

FABRICATION OF METAL OXIDE NANOSTRUCTURES FOR DEVICE APPLICATIONS BY THE THREE DIMENSIONAL REPLICATION OF BLOCK COPOLYMER TEMPLATES IN SUPERCRITICAL FLUIDS

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The development of well-defined porous metal oxides with nanometer-scale periodicity is of intense interest for a number of applications including photonics, sensing and detection arrays, catalysis, separations, microfluidics and low dielectric constant (low κ) thin films in microelectronics. To date, nearly all of these materials have been prepared by cooperative self-assembly of surfactants and metal oxide precursors in aqueous solution. While this approach has proven to be remarkably successful for controlling porosity at a local scale, difficult challenges for the fabrication of practical devices remain. These include the ability to form dimensionally stable, defect-free films of tailored composition over large areas, to control length scales, order and orientation in the pore structure and to produce films that can be directly patterned at dimensions much larger than the pore size. Here, we discuss a new approach to mesoporous silicates that satisfies these objectives. The process involves the infusion and selective condensation of metal oxide precursors within one phase domain of highly ordered, preformed block copolymer templates using supercritical carbon dioxide as the reaction medium. The template is then removed to produce the mesoporous oxide. To date we have replicated ordered spherical and cylindrical morphologies to yield silica, organosilicate and mixed silica/organosilicate mesostructures in films over 1 micron thick while maintaining all the structural details of the sacrificial copolymer template. The separation of the template formation and infusion steps is enabling. For example, structure on both the local and device levels can be achieved in three dimensions wholly in the polymer template using established techniques prior to infusion of the inorganic phase. This approach also offers flexibility with regard to framework chemistry and the nature of the copolymer template, which can now be chosen independently without regard to compatibility in solution or concerns about disrupting the coordinated self-assembly process. The implications of this process for the design and fabrication of nanostructured materials, including ultra-low dielectric constant thin films for application in microelectronics are discussed.