RESIST STUDIES FOR TCAD MODELING
1. NEGATIVE RESIST CORNER ROUNDING

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Abstract

A general overview is presented for future resist requirements from the submicron to the high nanometer regions. A brief introduction to polymer theory is given. As an example of taking into account more fundamental resist characteristics and processes, the corner rounding, prevalent in many negative resists, is investigated. Envelope sphere polymer molecule modeling describes the creation of the rounded profile at corners of resist lines during dissolution.

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1.0 Introduction

Resists are materials used in the IC and devices fabrication process to delineate circuit or other patterns on the surface of a silicon wafer or other suitable substrates. For an introduction to resists and the various lithographic processes the reader is referred to Wilson et al[24]. Briefly, resist patterns on a wafer act as masks for various fabrications steps e.g. for the etching of the underlaying oxide layer to the same pattern as that of the resist. The pattern is transferred on the resist by suitable irradiation through a mask and subsequent development. If the opaque parts of the mask are also retained in the final resist profile (i.e. no thickness loss due to development-etching), then we have what is called a positive resist, otherwise it is negative. If the irradiation that renders the resist soluble (positive) is visible light or UV radiation, then the resist is commonly called photoresist. E-Beam or x-ray resists, as their name implies, are sensitive to e-beams and x-rays respectively. It is immediately obvious that resists must have certain qualitative characteristics that render them suitable for this task. In particular they should be sensitive to the exposing radiation,

have good contrast qualities as manifested by differential development (etching) speeds between exposed and unexposed regions. High resolution capabilities is also a must for today's aggressive push for even lower minimum feature sizes, and the resist patterns should have well defined vertical walls and flat tops. Ideally the angle of the vertical wall with respect to both the substrate and the resist top surface should be 90°. Finally, they should be resistant to either wet chemical etchants or to ion etching. Those characteristics can only be obtained by a careful chemical design. In particular, since almost all of the resists in use are polymeric materials, molecular properties and polymer structure as well as the final synthesis play a crucial role towards the achievement of that goal. For a review of some of those aspects the reader is referred to Conley [46]. Last (but not least!), the exposure time factor is also of importance: A "fast" resist is a must for high throughput.

Resists have been around for along time, first as photosensitive materials for real lithography (i.e. printing patterns on paper using etched stones: λιθογραφια = λιθος [stone] + γραφη [enscription]), then used (briefly) on top of zinc printing plates and finally to this day on top of aluminum printing plates. While the minimum printable size hasn't changed in the printing industry for decades (around 60 to 100 lines/cm), the minimum device feature size of ICs has been shrinking steadily since the fabrication of the first ICs back in the 1960s. Currently the minimum feature size in the industry is around 0.25 μm while back at the early seventies it was around 2 μm. That has put a tremendous burden to resist designers and producers for a continuous upgrading of the resist chemical characteristics so that they would exhibit the aforementioned desired working specifications. Given the fact that all resist properties should simultaneously retain their desirable qualities, it is easy to see the difficulties encountered by the design chemists. This is especially true for photoresists which are now more appropriately called UV or Deep UV (DUV) resists. An extra constraint for DUV resists stems from the fact that the minimum resolvable geometric size is always comparable to the wavelength λ of the exposing radiation so diffraction effects have to be avoided by well designed optical systems; furthermore, in what concerns resists, they have to be sensitive to either a wide range of wavelengths (very desirable but usually unattainable) or be sensitive to the particular radiation.

The computational tools of TCAD, especially in the area of process technology have matured over the years. A manifestation of that fact is the collection of high performance algorithms that have been developed in connection with the Berkeley SAMPLE-3D program that is used to simulate lithography and 3-D topography. Central to SAMPLE-3D is the capability of incorporating the effects of the optical image, the lithography process, etching (and/or dissolution) and others. Of all processes, optical lithography and the etching or dissolution of the exposed resists, remain the most resistant to exact mathematical or physical modeling. For over twenty years, optical lithography has been modeled with a set of coupled differential equations with three parameters, A B and C, also called Dill's parameters. These are always extracted from experimental data, and they depend strongly on the kind of resist used. There is still no way to deduce those parameters just from the chemical composition of the resist used. Optical Lithography determines the energy absorbed at every point in the resist. The etching or development speed of the exposed resist is analogous (for positive resists) to the absorbed energy density. Again there are no exact models for dissolution of resists. In fact what is lacking is a general resist model, something that in my opinion is years away. This may not happen until a new breed of resists is developed.

In order for Technology CAD to fulfill its role as a design tool well into the nanometer region,

it has address the lack of a more accurate resist model(s). TCAD does an admirable work in having integrated in its tools the optical image and the etching and deposition. Both of them are rigorously represented with the appropriate mathematics and physics; However, in order to achieve an accurate final topography profile, it is important that all chemical-mechanical resist processes be integrated in the algorithmic tools, or as many as possible. SAMPLE-2D and SAMPLE-3D[32] do an excellent job in predicting etch profiles for most cases, but fail in some instances. A well known example is the corner rounding of developed negative resist profiles. As of yet, no available simulator predicts this effect. Deeper chemical processes must be taken into account. In a latter section we will analyze the problem of corner rounding and give a set of math equations to predict it.

In order to model a resist thoroughly, at least the following issues have to be addressed:
1. what is the mechanism with which the resist absorbs the incident radiation?
2. what kind of chemical and/or mechanical changes are produced in the body of the resist?
3. how are those changes related to an eventual dissolution (etch) rate in a suitable wet chemical etchant or plasma etchant?
4. how does the actual dissolution take place and proceed?

Those questions acquire increased importance as the geometries decrease and molecular level dimensions become more prevalent. A reverse engineering approach in manufacturing a resist does not exist and it is still almost impossible to implement; therefore, a top down approach to resist analysis is more appropriate. The question that naturally arises is: does a *general* resist model exist? In general, it does not; however, there exist models for specific tasks and /or a specific resist.

2.0 Resist models for TCAD

The ubiquitous presence of polymers as the basic building block for almost all materials used as resists warrants a brief review of some terminology which, even though well know to polymer chemists, eludes some of the users of resists.

2.1 Brief Introduction to Polymers

Resists are usually composed of high polymers. These are substances of very high molecular weight which may occur in nature or be chemically synthesized. High polymers, or macromolecules as they are sometimes called, are composed of very large molecules which are built up by the repetition of small simple chemical units called monomers. High polymers are said to be linear if the repetition of the repeating units in the molecule is similar to that of the links in a chain. Polymer molecules of this type are referred to as chain molecules or as polymer chains. The length of such polymer chains may be specified in terms of the degree of polymerization, i.e. the number of repeating units in the chain. Alternatively, the molecular weight of the polymer may be given (= degree of polymerization x molecular weight of repeating unit). Polymer chains may also be branched. Separate linear or branched chains may be joined together along the chains by crosslinks to give a crosslinked polymer. Extensive cross-linking may lead to the formation of a three-dimensional crosslinked or network polymer. Cross-linking considerably modifies such properties as tensile strength, elasticity and solubility.

Chemical formulas of polymer chains fail to indicate the ability of the chains to adopt any of a large number of possible coiled forms or configurations. This important characteristic is a consequence of considerable freedom of rotation about a single bond in the chain which results in a high degree of flexibility. In the absence of forces which keep the chains extended, irregular coiled forms are much more probable. In a given number of polymer chains many different coiled configurations will occur simultaneously. Due to the large number of possible and probable chain configurations, for any quantity that is defined as the dimension of a chain, only its average value over a large number of chains will reflect a unit of measure for the whole polymer volume[20,21]. The dimension most commonly used to describe the configuration is the end to end distance r, illustrated for a possible chain configuration in Figure 1. Another example of a measure of the dimension of the chain is the radius of a hypothetical volume that encloses completely the chain.
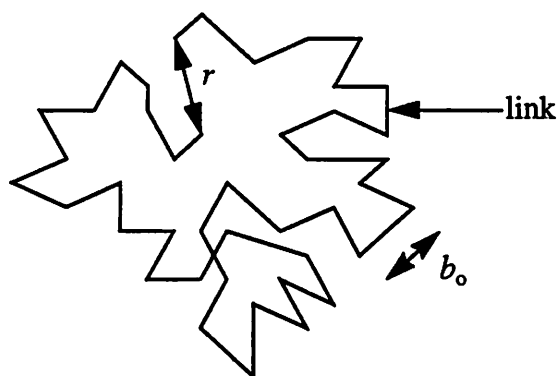

Figure 1. Representation of a possible chain configuration.

The distribution of values of r and the influences of chain structure and hindrance to rotation about bonds may be obtained by statistical methods; such information is essential in interpreting certain dilute solution properties of polymers. As shown in Figure 1, the simplest representation of a polymer chain consists of a series of n links, each of length b_o, joined in a linear chain without any restrictions on the angles between successive bonds. This model is a first level approximation since the macromolecule is completely free to move as it likes, a situation that might occur in dilute solutions. For this case it can be shown that the values of r are distributed according to a normal or Gaussian probability function and the root mean square $(\bar{r}^2)^{0.5}$ is equal to:

$$(\bar{r}^2)^{\frac{1}{2}} = b_o n^{\frac{1}{2}}$$

(1)

Figure 1 is just a visualization of the random flight chain model[30] for a polymer molecule, where each monomer unit is given a certain freedom of rotation about its axis of its preceding monomer unit, and this freedom allows the chain to take on a huge number of different conformations. This model then is a hypothetical chain made up of rigid thin rods (monomers) of equal length connected linearly by universal joints, where its rod can take any direction with equal probability. Each rod is referred to as a segment or bond. In the limiting case when the segments become infinitesimally small, the total contour is held constant and the bond angles approach 180°, the polymer chain is rendered continuous: a smooth space curve of certain length. This curved chain is called the continuous chain model. Sometimes this chain is also called

the wormlike chain[30].

In solid polymers intertwining of chains may restrict configurations. Interchain forces are of three types:

1. Dipole or orientation forces that cause attraction between polar groups on different chains. Dipole forces are strongly temperature dependent.

2. A dipolar group may cause slight displacement of the electrons and nuclei of a neighboring non polar, but polarizable, group on another chain, causing an induced dipole. Attractive forces between permanent and induced dipoles are called induction forces. These are small but not negligible.

3. A third type of force results from the fact that all molecules have time varying dipole moments, which average out to zero, arising from different instantaneous configurations of electrons and nuclei. These give rise to the so called London or dispersion forces. They are independent of temperature and make the main contribution to interchain attraction.

A particularly important type of interchain attraction may arise from hydrogen bonding[23], which may perhaps be regarded as an extreme case of dipolar attraction. Because of the positive charge on the nucleus of the hydrogen atom, the electrons in the bond between such an atom and an electron attracting atom or group tend to be somewhat displaced from the hydrogen atom. Since the electron is slightly displaced, the hydrogen molecule behaves as if it is positively charged (as if only the hypostatically charged nucleus remains). It can therefore exert a strong electrostatic attraction on such electronegative atoms as O, N and Cl. A well known example of hydrogen bonding in polymers results from attraction between OH groups on different chains (intermolecular bonding), and sometimes on the same chain (intramolecular bonding). It is precisely this property of OH groups[23,25] that renders the positive Diazonapthoquinone-Novolac based resists so important in Photo, UV and DUV lithography that decades of research still strive to unlock the exact mechanisms of their inner workings when used as resists. Also, resist hardening and spontaneous contraction of hardened resist features in submicron lithography that is due to the above forces[11] has been reported. In conclusion, interchain forces in polymers contribute a lot to their cohesion (and their cohesive energy). It is on those forces that many properties of polymers, including miscibility with liquids and solubility, depend.

Another form of "association" between adjacent chains is chain entanglements[44,45,29,30]. It is a very general term, and we postulate to define all sorts of intermolecular associative links, except for the extremely important form of intermolecular binding by crosslinks representing permanent bonds between what was originally separate molecules. Entanglements can behave for limited periods as equivalent permanent crosslinks. Figure 2 shows an entangled chain and its reptation tube. Reptation theories provide a set of constitutive equations for concentrated polymer solutions. It is based on the fact that the dynamics of each molecule must be affected by the many other molecules with which it is in intimate contact. The reptation tube is a topological constraint dictated by the physical constriction of a single chain to move only in a certain tubular volume because of the entanglements. The molecule is said to reptate. The reader is referred for a review of reptation theories to Larson[29] and Fujita[30]. It is propitious to emphasize at this point, that the knowledge of macromolecule displacements in concentrated solutions is important for understanding resist dissolution at a molecular level.
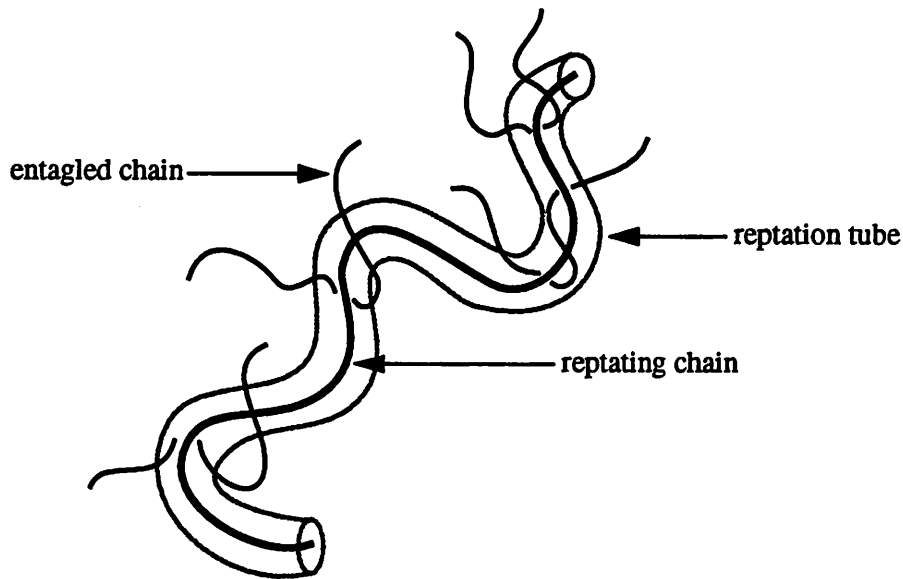
Figure 2. Entangled chain and its reptation tube.

2.2 Cross-linking of Polymers

Polymers can experience chain growth in more than one dimension. These polymers are far more complex than the linear polymers. At some stage, in the process of three dimensional cross-linking of individual chains, extremely large network structures will be formed. Such formation is shown by a sudden change in both the character of the polymers formed and in the properties of the reaction mixture. In the early stages of the three dimensional cross linking the polymers formed are soluble in appropriate solvents. The formation of the three dimensional networks results in gelation. At this stage the reaction mixture becomes much more viscous and will consist of two components: the gel, which is insoluble in solvents suitable for the polymer in its non cross-linked state, and the sol, containing polymers which are still soluble. The distinction between the two is that the gel consists of three dimensional networks, and the sol of branched structures. As polymerization proceeds beyond this point the amount of gel increases and the polymer becomes an even more complex structure with multiple cross-links) between the initial individual chains. It should be emphasized here that the onset of gelation is sudden, and, even though the average degree of increased polymerization immediately prior to gelation is low, the gel form corresponds to a very high degree of polymerization (i.e. a very high, almost infinite, molecular weight).

There are three main types of cross-linking of macromolecules that usually lead to a three-dimensional polymer network. These are:

1. Direct coupling of chains (homopolymerization) through the cross-linking site.
2. Direct coupling with propagation, resulting in multifunctional junctions. Junctions will join two or more chains.
3. Coupling through copolymerization with small monomers that can have an arbitrary distribution of molecular weight and functionality. Copolymerization is the process of the union of two or more suitable monomers. For cross-linking, the small monomer links two macromolecules by coupling with two monomers each belonging to the individual macromolecules.

Assuming a continuous chain polymer model, the Figures 3-6 are a visualization[2,3] of the above cross-linking types.

continuous chain with pendant
functional groups A's
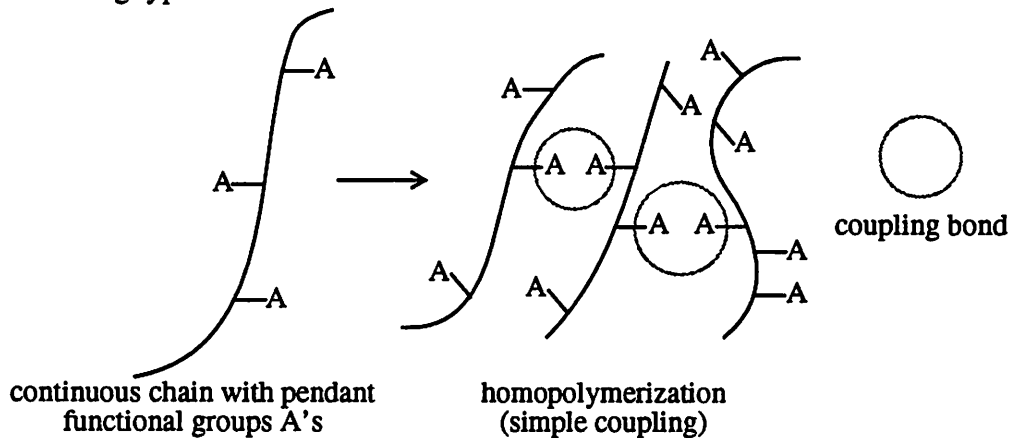
homopolymerization
(simple coupling)

coupling bond

Figure 3. Homopolymerization of long chains.

The homopolymerization of long chains is represented schematically in Figure 3 as the coupling of pendant functional (i.e. reactive) groups. These are represented by A's, distributed on each chain. An example of simple coupling is peroxide cross-linking of natural rubber[2].

coupling bond
(cross-linking junction)
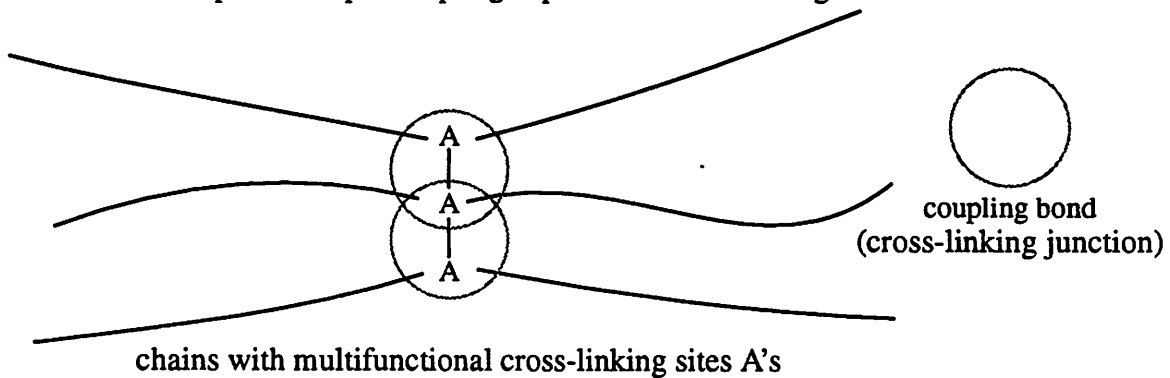
chains with multifunctional cross-linking sites A's

Figure 4. Coupling with propagation of long chains.

Figure 4 depicts coupling with propagation, another type of random cross-linking of long chains that involves two or more chains coupling at each crosslink. The cross-linking reaction is often an addition-type reaction (i.e. it involves chain reactions). Each crosslink junction involves a random number of chains. The multifunctional crosslinks are denoted again by A's.

Another process by which long chains may be cross-linked is via stepwise copolymerization with a small molecule. There are many examples of this type of cross-linking, including epoxy novolacs cured with amines, melamine cross-linking of acrylate copolymers with pendant OH groups, melamine cross-linking agent in SNR–248 resist with the poly (p-vinyl phenol) resin (acid catalyzed)[19], and as a last example, acid catalyzed cross-linking of novolac as the matrix resin with hydroxylmethylmelamine as the small molecule[24]. Photoacid generation is accomplished with the incorporation of diazonaphthoquinone which generates acid during exposure. Figure 5 describes the process of stepwise copolymerization with a small molecule and Figure 6 shows the chemical complexity of the acid catalyzed reaction between novolac and the hydroxyl-

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methylmelamine molecule, with subsequent cross-linking of the resist matrix.
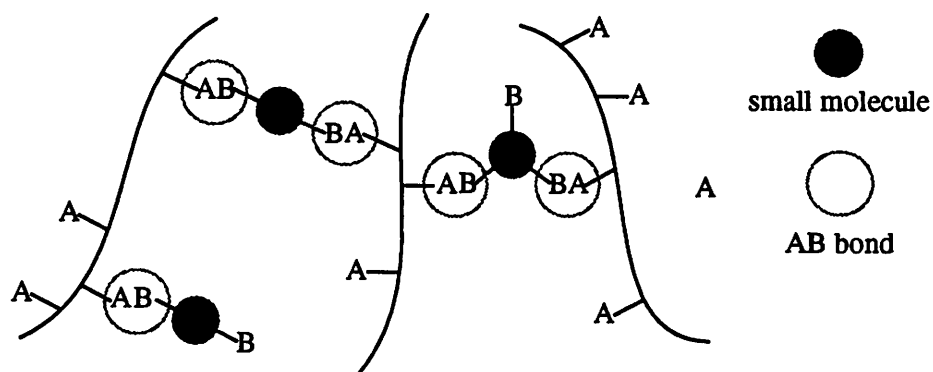

Figure 5. Coupling through small molecule copolymerization.
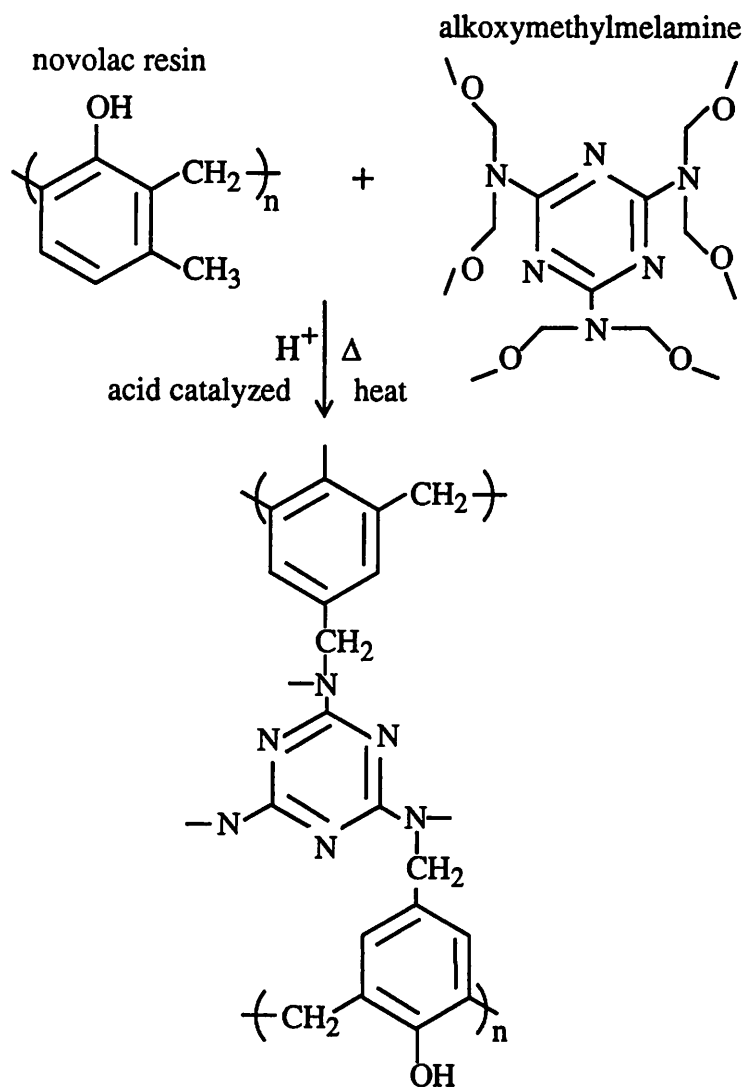

Figure 6. Cross-linking of novolac through hydroxylmethylmelamine.

Exposed areas of negative resists become insoluble to liquid developers precisely because the exposing radiation initiates a cross-linking process that renders them three-dimensional polymer networks. Areas that correspond to the opaque parts of the mask pattern dissolve in subsequent development. Therefore, the image pattern that gets transferred to the resist is the negative mask image. Cross-linking is usually the method that creates negative images on resists after exposure and development since exposed areas become insoluble.

As mentioned earlier, positive resists are characterized by the fact that exposed areas dissolve during a subsequent development process. Positive resists are usually of two kinds: a) one component resists such as Poly Methylmethacrylate (PMMA) which undergo chain scission upon exposure to ionizing radiation so that exposed areas have, in general, lower average molecular weight than the unexposed ones, or b) two component resists usually based on novolacs. The main result of exposure is to make various sites of the polymer molecules that contain OH groups accessible to an aqueous base developer that neutralizes the intermolecular bonds, thereby rendering the molecules dissolvable[35,33]. It should be emphasized here that a lot of research is still being conducted on the exact workings of novolac resists and also on the way the base reaches the "deprotected" i.e. accessible OH sites. It is also true for t–BOC type DUV positive resists that the exposure results in producing OH groups which contribute to their solubility in polar solvents. Percolation theory has been used to explain the workings of how deprotonation proceeds, albeit with no conclusive results[36,37,38,39,40,41,42]. However, the mechanism(s) by which the "dissolved" molecules escape from the polymer to the surrounding developer liquid, is (are) still part of the active investigation of polymer solution science and engineering.

2.3 Polymer Solutions

A developing liquid-usually an organic solvent- is needed for the dissolution of resists. The study of development, i.e the interaction of developer-resist, is part of the theory and experimental predictions of the field that is known as the study of polymer solutions. Briefly, a polymer solution is a mixture of polymer molecules with solvent molecules. The polymers are usually either dissolved in, or swollen by, the liquids. Dilute solutions are characterized by more or less non-interacting polymer molecules in a "sea" of solvent. Solvents can be either good or bad (or we can have mixtures of good and bad solvents). Assuming the random flight chain model of a polymer molecule, a solvent-segment interaction that favors solvent-segment contact over the segment-segment ones is defined as a good solvent (for the polymer considered), while if the reverse is the case, the solvent is said to be poor or bad.

The osmotic pressure[22] Π of a dilute solution of a monodisperse polymer with molecular weight M is expressed as a power series of polymer mass concentration c (weight of polymer per unit volume of solution) as

$$\frac{\Pi}{RT} = \frac{c}{M} + A_2 c^2 + A_3 c^3 + ...$$ (2)

where R is the gas constant, T the absolute temperature, and M the molecular weight of the polymer. This is the osmotic virial expansion series[21,30], with A_i (i = 2,3, ...) being referred to as the i-th virial coefficient of the solution. A_2 can be evaluated experimentally, and many studies have shown that it depends on M as well as T and the solvent species. It was also shown that for a given polymer there is a combination of poor solvent and temperature, called θ, for which A_2 vanishes

regardless of M (except for oligomers and similar low-molecular weight polymers). This special poor solvent at the theta temperatures is called the theta solvent. The theta condition is used synonymously with the theta temperature[21,20] (also called Flory temperature). The theta temperature for a given solvent-polymer combination can be viewed as the temperature below which the polymer becomes insoluble in that particular solvent.

Quantitative treatment of polymer solubility and solutions requires the application of thermodynamic principles. The quantity ΔG, the free energy change of dilution, is defined as the change of the Gibbs free energy when one mole of solvent is added to such a large amount of solution that the concentration in not effectively altered. ΔG is related to the heat (enthalpy) and entropy of dilution, ΔH and ΔS, respectively, by the equation

$$\Delta G = \Delta H - T\Delta S \tag{3}$$

Ideal solutions may be defined as those obeying Raoults's law, which may be expressed by

$$\frac{p_1}{p_{01}} = x \tag{4}$$

where p_1 is the partial vapor pressure of the solvent above the solution, p_{01} the saturation vapor pressure of the solvent at the same temperature, and x its mole fraction in the solution. This law is seldom obeyed; however, in practice x is sometimes replaced with $xf = a$ where a is the activity and f is the activity coefficient of the solvent for the law to become more realistic. If the ideal law is observed, equation (3) is reduced to:

$$\Delta S = -R\ln x \tag{5}$$

A polymer solution, far from being ideal, it is also irregular. For example, it is irregular when ΔH is positive (heat is absorbed) and $\Delta S \gg -R\ln x$. This departure from ideality in what concerns the polymers is primarily due to the very large entropies of dilution. Only infinitely dilute polymer solutions behave ideally. The large entropy changes are a consequence of the very large differences in size between molecules of solvent and polymer, and of the flexibility of the latter. Thermodynamic treatments of polymer-liquid (polymer-solvent) systems try to interpret theoretically the values of ΔS and ΔH and give expression for these and of ΔG in terms of concentration and other measurable quantities. The above quantities are important since they provide a measure of theoretical quantification of the solubility of polymers in particular solvents. The catch is, for resist work, that the most "accurate" theoretical derivation is valid for solutions which are neither dilute or really concentrated. We have defined the former as a solution where clusters of polymer molecules of even single ones are in a sea of solvent. The later are defined as solutions where the polymer molecules are not free to move as they please since there is a certain degree of entanglement among the molecules. Nevertheless, the advance of the study of polymer solutions to either side of the concentration spectrum was based on the relations derived by both Flory and Huggins for "regular" solutions.

Meyer suggested that entropies of mixing and dilution could be obtained from computations of the number of ways of arranging a flexible chain on the points of a lattice[20]. Flory and Huggins attacked the problem and after their computations they obtained[21,20]

$$\Delta S = -R\left[\ln(1 - \phi_2) + \phi_2\left(1 - \frac{1}{x}\right)\right] \tag{6}$$

where $\phi_1 = 1 - \phi_2$ and ϕ_2 are the volume fractions of solvent and polymer respectively ($_1$ denotes solvent and $_2$ denotes polymer).

Heat change occurs when a solute and solvent mix, or a solution is diluted, because of differing intermolecular forces between molecules of solute (polymer), molecules of solvent, and molecules of solvent and solute. If only dispersion forces are involved, or largely so, the heat of dilution is given by

$$\Delta H = V_1 (\delta_1 - \delta_2)^2 \phi_2^2 = \alpha \phi_2^2 \tag{7}$$

where V_1 is the molar volume of the solvent, α is a constant of the system, and δ is called the solubility parameter, and is defined as

$$\delta = \left[\frac{(L_e - RT)}{V} \right]^{\frac{1}{2}} \tag{8}$$

where L_e is the molar latent heat of vaporization, and V the molar volume, both at the absolute temperature T. It should be noted that the polymer solubility is inversely proportional to the molar volume ($V^{0.5}$) and hence, by extension, inversely proportional to the average molecular weight.

The goal is to find the free energy of dilution. It is appropriate to introduce here yet another term, the lattice coordination number z. For this treatment, we only consider "regular" solutions, i.e. neither too dilute or too concentrated. In this case the lattice coordination number is simply taken to be equal to the average number of nearest neighbors of a molecule. Values of z between six and ten are plausible. The formulae for regular solutions are insensitive to z. With this, the free energy of dilution as given by Huggins[20] is equal to:

$$\Delta G = RT \left[\ln 1 - \phi_2 + 1 - \frac{1}{x} \frac{z}{2} \ln 1 - 2 \frac{\phi_2}{z} + \frac{\alpha \phi_2^2}{RT} \right], \tag{9}$$

and if the logarithm is extended in series and only the first two terms are retained, then

$$\Delta G = RT \left[\ln (1 - \phi_2) + \left(1 - \frac{1}{x} \right) \phi_2 + \chi \phi_2^2 \right], \tag{10}$$

where, if x is large, χ is given by:

$$\chi = \frac{1}{z} + \frac{\alpha}{RT} \; . \tag{11}$$

This is the famous Flory polymer-solvent interaction parameter. Basically, $kT\chi$ denotes the difference between the energy of a solvent molecule surrounded by polymer molecules and the energy of the molecule surrounded by molecules of solvent (k is the Boltzmann constant). The value of χ depends on a number of factors. In equation (11), $1/z$ can be regarded as an entropy term, and α/RT as the heat term, so that

$$\chi = \chi_s + \chi_h \tag{12}$$

where s denotes entropy. Using (7) we arrive at

$$\chi = \chi_s + \frac{V(\delta_1 - \delta_2)^2}{RT} . \tag{13}$$

Expanding the logarithm in equation (10) and putting x equal to V_2/V_1, the ratio of molar volumes of polymer and solvent, then

$$-\Delta G = \frac{RTV_1\phi_2}{V_2} + RT\left(\frac{1}{2} - \chi\right)\phi_2^2 + \frac{RT\phi_2^3}{3} + \dots \tag{14}$$

Again, for "regular", i.e. not too concentrated solutions, ϕ_2^3 is small, and the higher terms are negligible, and the value of ΔG depends on χ. ΔG also depends on the molecular weight of the polymer through the term V_2/V_1 and through the solubilities δ (8).

For a polymer to dissolve in a liquid, it is a thermodynamic requirement that ΔG must be negative, and equation (14) shows that this requirement is met if the value of χ is less than approximately 0.5. If this value is exceeded, ΔG will be positive, and the polymer will not dissolve, rather it will swell. The degree of swelling decreases as χ increases in value. The greater the negative value of ΔG, the better the solvent in a thermodynamic sense. The critical value of χ, χ_c, above which dissolution cannot occur, rather uptake of solvent and swelling, depends on the RTV_2/V_1 term. This reflects the effect of molecular weight of polymer on χ_c. It is shown that

$$\chi_c = \frac{1}{2}\left(1 + \frac{1}{x^{0.5}}\right)^2 . \tag{15}$$

The above relation is valid for the *steady-state* case of solvent in equilibrium with the polymer. For the *transient* case of solvent uptake and swelling, Govindjee[31] attacked the problem from the viewpoint of a coupled field problem in which one accounts for the mass balance of the solvent and the momentum balance of the stressed mixture. Gao[13] proposed a numerical scheme that can predict the diffusion and swelling of the solvents into a one-dimensional polymer slab. In that, Fickian and non-Fickian diffusion models are used together with a concentration dependent mass uptake kinetics model for the viscoelastic response of the polymer. Zhogov[33] tackled the problem of dissolution of polymers with mass transport in the polymer-gel-liquid solution system. Diffusion in polymers was investigated in[14], and Rossi[16] described a macroscopic treatment of the kinetics of swelling for a cross-linked gel.

Taking z, the lattice coordination number, to be approximately equal to 4 (valid for flexible polymers) and using equation (7) for α, (11) becomes:

$$\chi = 0.25 + \frac{V_1(\delta_1 - \delta_2)^2}{RT} . \tag{16}$$

If χ is to be less than 0.5, then the solubilities of the solvent and the polymer should be very close (i.e. $\delta_1 - \delta_2$ should be small). It can be shown that for the critical value χ_c, the volume fractions of solvent and polymer in the liquid (solution) phase are:

$$(\phi_1)_c = \frac{x^{0.5}}{1 + x^{0.5}} \quad ; \quad (\phi_2)_c = \frac{1}{1 + x^{0.5}} \tag{17}$$

If x is large, the liquid in equilibrium with the swollen polymer will be practically pure liquid, as expected. This is immediately apparent from the fact that for large x, $(\phi_1)_c = 0$ and $(\phi_2)_c = 1$.

The rapid drop in solubility with increasing χ means that a linear homogeneous polymer will probably be either entirely soluble or completely insoluble in a given liquid.

If the value of χ for the system is greater than about 0.5, a linear polymer will only swell in the liquid. The condition for equilibrium between a swollen insoluble polymer and the liquid which causes swelling is that $\Delta G = 0$. Equating the right hand side of equation (10) to zero and neglecting ϕ_2/x, then

$$\ln \left(1 + \frac{1}{Q_m} \right) = (Q_m + 1)^{-1} + \chi (Q_m + 1)^{-2} \ ... \tag{18}$$

where Q_m is the maximum volume of liquid uptaken by unit volume of polymer. This has a positive solution if χ is greater than 0.5; hence, χ can be obtained from equilibrium-swelling measurements. If the polymer is cross-linked, it can only swell, however good the liquid may be as a solvent of the uncross-linked polymer. To reiterate, the main qualitative reason for the limited dissolution is that, a cross-linked polymer is more rigid than elastic, so it will swell only to a certain extent. For swelling cross-linked polymers[20], an additional term must be added to equation (10) for ΔG due to elastic deformation during swelling. This additional term is $RT\phi_2^{1/3}/M_c$, where M_c is the molecular weight of a section of the chain between two cross links. Neglecting ϕ_2/x we get

$$\Delta G = RT \left[\ln (1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \frac{\phi_2^{1/3}}{M_c} \right] . \tag{19}$$

At equilibrium swelling, $\Delta G = 0$ and we get

$$\ln (1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \frac{\phi_2^{1/3}}{M_c} = 0 . \tag{20}$$

$Q_m = \phi_1/\phi_2 = (1-\phi_2)/\phi_2$ so that if M_c is known, χ can be obtained from measurements of Q_m. Alternatively, if χ is known from experiments with uncross-linked polymer, M_c and the degree of cross-linking can be obtained. Note that the last term in the left hand side of equation (19), $\phi_2^{1/3}/M_c$, is proportional to the degree of cross-linking, hence it will render ΔG even more positive as cross-linking becomes more dense since, by definition, M_c will decrease and hence the fraction will increase. This is the main quantitative reason as to why cross-linked resists do not dissolve. It is also the qualitative and quantitative contributing factor to the extent of corner rounding in negative resists.

3.0 Negative Resist Corner Rounding

As mentioned previously, a very pronounced feature of negative resists is corner rounding. We will briefly review all the steps that lead to a negative resist developed profile.

3.1 Theoretical Background

An area of negative (chemically amplified) resist is exposed through a mask pattern. The exposing radiation will generate acid[19,34] (what is also called photoacid) in the bulk of the resist and at those areas that correspond to the mask open areas. The local concentration of the photoacid at any point in the resist is approximately proportional to the exposure dose at that

point. Continuing with the same train of thought that characterizes Ferguson's modeling[19] of the exposure and bake, the local extent of cross-linking that takes place at any volume point in the resist is related to the photo-generated acid concentration through chemical reaction kinetics at that point. The acid catalyzes the cross-linking process which proceeds using small molecules. For the case of the SNR–248 negative resist the small molecule is a melamine cross-linking agent, and cross-linking proceeds much like the example given in Figure 6 where the heat Δ is provided by the Post Exposure Bake (PEB). In general terms, the cross-linking of the whole exposed resist volume proceeds as shown in Figure 5. The third and final step of any resist characterization is the development (dissolution) of the unexposed negative resist or of the exposed positive resist. Here we will concern ourselves only with the first case, that of negative resists.

In our previous introductory exposé of polymers and polymer solutions we distinguished the following kinds of solvent-polymer solutions:

1. **Dilute solutions.** Here the macromolecules are more or less "free" in a sea of solvent. By definition, this picture corresponds to dissolved resist in the developing solvent. For our purposes, the solvent bath is considered infinite in size.
2. **Regular solutions.** Now the macromolecules are much closer to each other and polymer "clusters" may occur. Still there can be a steady state mixture of polymer molecules with solvent ones. This is often the starting point of most of the studies on polymer solutions. In what concerns resists, a regular solution might represent a heavier concentration of dissolved macromolecules just off the resist surface.
3. **Concentrated solutions.** The range of the definition is wide and its limits are the two extremes namely regular solutions and entangled-concentrated polymer–solution combinations. It is in this area that active research is increasing, since the combination of polymer-solvent is exactly what we find in the dissolution process of the resist. The undeveloped resist is a polymeric slab, extremely concentrated and usually entangled. It is immersed in the developer or it is sprayed with it – either way it is surrounded by it. The dissolution mechanism is extremely complex[25].
4. **Cross-linked polymer-solvent combination.** As it was mentioned previously, cross-linked polymers are almost impossible to dissolve; however, as it is also the case of entagled polymers, we can have solvent uptake, and subsequent swelling of the polymer (resist). The swollen cross-linked polymer (swollen gel) is in fact a solution, although an elastic rather than a viscous one[26].

Let us consider, in order, the main features of the dissolution of polymers in solvents[27]:

1. Adsorption of the solvent on the surface of the polymer.
2. Diffusion of the solvent within the polymer.
3. Chemical reaction of the solvent with various groups of the polymer (i.e. chemically unstable bonds, "deprotonation" as in the case of novolac resists, etc.).
4. Diffusion of the "dissolved" products (macromolecules) to the surface of the polymer.
5. Desorption of the dissolved products from the surface of the polymer.

A mathematical consideration of these processes is very difficult. It is usually assumed that one or at the most two stages are slow in comparison with the others, and consequently limit the course of the whole dissolution process[25,27]. The first and fifth stages usually take place more rapidly than the second, third, and fourth. As an example, an intense investigation effort is being conducted for positive Diazonapthoquinone–Novolac based resists of the workings of stages 2 and 3. For stage 2, one group of researchers uses mainly the mathematical tool of percolation[37,41,43],

which is an extension of the process of reaching a point in a volume via the most propitious path[28]. However, other researchers disagree[40]. This is just to show the difficulties one encounters in attacking those problems. Furthermore, little theoretical attention is paid to stage 4. Parallel investigations are conducted by polymer chemists of how polymer macromolecules move (or translate) in a very dense polymer. For non cross-linked resists, we usually assume that the dissolution takes place at an intermediate swollen layer, so thin and so close to the resist surface, so that there is no need to investigate how, how fast, and by which process or mechanism the macromolecules move to the surface of the resist and then onwards to the bulk of the solvent.

In general, most current resists are polymers composed of macromolecules and not of low order (up to 5-mers) molecules. In the later case, dissolution would have been straight forward: any bond of a "monomeric" resist has equal probability of "breaking" and subsequently extricating itself from the surface of the resist into the bulk of the developer. However, polymers, as we have described, can sometimes be dissolved, sometimes swollen. Furthermore, it is not known apriori that dissolution is always a surface phenomenon. If possible, it would be very desirable and advantageous to create monomeric resists provided that they have the same characteristics as the current ones in what concerns etch resistance, contrast, radiation sensitivity etc. If that can be achieved, then control of nanometer features will be much more precise.

Most of the dissolution models make use of an empirical etch rate equation that usually fits a set of experimental data points so that its "constants" can be determined. It is obvious that different resists and/or different developers and exposure parameters influence the value of the formula constants. The etch rate R for negative resists is given by:

$$R = \frac{R_o}{\left\{1 + \left(\dfrac{E}{E_o}\right)^\beta\right\}^\alpha} \tag{21}$$

where R_o is the unexposed resist etch rate, E is the absorbed energy density and β and α are the constants to be deduced from experimental data. R is a function of position. From our previous analysis, equations (14) and (17), among others, show clearly the connection between solubility of a polymer and its average molecular weight $\overline{M}_w$. Solubility is inversely proportional to $\overline{M}_w$ $\{R \propto 1/\overline{M}_w\}$. Therefore the etch rate R may be given by:

$$R = \frac{b}{\overline{M}_w^a} . \tag{22}$$

where b and a are empirical constants. The reason why no attempt is being made to give an analytic expression for either the a and b of eq. (22) or the α and β constants of eq. (21) in terms of polymer solutions theory is the fact that this theory was developed for regular solutions and not for concentrated solutions such as exposed resist–developer systems. Nevertheless, since the high extreme of regular solutions is the low extreme of concentrated ones, some of results apply at least *qualitatively* if not exactly *quantitatively* for the case of concentrated solutions.

The connection between equations (21) and (22) is the dependence of molecular weight on absorbed energy density. As long as a rigorous global model that quantifies the relationship of the molecular weight to the absorbed energy density is not available, equation (21) will always contain empirical parameters.

The problem that is often encountered during development of negative resists is that of corner rounding, depicted in Figure 7. Figure 7a represents a developed resist profile with no corner
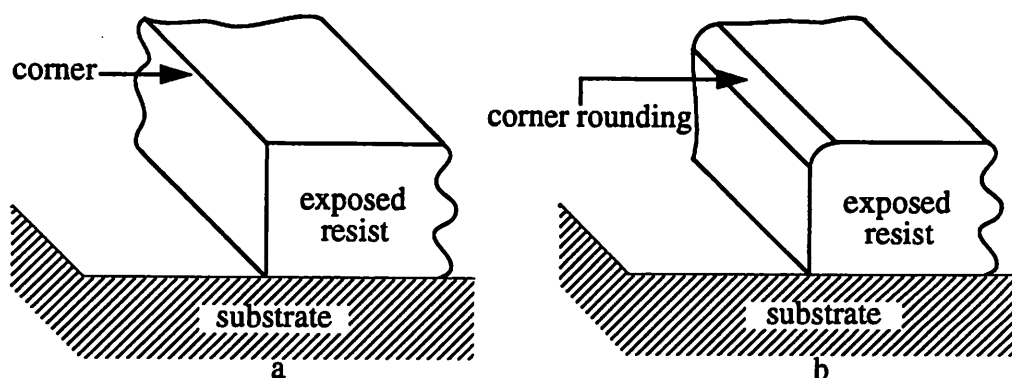

Figure 7. Definition of corner and corner rounding for negative resists.

rounding, while Figure 7b shows schematically the rounding of corners, Corner rounding has been observed by researchers in the field[9,10,18,19,35]. The phenomenon is also prevalent during polymer dissolution of radiation induced grafted resist in X–ray lithography, where subsequent post exposure bake to induce cross-linking still doesn't eliminate corner rounding[12]. To inhibit dissolution of less fully grafted resist components (mainly at the corners) as well as partial swelling, the resist was heated in order to induce cross-linking and hence resistance to dissolution. The experimental results corroborated to the fact that increased cross-linking decreases corner rounding. However, the profile characteristics deteriorated again when the temperature of heating was increased above a certain level, indicating that other chemical processes became important[12]. It is our conjecture that high temperatures changes the rheological characteristics of the resist so contrast is lost.

The studies that deal with cross-linking of polymers are usually probabilistic and statistical in nature and equations derived are valid in the bulk of a polymer. One assumption made by most researchers is that only *intermolecular* cross-links are important and not *intramolecular*, something that sometimes leads to erroneous results[4]. For cross-linking to occur, coupling of functional units should take place. Functional or reactive units denote, by definition, units of the macromolecule that can couple with other reactive units of different macromolecules and hence create cross-links. These are denoted by A's in Figures 3, 4, and 5. Note that for coupling through small molecules as shown in Figure 5, the B's denote the functional "units" of the small molecules. Whereas in Figures 3 and 4 A—A reactions are the norm, only A—B reactions are possible in Figure 5. An important coefficient in polymer cross-linking studies is α defined as the conversion coefficient i.e. the fraction of reactive or functional units that have reacted[2,3]. An equivalent definition is the probability that a functional unit has reacted[26].

As cross-linking proceeds, it is obvious that the weight average molecular weight $\overline{M}_w$ increases. The formula for $\overline{M}_w$ for the case of a monodisperse polymer where all the units are functional with equal probability of cross-linking and for the situation depicted in Figure 5 is given by[2]

$$\overline{M}_w = w_A \left\{ M + L \frac{\alpha m_b + r\alpha^2 M (L-1)}{1 - r\alpha^2 (L-1)(g-1)} \right\} + w_B \left\{ m_b + g \frac{r\alpha M + r\alpha^2 m_b (g-1)}{1 - r\alpha^2 (L-1)(g-1)} \right\} \quad (23)$$

where the above terms denote:

w_A Proportion of mass composed of the long chains with the A reactive units. (All units of the long chains are reactive in this case)

w_B Proportion of mass composed of the small molecules with the B reactive sites. (Actually the small molecule is a unit that has g reactive sites)

M Weight of the long chain (A chain).

m_b Weight of the small molecule (B).

r Stoichiometric imbalance ratio to be given below.

α Conversion coefficient, extent of reaction (cross-linking).

L Number of repeat units in a chain.

g Number of reactive sites in a small molecule.

The stoichiometric imbalance r is given by:

$$r = \frac{Lm_b}{gM}\frac{w_A}{1-w_A} \qquad \text{since} \quad w_A + w_B = 1 . \tag{24}$$

The gel point, or critical conversion α_c, is the conversion at which the weight average molecular weight diverges i.e. it becomes infinite. From equation (23) this is

$$\alpha_c = \frac{1}{\{r(g-1)(L-1)\}^{1/2}} . \tag{25}$$

The onset of gelation (three-dimensional network formation) is abrupt and equation (25) shows that the longer the molecules ($\Rightarrow$large L), the smaller the value of conversion required for the onset of gelation ($\Rightarrow$three-dimensional cross-linking), and the proportion of cross-linkages required for gelation becomes remarkably small[26]. It is important to note, however, that beyond α_c by no means all of the polymer will be combined into one infinite molecule. For example, in spite of the favorable probability of coupling, some chains might either remain uncoupled or coupled to a cluster of finite weight. This part of the polymer is defined as the *sol* and is soluble. The amount of soluble material in a polymer at a given extent of reaction can be computed[3]. However, again the derived formulas do not take into account the geometrical shape of the cross-linked polymer in question. Since the weight fraction soluble material is described in the basis of statistical models, the solubility behavior after the gel point is also described on the same basis[8].

For the more general case of a polydisperse polymer[5] that has a molecular weight distribution, it has been shown[7] that the network core is formed from the largest macromolecules whereas macromolecules of lower molecular weight remain uncross-linked or are engaged in cross-links which are not gel effective (mainly in the sol fraction but also in the gel)[7,26]. In the next section, a dissolution model is proposed that takes into account the topography of the developing resist.

3.2 Envelope Volume Molecular Dissolution Model

Figure 8 describes a first order approximation in representing an arbitrarily shaped coil chain as an envelope sphere whose diameter can be taken to be the statistical average of all the possible spherical envelopes of the arbitrarily shaped chains in the resist. The range of possible configurations extends from the globule to the elongated chain. This visual characterization of the macromolecules is helpful in describing the processes that take place near the corner of the resist lines. Besides their arbitrary shape, the molecules are also entangled, so usually the polymers are not crystalline in nature. Figure 9a shows the state of the exposed resist: Molecules are modeled as
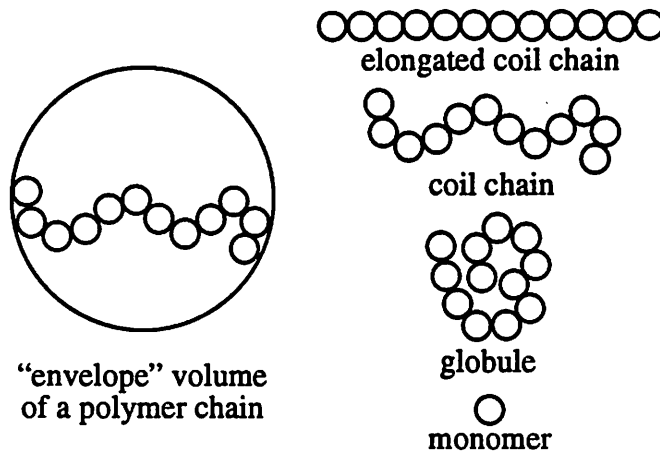
Figure 8. Spherical volume approximation of a coil polymer chain.

spheres and cross-linking is achieved via the intermediary of the small molecules. Note that the molecules are not arranged in any order, and also a molecule can physically be situated at the interface of the exposed-unexposed regions of the resist as shown in both Figures 9a and 9b. It is obvious that molecules situated at the surface of the resist do not have the possibility of cross-linking in an angle roughly 90° as shown in Figure 9a. This is due to the fact that the resist layer is physically terminated at the surface interface between resist and air. Carrying this analogy to the corner, the corner molecule has just half the probability of cross-linking compared to the surface molecule, since at the interface of the exposed-unexposed regions of the resist, no cross-linking can take place when the chain functional segments are "looking into" the unexposed area. The uncross-linked sites of the macromolecules and/or of the small cross-linking molecules at the corner and at the two interface surfaces (resist-air and exposed-unexposed resist) are depicted in Figure 9a.
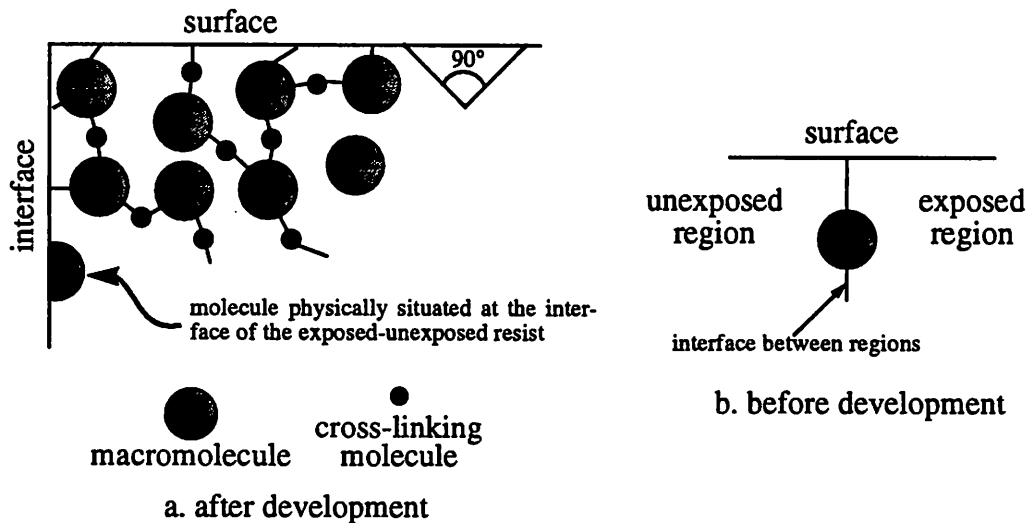

Figure 9. Cross-linking of the exposed region impedes dissolution during development.

In order to facilitate further the analysis of corner rounding during development, it is assumed

surface of resist

small
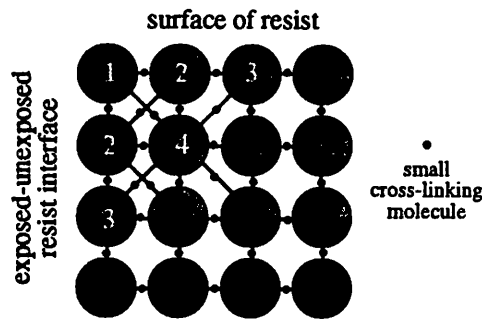cross-linking
molecule

exposed-unexposed
resist interface

Figure 10. Cross-linked resist
at corner rounding region

that the molecules are arranged in a regular array. This is shown in Figure 10. Note that the "bulk" molecule ❹ can have many cross-linking paths (bonds) with the three-dimensional network. The less loosely bound molecule is the corner one denoted by ❶. The surface and interface molecules denoted here by ❷ and ❸, plus all the others that are physicaly situated at those interfaces, are less tightly bound than the bulk molecule ❹ but more tightly than ❶.

Figure 11 describes the evolution of the corner rounding as development of the resist progresses in time. For simplicity, the cross-linking bonds are not shown. The dark spheres denote undissolved

a

b

c

d

e

● undissolved molecule
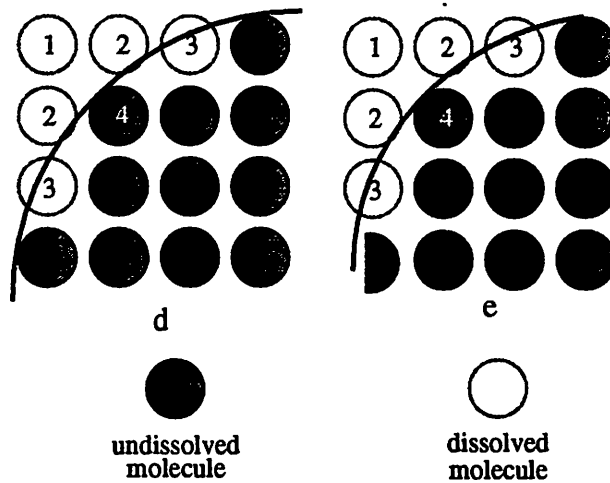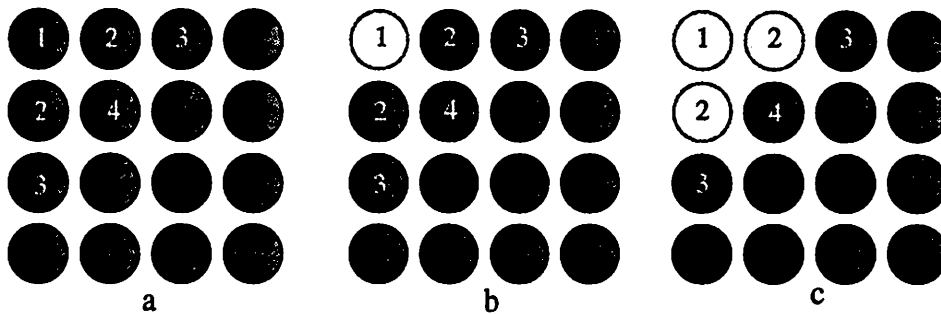
○ dissolved molecule

Figure 11. Model of the corner rounding during dissolution of negative resists.
Only the exposed region is shown.

molecules while the light ones are considered dissolved. The developed profile is the envelope curve of the undeveloped molecules. Note that, due to symmetry, a two-dimensional characterization of the process is sufficient. For three-dimensions the circles representing the molecules become spheres and coupling can occur in any direction. For surfaces and corners, the angles of non-coupling (like the 90° angle in Figure 9) become solid angles.

Development of the resist proceeds as follows: At time $t_d = 0$, the resist top surface extends over both the exposed and unexposed regions as shown in Figure 12. As time progresses, the unexposed (and hence noncross-linked) region is being etched away by the developer. The exposed region is inure to etching except at the corner region where it is being etched slowly.
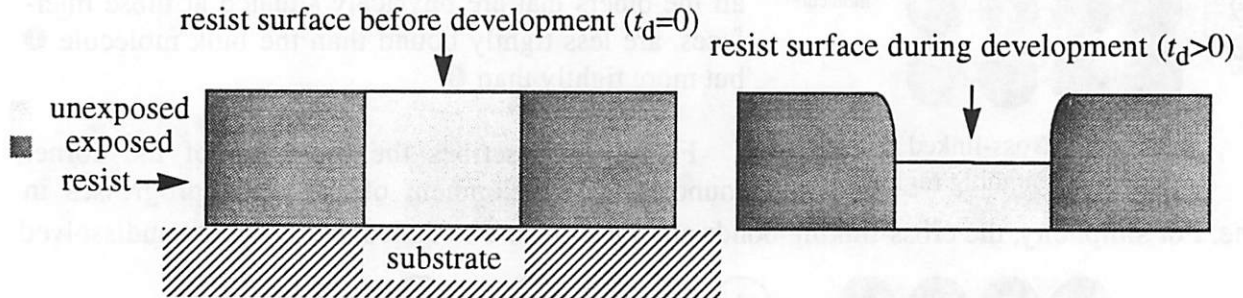
resist surface before development (t_d=0)

resist surface during development (t_d>0)

unexposed
■ exposed
resist →

substrate

Figure 12. Geometry of exposed and unexposed regions before and during development.

Below is a step by step description of the corner rounding as described graphically in Figure 11:

1. Figure 11**a** shows an exposed resist region right before development. All molecules have a high probability of being cross-linked with neighbouring molecules and being part of the three-dimensional network. As it was mentioned above, depending on how far cross-linked has progressed once gelation started, there is a certain amount of polymer, the sol fraction, that is soluble. However, formulas for the sol fraction give no clue as to the exact placement of the sol in a resist volume. It is postulated that the "corner" molecule ❶, even if it is not part of the sol, is a good candidate for dissolution based on the fact that, due to the geometry of the resist region as shown in Figures 9 and 10, it is the most loosely bound molecule. There exist various mechanisms that may achieve the desired result of prying loose (hence dissolve) the corner molecule from the rest of the resist: "Attack" by the developer both from the top and the side ($\Rightarrow$ the interface of the exposed–unexposed regions) and either weakening of the chemical bonds and finally disassociation, or topical swelling and forced translation of ❶ and mechanical breaking ("tearing apart") of the bonds.

2. Figure 11**b** shows the situation when the ❶ molecule has been dissolved. It is obvious form the figure that molecules ❷ are now the prime candidates for dissolution since they are the most exposed to the developer as ❶ was before it was dissolved. Note that now molecules ❷ have more couplings with the lattice when compared with what ❶ had. Thus, now it will take more time to pry loose molecules ❷.

3. Figure 11**c** shows the ❶s as being dissolved. Now the ❸s become the prime candidates for dissolution for the same reasons as given in 2.

4. Figure 11**d** shows the developed profile at the corner as the envelope curve of the still undeveloped resist. The model prediction of the corner rounding has been achieved. Even if a non-
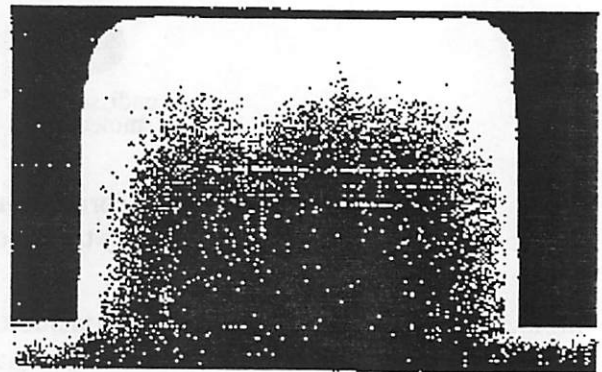

Figure 13. Tapering of side wall of INR2 negative resist from IBM (after Puttlitz[9] et. al.).

regularly spaced army of molecules is assumed, still the curvature remains cyclical as is shown by both published and our own experimental results to be presented in the next section.

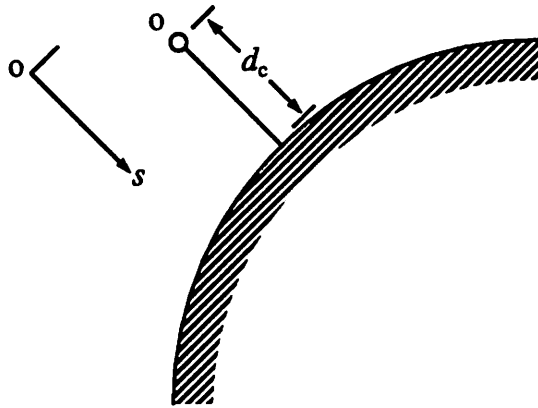5. Figure 11e shows the situation where it may happen that many molecules are situated at the

Figure 14. Definition of corner distance variable s.

interface of the exposed-unexposed resist. The probability of the molecules being uncross-linked or having far fewer couplings compared to the molecules which are wholly within the exposed region is greater. Therefore, this molecule will be easily dissolved. Such kinds of molecules are found only at the interface and not on the surface of the resist. The net result is a tapered profile of the vertical wall near the corner as shown in Figure 13.

In order to calculate the total corner etch distance d_c as defined in Figure 14, the corner etch speed $R_c(s)$ should be known. It can be found experimentally by interrupting the development process at regularly spaced time intervals and measure the etch distance corresponding to the partial development time elapsed. Still the ratio of the partial etch distance over the partial development time is equal to the average corner etch speed. Provided that a curve fit giving $R_c(s)$ can be achieved, then dc is given by the simple formula $d_c = \int_{t=0}^{t=T_{Dev}} R_c(s)\, dt$ where T_{Dev} (26) denotes the total development time.

4.0 Experimental Results

A series of exposures were performed on resist coated Silicon Wafers at the Microfabrication Laboratory using a stepper and a DUV source at 0.248 μm. The mask had a set of contiguous periodic lines as well as isolated lines. Both negative SNR–248 and positive APEX–E resists were used. The lines and spaces being reproduced ranged from 2.0 μm down to 0.20 μm. For each resist, the results are discussed bellow.

4.1 Positive Resist APEX–E

This resist worked very well down to a quarter micron (0.25 μm). The lines opened up nicely with vertical walls. The exposure dose was 9mJ/cm^2. Below are the SEMs for the 0.25 μm lines up to 0.40 μm:

Picture 1 shows the 0.25 μm line. As it is mentioned in the caption, the single line doesn't open up. Still the results demonstrate that this resist might be considered for the quarter micron lithography.
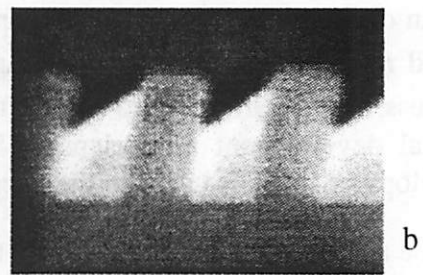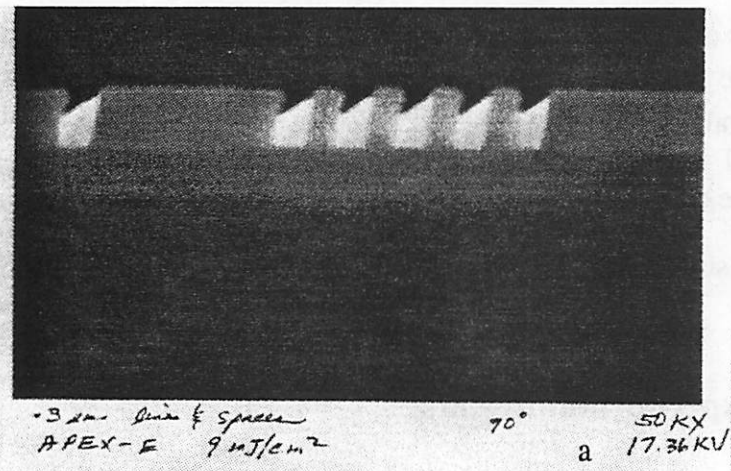
Picture 2 shows the 0.30 μm lines. Note that the single line has opened up nicely.

Picture 3 shows the 0.40 μm lines. The lines are excellent as expected.
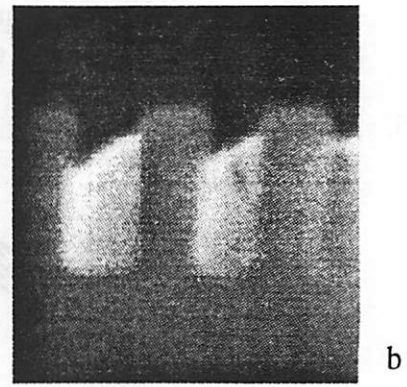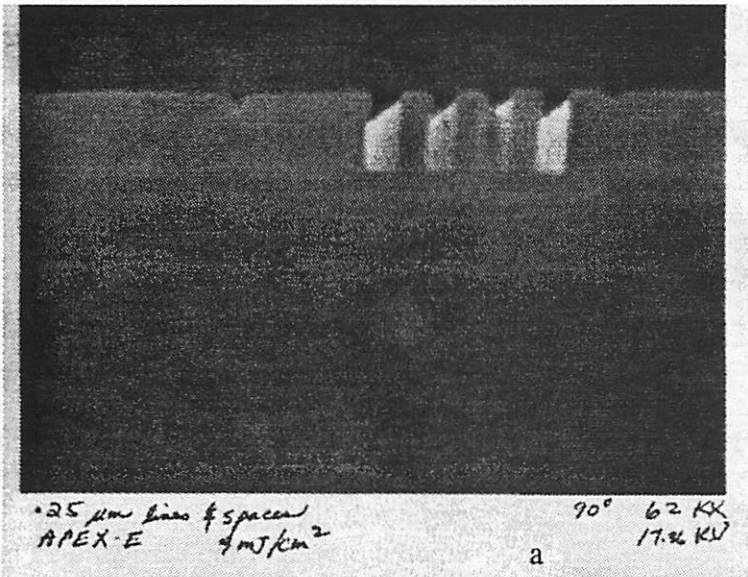
Picture 1. 0.25 µm lines and spaces. Note in a that the single line did not open up. A zoomed section of the lines is shown in b.
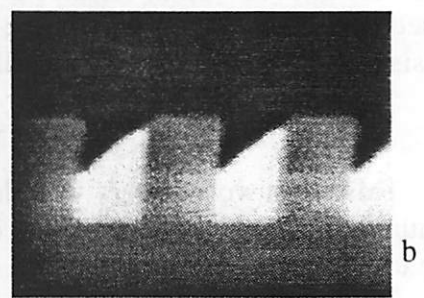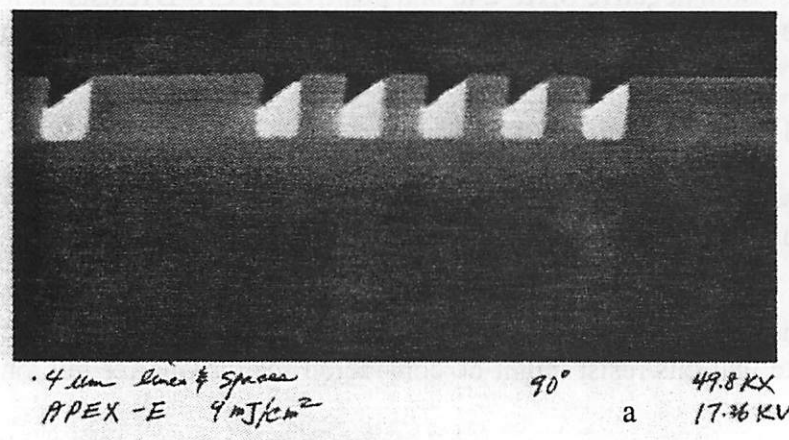

Picture 2. 0.30 µm lines and spaces. Note in a that the single line did open up. A zoomed section of the lines is shown in b.
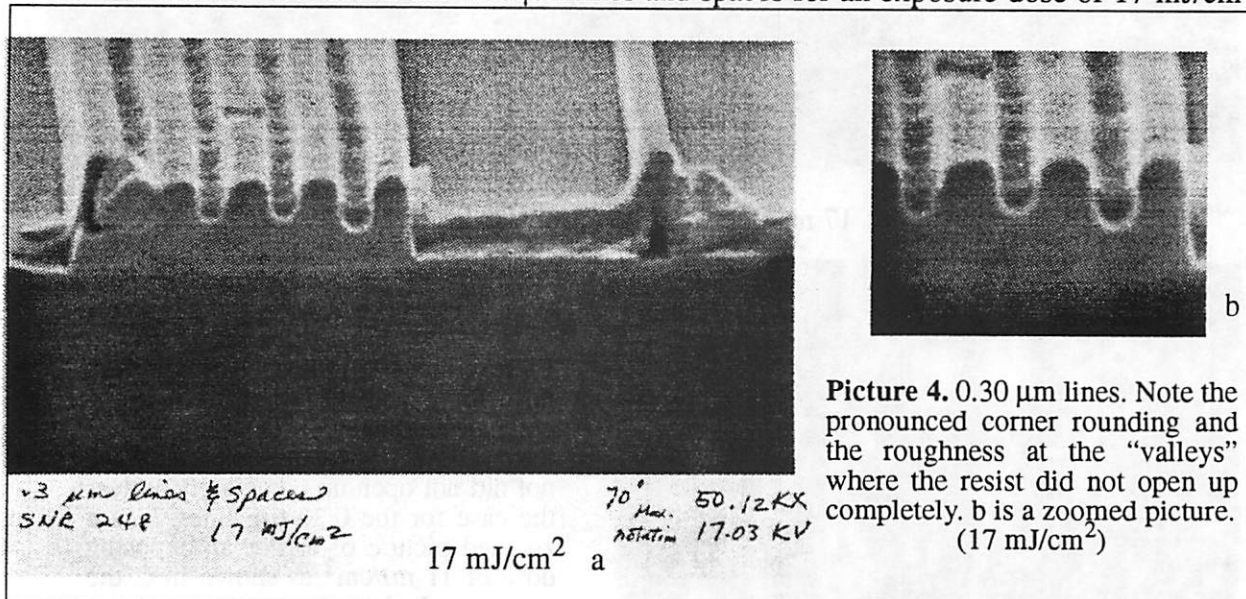

Picture 3. 0.40 µm lines and spaces. A zoomed section of the lines is shown in b.

4.2 Negative Resist SNR–248

This negative resist was exposed using two doses: 11 mJ/cm^2 and 17 mJ/cm^2. The higher dose was instrumental in strengthening the cross-linking and reducing corner rounding (but not erasing it completely). It also enabled the resist to show response down to 0.30 µm albeit not a perfect one! Another result is the fact that corner rounding does not depend on the line width, something to be expected from chemistry. Below are the experimental results:

Picture 4 shows the results for 0.30 µm lines and spaces for an exposure dose of 17 mJ/cm^2.

·3 µm lines & Spaces
SNR 248   17 mJ/cm2

17 mJ/cm^2 a

70° 50.12KX
Max.
notation 17.03 KV

Picture 4. 0.30 µm lines. Note the pronounced corner rounding and the roughness at the "valleys" where the resist did not open up completely. b is a zoomed picture. (17 mJ/cm^2)

Both the single line and the cluster of lines opened up, albeit with a pronounced corner rounding and, for the periodic lines, the development did not go all the way through. The texture of the valleys indicates that the length of the resist macromolecules are of importance in edge roughness and valley depth non-uniformity. The single line "opened" up completely. This indicates that the more free flow of developer around the single line is the cause of more rapid and thorough development and disassociation of surface molecules from the rest of the resist compared with the constricted and confined flow in the periodic cluster of lines. This is also to be compared with Picture 1 for positive resist where the single line did not open up.

Picture 5 shows 0.40 µm lines for exposure doses of 17 mJ/cm^2 and 11 mJ/cm^2. Note the improved profile over the 0.30 µm lines for the higher dose and the very bad profile for the lower dose. Corner rounding for the 17 mJ/cm^2 case has been minimized considerably from the 0.30 µm lines. As mentioned earlier, fabrications throughput time is of paramount importance, and using a higher dose (and hence more exposure time) to achieve better results might conflict with economics of scale.

Picture 6 shows 0.50 µm lines for the high dose of 17 mJ/cm2. Nice sidewalls and minimal corner rounding are evident. This picture is to be compared with Picture 7 for the same linewidths exposed with lower dose (11 mJ/cm2). Corner rounding is apparent.

Finally, 1 µm and 2 µm lines are shown in Picture 8.
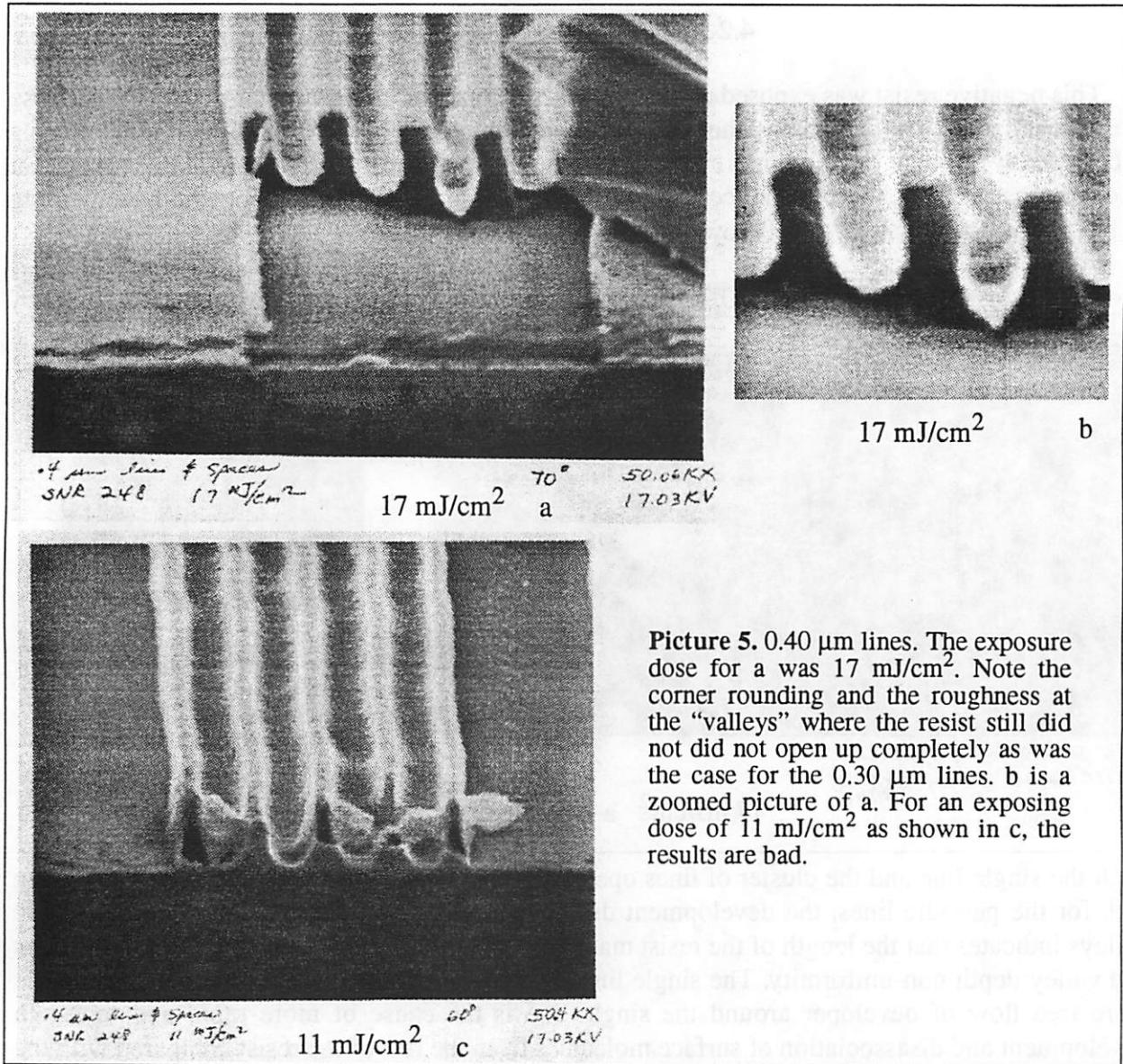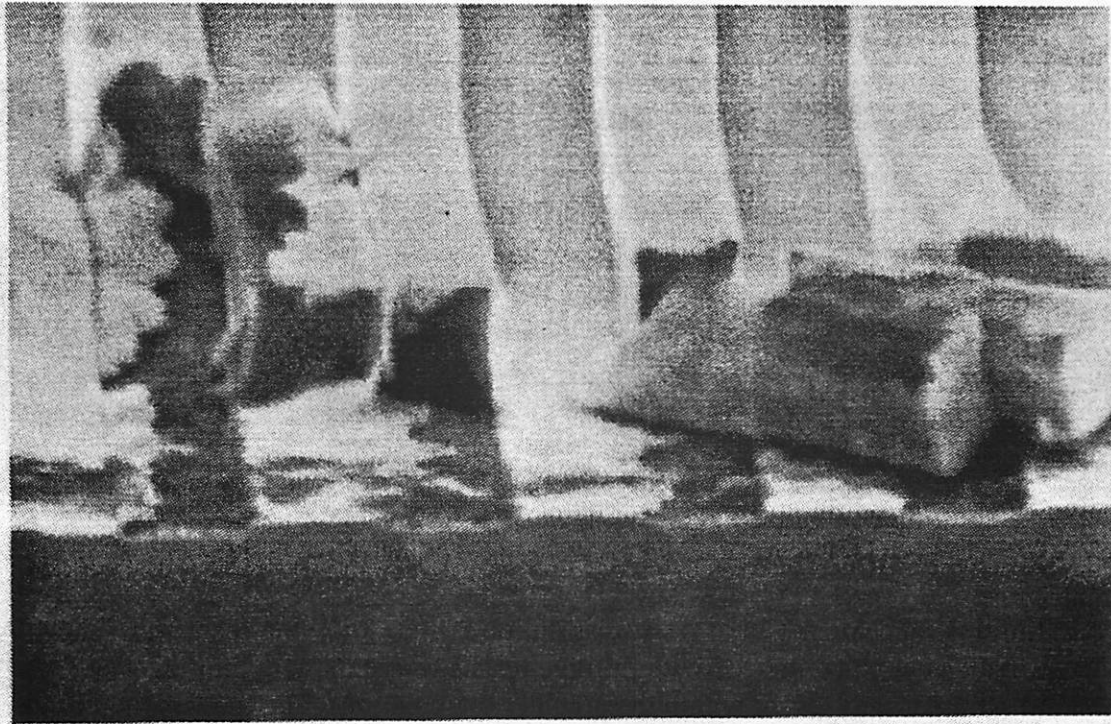
17 mJ/cm^2 b

17 mJ/cm^2 a

Picture 5. 0.40 μm lines. The exposure dose for a was 17 mJ/cm^2. Note the corner rounding and the roughness at the "valleys" where the resist still did not did not open up completely as was the case for the 0.30 μm lines. b is a zoomed picture of a. For an exposing dose of 11 mJ/cm^2 as shown in c, the results are bad.
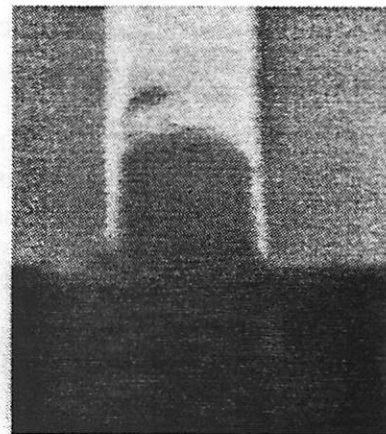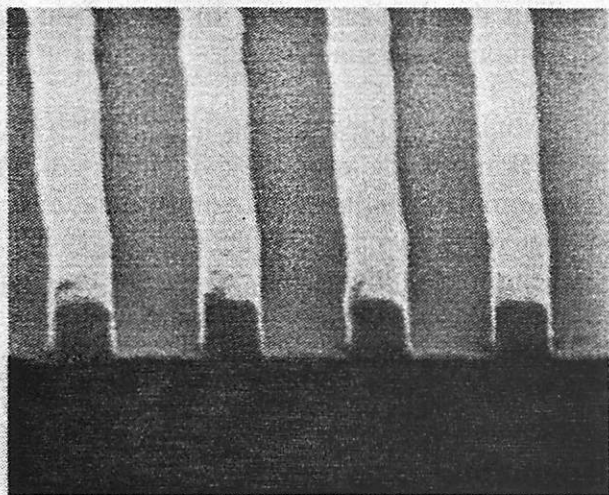
11 mJ/cm^2 c

5.0 Conclusions and Directions for Future Work

Guided by a desire for broad and fundamental characterization and modeling of the resist, an extensive literature search was conducted with regard to the general properties of resist base polymers, solution kinetics and cross–linking theories. There is a gap between general polymer research and transfer of those results and theories to resists. In particular due to the complexity of the physical and mathematical modeling of polymers, all pertinent results are usually valid in the bulk of the polymer. On the other hand, resists comprise surfaces of various shapes. As a paradigm of incorporating advanced chemical processes in modeling resists for TCAD a model of the corner rounding that is so pronounced in developed negative resist profiles was developed. The modeling of the corner rounding effect can provide extra insight on the dissolution mechanisms of cross-linked polymers. Experimental results with the negative resist SNR–248 for lines from 2.0 μm down to 0.20 μm confirm that corner rounding is not dependent on the line width. Also higher exposing doses restrict the rounding somewhat. This is an indication that higher

Picture 6. 0.50 μm lines with high dose exposure of 17 mJ/cm². Note minimal corner rounding.

a

b

Picture 7. 0.50 μm lines with low dose exposure of 11 mJ/cm². The walls are vertical and corner rounding is prominent.

stages of cross-linking affect (minimize) the rounding due to decrease in the sol level present at the corners.
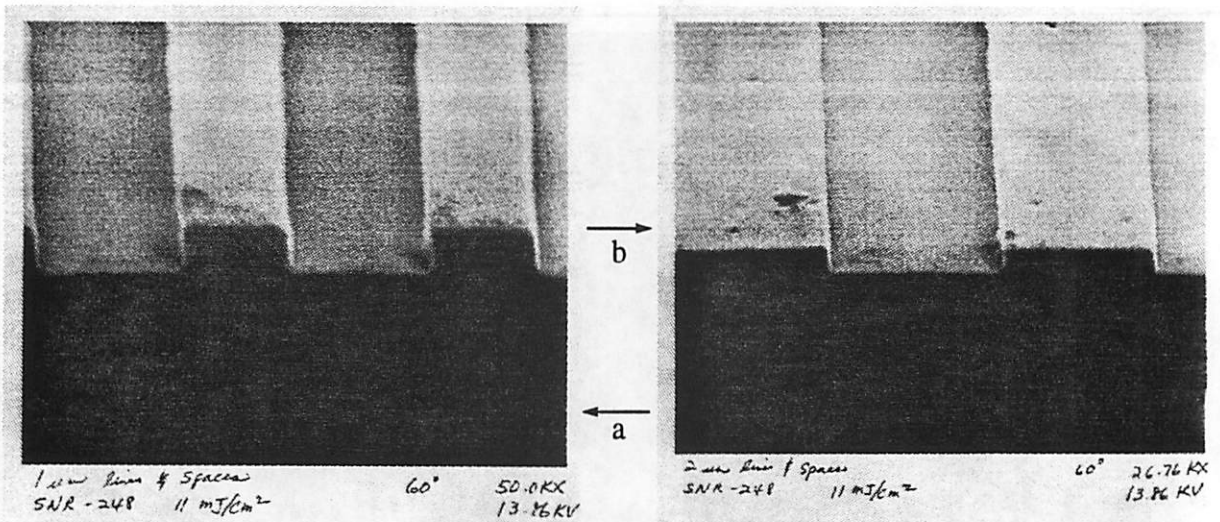
Picture 8. 1 μm (a) and 2 μm (b) lines. Note that corner rounding is always present.

The rate limiting step for negative resist dissolution is step 3 i.e. the reaction of the solvent with the resist. This is to be contrasted with positive resists where the rate limiting step for dissolution is the diffusion of the solvent within the polymer (percolation). The fundamental difference between the two dissolution mechanisms is that for positive (novolac) resists the developer weakens the attraction between different resist macromolecules while in negative resists the average molecular weight determines the rate of dissolution. Molecular weight does not play a dominant role in positive novolac resists.

Corner rounding is an unavoidable property of negative resists. It can be minimized with extra cross-linking which requires higher exposure doses at the expense of processing time. Experimental studies of corner rounding may yield clues for proprietary resists as to their probable chemical synthesis and/or speed (rate) of interaction with various developer solvents. In the dissolution model a corner correction factor should be included for more exact simulations.

A probabilistic-mechanistic model of cross-linking studies for a resist, especially at interfaces should be pursued. The exact mechanism of bond breaking for the cross-linked sol part of the polymer should be studied. A set of experiments to determine the influence of temperature, exposure dose and polydispersity is desirable. It should be determined which mechanism is responsible for the breaking of the bonds of corner molecules when those do not belong to the sol fraction. The envelope volume model for resist macromolecules may be further refined and developed. Studies of future monomeric resists will benefit from the above model since it readily adapts to any size molecule.

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I will miss Berkeley.

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