Task ID: 425.017
Task Title: Environmentally Benign Vapor Phase and Supercritical CO2 Processes for Patterned Low k Dielectrics
Deliverable: Report on the development of a photo-patternable template for SCF infusion and feasibility demonstration for a directly patterned ULK film

Abstract:

Simple and rapid fabrication of patterned dielectric films in an additive manner has tremendous potential to address integration challenges faced by ultra low k dielectrics. Recently Watkins et al., reported a new approach to mesoporous ultra low k (ULK) silicate films that involved 3-D replication of self-assembled block copolymer templates in supercritical carbon dioxide (scCO2). Films prepared using this approach have dielectric constant less than 2.2 and they were shown to survive a planar CMP test under conditions typically employed for dense carbon doped oxides. An enabling advantage of this approach is the separation of template preparation (via spin coating and self assembly) and silicate network formation into discrete steps. We have successfully extended the scCO2 replication technique to yield directly patterned ULK films that will eliminate or substantially reduce the need for dielectric etch and will offer good dimensional control in small features. These goals are accomplished by preparing photo-patternable templates based on block copolymer resist structures.

Technical Results and Data:

Mesoporous dielectric films with microscopic and nanoscopic features are fabricated by infiltrating silica precursors into patternable block copolymer templates containing photoacid generators (PAG). In our scheme the PAG serves two purposes: it deprotects the resist while simultaneously providing the acid catalyst required for silica network formation upon infusion of the precursor. Using selective irradiation, the presence of acid in the film can be spatially controlled, yielding in turn selective condensation of silica within the exposed regions. Moreover, because the acid segregates to the hydrophilic block of the deprotected resist, silica condensation is further localized to the hydrophilic domains in the block copolymer template. Since little silica condensation occurs in the hydrophobic domains, which serve as the porogen, mesoporosity is generated in the patterned film upon template removal. The process is shown schematically in Scheme 1.

Figure 1 shows an AFM image of a patterned dielectric lines of ~ 4 μm with interline spacing ~ 6 μm. These lines are prepared by exposure of poly (isobutylene-b-tertiary butyl methacrylate) (PIB-b-PtbMA) block copolymer to 254 nm UV radiation through a contact mask followed by infusion and condensation of tetra ethyl orthosilicate (TEOS) within the patterned template using CO2 as the carrier. Triphenyl sulfonium triflate was used as the photo acid generator. The chemical amplification process used to deprotect this PIB-b-PtbMA copolymer is essential to limit the diffusion of generated acid from exposed regions to unexposed regions. It is to be mentioned that our approach does not require a development step to dissolve the unexposed resist. The mesoporous structure of the silica films imparted by removal of the block copolymer template is shown in the TEM image shown in figure 2. In this case, chemically-amplifiable poly(styrene-b-tertiary butoxy carbonyloxy styrene) (PS-b-PtbocSt) block copolymer was used as a template. The pores are not well ordered due to weak microphase segregation in the template copolymer used for the feasibility study. The preparation of well-ordered mesoporous structures using suitable chemically-amplifiable block copolymer systems are now being explored. In conclusion, we have developed an efficient method to fabricate micro-patterned mesoporous silicate films by using a discrete two step approach. This method gains significant environmental safety and health (ES&H) benefits, as it can help to reduce cost and resources required, for example, in fabrication of fat lines for BEOL processes.Now that feasibility has been established, high resolution patterning is currently underway to achieve sub 10 nm features and ultimately to determine process resolution.

References:

1. R. A. Pai, R. Humayun, M. T. Schulberg, A. Sengupta, J. N. Sun, J. J. Watkins, *Science* **2004**, *303*, 507.
2. N. Sivakumar, J. K. Bosworth' C. K. Ober[†], T. P. Russell and J. J. Watkins, *Chem. Mater*. **2008**, 20, 604.

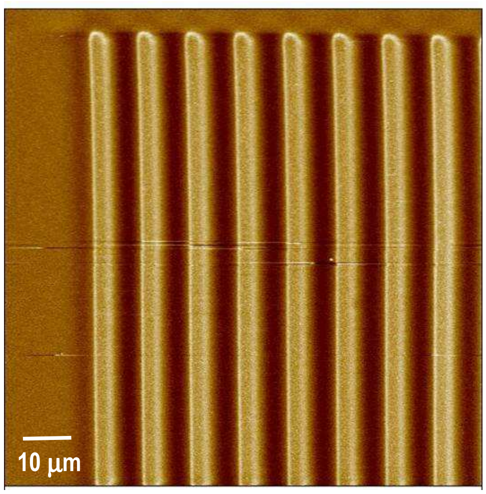


Figure 1: AFM image of patterned dielectric structures templated from P(IB-b-tbMA)

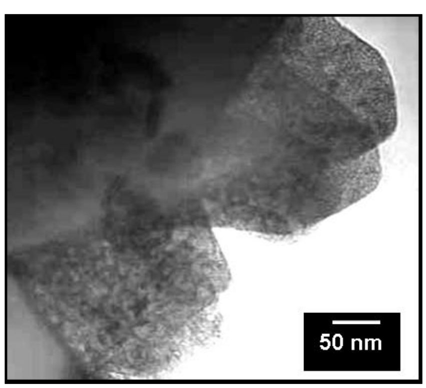
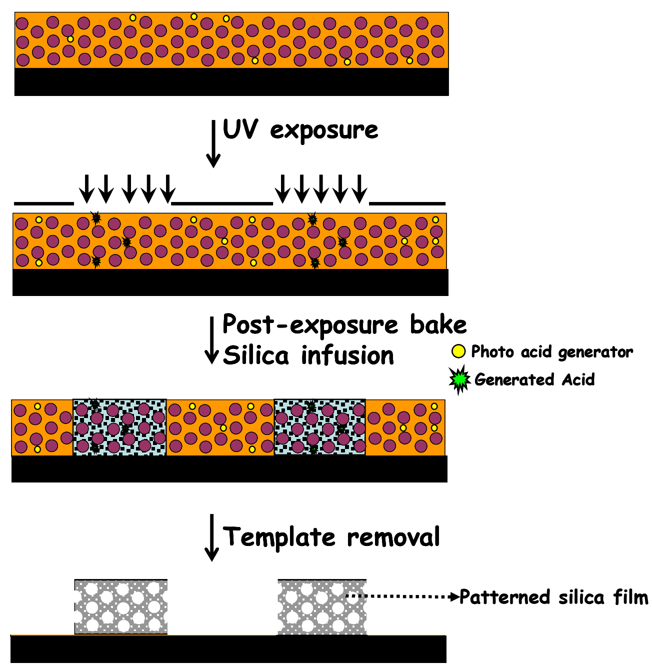


Figure 2:TEM image showing the Mesoporous structures present in the mesoporous silica film templated from P(S-b-tbocSt).



Scheme 1: Fabrication of patterned mesoporous silicate films from photo-patternable block copolymer films