

CHAPTER II

LITERATURE SURVEY

The silicon-based feed stock chemicals were firstly derived from the carbothermal reduction of silica to silicon metal (Si), as illustrated in eq. (2.1) by Kirk-Othemer (Kirk-Othemer, 1979).



The resulting metallurgical grade silicon (90-98% purity) must then undergo further processing to make other products, for example, to provide access to organosilicon compounds via reaction of Si with alkyl or aryl chlorides in the presence of catalyst:

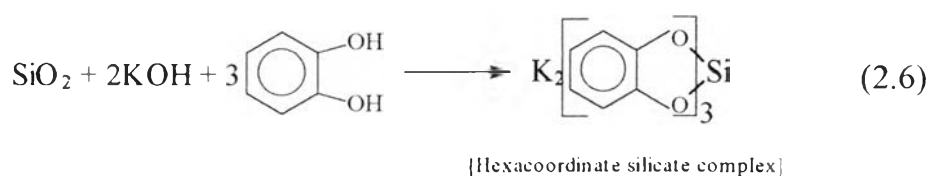


This reaction only works well when RCl is MeCl. Alternately, Si reacted with Cl₂ as eq. (2.3) or HCl as eq. (2.4) to make SiCl₄ can then be burned to make many of industrially useful (high purity) forms of silica as fumed or electronics grade silica[eq. (2.5)]:

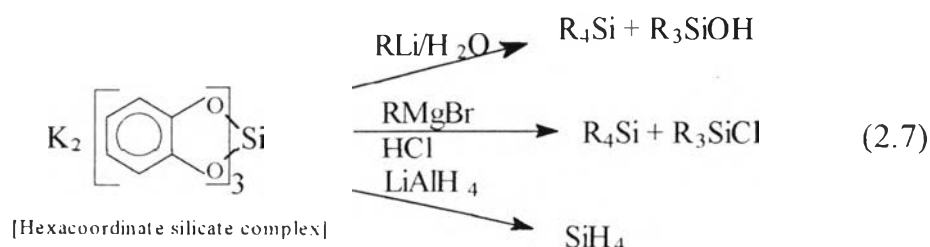


However, carbothermal reduction requires high heat and specialized equipment. The result is an energy and equipment intensive process. The preparation of useful silicon-containing compounds has thus been developed

which can be further reacted to produce a variety of useful soluble silicon products starting from silica and using a simple and inexpensive reaction. Rosenheim and coworkers (Rosenheim et al., 1931) were the first group to describe the direct reaction of silica with a coordinating ligand. They found that catechol could be used to transform a wide variety of metal oxides into catecholato complexes, as illustrated in eq. (2.6):



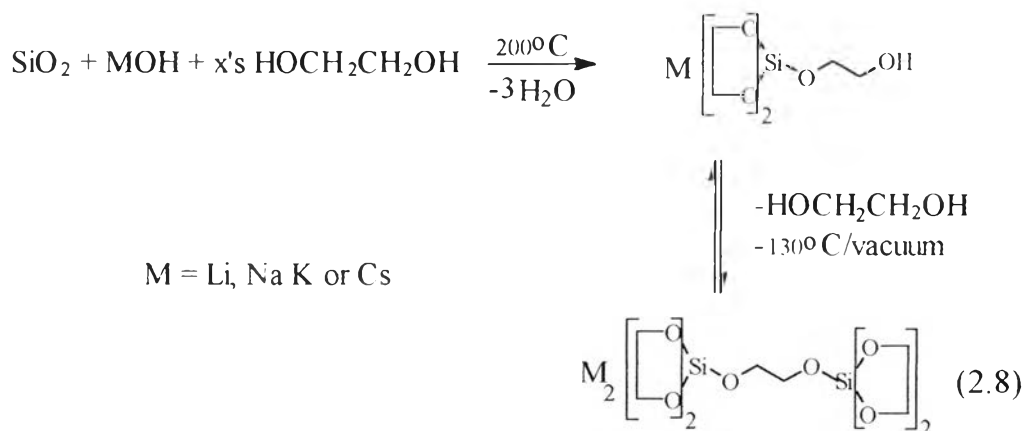
These reports showed that the reactions of silica with 1,2 aromatic diols provided hexacoordinate, monomeric silicon complex, which required lower temperature than that employed by carbothermal reduction. Corriu and coworkers (Corriu, et al., 1983, 1988, 1990) were able to search for new synthetic routes to silicon containing compounds, and explore methods of transforming the resulting tricatecholato silicates into a wide variety of Si-containing compounds by reaction with strong nucleophiles, such as aryl or alkyl Grignard or lithium reagents, as shown in eq. (2.7):



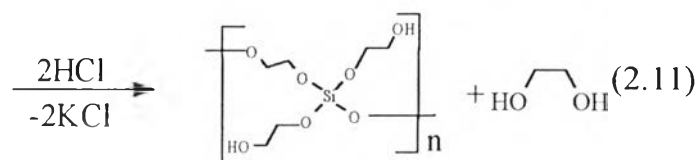
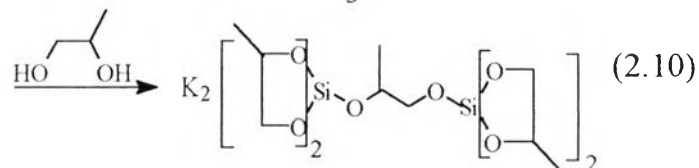
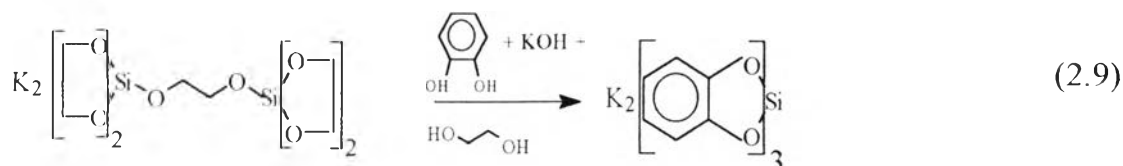
where R is alkyl, aryl or SnR'_3 group.

The problem with this approach is that, this catechol silicate complex is relatively expensive and stable. It can only be modified under forcing conditions using expensive reagents, and the products are limited to tri- or tetrasubstituted silicon. The large-scale utility is thus limited. Furthermore, formation of mono- and dialkyl derivatives that are primarily sought by industry for polymer synthesis was not possible.

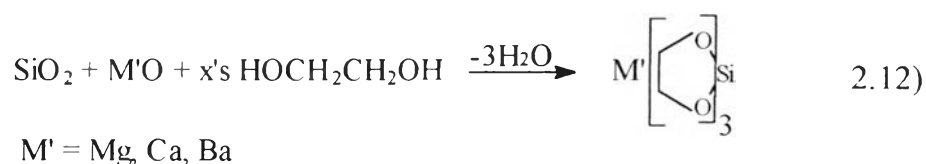
In principle, it would be desirable to develop more reactive complexes of silica. Laine and coworkers (Laine, et al., 1991, 1993) discovered a new inexpensive synthetic route to organosilicon compounds, using aliphatic 1,2 or 1,3 diols, such as ethylene glycol instead of catechol, in the presence of an alkali base. These complexes were found to contain one or more anionic pentacoordinate silicon atoms, as shown in eq. (2.8).



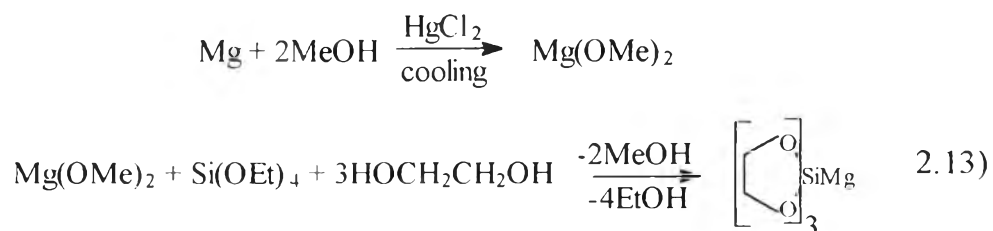
When M is an alkali metal such as Li, Na or K the product obtained was dimeric pentacoordinate anionic. However, if Cs was used, the product acted as monomeric species. Moreover, the products in eq. (2.8) can be used as reactant to further synthesize the derivatives of pentacoordinate spirosilicate, as shown in eq. (2.9), (2.10) and (2.11)



On the other hand, if the group II metal oxide ($M = \text{Mg}, \text{Ca}, \text{Ba}$) was used, the hexacoordinate dianionic silicate will be obtained [eq. (2.12)]



However, when MgO was used in reaction (eq. 2.12), the yields were very low. As a result, an alternative synthesis was developed, see eq. (2.13).



Based on previous research work, Suwankrughasn (Suwankrughasn, M., 1995) synthesized the glycolato siloxane polymer. It was found that suitable condition to synthesize crosslinked spiro-silicate was the reaction time of 24 hours using triethylentetramine, TETA, which was a base catalyst, 25 mole% as presented in eq (2.14):



As for the application, there have been many researchers trying to use these silicon derivatives. In 1993, Yoshino and coworkers (Yoshino, et al., 1993) discovered surface modification of glass that the contact angles on the surface of modified glass were dependent on the fluorocarbon chain length. From the modification of the glass surface by using the silane coupling agents, it was found that the hydrophilic glass surface could be covered effectively by the longer fluorocarbon chains. With the effect on the contact angles of the hydrocarbon moiety, Si-CH₂-CH₂- was reduced according to an increment of *n* of -(CF₂)_{*n*}CF₃. In addition, these data indicated that the fluorocarbon displayed water and oil repellence.

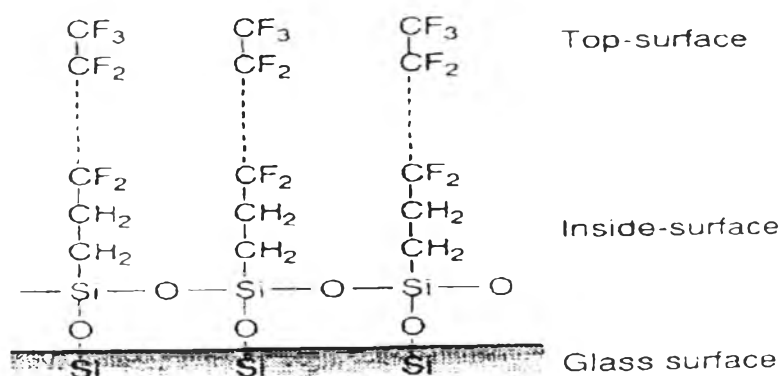


Figure 2.1 Illustration of the glass surface modified with (1H,1H,2H,2H-polyfluoroalkyl) trimethoxysilanes (Yoshino, et al., 1993).

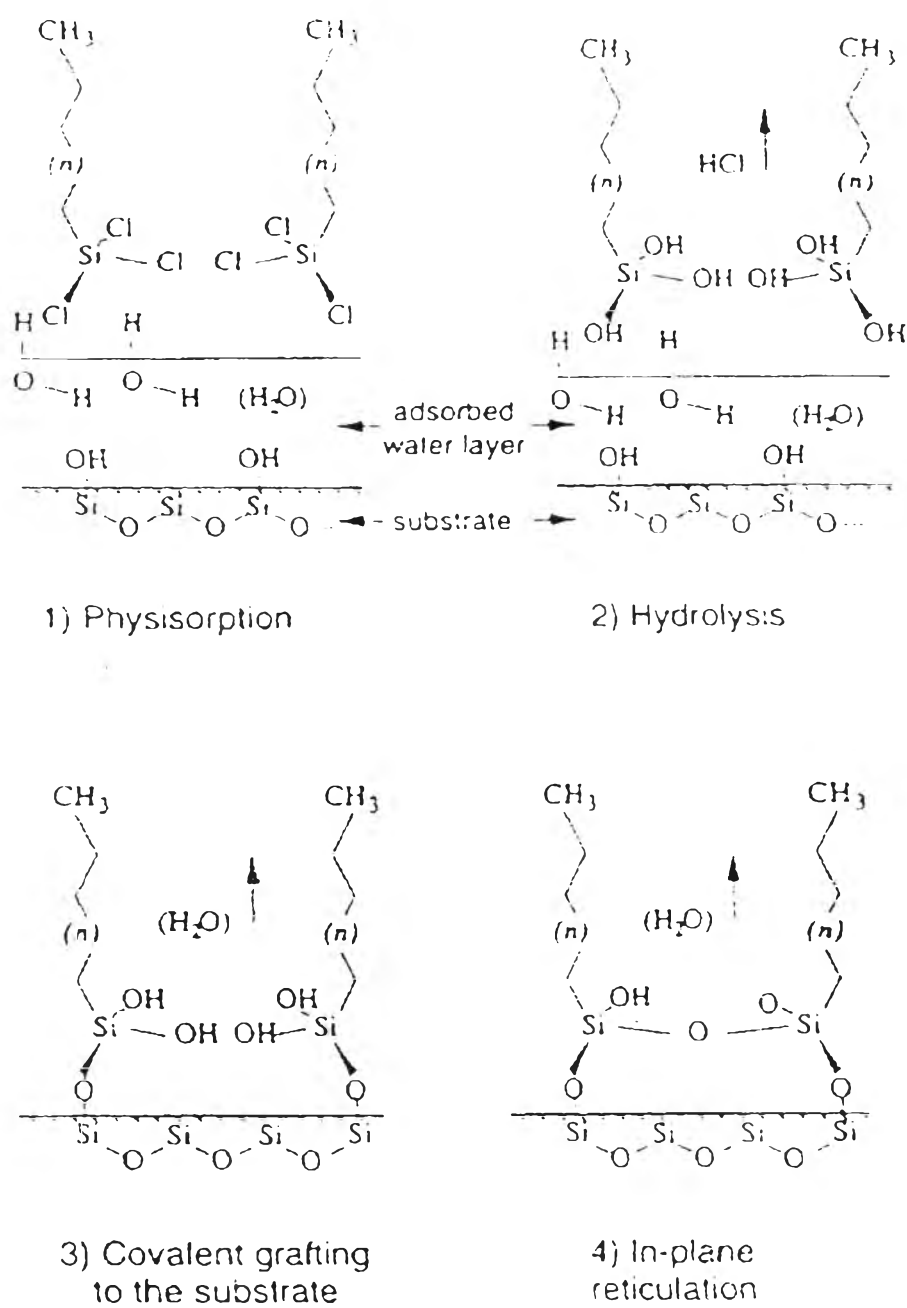


Figure 2.2 General schematic proposal for the silanization reaction. Note the presence of thin adsorbed water layer over the "bare" silica surface (Brzoska et al., 1994).

Brzoska and co workers (Brzoska et al., 1994) presented the effect of water absorption on SiO₂ wafer that the minimum amount of water was necessary for optimum monolayer deposition. In the case of octadecyltrichlorosilane (OTS), the proposed mechanism of silanization is summarized in the Fig. (2.2); there is an initial water layer present on the substrate onto which the organic molecules contained in the reactive solution can gradually absorb (stage 1). Following physisorption, the trichlorosilane head groups hydrolyze and form trisilanols (stage 2). Moreover, the presence of a thin film of fluid permits the in-plane lateral mobility of the long-chain silanes by Brownian motion. This leads to important in-plane reorganizations, in a manner analogous to Langmuir monolayers of short-chain surfactants submitted to lateral compression. Under the proper thermodynamic conditions (e.g. control of the temperature of the reaction), a uniform densely packed monolayer of vertical chains in their *all-trans* ordered conformation is formed. At later times, covalent siloxane bonds can take place at the head group-substrate interface (stage 3). The later becomes grafted to the solid surface. In addition, intermolecular crosslinking by the trisilanol head group can occur, providing the favorable distance and orientation between the groups. The end result is a 2D network of polysiloxane (stage 4). Stages 3 and 4 will obviously be facilitated by a moderate baking of the substrate, which will help to remove the water layer.

In 1996, the silane compound was mentioned in many cases of application, there were many interesting researches in photoresist area using metal to produce pattern on circuit board. However, in the application of biochip sensor the metallic photoresist has been limited due to not enough thickness formation, so the polymer was created to produce photoresist material. Chrisey and coworkers (Chrisey et al., 1996) used the created photoresist pattern for selective metallization of silane to form single DNA

surfaces. With positive-tone resist, Fig. (2.3), the DNA was ultimately bound wherever 405 nm light was allowed to impinge on the surface. For the negative-tone resist, the DNA was immobilized wherever the substrate was protected from 254 nm irradiation, as summarized in Fig. (2.4).

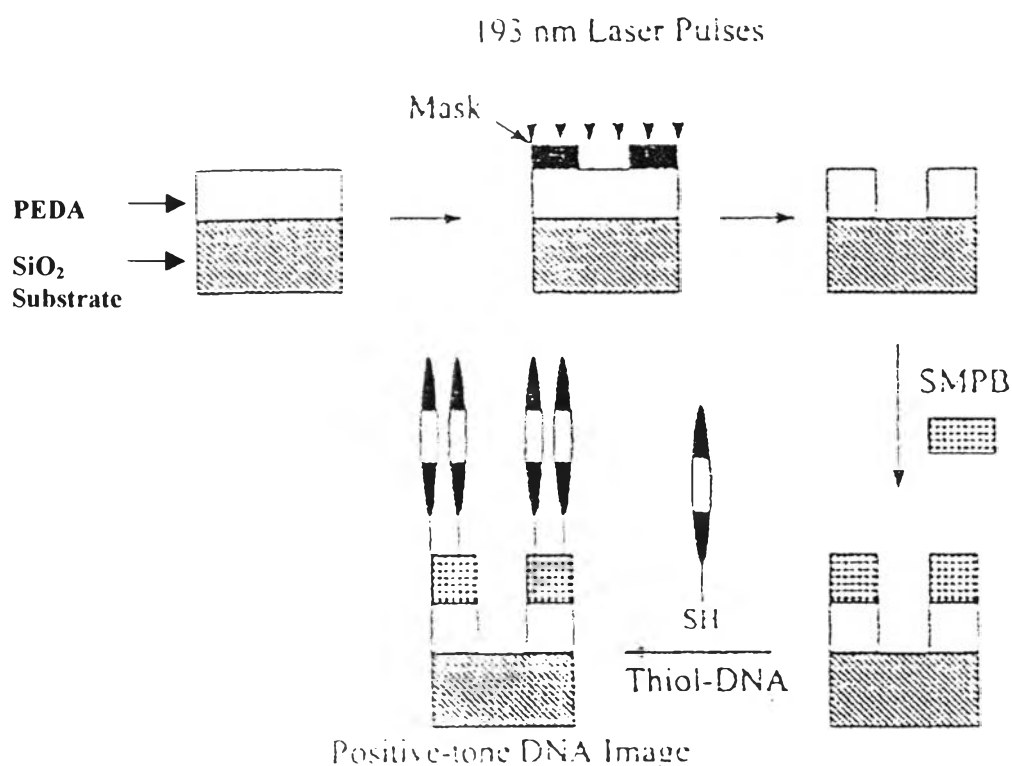


Figure 2.3 Schematic of the direct, deep UV (193 nm) method for patterning of PEDA films. An alternate configuration of process involves deep UV irradiation of a SMPB-modified PEDA film to produce a patterned surface which is then treated with thiolated DNA oligomer (Chrissey et al., 1996).

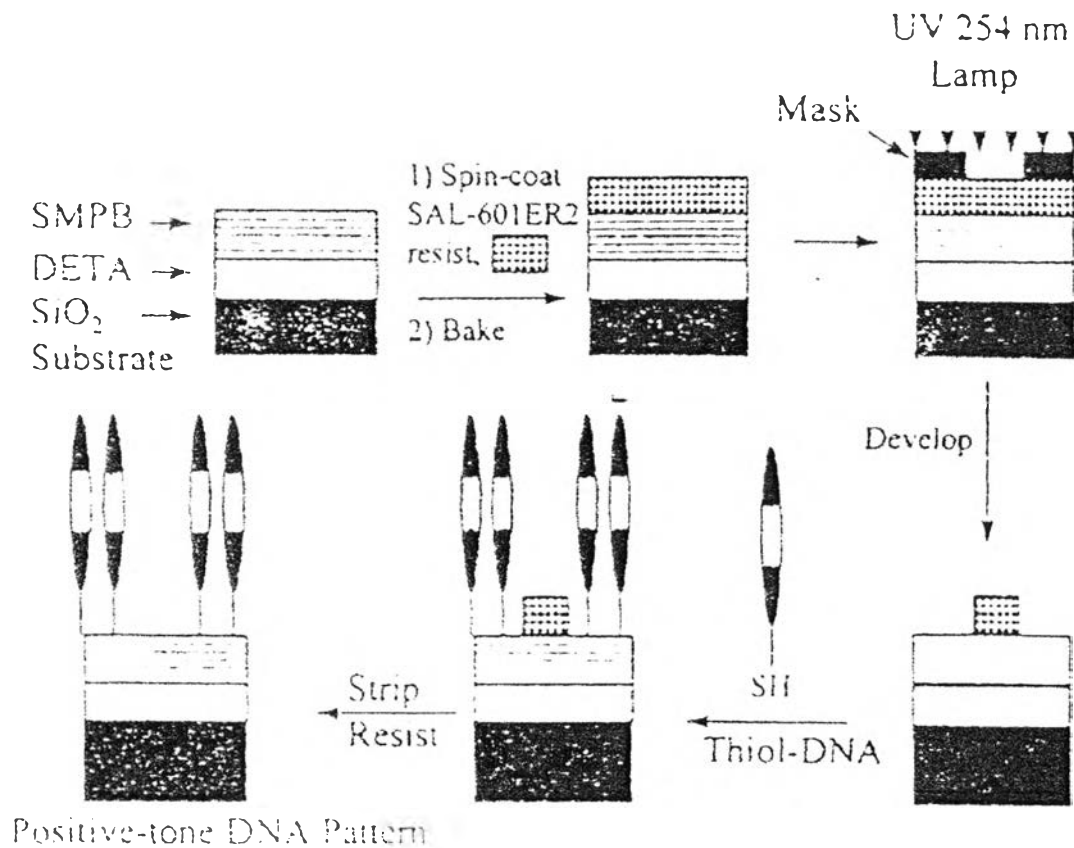


Figure 2.4 Schematic illustrating the UV lamp exposure of the photoresist SAL-601-ER to form DNA patterns on a DETA silane film (Chrisey et al., 1996).

Note: PEDA : [m,p(amino-ethylaminomethyl)phenethyltrimethoxysilane]

DETA : Triethoxysilylpropyl diethylenetriamine

SMPB : Succinimidyl 4-[maleimidophenyl]-butyrate

Although polymeric photoresist could be prepared, the resolution of polymeric photoresist was not enough to produce microchip. Then in 1998, Shirai and Tsunooka (Shirai, M. and Tsunooka, M., 1998) discovered that photoacid generating polymers which have iminosulfonate units in their side

chains were used as surface imaging resists, The steps of process for the surface imaging are shown in Fig. (2.5) (eq. 2.15 and 2.16). Upon irradiation, the surface of the polymers, having photoacid generating units, becomes hydrophilic because of the formation of silicic acid.

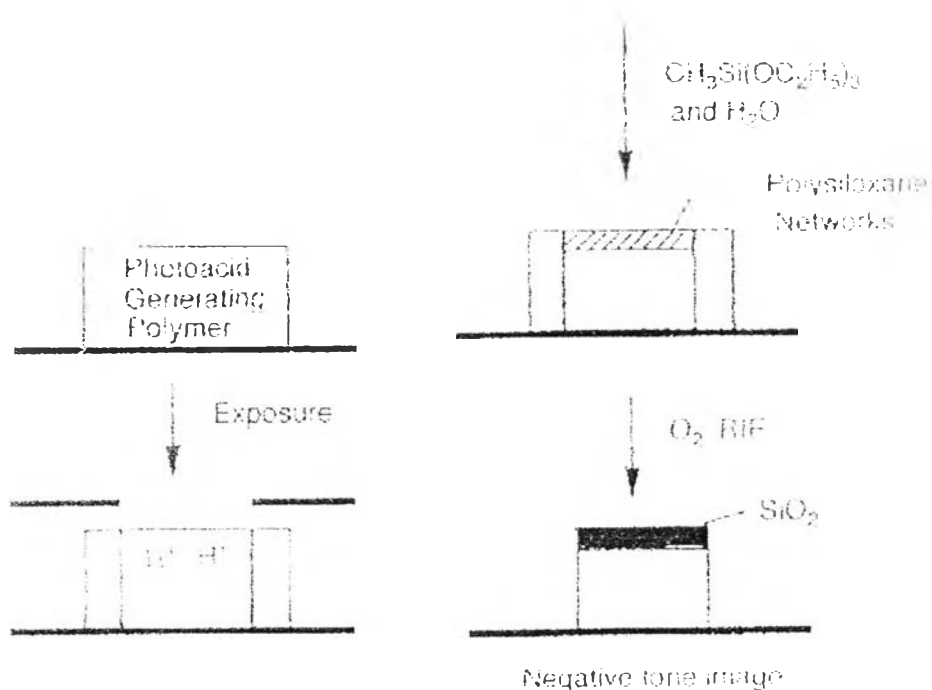


Figure 2.5 Schematic of pattern process using photoacid or photobase generator to produce resist material (Shirai, M. and Tsunooka, M., 1998).



Water sorption from the atmosphere occurs at the surface of the irradiated films. When the irradiated surface was exposed to the vapor of alkoxy silanes under humid conditions, polysiloxane networks were formed near the surface of the polymer films. No polysiloxane networks were formed at the irradiated

surface, since the photoinduced acids are essential for catalyzing the hydrolysis of alkoxy silanes. A negative tone image was obtained by using oxygen reactive tone ion etching (O₂RIE), since the polysiloxanes formed at the irradiated polymer surface act as a good etch barrier. In the microlithographic process, the use of deep UV light to provide higher resolution causes new problems due to decreased depth of focus and increased substrate reflectance. The surface imaging system is expected to eliminate or alleviate these problems.

Moreover, the more specific research work was discovered to the reaction of silane compound on the silicon substrate. Okumoto and Fujita (Okumoto, S. and Fujita, N., 1998) investigated two reactions of hydrolysis and condensation of silicon alkoxides. They discovered the hydrolysis of methylmethoxydihydroxysilane examining under neutral condition, and the water-trimer cluster was found to be reacted for ready bond interchange. The condensation of methyltrihydroxysilane was caused by the participation of the water dimer. Both of the observed reactions involved a front-side nucleophilic attack to the silicon center or a similar mechanism. In addition, acid- and base-promoted hydrolyses were also examined and their enhanced reactivities were ascribed to the stability of the silyl cation and a hypervalent intermediate, respectively.