Silicon Containing Organic-Inorganic Hybrid Materials as EUV Photoresists

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The opportunities posed by extreme ultraviolet (EUV) lithography are encouraging the development of new resist platforms. The absorbance characteristic of materials required for the EUV lithography demands the use of polymers containing highly transparent silicon atoms. At the same time, very low levels of outgassing of silicon containing fragments are required due to the vacuum environment present during exposure and the extremely high cost of the EUV tools. These two contradictory requirements have led us to pursue new types of silicon containing hybrid materials as a resist platform; chemically amplifiable polysilanes and silsesquiazanes. In the former case, the direct incorporation of acid sensitive groups into the polymer backbone allows for a solubility switch upon exposure. In the later system, a silicon-nitrogen backbone structure can be cleaved upon exposure to induce a solubility switch. These hybrid materials possess many useful properties including low absorbance, low outgassing, and high sensitivity. Silsesquiazanes having different substituents and branching ratios were synthesized. The properties of the polymers will be discussed in the context of their lithographic performance.

Keywords: EUV lithography, silicon-containing polymer, hybrid materials, polysilanes, silsesquiazanes

1. Introduction

Ongoing efforts for last 4-5 years on Extreme UV lithography (EUVL) have made this technique a contender for next generation lithography (NGL). Many barriers related to the light source, materials for the optical system and tools have been removed. Several prototype tools capable of 40 nm resolution have already been introduced to help researchers fully develop the technology for implementation around 2010.[1] Resist research has drawn relatively less interest from researchers because of the initial belief that traditional deep UV resists could be extended to EUVL. Since EUVL targets very small 40 nm feature size, a thinner film will be used considering the aspect ratio of the prepared pattern. With this reasoning in mind, people believed that the use of thinner films would eliminate the necessity for low absorbance. However, it is now understood that very low absorbance is required to achieve good side wall

profiles in EUVL. Therefore there is a renewed focus on preparing polymers having high transparency, and developing suitable EUV resists thus becomes one of the top materials issues that must be addressed. Because of the high energy level of the EUV beam, the absorbance of materials is related to their atomic composition instead of the bonding characteristics between them.[2] This simple characteristic makes it possible to design new highly transparent materials by reducing the atomic concentration of highly absorbing elements like O and F. Another important requirement for EUV resists is very low levels of outgassing. Outgassed materials can deposit on optical structures thereby reducing their reflectivity and lifetime. This is especially undesirable both because of the operational conditions of EUVL requiring exposure with very high energy under ultra high vacuum, and the very high cost of EUV tools. However, for the systems

studied to date, these requirements seem out of reach.

In our early studies, we tried to modify the conventional polymer systems used in previous generation lithography with low EUV absorbing elements. Based on a theoretical calculation of elements at this wavelength, silicon and boron were selected as those highly transparent elements. The modified hydroxystyrene based polymer systems met the requirement for high transparency along with high sensitivity and good imageability. [3] However, there was a concern about outgassing of silicon containing organics because the silicon was incorporated into the polymer as a simple substituent on the phenylene ring. This concern was based on previous studies of similar systems at the 193 and especially 157 nm exposure tests. The best silicon-containing polymer systems in terms of outgassing at 193 and 157 nm are silsesquioxane-based, but these have too high oxygen content to be applicable to EUVL. We have been looking at other silicon polymers as resists that could fulfill the requirements of EUVL. These systems include polysilanes, and polysilazanes. Strategies for modification of polysilanes with acid sensitive moieties have been developed to introduce chemical amplification features. Silsesquiazanes, a branched form of polysilazane with the general formula of $[\text{Si}_2(\text{NH})_3]_n$, have also been prepared as an analogue of silsesquioxanes. [4] Polysilazanes and silsesquiazanes have been used with various types of lithographic techniques, but in most methods they were used as a negative type of resist. [5], Although they lack oxygen, they are intrinsically acid sensitive, making them good candidates for oxygen-free positive tone resists. [6] The performance of these polymers as EUV resists is discussed with an emphasis on outgassing, transparency, imageability, and sensitivity.

2. Experimental

2.1 Characterization

IR spectra of samples were obtained with a Mattson Infinity Gold series FTIR as thin films coated on a sodium chloride cell or a silicon wafer. ^1H and ^{29}Si NMR spectra were measured in CDCl_3 . Spectra were recorded on a Varian Inova-400 spectrometer (400 MHz). For quantitative analysis of ^{29}Si NMR, chromium triacetylacetonate was used as a relaxation enhancer. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions of the resulting polymers. It was performed using a Waters liquid chromatograph system with a Waters 410 differential refractive

index detector using tetrahydrofuran as an eluent.

2.2 Materials

Silane compounds including dichloromethylphenylsilane, methyltrichlorosilane, dimethyldichlorosilane, chlorotrimethylsilane, phenyltrichlorosilane, and cyclohexyltrichlorosilane were obtained from commercial suppliers and used without further purification. Toluene, triflic acid, *tert*-butyl acetate, triethylamine, pyridine, methylene chloride, benzene, and ammonia were obtained from commercial suppliers as moisture-free.

2.3 Synthesis of Polysilane

Poly(methylphenylsilane) (PMPS) was synthesized following the standard Wurtz coupling reaction as previously described. [7] Poly(methylphenyl-*co*-methyl-*tert*-butylacetyl silane) (PMPMBAS) was synthesized from PMPS as follows: PMPS (1.9 g, 15.8 mmol) was dissolved in dry toluene (70 mL) inside a 100 mL air-free glass tube. The solution was cooled in ice, and triflic acid (0.70 mL, 7.9 mmol) was added dropwise under dry nitrogen using a syringe. The mixture was allowed to warm to room temperature and stirred for 3 hrs. Then a toluene solution (5 mL) of *tert*-butyl acetate (1.0 mL, 7.8 mmol) and triethylamine (1.1 mL, 7.8 mmol) was added dropwise using a syringe. The mixture was stirred for another 3 hrs and the polymer obtained by precipitation from methanol.

2.4 Synthesis of Silsesquiazane

To a three-neck flask equipped with gas inlet and condenser were added chlorosilanes in a predetermined ratio under moisture-free nitrogen. The mixture was diluted with a solvent to about 10% of silanes by weight. The mixture was cooled to 0 °C under constant stirring, and ammonia gas was introduced. After 3 hours of reaction, excess ammonia was removed by flowing nitrogen, and white solid salt was removed by filtration under nitrogen. A removal of solvent from the filtrate under vacuum rendered crude silsesquiazanes. The phenyl- or cyclohexyl- substituted silsesquiazanes with high T_g were dissolved in tetrahydrofuran and purified by successive precipitations from hexane or methanol. The resulting white powder was dried under vacuum overnight and stored in a drybox.

2.5 E-beam Lithography

The resist solution of polymer and photoacid generator (PAG) in propylene glycol methyl ether acetate (PGMEA) was prepared. To get a film with ~125 nm thickness, 7 % of polymer solution

in PGMEA was used. Triphenylsulfonium nonaflate (5 weight % to polymer) was used as PAG. The solution was spin coated on to untreated silicon wafer, and baked at 115 °C for 1 min. E-beam exposure was conducted using a Leica VB-6 e-beam tool operating at 100 KeV.

Hybrid polymers containing the inorganic elements, silicon and boron, were prepared as an initial solution to the high absorbance of organic polymers, including those for the previous generations of photoresists. Those polymers, where inorganic components are added as side chains, showed excellent performance as photoresists on testing at 248 nm. However, since there was a concern over outgassing of silicon-containing fragments during high energy EUV exposure in vacuum, we have developed a new generation of silicon containing materials based on silicon backbone polymers. These hybrid materials showed excellent absorbance properties in the EUV region (Fig. 1). Compared to conventional resist platforms like polyhydroxystyrene or polytrimethylsilylstyrene, silicon backbone polymers showed lower absorbance values at 13.5 nm, except for siloxanes that contain highly absorbing oxygen atoms. Even though the linear silicon backbone polymers possess excellent transparency, they could not be used as resist materials due to their low glass transition temperatures (usually $< 0\text{ }^{\circ}\text{C}$). [8] From these observations, we selected two platforms as our targets, polysilanes and silsesquiazanes.

Polysilanes have high T_g values thereby providing enough dimensional stability, even though they have a simple linear structure. Silsesquiazanes, a Si-N analogue of silsesquioxanes, have a branched structure, ideally a bridged ladder type and this increases T_g of the materials.

As reported in prior work, [3] the incorporation of chemically amplifiable units into a polysilane would allow their application as a resist material. In that initial study, we photochemically synthesized polysilane acrylate copolymers, where the acrylate section confers chemical amplification attributes to the polymers. Although, the strategy did produce chemically amplifiable resists, issues involving solubility in developer solutions was found. To address this issue we synthesized polysilanes in which a polar unit, like *n*-butylacetate, was incorporated into the silicon backbone. [9] Using similar strategies, we synthesized *tert*-butylacetate-modified polysilane. This polymer could introduce chemical amplification characteristics directly into the polysilane backbone and also give improved

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Fig. 3. ^1H -NMR spectrum of *tert*-butylacetate-modified polysilane

solubility in PGMEA. The synthetic strategy is presented in Fig. 2. The polymer shows the expected band in both FTIR and ^1H -NMR (Fig. 3). The ratio of incorporation was changed to fine tune the properties of the polymer. After incorporation of the acetate unit, a marked increase in solubility in polar solvents was observed. Previously, PGMEA-insoluble polysilanes (PMPS) became fully soluble in this solvent after chemical modification. Optical quality thin films could be easily deposited from PGMEA solutions.

Lithographic characteristics of the modified polysilane polymer were evaluated using E-beam lithography (Fig. 4). It was found that doses on the order of $150 \mu\text{C}/\text{cm}^2$ were necessary to create an image. The results prove that the concept of chemical amplification is feasible but some fine tuning is still needed to improve the resolution of

Fig. 4. Optical image of PMPMtBAS resist. Dose $150 \mu\text{C}/\text{cm}^2$. PEB: 115C. Developer: TMAH (0.26N) : isopropanol (2:1) 2 min.

the resist to achieve the desired critical dimensions for EUVL.

Polysilanes have been thought of as good materials for lithography. However they were principally thought of as a top layer in a bilayer resist system or as an e-beam resist.[10] With the advent of EUVL, polysilanes may be contenders for this technology. Although the Si-Si bond in polysilanes is photosensitive at 248 nm, studies have shown that it can withstand irradiation at 13 nm (91 eV) without outgassing silicon containing material.[11] We have tested a PMPS-acrylate copolymer using EUV beam and it has not shown significant outgassing of silicon containing fragments (Table 1). This is encouraging, especially when compared to acrylate or styrenic polymers with silicon side chain units in which the Si-C bond can be easily broken. It appears that at EUV wavelengths, the major concern would be outgassing of carbonaceous material. We are currently studying specific means to reduce any outgassing concerns.

Table 1. Outgassing test of PMPS-acrylate copolymer using EUV beam.

Detected compound	Concentration (molecules/ cm^2)	Percent
Benzene	7.69×10^{13}	90.36
Toluene	2.17×10^{12}	2.55
Dimethylbenzene	1.09×10^{12}	1.28
Ethylmethylbenzene	8.29×10^{11}	0.97
SO ₂	7.25×10^{11}	0.85
Trimethylbenzene	5.61×10^{11}	0.66
Fluorobenzene	4.31×10^{11}	0.51
Isobutene	3.49×10^{11}	0.41
Diphenyl sulfide	2.88×10^{11}	0.34
Acetone	2.42×10^{11}	0.28
Ethylbenzene	2.41×10^{11}	0.28
Xylenes	2.25×10^{11}	0.26
Benzaldehyde	1.88×10^{11}	0.22
Unknown	1.43×10^{11}	0.17
Sub benzene	1.31×10^{11}	0.15
Acetophenone	1.26×10^{11}	0.15
<i>tert</i> -butylbenzene	9.92×10^{10}	0.12
Unknown	9.21×10^{10}	0.11
Styrene	8.77×10^{10}	0.10
1-methylindan	7.63×10^{10}	0.09
Unknown HC	7.12×10^{10}	0.08
TOTAL	8.51×10^{13}	100

Fig. 5. Reaction Scheme for the synthesis of PSSQZ

3.2 Polysilazane based resists

Polysilazanes or silsesquiazanes (SSQZ) are silicon polymers similar to polysiloxanes or silsesquioxanes, in which the oxygen atoms of polysiloxanes have been exchanged for nitrogen. In the synthetic procedures used a chlorosilane precursor is condensed with ammonia to produce branched polymers. The general synthetic procedure is presented in Fig. 5.

One of the issues with SSQZs is their hydrolytic stability and T_g . To control these properties, SSQZs with methyl and phenyl substituents were prepared (Table 2). The hydrolytic stability of SSQZ dramatically improved by increasing the content of phenyl substituted chlorosilane. SSQZs with lower phenyl content (SSQZ-5 and -6) gelled even during solvent removal. On the other hand, SSQZs with more phenyl substituents showed good hydrolytic stability, and the 100% phenyl substituted material (SSQZ-1) is very stable to hydrolysis, showing no difference in solubility in organic solvent after being stored on the benchtop for several months. The T_g of SSQZ also increased with increasing phenyl content. The bridging density also affects the T_g of the SSQZ. When dichlorodimethylsilane (SSQZ-3) is used instead of trichloromethylsilane (SSQZ-2), the T_g of the resulting materials was lower due to its reduced bridging density. Another property that should be noted is the effect of the end group. SSQZ-2 with trimethylsilyl end groups has a lower T_g than SSQZ-4 without that end group,

even though the former has a higher content of phenyl substituted silane.

In a conventional chemically amplified system, the acid catalyst that drives the deprotection reaction is generated during the exposure process, while the deprotection takes place with thermal energy during the post exposure baking process. The parameters governing the degree of acid formation are temperature and time of baking. Likewise, in SSQZ, the catalyst (acid) is generated from the PAG on exposure. However, the acid formation reaction (hydrolysis) for SSQZ requires of H_2O as an additional component, so the relative humidity is another important parameter affecting image formation. In this scheme, the sensitivity of a resist could be controlled by changing three variables during post exposure steps: relative humidity, hydrolysis temperature and hydrolysis time. At our facility the relative humidity is maintained at approximately 40% and room temperature is controlled at 25 °C. Because it is relatively easy to control, we mainly tried to use post exposure time delays as a variable to ensure complete chemical change.

SSQZ with 50% methyl and 50% phenyl substituents (SSQZ-4) was tested using e-beam lithography. To determine optimal exposure, the dose was checked keeping the post exposure delay condition fixed. Over the dose range studied, 50 ~ 450 $\mu\text{C}/\text{cm}^2$, the optimal dose was found to be 100 ~ 150 $\mu\text{C}/\text{cm}^2$. Next, using a fixed dose of 100 $\mu\text{C}/\text{cm}^2$, the effect of the humidity was tested (Fig. 6). It was found that by changing the relative humidity from 40% to 60% the pattern was not completely cleared after 5 min, overexposed after 10 min and showing smeared images near boundary areas. The best approach was to keep the humidity at 40%, but extend the post exposure delay time to 50 min (Fig. 7a). The resulting image was better but there was still some level of diffusion to the unexposed area. The contrast between exposed and unexposed regions was improved by using a diluted developer (0.13 N TMAH). Using these conditions, it was possible to produce images down to 50 nm (Fig. 7b).

Table 2. Properties of prepared SSQZs

	T_{Ph}	T_{Me}	M_n ; PDI	T_g (°C)
SSQZ-1	100	0	2,700; 3.38	213
SSQZ-2*	80	19	2,100; 3.19	181
SSQZ-3*	80	19**		155
SSQZ-4	50	50	3,200; 2.47	192
SSQZ-5	20	80	gelled	-
SSQZ-6	0	100	gelled	-

* including 1 portion of M_{Me} (trimethylsilyl chloride)

** dimethyldichlorosilane (D_{Me}) was used instead of T_{Me} .

Fig. 6. Effect of Post Exposure Delay Conditions (a) 5 min at 60% RH (0.26 *N* TMAH developer) (b) 10 min at 60% RH (0.26 *N* TMAH developer) (c) 40 min at 40% RH (0.26 *N* TMAH developer) (d) 40 min at 40% RH (0.13 *N* TMAH developer).

We believe SSQZ is a promising resist material requiring continued study of issues such as modification of the structure by changing molecular weights, branching ratios, and substituents. These structural modifications will enhance polymer properties, including thermal and atmospheric stability. Since hydrolysis after exposure is very important for this new system, we are also trying to establish the relationship between structural variation and hydrolysis conditions, such as relative humidity delay, time, and temperature to achieve optimal conditions for high resolution images.

4. Conclusion

In this work we have described several approaches taken to silicon containing organic-inorganic hybrid materials as a photoresist in EUVL. The versatility of silicon backbone polymers allows specific modification to enhance properties like acid sensitivity and solubility in aqueous base, two key properties for lithography. *Tert*-butyl protected polysilanes have shown promising results to be used as chemically amplifiable resists, where the process is controlled by the photoacid instead of the photosensitive polymer. Silsesquiazanes have also shown

Fig. 7. E-beam images using PSSQZ. (a) Post exposure delay, 50 min (0.26 *N* TMAH developer). (b) Post exposure delay, 50 min; at room temperature (0.13 *N* TMAH developer).

excellent lithographic performance in e-beam lithography. Since SSQZs require new post exposure steps for image formation, more studies on the hydrolysis step should be performed to find the optimized process conditions for the ultimate performance of the materials. More testing at EUV wavelength is needed, but preliminary e-beam results are encouraging showing that silicon containing hybrid type positive tone resists are good candidates for EUVL.

Acknowledgements

This research was supported by Intel Inc. Lithographic studies using an e-beam tool were performed at the Cornell NanoScale Science & Technology Facility (CNF), which is a member of the National Nanofabrication Users Network and supported in part by the National Science Foundation.

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