

# ***Investigation of New Positive and Negative Electron Beam Resists for Microlithography***

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*The primary objective of this investigation was to obtain maximum electron beam resist contrast (gamma), maximum sensitivity, minimum thickness loss, and maximum plasma etch resistance for 10 KeV electron beam exposure process. This is to be achieved while maintaining a robust design. This study also compares the etch resistivity and etch rate of different electron beam resist materials to O<sub>2</sub>, Cl<sub>2</sub>, and SF<sub>6</sub> containing plasma conditions. Measurements of the resist thickness loss yield the results of resist sensitivity and gamma for various development conditions.*

## **I. INTRODUCTION**

Electron beam lithography offers a great potential in the making of next generation sub-micron devices. One current technology, using chrome masks fabricated with wet etching, can limit resolution due to isotropic etching effects. An alternative phase shift mask technology, requires reactive ion etching of chrome and fused silica. Common resists such as PBS, an alternating copolymer of sulfur dioxide and 1-butene, which is used for mask writing is not resistant to plasma etching.

PMPS/novolac, poly(dimethyl-pentene sulfone)/novolac, is a positive electron beam resist which operates by spontaneous depolymerization of the polymeric dissolution inhibitor in novolac resin. This process is activated by electron radiation. The sensitivity of this resist is  $\sim 5 - 50 \mu\text{C}/\text{cm}^2$  at 40 KeV. In addition, PMPS/novolac can withstand high resistance to aluminum, polysilicon, SiO<sub>2</sub>, doped SiO<sub>2</sub>, and Si<sub>3</sub>N<sub>4</sub> plasma etching due to the novolac component of the resist. This inherently good plasma resistance can be used for etch mask to deliver sub-micron features into the film substrates.

P(SI-CMS), a copolymer of trimethylsilylmethyl methacrylate with chloromethylstyrene, is a negative electron beam resist and deep-UV resist which can endure the erosion of O<sub>2</sub> and Cl<sub>2</sub> containing plasma environment. It is also known to be very useful as masking layer for hard-baked novolac in bilayer lithography. The silicon (SI) component

in P(SI-CMS) can withstand O<sub>2</sub> and Cl<sub>2</sub> etches due to the silicon containing component, while the CMS component reveals radiation sensitivity through radical influenced cross-linking reactions. Manipulation of the composition and molecular weight (Mw) permits regulation of the etch resistance and radiation sensitivity properties. A 90:10 mole of SI:CMS and Mw between 30 - 41 Kg/mol represent an optimal combination of the resist sensitivity, dry-etching resistance, and pattern resolution.

In this experiment, PMPS/Novolac and P(SI-CMS)'s characteristics have been investigated through a robust design for the determination of maximum gamma, maximum sensitivity, and minimum thickness loss for 10 KeV electron beam lithography process. Measurements of resist thickness loss yield resist sensitivity and gamma for various develop conditions. This experiment also compares the etch resistivity and etch rate of different electron beam resist materials to O<sub>2</sub>, Cl<sub>2</sub>, and SF<sub>6</sub> containing plasma conditions.

## **II. EXPERIMENT**

### ***Lithographic Processing***

Wafer preparations - All wafers (Si) were subjected to RCA clean and spin dry. They're then dehydration baked at 250°C for five minutes.

#### ***A. PMPS/Novolac***

**PMPS/Novolac Preparation** - The resist was obtained from AT&T Bell Laboratories for these experiments.

**Spin Coating** - The resists were spin-coated on four 3" wafers. The spin speed was determined to be 1200 RPM for 60 seconds, by trial and error to obtain a thickness of  $\sim 3000 - 3500 \text{ \AA}$ . Prior to the resist coating, HMDS-C20 was applied with the same spin speed for 60 seconds.

**Baking** - The wafers were prebaked on a hotplate at  $120^\circ\text{C}$  for 120 seconds.

**Exposure** - The resist was exposed using an electron beam system (MEBES-I) at doses sampling from  $2 - 32 \mu\text{C}/\text{cm}^2$  with 16 steps in increment of  $2 \mu\text{C}/\text{cm}^2$ . The beam size was set at  $0.5 \mu\text{m}$  and beam current of 40 nA with an energy of 10 KeV.

**PEB** - After exposure of the resist, post exposure baked (PEB) was done at  $70^\circ\text{C}$  for 120 seconds, also on a hotplate.

**Development** - The developer used for this resist was Shipley 312, an aqueous base developer. Different normality was used for each wafer. The normality ranged from 0.22N - 0.30N. The wafers were submerged in the developer solution for 60 seconds. The thickness loss of the resist was also measured.

**Image Evaluation** - The quality of the resist patterns was measured using the Nanoline for the critical dimension (CD) for each exposure dose. Also, the thickness loss of the resist was measured.

**Hard Baked** - Three wafers were hard-baked at  $130^\circ\text{C}$  for 120 seconds before plasma etch.

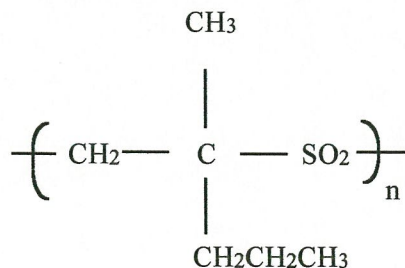


Figure 1: Chemical structure of the repeat units in PMPS/Novolac.

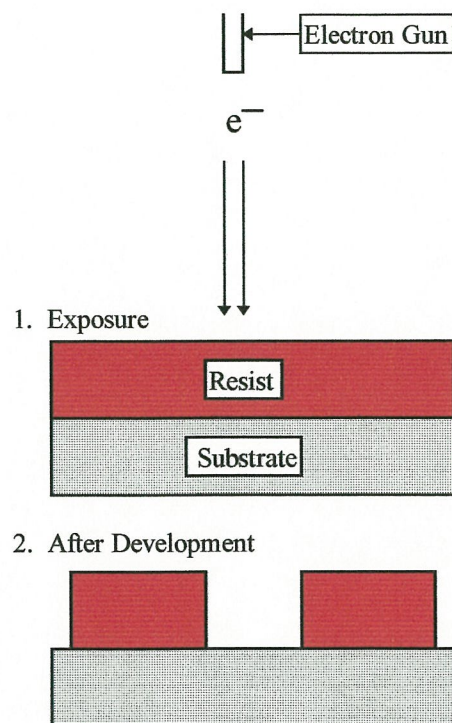


Diagram 1: Photolithography process for PMPS/Novolac.

### B. P(SI-CMS)

**P(SI-CMS) Preparation** - The resist was obtained from AT&T Bell Laboratories for the experiment.

**Spin Coating** - The resists were spin-coated on five 4" wafers by using a spinner. The spin speed was 2500 RPM for 60 seconds to get a thickness of  $\sim 2000 - 2200 \text{ \AA}$ . Prior to the resist coating, HMDS-C20 was applied with the same spin speed for 60 seconds.

**Baking** - The wafers were prebaked on a hotplate at  $90^\circ\text{C}$  for 120 seconds.

**Exposure** - The resist was exposed using an electron beam system (MEBES-I) at doses sampling from  $2 - 32 \mu\text{C}/\text{cm}^2$  with 16 steps in increment of  $2 \mu\text{C}/\text{cm}^2$ . The beam size was set at  $0.5 \mu\text{m}$  and beam current of 40 nA with an energy of 10 KeV. Wafer E10 was given the dose of  $2 - 32 \mu\text{C}/\text{cm}^2$  with 16 steps in increment of  $2 \mu\text{C}/\text{cm}^2$ . Wafer E11 and E12 were given the dose of  $1 - 16 \mu\text{C}/\text{cm}^2$  with 16 steps in increment of  $1 \mu\text{C}/\text{cm}^2$ .



PEB - No post-exposure bake was use before development.

Development - Using ethanol as the developer for this resist (for 30 - 60 seconds), followed by methanol (for 30 seconds), and then isopropanol-water with mixture of 7:3 volume ratio (for 30 seconds). The thickness loss of the resist was also measured.

Image Evaluation - The quality of the resist patterns was measured using the Nanoline for the critical dimension (CD) for each exposure dose.

Hard Baked - Three wafers were hard-baked at 130°C for 120 seconds before plasma etch.

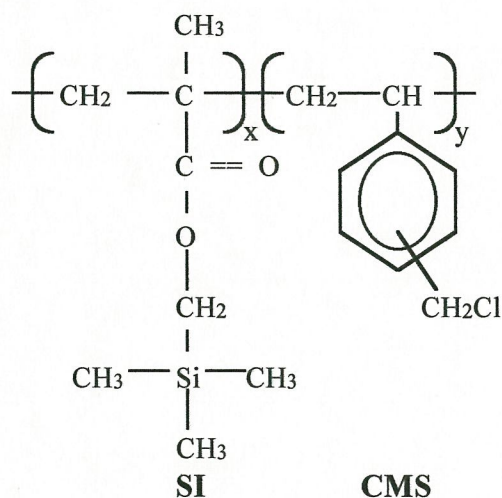
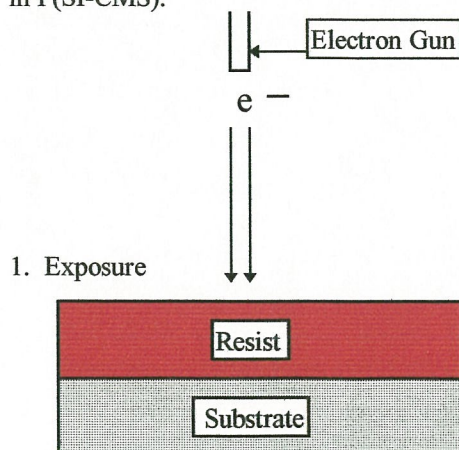


Figure 2: Chemical structure of the repeat units in P(SI-CMS).



## 2. After development

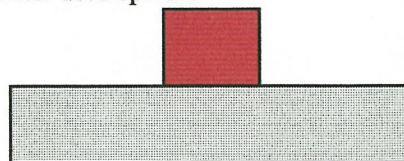


Figure 3: Photolithography process for P(SI-CMS).

## Plasma Etching

Figure 4 shows a schematic of a typical r.f. plasma chamber. The wafers to be etched are placed on the cathode. The chemical reaction with plasma radicals takes place under the influence of electric field. The by products are volatile and carried away.

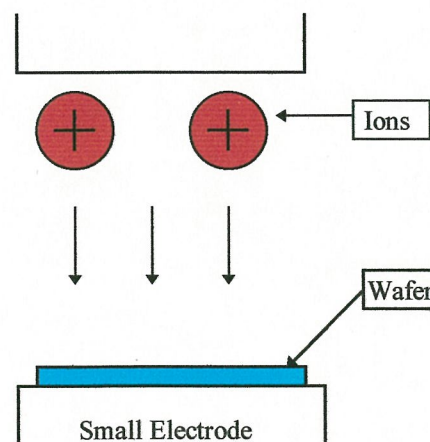


Figure 4: Etching processes for all resists.

### A. PMPS/Novolac

The resist PMPS/Novolac contain 1:10 (9% PMPS and 91% Novolac) were evaluated with O<sub>2</sub>, Cl<sub>2</sub>, and SF<sub>6</sub> containing plasma. The resist thickness was measured before the plasma etch and after the plasma etch to determine the etch rate and resistivity of the resist.

For typical etching conditions, the resist was etched for the following condition as follows:

Table I:

Gases	O <sub>2</sub>	Ar:Cl <sub>2</sub>	SF <sub>6</sub>
Flow Rate (sccm)	40	50:500	30
Pressure (mTorr)	250	100	300
Power (Watts)	50	150	50

### B. P(SI-CMS)

The resist P(SI-CMS) contain 90:10 SI:CMS mole ratio were evaluated in O<sub>2</sub>, Cl<sub>2</sub>, and SF<sub>6</sub> containing plasma. The resist thickness was measured before the plasma etch and after the plasma etch to determine the etch rate and resistivity of the resist.

Typical etching conditions for this resist are as shown in table I.

### C. Shipley 812, COP, and PBS

Conventional positive resist along with COP and PBS were evaluated to compare to the etch resistance of PMPS/Novolac and P(SI-CMS).

The etch conditions were similar to table I.

## III. RESULTS AND DISCUSSION

### Lithographic Results

#### A. PMPS/Novolac

Previous studies showed that the rate of dissolution of the novolac resin in aqueous alkaline solution is based on the molecular weight, its' structure, developer strength, dissolution temperature, prebake temperature and conditions. For different normality of the developer, the dose to clear (Dc) changes according to the developer strength.

For this experiment, the resist was exposed with a dose matrix composed of 16 steps. The dose arranged from 2 - 32  $\mu\text{C}/\text{cm}^2$  with increments of 2  $\mu\text{C}/\text{cm}^2$ . The resist was developed with different normality from 0.30N, 0.28N, 0.26N and 0.22N. Table II below shows the values for dose to clear, gamma, thickness loss (TL) and  $\Delta\text{CD}/\Delta\text{Dose}$  for different normality.

Table II: PMPS/Novolac

Normality	0.30	0.28	0.26	0.22
Dc ( $\mu\text{C}/\text{cm}^2$ )	16	16	51	N/A
Gamma	0.056	0.071	0.01	0.009
TL (Å)	479	794	396	166
$\Delta\text{CD}/\Delta\text{Dose}$	0.004	0.02	0.028	N/A

According to the experiment, the best parameters for this resist at 10 KeV is at develop normality of 0.28; dose to clear of 16  $\mu\text{C}/\text{cm}^2$ ; gamma of and thickness loss of 479 Å. For the  $\Delta\text{CD}/\Delta\text{Dose}$  parameter, as normality of the developer increased  $\Delta\text{CD}/\Delta\text{Dose}$  will decreased due to the space width become larger and the line width get smaller.

#### B. P(SI-CMS)

For P(SI-CMS), a negative acting cross-linking resist, optimal results can be obtain by working with the low molecular weight, 90:10 mole ratio of SI:CMS, for the optimal radiation sensitivity.

For this experiment, the resist was exposed with a dose matrix composed of 16 steps. The dose arranged from 2 - 32  $\mu\text{C}/\text{cm}^2$  with increments of 2  $\mu\text{C}/\text{cm}^2$ . The resist was then developed in ethanol for different develop time (30 seconds to 60 seconds). Table III below shows the values for dose to clear, gamma, thickness loss (TL) and  $\Delta\text{CD}/\Delta\text{Dose}$  for different development time.

Table III: P(SI-CMS)

Develop Time(sec.)	30	45	60
Dc ( $\mu\text{C}/\text{cm}^2$ )	5	6	5
Gamma	0.395	N/A	0.422
TL (Å)	2013	2059	2138
$\Delta\text{CD}/\Delta\text{Dose}$	0.009	0.016	0.027

According to the result of the experiment, the parameters for P(SI-CMS) stayed relatively constant. This is because P(SI-CMS) have good process latitude or a robust process. This is a desire characteristic for any resist.

For the  $\Delta\text{CD}/\Delta\text{Dose}$  parameter, it is opposite to PMPS/novolac because P(SI-CMS) a negative resist. As develop time increases,  $\Delta\text{CD}/\Delta\text{Dose}$  increases due to the resist line width become smaller and space width become larger.

### Plasma Etching Results

Table IV: Etching Results

Material	Etch Rates (Å/sec.)		
	O <sub>2</sub>	Cl <sub>2</sub>	SF <sub>6</sub>
Shipley 812	31	8	39
COP	52	15	52
PBS	110	10	131
PMPS/Nov.	31	6	36
P(SI-CMS)	0.7	3	62

Table IV shows the etch rates for different resists in O<sub>2</sub>, Cl<sub>2</sub>, and SF<sub>6</sub> gas containing plasma. COP - Poly(glycidyl methacrylate-co-ethyl acrylate).

The resist P(SI90-CMS10) was found to have superior etching resistance to O<sub>2</sub> and Cl<sub>2</sub> than the novolac based resists. The superior etch resistance to the O<sub>2</sub> and Cl<sub>2</sub> due to the silicon containing component, SI. However, when P(SI-CMS) is subject to SF<sub>6</sub> containing plasma, the etch rate dramatically increases. This is also due to the silicon containing component. This make perfect sense because SF<sub>6</sub> plasma is known to etch silicon, and when P(SI-CMS) was exposed to this plasma, the etch rate was very fast.

As for PMPS/Novolac, the etch rates for this resist is very much similar to the conventional positive resist, Shipley 812, due to the novolac based component of the NPR.

The etch rates for PBS were very fast compared to all the resists that were experimented with. This result came in no surprise since PBS is a fast scissioning resist as exposed to ionized radiation and a thermally unstable resist. As a result, PBS was proven to be a poor choice for dry etch.

#### IV. SUMMARY

A study has been presented on different types of positive and negative electron beam resists for microlithography using techniques such as measuring the D<sub>c</sub>, gamma, TL, ΔCD/ΔDose, and the etch rates for the different types of resist system.

As a recapped for the experiment, best results for PMPS/Novolac for 0.28 develop normality are: D<sub>c</sub> = 16 μC/cm<sup>2</sup>, gamma = 0.071, TL ~ 500 Å, and ΔCD/ΔDose = 0.02 μm/(μC/cm<sup>2</sup>). The results for P(SI-CMS) in D<sub>c</sub>, gamma, TL, and ΔCD/ΔDose stayed relatively constant for different development

time. Which means P(SI-CMS) have a large process latitude.

For etch resistance, P(SI90-CMS10) seems to have the best etch resistance to O<sub>2</sub> and Cl<sub>2</sub>, but not very resistance to SF<sub>6</sub> due to its' silicon containing component. PMPS/Novolac and Shipley 812 have similar etch resistance due to their novolac containing components. PBS was not at all resistance to plasma etch due to thermally unstable and unstable to ionized radiation.

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