Properties and Performance of Molecular Glass Photoresists

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Abstract:

Molecular glasses are small molecules that have the ability to form amorphous films. They are promising candidates as low line-edge roughness resists because of their small size compared to conventional polymeric photoresists. This is especially important as the critical dimensions of photoresist features become even smaller.

The objectives of this project are to find the right processing conditions and to evaluate their plasma etch resistance. Optimal exposure and development times were also found for these molecular glass resists. Profilometer measurements of resist film thickness were used in order to establish etch rates as well as post-development film thicknesses. 10x i-line stepper patterning was also performed to produce patterns for observation using SEM.

Introduction:

As smaller feature sizes are required for progress in the semiconductor industry and nanotechnology in general, new processes need to be developed in order to support these changes. The types of photoresist used are an integral part of the changes that occur with reduction of feature size.

Molecular glasses have many desirable properties. Their relatively small molecular size (1-2 nm), low crystallization tendency and exceptional uniformity give these glasses the ability to be incorporated into new photoresists for smaller features.

Molecular glasses are present in two varieties: positive tone and negative tone. Negative tone molecular glass resists require the use of a crosslinker molecule (Powderlink®) in order to create a polymer-like matrix upon exposure. (See Figure 1.)

Positive-tone molecular glasses work by having their tetrabutoxycarbonyl (tBOC) groups cleaved off when photoacid generator (PAG) replaces them with hydroxyl groups which can be dissolved in tetramethyl ammonium hydride (TMAH).

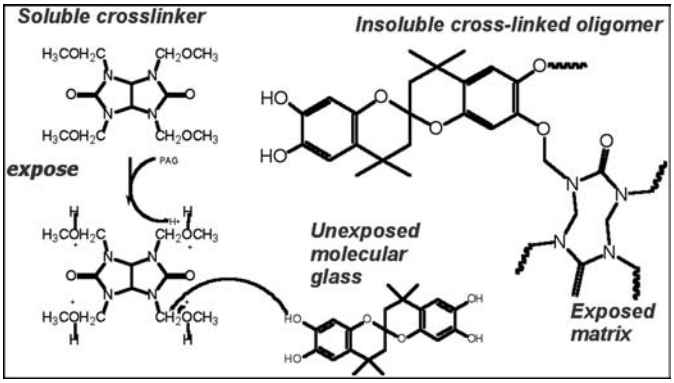

Figure 1: Schematic of a negative-tone molecular glass photoresist being exposed.

Experimental Procedure:

To prepare molecular glasses for dosage experiments, 10 percent (by mass) molecular glass and crosslinker (if necessary) were dissolved in propylene glycol methyl ether acetate (PGMEA) solvent. 5 mg photoacid generator (PAG) was then used per 100 mg of molecular glass. The resist was spun at 2000 rpm for 30 seconds. Positive-tone molecular glasses were spun onto HMDS primed silicon wafers whereas the negative-tone glasses were spun onto bare silicon. Exposure times of 0, 5, 20, 50 and 90 seconds were used on the 1.2 mW/cm^2 253 nm UV lamp with other times added as deemed necessary. Post-spin bake and post-exposure bake times and temperatures were held constant throughout the experiments.

Each molecular glass was subjected to an optimal development concentration test that involved varying concentrations and dilutions of 0.26N TMAH in H_2O. Film thickness measurements were subsequently taken by profilometer in order to establish contrast curves for the various molecular glass resists.

CHF_3/O_2 etching of the molecular glasses was done using polyhydroxystyrene, a polymer, as a standard. This was accomplished in 30s increments

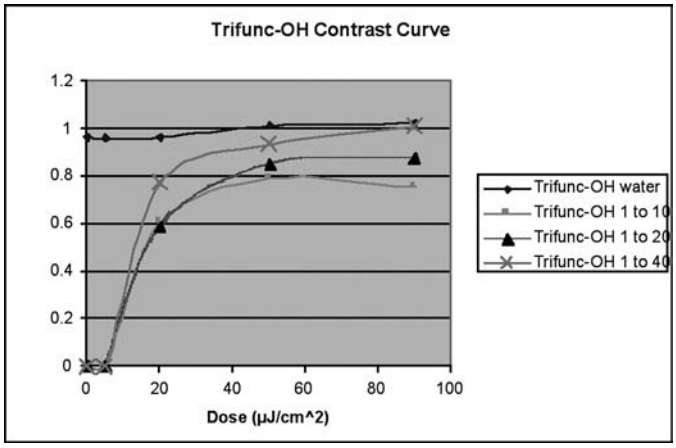

Figure 2: Negative-tone molecular glass contrast curve with various development concentrations.

with intermittent film thickness measurements until suitable etch rates could be determined for each of the molecular glasses after several minutes of etching.

Results and Conclusions:

The contrast curve of the particular molecular glass in Figure 2 demonstrates that a dilute solution of TMAH coupled with a UV light dose around 90μj/cm^2 provides optimal exposure and development conditions for this particular resist. Contrast curves were also developed for the other molecular glasses that had undergone experimentation.

The plasma etch rates in Figure 3 obtained for the molecular glasses were in the range of 20 to 30 nm per minute, which is a higher rate than desired. One particularly promising molecular glass demonstrated a lower etch rate around 10 nm/min.

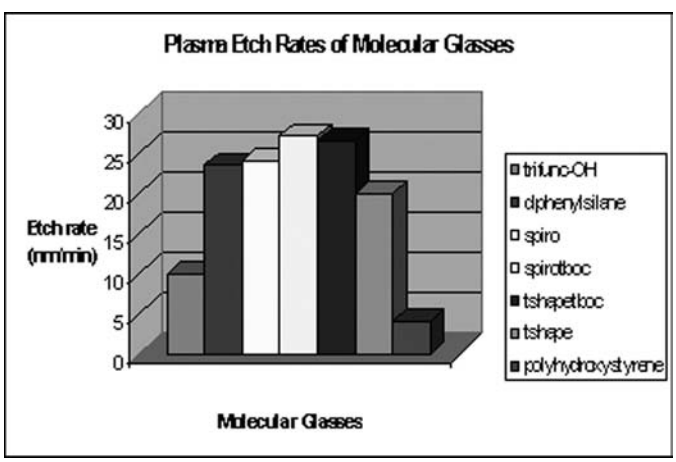

Figure 3: CHF_3/O_2 etch rates of molecular glasses against a polyhydroxystyrene standard.

SEM imaging of another resist (shown in Figure 4) was done after patterning on a 10x i-line (365 nm UV) stepper. This particular molecular glass resist has well-defined features and may very well be a viable alternative to polymeric resists. Further testing will need to be done on this resist in order to confirm this.

Future Work:

There is plenty of future work that can be done to further the characterization of these molecular glasses. Atomic force microscopy for line edge roughness, ellipsometer tests for refractive index and measurements for the dielectric constant of these films still need to be done to confirm the viability of these films in industrial applications. Additional patterning and etch work can be done as well as performing experimental runs on other molecular glasses.

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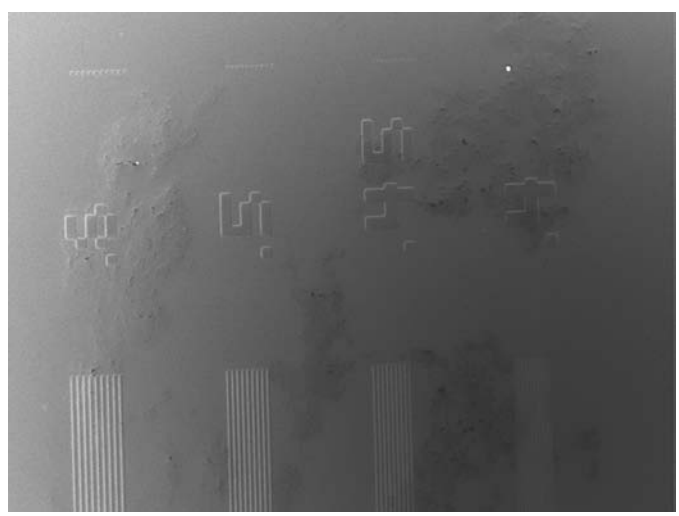

Figure 4: SEM of resolution lines taken with 10x i-line stepper.