High-Resolution, Supercritical CO₂-Developable Molecular Glass Photoresists

CNF Project # 386-90
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Abstract:

The use of supercritical CO₂ (scCO₂) in semiconductor manufacturing has many potential benefits from both an environmental and technical point of view. Along with being non-toxic and non-flammable, scCO₂ is a zero surface tension, high diffusivity fluid capable of processing features on the nanometer scale. However, finding photoresists and strategies suitable for CO₂ processing has proved to be a challenge. Until recently, patterning and development of sub 100 nm photoresist features has not been possible, and photoresists required fluorination to impart solubility. With the growing adoption of small molecule resists, also known as molecular glasses, the possibility of CO₂ solubility and high solubility contrast drastically increases. With scCO₂ development, we have been able to show positive- and negative-working resists patterned down to 50 nm features, all without the need for fluorine. This performance with an environmentally friendly solvent is comparable to current photoresist technologies.

Summary:

Molecular glasses are an innovative type of photoresist based on small, discrete molecules rather than polymers [1-3]. Because of this, they possess potential advantages over standard polymeric resists. The small, uniform size of molecular glass resists has the potential to alleviate the line-edge roughness problem facing next-generation lithography. Also, due to their small size, molecular glasses have the potential for supercritical CO₂ solubility without the need for fluorination. This greatly expands the range of materials that can be developed in scCO₂.

A high contrast molecular glass resist, hexa(hydroxyphenyl)benzene (HHPB) was used as a high contrast photoresist. Details of the synthesis are described elsewhere [4]. This molecule with six hydroxyl functionalities was protected with tert-butoxycarbonyl (tBOC), which is acid labile. Upon exposure, the resist is deprotected, rendering the molecule more polar and less soluble in scCO₂.

A 10 wt% solution of tBOC-protected HHPB was made in propylene glycol methyl ether acetate (PGMEA). To this solution, a 5 wt% loading of a photoacid generator, triphenylsulfonium perfluoro-1-butanesulfonate, was added. This was spin-coated to a 200 nm thickness, soft baked at 115°C for 60 s and patterned using CNF’s Leica VB6 electron beam system operating at 100 kV. Post-exposure bake was performed at 90°C for 30s and then developed in scCO₂. Supercritical CO₂ exists above 31°C and 1070 psi, and processing conditions were explored from 35°C to 65°C and 2000 psi to 10,000 psi. Using contrast curves, the optimal condition for development was found to be 35°C and 5000 psi.

After development at 35°C and 5000 psi for 3 minutes, features as small as 50 nm lines and spaces were resolved. This shows the high development contrast of the molecular glass resist in scCO₂ as well as the potential of scCO₂ processing. These features were at an aspect ratio of 3:1 without collapse, showing the ability of supercritical developers to alleviate pattern collapse.

This is the first reported instance of sub 100 nm resist features developed in scCO₂ and potentially brings supercritical processing to the same level as conventional resist development.

References:

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Figure 1: Reaction scheme of tBOC-protected hexa(hydroxyl phenyl)benzene upon exposure and acid generation. Exposure renders the photoresist more polar and therefore less soluble in supercritical CO₂.

Figure 2: After development in supercritical CO₂ at 35°C and 5000 psi for 3 min, 50 nm lines and spaces can be resolved in the resist. Aspect ratios of resist features are as high as 3:1, demonstrating the advantages of supercritical development.