CHAPTER I
INTRODUCTION

1.1 Photoresist

Generally, resists are imageable organic polymers that can be coated on or laminated to a substrate (Turner and Daly, 1989). After exposure and development a relief image is produced to protect the underlying substrate so that the geometry of the uncovered areas can be transferred into the substrate either by chemical or physical processes. The polymer image thus 'resists' the attacking of the etching process. Photoresists are polymers that are sensitive to light, and radiation sensitive resists are generally polymers that are sensitive to other higher energy sources of radiation, such as electron beams and X-rays.

The exposure of a resist produces a latent image that is later developed to produce the needed relief image pattern. Development of the image is nothing more than the selective dissolution of the polymer coating in the areas that is removed from the substrate. Depending upon the resist chemistry, combination of exposure and development can produce either positive or negative images. These image modes are shown in Figure 1.1. A positive image results when the exposed areas become more soluble in developer. Whereas for a negative process the exposed areas become less soluble and remain on the substrate. Both positive and negative processes are of commercial importance. However, this research dealt only with negative crosslinking process, thus only the negative process will only be described.

Resist chemistry implicitly covers many processes and technologies and it is quite important to put the polymeric resist into perspective as part of a system for transferring images onto a substrate. Included in the system are the exposure source, the coating process, any baking (drying) processes, the

developer chemistry and the development process, the image transfer process and finally a stripping process to remove the resist images. The fastest resist cannot be used if it cannot withstand the etching process used to transfer the image onto the substrate. High-resolution resists have little value if the resist image cannot be removed after the image transfer step and before the next processing step.
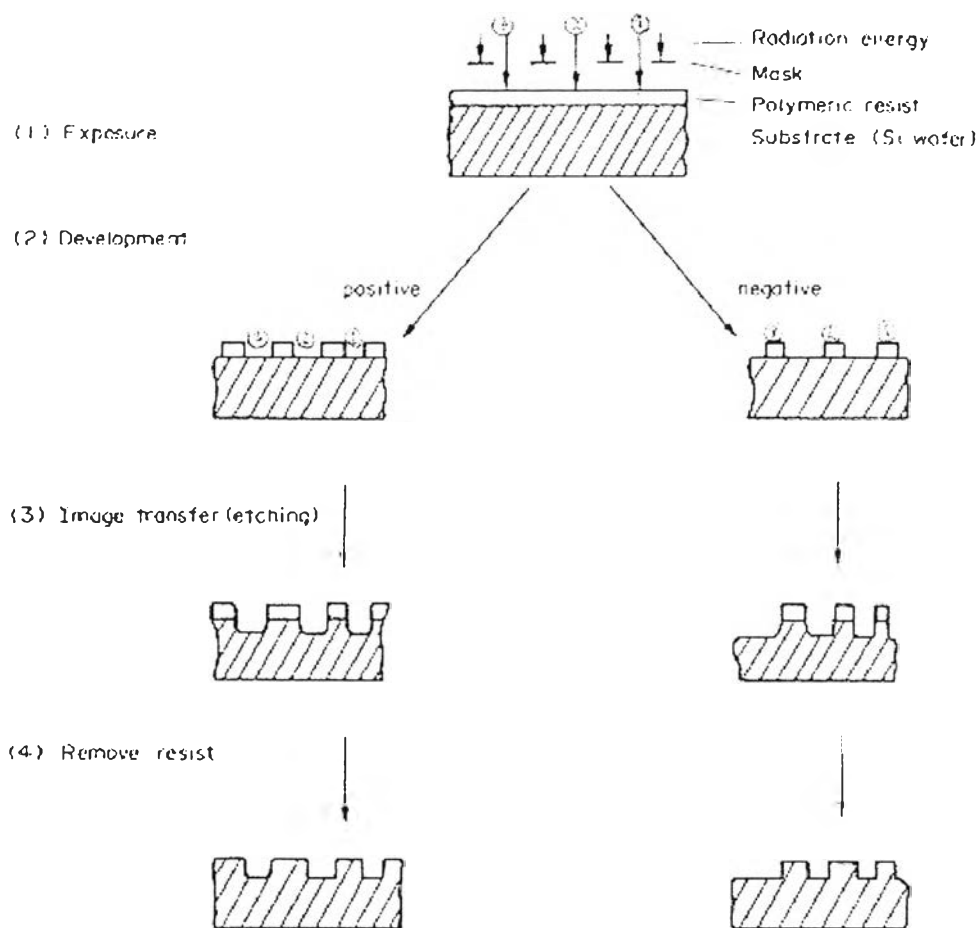
Figure1.1 Schematic of positive and negative image modes to form a relief image and subsequent transfer of image into substrate (Turner and Daly, 1989).

There is distinction between macroresists and microresists. Macroresists are used predominately for photomatchining, deep etch master

printing plates and circuit board fabrication. These technologies make use of both resist solutions and dry film laminates. The image sizes are in the range of 50 *u*m. to 10 mm. Microresists are used to fabricate the microchips which power the semiconductor revolution. Microresists must exhibit remarkable resolution (*ca.* 0.5 *u*m to 10 *u*m) and must resist extremely harsh image transfer processes, they represent the leading edge of resist science and technology. Again this work concentrated primarily on materials and processes used in microresists.

An outline of the process types, which can be envisaged to produce necessary physical changes in polymers and allowed the development of a high-resolution image, includes the following:

- Molecular weight increasing photoresists: (a) polymer-crosslinking processes; (b) polymer-forming processes.

- Molecular weight decreasing photoresists: (a) polymer-scissioning processes; (b) polymer ablative or erosion processes.

- Photofunctional change resists: (a) single photon processes; (b) chemically amplified processes.

- Post exposure process resists: (a) additive processes; (b) subtractive processes.

The first two represent chemistries which make up the majority of the polymers used in photoresists. In general, when the molecular weight of the resist polymer is increased by causing a polymerization to occur or by photo-crosslinking the soluble photopolymer into a network or a negative image is formed. Chain-scissioning chemistries decrease the molecular weight of the polymer yielding positive images. Degradation may occur by scissioning the polymer into smaller chain, unzipping the polymer back to monomer, or ablating away fragments to the polymer chain. Discrimination during development is brought about strictly because low molecular weight molecules, polymers and polymer fragments, dissolve faster than high

molecular weight ones and, in addition, they are usually soluble in a wider range of solvents.

The last two deal with chemistries that can produce either positive or negative resist images and can produce resists with processing and performance advantages. Photofunctional change resists are based on a photo-induced functional group change in the resist that can lead to a significant solubility difference. This kind of change can make the exposed polymer either more or less soluble in a developing solvent, resulting in positive or negative images.

Imaging systems that are classified as post-exposure process resists are those which an additional process step has been added after the exposure of the resist coating. In the additional process, a post-exposure chemical reaction occurs imagewise to alter the physical properties of the image. Subsequent processing or development discriminates reached from unreached areas. Subtractive processes operate by the imagewise removal of a component of the resist in a post-exposure process step. Theoretically, both of these processes can produce either positive or negative images.

Two of the most important requirements for resists used in lithography are sensitivity and resolution. The greater the sensitivity, the greater the tool throughput; the greater the resolution, the smaller the circuit pattern. Radiation-sensitive polymers can be patterned with photons from the visible to the x-ray region of the spectrum, and with electron and ion beams (Wong, 1993). Figure 1.2 schematically shows the effect of photon and ionizing radiation on a 1 μm thick positive resist coated on a silicon substrate both before and after image development.

When a polymer is exposed to photons (440 to 200 nm) through a mask pattern that is projected onto the surface of the polymer film, there is degradation of image caused by diffraction effects from the edge of the mask pattern, and losses due to the optical elements in the exposure tool. Because

of the degradation of the aerial image, and the effect of the UV light degradation through an absorbing photoresist material, the pattern after development is wider at the top than at the bottom. This broadening of the image minimizes the packing density, i.e. the number of lines, that can be formed in a given area, and limits the theoretical resolution limit for optical lithography to 0.25 um.
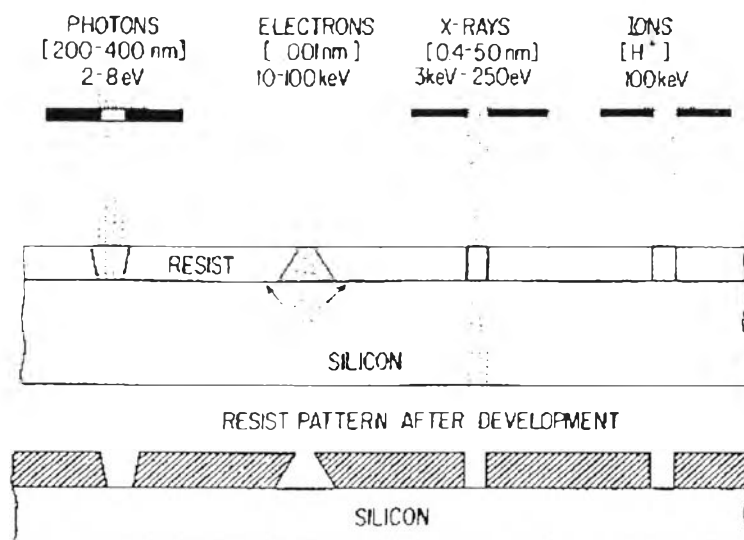
Figure 1.2 Effect of photon and ionizing radiation on the resist pattern (Wong, 1993).

Electron beam exposure is a direct-write method, where a focused beam of electrons (10 to 100 nm) is scanned over the surface of a resist-coated wafer, similar to the raster scanning of TV screen. There is no need for a mask, as the pattern is digitally encoded and computer-generated. Diffraction effects seen in optical exposures are eliminated, as the effective wavelength of an electron is only 0.001 nm. Owing to its small beam size, electron beam lithography is capable of patterning the smallest dimensions. As

an electron beam enters a polymer film, it loses energy through elastic or inelastic collisions. At 5-30 keV, the accelerating potential of most e-beam tools, practically all the kinetic energy, is lost via inelastic collisions. This ionization and excitation in the polymer film generate reactive species that can result in the crosslinking or scission of the polymer. Besides causing reactions in the polymeric film, the electrons will drive down into the silicon substrate to a depth dependent on the acceleration energy of the electrons (~10 um at 20kV), backscattering electrons into the polymer film and exposing the material to rediation as much as 5 um from the point of impact. Due to the contribution of these backscattered electrons, the developed image in a positive resist is larger at the bottom than at the top, the reverse of the optical image. This background cloud of electrons affects the ultimate resolution capability of e-beam resist materials.

Soft x-rays (0.4 to 5.0 nm.) are also not limited by diffraction effects, and high-resolution patterns with vertical walls can be obtained. However, as there are no x-ray lenses available, the x-rays cannot be focused, and pattern transfer relies on a flood exposure of x-rays through a special mask with the same pattern dimensions as those desired on the wafer (1:1 proximity printing). X-ray technology has not yet been implemented in manufacturing because of the difficulty in making these masks and the current requirement for high-flux x-ray synchrotron sources. However it is under much investigation in research laboratories around the world.

Ion beam lithography is also under investigation to achieve high resolution. This technology is similar to electron beam systems, but ions, rather than electrons, are electrostatically scanned over the resist film. As the ions scatter much less than the smaller electrons, high-resolution images are possible. High-brightness sources and high-speed deflection systems must be developed to make ion beam lithography competitive.

1.2 Applications

The mainly used of resist materials can be categorized below :

1.2.1 Semiconductor Circuit

1.2.1.1 Printed Circuit Boards

Circuit boards, due to their size and the volume of production, are the largest user of polymers in the semiconductor industry. The most widely used family of polymers for circuit board applications for the past 25 years has been the epoxy systems.
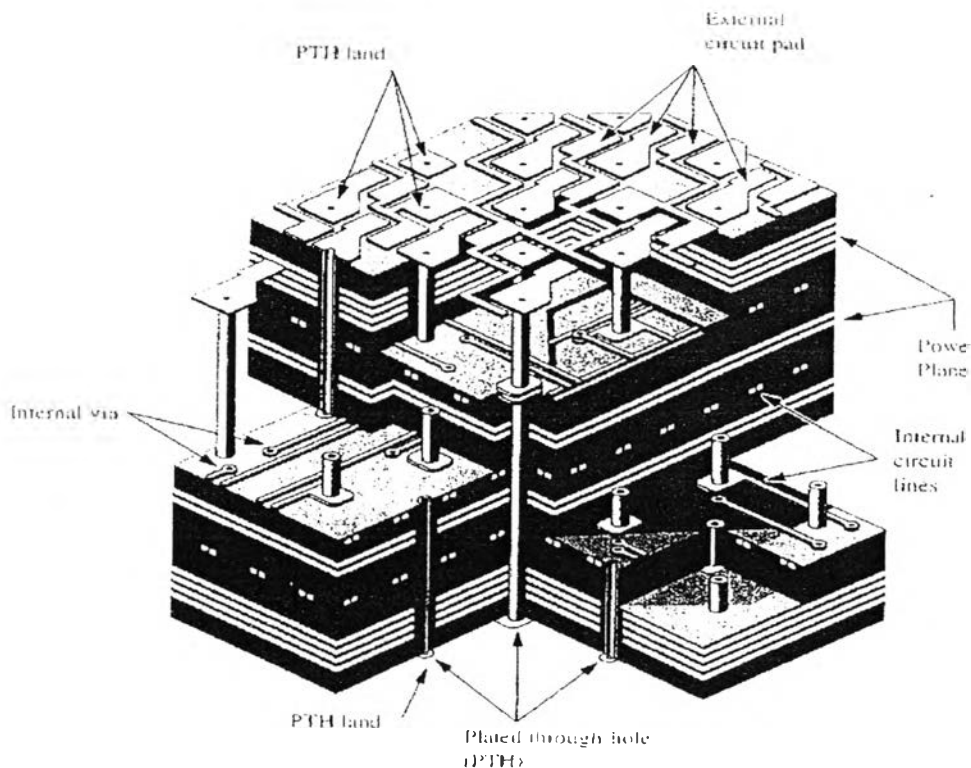

Figure 1.3 Schematic of a multilayer printed circuit board (Wong, 1993).

They have several advantages for this application: 1) excellent adhesion to many types of surfaces, 2) reactivity with a variety of curing agents, 3) rapid curing times and low shrinkage during cure, and 4) low cost. A printed circuit board consists of glass cloth for mechanical strength impregnated with an epoxy that has been partially cured to a "B" stage. This is called a "prepreg" and is used as the insulator between two copper sheets that are laminated to the epoxy. Holes are drilled through this material and plated with copper to form the vias, and the copper surfaces are patterned lithographically with a dry film resist to form the wiring circuitry. Several of these patterned prepregs or sublaminates will be laminated together to bring in power and redistribute the signal wiring. An example of a patterned sublaminate is shown in Fig. 1.3.

1.2.1.2 Singer-chip Packaging
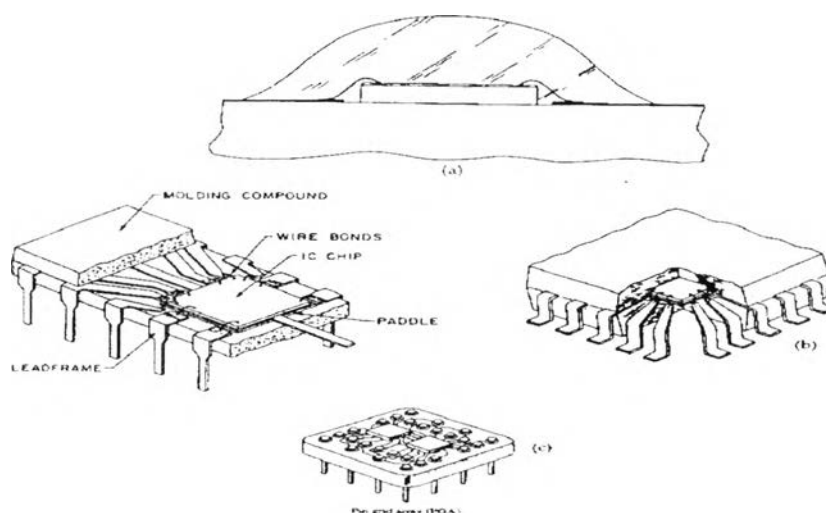
Figure 1.4 Schematic of single-chip packaging from polymer application (Wong, 1993).

The majority of chips are dices from a silicon wafer and after testing are packaged on single chip carriers. For this application polymers (Fig.1.4) are used as molding materials, encapsulants, and as a thin-film carrier for the chip itself. Plastic encapsulated devices were first introduced in the 1960s. To a great degree, the combination of their low cost and high production capability has been responsible for their widespread usage. The encapsulation materials must protect the chip from the environment, which can cause corrosion or degradation of chip performance. The materials must be resistant to radiation (ultraviolet, visible and alpha particles), water diffusion, and mobile ions, and they must protect the devices from solvents, fluxes, cleaning agents, and fire. They also must have excellent mechanical properties to reduce stresses, good dielectric properties, and be of very high purity.

1.2.2 Biochip Sensor Process

The notion of utilizing 'biochip arrays' for multiplexing biogical reactions has become common place over the past several years (Chrisey et.al,1996). This concept is evolved from the notion of using combinatorial synthetic approaches to create very large scale libraries of receptor molecules and to then screen the population for enhanced binding activity of individual members to a target of interest. Possible applications for large scale arrays of biomolecules include DNA sequencing-by-hybridization,. DNA-based sensors enzyme or antibody-based sensors, and peptides or nucleic acid oligomer libraries for screening ligand binding. Various schemes for the fabrication of such arrays have emerged, including the light-directed spatially resolved modification of surfaces using monolayer silane films. Silane films bearing a wide variety of functional groups may be formed on numerous types of surfaces. Certain photolabile silanes can be irradiated using a lithographic

mask, resulting in a pattern reactive surface. UV patterning of self-assembled monolayer (SAM) silane films has been demonstrated to sub-micron geometry and can also be extended to nanometer-scale dimension with proximal probe exposure tools. A patterned silane film can consist of spatially resolved regions bearing different functional groups or physical properties or may be silanized again to obtain a coplanar assembly of selected functional groups on the surface. This approach has been exploited to create patterned biomolecular surfaces modified with nucleic acids, protein, antibodies and living cells.

1.3 Photocrosslink

Photocrosslinking of monomers, oligomers and polymers constitutes the basis of important by commercial processes with broad applicability, including photoimaging and UV curing of coatings and inks. These processes require that light energy is absorbed by the photoactive agent and is used to form new chemical bonds (Pappas, 1989). Photocrosslinking may be accomplished by the use of photoinitiators, photocrosslinking agents and photocrosslinkable polymers, which represent the photoactive agents.

Photoactive agents absorb light in the UV-visible spectral region, generally 250-450 nm., to yield electronically excited states, which may undergo crosslinking directly or convert this light energy into chemical energy in the form of reactive intermediates, such as free radicals, reactive cations, nitrenes, etc. These subsequently initiate polymerization or undergo crosslinking reactions.

Photocrosslinkable polymer genereally undergo crosslinking by the reaction of an excited photoactive group on the polymer with the corresponding group in its ground state. Photoinitiators and photocrosslinking agents convert their light energy into chemical energy in the form of reactive intermediates, which participate in crosslinking reactions.
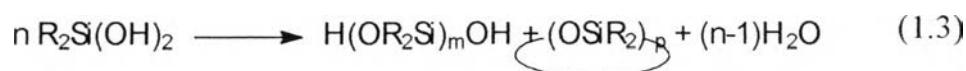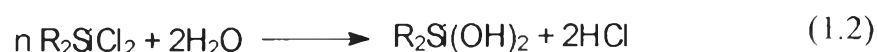
1.4 Synthesis of polysiloxane

Polycondensation processes are often applied for the synthesis of both linear siloxane polymers and cyclic siloxane oligomers used further as substrates in ring-opening polymerization (Clarson, 1993). A polysiloxane chain is most often formed as a result of two types of polycondensation; homofunctional polycondensation of silanediols and heterofunctional polycondensation involving the silanol group with another function. These reactions usually constitute the second step of the hydrolytic polycondensation of organosilanes having two hydrolyzable groups attached to silicon (eq. 1.1).

$$n\,R_2SiX_2 \quad \xrightarrow[-HX]{H_2O} \quad \underbrace{\left(\,SiR_2O\,\right)}_{n} \qquad (1.1)$$
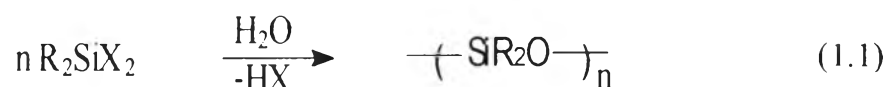
$$X = Cl,\ OR,\ OC(O)R,\ NR_2,\ SR \ \ etc.$$

Both steps, hydrolysis and polycondensation, usually occur in a one-step process. If the hydrolysis is much faster and an excess of water is used, then the silane is fully transformed into silanediol and the polymer is formed from the homofunctional silanediol polycondensation. This is the case in the hydrolytic polycondensation of diorganodichlorosilanes, which is the most often exploited reaction in synthesis of polysiloxanes(eq. (1.2) and (1.3)).

$$n\,R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl \qquad (1.2)$$

$$n\,R_2Si(OH)_2 \longrightarrow H(OR_2Si)_mOH \pm (OSiR_2)_R + (n-1)H_2O \qquad (1.3)$$
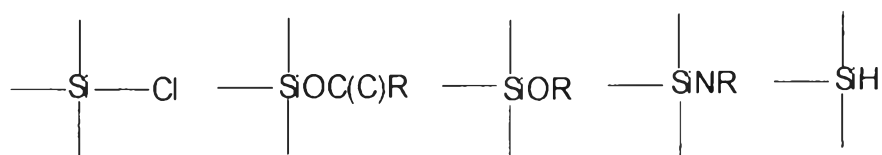
The most frequently used monomer is dimethyldichlorosilane. Industrial synthesis is carried out as either a batch process or a continuous process and may be performed in the gas phase or as an emulsion. The

hydrolytic polycondensation in the presence of bases is practiced for synthesis of polysiloxanes bearing substituents, which are reactive towards acids.

Heterofunctional polycondensation (equation 1.4) is favored in the process of equation (1.1) when the functional group is less reactive and a limited amount of water is used.

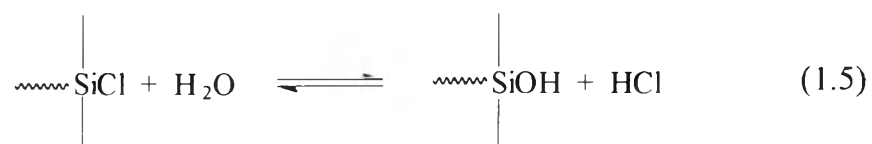$$\text{---}R_2SiX + HOSiR_2\text{---} \longrightarrow \text{---}R_2SiOSiR_2\text{---} + HX \qquad (1.4)$$
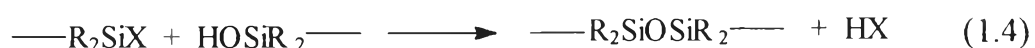
The silanol group is able to produce the siloxane linkage entering into the condensation with various silicon functional groups. Some of these reactions are exploited in synthesis of linear siloxane polymers and linear or cyclic oligomers. The functional group most often used for this purpose are following:

$$\text{---}\overset{|}{\underset{|}{Si}}\text{---}Cl \quad \text{---}\overset{|}{\underset{|}{Si}}OC(C)R \quad \text{---}\overset{|}{\underset{|}{Si}}OR \quad \text{---}\overset{|}{\underset{|}{Si}}NR \quad \text{---}\overset{|}{\underset{|}{Si}}H$$

R is a simple alkyl or aryl group. In contrast to homofunctional silanediol polycondensation, the heterofunctional process permits the synthesis of copolymers with pendant groups or sequences, which are regularly arranged along the chain. These heterofunctional condensation processes usually require catalysis. It was demonstrated that the spontaneous coupling reaction of the silanol and silyl chloride-ended oligosiloxanes in a neutral solvent, like methylene chloride, does not proceed at a detectable rate. Similarly acetoxysilyl-ended groups may coexist for a very long time with the silanol-ended groups when no catalyst or water is present. The use of an appropriate catalyst is often crucial to direct the process towards the heterocondensation as it competes with the silanol self-condensation and may be accompanied by the interconversion of the end-groups as well as the siloxane bond cleavage.

It is not appropriate to catalyze the silyl chloride and silanol process with a protic acid. The acid protonates the SiOH group much more easily than the silyl chloride group; thus promoting the homofunctional silanol condensation instead of the heterofunctional reaction. End-group interconversion may occur extensively in this system as a two-step process according to equation (1.5).

$$\text{\textasciitilde\textasciitilde\textasciitilde SiCl} + H_2O \; \rightleftharpoons \; \text{\textasciitilde\textasciitilde\textasciitilde SiOH} + HCl \qquad (1.5)$$

This polycondensation has been successfully employed for the synthesis of siloxane copolymers with regularly arranged side-groups and averaged $Mw = 10^5$.

The reaction of silyl and silanol-ended oligosiloxanes catalyzed with transition metal catalysts, in particular by rhodium complexes, in both a homogeneous as well as a heterogeneous system, is suitable for the synthesis of siloxane oligomers including those comprising functional groups. The reaction proceeds with a high yield since side reactions of the silanol homocondensation and the hydride disproportionation are suppressed in this system. This type of condensation is also promoted by tin ester catalysts. Another group of catalysts are inorganic salts, e.g. cadmium and zinc chlorides.

The aim of this research work, is to synthesize and characterize polysiloxane based on new photoresists process for a DNA detector to seek the DNA sequence of disease. This research work uses an organic base, which is triethylenetetramine, as catalyst to synthesize a new photoresist using condensed polysiloxane as a wall between each amino acid sequence.