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Task Title: Supercritical Carbon Dioxide Compatible Additives: Design, Synthesis, and Application of an Environmentally Friendly Development Process to Next Generation Lithography: Resists and Additives
Deliverable: Report on the Preparation of New Resist Systems and Lithographic Evaluation of Silazane Processes for $scCO_2$ Development
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Abstract:

Supercritical carbon dioxide ($scCO_2$) is considered as an environmentally benign replacement for organic solvents in many applications. Its unique properties are also beneficial to be used as a developing solvent for photoresists patterning. However, most conventional photoresists are generally not soluble in $scCO_2$ and require certain functional groups. In this report, we have shown the development of poly(hydroxystyrene-co-styrene-co-*t*-butylacrylate) (ESCAP) in $scCO_2$ by using a silylation agent. In order to achieve higher resolution patterning, a small molecular glass photoresist is also synthesized for $scCO_2$ processing.

Introduction:

Supercritical carbon dioxide ($scCO_2$) is the supercritical state (T_c=31.1°C, P_c=72.9 atm) of carbon dioxide and it is nontoxic, nonflammable, inert under most conditions. It has been used as an environmentally benign replacement for organic solvents in many applications[1]. It exhibits the unique properties as combining liquid-like densities with gas-like diffusivities. It also possesses zero surface tension that has the potential to eliminate common lithography problems such as pattern collapse. $ScCO_2$ is generally a good solvent for non-polar small molecules. However, most polymeric photoresists are not soluble in $scCO_2$ and certain fluorinated or silicon-containing functional groups are incorporated to increase the solubility of polymers in $scCO_2$. Previously, Ober et al. have showed the ability to develop fluorinated photoresists in $scCO_2$[2]. It is believed that the presence of fluorine increases the solubility of polymers in $scCO_2$, but high content of fluorine has an adverse effect on the etch resistance. Therefore, conventional photoresists generally are not fluorinated and require additives such as cosolvents to be developed in $scCO_2$[3].

In the previous reports, we have shown the development of two conventional photoresists, poly(4-*t*-butoxycarbonyloxystyrene) (PBOCST) and poly(hydroxystyrene-co-styrene-co-*t*-butylacrylate)(PHS-co-PS-co-PtBA) (ESCAP) in $scCO_2$ with quaternary ammonium salts(QAS)[4]. To increase the environmental friendliness of this process by reducing the use of fluorinated materials, we have also considered a new class of additives. In this report, we have demonstrated the patterning of ESCAP resist by using (N,N-dimethylamino) trimethyl silane (DMTS). In order to achieve higher resolution patterning, we have also designed and synthesized small molecular glass photoresists to be developed in $scCO_2$.

Experimental:

Materials. (*N*,*N*-dimethylamino)trimethylsilane (DMTS) were purchased from Gelest and used without further purification. Poly(hydroxystyrene-*co*-styrene-*co*-*tert*-butylacrylate) (ESCAP) was obtained from DuPont Electronic Polymers Inc. *N*-hydroxynaphthalimide triflate (NI-Tf) were purchased from Sigma-Aldrich. *C*-4-Hydroxyphenyl calix[4]resorcinarene (CHPB) and its fully *tert*-butoxycarbonylated (Boc) molecular resist (CHPB-BOC) were synthesized according to procedures reported in literature.[5]

Lithographic Evaluation. ESCAP resist film was spin-coated on an HMDS-primed silicon wafer and baked at 130°C for 60 seconds. Dose testing was performed by using a GCA Autostep 200 DSW i-line Wafer Stepper (500mW/cm^2). High-resolution patterning was done using a Jeol JBX-9300FS e-beam lithography system operating at 100 kV. After exposure, the resist film was baked at 115°C for 60 seconds.

Development in Supercritical CO_2. 0.5 ml of DMTS was dissolved in 50 ml scCO_2 at 50°C and 5000 psi for 15 minutes and was subsequently used to develop ESCAP resist film for 5 minutes by using a scCO_2 dissolution rate monitor described elsewhere[6].

Metrology. A Tencor P10 profilometer was used to measure the film thickness of each photoresist film before and after development. The developed patterns were examined using the Nikon Digital Sight D5-5M-L1 optical microscope and the LEO 1550 FESEM scanning electron microscope.

Results and Discussion:

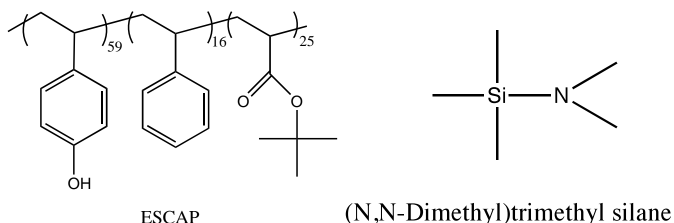


Figure 1 Chemical structures of ESCAP and DMTS

The chemical structures of ESCAP and DMTS are shown in Fig.1. ESCAP is insoluble in scCO_2 before and after exposure without any additives or co-solvents. It is well known that silicon-containing functional groups can increase the solubility of polymers in scCO_2 and therefore a silylation chemistry is applied here. DMTS is chosen because of its moderate boiling point and its high reactivity compared to hexmethyldisilazane (HMDS). As shown in Fig. 2, DMTS can react with the hydroxyl groups in ESCAP and incorporate silicon-containing trimethylsilyl (TMS) groups into the resist and increase its solubility in scCO_2.

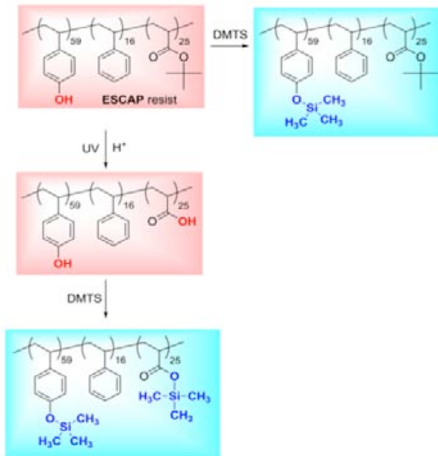


Figure 2 Reaction scheme of ESCAP with DMTS

Lithographic evaluation was done using 365-nm UV light and electron-beam lithography, as shown in Figure 3 and Figure 4 and high contrast patterns were observed in both images.

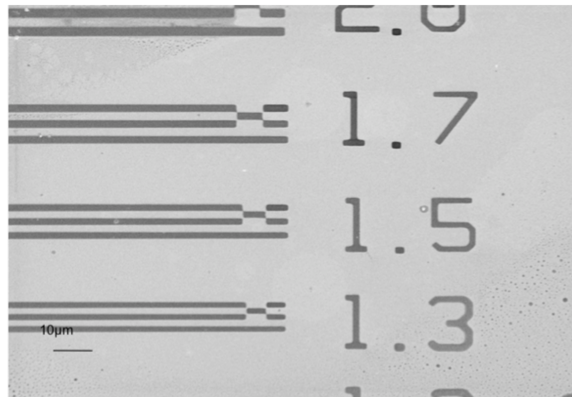


Figure 3 SEM image of ESCAP exposed under 365-nm light (dose: 50 mJ cm^{-2}) and developed in $scCO_2$

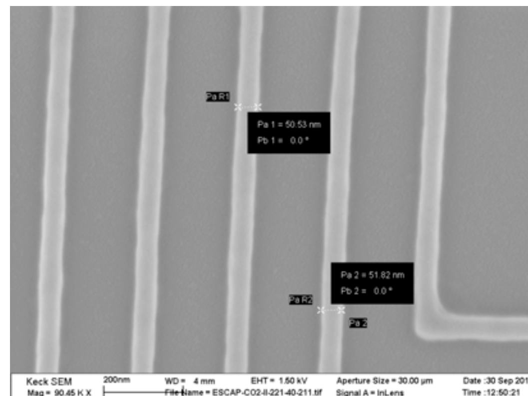
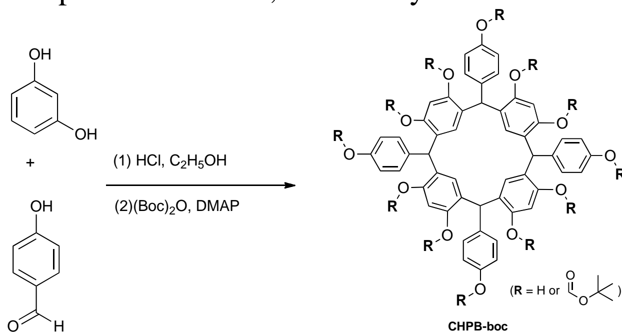


Figure 4 SEM image of ESCAP exposed under electron-beam (dose: 50 µC cm^{-2}) and developed in $scCO_2$

High-resolution patterning is achieved as shown in Figure 4 using electron-beam lithography. Feature size as small as 50 nm is shown in Figure 4 and we have therefore

demonstrated the high-resolution patterning ability of $scCO_2$ by using a simple silylation process.

It is believed that resolution limits and line-edge roughness (LER) are related to the molecular size of photoresists[7]. Our group has previous synthesized several small molecular glass resists for high resolution patterning.[5] Because of the small size of molecular glass resists, they are soluble in $scCO_2$ and can be used as a new type of photoresists for environmentally friendly processing. We have successfully synthesized t-boc protected CHPB, with the synthetic scheme shown in Scheme 1.



Scheme 1 Synthesis of t-boc protected CHPB[5]

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