

# Effect of a Deprotection Group on Acrylic Photoresist

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**Abstract:** This study is synthesized and investigated polyacrylate single layer resist (SLR) using *t*-amyl alcohol as a deprotection group. The *t*-amyl group of the copolymer resist and dissolution inhibitor (DI) in this chemically amplified photoresist (CAMP) was deprotected by a light stimulated photoacid generator (PAG) upon post exposure bake (PEB). The polarity change of the system from a hydrophobic to a hydrophilic property made the exposed region soluble in the base developer. KrF and ArF excimer lasers were used to test resists using two components (PR and PAG) and three components (PR, DI and PAG) in the resists. This study also investigated the different effects of exposure dose, developer concentration, and content between *t*-amyl and *t*-butyl methacrylate on lithographic performance of resists.

Keywords: *t*-Amyl methacrylate, *t*-Amyl cholate, Lithography, CAMP.

## Introduction

With the increased complexity and enhanced reliability of advanced integrated circuits has come increased need to manufacture a thinner critical dimension (CD), the light source required has moved from visible light (g-line, i-line) toward KrF (248 nm) and ArF (193 nm) for improved delicacy. However, the Novolac and PHS resists which were conventionally used in I-line and KrF (248 nm) respectively, cannot be used as ArF (193 nm) photoresists owing to their strong phenolic absorption in 193 nm wavelength. A resist of a non-benzene structure, such as methacrylate or cycloolefin [3], has been made using an ArF excimer laser and is claimed to enable the manufacture of 1G-bit DRAM with 0.13  $\mu\text{m}$  lithographic performance. Technically, though several types of photoresist, such as bilayer and thin film image [2], have been investigated worldwide, single layer resist (SLR) has the greatest potential for commercial use because of its processing simplicity, though its etch resistance and stability need to be improved in the future. Research on SLR methacrylate resist has mainly focused on improving etch resistance by incorporating the high C/H alicyclic group [7], such as isobornyl,

adamantyl, or the tricyclodecyl group, and on developing a better latitude by changing to a protective group, such as tetrahydrofuranyl, ethoxyethyl, or the Mevalonic lactone group [6]. However, there are questions remaining about using these strategies. Therefore, insight into 193 nm photoresist is crucially important.

In early 1992, IBM used *t*-butyl methacrylate copolymer as a prototype chemically amplified photoresist (CAMP) in 193 nm lithography. This copolymer changes the polarity of the exposed area, which will then dissolve in the developer and exhibit a positive tone pattern transfer. PAG within resin uses much less energy than a traditional photo active compound (PAC), and can magnify the energy by repeatedly catalyzing the deprotecting reaction of the photoresist. The sensitivity of developer concentration and instability of resin require another additives, such as DI or photobase, to make the resist suitable for application. This study focuses on *t*-amyl methacrylate, which has similar structure and deprotection behavior as *t*-butyl methacrylate. However, the lithographic performance of *t*-amyl methacrylate has not been studied. A dissolution inhibitor (*t*-amyl cholate) with the same protecting group was also synthesized and added to improve

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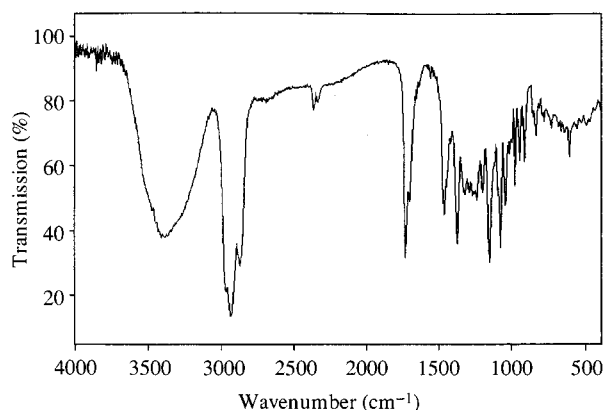


Figure 1. FTIR spectrum of *t*-amyl cholate.

the performance of the resist. This work aims to investigate systematically the performance of the copolymer of *t*-amyl methacrylate with MAA and MMA.

## Experimental

### 1. Materials

*t*-Amyl alcohol (30 g) and triethylamine (34.5 g) were mixed in tetrahydrofuran (THF) solution (400 mL). Drops of methacrylic chloride (36 g) were added to the solution at 0 °C and the solution was left to react for three hours. After filtration, rinsing with sodium hydroxide and water, and drying with MgSO<sub>4</sub>, the *t*-amyl methacrylate [1] (*t*AMA) was purified at 60 °C by vacuum distillation. The yield of the process, 70%. *t*-amyl methacrylate, was identified by FTIR with absorption peaks at 1722 cm<sup>-1</sup> (C=O), 1637 cm<sup>-1</sup> (C=C), and 1160 cm<sup>-1</sup> (C-O-C). <sup>1</sup>H NMR were further measured with peaks at 0.83 ppm [3H, t, -CH<sub>2</sub>CH<sub>3</sub>], 1.39 ppm [6H, s, -C(CH<sub>3</sub>)<sub>2</sub>], 1.68~1.79 ppm [2H, q, -CCH<sub>2</sub>CH<sub>3</sub>], 1.83 ppm [3H, s, -CH<sub>2</sub>CCH<sub>3</sub>], and 5.38~5.94 ppm [2H, d, -CH<sub>2</sub>CCH<sub>3</sub>].

*t*-Amyl cholate was synthesized according to the method of Bonar-Law et al. [9]. Hydroxy groups of cholic acid were first protected by reaction with trifluoroacetic anhydride and, after the *t*-amyl attached to the acid, were deprotected by ammonium hydroxide. Further purification consisted of extraction with ether, drying, and re-crystallization twice in acetonitrile and hexane. The yield, 65%. *t*-amyl cholate, was identified by FTIR with absorption peaks at 3385 cm<sup>-1</sup> (OH), 1730 cm<sup>-1</sup> (C=O), and 1153 cm<sup>-1</sup> (C-O-C), as presented in Figure 1. <sup>1</sup>H NMR were measured with peaks at 0.68 ppm [3H, s, 18-Me], 0.96~0.99 ppm [3H, d, 21-Me], 1.41 ppm [6H, s, -C(CH<sub>3</sub>)<sub>2</sub>], 3.36~3.58 ppm [1H, m,

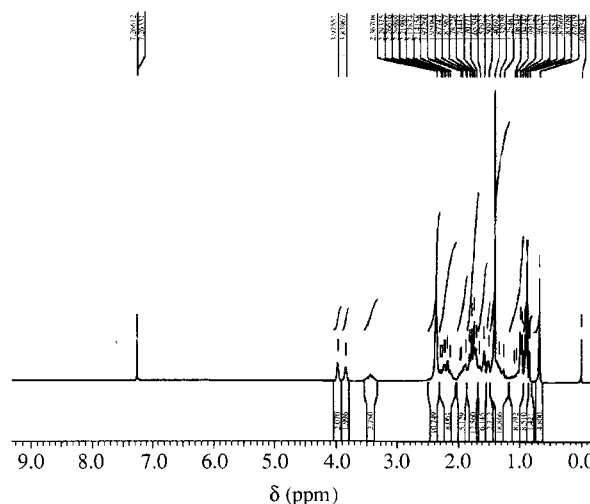


Figure 2. <sup>1</sup>H NMR spectrum of *t*-amyl cholate.

Table I. Composition and properties of copolymer.

MAA/MMA/ <i>t</i> AMA	AIBN (wt%)	$\bar{M}_n$	$\bar{M}_w$	T <sub>g</sub> (°C)
(a) 0.2/0.5/0.3	0.5	14800	58700	141
(b) 0.2/0.5/0.3	2.0	4700	11000	136
(c) 0.2/0.4/0.4	0.5	15700	58300	138
(d) 0.1/0.5/0.4	0.5	14300	55100	121

3-H], 3.84 ppm [1H, m, 7-H], and 3.98 ppm [1H, m, 12-H], as displayed in Figure 2. The melting points were measured by DSC at 147.4 °C and elemental analyses were measured with C, 72.94%; H, 10.59% (calculated: C, 72.76%; H, 10.53%).

PMMA copolymers of different compositions were prepared by adding an appropriate equivalent amount of monomer (MAA, *t*AMA, MMA) in dry THF, with AIBN as initiator (Table I). Reaction took place at 65 °C under a nitrogen atmosphere over 24 hours. After reaction, the polymers were precipitated twice in hexane and were then dried in a vacuum.

### 2. Measurement

Analyses of <sup>1</sup>H NMR spectra were carried out on a Bruker DMX-500SB using CDCl<sub>3</sub> as solvent. FTIR spectra were obtained using a BIO-RAD FTS-40. Thermal properties were assessed on Perkin-Elmer DSC-7 and TGA-7. Gel permeation chromatography (GPC) was performed on a SHOWA Shodex RI-71 using THF as solvent. Hitachi S-800 SEM was used to investigate the lithographic performance of the resist.

### 3. Lithographic evaluation

Acrylate copolymer, DI, and 1~5 wt% PAG

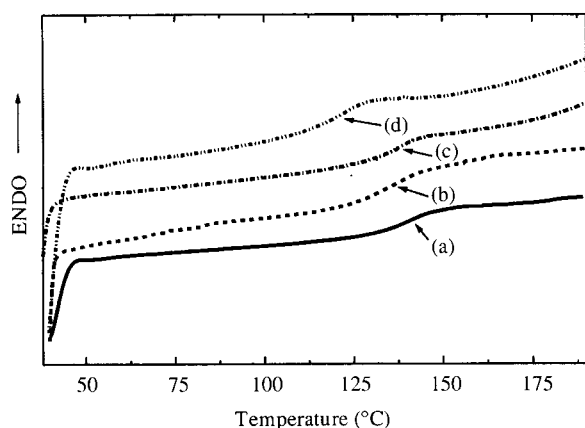


Figure 3.  $T_g$  of copolymer (a)–(d) measured by DSC.

(triarylsulfonium hexafluoro-antimonate) were dissolved in 2-(1-methoxy)propyl acetate (PGMEA) and were filtered to 0.2  $\mu\text{m}$  using a Teflon filter. The DI content was calculated as  $\text{DI}/(\text{DI}+\text{polymer}) \times 100\%$ . Wafers used in the experiment were cut to about 1 cm  $\times$  1 cm, washed, and then primed with hexamethyldisilazane (HMDS) for better adhesion properties. Resists were spun coated on the wafers and then pre-baked at 100  $^\circ\text{C}$  for 1 minute. Thickness was controlled by adjusting the solid concentration (about 1.8 g solid/10 g PGMEA for 1  $\mu\text{m}$  thickness). Samples were exposed to lambda Physik KrF and ArF excimer lasers through a 1  $\mu\text{m}$  line and space (L/S) contact mask, and were then subjected to a post exposure bake (PEB) at 120  $^\circ\text{C}$  for 1 minute. Resists were developed on different concentrations of TMAH and were then rinsed in water for 10 seconds.

## Results and Discussion

### 1. Characterization of photoresist

Four types of copolymer were manufactured for comparison, as displayed in Table I. Molecular weight measured by GPC indicated a polydispersity index from 2 to 4 for free radical polymerization. The amount of initiator that would influence the molecular weight of copolymer was about 55,000–60,000 with 0.5 wt% azobisisobutyronitrile (AIBN) and about 11000 with 2 wt% AIBN. The DSC of copolymer (a)–(d) were measured as displayed in Figure 3. Single  $T_g$  was observed, indicating that the resultant polymers are random copolymers. The  $T_g$ s of the copolymers range between 125 and 142  $^\circ\text{C}$ . This indicates that less MAA in the copolymer composition would result in a lower  $T_g$ , which follows the mixing rule. The TGA was conducted for

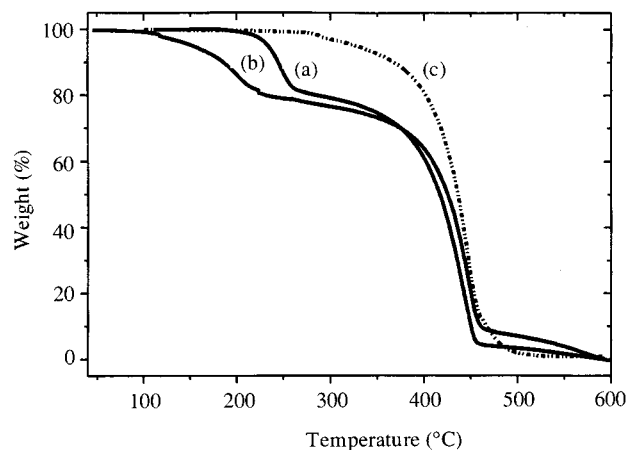


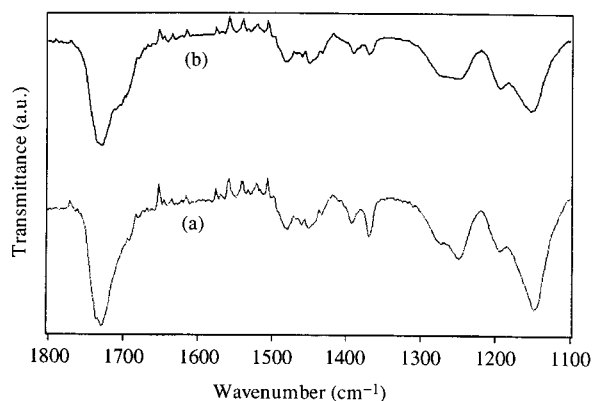
Figure 4. Thermogravimetry analysis of (a) unexposed resin, (b) resin exposed with excess KrF excimer laser and (c) PMMA/PMAA copolymer.

copolymer (a) and the result is presented in Figure 4(a). Two stages of degradation are observed. The first stage of degradation, starting at about 200  $^\circ\text{C}$  and with a 20 % weight loss of copolymer, reveals the theoretical loss of the *t*-amyl group in the copolymer, which has been observed in poly(*t*-amyl methacrylate) [1].

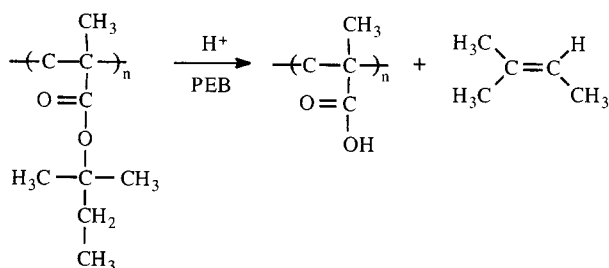
### 2. Characteristics of photoresist

Four types of photoresist (a)–(d) were tested in this study. Type (b) was easily stripped off the wafer during development. This effect is attributed to the dissolution of the unexposed area due to the lower molecular weight of the resist. Types (c) and (d) are insensitive to the developer. Evaluating the role of MAA in the resist demonstrates that the higher MAA fraction in type (a), compared to the fractions in types (c) and (d), produces better adhesion and more sensitivity to the developer. This result resembles the observations of previous investigations [6-16]. However, type (a) had better lithographic performance in this study and therefore these investigations were based on this resist.

The TGA was performed for the exposed and unexposed resist as illustrated in Figure 4. Two-stages of weight loss were observed, both in unexposed (a) and exposed resist (b). The first weight loss stage can be attributed to losing the deprotected *t*-amyl group in the resist. The protons released by PAG in the exposed resist accelerated the deprotection of photoresist, as described in the literature [1,4], and, therefore, the *t*-amyl group broke and evaporated from the exposed resist at a lower temperature, about 100  $^\circ\text{C}$  less than that of the unexposed resist. The onset of the deprotection reaction in this *t*-amyl resist is found to be slightly higher than that of the *t*-butyl resist. This may be attrib-

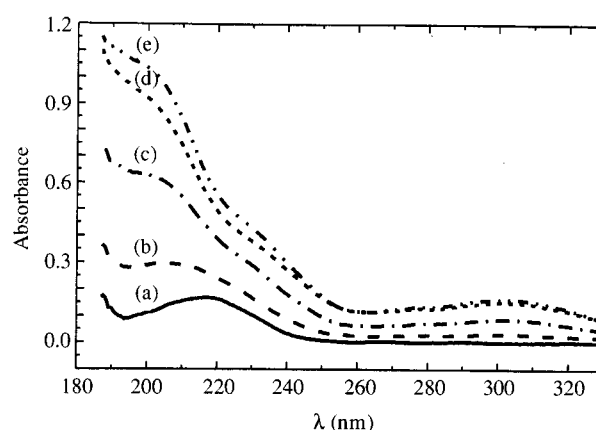


**Figure 5.** FTIR spectra of photoresist (a) before exposure and (b) after exposure to deep UV (248 nm).



**Scheme 1.** Acid catalyzed deprotection of *t*-amyl methacrylate.

uted to the higher boiling point of *t*-amylene (38 °C) compared to that of 2-methyl propene (-6.6 °C), so that higher energy is required to cause the deprotection reaction. Weight loss after the first stage was nearly the same for both unexposed (a) and exposed (b) resists at around 20 wt% of the theoretical value for losing the *t*-amyl group in the resin. The weight loss for the second stage (after heating to 300 °C) of both unexposed (a) and exposed (b) resists coincides with the weight loss of the MAA/MMA copolymer, which further confirms that the weight loss in the first stage was due to the deprotection of the *t*-Amlyl group in the photoresist. The FTIR analysis for the photoresist in Figure 5 shows the broadening of C=O around 1700 cm<sup>-1</sup> and the blue shift of C-O around 1150 cm<sup>-1</sup>. This further indicates the deprotection of the *t*-Amlyl group and the formation of acid and *t*-Amlylene, as illustrated in Scheme 1. The TGA thermograms of photoresist in Figure 4 also provided information for finding the range of the PEB temperature. The PEB temperature should be controlled to be between 100 °C and 200 °C, where only protonic acid released by PAG can catalyze the deprotection reaction. Since the thickness of photoresist spun-coated on wafers was only about 1 μm, the temperature difference in the resist film can be ignored. The PEB tempera-



**Figure 6.** UV spectrum of photoresist containing (a) 0% PAG, (b) 1% PAG, (c) 3% PAG, (d) 5% PAG and 40% DI, and (e) 5% PAG. Film thickness is 1 μm.

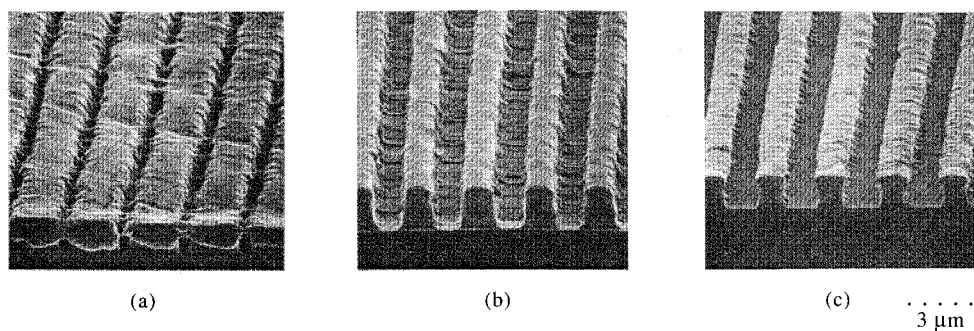
ture tests were performed at 120 °C on a hot plate for 1 minute, this proved to be a suitable process for the photoresists.

In order to adjust for adequate transmittance of UV light, photoresists containing different amounts of PAG and DI were tested for their UV absorption as presented in Figure 6. Without PAG, the absorption of the photoresist is small, about 0.1 μm<sup>-1</sup> at 193 nm wavelength, confirming its usefulness in deep UV. However, as the PAG content increases in the resist, the absorption increases considerably, to about 0.65 μm<sup>-1</sup>. Figure 6 also demonstrates that the introduction of 40% DI in the resist varies the absorption only slightly, illustrating that the addition of DI would not significantly change the light absorption strength in the photoresist.

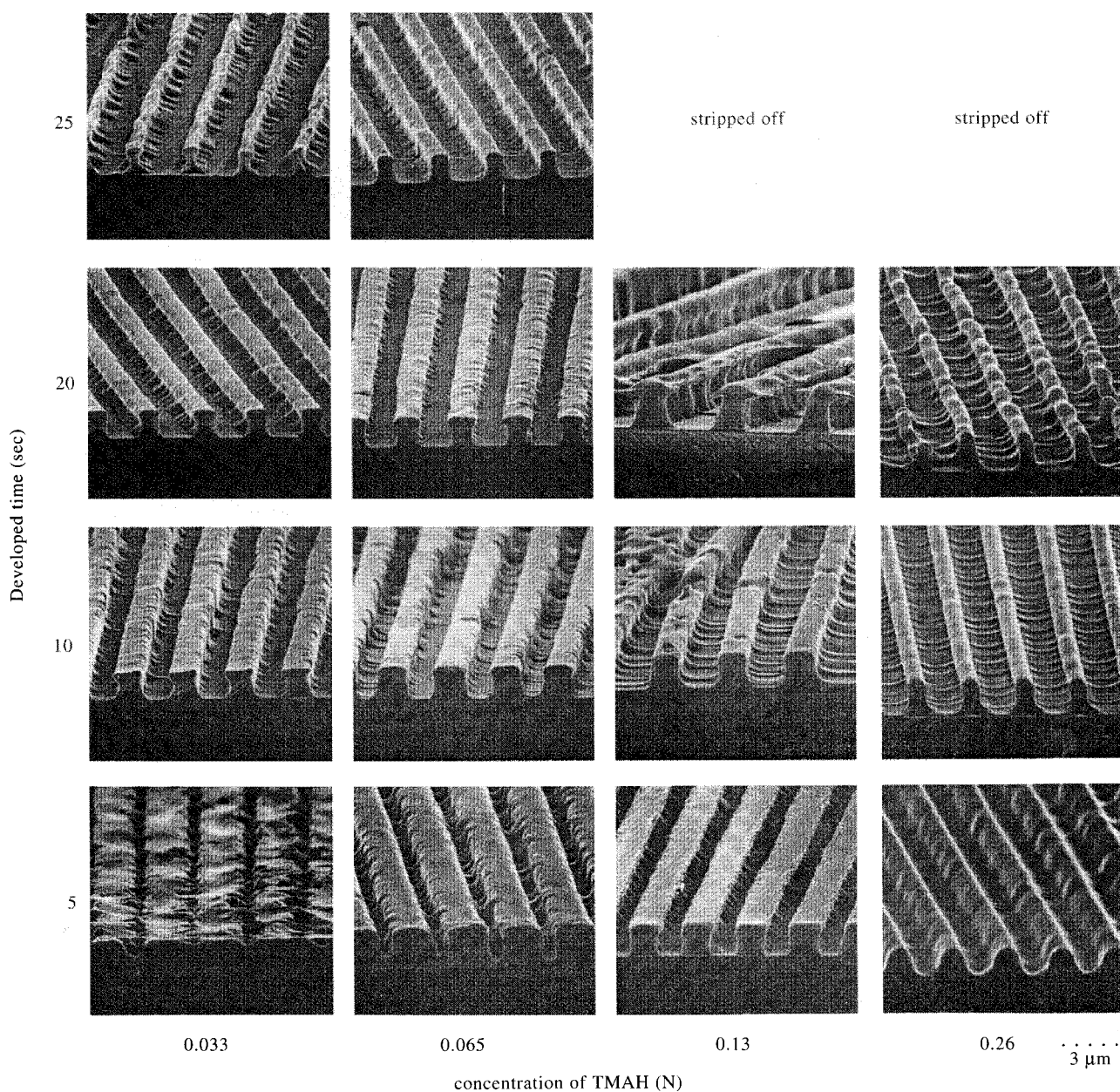
The acrylate photoresist was first tested at a 248 nm wavelength source with various strengths, as displayed in Figure 7. No observable patterns were found below the dose of 15 mJ/cm<sup>2</sup>, so such doses are not included in the figure. When the applied dose was increased to 25 mJ/cm<sup>2</sup>, the pattern became clearer, and none of the exposed zone was left on the surface of the wafer after development. Therefore, in this study, the discussion of the effect of developer on lithographic performance is based on a dose of 25 mJ/cm<sup>2</sup>.

### 3. Lithographic performance

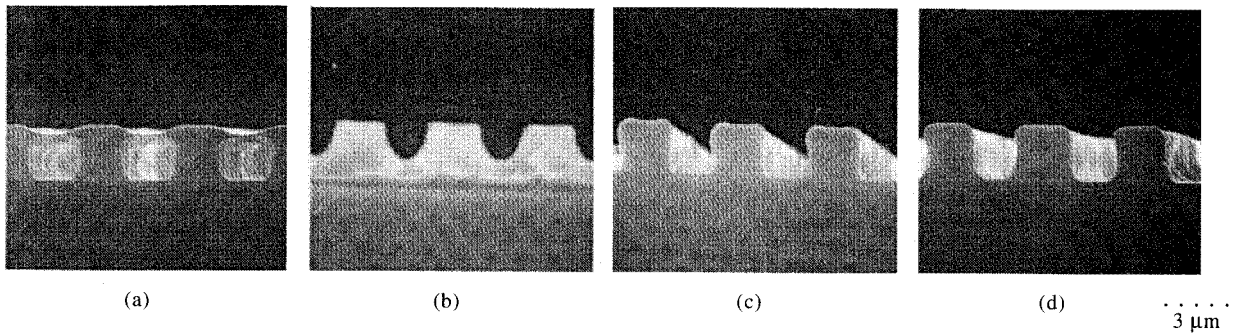
Patterns of photoresist (a) developed under different concentrations of developer and for different times are displayed in Figure 8. With conventional 0.26 N TMAH, which is usually applied for novolac and PHS photoresists, rounding and then thinning of the pattern (1 μm pitch width) are obvious in the right-hand column of Figure 8. This may be attributed to the unexposed resist dissolving in a highly



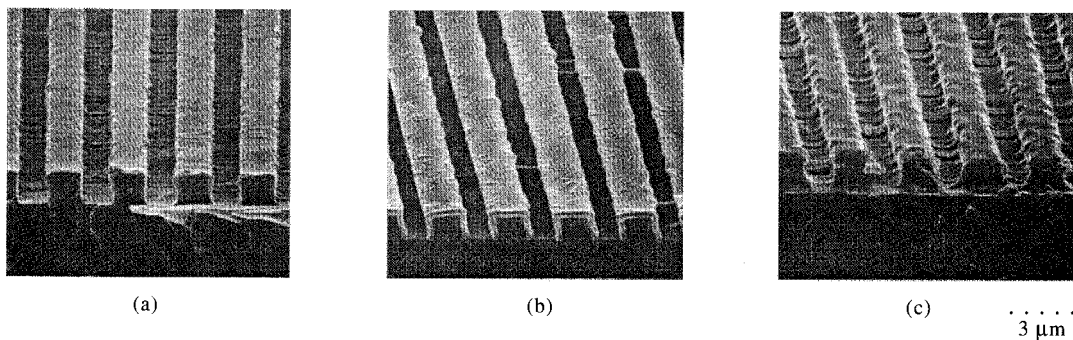
**Figure 7.** Acrylate photoresist exposed to KrF 248 nm light under 1 µm L/S mask with different doses (a) 15 mJ/cm<sup>2</sup>, (b) 20 mJ/cm<sup>2</sup>, and (c) 25 mJ/cm<sup>2</sup>, and developed with 0.065N TMAH for 20 seconds and rinsed for 10 seconds.



**Figure 8.** Photoresist exposed with 25 mJ/cm<sup>2</sup> under 1 µm L/S and developed at different times with various concentrations of TMAH.



**Figure 9.** Lithographic performance of resists (a) amine contamination, (b) resist exposed by 193 nm source with 25 mJ/cm<sup>2</sup>, and (c) and (d) side-view of resist with and without addition of dissolution inhibitor.



**Figure 10.** 1 μm L/S performance of resist containing 10% DI (a) developed by 0.13-0.033N TMAH, hot bake 10 minutes, (b) developed by 0.13-0.033N TMAH, post bake 1 minute, and (c) developed by 0.26N TMAH.

concentrated TMAH developer, so that the surface of the unexposed resist that came into contact with the developer would be dissolved by the TMAH solution. Resists were therefore stripped off the wafers in just about 25 seconds using 0.26 N and 0.13 N TMAH developers. The unsuitability of using concentrated TMAH was the same as its unsuitability for use in other PMMA resists [5], but the *t*-amyl resist was more sensitive to the developing condition than the *t*-butyl resist was. However, diluted TMAH developer did not dissolve the unexposed part as much and the photoresist stuck to the wafer for a longer time. Experimental results show that the photoresist developed by 0.065 N TMAH developer for 10-20 seconds exhibited the optimum performance. Our observations demonstrate that the window for suitable pattern transference is very narrow. The pattern was generated and then disappeared within a short period. The generated pattern distorted within a few seconds of processing.

A few other patterns, under various conditions, are also displayed in Figure 9. The T-topping shape, resulted from amine contamination (Figure 9(a)), was observed after a long post bake delay (PBD). This contamination can be eliminated with careful

processing. The photoresists in Figure 9(b) were exposed using an ArF excimer laser with the same dose of 25 mJ/cm<sup>2</sup> as the KrF excimer laser. The bottom of the exposed region in the pattern was not adequately clear because some resist still remained. This again demonstrates that to supply enough light to reach the bottom of the film, the absorption of the photoresist must be carefully controlled by either adding an appropriate amount of PAG or by using a greater dose of applied light. Figures 9(c) and 9(d) compares the resists with and without the addition of DI. With only 10% of DI, the contrast of exposed and unexposed areas was significantly enhanced.

Different amounts of DI were added to the photoresist (a) to investigate the performance. 10% DI content in the resist was proved to be the best for the developing process. The performance of the resist containing 10% DI is presented in Figure 10. The desired pattern was developed using a 0.13 N, 0.065 N, or 0.033 N TMAH solution from 5 to 40 seconds. It was surprising to find that adding DI can enhance the pattern contrast and widening the processing window so significantly. This enhancement is slightly different from the result of the IBM

version 1.5 resist [15], where *t*-butyl cholate (TB-1) did not work well in the MMA-TBMA-MAA terpolymer resist. This is attributed to the addition of DI increasing the dissolving rate of the exposed area due to the small molecular weight of DI. Thus, the deprotected DI dissolves more quickly in the developer and, at the same time, decreases the dissolving rate of the unexposed area by lowering the acid content in the resist. The longer carbon branch in *t*-amyl cholate-based resists may have higher hydrophobicity and thus 10% of *t*-amyl cholate enhances the contrast of patterns. Figure 10(b) demonstrates that the swelling pattern was much more significant when the resist contained DI. Three hydroxy groups of *t*-amyl cholate could easily absorb water during the developing process. In the experiment, a longer time for post bake was needed to remove the absorbed water in the pattern. Adjusting the dissolving rate of the resist by adding DI in the system may depress the sensitivity of the developer and improve the developing process.

## Conclusion

Our result show that *t*-amyl methacrylate has a similar lithographic performance and similar chemical properties as *t*-butyl methacrylate. Embedded PAG releases protons upon exposure and has proved to accelerate the deprotection reaction of the *t*-amyl group about 100 °C. The polarity change makes the exposed portion of the resist dissolvable in developer. However, the sensitivity of the developer to *t*-amyl methacrylate is less predictable than that of *t*-butyl methacrylate. This sensitivity to the developing condition can be modified with incorporating DI. It takes 10~20 seconds to achieve a 1 μm L/S pattern using 0.065 N TMAH without DI. Incorporating synthesized DI, *t*-amyl cholate enhances pattern contrast and widens processing latitude. A 10% DI content offers the widest process latitude. A developer concentration ranging from 0.13 to 0.033 N offers satisfactory lithographic performance.

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