## Production of sub-20nm Pitch Features from Directed Self Assembly of High $\chi$ Polymers via a Selective Block Removal Process Utilizing Atomic Layer Deposition

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Directed Self-Assembly (DSA) using the guided phase separation of block copolymers has rapidly gained attention as a possible route for producing sub-20nm features. The basic DSA technology has progressed to the point where impressive results demonstrating near 20 nm pitch features over full wafers have been demonstrated using the most commonly studied block copolymer system for DSA, i.e. polystyrene-b-poly(methylmethacrylate) or PS-b-PMMA. However, at this 20 nm pitch region, it appears that PS-b-PMMA materials are reaching their limits in terms of the thermodynamic driving forces that are responsible for the phase separation process to occur. As this limit is approached, significantly higher defectivity is experienced and ultimately loss of patterning capability occurs as the pitch is decreased further (i.e. which corresponds to use of lower and lower molecular weight polymers). Therefore, to progress to even smaller pitches, it is believed that block copolymers with higher  $\chi$  values will need to be used. However, as new block copolymers are introduced, methods for the selective removal of one of the polymer blocks is also required in order to produce a lithographically useful pattern.

One of the promising class of alternative, higher  $\gamma$  polymers are those which contain blocks containing hydrogen bonding groups such as phenols, carboxylic acids, and alcohols combined with blocks that do not contain any such hydrogen bonding character. For example, polystyrene-b-poly(hydroxystyrene) or PS-b-PHOST is predicted to have a significantly higher  $\chi$ value than that of PS-b-PMMA and thus is predicted to be capable of producing feature sizes down to roughly 8nm pitch. However, a common problem for many of the polymers in this class that are easily obtained from common controlled polymerization techniques is a lack of etch contrast between the two polymer blocks that would allow for selective block removal through plasma etching. This work has explored methods for achieving selective block removal in such polymers, and has specifically focused on PS-b-PHOST as a model block copolymer system. It has been found that such block copolymer films after phase separation are a perfect substrate on which to carry out area selective atomic layer deposition techniques (ASALDT). For example, it will be shown that very high quality, defect free titania features can be grown selectively on the PHOST regions of a PS-b-PHOST film using ALD and that such oxide features can serve subsequently as robust etch masks that allow for the plasma etch removal of the PS blocks in he polymer, thus producing very high aspect ratio patterned BCP films. The capabilities and optimization of this type of novel DSA-ALD approach using polymers containing one block possessing alcohol, phenol, or carboxylic acid functionality in conjunction with a second hydrophobic block will be discussed in detail. Acheivement of DSA pitches down to 10nm will be demonstrated in relief features obtained using the DSA-ALD process.