# Resist Materials Design: Base-catalyzed Chemical Amplification

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**Abstract:**
The search for advanced resists that can provide the high density of circuits and high throughput required for the new generations of microelectronic devices requires that highly stable chemically amplified materials be developed. In view of the high susceptibility of resists based on photoacid generation to environmental contamination, resulting in lessened performance, a program aiming at the development of chemically amplified resists utilizing photobase generation has been undertaken. In a first approach, the photogenerated amines we developed in the first stage of this project were used as catalysts for the decarboxylation of totally new resist systems containing active carboxylic acid pendant groups. The resists materials could be developed to afford negative tone images through wet development in aqueous base, or positive tone images through dry development using a gas-phase silylation reaction followed by oxygen plasma etching. The first patterning experiments carried out with two new resists utilizing photogenerated base have confirmed the validity of the approach.

**Subject Terms:**
PHOTORESIST, CHEMICAL AMPLIFICATION, PHOTOBASE GENERATOR, IMAGING MATERIAL, MICROLITHOGRAPHY

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Resist Materials Design: Base-catalyzed Chemical Amplification

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ABSTRACT

Many chemically amplified resists that function on the basis of acid catalysis of thermolytic reactions have been described as well as systems that function on the basis of free radical chain reactions. But there have been very few reports on the use of base catalysis of chemical transformations in resist materials. We describe here our initial results on base catalyzed chemically amplified deep-UV photoresists. Photogenerated amines were used as catalysts for the decarboxylation of carboxylic acids. Two approaches to building resists around this chemistry were investigated. 1) Decarboxylation of a low molecular weight carboxylic acid led to base induced dissolution inhibition of a phenolic polymer giving negative tone images. 2) A carboxylic acid polymer was synthesized which also is susceptible towards base catalyzed decarboxylation. Wet development of this resist material gives negative tone images. Site specific gas-phase silylation of the carboxylic acid allows the use of this material in a positive tone dry develop process. A 0.5μm line-space pattern obtained by this dry develop process illustrates the potential of base-catalyzed chemical amplification.

1. INTRODUCTION

Resist materials based on chemical amplification have become increasingly important in the microelectronics industry. Generally these materials are based on the photoinduced liberation of a strong acid which in a subsequent catalytic process leads to chemical changes in the resist film (e.g. unmasking of a dissolution enhancing functionality or crosslinking of the resist material).

Though acid-catalyzed chemically amplified photoresists have proven to be extremely useful in manufacturing, the performance of such systems can be degraded by absorbing airborne basic contaminants. Even weak bases, such as N-methyl pyrrolidone, widely used in microelectronics processing, cause performance degradation of chemically amplified resists. Due to the catalytic nature of the chemically amplified process, even very low concentrations of airborne contaminants have a severe effect on resist performance.

One interesting approach of avoiding the problem of basic airborne contamination is to design a base-catalyzed chemically amplified process. Here a catalytic amount of photogenerated base is used instead of the acidic catalyst to achieve the chemical change in the resist material. This report summarizes our recent efforts in designing such a resist system using deep-UV sensitive photobase generators and base induced decarboxylation of carboxylic acid sensitive polymers.
2. PROGRESS IN THE PHOTOGENERATION OF BASE AND PREVIOUS LITHOGRAPHIC APPLICATIONS OF PHOTOGENERATED BASE

2.1. Photogeneration of Base

Different classes of compounds are known to generate amines when exposed to light. Cobalt(III)ammine complexes (e.g. 1) have been shown to liberate multiple equivalents of amine upon photolysis along with a Lewis acid (Co$^{2+}$) and a radical (Br$^\cdot$). Unfortunately, the inorganic nature of these complexes limits their solubility in organic materials.

$$[\text{Co(NH}_3)_5\text{Br}]^{ll} \xrightarrow{\text{hu}} \text{Co}^{2+} + 5\text{NH}_3 + \text{Br}^\cdot \quad \Phi = 0.01$$

Another approach involves masking an amine with a photolabile protective group. The latter has been designed to give only inert byproducts upon irradiation. Thus, the ($\alpha$-$\alpha$-dimethyl-3,5-dimethoxybenzyloxy)carbonyl group has been used in compounds like 2. Photolysis of 2 gives cyclohexylamine, CO$_2$ and 3,5-dimethoxy-$\alpha$-methylstyrene.

The compounds used for the photo-liberation of amines throughout this work are 2-nitrobenzyl carbamates 3. The products of their photolysis are the amine, CO$_2$ and a nitrosobenzaldehyde. The latter results from the intramolecular redox reaction which follows the photoexcitation of o-nitrobenzylic compounds.

$$\text{R}_3\text{R}_4\text{NO}_2 \xrightarrow{\text{hu}} \text{R}_3\text{R}_4\text{CHO} + \text{CO}_2 + \text{HNR}_1\text{R}_2 \quad \Phi = 0.10 - 0.60$$

The quantum efficiency of this photo-process is influenced by the presence of a second o-nitro-substituent (2,6-dinitrobenzyl carbamates) and by the substitution of the benzylic position. These photo-base generators possess high quantum yields (up to $\Phi = 0.6$) and are readily soluble in common organic solvents.

2.2. Previous Lithographic Applications of Photogenerated Base

Resists based on the crosslinking of an epoxy resin have been described using cobalt(III)ammine complex 1 for the photogeneration of an amine. The products of the photodecomposition of the inorganic complex induce crosslinking of the glycidyl methacrylate / ethyl acrylate copolymer 4. Subsequent development with a mixture of 2-butanone and ethanol gives a negative tone image.
Photogenerated base has been used in another approach which is also based on crosslinking of the resist material. A p-hydroxystyrene / p-acetoxymethylstyrene copolymer 5 was mixed with a thermal acid generator and a photobase generator. This material is crosslinked thermally by the acid generator in the unexposed areas. In the exposed areas the action of the thermally generated acid is suppressed by the photo-liberation of amine. Positive tone images are obtained after development with aqueous base.

Negative tone images were obtained via base catalyzed imidization, to provide photosensitive polyimide materials. Imidization reduces the solubility of the polymeric material such that only the polyamic ester precursor remains soluble in the developer.

The central feature of the Monazoline image reversal process is base catalyzed decarboxylation of a substituted indene carboxylic acid. The latter is formed by photolysis of a diazonaphthoqui

Scheme 1: The Monazoline image reversal process.
none dissolution inhibitor in a phenolic resin based photoresist. Its decarboxylation is induced by imidazole or ammonia and baking the film at \( \approx 100^\circ C \). Subsequent flood exposure converts the remaining diazonaphthoquinone to the indene carboxylic acid rendering those areas soluble in aqueous base which have not been exposed in the first exposure step. A negative tone image is obtained (scheme I).

3. EXPERIMENTAL

Details of the synthesis of compounds 9 and 11 will be published elsewhere. The following resist solutions were used for the imaging experiments:
- dissolution enhancer 9, photo-base generator 10 and poly(p-hydroxy styrene) (71 wt% PHOST, 19 wt% 9 and 10 wt% 10) were dissolved in diglyme (total of 21.4 wt% solids) and spun at 1950 rpm to give a film of 1 \( \mu m \) thickness.
- carboxylic acid polymer 11 (90 wt%) and photo-base generator 10 (10 wt%) were dissolved in diglyme (total of 22 wt% solids), spun at 3000 rpm to give films of 1 \( \mu m \) thickness.

IR measurements were done using an IBM FTIR/32. The kinetic IR-data was collected using a custom made copper heating cell in conjunction with an Omega TC 2011 temperature controller. Contact prints were obtained using a mercury arc exposure tool and a 254 nm bandpass filter. The light intensity was monitored with an OAI 354 exposure monitor. Projection printing was done on a 0.35 NA, IX, UltraStep X-248E step-and-repeat projection system built by Ultratech. Gas phase silylation was carried out using a Monarch technologies universal vacuum processing module and N,N-dimethylamino-trimethysilane (Petrarch systems Inc.) as silylating agent (200 torr, 80°C). Scanning electron micrographs were recorded on an Amray 1850 FE.

4. RESULTS AND DISCUSSION

4.1. Base Catalyzed Decarboxylation Chemistry

Decarboxylation of carboxylic acids may proceed via several mechanisms dependent on the structure of the acid.\(^6\) There exists a subset of carboxylic acids in which the salt of the acid undergoes decarboxylation at a temperature below that of the free acid.\(^7\) In such systems the rate of decarboxylation may be correlated with the stability (\( pK_a \)) of the carbanion formed on decarboxylation (see table 1).\(^8\) Among the bases which have been used to induce the decarboxylation of carboxylic acids are amines. Some examples of decarboxylation reactions involving amines are given in table 2. Photogenerators of amines have been described in section 2.1.

4.2. Design Concepts

Two approaches have been pursued to demonstrate the utility of base catalyzed chemical amplified decarboxylation chemistry in microlithography. As in the Monazoline process, the first uses an
<table>
<thead>
<tr>
<th>acid</th>
<th>$pK_a$</th>
<th>$T$ [°C]</th>
<th>$t_{1/2}$ [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$^-$CO$_2$Na</td>
<td>17.9</td>
<td>-20</td>
<td>400</td>
</tr>
<tr>
<td>CO$_2$Na</td>
<td>22.6</td>
<td>30</td>
<td>7500</td>
</tr>
<tr>
<td>Ph$^-$C=NC=O$_2$Na</td>
<td>28.8</td>
<td>100</td>
<td>3600</td>
</tr>
<tr>
<td>Ph$_3$C=O$_2$Na</td>
<td>30.7</td>
<td>61</td>
<td>3300</td>
</tr>
<tr>
<td>Ph$_2$CH=CO$_2$Na</td>
<td>32.1</td>
<td>149</td>
<td>35000</td>
</tr>
</tbody>
</table>

*Table 1:* Correlation of decarboxylation rate with basicity of the carbanion formed.$^{17}$

<table>
<thead>
<tr>
<th>acid</th>
<th>$pK_a$</th>
<th>thermal decarboxylation</th>
<th>amine catalyzed decarboxylation</th>
<th>lit.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$^-$C=CC=O$_2$H $^6$</td>
<td>$\approx$22</td>
<td>125°C, $^1$BuOH, 110h, 90%</td>
<td>NH$_4^+$ carboxylate salt (25 mol%), 25°C, $^1$BuOH, 39h, 89%</td>
<td>19</td>
</tr>
<tr>
<td>PhSO$_2$C=O$_2$H $^7$</td>
<td>$\approx$32</td>
<td>290-320°C, neat, 96%</td>
<td>Et$_3$N (10 mol%), 175-195°C, 95%</td>
<td>20</td>
</tr>
<tr>
<td>Ph$^-$C=CO$_2$H $^8$</td>
<td>$\approx$23</td>
<td>$&gt;$140°C, DMSO, 100%</td>
<td>Et$_3$N (1eq.), DMSO, 80°C, 10min, 95%</td>
<td>21</td>
</tr>
</tbody>
</table>

*Table 2:* Specific examples of decarboxylation involving amine type bases.
indene carboxylic acid derivative as a base sensitive dissolution enhancer in a phenolic resin matrix. In the exposed areas, the photo-generated base catalyzes the decarboxylation of the enhancer converting it into a dissolution rate inhibitor (negative tone dissolution inhibitor).

The second approach employs a polymer with an appropriately substituted pendant carboxylic acid as the matrix polymer. In the exposed areas the amine liberated by the photo-base generator catalyzes the decarboxylation and causes a polarity change. This polarity change can be used to produce negative tone images by wet development. Furthermore, dry development is possible by selectively silylating the carboxylic acid moieties remaining in the unexposed areas. Subsequent plasma etching (O₂-RIE) gives positive tone images.

4.3. Negative tone dissolution inhibition

The dissolution enhancer used is derived from bisphenol A. The latter is transformed to the bis(diazo naphthoquinone sulfonester) which is photochemically converted to the indene carboxylic acid derivative 9 (scheme 2). Compound 9 is readily soluble in aqueous base while its decarboxylation product is not.

**Scheme 2: Synthesis of the bis(indene carboxylic acid) dissolution rate enhancer 9.**

Poly(p-hydroxy styrene) was used as a base resin to demonstrate the usefulness of the dissolution enhancer 9. Carbamate 10, which generates 1,6-hexane diamine upon irradiation with deep UV light was used for photo-base generation. Its action is based on the o-nitro
benzy1 chemistry previously described. The post-exposure bake leads to base-induced
decarboxylation of the dissolution enhancer 9 in the exposed areas which renders these areas less
soluble in the aqueous base developer solution. A negative tone image is obtained (figure 1a) dem-
onstrating the dissolution inhibiting effect of the product of decarboxylation of 9. The sensitivity
curve for this resist formulation is given in figure 1b.

Figure 1: a) Scanning electron micrograph of the negative tone image obtained with the dissolution
enhancer 9 in poly(p-hydroxy styrene) using 10 for photo-base generation (prebaked 2 min at 110°C
and exposed to 175 mJ/cm² at 254 nm (contact print); postbaked at 140°C for 15 min and developed
in 14% AZ400K (Hoechst-Celanese) for 2 min). b) Sensitivity curve for poly(p-hydroxy styrene) us-
ing the bis-indene carboxylic acid dissolution enhancer 9 and photobase generator 10.

4.4. Carboxylic acid polymer

As can be seen from table 2, 2-cyano-2-phenyl butanoic acid 6 has
a reasonable thermal stability but at the same time is very sensitive
towards amines. Alkyl substitution at the phenyl moiety, which is
necessary to build a styrenic polymer from this compound, should not
have a large effect on the rate of decarboxylation. Hence, this structure
was chosen for building a styrenic monomer which upon
polymerization should give a base sensitive carboxylic acid polymer.
The synthetic sequence leading to polymer 11 is outlined in scheme 3.

Scheme 4 summarizes the chemistry which occurs during the different lithographic steps using
poly(2-cyano-2-(4-vinylphenyl))butanoic acid 11 and the photo-base generator 10. Wet devlop-
ment (4.4.(a)) includes steps 1 and 2 while dry development (4.4.(b)) includes steps 1 through 4.
**Scheme 3:** Outline of the synthesis of poly(2-cyano-2-(4-vinylphenyl)butanoic acid II.

1. Expose
   ![Scheme 3 Expose](image)

2. Bake
   ![Scheme 3 Bake](image)

3. Silylate
   ![Scheme 3 Silylate](image)

4. O₂ Etch
   ![Scheme 3 O₂ Etch](image)

**Scheme 4:** Lithographic scheme for the use of the carboxylic acid polymer II in a base catalyzed chemically amplified process: (a) photo-base generation by deep-UV exposure; (b) post exposure bake leads to decarboxylation of the polymer in the exposed areas. At this point wet development generates a negative tone image; (c) gas-phase silylation gives silicon incorporation in the unexposed areas; (d) O₂ reactive ion etching produces a SiO₂ etch barrier and gives a positive tone image in a dry develop process.

4.4. (a) Carboxylic acid polymer: wet development giving negative tone images

Figure 2 shows the influence of photogenerated base on the decarboxylation rate of the carboxylic acid polymer II. Polymer II is not thermally stable at 120°C and undergoes very slow decarboxylation in the absence of photogenerated base. However where the resist film is exposed with 50 ml/cm² (254 nm) the photogenerated base induces complete decarboxylation after approximately 25 min. Figure 2 shows that after 25 min of heating the unexposed film still retains 85% of
the carboxyl moieties. This chemical contrast translates into a solubility difference in weak aqueous bases to allow for wet development. Figure 3a shows a relief image generated by this wet develop process along with the corresponding contrast curve. A contrast curve for the wet develop process is given in figure 3b.

![Contrast Curve](image)

**Figure 3a**: Relief image generated by the wet develop process along with the corresponding contrast curve.

**Figure 2**: IR-study on the extent of decarboxylation induced by the photogeneration of amine in photoresist films of carboxylic acid polymer 11 and PBG 10 (resist formulation in experimental section). Wafer was placed in a heated copper block (120°C) immediately after exposure and the intensity of the carbonyl band at 1753 cm\(^{-1}\) was monitored with time.

**Figure 3**: a) Scanning electron micrograph of a negative tone image obtained from carboxylic acid polymer 11 with photo-base generator 10. (1 µm resist prebaked at 110°C for 2 min, exposed to 33 mJ/cm\(^2\) at 254 nm (contact print), postbaked at 125°C for 14 min, developed by soaking in water for 3 min and treating with an aqueous solution of triethanolamine (2.3 g/l) for 12 sec.) b) Contrast curve for the wet develop process.
4.4. (b) Carboxylic acid polymer: dry development to yield positive tone image

Silylation of carboxylic acid groups has previously been used to generate dry develop resists. As seen from scheme 4 resist formulations of the carboxylic acid polymer 11 and photo-base generator 10 are also suitable for dry development. The carboxylic acid moieties left in the unexposed areas of the film can be transformed into the corresponding silyl esters by treatment with a suitable silylating agent. Subsequent O₂-reactive ion etching (O₂-RIE) transforms the silyl esters into silicon dioxide which acts as an etch barrier. The exposed area (which has been decarboxylated) is etched to the substrate leaving a positive tone image.

Figure 4 shows that gas-phase silylation of a 1 μm thick film of polymer 11 with dimethylamino trimethyl silane (Me₂NSiMe₃) gives the trimethyl silyl ester quantitatively. The bands at 1253 cm⁻¹ and 845 cm⁻¹ are due to the CH₃-Si vibration (figure 4 b). The silyl ester was found to be stable for at least 19 h when the sample was kept under dry nitrogen. However, exposure of the film to air for less than one hour leads to a rapid decomposition of the silyl ester (figure 4 c). As shown by figure 4 c the O-H-band of the acid as well as the second carbonyl band reappear while the bands due to the Si-CH₃ vibration decrease but do not disappear completely. Even exposure of the film to vacuum does not lead to the disappearance of these silicon-carbon bands. The IR results show that the silyl ester is not stable in a typical laboratory atmosphere, but even after decomposition of the silyl ester a non-volatile silicon species derived from hydrolysis remains in the film.

Preliminary results obtained from Rutherford backscattering indicate that silicon is incorporated into the unexposed areas (which contain carboxylic acid) with a selectivity of at least 10:1. In agreement with the results obtained from IR, the RBS data also indicates that there is a considerable amount of silicon retained in the unexposed area after hydrolysis of the silyl ester. The silicon content of films exposed to air for 1 hour, with respect to films transferred into vacuum immediately after gas phase silylation, is greater than 80 %. Finally it was found that silylation of the carboxylic acid films proceeds easily throughout the whole thickness of the film.

Figure 5 demonstrates the feasibility of this positive tone chemically amplified dry development scheme. This figure shows a 0.5 μm line-space pattern which was printed by projection lithography.

5. SUMMARY

The work presented here demonstrates the feasibility of a chemically amplified lithographic process which makes use of a base as the catalytic species. A bis(indene carboxylic acid), which is transformed into a dissolution inhibitor upon decarboxylation, as well as a carboxylic acid polymer have been shown to be imageable in the presence of a photogenerated amine. Wet development gives negative tone images. Dry development using the carboxylic acid polymer has been shown to give positive tone images with 0.5 μm resolution.

6. ACKNOWLEDGEMENT

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Figure 4: Monitoring the silylation of the resist formulation of polymer 11 by IR spectroscopy: a) film of the resist formulation after prebake; b) film after gas-phase silylation (200 torr Me₂NSiMe₃ at 80°C for 300 sec); c) silylated film after exposure to air for 50 min.

Figure 5: Positive tone image obtained with polymer 11 in a dry develop process (resist formulation see experimental section, post apply bake 2 min at 110°C, 75 mJ/cm² projection print, PEB 12 min at 125°C, gas-phase silylation with Me₂NSiMe₃ for 75 sec, O₂-RIE (0.5 kW, 6 torr, 10 sccm, 1.3 min)).
7. REFERENCES


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