## Task ID: 425.017

<u>Task Title</u>: Environmentally Benign Vapor Phase and Supercritical CO<sub>2</sub> Processes for Patterned Low k Dielectrics

<u>Deliverable</u>: Report on preparation and assess of new porogens for ULK materials compatible with scCO<sub>2</sub> processing

## Abstract:

Porogens and pore formation represent an important strategy for lowering the dielectric constant of low k materials. Porogens can be added to a low k material matrix to act as spacers and ultimately removed leaving air pores to reduce the dielectric constant. We are investigating molecular glass precursors and porogens that either decompose at low temperatures or can be extracted with scCO<sub>2</sub>. In this way, we hope to reduce the environmental impact of annealing porous dielectric films.

## Technical Results and Data:

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 themselves to the surrounding low-k matrix. The smallest of these compounds have a clean decomposition temperature of  $<200^{\circ}$ C, meaning that post-deposition processes can occur at much lower temperatures than used currently (Fig. 1). Also, all porogens should be independently soluble in scCO<sub>2</sub> given their small size and non-polarity.



Fig. 1. Decomposition temperatures and weight losses for two porogens synthesized. The porogens on the left decomposes cleanly below  $200^{\circ}C$ 

The synthesized porogens and a commercially available porogen norbornene were integrated by concurrent vapor deposition with vapor-deposited dielectric films and thermally annealed for decomposition. The thickness loss after the annealing was measured, and void percentage caused by the porogens was modeled using spectroscopic ellipsometry (Fig. 2). All new porogens reported here survived the vapor deposition process and integrated nicely into the dielectric film. After annealing, films with ~10% porosity were achieved.



Past work has demonstrated the solubility of small glass-forming molecules in  $scCO_2$ .<sup>1</sup> General trends of  $scCO_2$ -solubility could be inferred, which helps with the design of  $scCO_2$  soluble porogens. Though solubility data was not generated for these molecules, there should be no issues with supercritical CO<sub>2</sub> processing of these porogens.

1. Nelson M. Felix, Anuja De Silva, Camille Man Yin Luk and Christopher K. Ober, "Dissolution Phenomena of Phenolic Molecular Glass Photoresist Films in Supercritical CO2", *J. Mater. Chem.*, (2007), 17(43), 4598-4604.