

Chapter I



Introduction

1.1 General

Nowadays our lives are influenced by some aspect of the electronics revolution, which is based on a very small foundation i.e. the microchip. Automobiles, televisions, and many other home appliances are now controlled by the tiny electronic circuits of these microchips. The microchip is a precisely patterned array of conductors, insulators, and semiconductors that can be made to perform a wide variety of electronic functions. Modern day computers owe their existence to these electronic wonders. High resolution video and still electronic cameras are being developed that use sophisticated light-sensitive versions of microchips of the "film". These could be approached by improvement in radiation techniques and the use of radiation-sensitive polymeric materials that used in photolithography. While photolithography will continue to be the mainstay of the microelectronics industry for many years to come, there are a number of disadvantages inherent in it. Photolithography, using near-ultraviolet radiation in the range of 300-400 nm for exposure, is limited to the replication of fine structure with dimension of about 1-2 μm . Below approximately 1 μm , the resolution capability of photolithographic processing becomes increasingly limited by diffraction. But it can be improved in resolving power and reproducibility of patterns by virtue of high energy radiation, especially electron-beams and X-rays.

In order to appreciate the role of photosensitive negative resists playing in the fabrication of such devices and, in particular, the necessity for continuous developments in device lithography, it will be worthwhile to mention about the sequential steps in microlithography in which photoresist used.

1.1.1 Microlithography

Fig. 1.1 illustrates a typical procedure employed in the production of integrated circuits.

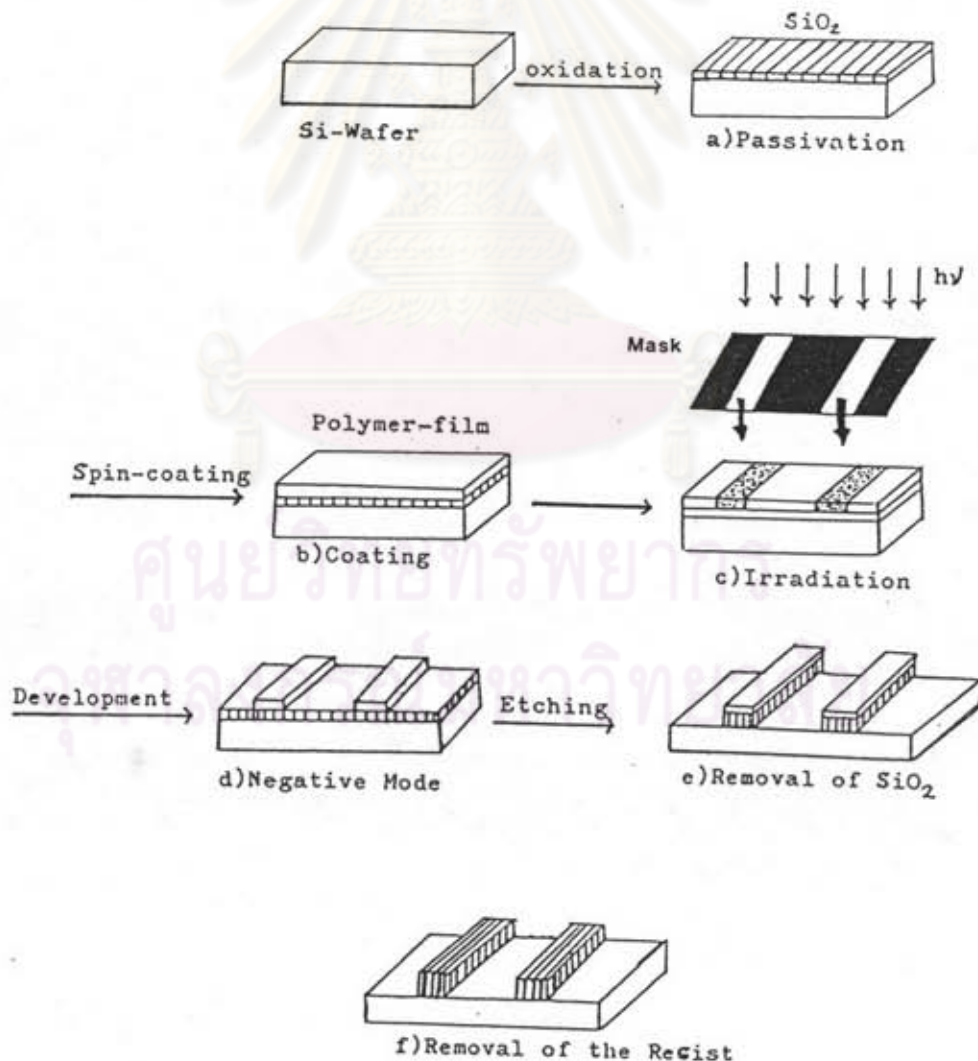


Fig. 1.1 Photolithography using a negative resist

1.1.1.1 Passivation

In order to protect the surface of silicon and to dope it only at the desired positions, the silicon wafer is covered with a thin layer of SiO_2 ($0.1 \mu\text{m}$). This oxide is impermeable to boron atoms and to impurities like oxygen. Silicon dioxide can be stripped by hydrofluoric acid (silicon itself is not attacked). Therefore, to strip selectively the oxide layer and to obtain the design of a circuit, given positions have to be protected.

1.1.1.2 Coating

The passivated silicon surface is spin coated with a polymer of about one μm thickness which is suitable for high resolution. The step is followed by an annealing to remove the solvent and favor the adhesion of the resist on the substrate. To obtain a uniform thickness, the resist and wafer have to be clean.

1.1.1.3 Irradiation

Subsequently, the polymer film is irradiated using a mask. The irradiation induces a modification of the polymer linked to the energy absorbed by it.

1.1.1.4 Development

Areas of the resist layer which are exposed to light, become detached in the subsequent development process. Depending on whether the irradiated or the nonirradiated regions of the

polymer remain on the substrate after development, the polymers are classified as negative or positive working.

1.1.1.5 Removal of SiO₂

In the non - protected zones, the silicon dioxide layer is etched away by hydrofluoric acid or by plasma.

1.1.1.6 Removal of the resist

The resist is removed and the substrate is only partially covered by the silicon dioxide layer. "Windows" have been opened which make the silicon substrate accessible for further treatment such as doping.

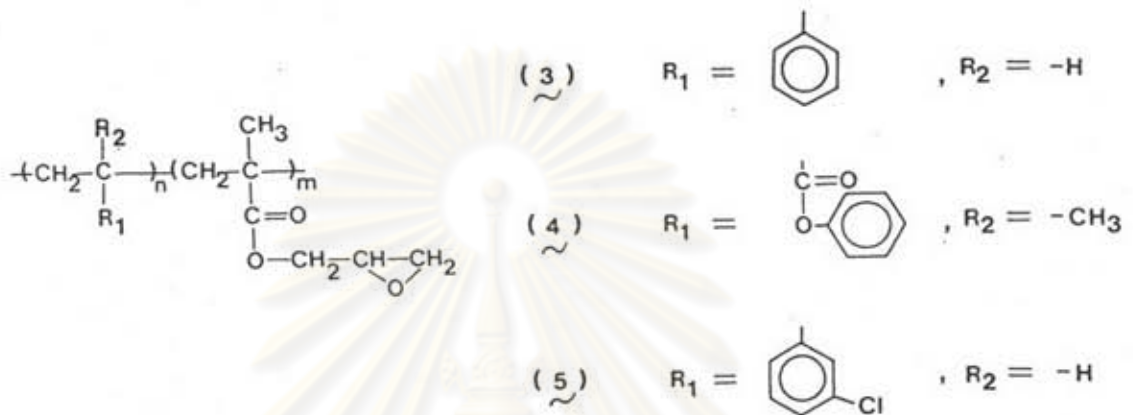
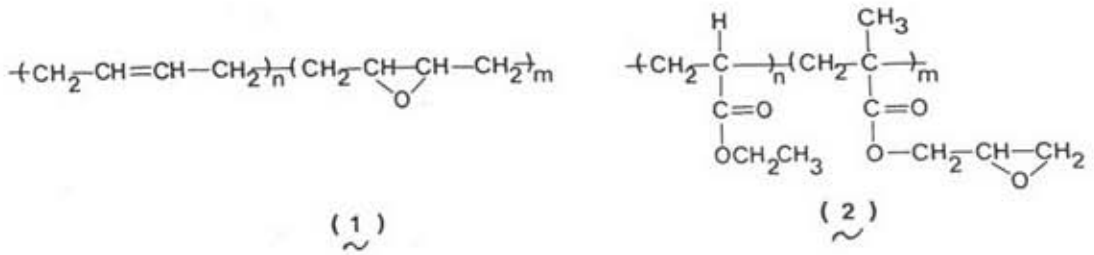
The manufacture of a transistor needs at least four lithographic steps. But often, up to twelve lithographic steps are necessary for more sophisticated circuits. Therefore, the precision of superposition is of great importance. The resists used must have very particular properties because the sharpness of the designs and their sizes will be dependent on the quality of these resists and on the radiation used.

1.2 A Literature Review of Negative Resists

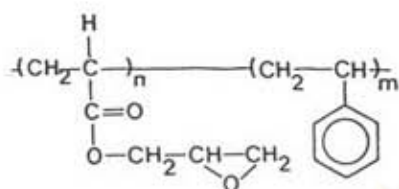
Much work on negative resists has been done. They could be classified into electron-beam, X-ray and photo-sensitive resist due to the energy exposure.

1.2.1 Electron-beam sensitive negative resists

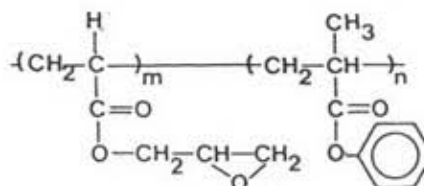
Though many classes of compounds was examined in the past as negative electron-beam resists [1], recent work has been concentrated on three major categories : epoxy group containing polymers, polymers with pendant unsaturation, and vinyl aromatic polymers. It has generally been shown that in the epoxy group containing polymer class, the placement of the epoxy groups as side chains of the polymer, as opposed to in the backbone, results in marked improvement in the contrast of the resist. Nonogaki.S and et al [2] synthesized the epoxide containing polybutadiene by epoxidation of polybutadiene (1). They had high sensitivity, but low contrast (lower than 1). As a consequence of this, current efforts in this area are directed toward synthesizing and evaluating polymers prepared from glycidyl ester monomers. Hamermesh and Crane [3] attempted to prepare poly (ethylacrylate-co-glycidylmethacrylate). It was known under the trade name "COP" (2) a copolymer that was studied in some detail by Thompson and co-worker [4,5]. They tried to solve the swelling problem by synthesizing copolymers of GMA and each of the other monomers, i.e., styrene (3), phenylmethacrylate (4), and 3-chlorostyrene (5). It was found that swelling was reduced, while contrast, resolution, thermal stability and etch resistance were better than that of COP. But sensitivity of these copolymers were decreased comparing to the one of COP, because of the presence of the phenyl ring. They also studied deeply in the spinning solvent used for the final wafer preparation. However, copolymerization in cellosolve acetate led to inhomogeneous polymer mixtures of two components, one with more ethyl acrylate and the other with more glycidyl methacrylate content.



Feit et al [6] attempted to characterize the resist response of glycidyl methacrylate (GMA) homopolymer and copolymers with ethyl acrylate (EA). This has been successful for features $5 \mu\text{m}$, and these parameters could be related to the molecular properties of the polymers. At lower feature sizes, however, other factor like solvent - induced swelling of images, wetting properties of developer and polymer and gel-rupture by forced development came into play. Thompson and co-workers [7] at Bell Laboratories examined copolymer of GMA and glycidyl-acrylate (GA) with styrene (6) and phenyl methacrylate (7) as negative electron resist materials. These copolymers had sufficient sensitivities for application and, in general, GA copolymers was more sensitive than the corresponding GMA copolymers. All these materials also showed better thermal stability than the (GMA-EA) copolymers.

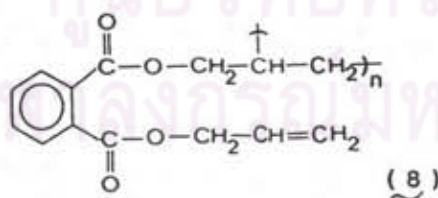


(6)

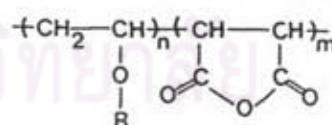


(7)

In the case of ethylenically unsaturated polymers, it has again been established that when the unsaturation is in the side chain of the polymer, the sensitivities of the resist are better than when they are in the backbone. One such polymer that has received wide spread attention is poly(diallyl-orthophthalate) (PXOP) (8), which is good thermal stability [8]. Recently, Yoneda et al [9] had optimized molecular weight and dispersity of this material for making high-resolution patterns. Vertical wall profile with 1 μm line widths were obtained with sensitivities of 4×10^{-6} C/cm² at 15 kV. This material showed acceptable fluorocarbon sputter etching resistance.



(8)



(9)

Cole and his associates at General Electric Co. had reported [10] highly sensitive negative resists prepared as alkenyl half-ester from copolymers of vinyl ethers and maleic anhydride (9). Sensitivities of the order of 10^{-8} C/cm² at 9 kV were reached. The importance of the ether group was evident in these polymers, although their exact function had not yet been

established. Despite their high sensitivity, the storage stabilities of these resists were quite good.

Vinyl aromatic polymers have been widely studied as negative electron resists. The simplest polymer of this rather large group is polystyrene and, although it has several disadvantages, it is one of the early candidates in electron-beam lithography applications. It has excellent processing properties but has a very low sensitivity ($2 \times 10^{-4} \text{ C/cm}^2$). Lai and Shepherd [11] had recently examined the effect of the molecular weight and its distribution on the performance of polystyrene as an electron resist. Their researches showed that the sensitivity increased with molecular weight and narrow dispersity gave improved contrast. Line widths $< 1.0 \mu\text{m}$ has been obtained with this negative resist. Sensitivities of $1 \times 10^{-5} \text{ C/cm}^2$ had been reported, and very good plasma etch resistance had been observed.

The rather poor sensitivity of polystyrene and yet its good processability and ready availability at a low price have prompted significant research in chemically improving its susceptibility to crosslink by electron-beam exposure. The strategy by which this problem is being commonly addressed is introducing electron-sensitive substituents into the phenyl rings. Halogenation of the phenyl rings has this effect, and the use of iodinated polystyrene for this purpose has recently been described [12]. Researches at Hitachi Ltd. had prepared iodinated polystyrene by direct iodination of polystyrene and found the sensitivity of the polymer to be increased through this process. The resist would not crosslink in a vacuum after

exposure, indicating a short lifetime of the active species produced by the irradiation. It was ion-millable and showed good thermal stability.

Feit and Stillwagon [13] had prepared a chlorinated polystyrene with narrow molecular - weight distribution and had observed that at 70% chlorination, the material was 5.4 times more sensitive than polystyrene. As in the case of polystyrene, the contrast was very sensitive to the dispersity of the polymer and the latter is broadened by the chlorination process.

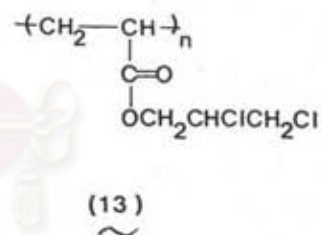
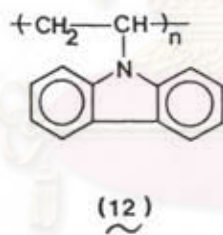
Imamura . S [14] studied chloro - methylated polystyrene (CMPS) which prepared by chloromethylation of polystyrene. It showed that the presence of a C-Cl bond (20% by weight of chlorine) increased the sensitivity. As expected for negative resist, the sensitivity increased with increasing molecular weight, while the contrast increased with decreasing molecular weight distribution. The resolution observed was about 0.3 μm and the plasma etch resistance was 40 $^{\circ}\text{A}/\text{min}$. Recently, Choong H.S. thoroughly examined poly(chloromethylstyrene) (PCMS) (10), whose lithographic properties was better than those of CMPS. Also its copolymer with styrene (11) improved the contrast and etch resistance because of the presence of phenyl ring.



Other vinyl aromatic polymers had been examined by Jagt and Sevrien [15], e.g., poly(vinyl-carbazole) (PVK) (12) and poly(3-bromo -N-vinyl carbazole). Poly(vinyl-carbazole), like

polystyrene (PS), had a high contrast and dry etching resistance properties, but the sensitivities were not sufficiently high unless molecular weights were very high. The bromo-derivative, however, has a much higher sensitivity (10^{-6} C/cm²). Experiments also showed that the addition of organic bisazides, e-g., 4,4-diazidostilbene, to polystyrene or poly(vinyl-carbazole) was effective in increasing the sensitivity of these resists tenfold, with no loss of contrast.

Gazard et al [16] had synthesized a poly(methyl methacrylate) (PMMA) which was grafted with acrylic acid. It formed a negative system on development with solvents for PMMA. Sensitivities as high as 2.8×10^{-8} C/cm² at 20 kV have been reported for this process.



1.2.2 X-ray sensitive negative resists

Taylor et al [17] examined chlorine-containing acrylate homopolymers and copolymers as resists for X-ray exposure at 3.5 mJ/cm^2 flux (1 C/cm^2 at $1 \text{ kV} = 10^6 \text{ mJ/cm}^2$). Highly sensitive materials, requiring less than a minute of exposure, had been found, but these showed rather low contrasts, attributed to competitive intramolecular crosslinking reactions. Optimum properties were obtained for

poly(2,3-dichloro-1-propylacrylate), (13), which also showed excellent stability. Lines and spaces of $1\mu\text{m}$ could be obtained with sensitivities of 7 mJ/cm^2 .

Several polyvinyl ethers have been reported as X-ray resists [18]. These polymers are prepared by the cationic polymerization method, and the exposures have been done at 5.4 \AA . The polymers with chlorine or vinyloxy group containing side chains gave good sensitivity ($\geq 18\text{ mJ/cm}^2$), while those with chlorine also showed good contrast (≤ 2.2).

The negative X-ray resists and their sensitivities were exhibited in Table 1.1.

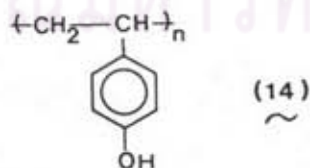
Table.1.1 Negative X-ray Resists

Polymer composition	Target wavelength, nm	Absorbing element	Sensitivity, mJ/cm^2
glycidyl methacrylate-ethyl acrylate (COP)	0.43 (Pd)		175
2,3-dichloropropyl acrylate (DCPA)	0.43 (Pd)	Cl	7.0
blend of COP and DCPA (DCOPA)	0.43 (Pd)	Cl	15.0
2,3-dibromopropyl acrylate-glycidyl methacrylate	0.46 (Rh)	Br	15.0
chloroethyl vinyl ether-ethyl vinyl ether	0.54 (Mo)	Cl	72
chloroethyl vinyl ether-vinyloxyethyl acrylate	0.54 (Mo)	Cl	18
chloromethylstyrene	0.43 (Pd)	Cl	25
allyl methacrylate-2-hydroxyethyl methacrylate	0.74 (W)		9

1.2.3 Photosensitive Negative Resists

Optical lithographic methods are most important for the manufacture of integrated circuits on a worldwide basis. The photoresists used are mainly sensitive in the wavelength from 300 nm to 500 nm. Some important research works could be reviewed as follows.

The photochemical reaction between polyvinyl alcohol (PVA) (14) and chromate species had been widely used in imaging devices. Steihler and Duncalf and Dunn [19] did some of the early mechanistic work on this system and more recently Branin and Fonger [20] had examined the photochemical process. Nice and Farlee [21] have studied the chromate ion reaction with PVA in aqueous solutions by UV and electron paramagnetic resonance spectroscopy. It was found that during irradiation, the charge - transfer absorptions of the chromate esters initiate the photochemical reaction. The results were compared with those of the previous mechanistic studies made on this system. A proposed step wise was a reduction of the Cr species to Cr (III), which finally forms complexes with PVA.



The sensitization of dichromated PVA to visible laser wavelengths had been investigated by Bloom and Burle [22]. They found that compounds that were used for sensitization were

sodium fluorescein, 2, 4, 6 - tritolpyrilium tetrafluoroborate, 2,4-dinitro-1-naphthol, and methyl orange.

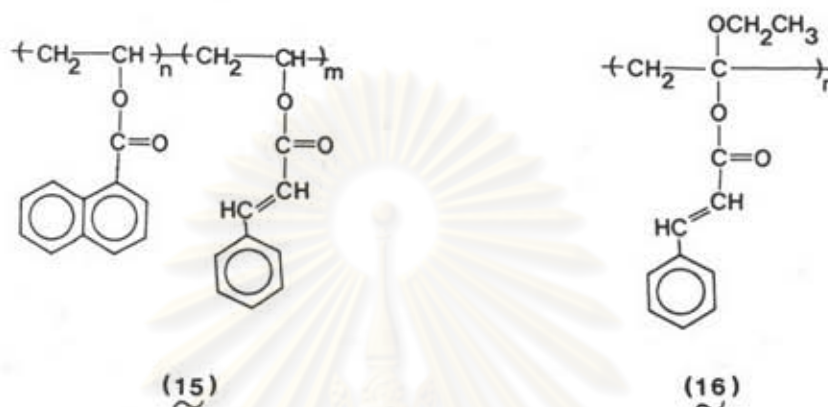
Slobodkin and co-workers [23] had examined the relative merits of different drying and curing modes of PVA-dichromate compositions. Undesirable post-polymerizations were found to appear to a large extent in infrared processes.

Several chemically modified derivatives of PVA had been developed recently to prepare negative photoresists. Thus, Daly and Engebrech [24] had prepared copolymers of vinyl cinnamate with vinyl naphthoate or vinyl-3-naphthyl acrylate (15) by coesterifying PVA1 with the appropriate acid chlorides, giving acid - resistant photoresists. After UV exposure and development, the remaining crosslinked polymer could withstand hot nitric acid "deep etch" conditions.

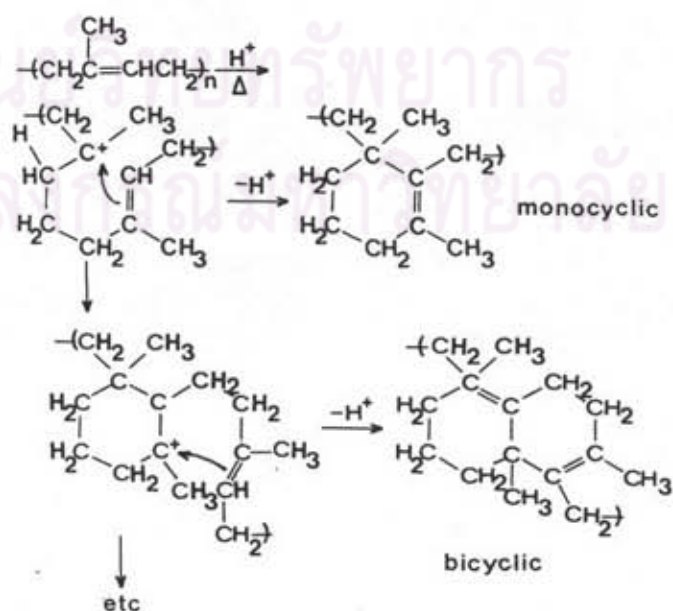
Polyvinyl ethers with sidechain unsaturation had been synthesized by Biryukova et al [25] by polymerization of the corresponding monomers with a cationic initiator like $\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. These polymers gave photochemical crosslinking with benzophenone - Michler's lactone and, as photoresists, resolution of $1 \mu\text{m}$ line widths were obtained.

Koto and Nakane [26] had recently described cationically polymerized 2-vinyloxyethyl cinnamates (16) as a negative photoresist with greater sensitivity than commercially available polyvinyl cinnamate resists, and about twice as much sensitivity as the rubber-based resists. Its resolution was comparable to a photoresist under the trade name "AZ-1350",

which was remarkable for a negative photoresist. The material was also reported to be excellent in terms of adhesion, thermal stability, and resistance to pin-hole formation.



Cyclized rubbers (Scheme 1.1) had been used extensively in the negative photoresist applications, and several commercial materials of this class are available, e.g., KMER, KTFR, Waycoat IC and SC, and Dynachem CMR and Micro-G. The most common composition in this family is a cyclized form of polyisoprene and a photoactive crosslinker, typically a bisazide, which photolyzes to the highly reactive dinitrene



Scheme 1.1

Treushnikov et al [27] had carried out theoretical and experimental studies to explain the important contributing factors that affect the photosensitivity of cyclorubber - bisazide system. It appeared from this work that, apart from more crosslink formations, parameters like the distribution of bisazide molecules in the film and the average number of structural formations per polymer molecule capable of functioning as effective molecular network units were important. This research group had also examined [28] the effect of such factors as the method of solution preparation, solvent removal from cast film, storage time of prepared solutions, and air vs vacuum exposure on the photosensitivity of cyclorubber - 2, 6 - bis (4-azidobenzal)cyclohexanone system, the changes in sensitivity of these materials with changes of drying temperatures may be attributed more to molecular conformational changes than to residual solvents. The effect of low-molecular-weight solvent in cyclized rubber and polystyrene coatings on the mobility of the nitrenes formed by photolysis had also been studied [29]. Coating containing stable microvoids did not require solvents for nitrene mobility and those that absorbed water inhibit this mobility by such absorption. Treushnikov and co-workers [30] found that the negative photoresist FN-11 and a bisazide showed the interesting property of increased light sensitivity of the unexposed regions accompanying the decreased sensitivity in the exposed areas. This was explained theoretically and experimentally by an oxygen-pumping mechanism from the dark parts to the exposed parts. Exposure in air gave much lower resolutions than in an inert atmosphere where the crosslinking reaction of dinitrene effectively competed with the much faster oxygen - nitrene reaction.

Shimizu and Bird [31] had contributed significantly to the understanding of the mechanism of photocuring of the cyclorubber-bisazide-system. At 100 °C, the oxidative crosslinking by polymerization of the cycloisoprenes was predominant over the thermal crosslinking produced by the bisazide. Significant crosslinking of the resin inhibited further bisazide decomposition by cage effect of the rigid matrix.

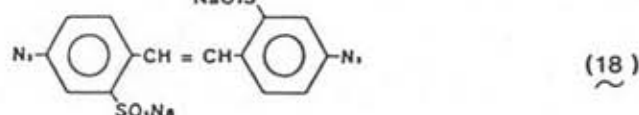
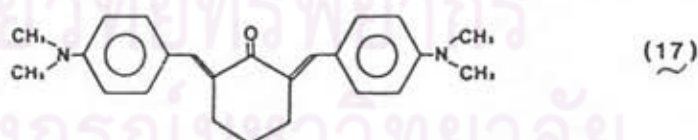
A 43 % quantum yield was established for the simultaneous cleavage of both the azide groups in a molecule of the bisazide, from the absorption of one photon of energy. The products of the azide decomposition were implicated in inhibiting further bisazide decomposition by an energy-transfer process. The chemical mechanism of crosslinking and reciprocity failure is evidenced by the appearance, on exposure, of a new absorption band at 410 nm, which was attributed to the bisamine crosslink from comparison with the model compound, 2,6-bis(p-dimethylaminobenzal) - cyclohexanone (17). The reciprocity effects were explained by competitive reactions of the nitrene with oxygen and polymer, the first being greater than 10^4 times faster than the latter. The sensitivity can be significantly enhanced by inert atmosphere or rapid exposure, both of which cause a low equilibrium oxygen content in the exposed areas. The azide-to-nitrene reaction is not affected by the oxygen content, but the consumption of the nitrene, once formed, can be decreased by minimizing the oxygen in the film.

Cyclized cis-1,4- polybutadiene has also been developed into a photoresist. This resist showed a higher UV sensitivity than cyclized polyisoprene and had good resolution properties (1.6 μm). The polymer showed no resist flow up to 250 °C, and the

decomposition temperature was higher than for polyisoprene. The polymer was prepared by cyclization of the monomer with organoaluminum catalysts. The photoinitiator used as 2,6-bis(4-azidobenzal)cyclohexanone.

Naumova et al [32] had photocrosslinked an oligomeric 1,3-cyclohexadiene using 2,6-bis(4-azidobenzal)-4-methylcyclohexanone as a catalyst. Images of resolution 100-200 lines/mm had been successfully made with this material for photofabrication of optical screens and scales.

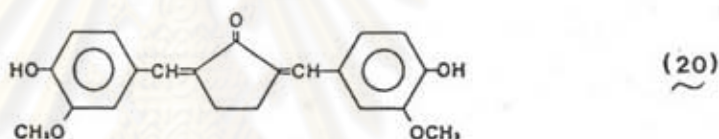
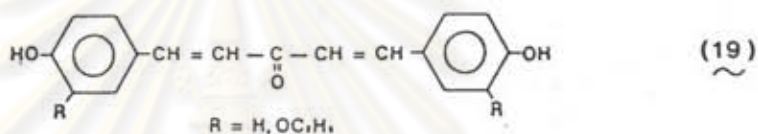
The bisazide system has been used to crosslink some non-rubber polymers to prepare negative photoresists in the recent past. Thus, Akagi et al [33] had used a formulation based on polyvinyl pyrrolidone, polyacrylamide, and 4,4-diazidostilbene-2,2-disulfonic acid disodium salt (18) to prepare a reciprocity-law-failing photoresist, the photosensitivity of which decreased rapidly with decrease in the light in the light intensity.



The mechanism involved generation of dinitrenes from the bisazide, which crosslinked the resin. As the light intensity was lower in the presence of oxygen, the dinitrene was effectively trapped. More oxygen therefore permeated into the layer and the

crosslinking was further inhibited. This explained the reciprocity-law-failing characteristics of the material.

Some polyesters had been recently described in the area of photoresists. These polyesters contain unsaturated ketone moieties in the diol portion, e.g., substituted and unsubstituted. Bis(4-hydroxybenzylidene) acetone (19), and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (20)



In the polyester derived from the latter, various metal atoms were incorporated by using metal dihalides to substitute partly the diacid chlorides in the solution condensation reaction.

The resulting polyesters were photosensitive and, coated on Al or Cu, could be exposed to UV-visible radiation and solvent developed to produce photoresists with 0.5-20% of the image being the metal.

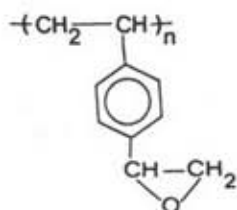
Stolyarova and co-workers [34] had observed that in ethylene propylene copolymers, bisazide photocrosslinkers caused increased sensitivity and contrast when exposures were carried out in an Ar atmosphere as opposed to that in air. From

turbidimetric titration data, the best solvent for this copolymers was a 3:1 mixture of pentene-xylene.

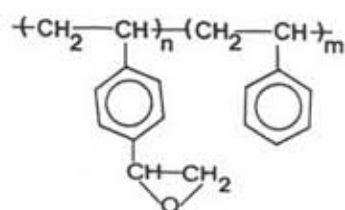
Crosslinking reaction through epoxy group ring opening has been demonstrated to be a feasible method of preparing negative resists if the ring-opening reaction can be photochemically triggered using a latent initiator. Thus, glycidyl methacrylate polymers were successfully crosslinked by photochemically generating PF_5 from p-chlorobenzene diazonium fluorophosphate. The system sensitivity depended on the diazonium salt concentration, glycidyl methacrylate concentration, and the molecular weight of the comonomers.

1.3 Objectives for this Study

The focus of this research is aimed to examine photosensitive negative resist that has high sensitivity and good contrast. So the objective of this investigation is to synthesize the photosensitive negative resists containing para-epoxystyrene. Though poly(para - epoxystyrene) (21) is expected to have high sensitivity due to the epoxy group, it was also worthwhile to improve the contrast by copolymerization with styrene monomer. Therefore, various ratios of the two monomers will be performed for the preparation of poly(p-epoxystyrene-co-styrene) (22).



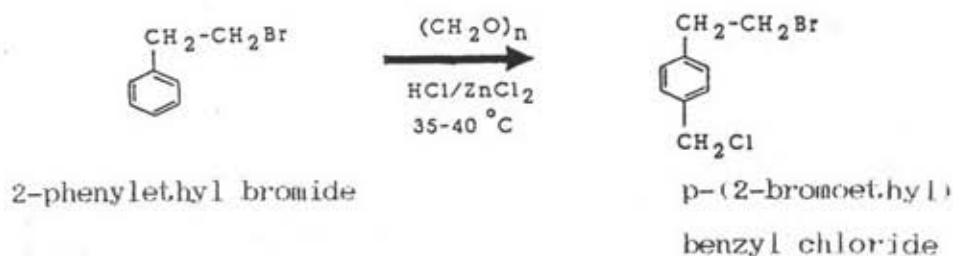
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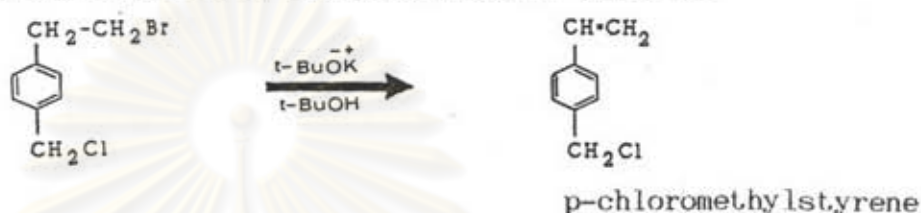
(22)

The synthesis consists of the following steps.

1. Chloromethylation of 2-Phenylethyl bromide

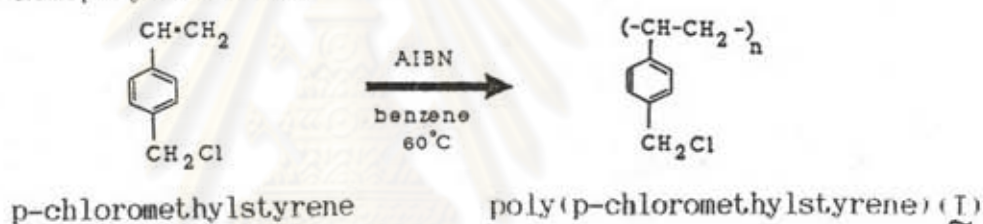


2. Dehydrobromination of p-(2-Bromoethyl)benzyl chloride

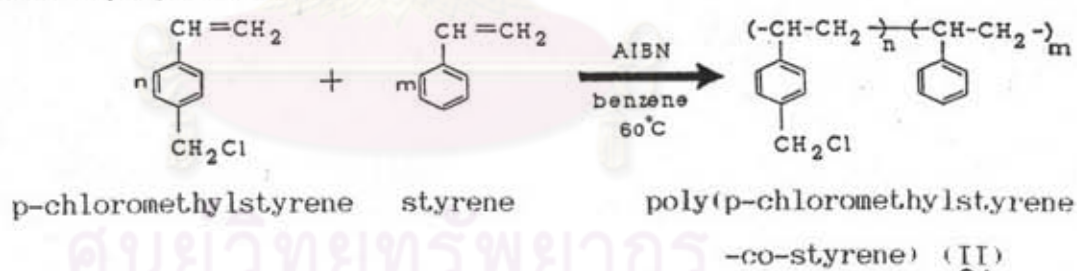


3. Polymerization

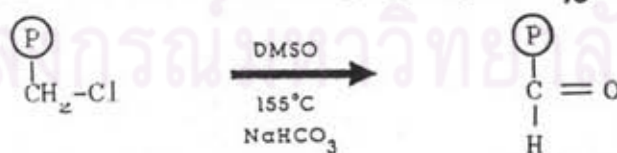
3.1 Homopolymerization



3.2 Copolymerization



4. Carboxylation of Chloromethyl group (Let. (I) and (II) = (P)-CH₂Cl)



5. Epoxidation of Carboxaldehyde group

