Positive-Tone Photoresist Process for Supercritical Carbon Dioxide Development

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Carbon dioxide has steadily emerged as a potential solution to several of today's important concerns in nanofabrication.[1] In addition to significant environmental benefits—reduction of water consumption and supplanting hazardous processing chemicals with an abundant, nontoxic, nonflammable, recyclable source—special properties of carbon dioxide in the supercritical state can enhance processing performance in photolithographic and cleaning stages of chip production. These attributes include a solvent with low viscosity and high density combined with the absence of surface tension[2] that eliminates pattern collapse in high aspect ratio submicrometer features.[3−5]

The pursuit of a $scCO_2$ developable photoresist has received widespread interest but is still in its early stages. The only $scCO_2$ developable resist that has to date demonstrated negative-tone 100-nm resolution was introduced by Ober et al. in recent publications.[6,7] Excessive swelling of patterns by aqueous solvents in *traditional* negative-tone resists, however, has driven the manufacturing industry toward the use of positive-tone systems. To the best of the authors' knowledge, the only prior $scCO_2$ developable positive-tone resist was based on the imaging of polysilane and was only capable of micrometer level resolution.[8]

In this communication, we describe a method to create a positive-tone photoresist by in situ chemical modification of poly(tetrahydropyranyl methacrylate-*co*-1H, 1H perfluorooctyl methacrylate) (THPMA-F7MA) through silylation. Surface silylation of aqueous base developable photoresists has been extensively reported in the literature.[9−14] Because of the types of resists used and the associated high silylation temperatures, polymer cross-linking and other barriers to diffusion render prior techniques useful mostly for top surface imaging (200 nm or less). THPMA-F7MA allows for longer time, lower temperature silylation without cross-linking such that complete image reversal is possible for original film thicknesses exceeding 600 nm.

Block copolymers of THPMA-F7MA ($M_n \sim 10000$ g/mol, 65:35 mole ratio) were synthesized by group transfer polymerization. Details of the synthesis and characterization have been published in the literature.[7] Pattern imaging at 248 nm generates acids in the exposed regions that cleave THP groups, resulting in methacrylic acid with significantly decreased solubility in $scCO_2$. During subsequent silylation, hexamethyl disilazane (HMDS) vapor diffuses into the film to react with free carboxylic acid groups, forming $O{-}Si(CH_3)_3$. Patterned regions thus regain solubility in $scCO_2$ due to the favorable polymer−solvent interaction enthalpy with the addition of the organosilicon protecting groups. A subsequent UV flood exposure step activates unreacted photoacid generators throughout the sample. Cleavage of nonpolar THP protecting groups then occurs everywhere except in the originally patterned regions. Development in $scCO_2$ thus removes the patterned regions, making this a positive-tone resist. Investigations of chemical reactions and diffusion during silylation were carried out using FTIR. Figure 1 shows FTIR spectra of a sample undergoing successive steps of the process. In the original and silylated films, carboxylic acid hydroxyl peaks are absent, indicating the presence of protecting groups. The hydroxyl peak is readily apparent in the deprotected sample. After silylation, however, the carbonyl $C{=}O$ stretch peak at 1725 cm^{-1} does not return to the shape of the same peak seen in the original protected film, likely due to the formation of anhydrides. Anhydride formation is unfavorable at this temperature and thus does not hinder the silylation reaction to a significant extent. The upper spectrum shows a film silylated without pattern exposure. In this case, HMDS molecules do not react in the absence of OH groups and thus the NH stretching peak of the HMDS molecule is strongly evident.

With a Nikon 248-nm stepper, achievable resolution for unsilylated THPMA-F7MA resist developed in $scCO_2$

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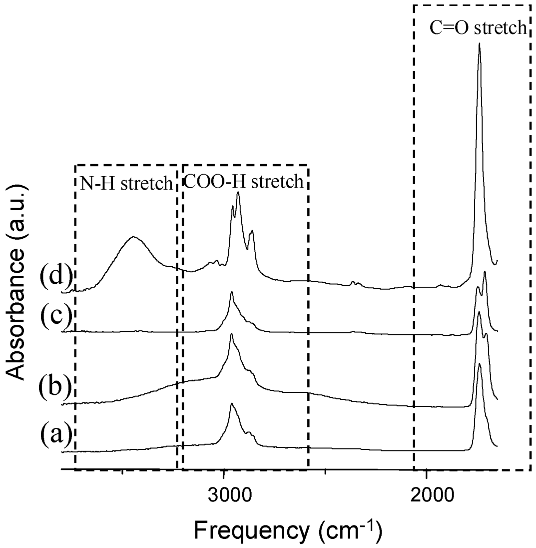

Figure 1. FTIR spectra of THPMA-*b*-F7MA: (a) original resist; (b) deprotected; (c) silylated; and (d) silylated without deprotection. At 1725 cm^{-1}, transformation of the C=O stretch as a result of deprotection and silylation, with possible anhydride formation evident in (c).

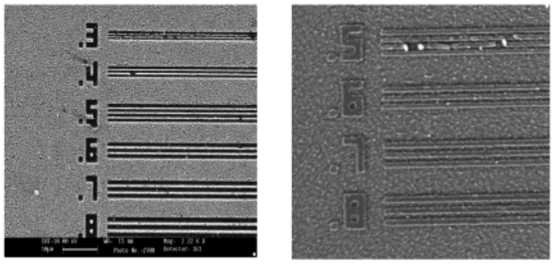

Figure 2. (a) THPMA-F7MA block copolymer resist exposed with 248-nm Nikon stepper and developed in scCO$_2$; (b) sample processed after silylation, showing positive-tone patterns.

is ~400 nm. Pattern deformation occurs at smaller dimensions, as shown in Figure 2a. A number of factors such as PAG type and concentration, the use of antireflective coating, film thickness, baking, and processing time and temperature, can be optimized to improve resolution for 248-nm exposure. The present achievable dimensions, however, suffice to demonstrate a simple yet highly effective method of producing a positive-tone scCO$_2$ developable photoresist.

With HMDS silylation and the subsequent flood exposure steps, the now positive-tone patterns retain good structural integrity to 500-nm lines/spaces. Figure 2b shows an SEM image of a sample developed in scCO$_2$ after silylation for 60 min at 90 °C. While image reversal is clearly achieved, incomplete film removal and excessive surface roughness are also apparent.

Some of the challenges posed by the use of block copolymers can be addressed by employing random copolymers, for which similar lithographic resolution has not yet been demonstrated. Random copolymers of THPMA-F7MA ($M_n \sim 14000$ g/mol, 60:40 mole ratio) were synthesized by free radical polymerization. These have advantages that include easy synthesis, good solubility in spin-coating solvent (trifluorotoluene), and high quality, uniform spin-coated films. During development in scCO$_2$, swelling and lower adhesion compared to block copolymers lead to image resolution no better than 600 nm, as shown by SEM images of lines/spaces in Figure 3a.

Silylation with HMDS was performed as before. Unexpectedly, while results obtained from block copolymers exhibited a decrease in resolution after silylation, the opposite is true for random copolymers. Image reversal was achieved with 400-nm lines/spaces, a significant improvement from the original negative-tone performance. However, as shown in Figure 3b, observable lateral swelling of features cause lines to be wider and gaps closer than originally patterned.

To further improve performance, tetramethyl disilazane (TMDS) was chosen as an alternative silylating agent. Two possible advantages might be expected for the smaller, somewhat more polar molecule. First, enhanced diffusion and better interaction with the polar carboxylic acid groups (to be protected) may result in greater silylation depth and completeness. Second, swelling can be reduced with a smaller protecting group. Lithographic performance improvement when using TMDS was remarkable, as shown in Figure 3.

Profilometry measurements (Tencor P10) were performed to gauge silylation depths. The extent of film

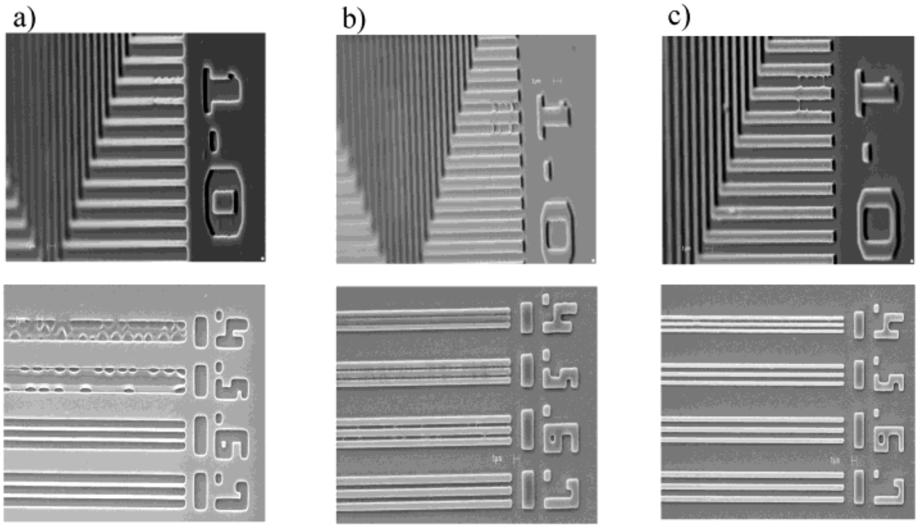

Figure 3. THPMA-F7MA random copolymer resist patterned by 248-nm exposure: (a) scCO$_2$ processed negative-tone images, (b) positive-tone images processed after silylation with HMDS, and (c) positive-tone images processed after silylation with TMDS.

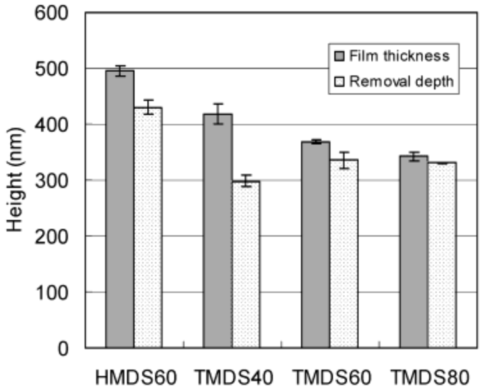

Figure 4. Profilometer measurements (Tencor P-10) comparing film thickness with the depth of patterned regions, which are removed during development in $scCO_2$.

removal during $scCO_2$ processing, measured by the depth of pattern trenches, is compared to the thickness of the bulk undissolved film after development. The two are equal only if the silylation reaction occurs throughout the entire film thickness and development, thus removing patterned regions completely from the silicon wafer surface. It was found that HMDS does not silylate the entire film thickness even after 60 min. Because of observed swelling of features, longer silylation times were not attempted. With TMDS, at 60 °C, incomplete removal was observed after 40 min and to a lesser extent after 60 min of silylation. However, after 80 min, film thickness and pattern depths were equal within measurement errors. At higher silylation temperatures, we observed the onset of pattern deformation in 400-nm features. Therefore, we concluded that, for THPMA-*r*-F7MA, which has a glass transition temperature of 65 °C, the optimal silylating conditions have been reached. The results are shown in Figure 4. Shown in Figure 3c are 400-nm lines and spaces produced with the reported conditions.

In summary, a process was developed for the formation of positive-tone submicrometer images developed entirely in $scCO_2$. Lithographic patterning at 248 nm generates acid groups in exposed regions of the resist film. Subsequent silylation of the acid groups causes the exposed regions to become soluble in $scCO_2$. In the flood exposure step, the remaining areas become insoluble in scCO2, thereby creating positive-tone images. Work is continuing to further understand the limits of the process and to improve overall resolution of the materials.

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