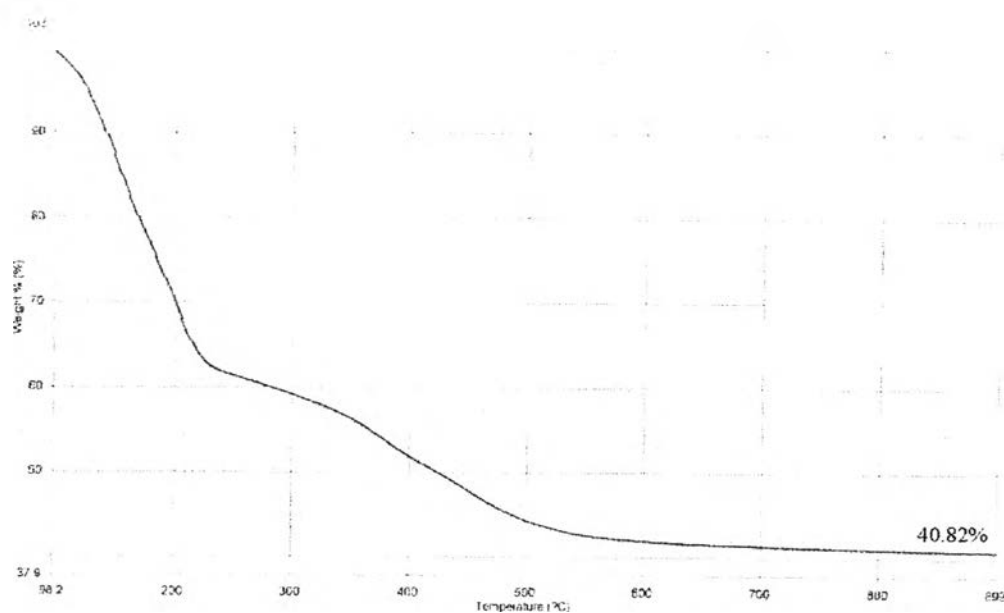


Figure 4.3 TGA thermogram presenting % ceramic yield of EG spirosilicate monomer.

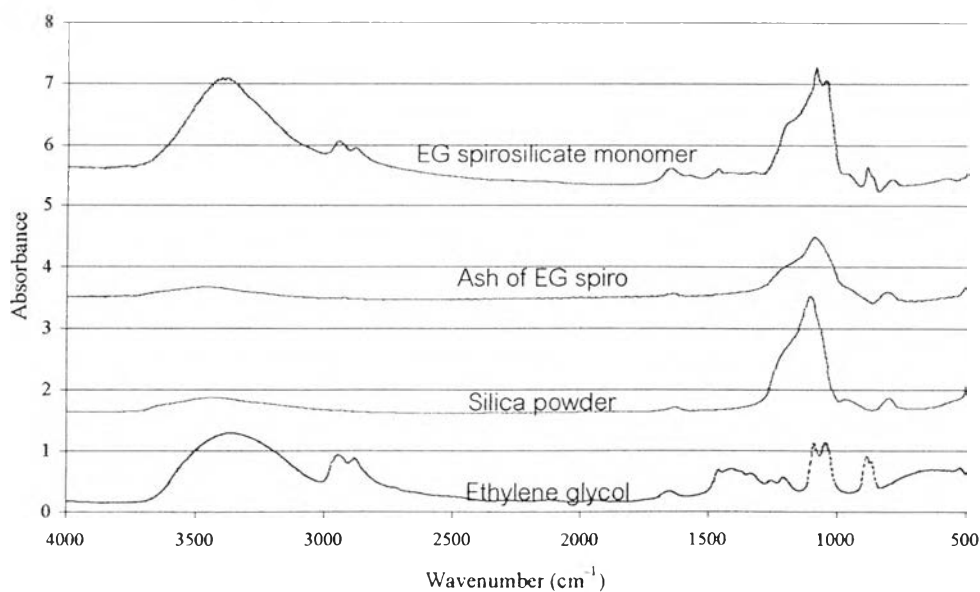
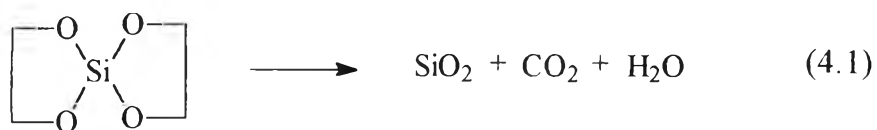


Figure 4.4 FTIR spectra of starting materials, spirosilicate monomer and the remaining ash of EG spirosilicate after characterized by TGA.

4.1.2 Crosslinking of EG spiro silicate

EG spiro silicate monomer synthesized in excess ethylene glycol without further purification was firstly crosslinked by variation of crosslinking temperature in vacuum oven. Table 4.2 shows results obtained from varying the reaction temperature. It was found that 100°C was the best condition for crosslinking EG spiro silicate monomer in vacuum oven. The reason was that at temperature below 100°C, EG was removed too slow and at temperature above 100°C, EG was removed too fast, resulting in too long crosslinking time or too short to control the crosslinking process.

Table 4.2 Variation of crosslinking temperature in vacuum oven.

Temperature (°C)	Result
80	Liquid EG cannot be removed
90	Liquid EG was very slowly removed
100	Liquid EG was removed faster
110	Liquid EG was too fast removed

Another studied condition of crosslinking EG spiro silicate was the crosslinking time. It was characterized using FTIR, DSC and TGA techniques. FTIR spectra in Fig.4.5 shows that the longer crosslinking time, the higher crosslinked peak according to the frequency at 1000-1200 cm^{-1} which indicated Si-O-C bond (Silverstein et.al., 1981). So another techniques used to confirm the degree of crosslink were DSC and TGA to find a more reliable crosslinking time.

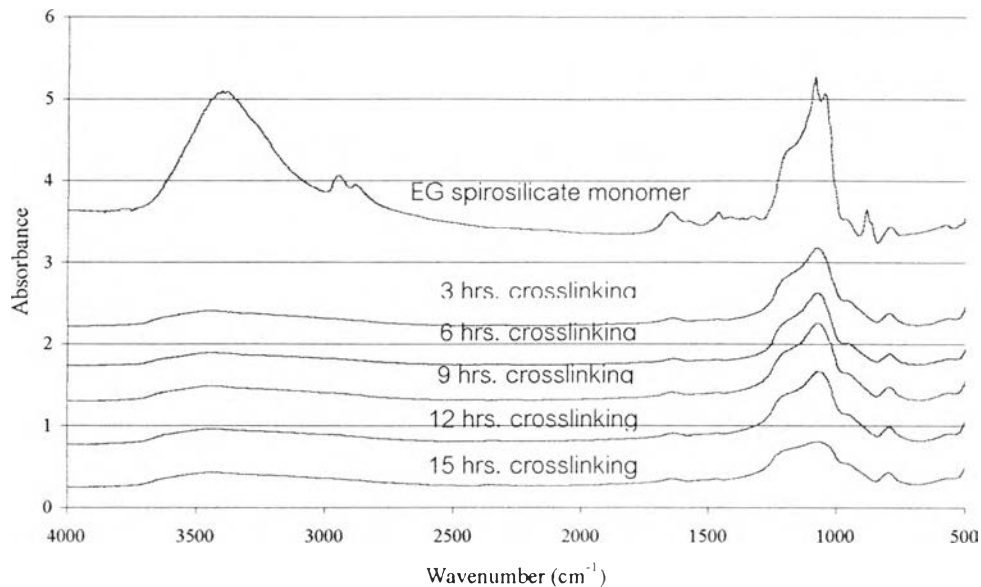


Figure 4.5 FTIR spectra from varying crosslinking time of EG spiro-silicate at 110°C under vacuum.

As presented by Fig. 4.6, DSC was employed to investigate characteristic Tg curve of crosslinked EG spiro-silicate. No change in characteristic Tg curve was observed at 6 to 9 hour crosslinking times and the lowest Tg obtained from these crosslinking reaction time was 5°C. TGA, in Fig.4.7, could confirm the particularly crosslinked time that 6 hours showed the best result referring to the highest % ceramic yield (Hatakeyama & Quinn, 1994).

4.1.3 Pattern process of EG spiro-silicate on SiO₂ wafer

After the thermal crosslinking conditions of EG spiro-silicate were obtained, the EG spiro-silicate was then exposed to UV radiation to get further more crosslinking. As compared to the thermal crosslinking, the UV

radiation resulted in much higher degree of crosslink on the surface of SiO₂ wafer, causing the breaking surface, see Fig 4.8. The longer exposure time, the more brittle surface affected by higher degree of crosslinking. Generally, when the structure contained too much crosslinks, polymer would be more rigid (Charrier, 1991), as displayed in Fig. 4.9.

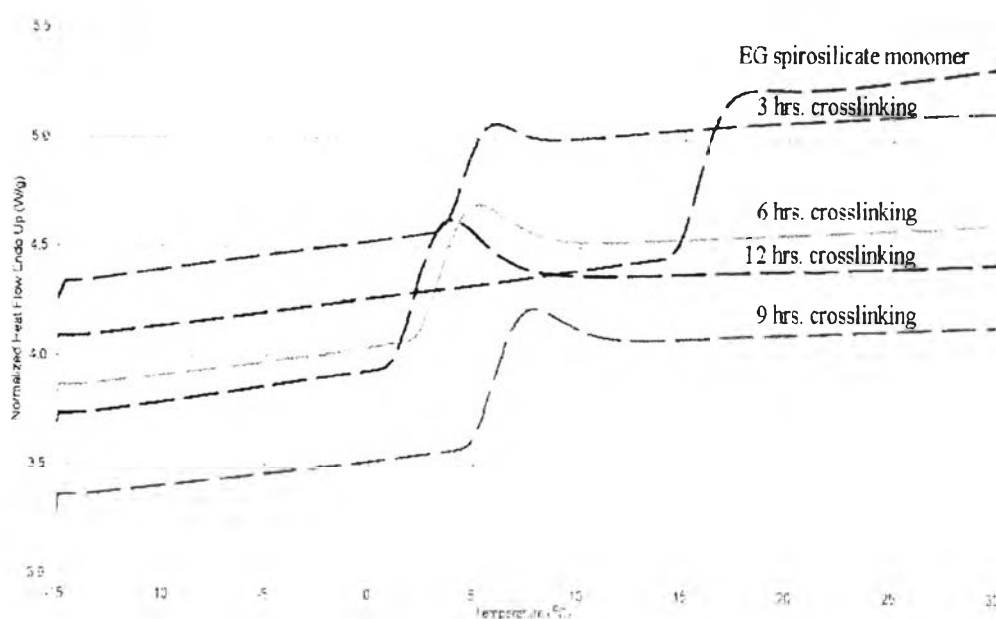


Figure 4.6 DSC thermogram of crosslinked EG spiro silicate at each crosslinking time.

To solve the problem of brittleness on the surface of crosslinked EG spiro silicate due to high stress of crosslinked structure formed, it was thus expected that the higher number of C-C bond in molecule, the more flexibility in the structure.

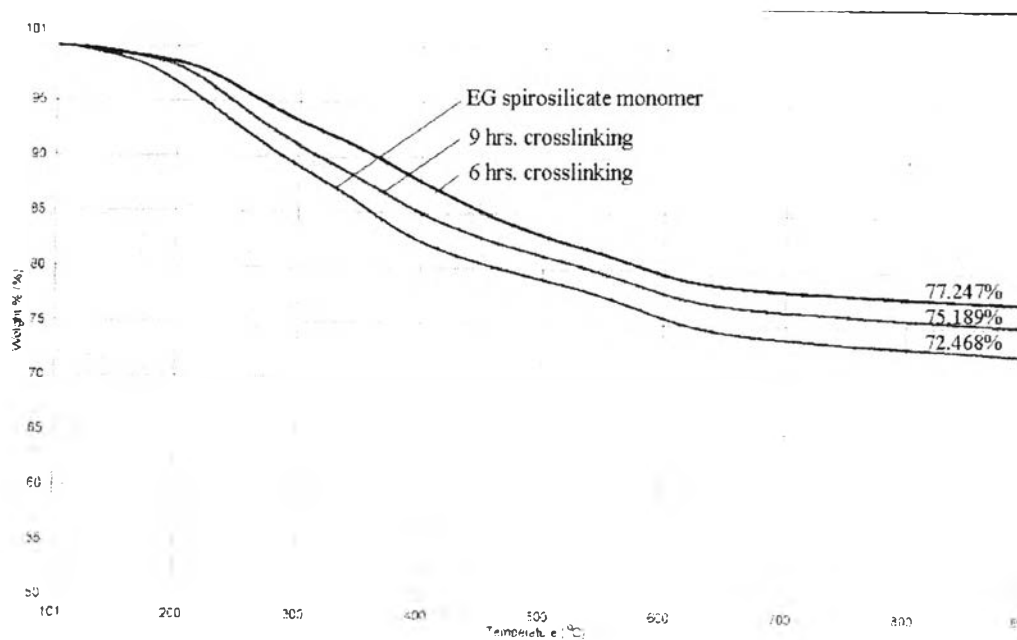


Figure 4.7 TGA thermogram of crosslinked EG spiro-silicate at each crosslinking time.

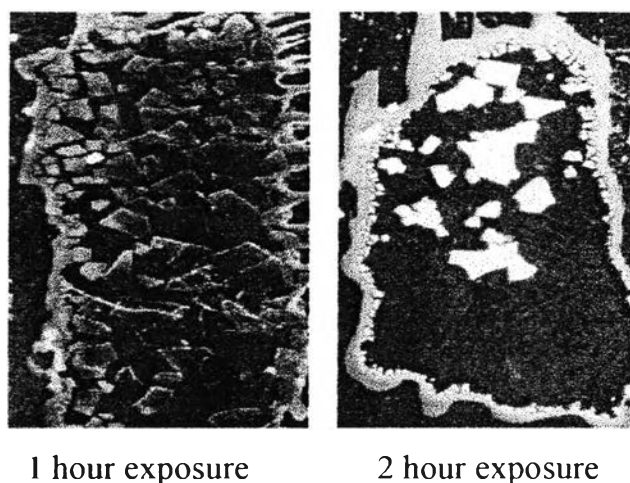


Figure 4.8 Image pattern of crosslinked EG spiro-silicate using UV radiation.

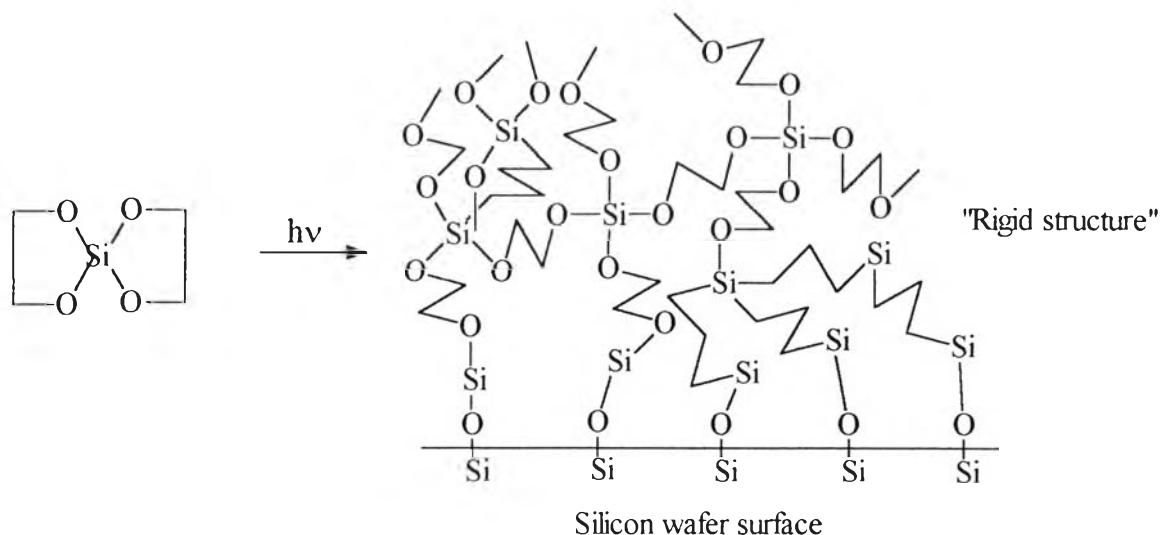


Figure 4.9 Structure of crosslinked EG spiro-silicate on the surface of SiO_2 wafer.

4.2 PG spiro-silicate photoresist

4.2.1 Synthesis and characterization of PG spiro-silicate monomer

PG spiro-silicate monomer could be synthesized using the same conditions used for EG spiro-silicate monomer, except that the reaction temperature was changed to the boiling point of PG (about 240°C). Energy used to form PG spiro-silicate monomer structure was higher than that used to form EG spiro-silicate monomer structure, as calculated by Alchemy Software Program, were 28.13 and 21.86 unit respectively. It means that the same condition for synthesizing EG spiro-silicate monomer can be adopted to synthesize PG spiro-silicate monomer.

To confirm the structure of PG spiro-silicate monomer, FTIR spectra were again employed, see Fig 4.10, to compare between spectra of PG

spirosilicate monomer and starting chemicals. It was found that spectrum of PG spirosilicate monomer showed the absorption peaks at 1100 cm^{-1} and 886 cm^{-1} frequency indicating to Si-O-C of spirosilicate (Silverstein et.al., 1991). For complete characterization PG spirosilicate monomer structure, $^1\text{H-NMR}$ technique (see appendix) using DMSO-d_6 as reference peak was used to clarify the structure, table 4.3 (Skoog & leary, 1992).

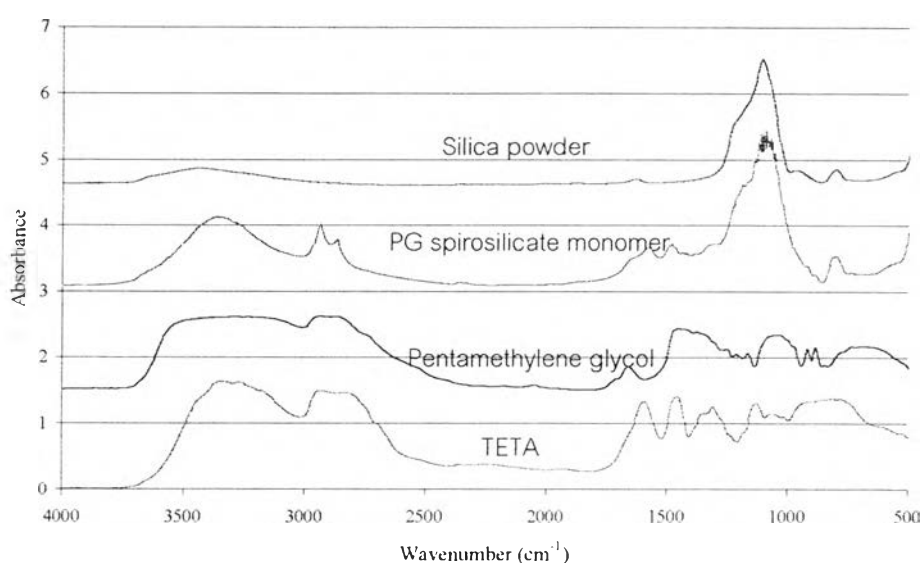
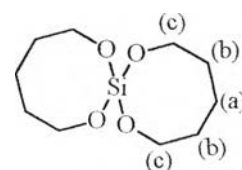


Figure 4.10 FTIR spectrum of PG spirosilicate monomer.

Table 4.3 $^1\text{H-NMR}$ result of PG spirosilicate monomer.

Chemical shift	Structure
a) 1.3 (m)	-CH ₂ (saturated)
b) 1.4 (m)	
c) 2.6 (m)	-CH ₂ -O-
2.5 and 3.3	DMSO-d_6 and H_2O of DMSO-d_6



4.2.2 Pattern process of PG spiro silicate on SiO₂ wafer

Crosslinking PG spiro silicate monomer was carried out using UV radiation. Without photomask, as shown in Fig.4.11. One and one and a half hour exposure time could produce enough crosslinked PG spiro silicate on the surface of SiO₂ wafer, while 2 hour exposure time showed little color, meaning decomposition of the crosslinked PG spiro silicate. The suitable crosslinking time using UV radiation was thus chosen at one and one and half hours. As expected, when comparing with exposed EG spiro silicate, crosslinked PG spiro silicate performed a better brittleness and moisture absorption properties after UV exposure. This was owing to the structure of PG spiro silicate containing more C-C bonds which affected on the flexibility of polymer chain and increased hydrophobic properties, as well, see Fig.4.12.

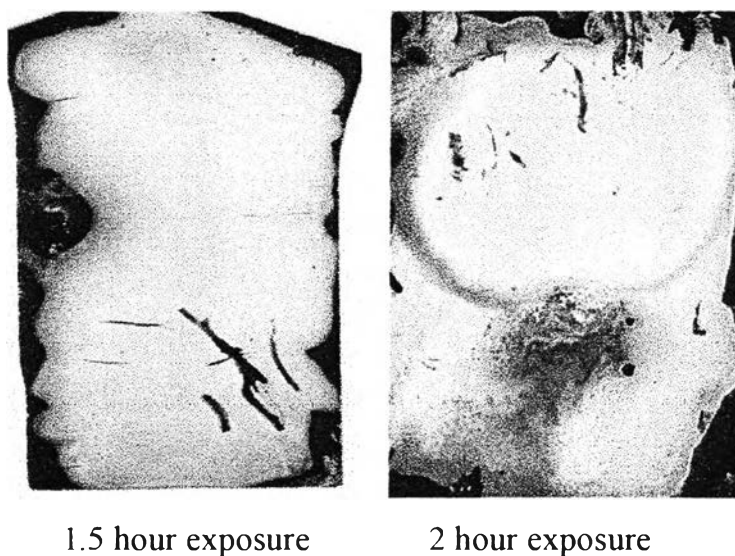


Figure 4.11 Crosslinked PG spiro silicate on the SiO₂ wafer using UV radiation without photomask.

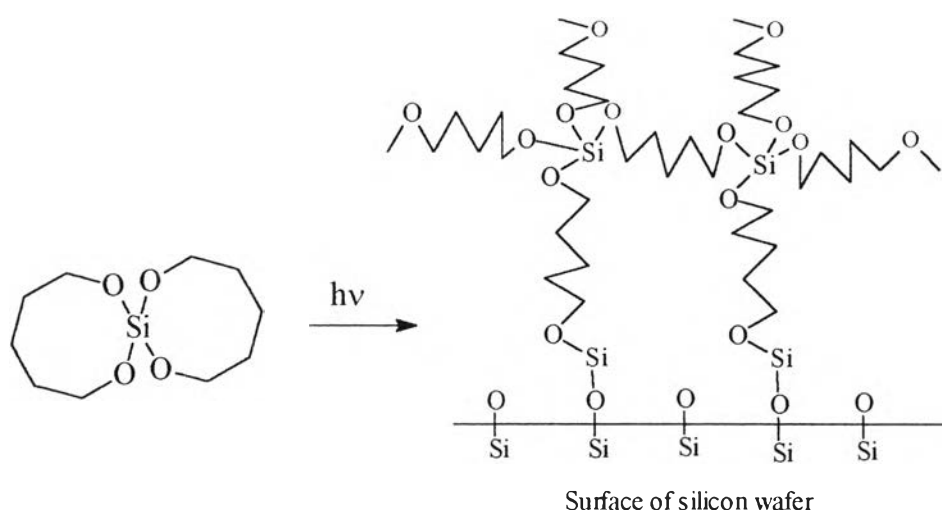


Figure 4.12 Schematic drawing of crosslinked PG spirosilicate structure.

4.2.3 Etching process of PG spirosilicate photoresist

After using photomask to cover the surface of polymer film during exposing UV, the suitable exposure time become longer, Fig.4.13. When using a suitable etching solution, which was 66% acetic acid in the solution of water, results showed that 3 hour exposure time was not enough for crosslinking because its surface was destroyed after passing through the 66% acetic acid etching solvent. Although, many results of crosslinked PG spirosilicate listed better properties than crosslinked EG spirosilicate, PG spirosilicate could not be used as polymeric photoresist because its properties, such as, low chemical durability and low resolution, would lead to bad quality of photoresist. Another solution was to look for a better side wall deposition polymer giving high resolution and enough thickness to use as a DNA detector.

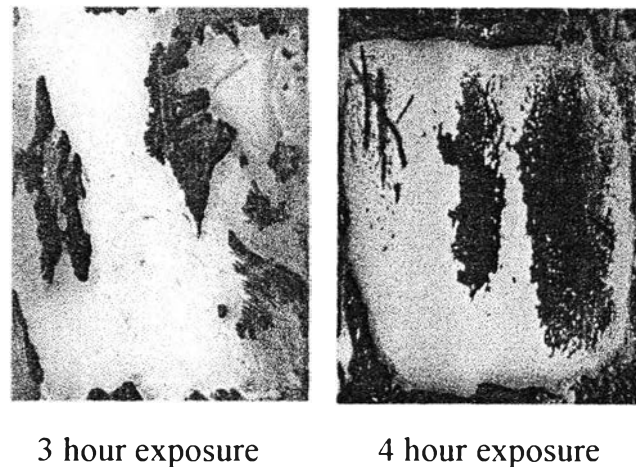
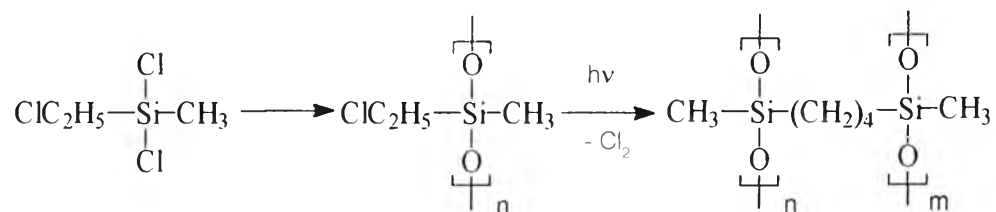


Fig 4.13 Image pattern after etching of crosslinked PG spiro-silicate.

4.2 2-Chloroethylmethyldichlorosilane photoresist



4.3.1 Pattern process of 2-chloroethylmethyldichlorosilane on SiO₂ substrate

Regarding problems of EG and PG spiro-silicate photoresist presented, 2-chloroethylmethyldichlorosilane was chosen to process polymeric photoresist on the surface of SiO₂ wafer. Exposure time was the first step of finding a suitable condition for uncovered and covered photoresists by photomask during processing of UV exposure. For uncovering photomask process, results of spectra, in Fig.4.14 and Table 4.4, indicated that the longer exposure time the higher crosslinked bond (Silverstein et.al.,1991).

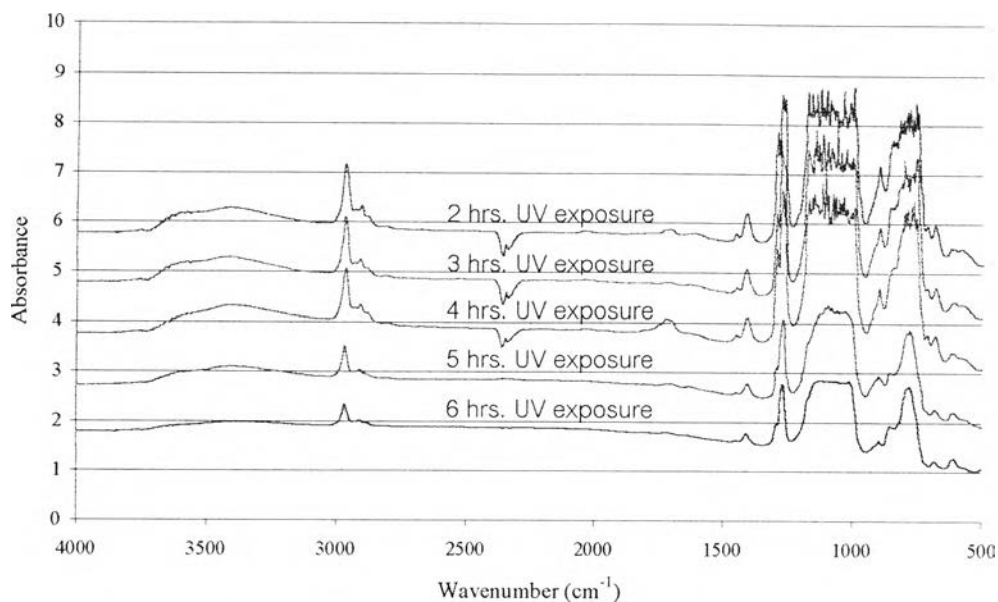


Figure 4.14 FTIR spectra of crosslinked 2-chloroethylmethyldichlorosilane using variation of UV radiation time without photomask covering.

Table 4.4 FTIR assignment of crosslinked 2- chloroethylmethyldichlorosilane in Fig 4.15.

Frequency (cm^{-1})	Functional group
2950	Saturated C-H stretching
1400	-CH ₂ - aliphatic
1270-1250	Si-CH ₂
1150-1000	Si-O- aliphatic
870-800	Si-X (X = Cl, F)

When using photomask to partially shield the ray of UV radiation, 2-chloroethylmethyldichlorosilane monomer coated SiO₂ wafer increased the exposure time to 4 hours, as exhibited in Fig.4.15. FTIR spectra indicated that the longer exposure time than 4 hours was preferred according to the decrease in peak intensity at the range of 608-674 cm⁻¹ relating to -CH₂-Cl bond (Koenig, 1992). From all results they can be summarized that the suitable time for UV projection was be 4 hours.

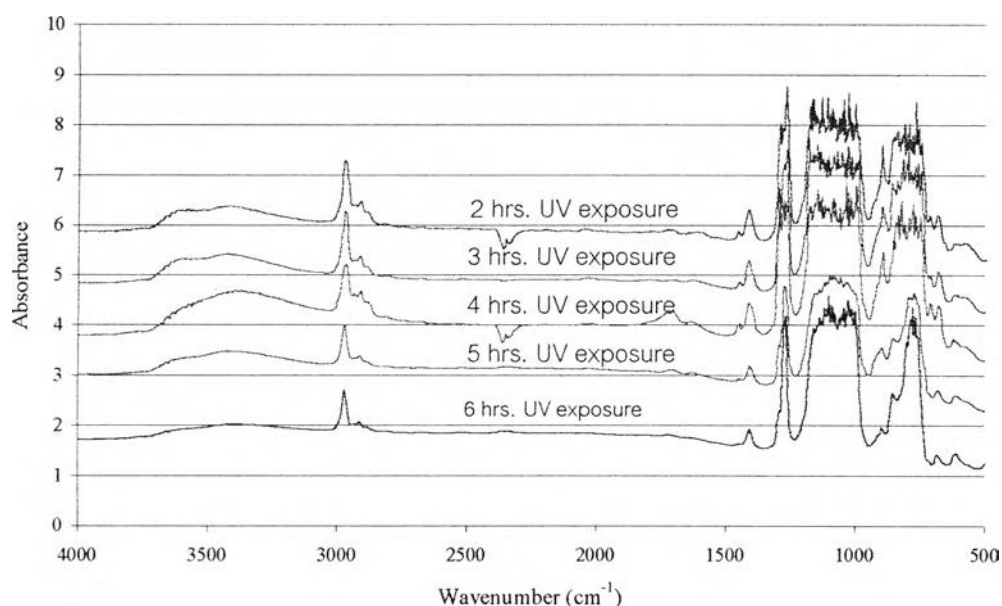


Figure 4.15 FTIR spectra of crosslinked 2-chloroethylmethyldichlorosilane using UV radiation with photomask.

TGA technique was also used to support the result that 4 hour exposure time was not enough to form completely crosslinked 2-chloroethylmethyldichlorosilane. By comparing calculated with experimental % ceramic yields, 69.0% and 50.7 %, respectively, the experimental data showed lower value, meaning that crosslinked reaction was not complete (Fig.4.16).

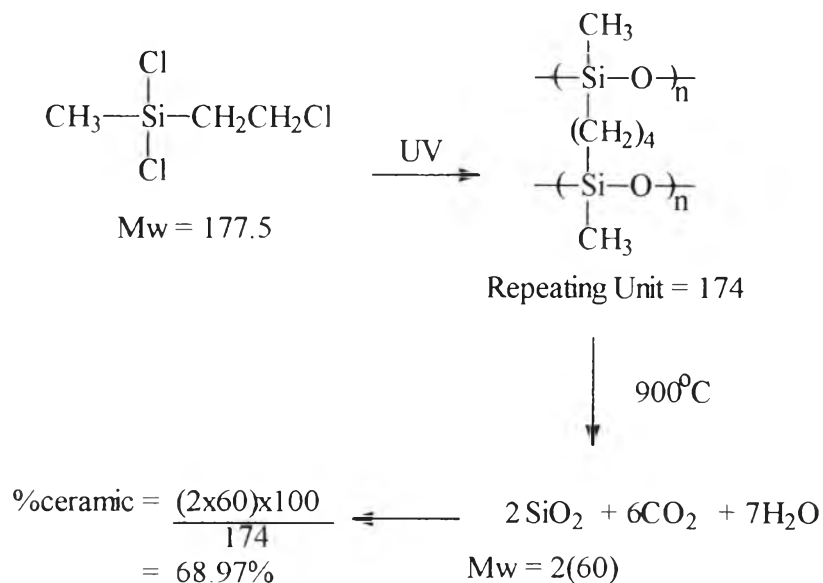


Figure 4.16 Theoretical % ceramic yield of the repeating unit of a fully crosslinked 2-chloroethylmethyldichlorosilane.

To support the structure of partially crosslinked 2-chloroethylmethyl-dichlorosilane, MS technique was used to explain, as shown in Fig.4.17. It showed that the base peak at $m/e = 314$ correlated to the structure rationalized in this figure.

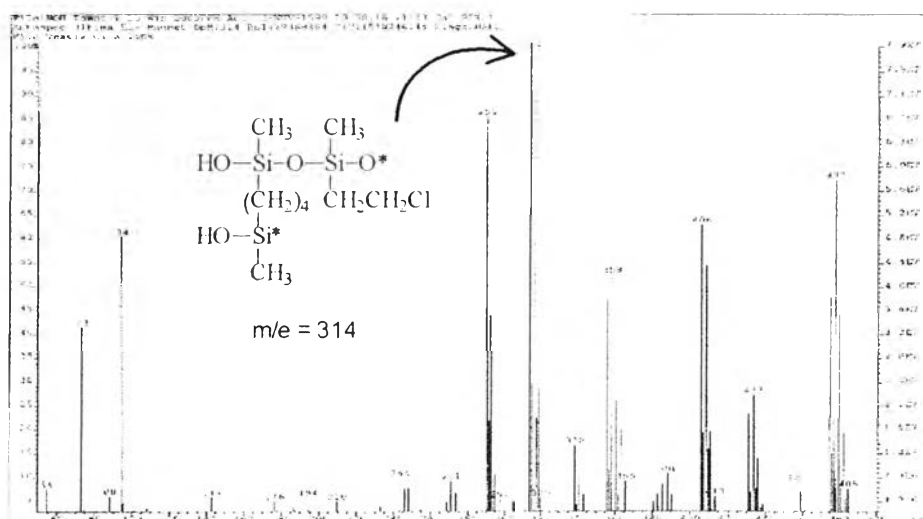


Figure 4.17 MS spectrum representing structure of partially crosslinked 2-chloroethylmethyl-dichlorosilane.

4.3.2 Etching Process of 2-Chloroethylmethyldichlorosilane Photoresist

After the exposure condition was obtained, the developing step was next investigated. This step was firstly varied the etching solvent by grouping as acidic, aromatic, aliphatic and mixed solvents to pattern crosslinked 2-chloroethyl-methyldichlorosilane on surface of SiO₂ wafer with variation of etching temperature. Table 4.5 listed a number of chemicals used as etching solvent. Acidic solvents were mostly effective agent of all etching reagent. It is worth nothing that at 80°C etching temperature, concentrated HCl gave pattern process of positive photoresist whereas less percentage of H₂SO₄ resulted in negative photoresist pattern.

Table 4.5 Effect of chemical etching solvents on lithographic process.

Type of solvent	Covered part		Uncovered part	
	Room Temp.	80°C	Room Temp.	80°C
Acidic solvent				
H ₂ SO ₄	O	O	O	O
95% H ₂ SO ₄	O	O	O	O
90% H ₂ SO ₄	O	O	O	O
85% H ₂ SO ₄	O	O	X	O
80% H ₂ SO ₄	X	O	X	X
75% H ₂ SO ₄	X	X	X	X
70% H ₂ SO ₄	X	X	X	X
HCl	X	X	X	O
HNO ₃	X	X	X	X
CH ₃ COOH	X	X	X	X
50%CH ₃ COOH	X	X	X	X
Aromatic solvent				
Benzene	X	-	X	-
Toluene	X	-	X	-

Table 4.5 (Cont'd)

Type of solvent	Covered part		Uncovered part	
	Room Temp.	80°C	Room Temp.	80°C
Aliphatic solvent				
Methanol	X	-	X	-
n-Propanol	X	-	X	-
Dichloroethane	X	-	X	-
Diethyl ether	X	-	X	-
Methylene chloride	X	-	X	-
Mixed Solvent (v/v)				
1:1 H ₂ SO ₄ +HNO ₃	X	X	X	X
1:1H ₂ SO ₄ +H ₂ O ₂	X	X	X	X
1:1 H ₂ SO ₄ +CH ₂ Cl ₂	X	-	X	-
1:1:1 H ₂ SO ₄ +CH ₂ Cl+ CH ₃ OH	X	-	X	-
1:1 H ₂ SO ₄ +Toluene	X	-	X	-
1:1:1 H ₂ SO ₄ +Toluene+ CH ₃ OH	X	-	X	-
1:1 HCl+diethylether	X	-	X	-
1:1 HCl+CH ₂ Cl ₂	X	-	X	-
Mixed Solvent (v/v)				
1:1 CH ₃ COOH+H ₂ O ₂	X	X	X	X
1:1 CH ₃ COOH+ Propanol	X	X	X	X
1:1 CH ₃ COOH + Diethylether	X	-	X	-
1:1:1 CH ₃ COOH + Propanol + Diethylether	X	-	X	-

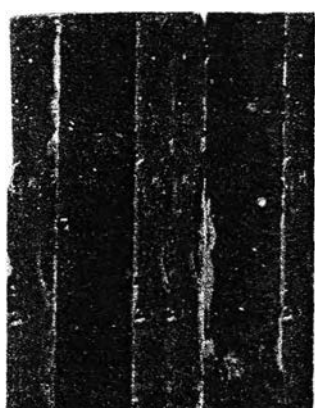
O = Can etch

X = Cannot etch

In addition, the variation of temperature in variable solvent was delicately investigated, as shown in table 4.6. Precisely, the highest resolution and the easiest etching processing were found in the condition of boiled 70% H₂SO₄ in solution of water for 2 minutes, as observed in Fig.4.18 exhibiting the pattern surface after etching.

Table 4.6 Effect of temperature on etching.

Type of solvent	Covered part	Uncovered part
Boiled 10% H ₂ SO ₄	X	X
Boiled 30% H ₂ SO ₄	X	O
Boiled 50% H ₂ SO ₄	O	O
Boiled 60% H ₂ SO ₄	X	X
Boiled 70% H ₂ SO ₄	X	O
Boiled 80% H ₂ SO ₄	O	O



Boiled 70% H₂SO₄



80% H₂SO₄ 80°C



90% H₂SO₄ 80°C

Figure 4.18 Image pattern of partially crosslinked 2-chloroethylmethyl-dichlorosilane at varied etching.

Coating 2-chloroethylmethyldichlorosilane on SiO₂ wafer was studied with/without using spincoater and using photomask to cover polymer film. Without using spincoater, pattern resulted after etching is shown in Fig. 4.19. Approximately the best condition should be 4 hour exposure time with enough thickness. 3 Hour exposure time was too short because the polymer was all etched whereas 5 and 6 hour exposure times were too long because side wall deposition pattern cannot be formed due to their brittleness.

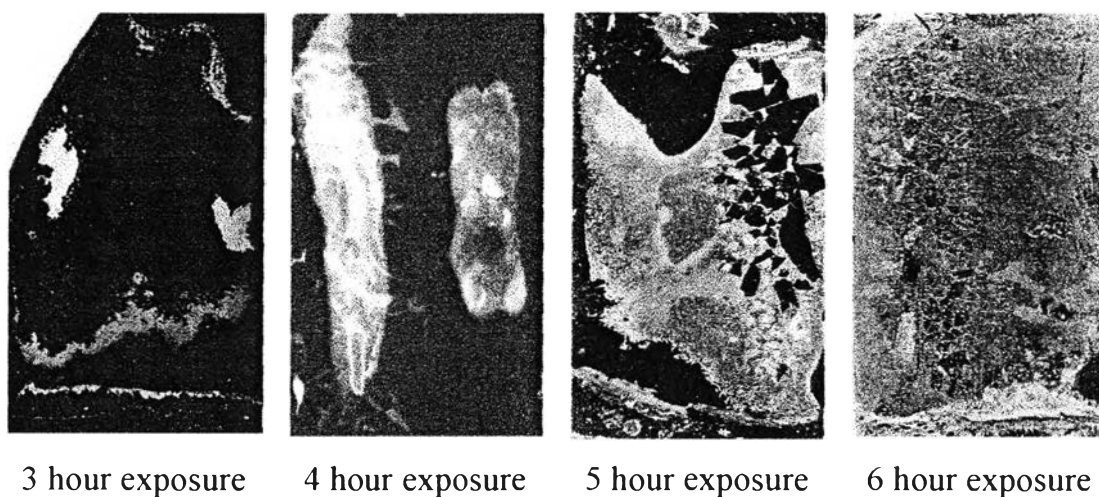


Figure 4.19 Image pattern of partially crosslinked 2-chloroethylmethyldichloro-silane without using spincoater at varied UV exposure time.

With using spincoater to control smoothness for coating 2-chloro-ethylmethyldichlorosilane on SiO₂ wafer, speed of spincoater was varied from 200 to 500 rpm with 100 rpm interval, as shown in Fig. 4.20, 4.21, 4.22, and 4.23, respectively. By comparing results of speed variation, the

speed of spincoater at 200 rpm gave the highest resolution pattern at 4 hour exposure time with the same etching condition. At higher speed than 200 rpm, they demonstrated the worse pattern. The higher the speed, the worse the resolution. According to more difficulty of etching when the spinning speed was increased, it resulted in a thinner film. The covered part, including all adjacent area of exposed region, became easier crosslinked due to easier heat transfer.

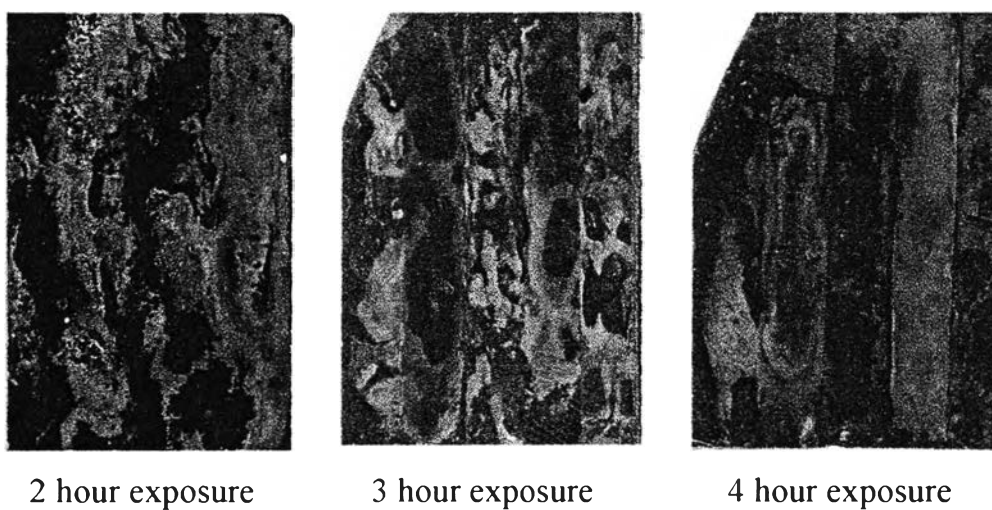


Figure 4.20 Image pattern of partially crosslinked 2-chloroethylmethyl-dichlorosilane using spincoater at 200 rpm, and varied UV exposure time.

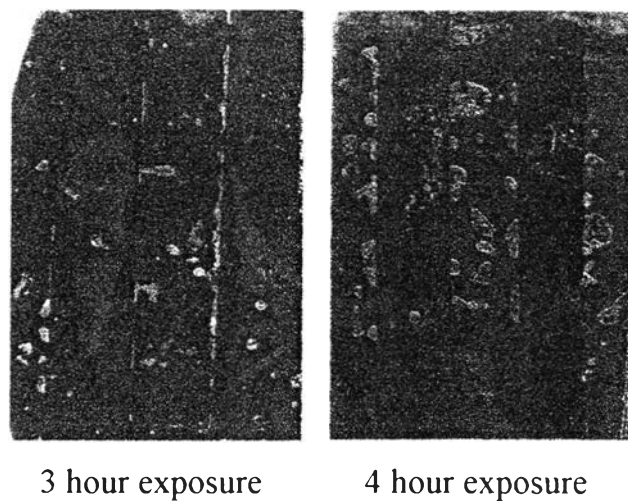


Figure 4.21 Image pattern of partially crosslinked 2-chloroethylmethyl-dichlorosilane using spincoater at 300 rpm, and two different UV exposure time.

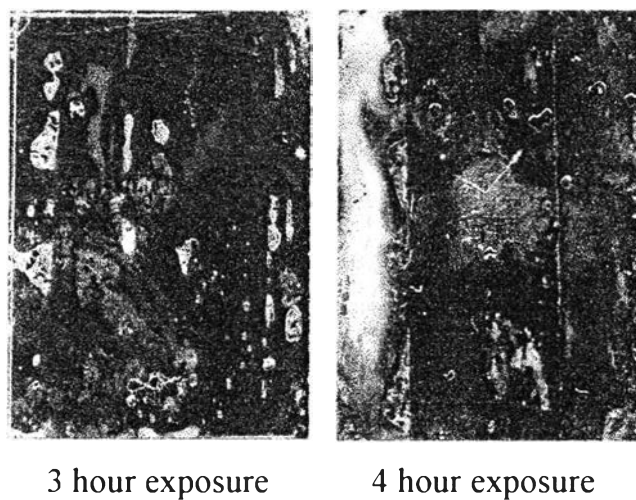


Figure 4.22 Image pattern of partailly crosslinked 2-chloroethylmethyl-dichlorosilane using spincoater at 400 rpm, and two different UV exposure time.

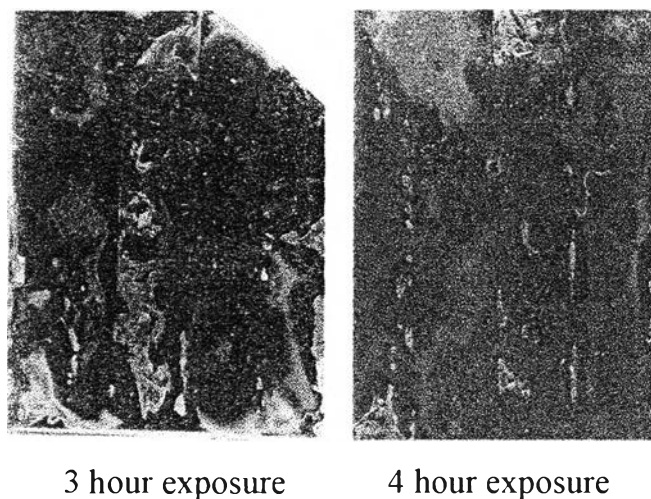


Figure 4.23 Image pattern of partailly crosslinked 2-chloroethylmethyl-dichlorosilane using spincoater at 500 rpm, and two different UV exposure time.

4.3.3 Effect of type of photomask on 2-chloroethylmethyldichloro-silane photoresist

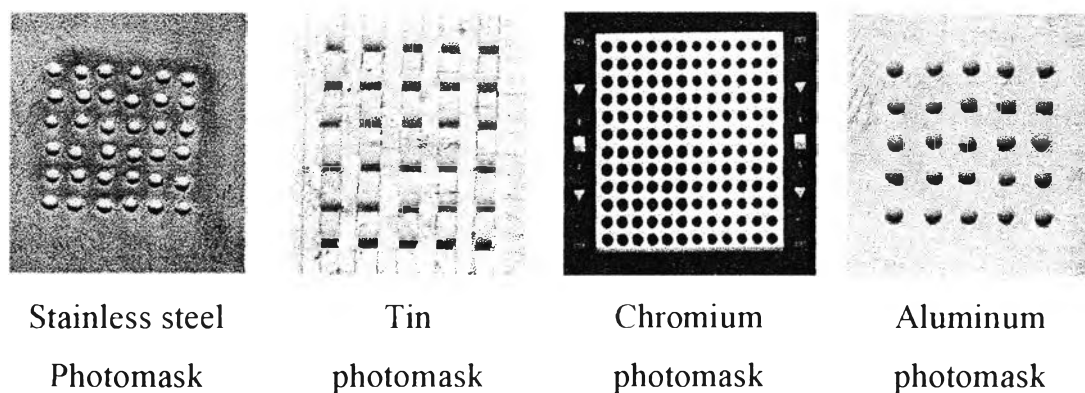


Figure 4.24 Pattern of photomasks used.

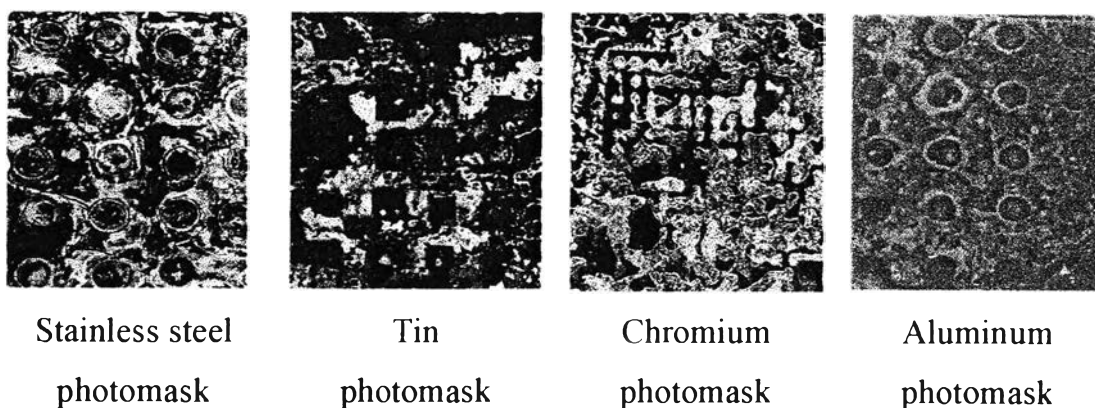


Figure 4.25 Image pattern of partially crosslinked 2-chloroethylmethyldichlorosilane using spincoater at 200 rpm with varied type of photomask.

Another effect studied was type of photomask whether its thermal conductivity has any effect on the photoresist. Fig.4.24 shows different type of photomask having different thermal conductivity, and Fig.4.25 shows that stainless steel and tin photomasks which have lower thermal conductivity, 0.187 and 0.666 W/cm K, introduced negative photoresist patterns, whereas chromium and aluminum photomasks which have higher thermal conductivity, 0.937 and 2.37 W/cm K, produced positive photoresist pattern. It could be explained by simulation of forming negative and positive photoresist patterns in Fig. 4.26 and 4.27, respectively.

For negative photoresist, the exposed areas could be directly formed crosslinked structure while the shielded areas much less crosslinked reaction was occurred. After etching process with boiled 70% H_2SO_4 solution, the crosslinked 2-chloroethylmethyldichlorosilane was left on a surface of SiO_2 wafer generating negative photoresist pattern.

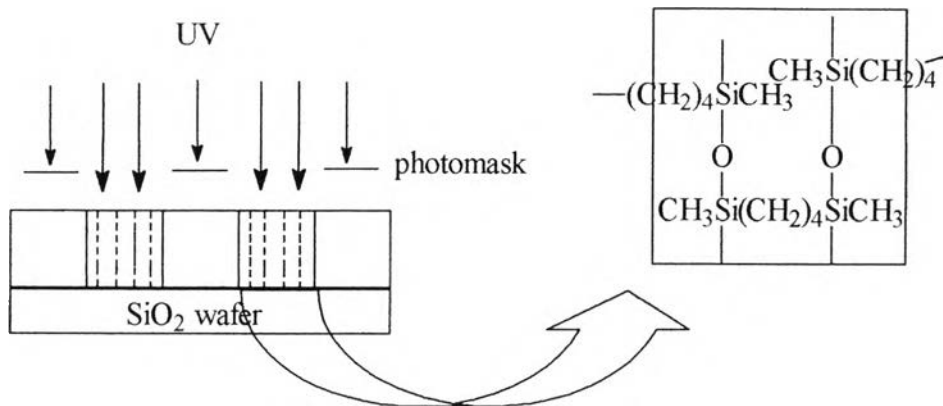


Figure 4.26 Simulation of negative photoresist formation using stainless steel and tin photomasks.

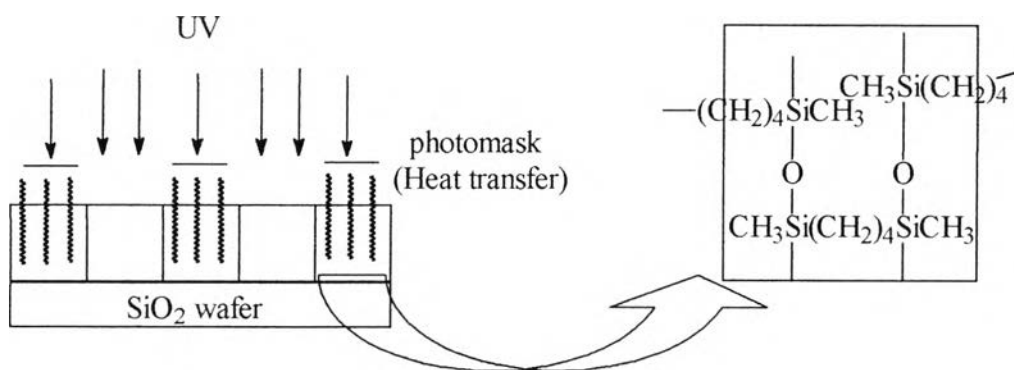


Figure 4.27 Simulation of positive photoresist formation using chromium and aluminum photomasks.

On the other hand, for positive photoresist, the reaction at the uncovered area occurred much less crosslinking than the embedded areas due to the higher heat transfer from metal to the polymer. After etching process with boiled 70% H₂SO₄ solution, the highest crosslinked part, covered area of 2-chloroethylmethylchloro-silane would be left on the surface of SiO₂ wafer exhibiting positive photoresist pattern.