Optimization of solvent development in radiation induced graft lithography of poly(methylmethacrylate)

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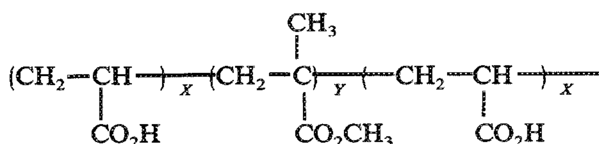
Irradiation of poly(methylmethacrylate) film, PMMA, with e-beam, H^+, x ray, and deep UV creates reactive centers which combine with acrylic acid vapor to form graft and/or block copolymers with solubilities different from that of PMMA. Dissolution rate studies of modified PMMA using a variety of solvents have revealed that while toluene forms good negative-tone images, it develops too slowly, and that a mixture of methylisobutylketone and isopropanol is not selective enough to give images with good contrast. Consideration of the solubility parameters of pure PMMA and pure poly(acrylic acid) (PAA) indicates that organic esters such as methylformate (MF), ethylacetate (EA), and a commercially available mixture (Dupont Co.) of dimethylsuccinate, dimethylglutarate, and dimethyladipate (DBE) could be useful development solvents for the samples under discussion. The data obtained reveal that toluene gives the best image, but also reveal that the dissolution rates decrease as the development fronts proceed into the body of the film.

I. INTRODUCTION

We have been studying new ways to increase radiation sensitivity of resists used in microlithographic fabrication of integrated circuits.[1–3] In the usual positive processes, incident radiation, whether focused or masked, degrades the polymer film to small fragments which are either directly volatile (e.g., olefin–sulfur dioxide copolymers) or selectively dissolvable (PMMA) in the presence of the unirradiated matrix. Because of the nature of chain polymerization, the introduction of a polymerizable monomer into the vicinity of the reactive fragments before they decay presents the possibility of drastically modifying the solubility of the fragments at very low dose levels of radiation. We have found that the same reactive free radical fragments are generated, irrespective of the source of radiation[3] (e-beam, H^+ beam, x ray, deep UV) and that sensitivities enhanced by a factor of ~ 1000 are obtained using acrylic acid (AA) as the reactive monomer.[1,2] The first results on the grafting of AA onto irradiated PMMA were given by Gazard *et al.*[4] At low doses the normal developers for PMMA such as methylisobutylketone–isopropanol mixtures do not give good contrast in our negative-tone system while aromatic solvents such as toluene give good images but are very slow developers.

In this process it is believed that we are forming block copolymers of poly(acrylic acid) (PAA) and PMMA as shown below:



where $X > Y < X'$. Thus, the ideal developer would be a very good solvent for PMMA and a complete nonsolvent for PAA.

In this paper we report on detailed dissolution studies for various solvents for AA modified PMMA irradiated by e-beam, H^+ ions, x rays, and deep UV. We also include scanning electron microscope (SEM) studies of several different radiation sources.

II. EXPERIMENTAL MATERIALS

A 9% chlorobenzene solution of poly(methylmethacrylate) (PMMA), molecular weight 500 000, was obtained from KTI Chemical Corporation and diluted with chlorobenzene to a 7% solution.

Acrylic acid (Aldrich) was distilled at reduced pressure under nitrogen flow (2 Torr, 45 °C). The column and condenser were packed with copper helices and CuCl was added to the distillation flask to prevent polymerization during distillation. The distilled monomer was stored in a refrigerator at -20 °C.

III. SAMPLE PREPARATION

Poly(methylmethacrylate) was spin coated on silicon wafers which were dehydrated in an oven at 260 °C for 1 h. HMDS (hexamethyldisilazane) was spin coated and then 2 ml of PMMA solution was applied. The coated wafers were baked at 120 °C for 1 h and the resist thickness was measured with a surface profilometer. Films with $0.8(\pm 0.2)\,\mu$m thickness were obtained.

IV. EXPOSURE

The PMMA films were irradiated (e-beam, proton beam, x ray, and deep UV) at various incident doses.

Beam	Energy	Incident dose range
Electron	25 keV	10^{-6}–10^{-7} C/cm^2
X ray	0.27 keV	10^{-3}–10^{-2} J/cm^2
Proton	65 keV	10^{10}–10^{12} H^+/cm^2
Deep UV	5.3 eV	1–6 mJ/cm^2

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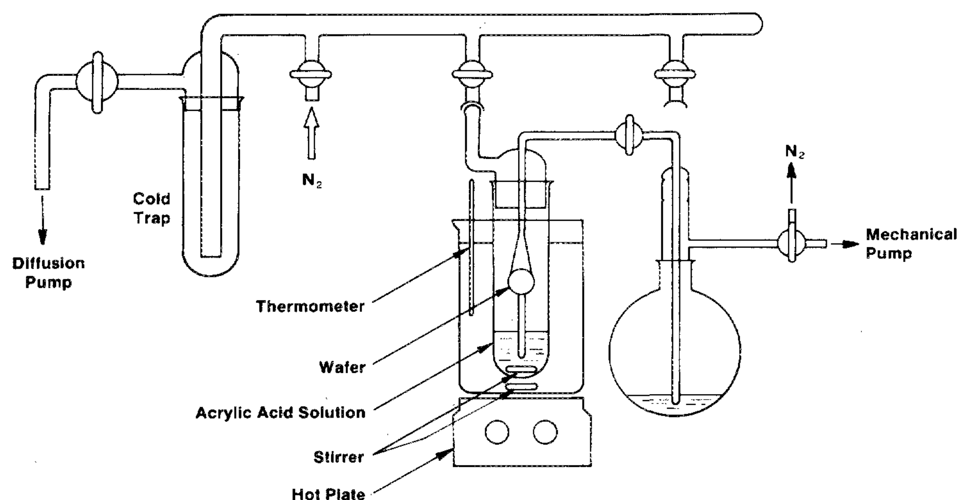

FIG. 1. Reactor for modification of irradiated PMMA.

The irradiated PMMA film was exposed to AA within 1 h after irradiation. If the time lapse between radiation and grafting exceeded 1 h, the irradiated wafers were stored in liquid nitrogen.

The samples for dissolution rate studies were irradiated over an area of 1×1 cm. In those instances where patterns were generated, appropriate masking procedures were used, except for focused e-beam exposures.

V. ACRYLIC ACID (AA) TREATMENT

The irradiated sample was mounted on a wafer holder and placed in the upper part of the reaction chamber (Fig. 1). The reaction vessel was then evacuated (10^{-6} Torr) prior to the reaction. An acrylic acid solution (10% in water) was added to the monomer reservoir and was degassed by first freezing the solution with liquid nitrogen and then allowing the temperature to rise slowly to room temperature at a pressure of 10^{-2} Torr. The degassed monomer was siphoned directly into the reaction chamber with the reaction vessel immersed in a water bath and the temperature was raised from 25 to 60 °C. After the desired temperature was attained the reaction with acrylic acid was continued for 5–20 min, until the pattern on the PMMA film could be detected visually. The wafers were removed from the reaction chamber, rinsed with methanol and deionized water and blown dry with nitrogen. The modified samples were baked at 120 °C for 1 h and the thickness of modified PMMA was measured with a surface profilometer.

TABLE I. Dissolution rate of PMMA and PAA.

Solvent	Polymer	
	PAA (Å/min)	PMMA (Å/min)
Methylformate (10 °C)	10	4750[a]
Ethylacetate (17 °C)	13	2180[a]
Toluene (RT)	20	250
DBE[b] (25 °C)	···	700

[a] Data obtained with an end point detector.
[b] Dibasic ester (Dupont), $H_3CO_2C(CH_2)_nCO_2CH_3$, $n = 2,3,4$.

VI. DEVELOPMENT

Development was carried out by immersing the samples in various solvents including toluene, methylformate, ethylacetate, and DBE (a mixture of dimethylsuccinate, dimethylglutarate, and dimethyladipate produced by the Dupont Co.) at different temperatures.

After development at time intervals of 5, 10, and 15 min, samples were baked at 120 °C for 1 h and the remaining thickness of modified PMMA was measured with the surface profilometer. Patterns were observed using a scanning electron microscope.

A consideration of the solubility parameters of pure PMMA and pure PAA reveal that esters such as methylformate (MF) and ethylacetate (EA) should be good solvents for PMMA and poor solvents for PAA. These solvents are rela-

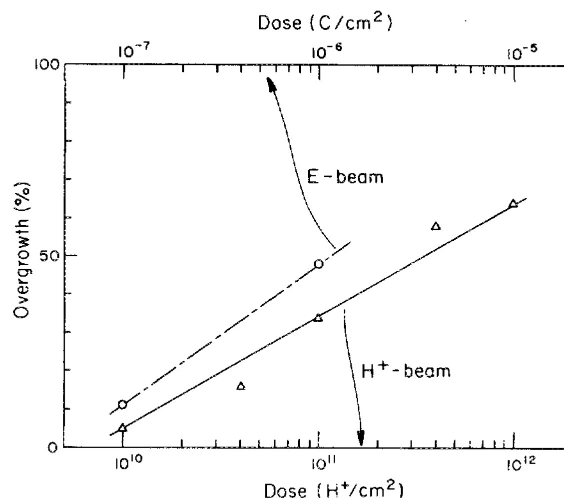

FIG. 2. Growth of modified PMMA film by H^+ beam and e-beam.

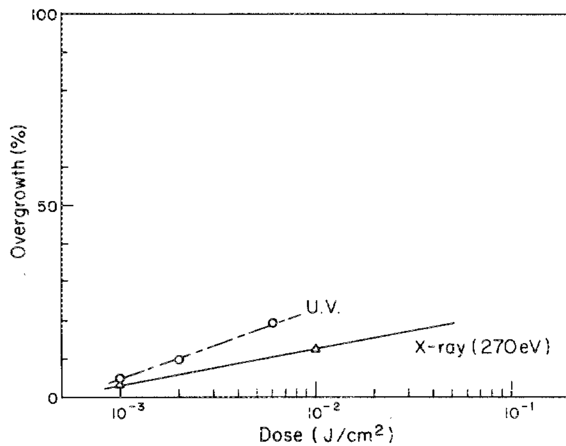

FIG. 3. Growth of modified PMMA film by x ray and deep UV.

tively volatile so a commercially available mixture of high boiling esters (designated DBE by Dupont) consisting of dimethylsuccinate, dimethylglutarate and dimethyladipate was also studied. Prior work[1,2,5] has shown that toluene gave good electron micrographs even though it was a very slow developer and so it was also included in the present study as a point of comparison.

VII. RESULTS AND DISCUSSION

Table I shows a comparison of the dissolution rates of PMMA and PAA with the solvents in question. Clearly, the ester solvents are good candidates for this system because of their clearly defined selectivities. By using a surface profilometer it can be seen, (Figs. 2 and 3 and Table II) that not only do the irradiated regions become insoluble after treatment with AA (negative tone) but that the film thickness in the vertical dimension increases in proportion to the radiation dose used. Because the number of active sites generated upon irradiation should depend directly on the impinging radiation dose it is to be expected that more acrylic acid should be polymerized at higher doses. Preliminary examinations of image fidelity in the lateral dimension have not revealed substantial growth. These experiments are still in progress and details will be reported in a future publication.

TABLE II. Growth of modified PMMA film (in microns).

E-beam (25 keV)	Dose (C/cm²)		
	10^{-6}		10^{-7}
PMMA (original thickness)	0.74		0.70
Modified PMMA	1.09		0.78
Growth	0.35		0.08
H^+-beam (65 keV)	Dose (H^+/cm²)		
	10^{12}	10^{11}	10^{10}
PMMA	0.77	0.74	0.81
Modified PMMA	1.26	0.99	0.85
Growth	0.49	0.25	0.04
UV	Dose (mJ/cm²)		
	6	2	1
PMMA	0.80	0.80	0.80
Modified PMMA	0.95	0.88	0.84
Growth	0.15	0.08	0.04
X ray	Dose (mJ/cm²)		
	10		1
PMMA	0.70		0.72
Modified PMMA	0.80		0.74
Growth	0.1		0.02

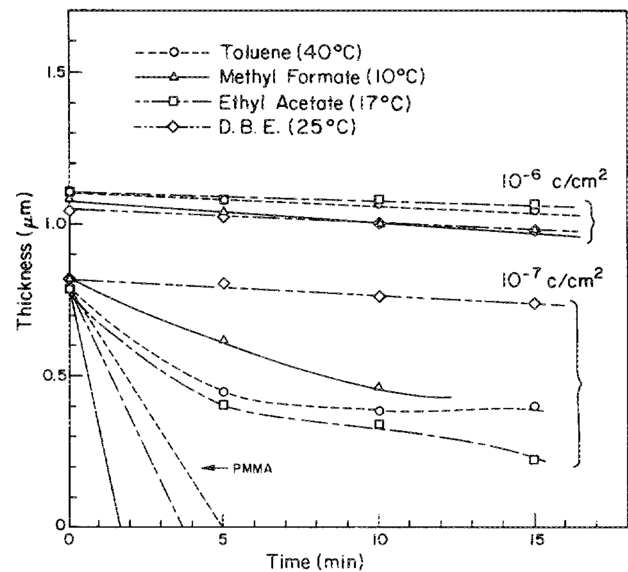

FIG. 4. Dissolution curve of e-beam modified PMMA.

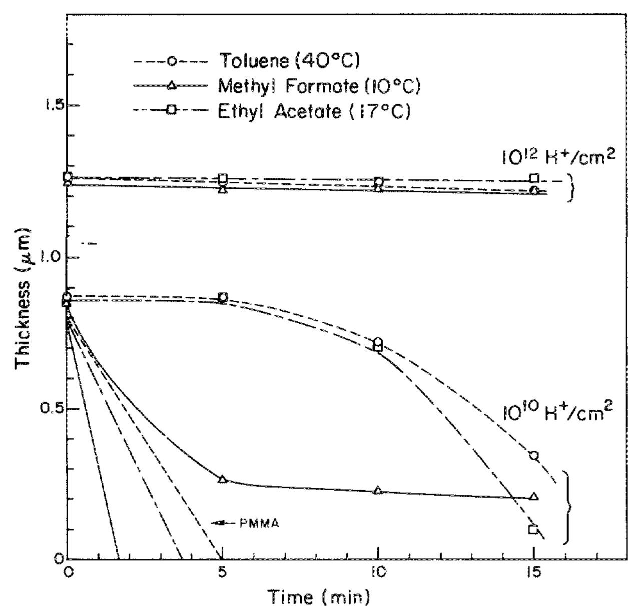

FIG. 5. Dissolution curve of H^+ beam modified PMMA.

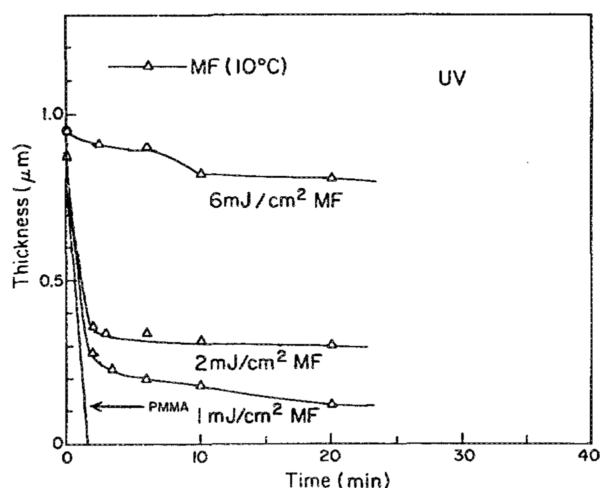

FIG. 6. Dissolution curve of deep UV modified PMMA.

TABLE III. Dissolution rate of e-beam modified PMMA.

Solvent	Time (min)	Incident dose (C/cm^2)	
		1×10^{-6} (Å/min)	1×10^{-7} (Å/min)
Methylformate	5	80	360
(10 °C)	10	80	360
	15	65	...
Ethylacetate	5	39	760
(17 °C)	10	20	440
	15	13	370
Toluene	5	0	680
(40 °C)	10	20	400
	15	27	253
DBE	5	31	40
(25 °C)	10	40	59
	15	40	53

Figures 4–6 and Tables III–V show data for the dissolution rates of the PAA modified PMMA with the solvents in question. In all cases, at the highest doses used, the esters appear to leave the modified area essentially untouched. Thus it is to be expected that acceptable levels of contrast will be defined by these solvents in imaging experiments in reasonably short development times. A most interesting phenomenon is revealed at the lower doses. The overgrowth is essentially eroded in times comparable to those of the unmodified PMMA in the particular solvent and then the rate of dissolution decreases dramatically as the development front progresses into the bulk of the film. One explanation for these observations is that more polymerization sites are active within the interior of the film than at the surface, so more acrylic acid is polymerized and the copolymer is less soluble. It is tempting to attribute this effect to enhanced radiation effects arising from backscattering for e-beam irradiation. However, this explanation is not in keeping with the fact that similar behavior is observed for UV and H^+ beam irradiation where there is not a similar deposition of energy with depth as for e-beam. An alternative rationalization is that after the reactive sites are generated, some of them (at the surface) are scavenged by adventitious oxygen and are deactivated, but those formed in the bulk of the film remain active and incorporate larger (relative to the surface) amounts of acrylic acid and are therefore less soluble. This rationale is not without its stumbling blocks, because it implies that AA diffuses into the bulk of the film faster than O_2. Specific solvation arising from hydrogen-bonded interactions with water used in the process may contribute to this effect. Experiments to test this point are in progress.

It is expected that the solvent with the highest selectivity gives the best image. Thus far we have completed selectivity experiments only with deep UV and toluene, ethylacetate, and methylformate developers. However, SEM micrographs shown in Figs. 7–10 indicate that toluene gives better images than any of the other solvents used. The results in Figs. 7–9 are for 65 keV H^+ exposure of PMMA to a dose of 10^{10} H^+/cm^2, with postirradiation grafting with AA while Fig. 10 is for irradiation with 5 mJ/cm^2 of deep UV light and postirradiation (AA) grafting. Only data for methylformate are reported in Fig. 10 for the sake of clarity. One explanation for this result is that there is a distribution of reactive radicals in the irradiated volume, in which the outside surface has less reactive sites than the inner volume. In addition,

TABLE IV. Dissolution rate of H^+ modified PMMA.

Solvent	Time (min)	Incident dose (H^+/cm^2)		
		10^{12} (Å/min)	10^{11} (Å/min)	10^{10} (Å/min)
Methylformate	5	39	30	1180
(10 °C)	10	20	40	620
	15	13	53	427
Ethylacetate	5	0	0	0
(17 °C)	10	20	20	150
	15	0	13	500
Toluene	5	39	37	0
(40 °C)	10	19	0	150
	15	26	40	353

TABLE V. Dissolution rate of deep UV modified PMMA.

Solvent	Time (min)	Incident dose (mJ/cm²)		
		6 (Å/min)	2 (Å/min)	1 (Å/min)
Methylformate	2	160	2600	2800
(10 °C)	6	83	900	1067
	10	130	560	660
Ethylacetate	5	0	220	260
(17 °C)	10	0	120	280
	15	0	193	327
Toluene	5	40	160	800
(40 °C)	10	30	320	460
	15	20	227	293

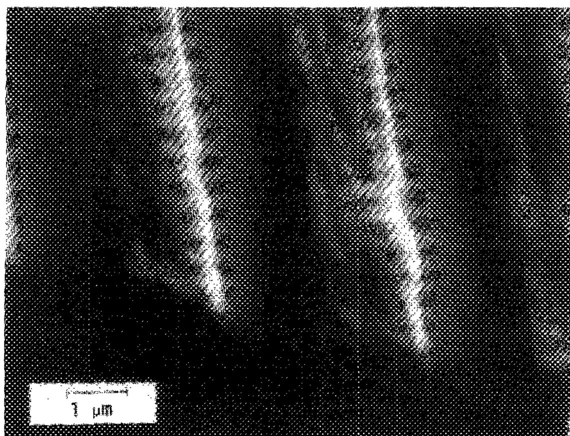

FIG. 7. SEM micrograph of AA modified PMMA after exposure to 10^{10} H^+/cm^2 65 keV ions (developed in toluene).

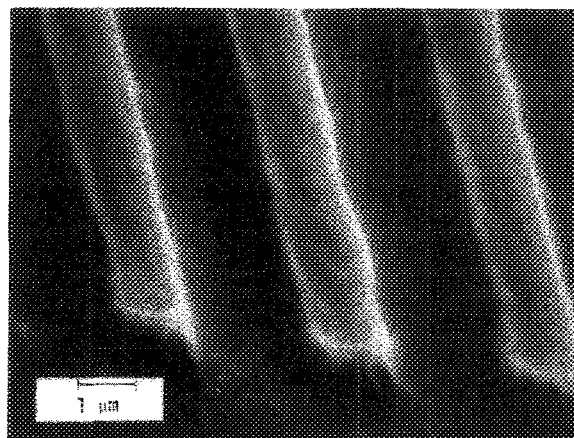

FIG. 8. SEM micrography of AA modified PMMA (same H^+ dose as in Fig. 6, but developed in methylformate).

at the surface, some of the reactive radicals combine with oxygen forming relatively stable peroxy radicals[6] and are deactivated. Therefore, the outer surface has less acrylic acid

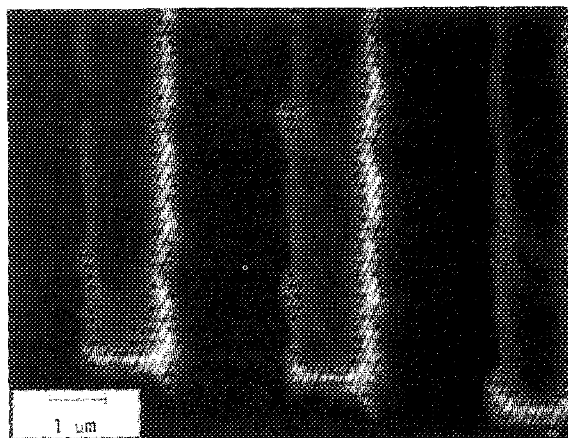

FIG. 9. SEM micrography of sample in Fig. 7, but at a different sample orientation.

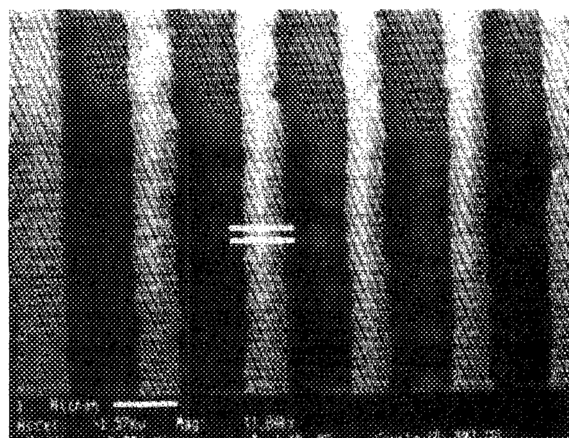

FIG. 10. SEM micrograph of AA modified PMMA after exposure to 5 mJ/cm² of deep UV (developed in toluene).

(more PMMA) relative to the inner volume and the surface becomes susceptible to the highly reactive solvents which rapidly dissolve the PMMA.

VIII. CONCLUSIONS

1. Toluene developer gives the best lithographic images for AA modified PMMA.

2. As a negative-tone resist AA modified PMMA before developing exhibits very small growth at low doses as can be seen in Table II. After developing there is no swelling in the pattern for low doses.

ACKNOWLEDGMENTS

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