Photosensitive Polyimides Developable with Basic Aqueous Solutions (II)

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SYNOPSIS

Positive and negative photosensitive polyimides developable with basic aqueous solutions are reported. The results consist of poly amic acids and naphthoquinone diazides in which sulfonate groups have to be substituted at 4-position. It depends on the naphthoquinone structures whether positive or negative patterns are obtained. In order to fabricate resist patterns, High-Temperature-Post-Exposure-Process (HIT-PEB) must be utilized. The reaction mechanisms are also discussed. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides have many desirable properties for use in the microelectronics industry. For example, polyimides are one of the excellent high-temperature heat-resistant polymers in organic materials and have good planarization capability and electrical insulating properties.[1]

Photosensitive polyimides (including photosensitive polyimide precursors as well) have attracted great interest because the photosensitive polyimides simplify processing by eliminating the need for separate resist application and removal steps.[2]

Negative working polyimides are quite common.[2] However, they need much solvent to develop the patterns. This has not been compatible with existing photoresist processing technology in microelectronics where dilute organic base aqueous solutions have been put into use.[3] Our goal is to find polyimide resists that can be developed with basic aqueous solutions.

In order to realize the resists developable with the aqueous solutions, diazonaphthoquinones were promising photoactive compounds.[4] Khanna and Mueller have reported on the use of hydroxy polyimides and polyamides for positive working diazonaphthoquinone-sensitized resists.[5a,5e] Positive polyimide resists, in which diazonaphthoquinones are bonding partially to the hydroxy groups on the polyimide backbone, have been also reported.[5b,5c] However, these polymers had to bear phenolic moieties either on the polymer backbones or in the side chains, which have made polymer syntheses complicated.

These diazonaphthoquinones act as dissolution inhibitors to base-soluble binder polymers, such as phenol novolac resins.[4] Considering this point of view, these diazonaphthoquinones may also act as the dissolution inhibitors to polyamic acids, which are precursors to polyimides, because the polyamic acids have carboxylic acid moieties that make it possible for the polymers to be soluble in dilute basic aqueous solutions.

However, this has not worked yet for conventional polyamic acids prepared from benzophenone tetracarboxylic acid anhydride and diaminodiphenyl ether and so on because they are too soluble in the basic solutions. Therefore, both exposed and unexposed areas are usually washed away during the development.

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To achieve positive resists consisting of polyamic acids, some specific polyamic acids have been synthesized. It has been reported that these polyamic acids are partially imidized during soft baking process before exposure, so as to adjust (decrease) the polymer solubility in the basic aqueous solutions. These polyamic acids have been reported to give positive tone resists when coupled with diazonaphthoquinones.[5d,5e,5f] This method has come up with a new idea about the decrease in the solubility, however, which has a limit. Because common diazonaphthoquinones decompose rapidly above 135°C, the soft bake process has to be accomplished below 135°C, at which temperature conventional polyamic acids are not converted to the imide structure at all.

Recently, the authors found another approach, high-temperature–postexposure bake (HIT–PEB) process, which made it possible to develop the conventional polyamic acids with basic aqueous solutions and gave negative-tone patterns.[6] The resist consists of conventional polyamic acids and naphthoquinone diazides. More than two naphthoquinone diazide moieties are bonding to a benzophenone group through sulfonate linkages and the substitution had to be at 4-position on the naphthoquinone diazide group [(4)-NAC]. Naphthoquinone diazides on which a sulfonate group is substituted at 5-position [(5)-NAC] did not work at all even if the HIT–PEB process was applied.

In the course of this study it was found that positive tone resists were also realized, depending on the structure of the naphthoquinone diazides.

This report discusses how resist properties are affected by the structures of naphthoquinone diazides and HIT–PEB process conditions.

EXPERIMENTAL

All photoactive compounds used in this study were purchased from Toyo Gousei (Table I) and used without any purification.

Polyamic acid (PA1) was synthesized by reacting 0.3 mol of pyromellic acid anhydride and 0.7 mol of benzophenone tetracarboxylic acid anhydride with 0.9 mol of diaminodiphenyl ether and 0.1 mol of di(aminopropyl)tetramethyldisiloxane. The intrinsic viscosity was 0.65 (dL/g) (0.5 g in 100 mL of NMP) at 30°C. Ultraviolet exposure was carried out by using CA 800 (Cobilt contact printer) equipped with an Xe lamp.

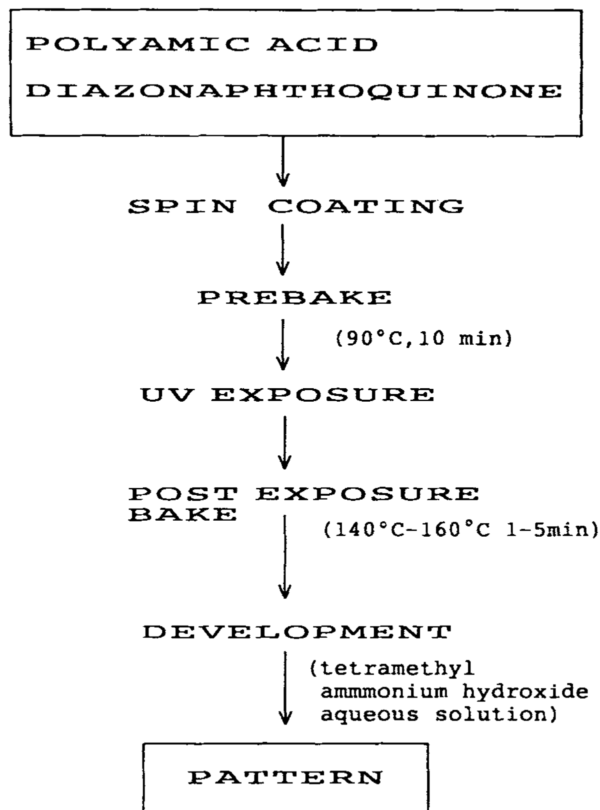
HIT–PEB Process

Resists consisting of the polyamic acids and naphthoquinone diazides were spin coated on a Si wafer and the wafer was soft baked at 90°C for 10 min, followed by exposure. The wafer was again baked at

Table I Structures of Photoactive Compounds

NAC 1	O, C, OH, OR	NAC 2	O, C, OR, OH, OR
NAC 3	RO, O, C, OR, OH, OR	NAC 4	OR, Me
NAC 5	RO, OR	NAC 6	ROBu
NAC 7	CH_3, N—R	NAC 8	HO, CH_3, C, CH_3, OR

R= O, N_2, SO_2



Scheme 1

140–150°C for 2–5 min (Scheme 1). The precise conditions are described in the figures. The wafer was developed with tetramethylammmonium hydroxide aqueous solution and linsed with deionized water. These conditions are also described individually.

Dissolution rates of each resist were calculated from the resist thickness before and after immersing in the basic solution, followed by dividing the decreased thickness by the time involved. In all sensitivity curves, normalized thickness was defined so that the resist thickness after the postexposure baking would become unity.

RESULTS AND DISCUSSION

Figure 1 shows the exposure dose-normalized thickness curve for various resists consisting of one (NAC 1), two (NAC 2), and three (NAC 3) naphthoquinone diazide moieties bonding to the same benzophenone structure, respectively. There was almost no difference among these sensitivity curves, and even if the photoactive compound has only one naphthoquinone diazide moietie (NAC 1), it worked pretty well. However, naphthoquinone diazide bonding to benzene group acted differently, com-

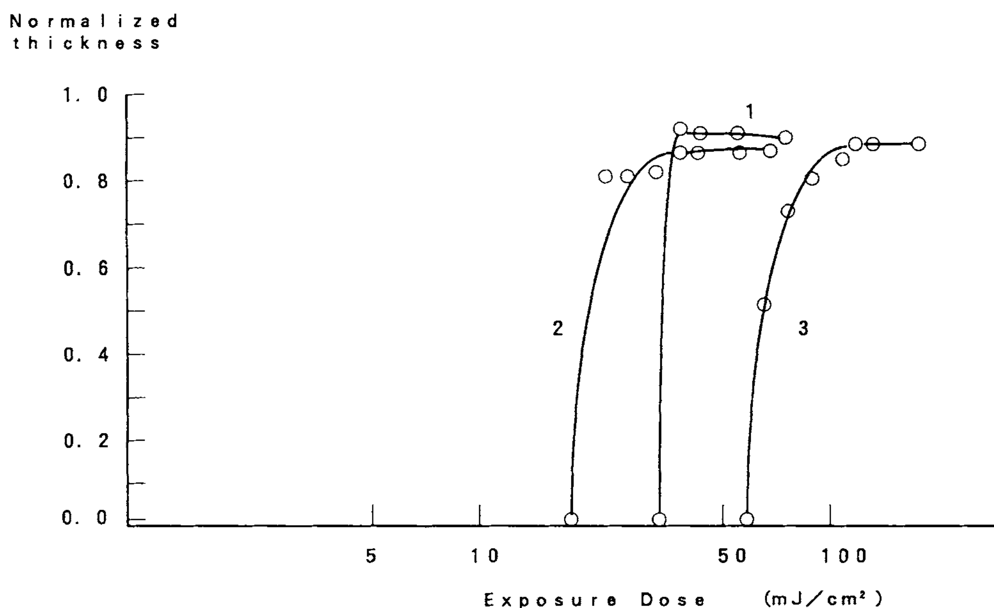


Figure 1 Sensitivity curves for resists containing one, two, and three naphthoquinone diazides bonding to a benzophenone group. HIT–PEB 140°C, 5 min. (1) NAC 3/PA1 = 3 : 7, development, 1.79% TMAH aqueous solution; (2) NAC 2/PA1 = 3 : 7, Development, 1.79% TMAH aqueous solution; (3) NAC 1/PA1 = 3:7, Development, 2.38% TMAH aqueous solution.

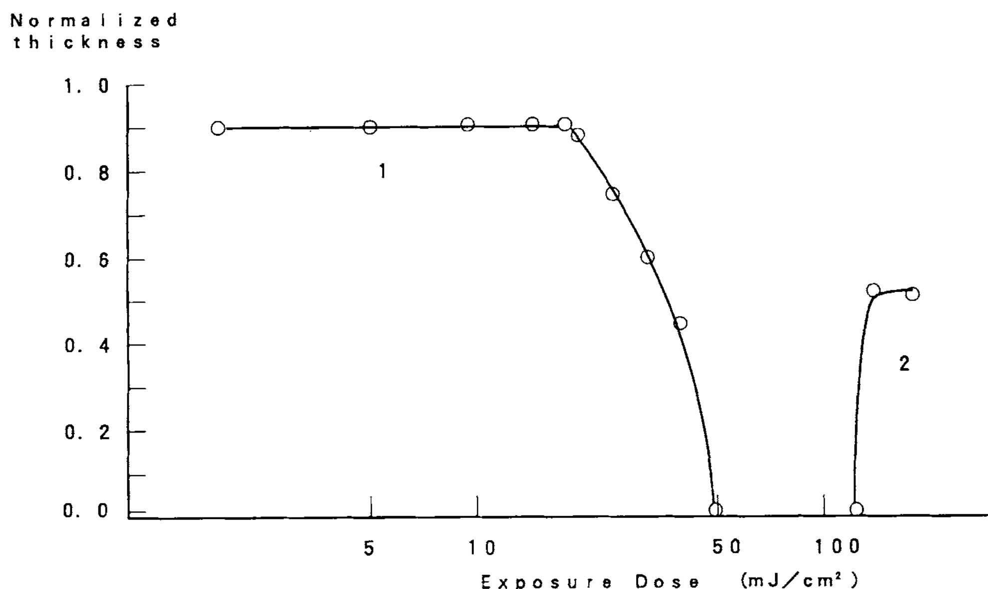


Figure 2 Sensitivity curves for resists containing naphthoquinone diazides without a benzophenone group. (1) NAC 4/PA1 = 3 : 7, HIT–PEB 140°C, 3 min. Development, 0.79% TMAH aqueous solution; (2) NAC 5/PA1 = 3 : 7, HIT–PEB 140°C, 5 min. Development, 1.19% TMAH aqueous solution.

pared to that bonding to the benzophenone moiety. Figure 2 shows the sensitivity curves for resists containing one (NAC 4) and two (NAC 5) naphthoquinone diazide moieties bonding to one benzene ring. Photoactive compound (NAC 5) showed a negative tone feature that was inferior to that shown in Figure 1.

Surprisingly, photoactive compound (NAC 4) showed pretty different behavior. The resist pattern fabricated by the HIT–PEB process was positive tone (Plate 2). NAC 8, in which a carbonyl group of NAC 1 is replaced with a isopropyridene group, showed the same behavior. However, trials to get resist patterns by using naphthoquinone diazides bonding to alcohols such as butanol (NAC 6) and that bonding to a aniline derivative (NAC 7) were in vain. Various HIT–PEB processes were tried; however, any pattern, which looked positive tone at the first stage of the development, was washed away completely at the end of the development. These results show that in order to get positive patterns naphthoquinone diazides have to be bonding to phenyl moieties without carbonyl groups.

In the resist system consisting of polyamic acids and NAC 4, HIT–PEB process also plays a significant role in fabricating patterns. Plate 1 shows clearly the usefulness of the process. Without the HIT–PEB process, only unclear patterns were obtained. After 1 min HIT–PEB process, the patterns

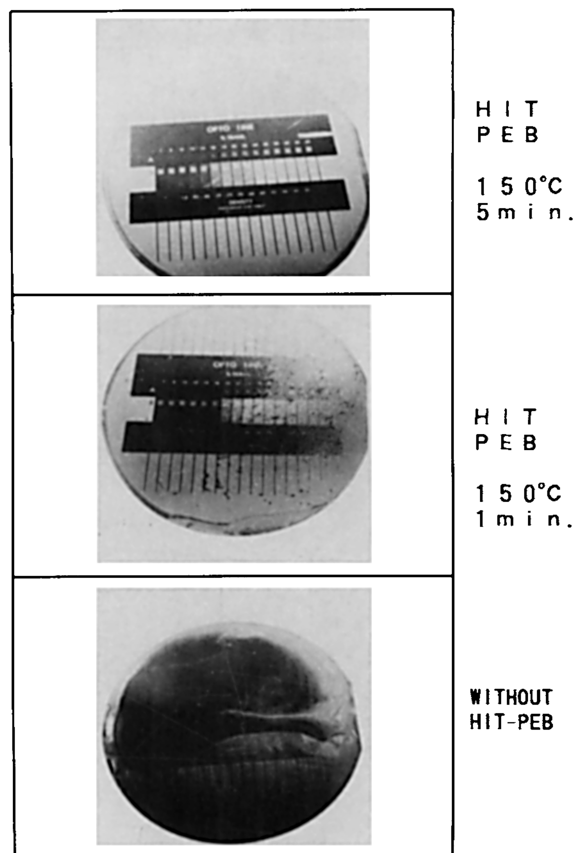


Plate 1 High temperature postexposure bake process (HIT–PEB).

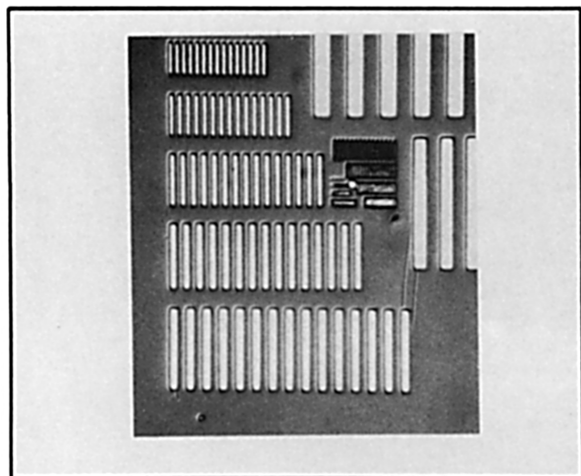


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Plate 2 Positive patterns fabricated by HIT–PEB process.

became clearer; however, some parts of the resist patterns were removed during rinsing. Completely clear patterns were obtained by 5 min HIT–PEB process.

In order to elucidate the difference between the resist systems, solubilities of the resist films containing various naphthoquinone diazides were measured in detail. Figures 3 and 4 show the relations between the solubility of resist films and HIT–PEB time in the exposed region and unexposed region, respectively. HIT–PEB temperature was 150°C and the development was carried out with 2.38% tetramethyl ammonium hydroxide (TMAH) aqueous solution.

In the exposed area the decrease in the solubility became remarkable as for naphthoquinone diazides bonding to a benzophenone moiety (NAC 1,3). The introduction of *m*-dioxybenzene (NAC 5) instead of the benzophenone moiety also decreased the solubilities, which, however, were not as low as those

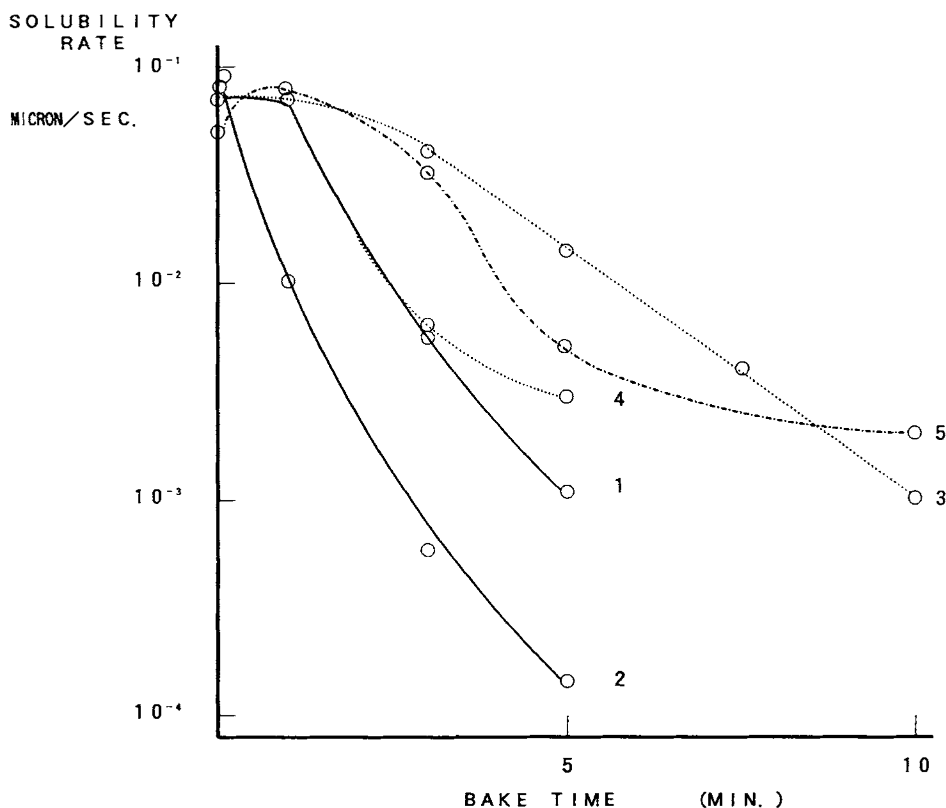

Figure 3 Solubilities of resist films in exposed areas after HIT–PEB process. HIT–PEB temperature, 150°C, development, 2.38% TMAH aqueous solution. (1) NAC 1/PA1 (3/7), (2) NAC 3/PA1(3/7), (3) NAC 4/PA1(3/7), (4) NAC 5/PA1(3/7), (5) NAC 6/PA1(3/7).

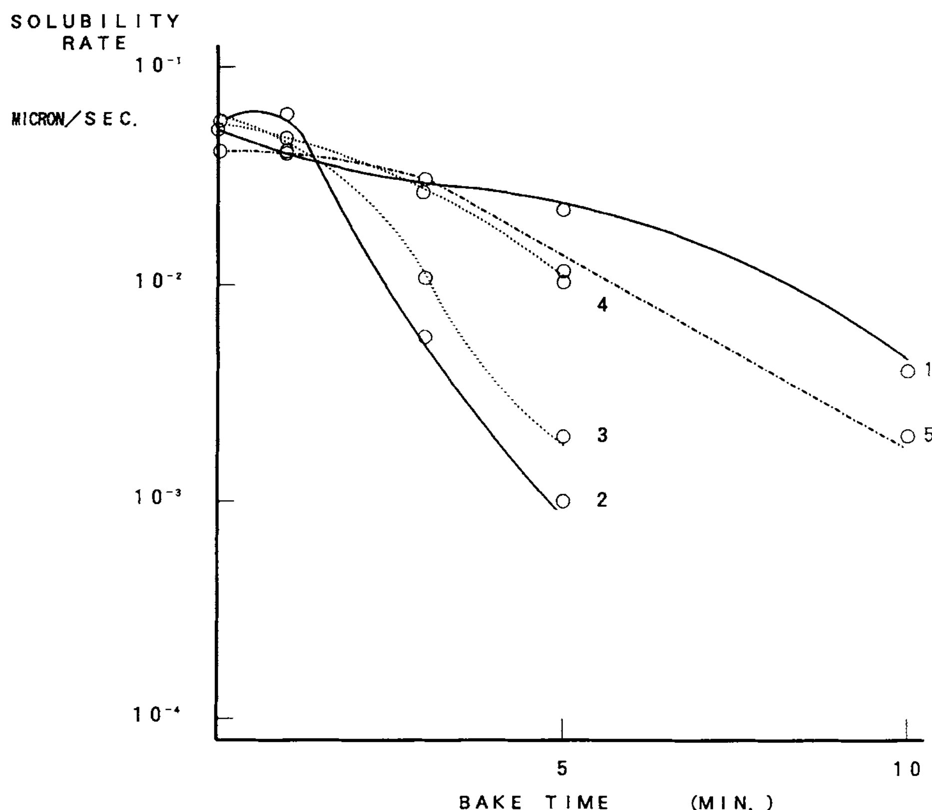

Figure 4 Solubilities of resist films in unexposed areas after HIT–PEB process. HIT–PEB temperature, 150°C, development, 2.38% TMAH aqueous solution. (1) NAC 1/PA1 (3/7), (2) NAC 3/PA1(3/7), (3) NAC 4/PA1(3/7), (4) NAC 5/PA1(3/7), (5) NAC 6/PA1(3/7).

for NAC 1 and NAC 3 and was a little less than those for NAC 4 and NAC 6.

On the contrary, in the unexposed area the decrease in the solubilities was lower for NAC 4 and NAC 3, and higher for NAC 1, NAC 5, and NAC 6. Comparison of NAC 1 with NAC 3 was remarkable, where they have almost the same benzophenone moiety, and the difference was only in the number of the naphthoquinone diazide bonds to the moieties. The other remarkable result was large decrease in the solubility on NAC 4 having a *m*-oxy toluene moiety whose solubility was the largest among the NACs in the exposed area.

Figure 5 shows very clearly the difference in the resist properties, depending on the structure of photoactive compounds. In case of NAC 4, the ratio (the dissolution rate in exposed area/the dissolution rate in unexposed area) increased as the bake time after exposure became longer, which means that this resist system is working as positive tones. The development was carried out with rather concentrated TMAH 2.38% aqueous solution for the resists. Therefore, these absolute ratios themselves do not mean the best one. It is possible to increase the ratios by using low-concentrate TMAH aqueous solutions. The other photoactive compounds also lay in the regions over 1.0 in the initial HIT–PEB time, however, the value decreased rapidly below 1.0 as the bake temperature became longer, which suggests that these resists act as negative tones.

Reaction mechanism is still in the dark. However, the following reaction scheme of naphthoquinone diazides reported so far and the naphthoquinone diazide structure dependence on the resist properties may have something to do with the mechanism.

Buhr and Grunwald et al.[7] have reported that in the image reversal process in the resist technology, crosslinking of phenol novolac resins with crosslinker was accelerated by sulfonic acid photogenerated from (4)-NAC. The acceleration was best when using NAC 1 or 3 structure, namely, the structure bearing a benzophenone moiety. On the other hand,

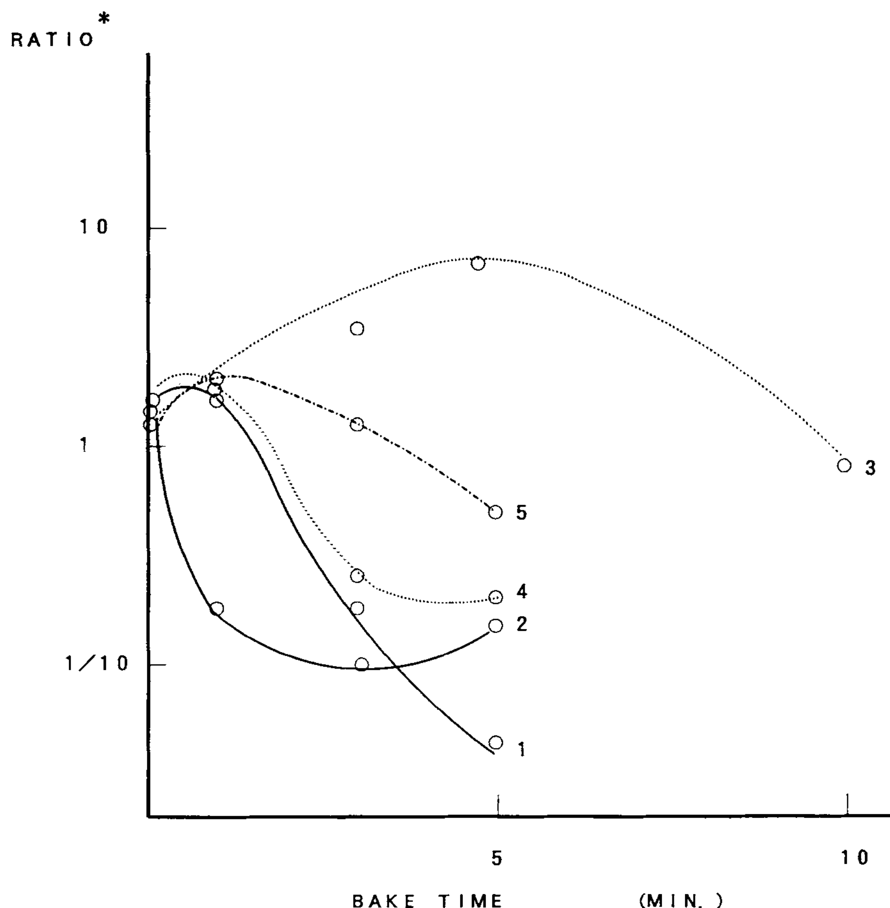

Figure 5 The ratios (the dissolution rate in exposed area/the dissolution rate in unexposed area) vs. HIT–PEB time. HIT–PEB, 150°C, development 2.38% TMAH aqueous solution. Each dissolution rate was taken from Figures 3 and 4. (1) NAC 1/PA1(3/7), (2) NAC 3/PA1(3/7), (3) NAC 4/PA1(3/7), (4) NAC 5/PA1(3/7), (5) NAC 6/PA1 (3/7). The development was carried out with rather concentrated TMAH 2.38% aqueous solution. Therefore, the absolute values do not mean the best one.

the crosslinking rate of the resist in which naphthoquinone diazides are bonding to bisphenol-A moieties were more than 10 times lower, compared to that containing NAC 3.

This has been explained as follows (Fig. 6): Naphthoquinone diazides photodecomposed to form indene carboxylic acid derivatives. Then the photolysis compounds further decomposed to form compounds with both carboxylic acids and sulfonic acids. The presence of carbonyl groups in the indene carboxylic acid derivatives facilitates proton acceptance and thus promotes the Lewis base behavior. Therefore, NAC-4-type photoactive compounds produce much sulfonic acids and facilitate the crosslinking by acid catalysis. However, in case of NAC 8, there are no proton acceptors such as carbonyl groups. For this reason the rate of sulfonic acid generations from the indene carboxylic acid derivatives decreases and the crosslinking is not carried out effectively.

In order to ascertain the effects of photogenerated sulfonic acids, solubilities of polymer films with and without *p*-toluene sulfonic acid after HIT–PEB were measured. The results shown in Figure 7 imply the following facts.

1. In the course of 150°C bake process, polyamic acid itself imidized partially, which decreased its solubility to basic aqueous solutions (No. 5). The imidization and the decrease in the solubility prevent the polyamic acids from swelling in the developers or detaching out of a Si wafer surface during the development process. This thermal imidization has

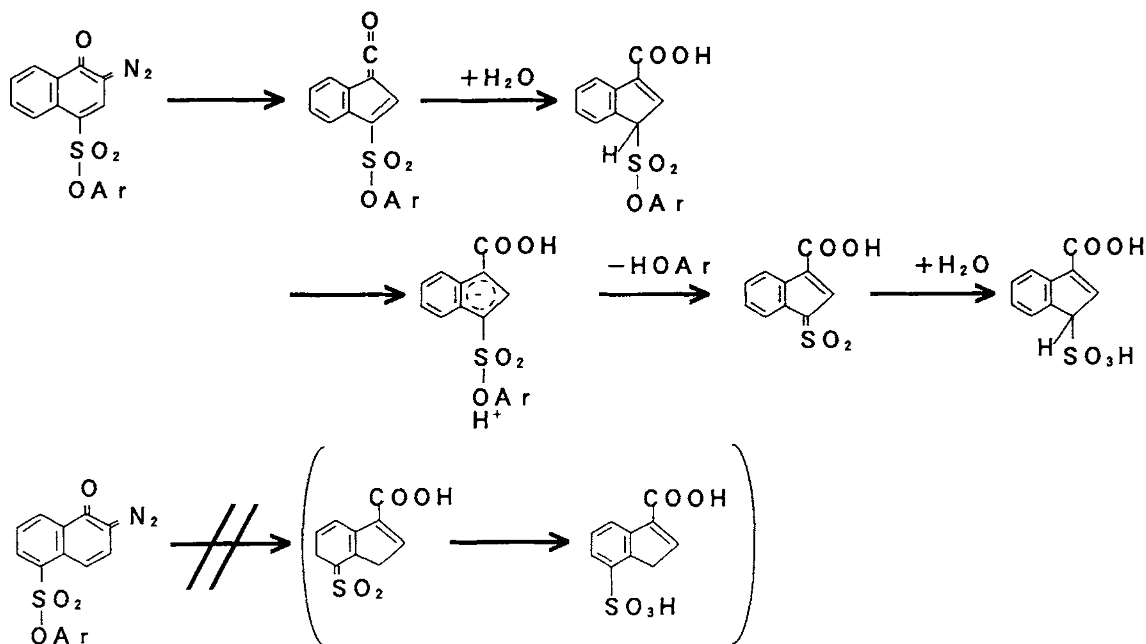

Figure 6 Photolysis mechanism for naphthoquinone diazides proposed by Ref. 7.

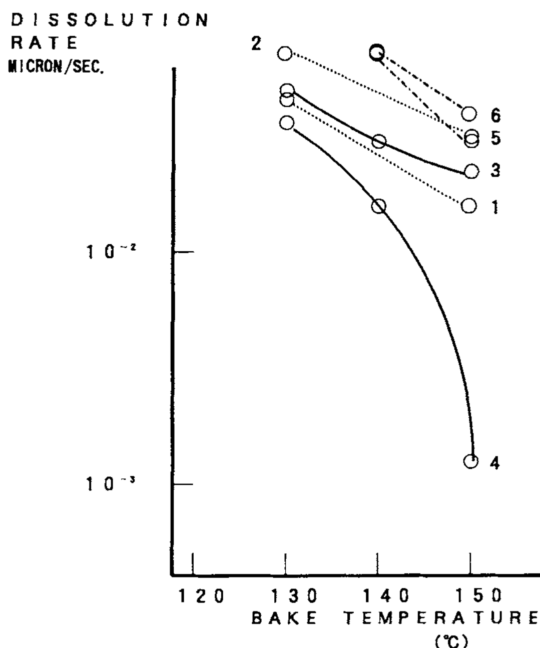

Figure 7 Comparison of dissolution rates for films with and without p-toluene sulfonic acid. (1) NAC 4/PA1 prebake 90°C, 10 min, TMAH, 2.38% aqueous solution. (2) NAC 4/PA1 + p-toluene sulfonic acid 5%, prebake 90°C, 10 min, TMAH, 2.38% aqueous solution. (3) NAC 3/PA1 prebake 90°C, 10 min, TMAH, 2.38% aqueous solution. (4) NAC 3/PA1 + p-toluene sulfonic acid 5%, prebake 90°C, 10 min, TMAH, 2.38% aqueous solution. (5) PA1 only, prebake 90°C, 10 min, TMAH, 2.38% aqueous solution. (6) PA1 only + p-toluene sulfonic acid 5%, prebake 90°C, 10 min, TMAH, 2.38% aqueous solution.

been also suggested by Grunwald and Buhr et al.[7]

2. Imidizations of polyamic acids were not accelerated even if the catalytic amount of p-toluene sulfonic acids were added (line 5 and 6). This means that even if sulfonic acids are photogenerated from the naphthoquinone diazides, the sulfonic acids do not act directly to imidize the polyamic acids and decrease the solubility of the polyamic acids.

3. Decrease in the solubility became remarkable when p-toluene sulfonic acid was added to the mixture of polyamic acids and NAC-3-type naphthoquinone diazides (line 3, 4).

4. The decrease in the solubility was not seen when p-toluene sulfonic acid was added to the mixture of polyamic acids and NAC 4 (line 1, 2).

From these results the following mechanism would be deduced (Fig. 8). In the exposed area NAC-1- and NAC-3-type naphthoquinone diazides photodecompose to form sulfonic acids partially. In the course of high-temperature postexposure bake, the polyamic acids and remaining naphthoquinone diazides crosslink, catalyzed by photogenerated sulfonic acids. In the unexposed area there are no sulfonic acids, therefore, the decrease in the solubility is small compared to that in the exposed area.

On the other hand in case of NAC 4, it is not very important whether the sulfonic acids are photogenerated. In the exposed area NAC 4 naphthoquinone diazide photodecomposes to form indene carboxylic acids, which may further decompose to sulfonic acids. What is different from NAC 3 is that the re-

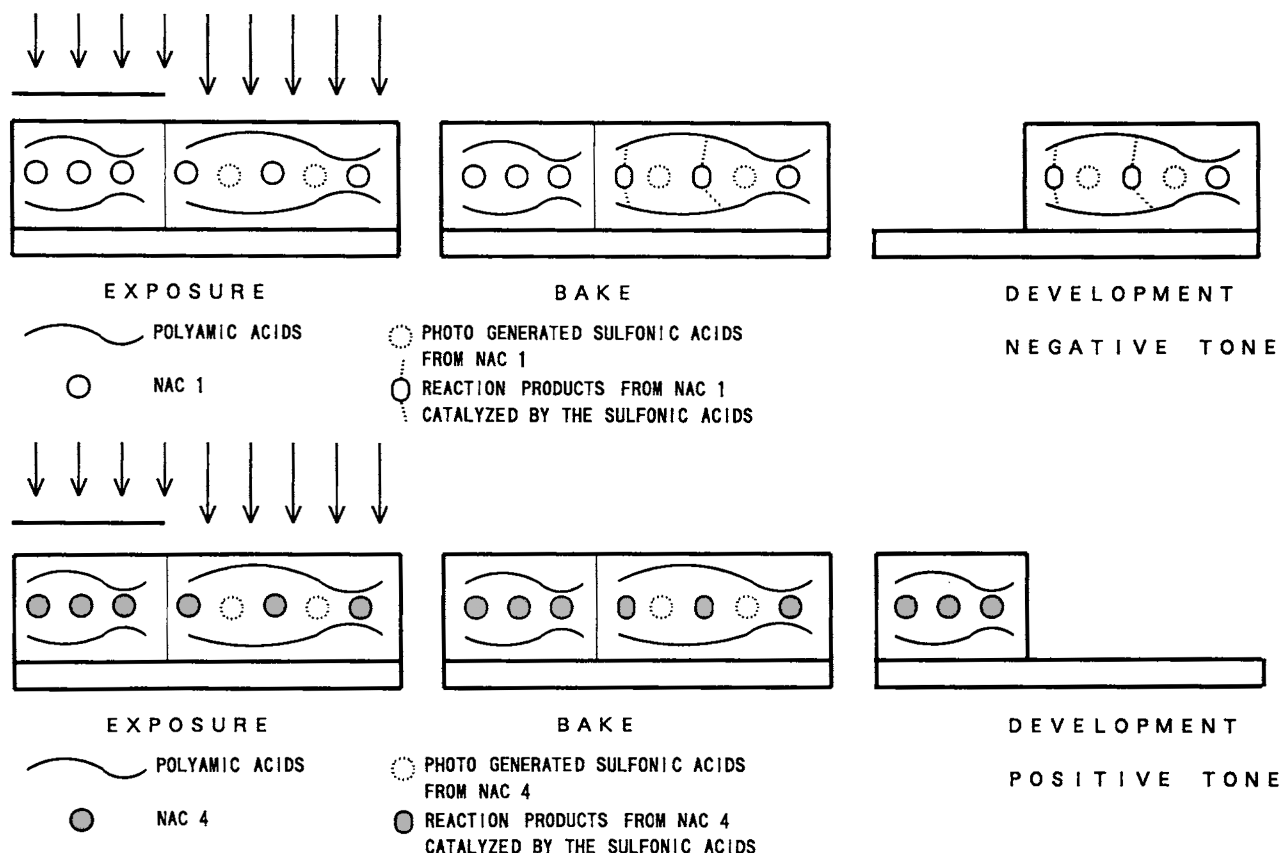

Figure 8 Proposed reaction mechanisms for positive and negative tone resists.

maining naphthoquinone diazides do not react with polyamic acids to cause the decrease in the solubility even if the sulfonic acids are photogenerated. If sulfonic acids are photogenerated, the sulfonic acids may accelerate the decomposition of the remaining naphthoquinone diazides to form indene carboxylic acids that made the exposed area more soluble to basic aqueous solutions. Because in the unexposed area naphthoquinone diazides probably act as dissolution inhibitors to the base-soluble polyamic acids, this resist system acts as positive tone.

How the polyamic acids react with naphthoquinone diazides in the presence of sulfonic acids is still in the dark and under investigation. Anyway, what is important is that the sulfonic acids once photogenerated facilitate the decomposition of the remaining (4)-NAC during postexposure baking.

The resist containing (5)-NAC gave only poor images. This result is also supported by the reports that naphthoquinone diazides never photodecomposed to form sulfonic acids. However, a little attention should be paid to the fact that negative tone patterns were obtained faintly. Probably, in this case, the reaction between photoreacted naphthoquinone diazides and unreacted (remaining) naphthoquinone diazides form lactone rings and azo compounds, which have been suggested by Yamada, and decarboxylation reactions may take place, which makes the exposed areas a little insoluble, compared to the unexposed areas.[8] This is one of the reasons for giving negative tones; however, it seems likely that the mechanism to generate sulfonic acids will be a major reason.

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