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Bilayer Resist

for Sub-65 nm Lithography

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With immersion lithography gaining acceptance, 193 nm lithography is being investigated for use in sub-65 nm technology nodes. As feature sizes continue to shrink, thin imaging layers are required to deliver high resolution and sufficiently wide process windows. Therefore, the etch selectivity in pattern transfer becomes a critical concern.

Several different types of processing schemes have been proposed to meet the increased etch resistance demands, including multilayer resist (MLR) and bilayer resist (BLR) processes. One of the most desirable aspects of the MLR process is that it typically uses a single-layer resist for imaging. An underlying, ultrathin inorganic layer acts as a hard mask during the etch pattern transfer step. This hard mask layer can be a silicon-con-

taining, spin-coatable polymer or CVD film. The third layer is typically an organic film. The key disadvantage to MLR approaches is the complexity that arises from the need for three separate layers and the requirement to integrate the processing steps for good imaging and pattern transfer.

The bilayer approach is a promising alternative to the MLR scheme. Various types of BLR systems have been developed and previously reported involving acrylate,^{1,2} cyclic-olefin maleic anhydride,^{3,4} vinyl ether maleic anhydride^{5,6} and poly(silsesquioxane)⁷⁻¹⁰ resist platforms. All the chemistries developed in

these studies have advantages as well as limitations. The two properties of primary concern are etch resistance and image resolution. Optimization of the etch resistance typically has been achieved by increasing the weight percent of silicon in the polymer.¹¹ Image reso-

lution has been obtained by balancing the various chemical components and functionalities within the polymeric system, such as the amount of protecting group and base solubilizer.

Another important polymer property of interest is the glass transition temperature caused by the predominate use of the chemical amplification mechanism for image formation. The desire has been to develop a high-silicon-content polymer backbone that has not only the same image-forming properties as a well-understood single-layer resist, but also the ability to resolve fine images for film thicknesses approaching 50 nm. This is only possible by adjusting the polymer structure to give both resolution and high etch resistance.

Outgassing of silicon-containing components during 193 nm exposure is a major concern of silicon-containing polymers and the topic of many research studies.^{8,12-15} Pendant silicon groups can be cleaved during exposure, causing silicon-containing moieties to outgas and possibly deposit on the optics of the exposure tool.⁴ However, poly(silsesquioxane)-based photoresists are not prone to outgassing be-

At a Glance

A new class of photoresists with high silicon content (23 wt%) achieved 55 nm features with high etch resistance and low line edge roughness. It also demonstrated compatibility with the immersion lithography process.

cause of the incorporation of silicon in the polymer backbone and bonding to multiple oxygen sites within the polymer structure.⁸

Working in close collaboration, lithography experts at TOK and silicon chemistry experts at Dow Corning developed a high etch resistant, high glass transition temperature ($T_g \sim 135^\circ\text{C}$) BLR system capable of imaging films as thin as 50 nm, while maintaining the ability to transfer the images to the thick underlayer during the etching step. Silicon contents of >23 wt% were effectively incorporated into the polymer backbone by optimization of the silsesquioxane (SSQ)-based structure. As with other poly-SSQ-based polymer systems, placement of silicon into the polymer backbone allows the incorporation of very high levels of silicon, with no detectable levels of outgassing, which will be shown.

The structure and composition of SSQ-based resin were determined (Fig. 1). High-silicon-content resins were formulated, and the values of n , m , x and y , ranging from 0.0 to 0.5, were optimized for best lithographic performance. For example, a unique base solublizer was selected not only to maximize dissolution rate upon exposure, but also to provide high silicon content.

Etch resistance

The optimized resin system has a silicon content of ~23 wt%, and the formulated resist has a silicon content of ~21.5 wt%. The silicon-containing ratio was higher than that of currently reported SSQ-backed BLRs.⁸⁻¹⁰ Etch rate by O_2/N_2 (60/40) gas in an ICP chamber demonstrated gradual saturation. Resins with >15 wt% silicon are etch-resistant enough for pattern transferring to the phenol-based bottom layer. For the resist with the

silicon content of 21.5 wt%, the initial etch rate of the resist is 11 nm/min (first 60 sec), and the etch rate of bottom layer is 127 nm/min (first 60 sec).

In actual etching of the bottom layer, the etching time is longer than it was in blanket etch tests. In the case of a 300 nm thickness of bottom layer, 144 seconds were needed to clear the film under our standard etching conditions. The etch rate of the bottom layer was found to be independent of etching time and almost constant. On the other hand, the etch rate of the silicon-containing resist strongly depends on etching time. For example, during the first minute, the average etch rate was determined to be 11 nm/min, but during the second minute, the etch rate averaged 7 nm/min, and during the third minute, the average etch rate was 5.5 nm/min. From these results, the selectivity was determined to be ~20:1 just as the film cleared. Even at a 50 nm thickness for the imaging layer, the etching tolerance (resistance) was high enough for pattern transferring to a 210 nm bottom layer.

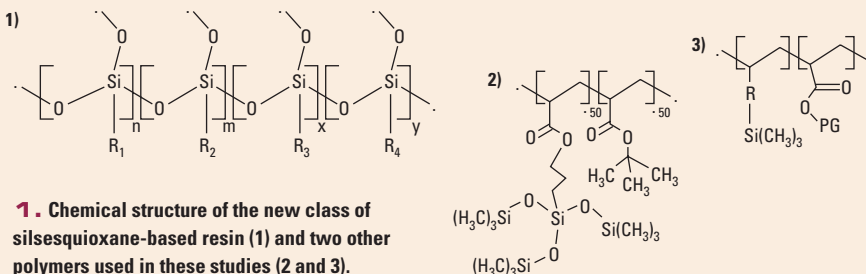
Figure 2 demonstrates the resist's superior etch resistance and pattern-transfer capability. A 90 nm thick film at a pattern size of both 110 nm and 70 nm could be effectively transferred to the 225 nm bottom layer with a loss of only 11 nm of photoresist. The transferred CD is within 5 nm of the imaged top layer.

Outgassing concerns

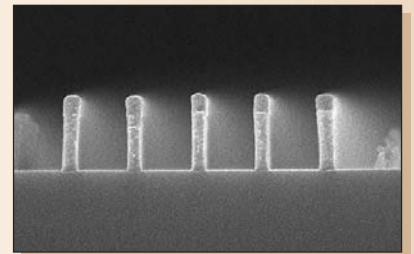
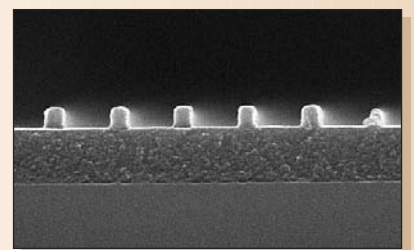
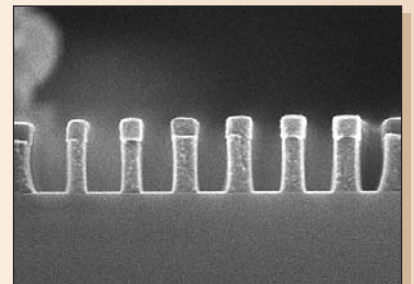
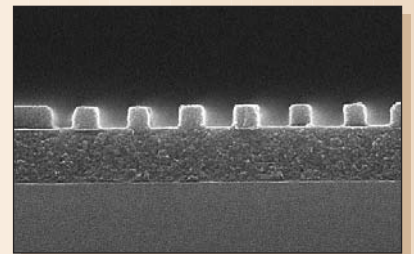
Outgassing exists almost unavoidably in all ArF lithographic processes because the 6.4 eV (193 nm) photon energy is high enough to activate organic photochemical reactions that are not possible at longer wavelengths. This may not be a major concern for single-layer applications, since the low-level organic species can be purged with nitrogen. On the other

hand, outgassing remains one of the main concerns for the implementation of a bilayer lithographic process in production, because the silicon species generated during irradiation could potentially contaminate the optics irreversibly. Recent studies,^{8-10,14} however, have shown that the structure (or location of silicon atoms) within the silicon-based polymer is critical to the outgassing of silicon species during the UV exposure, and that no detectable outgassing of silicon is observed if silicon is incorporated into the polymer backbone as in SSQ-based resins. The outgassing study in this report was per-

SILICON-CONTAINING POLYMERS



1. Chemical structure of the new class of silsesquioxane-based resin (1) and two other polymers used in these studies (2 and 3).



2. Patterning of 110 nm lines/spaces (L/S, top) and 70 nm lines with 265 nm pitch (bottom).

formed to confirm that the developed SSQ-based resists have little or no outgassing compared to silicon-containing resists in which silicon species are contained in pendant group positions.

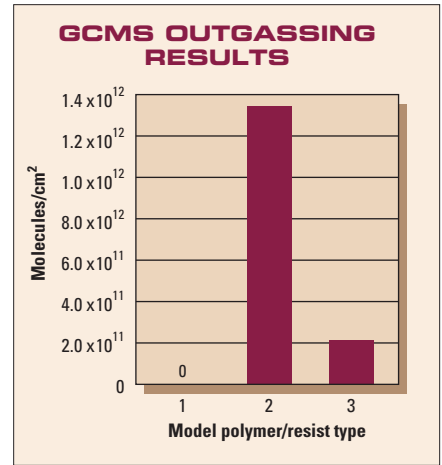
Outgassing experiments were carried out for the SSQ-based resist (1), along with model resist compounds shown in Figure 1. The polymers (2) and (3) consisted of acrylate-polymer backbone with a siloxane or a silane (silicon) pendant group, respectively. On the other hand, the polymer (1) is an SSQ-based resin with silicon incorporated into the backbone. The polymers were formulated with photo acid generators (PAGs), quenchers and other additives in the solvent propylene glycol methyl ether acetate (PGMEA). For outgassing studies, the films

3. Only the new resist, with silicon in the backbone of the polymer, had no detectable levels of outgassing on 193 nm irradiation.

The major species detected upon exposure were hexamethyldisiloxane ((CH₃)₃SiOSi(CH₃)₃) for 2 and fluorotrimethylsilane ((CH₃)₃SiF) for 3. These observations are consistent with their molecular structures, and are in good agreement with other literature reports.

Lithography performance

Our ArF BLR platform demonstrated good etching capability. We optimized the resist formulation for 100 nm thickness with a resin platform that has >20 wt% silicon content. This platform was evaluated with a trench pattern. Figure 4



a 250 nm thick bottom layer. After coating, the resist film was exposed with a 193 nm two-beam interference exposure system (Nikon LEIES 193-1). DI water was used as fluid media. The 45 nm lines and spaces were patterned for a calculated NA of 1.07 (Fig. 6).

To confirm the capability of pattern transfer with immersion, etching was demonstrated on a 55 nm L/S pattern. Figure 7 shows post-develop and post-etch results.

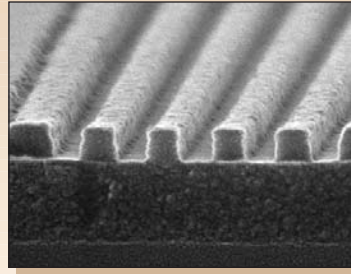
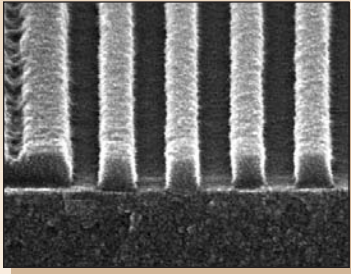
Conclusions

Collaborative work between two companies gave rise to a new class of SSQ-based resists with high silicon content for bilayer applications at 193 nm. The lithographic evaluation showed that the lithographic performance was good, but with much higher etching resistance, lower LER and higher etch selectivity to the bottom layer than was achieved with previous bilayer approaches. We also demonstrated that an imaging layer of 60 nm was thick enough to allow for the pattern to be transferred to a 210 nm bottom layer. A 45 nm L/S pattern

was achieved under immersion lithography conditions for a calculated NA of 1.07, and a 55 nm etched pattern could be observed.

In addition, for these SSQ-based resists, there was no silicon outgassing species detected when exposed to 193 nm light. •

5. Depth of focus is quantified, and the linewidth roughness is <5 nm (3σ=4.6 nm).



4. 80 nm L/S using a 100 nm silicon-based top resist and 210 nm bottom layer (0.78 NA dipole illumination).

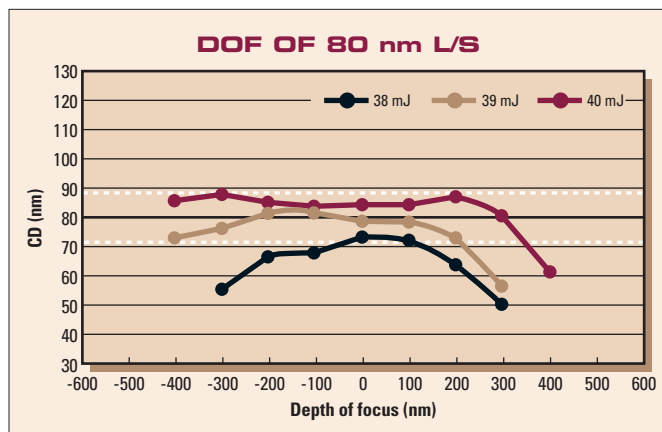
were cast on bare silicon wafers, followed by baking at 85-110°C for 90 seconds.

Outgassing species were observed for all three samples cast from polymers 1-3 because of the deprotection chemistry that occurred on UV exposure. The major species detected were organic fragments and/or derivatives of the protection groups (isobutene or cyclohexene and their derivatives or isomers, etc.), PAGs (benzene, sulfonium salts, etc.), and quenchers (amines, etc.).

However, what set apart the three polymers studied were the silicon species detected (Fig. 3). For polymers 2 and 3, significant silicon species were detected on irradiation, corresponding to 1.33×10^{12} molecules/cm² and 2.12×10^{11} molecules/cm², respectively. For polymer 1, no silicon species was detected using the gas chromatography mass spectrometer (GCMS) used throughout this study.

shows the 80 nm line and space (L/S) pattern using a 100 nm top resist on a 250 nm thick bottom layer with 0.78 NA dipole illumination. The depth of focus was almost comparable to that of an ArF single-layer resist, with linewidth roughness (LWR) of <5 nm (3σ=4.6 nm, Fig. 5).

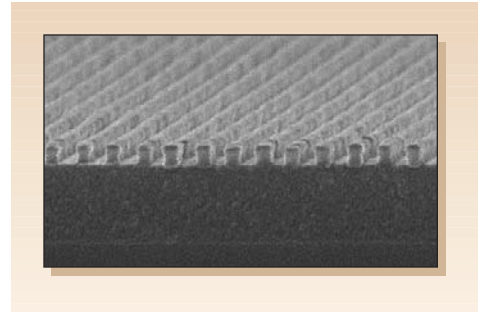
We also studied the possibility of using BLR for immersion lithography. We used the same resin platform with the resist coated at 60 nm (85°C bake) thickness on



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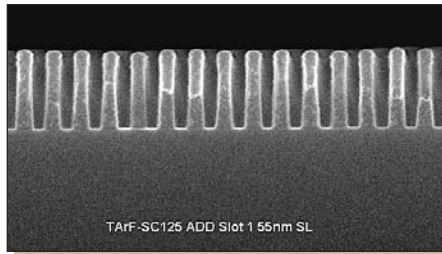
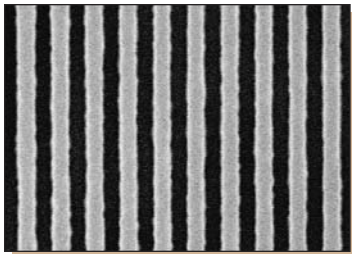
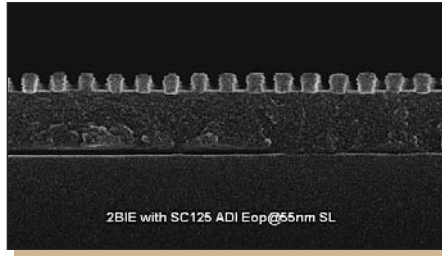
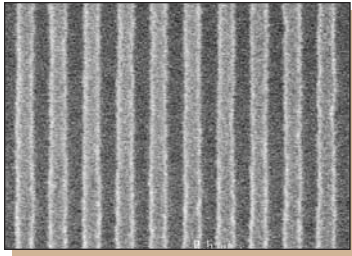
6. 45 nm L/S pattern using a dual-beam interference exposure system (calculated NA=1.07).

Vol. 18, No. 3, p. 1306.

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7. 55 nm L/S after first layer patterning (top) and after etch (bottom).

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