Positive-tone photoresist process for supercritical carbon dioxide development

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ABSTRACT

A new process is described for the development of positive photoresist materials using the environmentally benign solvent, supercritical carbon dioxide (scCO2). The main objective of this work is to introduce a method to produce a high-resolution scCO2 developable positive-tone photoresist that is compatible with current fabrication methods. scCO2 developable block and random copolymers of poly(tetrahydropyranyl methacrylate-co-1H, 1H perfluorooctyl methacrylate) [THPMA-F7MA] were silylated to produce positive-tone submicron features. Lithographic performance increased markedly when random copolymers were silylated after 248 nm exposures using scCO2 development. Film swelling and diffusion depth of silylating agents were investigated. Tetramethyl disilazane (TMDS) showed complete silylation of films with 600 nm original thicknesses. Complete removal of exposed regions was observed.

SUMMARY AND RESULTS

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 that eliminates pattern collapse in high aspect ratio sub-micron features [2].

The pursuit of a scCO2 developable photoresist has received widespread interest but is still in its early stages. Today, the only scCO2 developable resist that has to date demonstrated negative-tone 100nm resolution was introduced by Ober et al. in recent publications [3]. Excessive swelling, difficult to control crosslinking, non-uniform molecular weight in patterned areas, et cetera, in traditional negative-tone resists, however, has driven the manufacturing industry towards the use of positive-tone systems. To the best of the authors’ knowledge, the only prior scCO2 developable positive-tone resist was based on the imaging of poly(silane) and was only capable of micron level resolution [4].

In this abstract, we describe a method to create a positive-tone photoresist by 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 [5,6]. Because of the types of resists used and the associated high silylation temperatures, polymer crosslinking...
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 crosslinking such that complete image reversal is possible for original film thicknesses exceeding 600 nm.

Block copolymers of THPMA-F7MA (Mn ~ 10,000, 65:35 mole ratio) were synthesized by group transfer polymerization. Pattern imaging at 248 nm generates acids in the exposed regions that cleave THP groups, resulting in methacrylic acid with significantly decreased solubility in scCO₂. During subsequent silylation, hexamethyl disilazane (HMDS) vapor diffuses into the film to react with free carboxylic acid groups, forming O-Si(CH₃)₃ groups. Exposed regions thus regain solubility in scCO₂ due to the favorable polymer-solvent interaction enthalpy with the addition of the organosilicon protecting groups. A subsequent UV flood exposure step then activates unreacted photoacid generators throughout the sample. Deprotection and solubility switch then occur everywhere except in the originally patterned regions. Development in scCO₂ thus removes the exposed regions, making this a positive-tone resist. Investigations of chemical reactions and diffusion during silylation were carried out using FTIR. In figure 1, FTIR spectra of a sample undergoing successive steps of the process with carbonyl and hydroxyl peaks show evidence of deprotection and silylation, as expected.

Using a Nikon 248 nm stepper, achievable resolution for unsilylated THPMA-F7MA resist developed in scCO₂ is ~ 400nm. Pattern deformation occurs at smaller dimensions, as shown in figure 2a. A number of factors such as PAG type and concentration, the use of anti-reflective coating, film thickness, baking and processing time and temperature, can be optimized to improve resolution for 248nm exposure. The present achievable dimensions, however, suffice to demonstrate a simple yet highly effective method of producing a positive-tone scCO₂ 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 scCO₂ after silylation.
for 60 minutes 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. Random copolymers of THPMA-F7MA (Mn ~ 14,000, 60:40 mole ratio) were synthesized by free radical polymerization. These have advantages that include easy synthesis, good solubility in spincasting solvent (trifluorotoluene) and high quality, uniform spincasted films. During development in scCO2, swelling and lower adhesion compared to block copolymers lead to image resolution no better than 600nm, 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 400nm 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, more polar molecule. First, enhanced diffusion and better interaction with the polar photoresist film 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.

![image](a) ![image](b) ![image](c)

**Figure 3.** THPMA-F7MA random copolymer resist patterned by 248 nm Nikon exposure. (a) scCO2 processed negative-tone images, (b) positive-tone images processed after silylation with HMDS, and (c) positive-tone images processed after silylation with TMDS.

Profilometry measurements (Tencor P10) were performed to gauge silylation depths. The extent of film removal during scCO2 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 remove patterned regions completely from the silicon wafer surface. It was found that
HMDS does not silylate the entire film thickness even after 60 minutes. Because of observed swelling of features, longer silylation times were not attempted. With TMDS, at 60 °C, incomplete removal was observed after 40 minutes and to a lesser extent after 60 minutes of silylation. However, after 80 minutes, film thickness and pattern depths were equal within measurement errors. The results are shown in figure 4. Shown in figure 3c are 400nm lines and spaces produced with the reported conditions.

Figure 4. Profilometer measurements (Tencor P-10) comparing film thickness with the depth of patterned regions, which are removed during development in scCO₂.

In summary, a process was developed for the formation of positive tone images developed entirely in scCO₂. Solubility in the exposed regions was achieved by exposure to a silazane of the acid groups present in the film. The subsequent silylation rendered the exposed region soluble in scCO₂. A second process step involving flood exposure rendered the remaining resist sections insoluble in scCO₂ thereby creating the positive image. Work is continuing to further understand the limits of the process and to improve overall resolution of the materials.

REFERENCES