Percolation View of Novolak Dissolution. 5. The Dissolution of Exposed Resist Films

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Received November 3, 1995; Revised Manuscript Received December 18, 1995[⊗]

ABSTRACT: Dissolution inhibition produced by diazonaphthoquinones in novolak and in other phenolic resins is based on the formation of phenolic clusters. The principal result of the exposure of novolak−diazoquinone resist films to light is the dispersal of these clusters. It occurs through the thermal effect of the Wolff rearrangement that follows the photolysis of diazonaphthoquinone. Indenecarboxylic acid, which is the final product of irradiation, is converted to indenecarboxylate ion in the penetration zone of the dissolving films, where it adds to the concentration of hydrophilic percolation sites. This causes the dissolution rate of exposed resist films to be accelerated above that of pure novolak.

Introduction

Positive working novolak−diazoquinone resists currently are the most important imaging materials of the semiconductor device industry.[1] They were discovered in the 1940s by Oskar Suess, a leading organic chemist at Kalle, Wiesbaden, Germany, who observed that the introduction of diazonaphthoquinone derivatives into novolak strongly inhibited the dissolution of novolak films in aqueous bases. However, when the films were exposed to light, they dissolved even more rapidly than pure novolak. Suess realized the potential of these materials as imaging systems: when he exposed diazoquinone-containing novolak films to a pattern of light and shade, the exposed and unexposed areas could be distinguished by a very large differential in dissolution rate. On the basis of these observations, Suess developed a positive working lithographic printing plate[2] and also a photosensitive varnish (Kopierlack), which we now call a photoresist.[3]

Although novolak resists have been used for some 50 years, their functional mechanism was not known until recently. In earlier papers of this series, we have presented a model of novolak dissolution based on the percolative diffusion of base into the resin matrix.[4,5] This paper is concerned with the mechanism by which exposure to light affects the dissolution of novolak films.

In the percolation model of novolak dissolution, the rate of dissolution depends on the concentration of hydrophilic sites (OH groups) and declines if hydrophilic sites are removed from the system, e.g., by the partial methylation of phenolic OH groups.[6] In light of this observation, it was thought that inhibitors, such as diazonaphthoquinones (DNQ), function by blocking some of the hydrophilic percolation sites.[7] However, when this idea was investigated in more detail, it could not account for the large inhibition effects routinely observed with commercial inhibitors. For example, in terms of the blocking model, a monofunctional DNQ inhibitor would have to disable seven OH groups to produce the observed degree of inhibition.[8] The corresponding "blocking numbers" for other inhibiting additives in a typical novolak resin are given in Table 1 of ref 8. Clearly, one-to-one site blocking is not an adequate explanation for the change in dissolution rate in the presence of inhibitors. A mechanism is required that would enable inhibitors to interact with several hydrophilic sites simultaneously. In this spirit, Honda et al.[9] suggested the formation of a calixarene-like supramolecular structure (the so-called "octopus pot"), where up to 18 phenolic units can interact with a single diazoquinone functionality. A somewhat similar view was taken by Dammel.[10]

Table 1. Effect of Different Inhibitors on the Glass Transition Temperature of the Penetration Zone of a Novolak Resist (90% *o*-Cresol, 10% *p*-Cresol, Inhibitor Content 2%)

		f_{ij}	T_g' (°C)
	Novolak		30
1	flavanone	6.8	32
2	diazonaphthoquinone	3.1	34
3	flavone	18.3	34
4	diphenylindenone	23.6	37
5	2-benzoylnaphthalene	32.0	40
6	α-naphthoflavone	49.1	44

We have recently found a different mechanism that allows an additive to affect more than one OH group of a phenolic resin, namely, the inductive polarization of hydrogen bonds. This phenomenon is based on the dualistic nature of OH groups, which can act simultaneously as hydrogen donors and as hydrogen acceptors. As a result, phenols can form hydrogen-bonded strings or clusters. Intermolecular clustering of OH groups can be observed in nonpolar solutions of phenols, where hydrogen bonding does not stop at the dimer but immediately leads to the formation of larger aggregates.[11] Similar phenolic clusters form in solutions of novolak and of other phenolic resins.

The basis of cluster formation in phenolic systems is the fact that interacting OH groups polarize each other; when a hydroxyl group acts as hydrogen donor, its oxygen atom carries a larger partial negative charge and is a better hydrogen acceptor than the oxygen of a free phenol group. A hydrogen-bonded OH group therefore is a more attractive partner for further hydrogen bonding, and the inductive autopolarization of hydroxyls stabilizes hydrogen-bonded clusters in phenolic solutions. In the presence of strong hydrogen acceptors, such as diazoquinones or other aromatic ketones, this polarization effect is much intensified. When a strong acceptor is introduced into a novolak solution, it forms a hydrogen bond with the nearest OH group and, in so doing, inductively polarizes it, as mentioned before. The oxygen of the polarized OH group in turn interacts with the next OH group, polarizes it, etc. In this way, the inductive effect of the inhibitor propagates some dis-

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

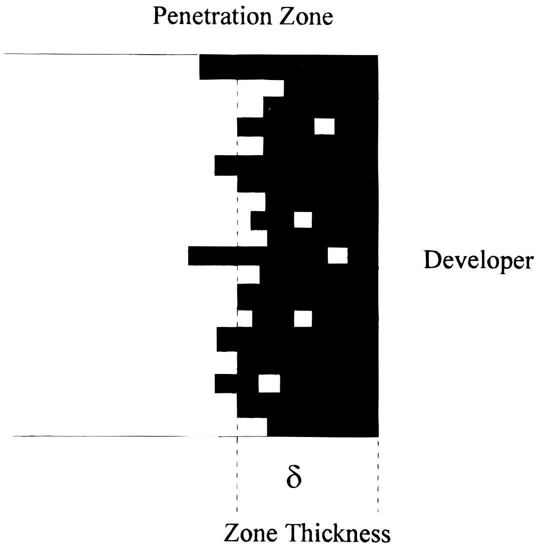


Figure 1. Percolation field in the penetration zone of a dissolving novolak film. The black squares are percolation cells containing phenolate ions.

tance into the neighborhood and leads to the formation of larger and more tightly bound phenolic clusters. In the preceding paper,[8] we went to some length demonstrating the reality and the importance of the inductive polarization effect.

How can the formation of phenolic clusters in the resist film affect the dissolution rate? The coming together of hydrophilic sites in clusters depletes the surroundings of the clusters of percolation sites and lowers the site connectivity of the percolation field.[8] As a result, the diffusivity of base and the dissolution rate of the resist film decrease.[8] A systematic study of percolation in nonuniform and nonrandom fields is currently underway at the Department of Physics of the University of Kazan, Russia, under professor Alexandr Kessel.[12]

Penetration Zone

We have so far ignored the fact that the diffusion process that controls dissolution does not take place in the phenolic matrix, but in a thin penetration zone at the interface of the film with the developer (base) solution. Arcus,[13] who conceived of the penetration zone, called it the "membrane" of the dissolving novolak film and demonstrated its real existence by an elegant laser interference experiment.[13] The penetration zone is formed when the resist film is immersed into aqueous alkali. As soon as base ions enter the matrix, they encounter phenolic OH groups and turn these into phenolate ions:

$$\mathrm{POH} + \mathrm{OH}^- \rightleftharpoons \mathrm{PO}^- + \mathrm{H_2O}$$

In this process, base disappears and is replaced by a molecule of water. The interface of the zone with the resin matrix is a fractal surface,[14,15] reflecting the statistical fluctuations of base diffusion (see Figure 1). As the penetration zone grows, the ionized novolak chains at the back of the zone detach themselves and float off into the developer. When the rate of mass transfer at the back of the zone balances the rate of diffusion at the front of the zone (i.e., when both occur at the same speed), a stationary regime is established in which the zone travels forward without changing its thickness (it is on the order of 100 Å) or concentration profile. By definition, the rate of dissolution (cm/s) of the resist film equals the rate of forward travel of the zone, and that depends entirely on the rate of supply of base to the frontal interface of the zone with the matrix. Base can reach this interface only by diffusing through the percolation field of phenolate sites in the penetration zone. *The rate of dissolution thus is controlled by the rate of diffusion of base through or across the penetration zone.*[16]

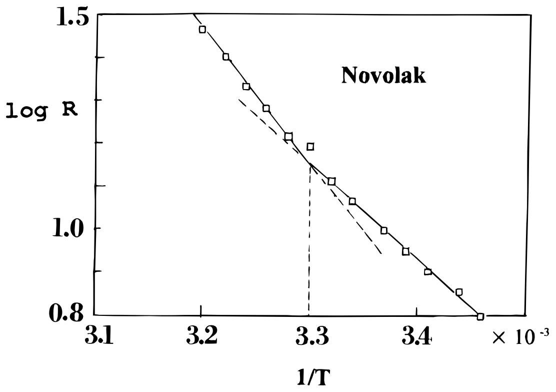


Figure 2. Arrhenius plot of the temperature dependence of the dissolution rate of novolak: log *R* vs 1/*T*. The intersection of the two straight lines corresponds to the glass transition temperature of the penetration zone. In this sample, $T_g' = 30$ °C.

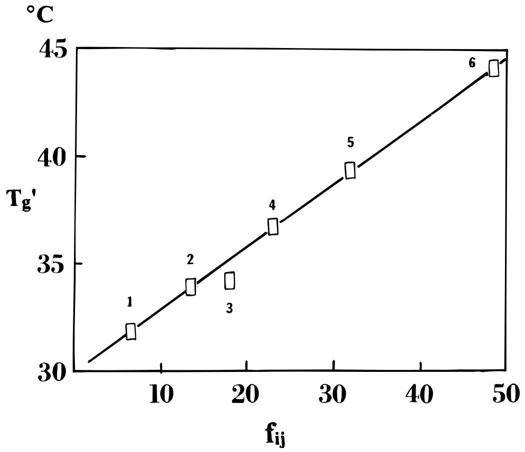


Figure 3. Glass transition temperature of the penetration zone in novolak films containing 2% of the inhibitors listed in Table 1.

If the rate-determining diffusion process occurs in the penetration zone, and if dissolution inhibition is caused by site clustering, clusters of hydrophilic sites must exist in the zone. It is our contention that the hydrophilic clusters originally formed in the coating solution and preserved in the phenolic matrix survive as phenolate clusters in the penetration zone. They do so because the zone is in the glassy state.

We can demonstrate the glassy state of the penetration zone by determining its glass transition temperature.[7] In Figure 2, the temperature dependence of the dissolution rate of novolak is presented in the form of an Arrhenius plot, log *R* vs 1/*T*. The plot consists of two straight lines separated by a discontinuity. The temperature corresponding to this discontinuity is the glass transition temperature, T_g', of the penetration zone. We have identified the glass transition temperature of the penetration zone in an earlier publication.[7] For the novolak sample of Figure 2, T_g' is 30 °C. We note in passing that the glass transition temperature of the bulk of the novolak film is 105 °C.

The glass transition temperature, T_g', is a sensitive probe of the internal cohesion of the penetration zone. Cohesion in the penetration zone is based on the electrostatic attraction between phenolate ions and the counterions of the base. The strength of the electrostatic field depends on the charge density, and that is higher within the phenolate clusters than in the rest of the zone. If inhibitors produce phenolic clusters in the resin matrix, they may be expected to increase the glass transition temperature of the zone. That is indeed the case. For example, the presence of 2% of the inhibitor α-naphthoflavone increases T_g' from 30 (pure novolak) to 44 °C. That increase in cohesion does not occur uniformly throughout the zone, but locally at the sites of the phenolate clusters. We assume, paraphrasing T. K. Kwei,[17] that the overall glass transition temperature T_g' is the weighted sum of contributions from the clusters and from other regions of the matrix:

$$T_g' = xT_g'(\text{cluster}) + (1 - x)T_g'(\text{noncluster})$$

Here x is the volume fraction of the clusters in the system, and T_g'(cluster) and T_g'(noncluster) refer to the two regions of the zone. The glass transition temperature of the cluster region can now be estimated. For example, in a resist with 6 wt % DNQ, we found a glass transition temperature $T_g' = 43$ °C. The molar concentration of inhibitor in this film is approximately 2%. If the clusters associated with the inhibitor contain some 10 phenolate centers,[18] the volume fraction of the clusters in the film is about 0.20. In taking a value of $T_g' = 30$ °C for the glass transition temperature of the noncluster region, (i.e., approximating it with pure novolak), we find that in the region of the clusters T_g'(cluster) = 95 °C. This signals a massive increase in cohesion within the clusters.

The inhibiting effect of an additive is measured by the inhibition factor f_{ij}, defined by the following derivative:[7]

$$f_{ij} = -\frac{d \log R}{dc_i}$$

where R is the dissolution rate (e.g., in micrometers per minute) and c_i is the concentration of inhibitor in the solid resist film. We have shown previously that the inhibition factor is directly proportional to the ability of the inhibitor to form hydrogen bonds with phenolic OH groups. The acceptor strength of the inhibitor determines the size and the phenolic clusters in the coating solution; stronger acceptors form larger and more tightly bound phenolic clusters. We now find that, in a group of inhibitors, the increase in T_g' is linearly related to the inhibition factor f_{ij}. This can be seen in Figure 3. The inhibitor has a powerful effect on the physical state of its immediate surroundings.

Dissolution of Exposed Resists

After these preliminaries, we are ready to consider the behavior of exposed resist films. The experimental facts are summarized in Figure 4. This is a so-called Meyerhofer plot[19] of log R as a function of the inhibitor concentration. The figure shows the effect of increasing concentrations of a standard monofunctional diazonaphthoquinone inhibitor on the dissolution rate of a typical novolak, before and after exhaustive exposure to light (437 nm). What happens in the exposure step that alters the dissolution rate of the films so dramatically?

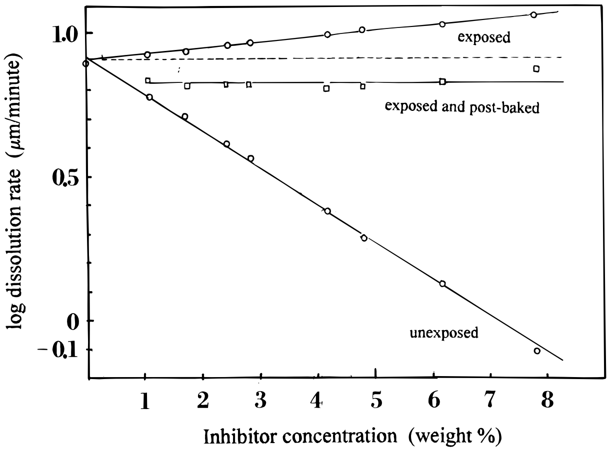


Figure 4. Meyerhofer plot of the logarithm of dissolution rate vs inhibitor concentration in films of a novolak made of 90% *o*-cresol and 10% *p*-cresol, containing increasing concentrations of a monofunctional inhibitor. Lower branch, before exposure; upper branch, after exhaustive exposure; horizontal line, after exposure and postbake at 70 °C for 2 h.

We know from the classical work of Suess[20] that diazonaphthoquinone is converted to indenecarboxylic acid upon exposure. Pacansky and Johnson,[21] and also Erlikh et al.,[22] have shown that unwanted side reactions occur if the water content of the films is insufficient, but that in films exposed to a typical laboratory atmosphere the formation of carboxylic acid is by far the most important process. Indenecarboxylic acid formed in the resin matrix is deprotonated in the penetration zone to indenecarboxylate, and the carboxylate ions provide additional percolation sites in the penetration zone. However, an increase of some 10% in the concentration of hydrophilic sites can hardly account for a 4000% change in dissolution rate, as is commonly observed upon exposure of commercial resist films. We believe that such a change must in some way be connected with the elimination or weakening of the hydrophilic percolation clusters, which are chiefly responsible for the inhibition effect.

It is possible to eliminate the effect of carboxylate from the exposed resist films by an experiment based on the thermal instability of carboxylic acids. The decarboxylation of indenecarboxylic acid to indene and to indene dimer was observed by Pacansky and Lyerla[23] in 1979. The reaction is so facile that it can be used to design a practical image reversal process.[24] We investigated the kinetics of decarboxylation in exposed resist films containing 6.2% indenecarboxylic acid (generated in situ by exhaustive exposure of DNQ). The films were heated to 70 °C, and the dissolution rate was monitored as a function of heating time. At first the rate decreased rapidly, but after about 60 min it settled to a fairly constant value. One of the wafers was kept at 70 °C for 17 h, and during this long period the dissolution rate decreased further (see Figure 5). It seems that two processes occur simultaneously during postexposure bake: the decarboxylation of indenecarboxylic acid and the gradual densification of the resist film. Both processes lower the dissolution rate, but they do so with very different time constants. From the data in Figure 5, one may conclude that the decarboxylation of indenecarboxylic acid is complete after the resist films have been heated for 1 h to 70 °C.

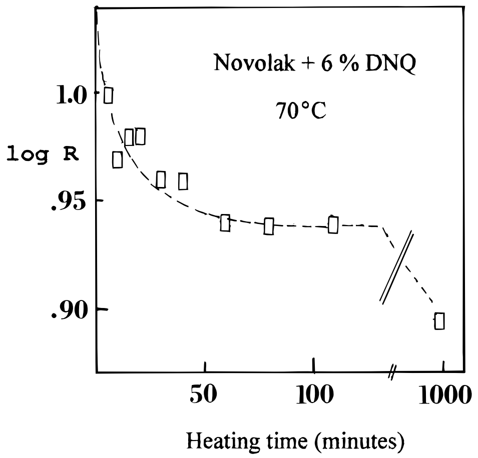


Figure 5. Dissolution rate of a resist containing 6% of the standard DNQ of this study, exposed and postbaked at 70 °C for the time indicated on the abscissa.

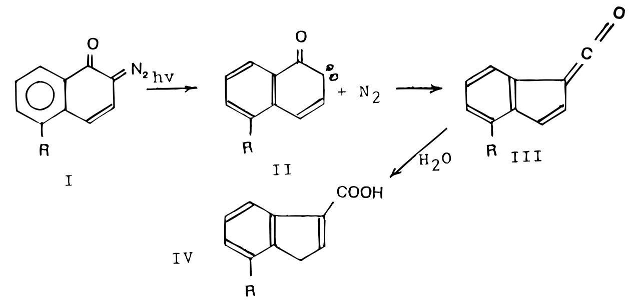
Having obtained this information, we exposed a series of resist films of increasing inhibitor content and subjected the exposed films to a postexposure bake at 70 °C for 120 min. When the dissolution rate of these films was subsequently measured, all of the films (irrespective of their earlier inhibitor content) dissolved at the same rate. The results of the experiments are included in Figure 4 and appear as a horizontal line. The small difference in the dissolution rate of these samples compared with that of the original novolak is caused, we believe, by a minor film densification effect. To summarize the data in Figure 4, it appears that the main change in dissolution rate during exposure is associated with the dispersal of the phenolate clusters in the penetration zone. This interpretation is also supported by the fact that the glass transition temperature of the penetration zone has the same value, $T_g' = 30$ °C, for *all* exposed and postbaked samples! The cohesive state of the system has reverted to that of pure novolak.

What is the mechanism responsible for the dispersal of phenolate clusters? The results of the postexposure bake experiments imply that the dispersal of site clusters is not linked to the presence of indenecarboxylic acid and that it must have happened before the postbake step, in the dry phenolic matrix and not in the penetration zone. We first considered the possibility that the presence of indenecarboxylic acid may have lowered the glass transition temperature of the matrix (not of the penetration zone!) below room temperature, but that could not be confirmed. However, it occurred to us that the energy released by the transformation of DNQ into indenecarboxylic acid may be the crucial factor.

Thermal Effect of DNQ Photolysis

The conversion of diazonaphthoquinone to indenecarboxylic acid occurs in three steps. First, the photolysis of diazoquinone I leads to the elimination of molecular nitrogen and to the formation of a highly reactive carbene II. The carbene immediately undergoes an intramolecular rearrangement, the Wolff rearrangement,[25] to ketene III. Finally, the ketene is hydrated to carboxylic acid IV.

The photoreaction produces the carbene in an excited singlet state (the ground state of the carbene is a triplet), which allows insertion into an available C−C bond. This reaction is not only very fast but also highly



exothermic. We have estimated a lower bound to the enthalpy change associated with the rearrangement of the carbene to the ketene from bond energies and heats of atomization.[26] From these data, the molar heat of reaction of the Wolff rearrangement is found to be not less than $\Delta H^\circ_{298} = 95 - 160 = -65$ kcal/mol, and the molecular enthalpy of reaction is in excess of $\Delta h^\circ_{298} = (-65 \times 10^3)/(6 \times 10^{23}) = -11 \times 10^{-20}$ cal/molecule. Δh° represents the heat released into the immediate environment of a single molecule of DNQ. Let us define that environment as the phenolic cluster associated with the DNQ, and let us assume that the cluster contains, say, 10 phenolic units. Each phenolic unit occupies on average a volume of 200 Å^3, and a 10-fold cluster will occupy a volume of about 2000 Å^3, corresponding to a mass of 2000×10^{-24} g. The specific heat of the material is approximately 0.25 cal/°C, which leads to a heat capacity for the cluster of $c = 2000 \times 10^{-24} \times 0.25 = 500 \times 10^{-24}$ cal/°C.

If the molecular heat of reaction, $q = 11 \times 10^{-20}$ cal, is released into the cluster "instantaneously", and if heat losses into the surroundings can be neglected, the temperature of the cluster will increase by $\Delta T = q/c = (10.8 \times 10^{-20})/(500 \times 10^{-24}) = 220$ °C. The cluster is embedded in the polymer matrix, and the assumption of an adiabatic transaction between the reacting DNQ and the associated phenolic cluster may be questionable. Let us then assume that the DNQ and its associated cluster are contained in a sphere of volume 2000 Å^3, which is enclosed in a spherical layer of thickness $s = 1$ Å. Let the temperature inside the enclosing sphere by 200 °C higher than outside, so that the temperature gradient across the enclosing layer is $\mathrm{d}T/\mathrm{d}s = 2 \times 10^{10}$ °C/cm. Fourier's law gives the heat flow out of a hollow sphere of radius r as[27]

$$Q = 4\pi r^3 k(\mathrm{d}T/\mathrm{d}s)$$

Here k is the thermal conductivity of the matrix material (for common polymers, k is on the order of 3×10^{-4} cal/grad cm s).[27] If we assume that the temperature gradient across the cover layer will be maintained for a full second, the quantity of heat that flows out of the sphere *in 1 s* is $Q = 12.6 \times 0.64 \times 10^{-21} \times 3 \times 10^{-4} \times 2 \times 10^{10} = 5 \times 10^{-14}$ cal.

The quantity of heat released at the center of the sphere is $q = 10^{-19}$ cal, but it is released within a time period on the order of picoseconds. By allowing some 1000 ps for the new temperature to establish itself in the sphere, the outflow of heat within 1000 ps (10^{-9} s) is $\mathrm{d}Q = 10^{-14} \times 10^{-9} = 10^{-23}$ cal. This heat loss represents less than one-tenth of one percent of the reaction heat of the Wolf rearrangement of a single DNQ. In light of this, the assumption of adiabatic heating within the cluster is not unreasonable. With this assumption, the pulse of thermal energy that the photoreaction injects into the cluster produces a temperature spike in excess of 200 °C. That releases the

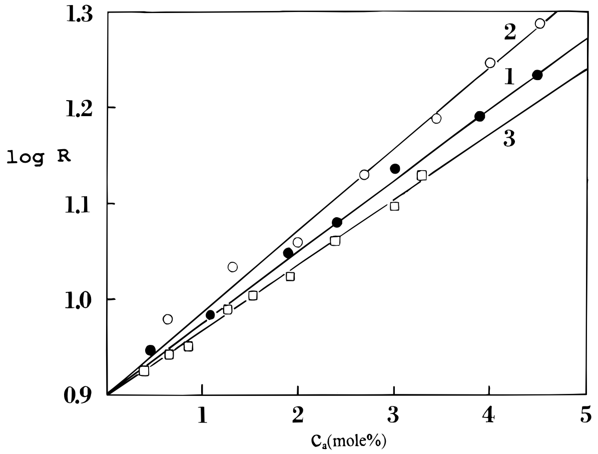


Figure 6. Plot of the logarithm of dissolution rate as a function of the molar concentrations of (1) 3-hydroxybenzophenone, (2) 4-hydroxybenzophenone, and (3) indenecarboxylic acid (generated in situ by exposure of a monofunctional DNQ).

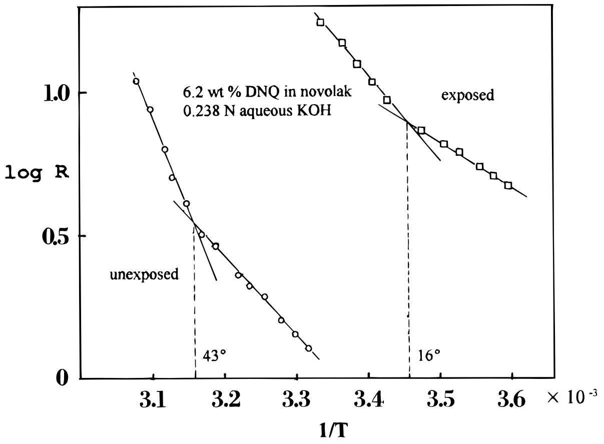


Figure 7. Arrhenius plot of resist films containing 6% of the standard monofunctional DNQ of this study, before and after exhaustive exposure, and after exhaustive exposure and a 2 h postbake at 70 °C.

polymer chains in the vicinity of the reacting DNQ and causes the dispersal of the phenolic cluster.

Effect of Indenecarboxylate on the Penetration Zone

Films that have been exposed, but not postbaked, dissolve faster than films of pure novolak. This can be seen in the upper line of Figure 4. This dissolution promotion (acceleration) effect is associated with the emergence of newly generated carboxylate ions, which function as added percolation sites. Figure 6 compares the acceleration effect of carboxylate to those of 3-hydroxybenzophenone and 4-hydroxybenzophenone introduced into the same novolak resin.

The presence of carboxylate has yet another effect on the penetration zone: it lowers the cohesion within the zone. This is reflected in a lowering of the glass transition temperature T_g' of the penetration zone of the exposed films. Figure 7 refers to films containing 6.2% of a standard monofunctional DNQ inhibitor. It shows Arrhenius plots of the temperature dependence of the dissolution rate of the films before and after exposure. From the break in the plots, we find that the glass transition temperature of the zone before exposure is $T_g' = 43$ °C; after exposure it is $T_g' = 16$ °C. This means that, in the exposed films, the penetration zone is well above its glass transition temperature during development and that, in exposed resists, base percolates in a field of mobile sites.

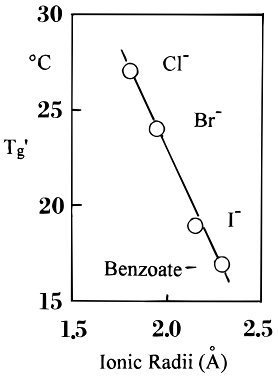


Figure 8. Effect on T_g' of electrolytes added to the developer. To a 0.24 N KOH developer was added 0.06 N of four different potassium salts, as indicated. T_g' is plotted as a function of the ionic radius of the anion of the added salt.

The lowering of cohesion in exposed resists is analogous to the behavior of solutions of polyelectrolytes where the introduction of salt is known to lower solution viscosity. We can demonstrate a similar effect directly in the penetration zone by adding various salts to the developer base and monitoring the effect on the dissolution rate. For example, the addition of KCl to a 0.24 N KOH developer lowers T_g' in proportion to the KCl concentration. The electrolyte intercalates itself between the phenolate ions and the K^+ counterions and interrupts the lines of force of the electrostatic field, which are the source of cohesion in the zone. If this interpretation is correct, larger anions should have a greater effect on T_g': in Figure 8 we have plotted T_g' values of films dissolving in 0.24 N KOH, to which was added 0.06 N of different potassium salts. The effect of the added salt on T_g' appears to increase linearly with the radius of the salt anion.

Summary

In the preceding paper of this series, we showed that the inhibition effect of diazoquinones and other addenda is caused by the formation of phenolic clusters, which lower the connectivity of the percolation field and reduce the rate of dissolution. Diazonaphthoquinones, which are the usual photoactive compounds of novolak resists, are converted to indenecarboxylic acids upon exposure to light or UV radiation. At the same time, the dissolution rate of the films in aqueous base (the developer) increases dramatically. It has been generally assumed that this effect is the result of the photochemical transformation of diazoquinone into indenecarboxylic acid, with the associated formation of a new ionized species. We have now found that this is not the case and that the most important event during irradiation is the elimination of the phenolic clusters. This occurs as a result of the heat effect that accompanies the Wolff rearrangement, which follows in the wake of the photolysis of diazonaphthoquinone. The Wolff rearrangement of a carbene to a ketene injects a heat pulse into the phenolic cluster. The resulting transient temperature spike releases the polymer chains in the vicinity of the reacting DNQ and causes the cluster to disperse. This event takes place during exposure in the resist matrix and not in the penetration zone.

The carboxylate ions that appear in the penetration zone after exposure increase the concentration of hydrophilic percolation sites and on that account contribute to the rate of dissolution. They also decrease the cohesion in the zone, as indicated by a lowering of T_g'.

Experimental Section

All experiments were carried out with a *m*-cresol-based novolak supplied by Hoechst Celanese Corporation. The inhibitors and all solvents were purchased from Aldrich Chemical Co.

Resin films were cast from 28% (weight) solutions in isoamyl acetate. The solutions were spin-coated onto silicon wafers at about 2000 rpm. The wafers were then kept at 90 °C for 1 h, except where otherwise indicated.

Dissolution rates were measured in 0.20 N solutions of KOH. The thickness of the dissolving films in the developer solution was monitored by laser interferometry. The apparatus is described in ref 28. The temperature of the developer solution was controlled to within +0.2 °C. The dissolution rate was derived by the method of Rodriguez et al.[20] from the recorder trace produced by the interferometer.

Acknowledgment. We thank the Semiconductor Research Corp. and also Hoechst Celanese for financial support of this work and Jim Gentleman of Silicon Valley Group, Inc., San Jose, CA, for the gracious gift of an advanced hotplate. We have benefitted greatly from extensive discussions with Ralph Dammel of Hoechst Celanese and with Rodney Hurditch and others at OCG, East Providence, RI.

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MA951668E