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Characterization of safe solvent PMMA resist variables for electron beam application

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ABSTRACT

Polymethylmethacrylate (PMMA) materials have been utilized for electron beam lithography for many years, offering high resolution capability and wide process latitude. Their poor sensitivity has, however, limited them until recently to R&D applications. MOSFET 0.25 μm T-gate fabrication utilizing PMMA in a multi-layer system has caused an increase in the volume of resist used in commercial applications, prompting a need to evaluate formulations for optimum process performance.

Results are presented from a study undertaken to evaluate resist casting solvent composition and molecular weight variation in PMMA for electron beam exposure. PMMA cast in several solvent systems have been evaluated for lithographic performance. Additionally, formulations in chlorobenzene with minor variations in molecular weight have been evaluated for batch-to-batch uniformity. A 10 KeV MEBES electron beam system has been used to study resist sensitivity, contrast, and process latitude. Using a two-factor, three level factorial designed experiment, prebake and development time have been varied as controlled process factors. Samples with varying molecular weights were shown to have wide process latitude. These samples gave comparable performance while their molecular weights varied from 539K to 614K, and polydispersity varied from 3.3 to 6.1. Resist samples with chlorobenzene, PGMEA (propylene glycol monomethyl ether acetate) and anisole as the casting solvent resulted in equivalent performance.

1. INTRODUCTION

The T-shaped gate structure has been utilized in FET applications in order to decrease gate resistance and noise. A tri-layer structure for fabricating these T-gates was first described by Chao *et al*¹, utilizing PMMA and P[MMA-co-MAA]. Since the introduction of these processes, emphasis has been placed on manufacturability and reproducibility for structures at and below 0.25 μm . This in turn has placed demand on the reproducibility of resin materials. The emphasis of this research has been directed toward investigation of PMMA resin parameters, specifically molecular weight variation and casting solvent. The sensitivity of processes to variations in molecular weight dispersity becomes critical, as resins not specifically produced for microelectronic application are commonly utilized as resist materials. Furthermore, it has been well established that the toxicity of chlorobenzene as a casting solvent makes PMMA less than attractive for volume manufacturing. The aim of this investigation has been to evaluate and lithographically compare PMMA materials with varying molecular weight variations, cast in chlorobenzene and environmentally safer propylene glycol monomethyl ether acetate (PGMEA) and anisole solvent systems.

2. EXPERIMENTAL DESIGN

Critical factors chosen for study of lithographic performance of PMMA formulations were prebake temperature and develop time, in 1:1 IPA:MIBK. The 1:1 development chemistry was chosen to optimize for sensitivity and contrast, using solubility parameters for IPA and MIBK, along with solvent maps for PMMA². A full-factorial design approach was taken, using 3² (three level, 2 factor) designs for each sample of study. Two responses were chosen: resist sensitivity (E_0) and contrast (γ). For each PMMA formulation, 10 experimental runs were conducted to allow for all levels of each factor, along with a replicated center run point for measurement of variation. Each run consisted of a single Si wafer, coated and prebaked according to design specification, then exposed in a MEBES electron beam system, at 10KeV, 40 nA, and with a 0.25 micron beam diameter. Energy doses ranged from 5 to 120 $\mu\text{C}/\text{cm}^2$, which was achieved through repeat exposure passes. Development followed immediately, at experimentally designed development times.

PMMA formulations in chlorobenzene with minor molecular weight and dispersity variations were evaluated. Five samples were prepared with molecular weights of 539, 577, 589, 590, and 614 at dispersities of 4.0, 3.3, 3.3, 6.1, and 5.4 respectively (average Mw 582 ± 27). Additionally, two samples were prepared in alternative casting solvents: PMMA cast in PGMEA and in anisole both at 589K molecular weight with dispersities of 3.3. PMMA cast in chlorobenzene at 4% solids (11.2 cst), anisole at 6% solids (31 cst), and PGMEA at 6% solids (41.7 cst) yielded thickness characteristics suitable for 4000 Å coatings. Figure 1 shows spin speed characteristics for these formulations. Evaporation rates of PMMA in the three solvent systems at 150 °C, 175°C, 185°C, and 200°C were used to determine prebake ranges for experimental runs. Percent weight remaining after baking of "standard" PMMA materials (in chlorobenzene) was used as a target point for alternative solvent systems. Both PGMEA and anisole formulations required a 15°C to 20°C higher temperature to match chlorobenzene formulations. Prebake temperatures for chlorobenzene formulations were chosen at 160°C, 170°C, and 180°C for 90s. Temperatures of PGMEA and anisole formulations were chosen at 175°C, 185°C, and 195°C for 90s. Develop times for all samples were chosen at 30s, 45s, and 60s.

Figure 1. Spin speed vs. thickness curves for PMMA samples, chlorobenzene, PGMEA, and anisole.

Randomized experimental worksheets for the seven PMMA formulations are shown in Tables 1 and 2. Response data for E_0 (clear dose, in $\mu\text{C}/\text{cm}^2$) and contrast (γ) are shown for each of the ten runs. Analysis of variance (ANOVA) for each sample showed *develop time* to be significant for both responses, (*prebake temperature*)² to be significant for γ , *prebake* to be significant for E_0 for Chlorobenzene samples S1, S3, and S4 and the Anisole sample, and (*prebake temperature*)² to be significant for E_0 for Chlorobenzene sample S2 and the Anisole sample. All levels of significance are for $\alpha=0.10$.

PMMA in Anisole, Mw = 589, Mw/Mn = 3.3

Run #	PreBake (C)	Dev. Time (s)	Eo ($\mu\text{C}/\text{cm}^2$)	Contrast
1	185	45	66	5.68
2	185	45	66	5.68
3	195	45	69	5.68
4	175	60	60	5.04
5	175	45	65	5.57
6	195	60	66	5.09
7	185	30	73	6.08
8	185	60	60	5.35
9	195	30	77	5.96
10	175	30	73	6.08

PMMA in PGMEA, Mw = 589, Mw/Mn = 3.3

Run #	PreBake (C)	Dev. Time (s)	Eo ($\mu\text{C}/\text{cm}^2$)	Contrast
1	195	45	66	5.02
2	195	60	60	4.51
3	195	30	75	5.41
4	175	60	61	5.15
5	185	45	66	5.57
6	185	45	65	5.79
7	185	60	63	5.27
8	175	45	65	5.57
9	175	30	73	5.78
10	185	30	70	5.94

PMMA in Chlorobenzene S1, Mw = 577, Mw/Mn = 3.3

Run #	PreBake (C)	Dev. Time (s)	Eo ($\mu\text{C}/\text{cm}^2$)	Contrast
1	180	60	64	5.07
2	160	45	67	4.93
3	170	60	62	5.15
4	180	30	75	5.54
5	170	45	68	5.58
6	160	60	60	4.76
7	170	45	67	5.48
8	170	30	75	5.97
9	160	30	72	5.49
10	180	45	67	5.07

Table 1. Randomized experimental worksheet for PMMA formulations.

PMMA in Chlorobenzene S2, Mw = 614, Mw/Mn = 5.4

Run #	PreBake (C)	Dev. Time (s)	Eo (uC/cm^2)	Contrast
1	170	45	65	5.58
2	180	45	63	4.44
3	180	60	57	4.05
4	180	30	70	5.78
5	160	30	70	5.58
6	160	45	63	5.36
7	170	60	60	4.98
8	170	45	65	5.57
9	160	60	60	4.76
10	170	30	70	6.1

PMMA in Chlorobenzene S3, Mw = 539, Mw/Mn = 4.0

Run #	PreBake (C)	Dev. Time (s)	Eo (uC/cm^2)	Contrast
1	170	45	65	5.27
2	160	60	58	5.23
3	180	30	75	5.59
4	170	45	66	5.47
5	160	30	72	5.68
6	160	45	67	5.48
7	180	60	63	4.8
8	180	45	70	5.05
9	170	60	61	5.15
10	170	30	73	5.97

PMMA in Chlorobenzene S4, Mw = 589, Mw/Mn = 3.3

Run #	PreBake (C)	Dev. Time (s)	Eo (uC/cm^2)	Contrast
1	160	45	68	5.78
2	180	45	68	5.12
3	170	45	70	6.08
4	170	45	69	5.78
5	180	60	63	4.8
6	160	30	73	5.98
7	180	30	76	5.25
8	160	60	63	5.57
9	170	60	65	5.57
10	170	30	74	6.29

PMMA in Chlorobenzene Control, Mw = 590, Mw/Mn = 6.1

Run #	PreBake (C)	Dev. Time (s)	Eo (uC/cm^2)	Contrast
1	180	60	61	4.87
2	180	45	66	5.48
3	160	30	70	5.78
4	170	30	73	5.97
5	160	60	60	5.04
6	160	45	64	5.27
7	180	30	73	5.78
8	170	60	58	5.12
9	170	45	65	5.57
10	170	45	65	5.57

Table 2. Randomized experimental worksheet for PMMA formulations.

Response surfaces were generated and are displayed in Figures 2 and 3. Additionally, optimization was performed for each sample for two criteria: 1) maximum γ and 2) minimum E_0 . Table 3 shows results of each optimization.

Sample	$\gamma_{\max}$	E_0	Prebake °C	Develop sec.	$E_{0 \min}$	γ	Prebake °C	Develop sec.
Chlorobenzene 4% - Control	5.9	71	167	30	59	5.1	165	60
Chlorobenzene 4%-S4	6.2	74	167	30	63	4.8	165	60
Chlorobenzene 4%-S3	5.9	72	168	30	59	5.3	165	60
Chlorobenzene 4%-S2	6.2	71	170	30	57	3.9	165	60
Chlorobenzene 4%-S1	5.9	74	167	30	60	4.7	160	60
PGMEA 6%	6	72	182	30	61	4.9	190	60
Anisole 6%	6.1	73	181	30	60	5.2	180	60

Table 3. Optimization of γ and E_0 for PMMA samples. Samples Control, S4, S3, S2, and S1 correspond to 590, 589, 539, 614, and 577 K molecular weight and 6.1, 3.3, 4.0, 5.4, and 3.3 Mw/Mn.

Figure 2. Response surfaces for PMMA formulations. Responses γ (C) and E_0 (E) are plotted against prebake temperature (°C) and develop time (sec). From top, PMMA in Anisole and PMMA in PGMEA.

Figure 3. Response surfaces for PMMA formulations. Responses γ (C) and E_0 (E) are plotted against prebake temperature ($^{\circ}\text{C}$) and develop time (sec). From top, PMMA in Chlorobenzene S1, S2, S3, S4, and control.

3. LITHOGRAPHIC PERFORMANCE

Following response surface analysis and optimization, lithographic performance was evaluated through pattern transfer integrity and uniformity. A series of fifteen exposures, made over a 4" array on silicon substrates, was performed for each sample. Exposure patterns consisted of isolated and dense line patterns, ranging from 0.5 to 10 μm . Sample prebake temperatures, exposure doses, and develop times were determined individually to give maximum latitude to maintain high contrast and low E_0 . After development, linewidth data from a Nikon 2I laser scanning system was used to compare CD uniformity across the array. CD linearity existed down to 2 μm , at which point proximity effects became measurable. CD variation for 2 μm features, as a function of feature linewidth is given in table 4.

Sample	Prebake $^{\circ}\text{C}$	Dose $\mu\text{C}/\text{cm}^2$	Develop sec.	2 μm CD σ ($\mu\text{m}/\mu\text{m} \times 100$)
Chlorobenzene 4% - Control	170	80	45	3.53
Chlorobenzene 4% - S4	167	95	40	2.93
Chlorobenzene 4% - S3	166	90	45	2.67
Chlorobenzene 4% - S2	168	85	50	2.71
Chlorobenzene 4% - S1	171	95	42	2.35
PGMEA 6%	182	85	45	3.33
Anisole 6%	182	90	45	2.73

Table 4. CD uniformity results across 4" array for PMMA samples.

4. ANALYSIS OF RESULTS

Evaluation of data shows variations over the range of molecular weights and between the solvent systems studied to be small. Using small sampling theory (t-distribution testing) it is seen that processes optimized for γ_{max} have an average γ of 6.03. All samples optimized produced γ values within 95% confidence limits, or 6.03 ± 0.138 . Corresponding E_0 values average 72.4 and all samples produced E_0 values within 95% limits, or 72.4 ± 1.27 . When processes were optimized for minimum E_0 , average E_0 was 59.9 and 95 % limits were 59.9 ± 1.86 , containing all sample values except sample S2, which corresponds to the highest molecular weight PMMA sample in chlorobenzene, at $M_w = 614\text{K}$. Corresponding γ values also fall within 95% limits if sample S2 is removed (4.84 ± 0.46). Without further data, it can be determined that at least a 6% variation in molecular weight and a M_w/M_n range of 2.8 produces no significant difference for 95% confidence limits. At 99%, all samples fall within

confidence limits. For CD uniformity, values of all samples fall within 99% confidence intervals of the mean, or 2.89 ± 0.64 , showing little significant difference in lithographic performance within the ranges of samples.

The implication of these results is that small variations in Mw and Mw/Mn have little impact on PMMA resist performance. The results also show that when properly baked, different casting solvents can give identical resist performance. Thus replacement of chlorobenzene as a PMMA solvent with a safer solvent is expected to be a viable consideration. Furthermore, results show that resist contrast can be maximized with properly chosen bake temperature. Optimization of development composition is expected to allow further optimization.

5. CONCLUSIONS

A study has been carried out to investigate the influence of PMMA resin parameters and solvent systems on lithographic performance. Resist contrast and dose-to-clear have been studied as responses for input factors: prebake temperatures and develop time. It has been shown that small changes in molecular weight and dispersity produce little change in resist performance. It has also been shown that safer solvent systems, PGMEA and Anisole, have potential as replacements for chlorobenzene, allowing similar lithographic performance.

6. REFERENCES

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