Characterization and Acid Diffusion Studies of Cyclodextrin and its Carborane Inclusion Complex

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Abstract:

In order to move forward, the semiconductor industry is dependent on improvements in the lithographic process, most importantly the development of new resist materials. As pattern dimensions continue to decrease, issues of line edge roughness arise. Molecular glasses are an attractive alternative to polymeric resists, as they are able to incorporate an amorphous structure and high transition temperature (T_g) with a small size that can show improved line edge roughness. Cyclodextrin has shown promise as a 193 nm resist, though it exhibits poor etch resistance. By introducing carborane into the cyclodextrin core, we have shown that the etch resistance of cyclodextrin is around that of PHOST, an industry standard photoresist. However, we also see an increase in line edge roughness. We intend to observe the differences in acid diffusion between the non-carborane and carborane resist by creating bilayers and measuring film thicknesses before and after development. Using this data, we can now modify cyclodextrin core with carborane to inhibit acid diffusion and show improved patterning capability with high etch resistance.

Introduction:

tert-butyl ester protected methyl β cyclodextrin has been used as a 193 nm molecular glass resist and has good patterning abilities. Unfortunately, this resist exhibits poor etch resistance, so carborane was added. The addition of carborane increased the etch resistance to the equivalence of polyhydroxystyrene but increased the line edge roughness. We believe that the photoacid generator sits in the pocket of the cyclodextrin molecule, which inhibits the acid from diffusing beyond exposed regions. We hypothesize that the carborane sits in the cyclodextrin pocket, which blocks the photoacid generator's ability to do so, increasing the acid diffusion.

Experimantal Procedure:

Our studies were carried out using *tert*-butyl ester protected methyl β cyclodextrin, shown in Figure 1. Carborane was added to the cyclodextrin core, creating a host-guest complex. The complex was dissolved in Ethyl-l-Lactate to make a 5% weight solution. The photoacid generator used was triphenylsulfonium triflate (5% weight with respect to resist). We then spun this solution on HMDS primed silicon wafers. In order to find optimal post application bake (PAB) and post exposure bake (PEB) temperatures, we used a combinatorial tool. The setup consists of an aluminum plate with an ice bath and a hot plate on either end. The combinatorial tool allows us to have a temperature gradient across the wafer, so we can find the optimal PAB and PEB temperatures on one patterned wafer. The optimal exposure dose used for patterning was 30.45 mJ/cm^2. An ABM contact aligner with a 254 nm mirror was used to expose the resist and create patterns. Supercritical carbon dioxide ($scCO_2$) was used to develop the exposed resist, at 5000 psi for 5 minutes.

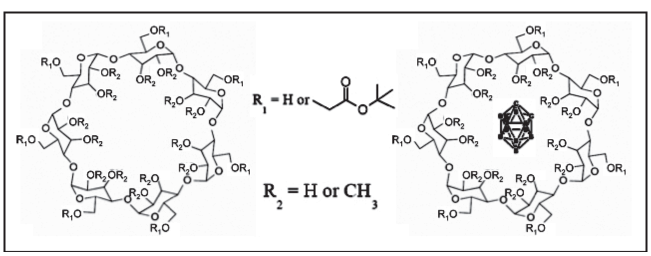

Figure 1: tert-butyl ester protected methyl β cyclodextrin without carborane (left) and tert-butyl ester protected methyl β cyclodextrin with carborane (right).

The acid diffusion studies were done using bilayers of resist, with and with out photoacid generator (PAG). Bilayers of resist were made by spinning the cyclodextrin resist with PAG on a silicon wafer. Next we spun cyclodextrin without PAG on a polydimethylsiloxane stamp that had been cleaned using oxygen plasma. The wafer and stamp were pressed together and let sit until fully wetted. Pressure and heat were applied for twenty seconds, and then the set was cooled. Finally the stamp was peeled off, leaving two layers of resist on the wafer, with the resist with PAG on the bottom. These were then exposed at varying doses and post exposure baked which started the diffusion of the acid. The wafer was then

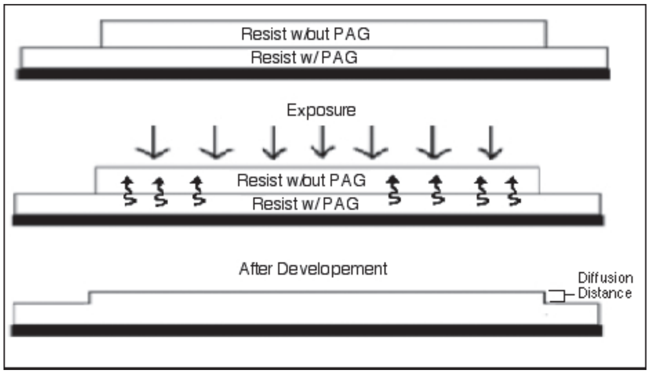

Figure 2: Patterns generated from the ABM contact aligner. Cyclodextrin without carborane on left and carborane complex on right.

developed using $scCO_2$ at 5000 psi for 5 minutes. With this type of development, the polar, or exposed portion of the resist remains, so the areas where the acid had traveled would also remain allowing us to see how far the acid diffused (Figure 2). Measurements were taken on the wafer with only the bottom layer containing resist with PAG, the wafer with both layers of resist, and after development on each exposure section. The vertical diffusion will replicate the horizontal diffusion, and we should be able to see a difference in diffusion between cyclodextrin with and without carborane.

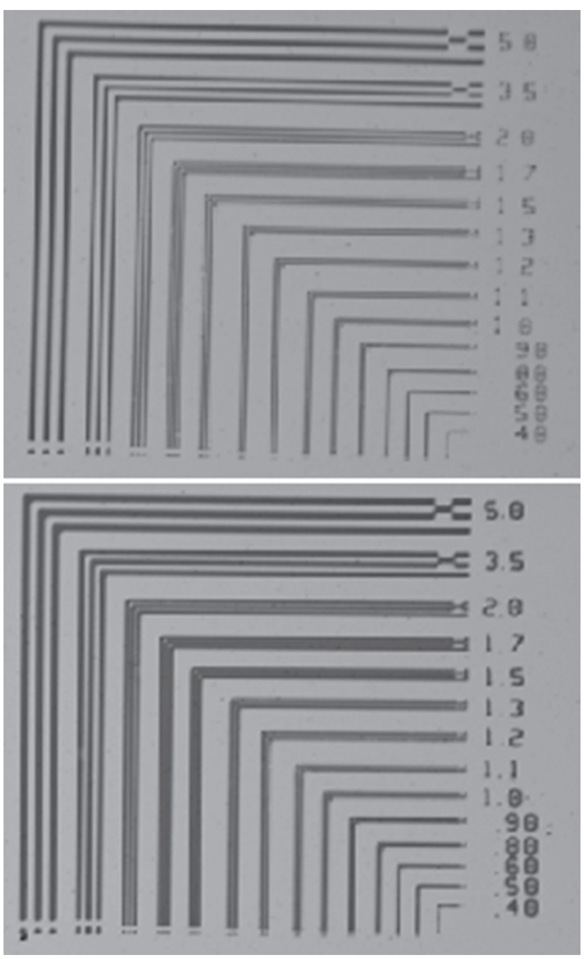

Figure 3: Diagram of bilayers.

Results:

Based on results obtained using the combinatorial technique, the optimal patterns for cyclodextrin without carborane (Figure 3, top) were observed at PAB of 109°C and PEB 99°C. The optimal patterns for cyclodextrin with carborane (Figure 3, bottom) were observed at a PAB of 107°C and a PEB of 99°C.

In order to obtain the data for the acid diffusion tests, we subtracted the resist thickness with PAG (no bilayer) from the resist thickness after development. We ran the experiment with the first batch of cyclodextrin, but the results were inconclusive. The second batch of cyclodextrin was more consistent and we can definitively say that the diffusion of acid is greater in the carborane complex than without carborane (Figure 4). Even when the swelling from development was taken into account, the data still showed that the acid diffusion was greater in the carborane complex.

Future Work:

Now that we have proven that acid diffusion is the cause of the patterns having greater line edge roughness, we can modify our cyclodextrin molecule to include PAG groups incorporated in the structure. This should decrease the acid diffusion so we can have a resist that is both etch resistant and produces high resolution patterns.

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References:

[1] Ito, Hiroshi. Chemical Amplification Resists for Microlithography, Advanced Polymer Science (2005) 172: 37–245.

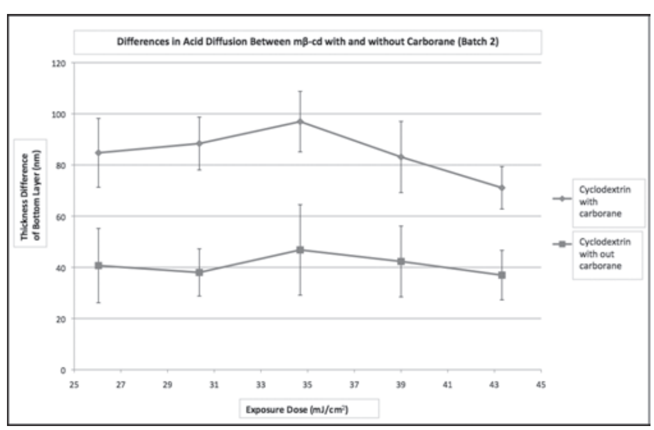

Figure 4: Batch 2 diffusion results.