546f Comparative Study of Covalent Molecular Assembly of Oligoimide Ultrathin Films in Supercritical Carbon Dioxide and Liquid Solvent

Sreenivasa Reddy Puniredd and M. P. Srinivasan

We have performed a comparative analysis of molecular assembly with covalent bonding using conventional and supercritical solvents. An ultrathin film of oligoimide has been fabricated on amine-modified substrates of silicon and quartz through alternate layer-by-layer (LBL) assembly of pyromellitic dianhydride (PMDA) and diaminodiphenylether (DDE), with inter-layer links established by covalent bonds. The assembly was formed in supercritical carbon dioxide (SCCO2), and in solution (dimethyl acetamide, DMAc). The amide links were converted to imide bonds by imidization. X-ray photoelectron and UV-visible absorption spectroscopies, atomic force microscopy (AFM), and ellipsometry were employed to study the interfacial chemistry, growth, morphology, and thickness of the assembled film. The comparison is further extended to carrying out the imidization reaction by various methods. XPS clearly indicated the formation of interlayer covalent linkages and formation of functional surfaces for immobilization of the next layer. The extent of recreation of functional groups and imidization are consistently high as long as supercritical fluid (SCF) is involved in the processing. The highest conversion is observed for the sample which has the maximum SCF involvement (i.e., deposition as well as imidization in SCF medium). UV-visible spectroscopy performed on assemblies deposited on quartz showed increase in absorption with number of layers, thus confirming layer-wise growth. This was corroborated by the measurements of film thickness performed by ellipsometry. The films that underwent SCF processing during imidization were substantially intact, whereas those formed and imdized conventionally showed significant decrease in thickness and absorption intensity. AFM images showed that both PMDA and DDE molecules were also assembled in more organized manner in SCF.

We are able to obtain robust ultrathin films of oligoimide by layer-wise deposition of PMDA and DDE in SCCO2. Covalent bonding between the layers provides strength while utilization of a supercritical medium facilitates a solvent-free environment and avoids problems related to residual solvent, thereby improving film quality when compared to conventional films. The advantageous role of supercritical fluids in covalent molecular assembly is evidenced by greater conversion and less topographic change during imidization, greater thickness and absorption intensity, and enhanced stability.