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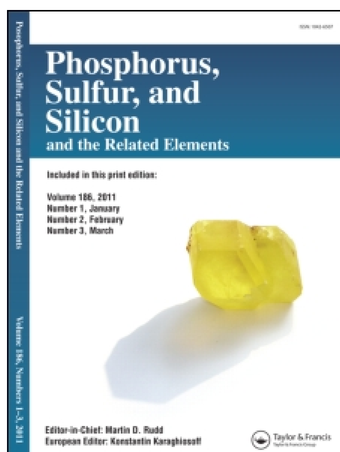

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The Application of Phosphazene Containing Polymers as Negative Resists in Microlithography

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THE APPLICATION OF PHOSPHAZENE CONTAINING POLYMERS AS NEGATIVE RESISTS IN MICROLITHOGRAPHY

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ABSTRACT New terpolymers containing phosphazene, epoxy and silicon moieties have been synthesized which were used as negative resists in microlithography. In addition to synthesis and characterization, lithographic properties are discussed.

INTRODUCTION

Reduction of feature sizes in VLSI (Very Large Scale Integrated) chips has resulted in the design of new techniques and resists which could fulfil the sub-micron dimensions of future DRAM's (Dynamic Random Access Memories)[1]. One of these new techniques consists of a double layer resist system with a radiation and acid sensitive silicon containing polymer film as the top imaging layer[2,3]. Using this double layer system with a silicon containing resist based on chemical amplification, the possibility is offered to create high resolution patterns with high aspect ratios combined with a high sensitivity[4].

EXPERIMENTAL

Polymerization

The synthesis of styrene substituted chlorocyclotriphosphazene, gem-methylvinylbenzyl-tetrachlorocyclotriphosphazene (STP), will be published

elsewhere[5]. The silicon containing macromers were synthesized as described in ref. 6. In the experiments described here a macromer with a molecular weight of 15000 $g.mol^{-1}$ (D = 1.3) was used as the silicon containing monomer (m1). Phosphazene containing terpolymers were synthesized using radical polymerization conditions (Scheme 1). Table 1 summarizes the characterization results of the polymers synthesized.

Pattern fabrication in phosphazene containing resists

A solution of 9.5 wt% terpolymer in PGMEA (1,2 propanediol monomethyl etheracetate) with 3 wt% triphenylsulfoniumhexafluoroantimonate, $(Ph)_3S^+SbF_6^-$, was spun on a silicon wafer, casted with a 750 nm thick hard-baked AZ-resist layer, and prebaked at 100 ^{0}C for 3 min on a hot plate to form a 300 nm thick layer. Electron beam exposure was carried out using an EBPG/03 (Philips) operating at 50 keV. After exposure the resist layers were postbaked at 90 ^{0}C for 3 min. The patterns were developed with PGMEA and subsequently etched in an oxygen plasma using a plasma reactor (Leybold Heraeus, Z-401) operating at 13.56 MHz in the RIE-mode (pressure 3 μbar, power 20 Watt, oxygen flow 20 sccm).

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RESULTS AND DISCUSSION

Scheme 1 shows the synthesis of the phosphazene containing terpolymers.

The terpolymers synthesized consist of three entities that are essential for their behaviour as negative resist in e-beam microlithography. First of all, the silicon containing branch is necessary for sufficient oxygen plasma resistance. During O_2-RIE the top layer of the silicon containing resist film is converted to SiO_2 that acts as a mask preventing further etching of the irradiated regions. The necessity of silicon has been tested using a copolymer of STP-glycidylmethacrylate (GMA) in a bi-level system. In this case, the created patterns were completely vanished after O_2-RIE. Secondly, epoxy moieties are required for a high sensitivity. The resist action is based on chemical amplification which means that upon irradiation an acid is generated which catalyzes the ring opening of the epoxy groups. A copolymer consisting of STP and m1 was not suitable as resist because no patterns could be

created after irradiation and development. Thirdly, incorporation of phosphazenes raises the Tg of the polymers by 20 ^{0}C which is an advantage since lithographic processes take place at high temperatures.

TABLE 1 Characterization results of the synthesized co- and terpolymers

	M_n (x 10^{-3})	D	Tg (^{0}C)	Elemental Analyses		
				Calc.	Found	
STP-GMA	57.5	2.1	95	19.16	19.29	(%Cl)
STP-m1	49.3	1.8	102	5.97	5.47	(%N)
STP-GMA-m1[a]	70.0	2.1	90	11.65	12.76	(%Cl)
STP-GMA-m1[b]	65.0	2.0	95	18.01	18.28	(%Cl)

a Terpolymer **1** containing 33 wt% STP, 33 wt% GMA and 33 wt% m1
b Terpolymer **2** containing 47 wt% STP, 20 wt% GMA and 33 wt% m1

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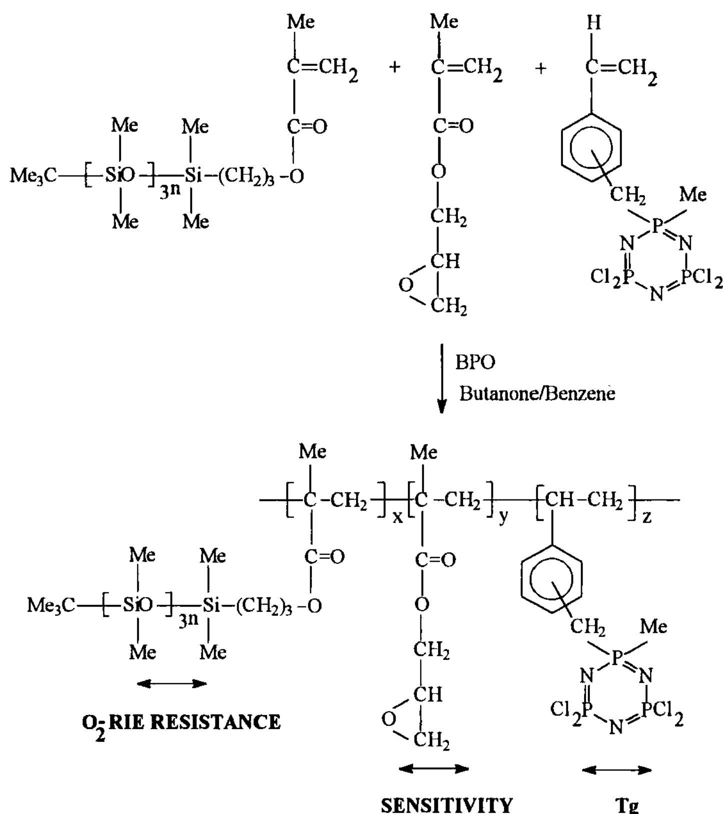
In addition to the effect of raising the Tg of the polymers, incorporation of phosphazenes enhances the lithographic behavior. Resolution of terpolymer **1** is limited to 1.0 μm as a result of swelling of cross-linked areas after development of the unexposed areas. Terpolymer **2** showed a higher resolution (0.5 μm) and less swelling. Raising the amount of phosphazene groups causes a 'diluting' effect that reduces the amount of epoxy groups that can take part in the acid-catalyzed cross-link reaction. Without phosphazenes, as an example a copolymer of GMA and m1, the cross-link reaction is not limited to the irradiated regions resulting in loss of resolution.

Sensitivities ($Dg^{0.5}$) for the terpolymers **1** and **2** equal to 18.0 μC/cm^2 and 23.0 μC/cm^2 at 50 keV, respectively. Terpolymer **1** possesses a contrast value of 1.4 whereas terpolymer **2** shows a value of 1.1 as a result of the decreased amount of epoxy groups.

The oxygen etch ratios of the terpolymers **1** and **2** compared with AZ-type resists are 10 and 12, respectively. These etch ratios are sufficient to withstand the oxygen RIE necessary for removing the underlying AZ resist layer in a bi-level resist system. Further studies are in progress to determine the effect of phosphazene and epoxy content that may lead to subhalf micron patterns in e-beam lithography.



SCHEME 1 Synthesis of phosphazene containing terpolymers

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