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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	Materials Science and Engineering 系 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of Engineering
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis titled, "Real-Time and Real-Space Tracking of the Self-Assembly of Block Copolymer Thin Films", the challenges set forth by academic interests in the bottom-up nature of BCP self-assembly and the industrial need for novel resist applications are addressed. As the need for stronger and faster computers fuels the demand for patterning capabilities at ever smaller dimensions, novel technologies that can overcome the limitations of conventional photolithographic technologies need to be developed. To that end, the 5 – 300 nm scale nanostructures formed through the self-assembly of block copolymers (BCPs) hold great potential as sub-10 nm resists for next generation lithographic applications. However, a number of challenges remain, including the reduction of defects in the thin film nanopatterns and the development of BCPs that are capable of forming sub-10 nm perpendicular lamellar structures with simple thermal annealing processes.

Chapter 1 "General Introduction" introduces the background behind the need for sub-10 nm patterning capabilities, along with a comparison of various competing next-generation technologies. Additionally, previously proposed solutions to the specific challenges imposed on the field of BCP lithography is discussed.

Chapter 2 "Evolution of Ordered Structures in PS-*b*-PMMA Thin Films on Unpatterned and COOL Process DSA Substrates" examines the evolution of ordered structures of the chosen workhorse BCP for the field, polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) on unpatterned and Coordinated Line Epitaxy (COOL) directed self-assembly (DSA) thin films. The evolution of perpendicular lamellae from a disordered to an ordered state is tracked in real-time and real-space with a high-speed atomic force microscope (AFM) on a heating stage and custom-built nitrogen environment chamber. However, on simple unpatterned substrates, the perpendicular lamellae adopt a highly random fingerprint-like pattern riddled with defects. To direct the self-assembly of the microdomains, PS-*b*-PMMA thin films are also prepared on chemically pre-patterned DSA substrates fabricated using the COOL process. The development of ordered structures from the initial disorder-like state is once again investigated using high-speed in situ AFM. While certain areas with long-range alignment of the perpendicular lamellar structures are detected, the thin films exhibit a mixed orientation likely due to disparate interfacial affinities between the BCP, substrate, and free interface.

Chapter 3 "Real-Time and Real-Space Evolution and Alignment of Lamellae on Chemically Pre-Patterned SMART^{TM} Process DSA Substrates" builds upon earlier work and the DSA of PS-*b*-PMMA is evaluated on chemically pre-patterned substrates prepared via the Surface Modification for Advanced Resolution Technology^{TM} (SMART^{TM}) process. Using high-speed in situ AFM, the microphase separation, growth, and long-range alignment of perpendicular lamellae is studied over a large temperature window that starts below the glass transition temperatures of the BCP, before increasing to high temperatures that expedite the self-assembly of the microdomains.

Chapter 4 "Defect Dynamics and Annihilation Pathways of Lamellar Patterns under the Influence of SMART^{TM} Process Chemoepitaxial DSA" examines the self-assembly behavior of nanostructures at characteristic annealing temperatures via high-speed in situ AFM. Large area and high resolution imaging reveal the sources of the defects, the nucleation and growth mechanisms, and the annihilation pathways of typical defects found in the self-assembly of BCPs. Furthermore, with ultra-high-speed AFM imaging, a movie highlighting the stochastic linking and breaking of the microdomains is recorded at a rate of one frame every two seconds.

Chapter 5 "Evolution and Hexagonal Arrangement of Dot Patterns in Perpendicular Cylinders on Chemically Pre-Patterned DSA Substrates" extends the study to perpendicular cylindrical structures which form hexagonal patterns on pre-patterned DSA substrates. The first report of the in situ, real-time, and real-space growth of PS-*b*-PMMA cylindrical structures, perpendicular reorientation, and long-range alignment is presented.

Chapter 6 "Synthesis of Poly(3(2,2',2",4,4',4",6-heptaethyl polyhedral oligomeric silsesquioxane)propyl methacrylate)-*block*-poly(2,2,2-trifluoroethyl methacrylate) (PMAPOSS-*b*-PTFEMA)" explores the optimal synthetic route for the preparation of PMAPOSS- and PTFEMA-containing BCPs. Moving beyond the limitations of PS-*b*-PMMA while maintaining the similar concept of BCPs with similar surface affinities for perpendicular

orientation, a silicon (Si) and fluorine (F) containing hybrid BCP, PMAPOSS-*b*-PTFEMA, is developed and the synthesis via the reversible addition-fragmentation chain transfer (RAFT) process is optimized.

Chapter 7 “Disorder-Order Evolution of Sub-10 nm Perpendicular Lamellar Structures of PMAPOSS-*b*-PTFEMA on Bare Silicon Substrates” then investigates the evolution of the 16 nm full-pitch lamellar structures via combinatorial studies. With heteroatomic Si- and F-containing components, PMAPOSS-*b*-PTFEMA was reported to be capable of forming self-assembled nanostructures with full-pitch periodicities down to 11 nm. Furthermore, with similar surface affinities, PMAPOSS-*b*-PTFEMA orients perpendicularly on a variety of substrates without needing chemically modifying neutral layers and using simple ambient thermal annealing. The combinatorial analysis reveals insights into the self-assembly behavior on not just the surface but also in the depths of the thin films.

Chapter 8 “Conclusion and Future Prospects” summarizes and reviews the results of this study, and a commentary on the future pathways available for the field of BCP lithography and DSA is discussed.