Task ID: 425.017
Task Title: Environmentally Benign Vapor Phase and Supercritical CO_2 Processes for Patterned Low k Dielectrics
Deliverable: Report on the synthesis and evaluation of molecular glass precursors for low k materials

Abstract:
We are investigating molecular glass precursors and porogens for low k materials. Molecular glasses are large molecules (500 to 1000 g/mol) that form non-crystalline bulk and thin film structures. As film formers they have many of the properties of polymers. Molecular glasses formed from non-polar hydrocarbon or inorganic materials make ideal components for a new generation of low k materials. New structural concepts from organic and inorganic materials that provide low k, high T_g, thermal stability and mechanical robustness can be developed from these platforms. Impressive patternability, along with the ability to be vapor deposited and $scCO_2$-developed, shows the versatility of these materials.

Porogens and pore formation represent an important strategy for lowering the dielectric constant of low k materials. Porogens are added to a low k matrix to act as spacers and are ultimately removed leaving air as a key part of the dielectric. Porogens, dispersed during deposition into low k materials, will be derived from a number of materials including small molecules and molecular glasses.

Technical Results and Data:

Past work has demonstrated the solubility of small glass-forming molecules in $scCO_2$. From this, general trends of $scCO_2$-solubility could be inferred. However, more specific solubility properties need to be calculated in order to design appropriate molecular glass precursors and porogens for $scCO_2$ processing. A supercritical CO_2 dissolution rate monitor (DRM) was used in order to study and compare the dissolution rates of molecules with different sizes and functionalities.

Hexa(hydroxyphenyl)benzene (HHPB) derivatives have shown excellent $scCO_2$ solubility while still showing patternability like a photoresist. Using the DRM, dissolution rates of these fully-protected molecules at some conditions were above 400 nm/min. In contrast, HHPB derivatives protected less than 70% dissolved at less than 10 nm/min. This suggests that any small molecule with more than one free hydroxyl group is sparingly soluble in $scCO_2$, while molecules with 0 or 1 free hydroxyl groups can have excellent solubility (Fig. 7). This was also investigated using a trisphenol-based molecular glass.

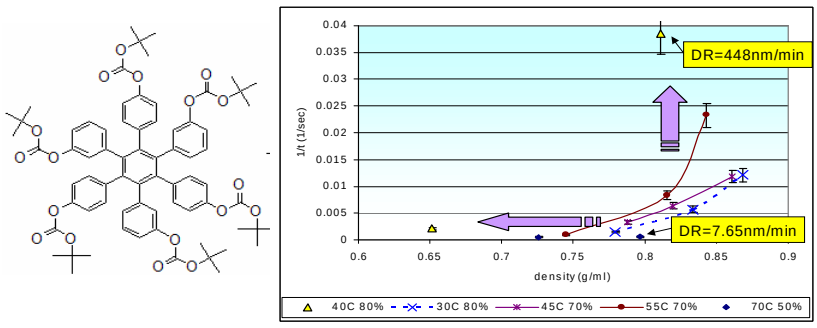

Fig 1. Dissolution rates of various protection ratios of HHPB in $scCO_2$. Above 70% protected, these molecules are very soluble in $scCO_2$.

Molecular glasses of this type have also shown versatility in their method of deposition. Because of their small size, these molecules do have a nonzero vapor pressure at elevated temperatures. Using this fact, one can conceive of vapor depositing these materials onto a cooled substrate. In this way, small molecule photoresist components have been deposited using a vacuum chamber equipped with individually-heated material sources to evaporate the components. Photoresist films created using this physical vapor deposition (PVD) process have been patterned and developed with submicron features shown. These concepts can easily be applied to low-k analogs of these components. As an added ESH benefit, the system shown in Fig. 7 was developed in pure water.

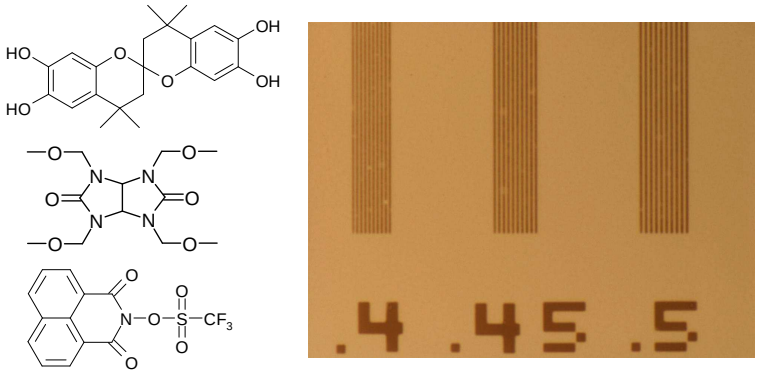

Fig 2. A three-component photoresist system applied using PVD, patterned using an i-line stepper, and developed in water.

Materials based on simple sugars have been synthesized in an effort to make porogens that can be vapor deposited and have a low decomposition temperature. These porogens can be inert in type or have reactive groups to chemically bind it to the surrounding low-k matrix (Fig. 8). The smallest of these compounds have a clean decomposition temperature of <200ºC, meaning that post-deposition processes can occur at much lower temperatures than used currently. Also, all porogens should be independently soluble in $scCO_2$ given their small size and non-polarity.

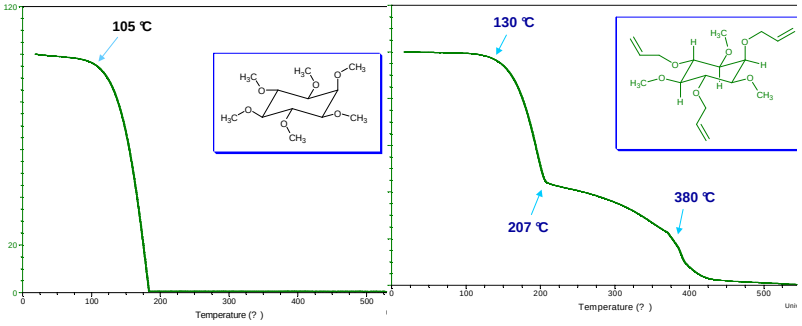

Fig. 3. Decomposition temperatures and weight losses for two porogens synthesized. The porogens on the left decomposes cleanly below 200ºC.