The Molecular Mechanism of Novolak Resists

Arnost Reiser*

Institute of Imaging Sciences, Polytechnic University, Brooklyn, New York 11201

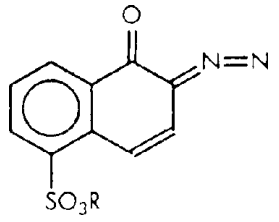
The molecular mechanism of Novolak-diazoquinone resists depends on the diffusion of base into the resin matrix. In this context the novolak film may be viewed as a percolation field where the percolation sites are the phenolic OH groups of the resin. The rate of percolation depends on the density (concentration) of percolation sites and on their steric accessibility. When diazonaphthoquinone inhibitors are introduced into the system they cause the formation of hydrogen-bonded strings of phenolic OH groups. The polarized hydroxyls are less available to the advancing base, that lowers the site connectivity of the field, and with it the dissolution rate. On exposure, the photolysis of the diazoquinones is followed by a very fast and very exothermic reaction, the Wolff rearrangement. The heat liberated in this thermal process produces an intense temperature spike, in excess of 200°C at the location of the inhibitor. At the high temperature the phenolic strings are severed from their anchor. The disconnected OH groups are no longer polarized by the inhibitor, and the inhibition effect is suspended. The dissolution rate of the exposed resist returns to that of novolak, except for a slight increase in dissolution rate caused by the presence of newly formed indenecarboxylic acid that contributes some additional percolation sites to the exposed film.

Journal of Imaging Science and Technology 42: 15–22 (1998)

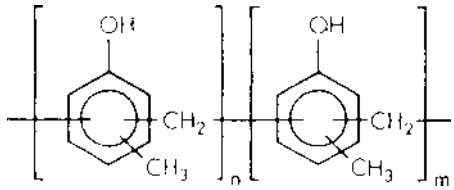
Introduction

Novolak-diazoquinone resists are the imaging materials of the computer chip. They are light-sensitive resins used to transfer the high-resolution pattern of modern integrated circuits from a transparency onto a silicon wafer. They were discovered in the 1940s by Oskar Sues, a leading organic chemist at Kalle in Wiesbaden, Germany. Sues had found that the addition of light-sensitive diazonaphthoquinone (DNQ) derivatives (1 below) to novolak, a phenol-formaldehyde condensation polymer (2 below), slowed down the dissolution of the resin in base to a spectacular degree. However, when novolak-DNQ films were exposed to sunlight, DNQ lost its ability to inhibit the dissolution of the resin, and the exposed films dissolved even somewhat faster than pure novolak films. Sues realized the potential of his observation, and on the strength of it formulated a light-sensitive varnish (Kopierlack), which we now call a resist.

The use of resists in building semiconductor devices is illustrated in Fig. 1. A silicon wafer carrying a thin layer of silicon oxide (glass) is coated with a resist film. The dry film is exposed to UV radiation through a transparency that defines the desired pattern and is then immersed in a solution of base, just long enough to remove the material in the irradiated areas. The film is washed and dried and becomes a template that protects the covered area of the wafer, but allows chemical action to occur in those areas that were uncovered by exposure and development. Novolak resists are used today in the making of some 95% of all integrated circuits worldwide. They have become an indispensable



1



2

ingredient of modern technology, yet, until quite recently, their functional mechanism was not understood. At the Institute of Imaging Sciences of Polytechnic University we have developed a model of the molecular mechanism of Novolak-DNQ resists that appears to fit all the principal aspects of these intriguing systems.[1] Such a model must be able to answer three basic questions:

1. What is the mechanism of novolak dissolution?
2. How does the DNQ derivative inhibit novolak dissolution?
3. What happens on exposure of the resist films?

We shall consider each of these in turn.

The Mechanism of Novolak Dissolution

The key to an understanding of novolak resists is the recognition that novolak is an amphiphilic material that

Original manuscript received April 2, 1997

* IS&T Fellow

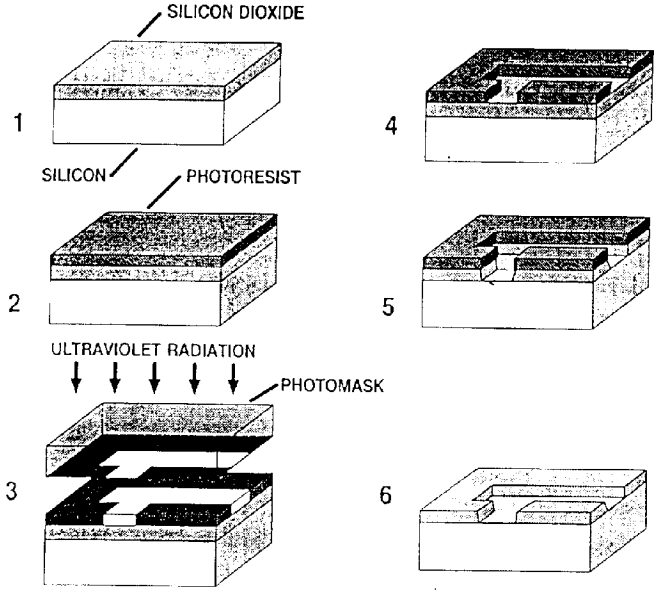


Figure 1. The basic steps of microlithography: (1) Oxidation of the silicon wafer, (2) coating with resist, (3) irradiation through a patterned mask, (4) development of the exposed film in aqueous base, (5) etching away the SiO_2 layer, (6) system ready for localized chemical action. (Reproduced with permission from "Electronic and Photonic Applications of Polymers" in *Am. Chem. Soc. Chem. Series* **218**, 5 (1988).

contains hydrophobic as well as hydrophilic components. In fact, a novolak film may be regarded as a hydrophobic solid in which hydrophilic sites, the OH groups of the phenols, are embedded. Base, an ionic species, is attracted to the hydrophilic sites and repelled by the hydrophobic regions, and as a result it migrates in the film by transferring from one hydrophilic site to the next.[2] This type of progression is a typical percolation process,[3] and if this view is correct, base diffusion in novolak films, and by implication their dissolution, will be governed by the rules of percolation theory.

The basic concept of percolation theory is the percolation field, an ensemble of cells that are either occupied or empty. Figure 2 shows a two-dimensional percolation field where only the occupied cells are indicated as open circles. A mobile particle (black circle) can reside only in an occupied cell and can transfer from an occupied cell to its occupied neighbor, but cannot pass through an empty cell. As a result, a mobile cell is confined to the cluster of occupied cells in which it happens to find itself.

The state of the percolation field is characterized by a percolation parameter p that is simply the fraction of occupied cells. If the concentration of occupied cells in Fig. 2 is increased, the cell clusters become larger and at a certain point some of the clusters will coalesce and connect opposite sides of the field. At that point macroscopic diffusion (percolation) sets in. The value of p at which this happens is called the percolation threshold, p_c. Figure 3 shows a quadratic percolation field just below and just above the percolation threshold.

Percolation theory asserts that all macroscopic properties of a percolation system are functions of the difference $(p - p_c)$, and that in most cases that function has the form of a *scaling law*,

$$\text{property} = \text{constant}\ (p - p_c)^n. \qquad (1)$$

The exponent n differs for different properties. For diffusion in three dimension and hence for dissolution, the

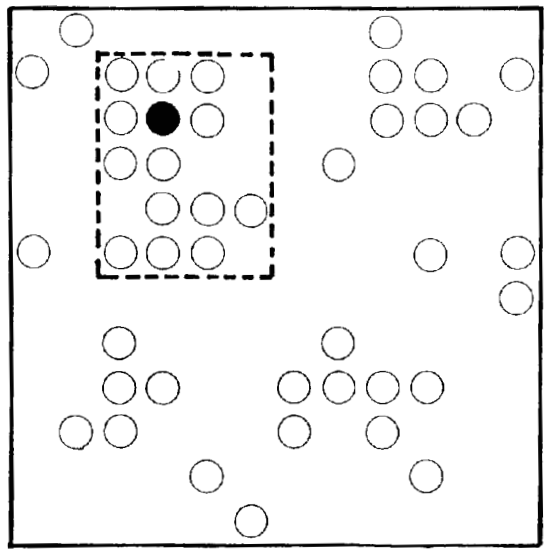


Figure 2. Two-dimensional percolation field. Only the occupied cells are marked by open circles. The mobile particle is represented by the filled circle.

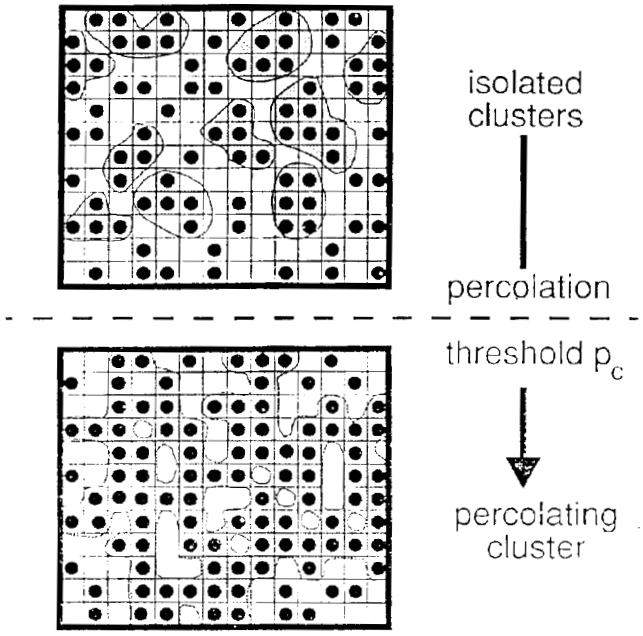


Figure 3. Transition from a percolation field below the percolation theshold p_c where the cell clusters are isolated, to a field above the percolation threshold where some of the clusters merge into an infinite cluster connecting two opposite sides of the field. (Reproduced with permission from Ralph Dammel Diazonaphthoquinone-based Resists" (SPIE Press, Tutorial Text No. 11, Bellingham, WA 1993). p. 63.

exponent equals two, and the dissolution rate R becomes a quadratic function of $(p - p_c)$,

$$R = \text{constant}(p - p_c)^2. \qquad (2)$$

We can test the applicability of the percolation theory to novolak dissolution by modulating p and observing the effect on the dissolution rate. Because the occupied sites are the OH groups of the resin we can modulate p by altering the concentration or the accessibility of the hydrophilic sites, e.g., by methylating some of the OH groups or

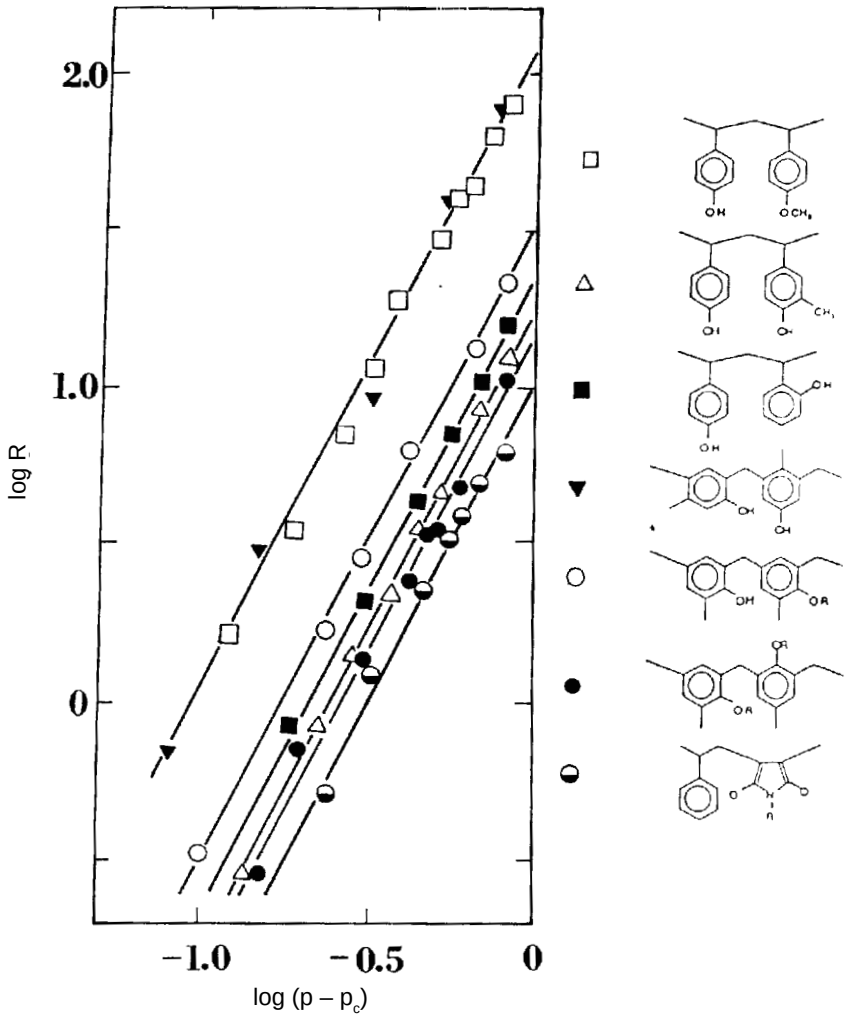


Figure 4. Plotting log$R$ against log$(p - p_c)$ for seven series of polymers, the structures of which are indicated in the margin.

by introducing steric hindrance in their surroundings.[4] In Fig. 4 we have plotted log$R$ against log$(p - p_c)$ for seven series of resins. Percolation theory predicts a linear correlation between the two logarithmic variables and a slope of two for the correlation line. The plots in Fig. 4 are linear and have the correct slope. Introducing a reference resin, it is possible to generalize the scaling law in the form shown below.

$$\log \frac{R}{R_0} = \log \frac{p - p_c}{1 - p_c} = f(p). \qquad (3)$$

Here R_0 is the dissolution rate of the reference resin (polyvinylphenol). The percolation threshold in all our systems was found to be $p_c = 0.20$. In the generalized plot of Fig. 5, the experimental points of all 52 resins of this study fall closely onto a solid line which represents the prediction of percolation theory. The percolative character of novolak dissolution seems well established.

How Does the DNQ Derivative Inhibit the Dissolution of Novolak?

Meyerhofer was the first to study the effect of inhibitors on the dissolution rate of novolak and he found that, over a significant range, a plot of log R against the concentration of the inhibiting additive is linear[5] (Fig. 6). We are using the slope of the linear plot as a concentration-independent measure of the inhibition strength of the additive, and call the negative slope the inhibition factor, f_{ij}, of inhibitor i in resin j.

TABLE I. Inhibition Factors and Site Blocking Numbers

Inhibitor	f_{ij}	blocking No.
Benzophenone	0.5	1
Xanthne	2.3	2.1
Flavanone	6.8	3.8
DNQ inhibitor	13	6.8
Flavone	18	7.7
2,3-Diphenylindene	24	9.7
b-Naphthoflavone	47	16
a-Naphthoflavone	49	17

If the rate of dissolution depends on the concentration of hydrophilic percolation sites, the answer to the question at the head of this section seems a foregone conclusion: the additives inhibit dissolution by simply blocking some of the percolation sites of the resin.When we tried to test this idea quantitatively we found that the usual diazoquinone inhibitors would have to block six to eight percolation sites to produce the observed inhibition effect; our most effective inhibitor, α-naphthoflavone, would have to block 16 percolation sites. Table I is a listing of inhibition factors and of blocking numbers for a group of inhibitors.

Several solutions to this problem were suggested.[6,7] All the solutions involve supramolecular configurations where a single inhibitor interacts simultaneously with a suitably arranged group of phenols. The difficulty here is that

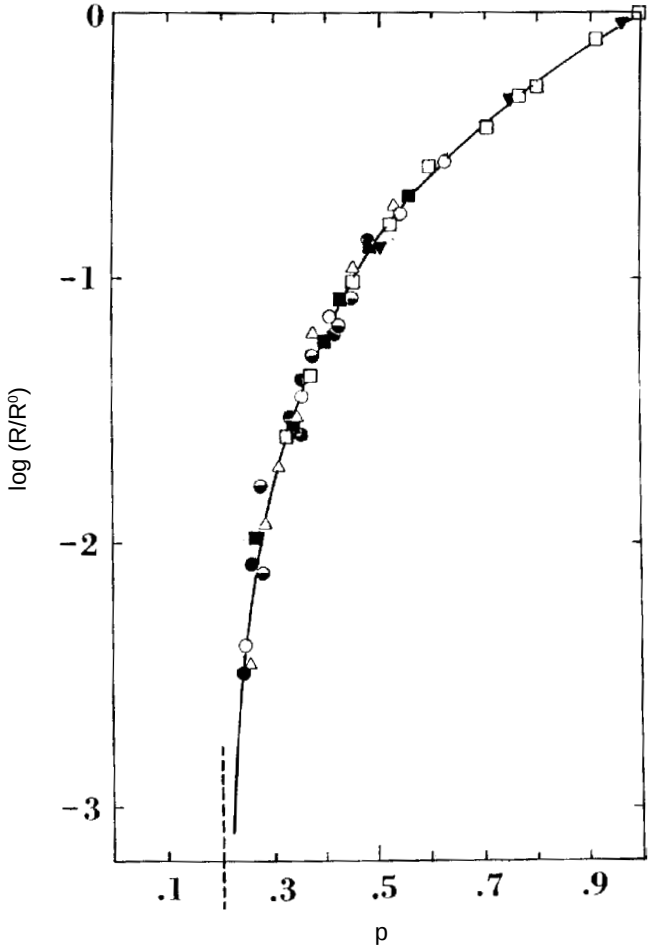
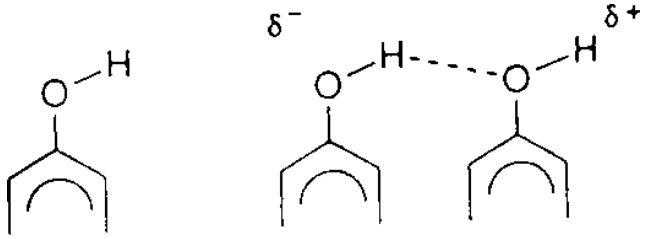


Figure 5. Generalized presentation of the scaling law of percolative dissolution. The experimental points refer to 52 phenolic resins of the groups indicated in Fig. 4.



the inhibitors interact with the phenol groups by hydrogen bonding, and hydrogen bonds connect hydrogen donors with hydrogen acceptors strictly on a one-on-one basis.

We found another mechanism that allows a single inhibitor to influence several phenolic OH groups.[8] It is based on the dual character of phenol groups that can act simultaneously as hydrogen donors and acceptors. When a hydrogen bond is formed between two phenol groups, the proton of the hydrogen acceptor phenol carries a larger partial positive charge than in an isolated phenol; that is the mechanism responsible for the well known hyperacidity of novolak.[7] At the same time, the oxygen atom of the hydrogen-donating phenol carries a larger partial negative charge than the oxygen of an isolated phenol. Consequently, phenolic dimers are better partners than isolated phenols for hydrogen bonding. In fact phenolic dimers are quite unstable in solution and are immediately included in larger strings or clusters of mutually hydrogen bonded phenols.

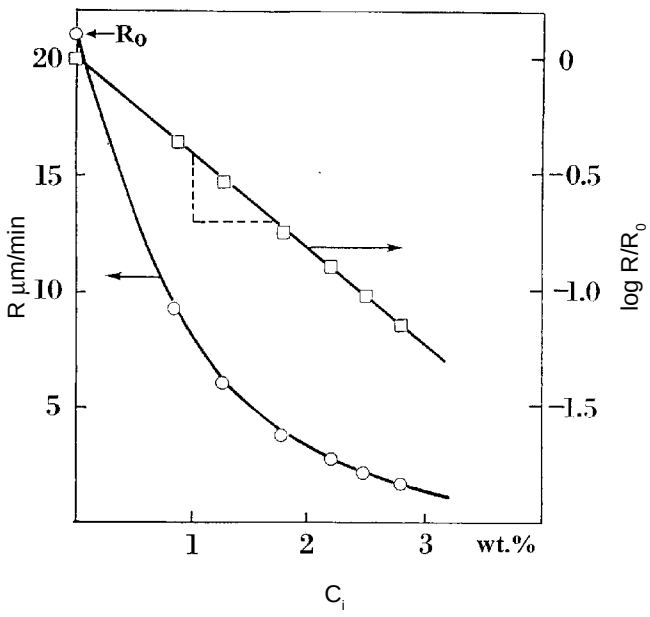
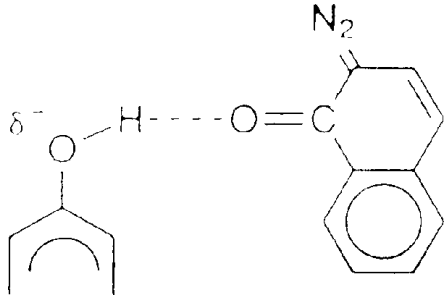


Figure 6. Plot of R and of logR as a function of the concentration of inhibitor in the resin film. The negative slope of the logarithmic plot defines the inhibition factor f_{ij}.



DNQ inhibitors are fairly strong hydrogen acceptors. When they are introduced into a novolak solution, they form hydrogen bonds with the nearest phenol which is thereby polarized and which itself becomes a much stronger hydrogen acceptor. In this way the inductive effect of the inhibitor propagates some distance into the surroundings. As the interaction between the phenols in the resulting strings are intensified in stronger inhibitors, larger and more tightly bound phenolic strings are formed.

It can be shown that the inhibition effect is linked to the hydrogen-bonding interaction between inhibitors and OH groups. We have measured the equilibrium constants of the interaction of various inhibitors (acceptors, A) with phenols (POH).

In Fig. 7 the two quantities are plotted against each other and can be see to be linearly correlated.

The existence of an inductive polarization effect between the inhibitor and the OH groups of novolak is confirmed e.g., by the effect inhibitors have on the viscosity of novolak solutions (Fig. 8). The observed large increase in viscosity arises from the formation of transient hydrogen bonds between hydroxy groups attached to different polymer chains.[9]

How can the formation of hydrogen-bonded phenolic strings change the dissolution rate of a resin film? It does so by altering the structure of he percolation field. The polarized OH groups in the phenolic strings are less available as percolation sites. They are less easily reached by

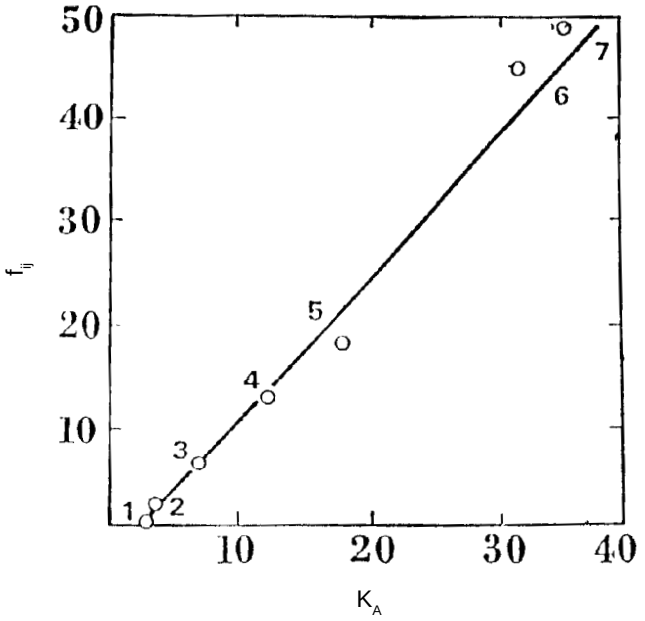


Figure 7. Correlation of the inhibition factors of a group of inhibitors with the equilibrium constant, K_A, of the hydrogen bonding process. (1) Benzophenone, (2) Xanthone, (3) Flavanone, (4) DNQ inhibitor, (5) Flavone, (6) β-Naphthoflavone, and (7) α-Naphthoflavone.

the advancing base ions, and as a result the connectivity of the percolation sites in the field is lowered, and with it the dissolution rate.

Up to this point we have ignored the existence of the so-called penetration zone of the dissolving resin film.[10] The penetration zone is a thin layer of phenolate ions formed at the interface of the film with the developer solution. Figure 9 is a schematic representation of the penetration zone where the black squares are cells filled with phenolate sites. The penetration zone is a polyelectrolyte of very high ionic strength, and because of that it is in a glassy solid state. One can determine the glass transition temperature of the zone by measuring the dissolution rate as a function of temperature and plotting log$R$ against 1/T. Such a plot, shown in Fig. 10 for a standard novolak resin, has two branches. The temperature corresponding to the intersection of the the two lines is the glass transition of the penetration zone. (For the resin to which Fig. 10 refers, this temperature, T_g' is 30C°). The glass transition temperature of the bulk of the film was 110C°. The glass transition temperature T_g' is an indication of the cohesive state of the penetration zone. Evidently, the presence of an inhibitor in the film makes for a more cohesive system. We find that T_g' increases linearly with the inhibition factor of an additive (Fig. 11).

What Happens on Exposure of the Resists Film ?

Until recently the conventional wisdom was that the dramatic change in dissolution rate that occurs on exposure is caused by the transformation of diazonaphthoquinone into indene carboxylic acid Diazoquinone is not soluble in base while indene carboxylic acid is. That seemed a sufficient explanation for the effect of exposure.

It can be shown that this is not true.[11] We prepared a series of resists by adding increasing quantitites of a standard diazoquinone inhibitor to novolak and we measured their dissolution rate, (see the lower trace of Fig. 12). We then exposed an identical series of resist films to completion, when all diazoquinones had been transformed into indene carboxylic acid, and we measured the dissolution rate again (see the upper trace of Fig. 12). Finally, a third series of these resists was exposed to completion and subsequently heated for 2 h to 70C°. This post-exposure bake decomposed

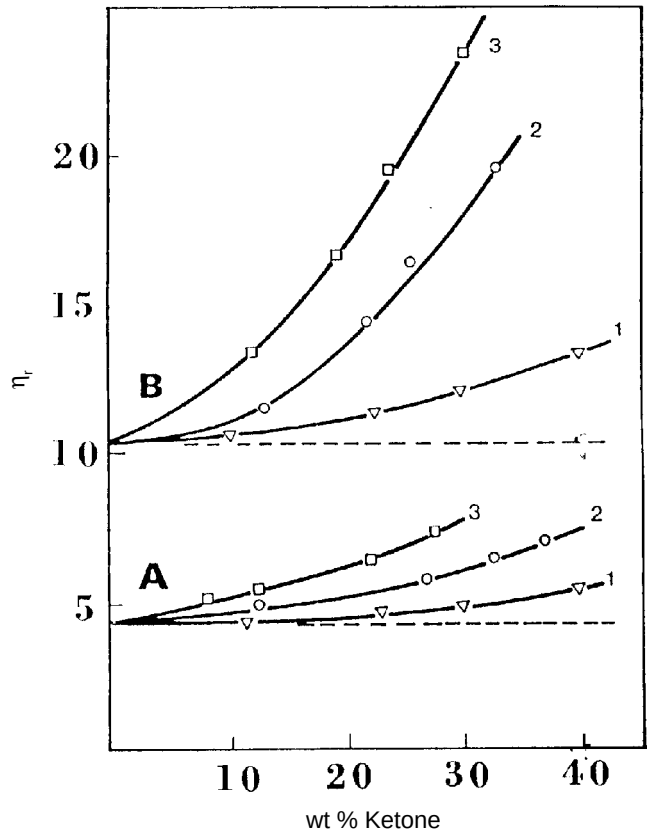


Figure 8. The effect of the inhibitors flavanone, flavone, and naphthoflavone on the viscosity of an 18% and 24% solution of novolak in iso-amylacetate.

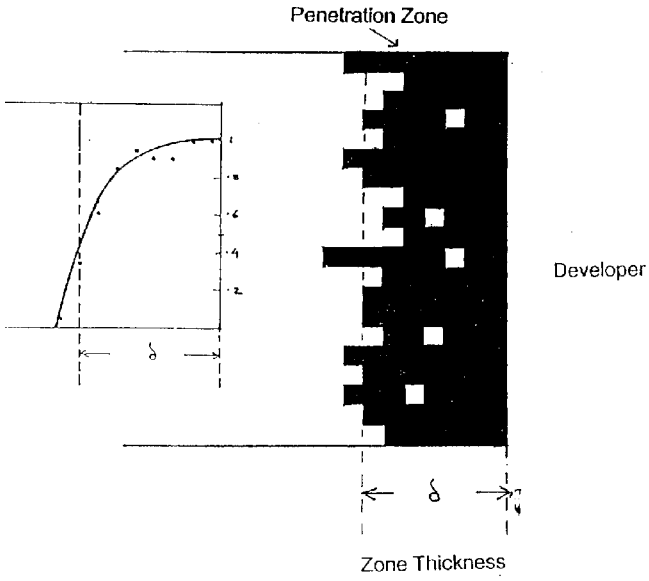


Figure 9. The penetration zone formed in the dissolving novolak film at the interface of the film with the base solution. The black squares represent phenolate ion sites, the white squares are phenol sites. The inset shows the concentration profile of phenolate sites at the front of the zone.

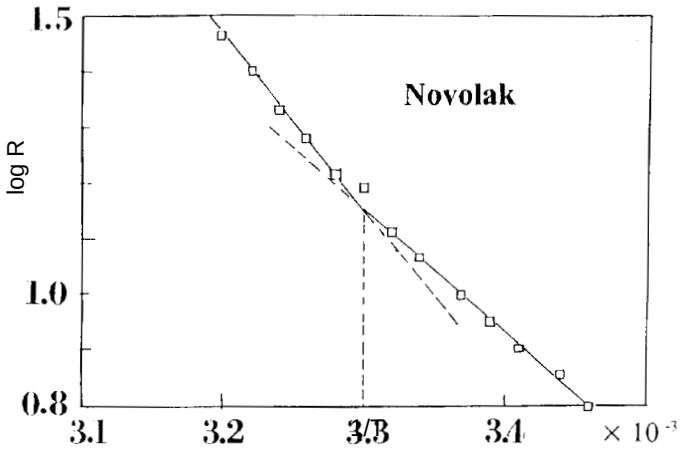


Figure 10. Arrhenius plot of log$R$ versus 1/T for a novolak resin dissolving in 0.2 N KOH. The discontinuity of the plot corresponds to the glass trasntion temperature of the zone. In this case it is T_g' = 30C°.

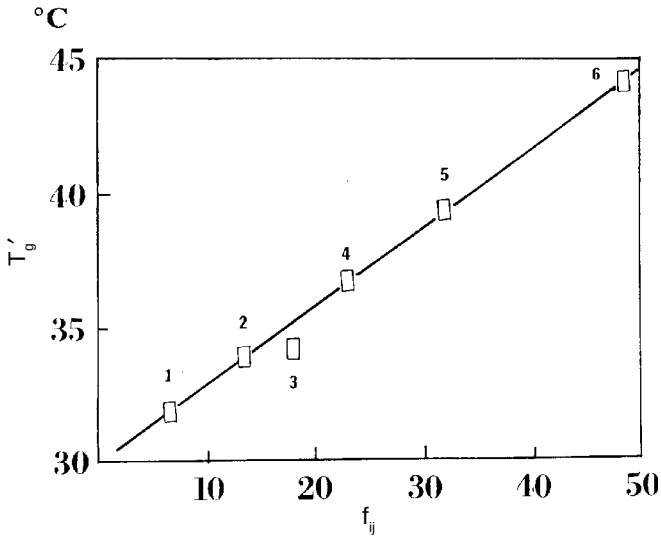


Figure 11. The glass transition temperature of the penetration zone of novolak films containing 2% of various inhibitors, plotted as a function of the inhibition factors of the additives. (1) Flavanone, (2) Diazonaphthoquinone inhibitor, (3) Flavone, (4) 2,3-Diphenylindenone, (5) 2-Benzoylnaphthalene, and (6) α-Naphthoflavone.

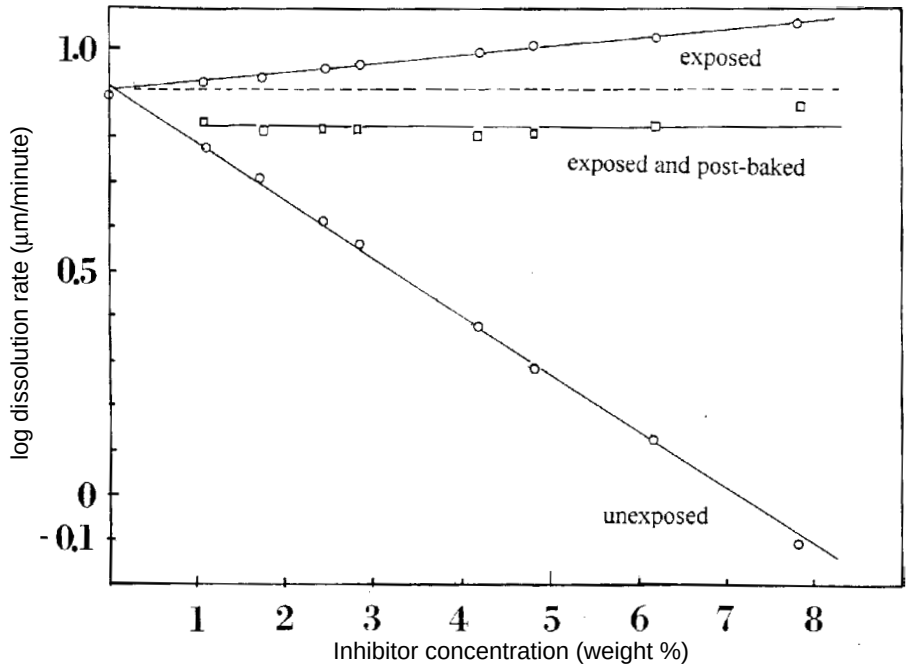


Figure 12. Plot of the logarithm of the dissolution rate in a series of resist of increasing inhibitor concentration: (a) before exposure, (b) after exposure to completion, and (c) after exposure to completion and a 2-h postbake at 70°C.

all the carboxylic acid in the films, (we had made sure of that in some preliminary experiments). When we measured the dissolution rate of these films, they dissolved all at the same rate, irrespective of the quantity of diazoquinone they had originally contained. Furthermore, the dissolution rate was very nearly that of pure novolak. (See the horizontal trace in Fig. 12).

We interpret these result as follows: if inhibition is caused by the presence of hydrogen-bonded strings of phenolic OH groups, the suspension of inhibition must be associated with the dispersal or deactivation of the strings. There is other evidence to support this interpretation. Figure 13 shows an experiment in which the glass transition temperature of the penetration zone of a resist film containing 6% of a standard DNQ inhibitor was determined in three states: before exposure the glass transition temperature was T_g' = 43C°, after exposure it was T_g' = 16C°, and finally, after exposure and post-bake the glass transition temperature of the penetration zone reverted to its value in pure novolak, T_g' = 30C°. It appears that the main effect of exposure is the functional disappearance (the dispersal, or inactivation) of the phenolic strings in the film.

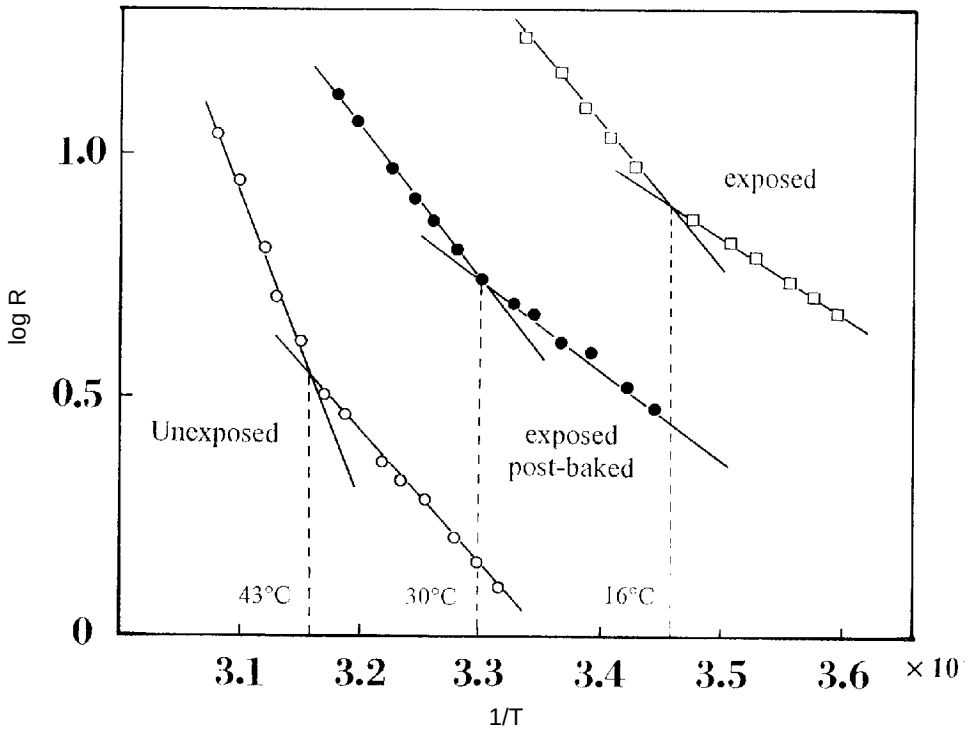
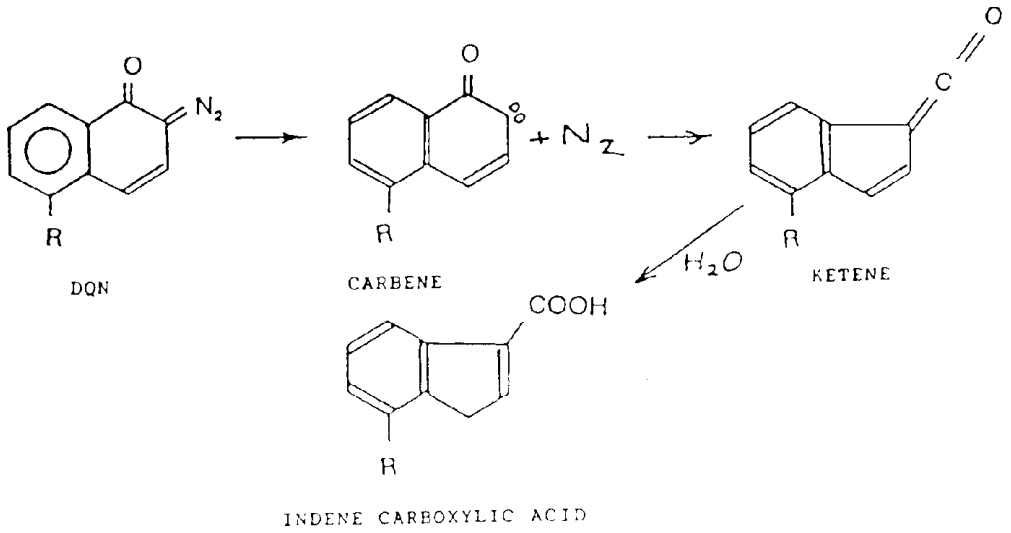


Figure 13. Determination of the glass transition of the penetration zone in a resist containing 6% of a standard DNQ inhibitor: (a) before exposure, (b) after exposure to completion, and (c) after exposure to completion and a post exposure bake for 2-h at 70°C.



By what mechanism is the dispersal of phenolic strings achieved? We know from the classical work of Sues[12] that the transformation of diazoquinone to indene carboxylic acid takes place in three stages.

(1) The photoreaction proper expells a molecule of nitrogen from the DNQ and produces a carbene.
(2) The carbene rearranges to a ketene (the Wolff rearrangement).
(3) The ketene is hydrated to a carboxylic acid.

The Wolff rearrangement that follows directly on the photolytic step is not only very fast, but also highly exothermic. ($\Delta H°$ is at least –66 kcal/mol). The sudden appearance at the location of the inhibitor of a heat pulse of that magnitude causes a temperature spike of not less than 220C°. At the high temperature the phenolic string is severed from its anchor at the DNQ and becomes inactive (dispersed), because it is no longer held together by the inductive effect of the inhibitor.

Let me summarize the basic features of our model of Novolak–DNQ resists:

1. Novolak dissolution is a percolation process in which base moves in the resin film by transfering from one hydrophilc site to the next.
2. The observed inhibition of dissolution is based on the formation of phenolic strings by the interaction of the strong hydrogen acceptor which is the inhibitor with the OH groups of the resin.
3. On exposure, the phenolic strings are severed from their anchor by a thermal effect: the Wolff rearrange-

ment, which follows photolysis of the diazoquinone moiety of the inhibitor molecule. ▲

Acknowledgments. We are grateful to the National Science Foundation, to the Office of Naval Research, to the Semiconductor Research Corporation, to Eastman Kodak, to the 3M Company and to Hoechst Celanese Corporation who supported us over the years. We acknowledge the help of Ralph Dammel (Clariant), Grant Willson (University of Texas at Austin), Kenji Honda (Olin Microelectronic Materials) and of our colleagues at Polytechnic University who shaped our ideas in dicussions and provided enthousiasm and encouragement.

References

1. A. Reiser, Y. Shih, T. F. Yeh, and J. P. Huang, *Angew. Chem. Int. Ed. Engl.* **33**, 2428 (1996).
2. T. F. Yeh, H. Y. Shih, and A. Reiser, *Macromol.* **23**, 5345 (1992).
3. D. Stauffer, "Introduction to Percolation Theory," Taylor & Francis, London, 1985.
4. T. F. Yeh, A. Reiser, R. R. Dammel, G. Pawlowski, and H. Roeschert, *Macromol.* **26**, 3862, (1993).
5. D. Meyerhofer, *IEEE Trans. Electron. Devices*, **ED-27**, 921 (1980).
6. K. Honda, B. T. Beauchemin, Jr., Y. Kawabe, and T. Kokubo, *Proc. SPIE* **1262**, 493 (1990).
7. R. R. Dammel, "Diazonaphthoquinone-based Resists", Tutorial Text No. 11, SPIE Press, Bellingham, WA, 1993.
8. H. Y. Shih, A. Reiser, R. R. Dammel, H. J. Merrem, and G. Pawlowski, *Macromol.* **27**, 3330 (1994).
9. H. Y. Shih and A. Reiser, *Macromol.* **28**, 5595 (1995).
10. R. A. Arcus, *Proc. SPIE* **631**, 124 (1986).
11. H. Y. Shih and A. Reiser, *Macromol.* **29**, 2082 (1996).
12. O. Sues, *Annalen Chem.* **556**, 65 (1944); O. Sues, J. Munder and H. Stephan, *Angew. Chem.* **74**, 985 (1962).