POSITIVE-TONE RESIST FOR SUPERCRITICAL CO_2 PROCESSING

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Introduction

Carbon dioxide is widely recognized today as a "Green Chemistry" solvent. The unique physical and chemical properties of carbon dioxide in its supercritical state, namely the absence of surface tension, low viscosity, high diffusivity, and easily tunable solvent strength provide for utility in a variety of industrial and scientific applications. In the microelectronics fabrication industry this non-toxic, environmentally friendly solvent is being heavily investigated as an alternative agent for device cleaning, micro-electromechanical systems (MEMS) drying, and lithographic processing. With the emerging advances in fabrication techniques and materials, microelectronic device features with dimensions below 100 nm are now possible to produce. At the sub-micron scale, the strong surface tension of current aqueous based solvents frequently causes pattern collapse and stiction during and after wet processing [1,2]. The introduction of supercritical carbon dioxide ($SCCO_2$) to supplant more toxic aqueous solvents, especially in the lithographic steps, eliminates such adverse effects.

Fortunately, fluorinated photoresist systems that are transparent at the advanced 157 nm deep ultraviolet (DUV) optical lithography exposure wavelength, while insoluble in most common solvents, readily dissolve in $SCCO_2$. In previous publications we have introduced a model fluorinated 157 nm resist system that is imageable by 193 nm and E-beam exposure tools. This negative-tone resist, poly(tetrahydropyranyl methacrylate-*b*-1H, 1H – dihydroperfluorooctyl methacrylate) [THPMA-F7MA], was processed in $SCCO_2$ to produce feature with dimensions ~ 100 nm [3].

Negative-tone systems, however, have been associated with excessive swelling in wet development since the region exposed to DUV light is prevented from dissolution by cross-linking mechanisms. The cross-linked polymers form swollen gels, sometimes absorbing large volumes of solvent. The work presented here involves a strategy to create a positive-tone resist system. Our method closely resembles the diffusion enhanced silylated resist (DESIRE) process [4-5] that has shown successful results in converting systems from positive to negative-tone in aqueous base development. In this process OH bonds of methacrylic acid, created by acid cleavage of the THP protecting groups from THPMA-F7MA resist upon exposure to DUV and heat, are replaced by $OSi(CH_3)_3$ [TMS] groups introduced into the polymer by hexamethyl disilazane $(CH_3)_3SiHNSi(CH_3)_3$ [HMDS] vapor. Regions containing MAA-F7MA are insoluble to $SCCO_2$, while those converted to TMSMA-F7MA are soluble in $SCCO_2$.

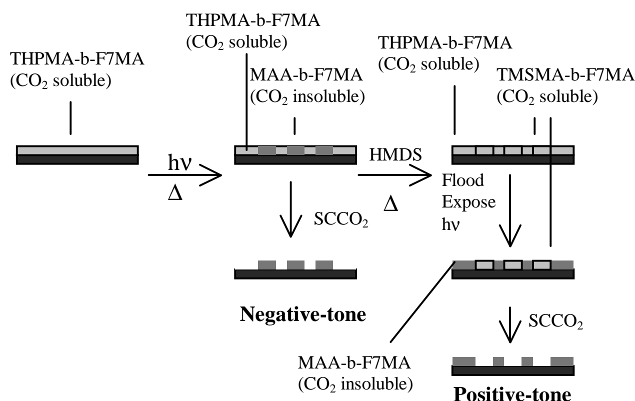

Figure 1. Scheme to achieve image reversal and positive-tone CO_2 resist.

Figure 1 illustrates the chemical amplification scheme and silylating steps. We have demonstrated a solubility switch using this process with the originally negative-tone THPMA-F7MA resist. Fourier transform infrared spectroscopy (FTIR) and Rutherford backscattering spectroscopy (RBS) were used to provide insights to the chemistry and physical phenomena of the silylating process.

Experimental

Block copolymers THPMA-F7MA were synthesized in-house by group transfer polymerization. Details of synthesis and characterization have been published in the literature [6]. Measured MW ranged from 7-12 kD by gel permeation chromatography (GPC). The molar composition of THPMA:F7MA groups vary from one batch to another, with minor deviations from the desired 34:66 ratio that was found to have optimal lithographic performance [7].

Solutions were prepared by dissolving 10 wt% polymer in α,α,α-trifluorotoluene (TFT) with ~ 5 wt% loading of iodonium perfluorooctyl sulfonate photoacid generators. The solution was stirred for 0.5 hr then filtered repeatedly until easily dispensed from a filter-capped syringe. For RBS studies and $SCCO_2$ development, the solution was then filtered directly onto a silicon wafer for greater film uniformity immediately before being spincoated at 2,500 – 3,500 rpm for 60 seconds. Post-apply bake (PAB) followed at 115 ^oC for 60-120 seconds, depending on film thickness. Exposure was done with an HTG contact aligner at 248 nm. During flood exposures high doses, ~100 mJ/cm^2, were used to ensure high rates of deprotection. Post-exposure bake (PEB) to mobilize acid was done at 115 ^oC for 90 seconds.

A tightly sealed cylindrical glass container was used to hold liquid HMDS. N_2, a carrier gas, was introduced into the gas cylinder with one end of the connecting tube submerged in HMDS liquid. Saturated gas was transported to a glass container that enclosed samples on top of a hotplate. N_2/HMDS gas constantly flowed into the container and escaped through a valve opening. Pressure was regulated by the flow rate of N_2 gas. Samples were heated on the hotplate inside the glass container during silylation.

IR data were collected with a Mattson Infinity Gold® FTIR instrument. Thin-film samples are applied on a polished NaCl plate manually. The baking processes involved samples raised <0.25 mm above the hotplate with coated side facing the heating surface. When transporting samples from hood to IR spectrometer, airborne contamination and evaporation might have occurred but are unlikely to have major affects on the important peaks relevant to our study.

RBS experiments were performed with a 1.0 MV tandetron He^{++} accelerator at the Cornell Center for Materials Research. Because polymer films are easily degraded by high-energy sources, sampling was done at multiple locations on the sample in small doses, and spectra are added linearly to produce an averaged plot. Experimental data are compared with simulations performed by RUMP, a software developed at Cornell for RBS analysis. Details on RBS can be found in literature [8].

Results and Discussion

We initially investigated image reversal and $SCCO_2$ processing on a macroscopic scale with conditions that have yielded prior successful lithographic results. First, a silicon wafer sample with spincoated resist is half-covered by an aluminum foil and flood exposed. Exposure, PAB, PEB, conditions are given in the experimental section. The sample was then processed in $SCCO_2$ (45 ^oC, 4000 Psig). As expected, the unexposed side dissolved; and the exposed side, CO_2-phobic after the removal of THP protecting groups, remained. Next, a sample similarly half-exposed and subsequently treated with HMDS (10 minutes, 115 ^oC) was developed in $SCCO_2$. Both sides dissolved in this case, indicating that the HMDS reacted to replace the insoluble OH groups with $SCCO_2$ soluble $OSi(CH_3)_3$. Lastly, a third sample was treated to the same steps as the second sample but with a final flood exposure before processing. This time, the solubility is exactly opposite of that in the first sample, signifying successful image reversal. Figure 2 shows a photograph of the samples discussed.

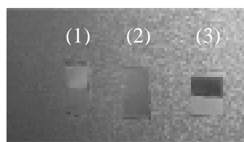

Figure 2. Samples showing successful image reversal with HMDS treatment. White regions: polymer, dark regions: surface of Si wafer. (1) Negative tone, (2) both sides dissolve, (3) positive-tone.

FTIR experiments were performed in transmission mode to probe the chemistry changes associated with silylation. Our interest is mainly to detect the presence of functional groups that indicate resist deprotection and silylation. The commonly observed Si-CH_3 peaks signal the presence of either HMDS or silylated polymers but it is difficult to differentiate one from another. The highly fluorinated polymer (THPMA-F7MA) and TFT solvent peaks densely populate regions where SiO bond peaks commonly occur. Better indicators are the broad carboxylic acid OH stretch that occurrs at 3300–2500 cm^{-} for deprotected polymers and the NH stretch at 3300 – 3030 cm^{-1} for unreacted HMDS present in the film. Additionally, changes in the carbonyl C=O stretch peak(s) at around 1740 cm^{-1} provide insights to whether the resist is protected, deprotected, silylated, or formed anhydrides.

The presence of carboxylic acid side groups may result in anhydride formation during the baking processes. Because anhydride formation is expected to occur at higher temperatures, and since no C=O peaks occur near 1818 cm^{-1} in our IR plots to indicate the presence of noncyclic anhydrirdes, we rule out this reaction.

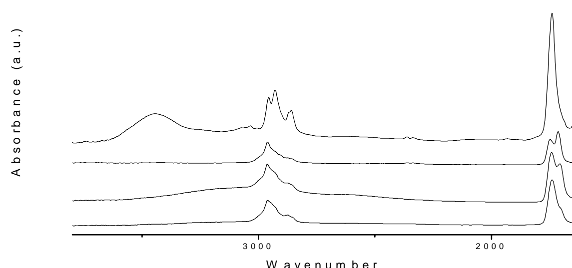

Figure 3. IR plots of different stages of silylating process. Data sets are numbered 1-4 from the bottom up. 1) After PAB, 2) after PEB, 3) silylated, and 4) treated with HMDS but without prior DUV exposure and PEB.

In figure 3, four FTIR plots are shown for the different stages of the silylation process. For ease of reference, the data sets are numbered 1-4, starting with 1 at the lowest position. In the mentioned regions, the first set, from a resist film applied on the NaCl plate and after post apply bake (PAB), shows a small peak around 3500–2500 cm^{-1}, belonging to the OH stretch of the carboxylic acid groups. The single carbonyl C=O stretch peak at 1740 cm^{-1} shows that most of the THP protecting groups are intact, as expected, before exposure to DUV. The carbonyl groups, one from THPMA and the other from the F7MA blocks of the copolymer, appear at a single location since both are from esters of methacrylates.

The second set from the bottom (number 2) is that of the sample after exposure to DUV and PEB step. A large increase in the carboxylic acid OH peak is readily observable after deprotection reactions that removed the THP protecting group. The appearance of a second C=O peak at around 1705 cm^{-1} due to the presence of carboxylic acid indicates the same. The C=O peak from F7MA remains in the same position as in plot 1 since no chemical changes occurred in this block.

Data set number 3 shows FTIR peaks of the sample after silylation for 10 minutes under HMDS vapor at 115 ^{o}C. The disappearance of the carboxylic acid OH peak at 3500–2500 cm^{-1} and a slight shift of the C=O stretch to 1715 cm^{-1} suggest silylation where SiO bonds replace OH bonds of carboxylic acid groups. Surprisingly, the OH peak totally disappears, indicating a nearly 100% reaction where all COOH groups are silylated.

The final data set (topmost) is used to verify the assumptions made above. It is a plot of a THPMA-F7MA polymer sample subjected to HMDS vapor at 115 ^{o}C but without prior exposure to DUV light. A combination of (a) no changes in the C=O stretch at 1740 cm^{-1}, (b) the absence of carboxylic OH peak at 3500–2500 cm^{-1}, and (c) a large NH peak at 3700–3300 cm^{-1} strongly suggests that thermal deprotection did not occur, silylation was absent, and the presence of HMDS in the film is by absorption alone. A comparison of this data set to the first three seems to confirm very well our interpretations of the FTIR plots.

Another analytical method available to investigate diffusion of HMDS or silylating agents into thin polymer films is RBS. With this analytical technique we can probe the diffusion length, depth concentration profile, and density changes in films subjected to silylation. Figure 4 shows an RBS plot comparing Si concentrations in THPMA-F7MA films spincoated on Si wafer, originally and those subjected to HMDS vapor at 115 ^{o}C for 20 and 40 minutes. Spectra for the latter show that Si concentrations in the films vary little between the two silylation times. RUMP simulations indicate that the resist film has a low atomic concentration of Si, ~1 %, in the bulk and up to ~5% in the top 150-250 nm layer. At the time of this writing, more RBS experiments are planned to verify these initial findings.

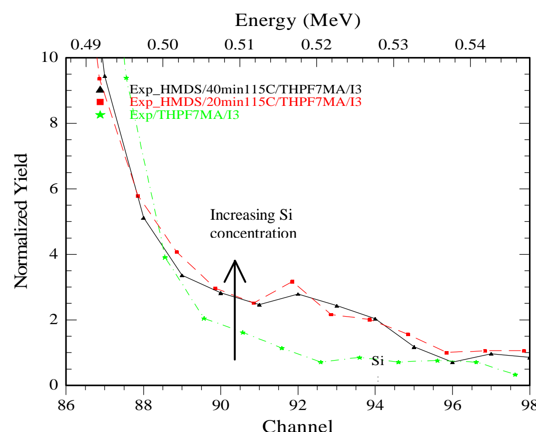

Figure 4. RBS spectra of resist samples. The lower data set is from original resist while the top two are from resist samples after DUV exposure and HMDS/heat treatment.

Conclusions

Our effort at creating a positive-tone CO_2 developable resist has yielded encouraging results. FTIR experiments show that cross-linking due to anhydride formation is unlikely and that silylation does indeed take place when carboxylic acid groups are present when exposed to HMDS vapor at elevated temperatures. With RBS we can begin to understand the diffusion process as well as obtain essential information such as depth concentration profiles of Si-containing molecules. We showed image reversal with large samples. Image reversal at micron and sub-micron length-scales is inherently more challenging since it involves process optimization in a large, multidimensional parameter space. However, the results obtained to date seem to suggest that such is a strong possibility in the foreseeable future.

References

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