

## A membrane model for positive photoresist development

R. A. Arcus

Research Laboratories, Eastman Kodak Company  
Rochester, New York 14560

### Abstract

The mechanism of development for positive photoresists can be described using a membrane model for the thin polymer film dissolution process instead of a simple surface-dissolution model. The model is consistent with previous findings on the factors controlling the dissolution, i.e., solubility changes due to quinone-diazide photochemistry, creation of free volume due to nitrogen gas evolution, dissolution rate effects due to cation size, and surface modification by adsorption of chemicals. One of the key reactions of the membrane model, the conversion of the phenol to a phenolate on the novolac polymer, seems to have been overlooked in previous studies. This reaction must go to completion for any dissolution process to occur, and it requires a pH greater than 12.5. The membrane model will be presented and specific, supporting experiments will be discussed.

### Introduction

It is enlightening to look at a technological process from a modified or new perspective. Besides being an intellectual exercise, it often permits the reconciliation of conflicting pieces of data into a more unified theory and promotes a better understanding of the processing variables and how changes in those variables can modify the product. This can be extremely fruitful in a multidisciplinary field such as the study of positive photoresist development.

This paper discusses a new framework for the study and understanding of positive photoresist development. The current literature emphasizes that the development discrimination is due to the dissolution of photochemically generated acid into the aqueous base developer.<sup>1</sup> The concept is not wrong, but it is incomplete because it neither predicts nor explains many processing observations. A better conceptual framework is to consider the photoresist as a thin-film membrane that can be modified by the built-in photochemistry as well as by processing techniques. Almost all photoresist development phenomena can be<sup>2</sup> adequately and simply described by the physical chemistry of an ion-permeable membrane that also can undergo dissolution. In retrospect, the membrane concept can be viewed as an extension of the current theory and the validity of the new concept rests heavily on the reinterpretation of excellent work discussed in the literature.

A workable positive photoresist can be made from only three materials: a photoactive compound (PAC), a polymeric binder, and a coating solvent.<sup>3</sup> Polymeric images can be made with a wide range of materials. However, a unique combination of a naphthoquinone diazide PAC with a novolac polymer as the binder seems to provide the best combination of any that have been tried over the years. The majority of the commercially available photoresists contain these materials in some form. The naphthoquinone diazide undergoes photochemistry in the near ultraviolet, and it is also sensitive to thermal decomposition above 100 °C.

### Concepts

#### Previous concepts

The photoresist literature describes two processes that allow the generation of the positive photoresist relief image. The first process is the photochemical conversion of the quinone diazide to an indene carboxylic acid as shown in Fig. 1. A detailed study of the reaction was conducted by Pacansky and Lyerla.<sup>4</sup> They conclusively demonstrated the importance of residual water in the photoresist film for acid formation. The second process is the surface<sub>5</sub> dissolution of the photoresist regions that have undergone the photochemical conversion. These two concepts are the basis for the successful modeling of the exposure and development processes of early positive photoresists by the computer program, SAMPLE, from the University of California at Berkeley.<sup>6</sup> The modeling can become a very complicated curve-fitting effort that does not shed light on the processes that are occurring.<sup>7,8</sup>

The addition of a molecule that has an unexposed quinone diazide moiety to a novolac polymer substantially slows the dissolution rate of the polymer in the aqueous base developer. Other authors have called the quinone diazide molecule a "development inhibitor".<sup>9</sup> As expected, incorporation of the photochemically generated indene carboxylic acid increases the dissolution rate of the novolac polymer. The differential rate of dissolution of the

photoresist with amount of photochemically generated acid was believed to be the major phenomenon used to generate the photoresist images.<sup>1,3</sup>

### Unexplained photoresist processing behavior

The photoresist development model based on the above two processes does not adequately predict several processing observations. In simple, surface dissolution, one would expect the dissolution to be linearly proportional to the amount of converted photoactive compound. The SAMPLE curves of dissolution rate versus the normalized PAC concentration are curved, not linear.<sup>7,10</sup> In addition, there is a pronounced decrease in the dissolution rate when the cation of the aqueous base increases in size.<sup>11</sup> Significant processing differences have been observed between metal hydroxide developers and developers based on quaternary ammonium hydroxide.<sup>12,13</sup> The addition of dyes<sup>14</sup> and the variation in the molecular weight of the novolac resin have very significant effects on the dissolution behavior of the photoresist. The aqueous base developer must be in a very tight pH range. If the pH is too low, there is no development of the exposed regions. If the pH is too high, the contrast between the exposed and the unexposed regions is lost. Besides variations in pH, variations in the total ion concentration of the developer will alter the development rate of the photoresist. A simple surface treatment of the photoresist with chlorobenzene can decrease the thickness loss in the unexposed regions.<sup>15</sup> Obviously, the photoresist development process is more complex than discrimination by simple surface dissolution between the photochemically generated acid and unconverted naphthoquinone diazide.

### The "forgotten" reaction - novolac dissolution

An additional reaction occurs in the development of positive photoresists besides the photochemistry, and it is at least as important as the acid formation for explaining some of the behavior of photoresist development. The "forgotten" reaction in the development of typical positive photoresists is the removal of the phenolic proton by the aqueous base to form the phenolate anion (Fig. 2). This reaction is important! The novolac polymer does not require organic acid groups for aqueous base solubility. However, the novolac polymer would not be soluble in the aqueous base if this reaction did not go to completion. The concentration of the phenolic groups is at least ten times that of the quinone diazide chromophore in a typical photoresist formulation. The formation of the phenolate anion on novolac polymers requires a pH of at least 12.5.<sup>16</sup> This is the lower pH limit for a useful aqueous base developer. The pH required for the aqueous solubilization of organic acids is lower.

Modifications of the novolac polymer significantly affect photoresist performance. It has been demonstrated by several authors that the log of the dissolution rate of an organic polymer is linearly related to the log of the molecular weight of the polymer for dissolution in organic solvents.<sup>17,18</sup> This variation in dissolution rate with molecular weight also holds true for novolac polymers with aqueous base developers (Fig. 3) even though the ionization reaction must also occur (Fig. 2). The slope of the line is significantly greater for the novolac polymers compared to the organic polymers with organic solvents,<sup>19</sup> as developers, but similar to the dissolution of other phenolic polymers in aqueous base. The addition of small molecules, especially PAC's, to the novolac, alters the dissolution rates. Of the many classes of phenol-containing polymers that we have studied, the cresol novolac polymer has the slowest dissolution rate for equivalent weight samples. This is true even for an isomeric polymer such as poly(p-hydroxy styrene).

### Membrane model concepts

The membrane model for photoresist dissolution is based on a few very simple concepts. (1) The formation and stabilization of the phenolate anion is the major chemical reaction for the dissolution of photoresist films. (2) There has to be a concentration gradient of developer across the photoresist film thickness, and only at gradient locations with pH 12.5 or greater can true dissolution of photoresists occur. A direct consequence of the gradient is that positive photoresists do undergo some surface swelling during dissolution. (3) The primary role of the naphthoquinone diazide chemistry for dissolution rate differentiation is the photochemical modification of the transport rates of water, ions, and base into the organic photoresist membrane. The transport is facilitated by the ionized organic acid groups, void volume generation by nitrogen gas evolution,<sup>20</sup> and molecular movement in the polymer matrix. It has also been reported that volatile products from the electron bombardment of positive electron-beam resists may enhance the dissolution of the irradiated areas.<sup>21</sup> (4) Differences in photoresist formulation (coating solvent, novolac molecular weight and polydispersity, additives such as dyes, etc.) and processing (prebake conditions, developer type, developer concentration and temperature, intermediate treatments, etc.) modify the transport of developer into the photoresist film.

## Membrane attributes

The inclusion of the ionization of the phenolic proton as one of the key photoresist development phenomena opens up an alternate and more complete description of the process. This alternate perspective is that the photoresist film behaves as a membrane. The cresol novolac polymer seems to be a unique membrane material because the isomeric polymer, poly(p-hydroxy styrene), has not been formulated into a photoresist with properties equivalent to the novolac-based systems.<sup>22</sup> In turn, the naphthoquinone photochemistry controls the properties of the photoresist membrane and is itself uniquely qualified for this task.

The model is best described in terms of the physical chemistry of an organic, ion-permeable membrane. The solubilization of the novolac polymer in the photoresist requires the ionization of the phenol at pH 12.5 or greater. The only way for this to occur is for the base in the developer to be transported into the membrane via some mechanism such as diffusion or infiltration into voids. Therefore, there is a gradient in the concentration of base ions across the thickness of the photoresist film. (A broad gradient with inclusion of water molecules would be identified as the gel layer.) The photoresist membrane can differentiate between the ions of aqueous basic developers due to variations in the size, composition, and charge of the ions. The membrane properties can be modified by chemical surface treatments, changes in the total ion concentration and composition of the developing solution, and, most importantly, the photochemistry of the included naphthoquinone diazide.

## Results and discussion

### Size of base cation

Hinsberg and Gutierrez<sup>11</sup> studied changes in the dissolution rate of photoresists with metal hydroxides that varied in cation size. They found that the dissolution rate decreased with increasing cation size. Figure 4 is a plot of the dissolution rate at 20 °C of bleached (360 mJ/cm<sup>2</sup>) Kodak micro positive resist 820 vs. the specific volume of the cation for the following developers: sodium hydroxide (NaOH) (I), tetramethylammonium hydroxide (TMAOH) (II), tetraethylammonium hydroxide (TEAOH) (III), and tetrapropylammonium hydroxide (TPAOH) (IV). The data are consistent with those reported by Hinsberg and Gutierrez.<sup>11</sup> As the cation size increased, the dissolution rate decreased. The effect was nonlinear for both cation specific volume and cross-sectional area. Development by TPAOH was very slow, and no development was observed for the tetrabutylammonium hydroxide.

### Photoresist discrimination of NaOH and TMAOH developers

The speed and contrast data for this resist can be plotted to demonstrate relative thermodynamic trends for the dissolution phenomenon.<sup>12</sup> Figure 5 is a pseudo-Arrhenius plot for data on the two developers. Figure 5 is considered a pseudo-Arrhenius plot for several reasons.<sup>23</sup> The values plotted for the y axis are the dissolution rates of the photoresist, not reaction rates or rate constants. This involves two assumptions. (1) The dissolution rate is related, or similar, to the statistics of a chemical reaction. (2) The rate constant for the process is directly proportional to observed rates. The first assumption is correct if the concentration of the "reactants" do not vary during the dissolution process. This is the case because the developer concentration was always 0.15 M and the concentration of the photoresist is the surface area of the resist film.

Examination of the relative slopes of the two lines shows that the activation energy for the NaOH developer is 1.9 times greater than for the TMAOH developer. Thermodynamically, NaOH is a poorer developer, requiring more energy to perform the same dissolution as the TMAOH developer. A possible rationalization for this effect is that the cation of TMAOH, Me<sub>4</sub>N<sup>+</sup>, is more soluble in the organic photoresist film than the Na<sup>+</sup> cation for the NaOH developer. The solubility of a solute in a medium is a thermodynamic property. However, the kinetics would favor the smaller cation at higher temperatures. This agrees with the observed higher "frequency factor" for the smaller cation. The values predict that Na<sup>+</sup> is statistically twice as likely to cause dissolution.

### Membrane modification

(1) Solvent removal during prebake. A membrane modification process that is universal to the semiconductor industry is the prebake step for the removal of the coating solvent from the resist film prior to the imaging step. Removal of the solvent is typically done below the boiling point of the solvent and, more importantly, below the glass transition temperature of the photoresist formulation. The resultant film cannot be in a totally thermodynamically relaxed state. The semiconductor industry has developed several different types of equipment for prebake (i.e., forced-air convection ovens, IR ovens, hot-plate cold-plate tracks) in an effort to reduce the processing variability attributed to this step.

Residual coating solvent is the most often mentioned culprit for processing nonuniformity from coating to coating. Several conflicting mechanisms can be proposed for the behavior of coatings with residual solvent. Residual solvent in a thin photoresist film is usually regarded as a plasticizer.<sup>21</sup> In this role, it would lower the glass transition temperature of the package and increase the diffusion rate of organic solvents into the film. However, the developer is an aqueous base and the diffusion of the aqueous base would be inhibited by the hydrophobic environment of additional organic solvent. Conversely, a solvent that stabilized the charges of the ions in the aqueous base would probably tend to increase the dissolution rate. Typical solvents that would stabilize the ionic charges such as alcohols and acids would also be miscible with water.

Walker<sup>24</sup> demonstrated that the standing wave effects due to monochromatic light exposure could be reduced by a post-exposure bake. He and Dill and Shaw<sup>25</sup> have postulated that the mechanism is the diffusion of the photoactive compounds from regions of high concentration to low-concentration regions, thereby providing a more uniform inhibitor concentration across the film thickness, and subsequently, more uniform development. Alternative interpretations of the data are reasonable with the membrane model for photoresist response to development. For example, the post-exposure bake could "anneal" out the effects of the evolution of the nitrogen gas and the molecular movement during the photochemical reaction. This would decrease the ease of transport of the ionic developer into the layers that received higher localized exposure because of the standing wave effects, and would produce more uniform development across the whole thickness of the photoresist film.

(2) Chlorobenzene surface treatment. Hatzakis et al.<sup>15</sup> demonstrated that soaking the photoresist film in chlorobenzene increased the differential development. The dissolution of the unexposed regions was halted, and exposed regions which had generated the acid underwent dissolution. The chlorobenzene is highly hydrophobic and non-ionic. We feel the adsorption of such materials further inhibits the transport of aqueous ions into the membrane and, therefore, halts dissolution.

(3) Quaternary alkyl ammonium halide additives. Guild<sup>26</sup> has demonstrated the utility of adding small amounts of tetraalkylammonium halide salts to TMAOH developers. Variable-temperature development-rate-monitor work has helped in understanding the possible mechanisms. The increased contrast appears to be directly due to the phase distribution of the quaternary alkyl ammonium halide salt between the organic photoresist film and the aqueous developer.<sup>12</sup> The quaternary salt behaves as an uncharged, organic molecule in the organic phase and as an ionic, charged species in the aqueous phase. It appears that the quaternary salt in a photoresist system can adsorb onto the surface of the photoresist film (organic phase), and thereby inhibit dissolution. The degree of adsorption and inhibition appears to be inversely related to the amount of exposure and photochemistry. Visually the surfaces are different. Standard TMAOH developer does not wet areas of low exposure that have been treated with a tetrabutylammonium chloride salt solution. Such low-exposure areas would ordinarily undergo uniform but slow dissolution.

Figure 6 shows a typical change in the plot of dissolution rate vs. exposure for a developer with TBACl salt added. Changes in the tetraalkylammonium cation at equivalent concentrations will change the plot dramatically. Varying the halide anion from chloride to bromide or iodide has little effect. Experimentally such a system shows very good differential dissolution.

#### Increased ionic strength of aqueous-base developers

Increasing the ionic strength of the developer solution by the addition of sodium chloride to the TMAOH developer increases the dissolution rate of the developer (Fig. 7). This is the same trend observed for the inorganic developers studied by Hinsberg and Gutierrez.<sup>11</sup> We have observed similar increases in dissolution rate by adding NaCl to NaOH developers and by adding tetramethylammonium chloride (TMACl) to tetramethylammonium hydroxide (TMAOH) developers. For equivalent exposures of 40 mJ/cm<sup>2</sup> to 1200 nm thick Kodak micro positive resist 820 photoresist films, the dissolution at 20 °C was 41 nm/sec for 0.15 M NaOH and 100 nm/sec for the same developer with NaCl added to a concentration of 0.15 M. With exactly the same samples and processing conditions, the dissolution rate was 28 nm/sec for 0.15 M TMAOH and 78 nm/sec for 0.15 M TMAOH with an added concentration of 0.15 M TMACl.

In each case, adding a salt to the basic developer increased the dissolution rate. This would not be expected for surface dissolution of an organic acid. The exact mechanism of this increase is unknown. Several mechanisms can be postulated for this phenomenon using the membrane model. This could include stabilization of the charge of the phenolate anion once the proton is removed by the base. Also, the higher salt concentration would provide a greater chemical potential to drive and maintain the ion gradient into the photoresist

membrane. The additional ions from the salt must aid in the dissolution of the ionized novolac polymer, because neither NaCl nor TMACl are developers for the photoresists nor are they capable of ionizing the novolac polymer.

#### Concentration gradient of developer in photoresist film

The concept of a concentration gradient of developer and swelling in the positive photoresist film during dissolution appears to be novel. However, control of chemical concentration gradients is one of the important uses of membranes.<sup>2</sup> Recently, Rodriguez et al.<sup>27</sup> have reported the ability to detect swelling during interferometric dissolution experiments of organic polymer films (electron-beam photoresist materials) in organic solvents. They call the swollen material at the polymer-developer interface the transition region. The distinguishing characteristic of swelling in that experiment was a decrease in the interferogram amplitude due to less reflectivity of a swollen polymer-developer interface compared to a solid polymer-developer interface. We have also observed this effect during positive photoresist development with aqueous base developers.

Intuitively, the developer concentration gradient must exist. The concentration of the hydroxyl ion in the developer is typically  $\sim$ pH 13 ( $0.1 \text{ N CH}_3^-$ ) and the concentration of the free hydroxyl beyond the transition zone in the film is essentially zero. However, the ionization of all of the phenols to phenolate anions on the novolac polymer chain is a requirement for solubility. The polymer chain occupies a three-dimensional volume and the pH must be 12.5 or greater across the entire volume for phenolate to exist at all possible chain locations. This requires the transport of the developer into the film by some mechanism, i.e. diffusion, capillary action through voids, etc. The transport of the developer into the film establishes a concentration gradient of developer into the photoresist film.

In the case of gel layer formation using an aqueous-base developer, it was possible to directly observe the swelling of the polymer film and three separate interferograms in the first part of the spectrum (Fig. 8). (The polymer was a high molecular weight, phenolic polymer that was similar to materials described by Turner, et al.<sup>19</sup>) The three reflections required for the three interferograms are from (1) interface A between the silicon wafer and the unswollen polymer, (2) interface B between the unswollen polymer and the swollen polymer, and (3) interface C between the swollen polymer and the developer solution. It is unusual to have such well-defined B and C interfaces in one sample. Once the B interface reaches the A interface, it disappears. The lower-amplitude continuing interferogram is due to the reflection from interface A' (between the silicon wafer surface and the swollen polymer) and the reflection from the C interface. This continuing interferogram is caused by continued swelling of the polymer film and/or dissolution of the swollen polymer film. Single-wavelength interferometry cannot distinguish between the two cases. Figure 9 is an expansion of the initial rapid interferometric event shown in Fig. 8. The periodicities of the three separate interferograms are marked above the spectrum.

#### Uniqueness of naphthoquinone chemistry

We postulate that the major mechanism for the developer discrimination between exposed and unexposed regions of a positive photoresist is the increased ability of the exposed regions to transport ions, base, and water through the photoresist film that is acting as a membrane. The photoresist can be considered a membrane that can be photochemically modified. In such a system, the dissolution rate does not have to be linear with the degree of photoactive compound conversion. In fact, the membrane concept accommodates several processes occurring simultaneously and it would be highly improbable to obtain a linear correlation.

The contribution of the naphthoquinone diazide photochemistry to the membrane modification can be broken down into at least four categories. (1) The original concept of increased aqueous-base solubility due to the photochemical generation of an organic acid (indene carboxylic acid) is a contributor to the increased dissolution rate. (2) The increased rate, however, is also due to the increased ability of the photoresist film to transport the ionic developer into the film. The photochemically generated acid groups provide a mechanism for ion transport. (3) The evolution of nitrogen gas during the photochemistry probably leads to an increased void volume for the film and possibly creates<sup>20</sup> physical channels into the film. This has been discussed previously by Hinsberg et al. (The choice of the word transport over the word diffusion in this paper was made to accommodate the possibility of the channel mode of transport.) (4) The photochemistry and the nitrogen gas evolution cause motion in the photoresist matrix on a molecular level.

## Conclusions

The membrane model for positive photoresist development is consistent with previous findings on the factors controlling the dissolution, i.e. solubility changes due to quinone-diazide photochemistry, creation of free-volume due to nitrogen gas evolution, dissolution rate effects due to cation size of the developer, surface modification by adsorption of chemicals, and thermal treatments. The importance of the formation of phenolate and the concentration gradient of developer into the photoresist film are emphasized and discussed. Some experiments that support the membrane model are described and the results are interpreted using the membrane model.

## Experimental

### Instrumentation

Two different interferometers were used in this study. The early data were obtained with a simple fiber-optics design similar to that described by the IBM workers.<sup>3</sup> It has a single data channel, a He-Ne laser for illumination, and a photodiode for signal measurement. The constant-temperature bath keeps the temperature of the 50 ml of stagnant developer within  $\pm 0.05$  °C.

The later data were obtained on an interferometer that is a preproduction model of the development rate monitor from the Applied Optics Division of Perkin-Elmer. The basic features of this machine have been described elsewhere.<sup>28</sup> For project continuity, all data were collected with the initial vibrating diaphragm pump and were collected and reduced with version 1.2 of the software package.<sup>12</sup> The instrument was modified in-house for variable temperature use between 2 and 40 °C.

Variable-temperature runs were done with the same temperature cycling schedule for time and order of temperatures. The sequence for temperature cycling was 20, 35, 25, 15, 5, and back to 20 °C over a period of 7 hr. Potentiometric titration data demonstrated that the developers picked up insignificant carbonate during the described temperature cycling.<sup>12</sup>

Each photoresist-coated wafer was given 15 different exposures through a movable slit. The intensity of the Oriel 200 W mercury lamp was monitored by an OAI intensity meter. All exposure data were corrected for lamp-intensity fluctuations.

### Materials

Kodak micro positive resist 820 was diluted to 31 wt% solids and filtered through a 0.5- $\mu$ m filter before coating. The resist was coated on new silicon wafers. The wafers were prebaked in convection air ovens for 30 min at 90 °C. The photoresist thicknesses were measured on a Nanometrics film thickness analyzer; all were  $1,225 \pm 15$  nm. Samples were developed within 1 hr of UV light exposure. The developer temperature was 20 °C unless specified.

All developer materials were diluted to 0.15 M (moles/liter) total alkalinity. The sodium hydroxide and sodium chloride were reagent grade, white, free-flowing pellets or crystals (Fisher Scientific, Pittsburgh, PA). The tetramethylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium chloride, and tetrabutylammonium iodide were free-flowing, white crystals (Kodak Laboratory Chemicals, Rochester, NY). Tetramethylammonium hydroxide was a 6 wt% aqueous solution (Synthetic Chemicals Division, Eastman Kodak Company, Rochester, NY). The tetraethyl, tetrapropyl, and tetrabutylammonium hydroxides were 10 wt% aqueous solutions (Kodak Laboratory Chemicals, Rochester, NY). Developer solutions were titrated with standardized HCl solutions with phenolphthalein indicator and again by potentiometric titration in a mixed solvent with standardized perchloric acid. Stock solutions were diluted to 0.15 M total alkalinity with distilled water, retitrated to verify the concentration, and stored in full, tightly closed plastic bottles. Developer additives for specific runs were added as salts at time of dilution. Specifics on the developers are listed in Table I.

Table I. Developer Compositions

No.	Developer	Abbreviation	Total Molar Base Conc.	Added Salt Molar Conc.
I	Sodium hydroxide	NaOH	0.15	----
II	Tetramethyl ammonium hydroxide	Me <sub>4</sub> NOH	0.15	----
III	Tetraethyl ammonium hydroxide	Et <sub>4</sub> NOH	0.15	----
IV	Tetrapropyl ammonium hydroxide	Pr <sub>4</sub> NOH	0.15	----
V	Tetrabutyl ammonium hydroxide	Bu <sub>4</sub> NOH	0.15	----
VI	Sodium hydroxide + Sodium chloride	NaOH + NaCl	0.15	0.15
VII	Tetramethyl ammonium hydroxide + Sodium chloride	Me <sub>4</sub> NOH + NaCl	0.15	0.015
VIII	Tetramethyl ammonium hydroxide + Sodium chloride	Me <sub>4</sub> NOH + NaCl	0.15	0.075
IX	Tetramethyl ammonium hydroxide + Sodium chloride	Me <sub>4</sub> NOH + NaCl	0.15	0.15
X	Tetramethyl ammonium hydroxide + Tetramethyl ammonium chloride	Me <sub>4</sub> NOH + Me <sub>4</sub> NCl	0.15	0.15

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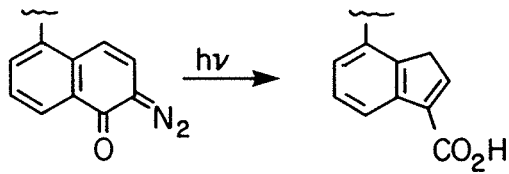
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## PHOTOCHEMISTRY

Typical chromophore

Typical product

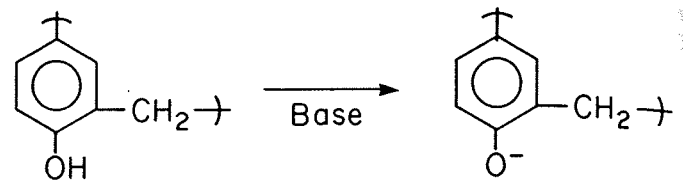


UV Absorber

Bleached

Figure 1. Photochemistry of naphthoquinone diazide, a typical chromophore in positive photoresists.

## THE FORGOTTEN REACTION



Requires pH > 12.5

Hydroxyl concentration at least ten times greater than that of chromophore.

Figure 2. The "Forgotten Reaction", the formation of the phenolate anion by the removal of the phenol hydrogen by base. The ionized polymer is soluble in the aqueous base.

### MW vs RATE (LOG-LOG PLOT) FOR NOVOLAC POLYMER

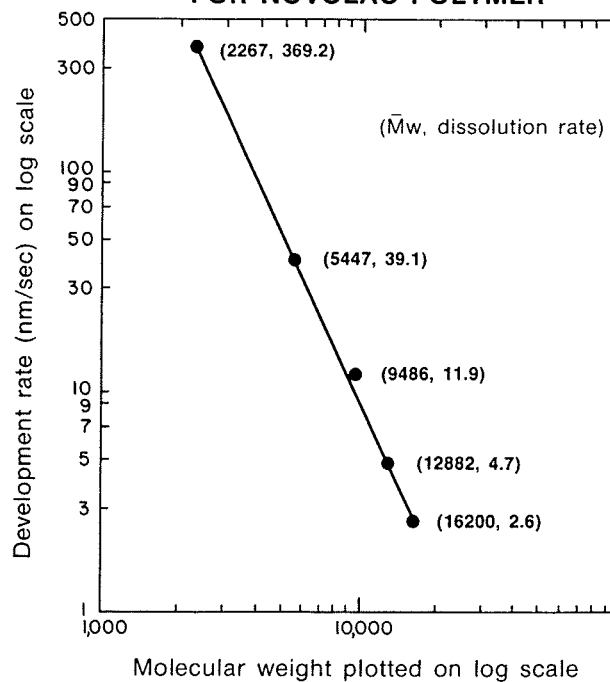


Figure 3. A plot of the development rates of a series of cresol novolac polymers vs. the weight-average molecular weight of the polymers on a log-log scale.

DISSOLUTION RATE OF BLEACHED PHOTORESIST FILM vs. SPECIFIC VOLUME OF BASE CATION

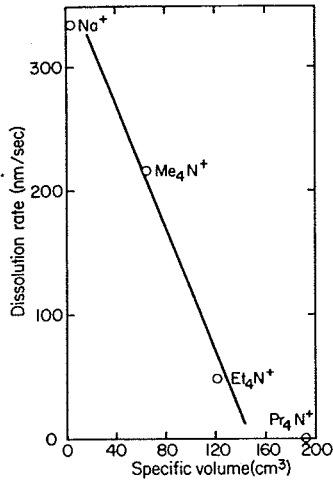


Figure 4. A plot of the dissolution rate of bleached photoresist film vs. the specific volume of the base cation. The smaller the base cation, the faster the dissolution rate.

LOG DISSOLUTION RATES OF KMPR 820 FILM vs. 1/T °K FOR 0.15M NaOH AND 0.15M Me₄NOH DEVELOPERS

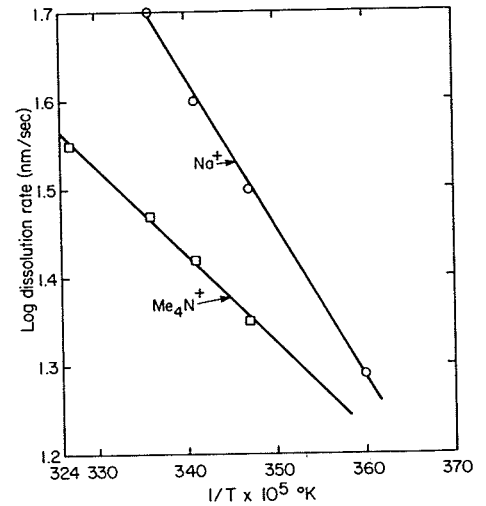


Figure 5. Pseudo-Arrhenius plots used to obtain relative activation energies for the dissolution of KMPR 820 film by two different developers, 0.15 M NaOH and 0.15 M Me<sub>4</sub>NOH. The activation energy for dissolution by NaOH is 1.9 times larger than the activation energy by Me<sub>4</sub>NOH. The UV 40 mJ/cm<sup>2</sup>.

DISSOLUTION RATE vs. EXPOSURE TIME

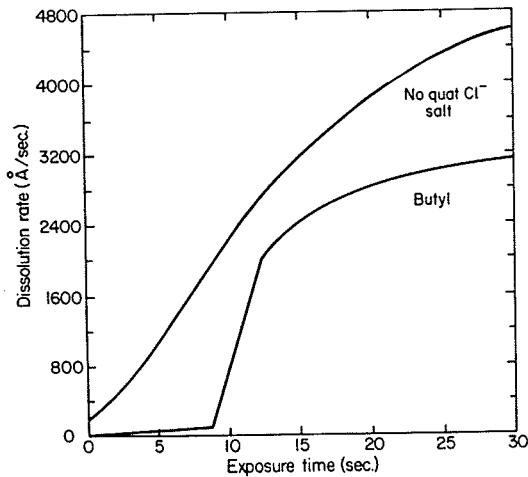


Figure 6. Dissolution rate vs. exposure time for Kodak micro positive resist 820 in TMAOH developer with and without TBuACl salt decreases the dissolution rate of the photoresist that has received low or no UV light exposure.

TIME TO CLEAR FOR UNEXPOSED PHOTORESIST FILMS vs. CONCENTRATION OF NaCl IN DEVELOPER

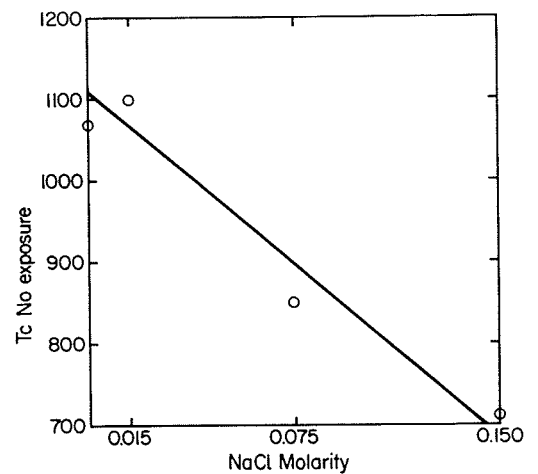


Figure 7. A plot of the time to clear for unexposed photoresist films vs. the concentration of added NaCl salt in the developer. The addition of NaCl salt increases the dissolution rate of the photoresist film in the same pH developer.

COMPLEX INTERFEROGRAM WITH OBSERVABLE  
GEL LAYER - EXPERIMENTAL BASE-SOLUBLE POLYMER

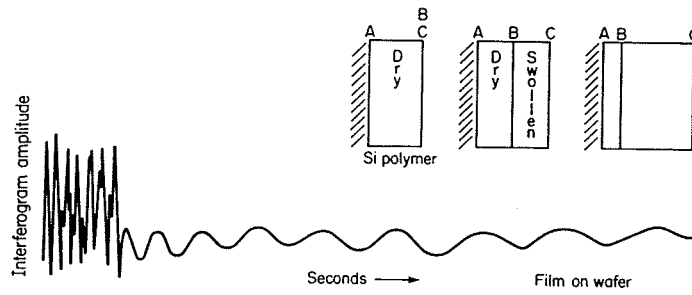


Figure 8. The complex interferogram of a phenolic polymer that is rapidly swelling and has a very distinct interface, B, between the swollen and dry polymer as labeled in the accompanying sketch.

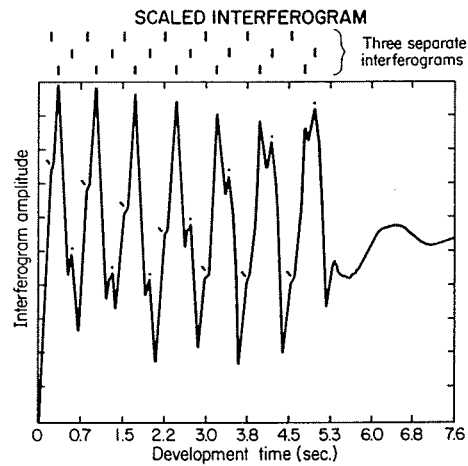


Figure 9. An expansion of the beginning portion of the interferogram in Figure 8.