Etch Resistance of Polymers used in Supercritical Carbon Dioxide Development

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Abstract:

Photoresists are commonly developed in such corrosives as tetra-methyl ammonium hydroxide. Supercritical carbon dioxide ($SCCO_2$) development offers a more environmentally-friendly alternative, as it is readily available for use and very easy to recycle or discard. Reactive Ion Etch testing, using oxygen and trifluoromethane gases, is being performed on photoresists that become soluble or insoluble in $SCCO_2$ upon ultraviolet exposure. The photoresists being analyzed include positive-tone fluorinated resists containing perflurooctyl methacrylate groups, negative-tone silicon-containing polystyrene-based resists and positive-tone polysilesquiazane resists.

Current research yields data that shows the fluorinated photoresists have the least etch resistance of the three sets previously mentioned. The silicon-containing polystyrene-based photoresists etch at about half the speed of the fluorinated resists, most likely due to their lack of fluorine and negative-tone behavior. This etch data is currently being used to further the characterization of these photoresists for their use in development in $SCCO_2$.

Introduction:

Research of $SCCO_2$ as a developer is dependent upon the photoresists used in the development process. The purpose of this research project is to investigate one of the fundamental process characteristics of photoresists used in development with $SCCO_2$. The specific photoresists discussed include those found to be soluble in $SCCO_2$—a set of fluorinated resists shown in Figure 1, a polystyrene-derived silicon resist and a polysilesquiazane resist.

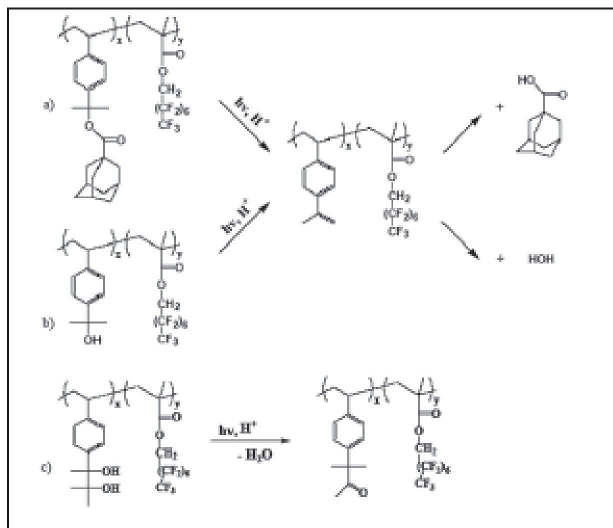

Figure 1: a) P1, b) P2 and c) P3 and their solubility switches.

Procedure:

Photo Acid Generators (PAG) and resist were dissolved in a 10% PAG to resist ratio in roughly 1 ml of solvent (methyl isobutyl ketone for silicon resists or triflurotoluene for fluorinated resists). Wafers (150 mm) were primed with HMDS for fluorinated resists, left clean for silicon resists. Photoresists were spun on a table-top spinner at 2000 or 2500 rpm. The wafers were post-baked at 115°C for one minute. Flood exposures of varying lengths (to ensure good exposure) were then performed on half of the wafers, generally at 235-260 nm for the fluorinated photoresists and 405 nm for the silicon photoresists. The film thickness of the photoresist was then measured with a profilometer. The silicon wafers were then placed into an RIE plasma etcher and etched for 1:30 (fluorinated resists) minutes or 3 minutes (silicon resists) at a time with a CHF_3 and O_2 etch (40 sccm). The film thickness on the silicon wafer was then re-measured.

Results and Conclusions:

By dividing the difference in thickness by the time etched, we determined the etch rates of these photoresists.

P1, also known as 2-(4-ethylphenyl)-2-propyl adamantoate with perfluorooctyl methacrylate groups, the first fluorinated photoresist, had average etch rates between 15 nm/min (unexposed) and 19 nm/min (exposed).

P2, also known as 2-(4-ethylphenyl)-2-propanol with perfluorooctyl methacrylate groups, had etch rates of anywhere from 0.5 nm/min to 33 nm/min. The reason for the large variation is that we did three trial runs of P2 using different percentages of perfluorooctyl groups on the main chain polymer. The first, V5, which was 80% fluorinated, gave etch rates of 8.5 nm/min to 33 nm/min. The second, V7, which was 35% fluorinated, gave etch rates of 0.5 nm/min to 15 nm/min. The last, V11, which was 65% fluorinated, surprisingly gave etch rates of 12 nm/min to 29 nm/min. When averaged and graphed, we get a graph like that of Figure 2. While there does not seem to be a correlation from the data, there is a possibility that the %

fluorine has a direct relationship with the etch rate, as you can tell from the error bars present. From this, it could be possible that the more perfluorooctyl groups in the resist, the faster it etches.

P3, also known as 2-(4-ethenylphenyl)-3-methylbutyl-1,2 diol with perfluorooctyl methacrylate groups, had etch rates slower than the other two groups of fluorinated resists, most likely because it was only 35% fluorinated. P3 had etch rates between 5.5 nm/min and 11 nm/min.

S1, also known as poly(chloromethylstyrene-co-trimethylsilylstyrene), had etch rates that were generally slower than those of the fluorinated resists, between 3.5 nm/min and 18 nm/min. We performed three trials using different molecular weights of S1, 11,000 g/mol, 22,000 g/mol and 100,000 g/mol. The 11k trial gave exposed etch rates of 2.8 nm/min to 9.2 nm/min. The 22k trial gave exposed etch rates of 2.4 nm/min to 10 nm/min. The 100k trial gave exposed etch rates of 2.3 nm/min to 8.2 nm/min. Graphing the etch rates versus the molecular weights of S1, we get Figure 3. It is hard to define a relationship between the etch rate and molecular weight of S1, but within the error bars, it could be suggested that as the molecular weight increases, the etch rate decreases.

S2, a polysilesquiazane, had etch rates between 10 nm/min and 16 nm/min.

The graph comparing the discussed etch rates to the control Shipley 1813 resist is shown in Figure 4.

Future Work:

More research should be pointed at determining the relationships between % fluorine and etch rates presented in the fluorinated resists found in this research. Research should also be performed on the relationship between molecular weight of S1 and etch rate of S1.

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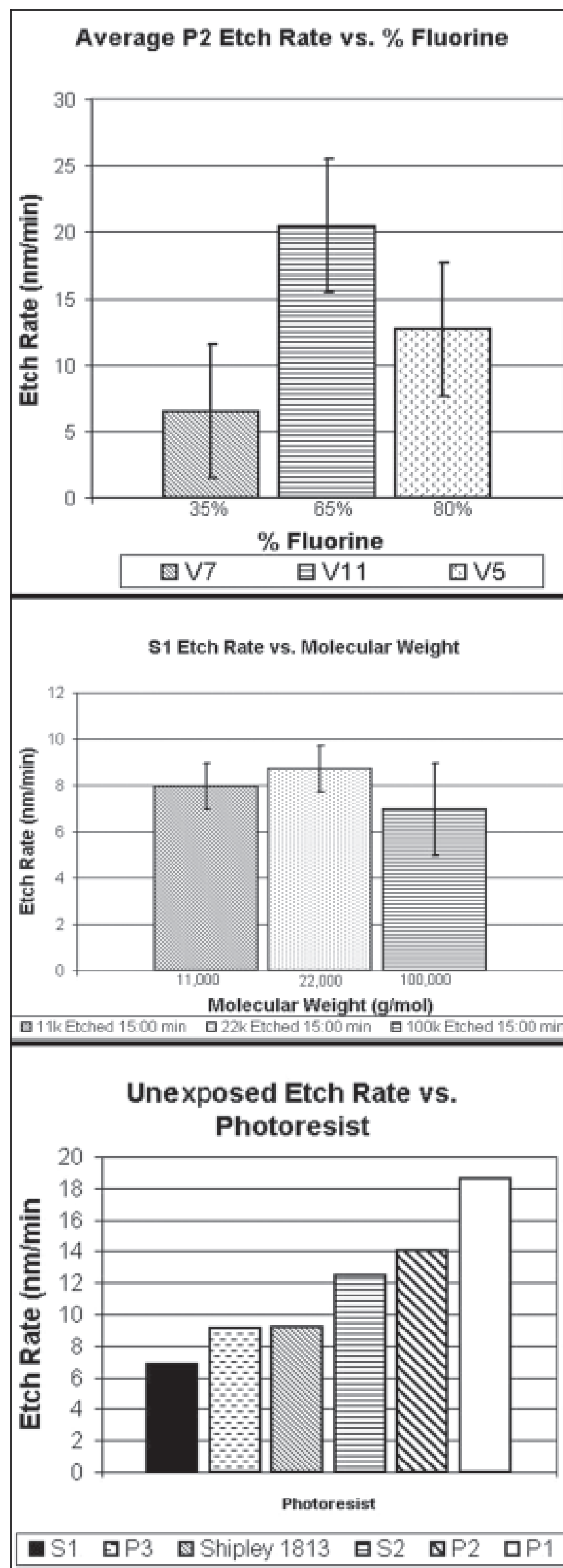

Figure 2, top: Average P2 etch rate vs. % Fluorine in trials V5, V7 and V11.

Figure 3, middle: S1 Etch Rate vs. Molecular Weight.

Figure 4, bottom: Unexposed Etch Rate vs. Photoresist.