New Photoresist Platforms Developable in Super-Critical CO\textsubscript{2}

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Abstract

For more than a decade, the idea of using supercritical fluids in semiconductor processing has been actively explored by many researchers. Super-critical carbon dioxide (scCO\textsubscript{2}) in particular is well-known as an environmentally benign solvent, but it also has many potential performance advantages. With its low critical temperature, zero surface tension, and non-polar inert character, scCO\textsubscript{2} shows great potential for its ability to process sensitive materials with patterned features on a very small length scale.

However, barring excessive fluorination, most materials traditionally used by industry show poor solubility in this solvent. This is where molecular glass resists show their unique nature. Because of their small size, molecular glasses have the potential for scCO\textsubscript{2} solubility while still showing equal performance to polymer photoresists [1]. Also, because of their small, discrete structures, these materials can show lower line-edge roughness compared to traditional polymer resists.

We demonstrate some recent successes in developing photoresist features in the sub-65 nm range with only scCO\textsubscript{2} as the developer solvent [2]. Additionally, we evaluate the effect of molecular structure on photoresist dissolution rate and show the consequences of protecting groups, glass transition, and pi-pi stacking on dissolution.

Experimental

The setup and use of the scCO\textsubscript{2} dissolution rate apparatus is described in a previous paper [3]. Briefly, a 1 cm by 1 cm piece of a silicon wafer coated with molecular glass film is placed into a 25 ml observation chamber, which is aligned with a laser and fitted with a quartz glass observation window for the laser beams to pass through. At the start of the experiment, CO\textsubscript{2} is quickly introduced into the observation chamber at the specific temperature and pressure. The reflected intensity of the laser on the film (at a measured incident angle of 3° from normal) is continuously logged until complete dissolution, when the reflected intensity from the bare silicon constitutes a steady maximum. For simplicity, the time from when the CO\textsubscript{2} is introduced until the time when the film is completely dissolved is taken to be the dissolution time. Comparison with the original film thickness allows one to calculate the dissolution rate with an estimated ± 3% observational error.

Patterning was performed by including 5 wt% (with respect to molecular glass) of a photoacid generator, triphenylsulfonium perfluoro-1-butanesulfonate, into the molecular glass solution before spin-casting. When exposed to ultraviolet or electron-beam radiation, the photoacid generator generates a proton that subsequently catalyzes the cleavage of tboc groups from the molecular glass. This renders the molecule relatively polar and therefore relatively insoluble in scCO\textsubscript{2}. High-resolution patterning was performed with a Leica VB6-HR operating at 100 kV, followed by a post-expose bake at 90°C for 30 seconds to activate the deprotection. Development was performed in the same scCO\textsubscript{2} chamber used for DRM measurements.

Results

In general, the solubility of all molecular glasses should be dependent on their molecular weight. This effect may be seen in their respective dissolution rates, which are plotted on one master plot in Figure 1. For simplicity, the required pressure at 40°C for each molecular glass to reach a dissolution rate of 400 nm/min is plotted against molecular weight.
In general, for the majority of the data there is an expected linear dependence of dissolution rate on molecular weight. However, there are three outlying points in this case where dissolution is inhibited. Further inspection of the thermal properties indicates this may also be loosely correlated to material glass transition temperature (T_g). This observation suggests that these particular films still exist above their T_g when exposed to scCO_2, unlike the lower T_g materials that are plasticized to a T_g below the scCO_2 temperature. These correlations suggest that in situ T_g is a very important factor in predicting film dissolution rate in scCO_2.

Due to excessive plasticization of these particular molecular glass resist films under scCO_2, using them to form stable, high-fidelity patterns remains a challenge. As a result of their un-crosslinked nature, flow and pattern distortion happens quickly near the T_g. Therefore, only molecular glasses with very high T_g’s can be patterned and developed reliably with scCO_2. Of course, this limitation can be mitigated if the molecular glass is crosslinked upon patterning, as Shiraishi et al. have shown [4]. From the molecular glasses reported in this paper, hexa(hydroxyphenyl)benzene-tboc has been reliably patterned and developed without the assistance of crosslinking. The resulting pattern is shown in Figure 2. Success with this molecular glass is due to the high T_g of the material, which increases upon deprotection and leads to a patterned material that resists plasticization.

Figure 1: Correlation of dissolution rates with molecular weight. In general, most points follow a trend, with outliers due to specifics of molecular architecture.

Figure 2: Results of e-beam patterning of hxph-mp-tboc followed by development in scCO_2 at 40ºC and 300 bar. 150 nm lines and spaces are shown.

References