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Silicon-containing block copolymers for lithographic applications

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ABSTRACT

This comprehensive review, summarizes recent advances in the fabrication of well-ordered block copolymer (BCP) thin films by different methods, focusing on the development of silicon-containing BCPs as candidates for lithographic applications. With the advantage of Si-containing blocks, these BCPs offer much smaller feature sizes due to large segregation strength and high etch contrast for the fabrication of well-defined nanopatterns with high resolution. Considering that poly(dimethylsiloxane) (PDMS)-containing BCPs are widely studied systems among Si-containing BCPs, the possibility of using PDMS-containing BCPs for lithographic applications is demonstrated through previous and ongoing key research.

BCP lithography will lead to the development of next-generation microelectronic devices by providing a simple and scalable nanopatterning method for the fabrication of microelectronic devices in which the feature sizes and geometries are controlled by tuning the chain lengths and volume fractions of the block copolymers. The control of microdomain orientation and alignment in thin film BCPs is crucial for lithographic applications. The principles and limitations of various methods to orientation are discussed, including temperature-gradient, surface modifications, solvent annealing/evaporation and other new types of annealing process.

Directed self-assembly (DSA) of BCP on topographic or chemically patterned substrates has attracted a great attention from academic and industrial research since it offers the advantage of defect free nanopatterning at large scales. The key achievements in DSA methods are elaborated in the subsequent parts of this review. New trends for lithographic applications and the applications beyond lithography using Si-containing BCPs for nanopatterning are also discussed, and finally, concluding remarks and perspectives for BCP lithography are presented.

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Nomenclature

AES	Auger electron spectroscopy.
AFL	Anti-symmetric surface-parallel lamella
AHY	Anti-symmetric hybrid structure
BCP	Block copolymer
C	Cylinders
CPS	Close-packed spheres.
CZA-SS	Cold zone annealing-soft-shear
DBP	Di-*n*-butyl phthalate
DDFT	Dynamic density functional theory
DEP	Diethyl phthalate
DOP	Bis(2-ethylhexyl) phthalate
DSA	Directed self-assembly
EUV	Extreme ultra-violet lithography
f	Volume fraction
FL	Symmetric surface-parallel full lamella
G	Gyroid
HL	Half-lamella
HY	Symmetric hybrid structure
ICs	Integrated circuits
ITRS	International technology roadmap for semiconductors
L	Lamellae
L_0	Domain spacing
MIRS	Multiple internal reflection infrared spectroscopies
N	Degree of polymerization
ODT	Order- disorder transition
OOT	Order-order transition
PE	Poly(ethylene)
PEDOT:PSS	(poly(3,4-ethylenedioxy thiophene): poly(styrenesulfonate)
PFS	Polyferrocenylsila
PI	Polyisoprene
PL	Perforated-layer
PL	Surface-perpendicular lamellae
PMOST-PTMSS	Poly(4-methoxystyrene)-*b*-poly(trimethylstyrene)
POSS	Polyhedral oligomeric silsesquioxane
PS-PB-PS	Polystyrene-b-polybutadiene-b-polystyrene
PS-PDSS	Polystyrene-*b*-poly(pentamethyl disilylstyrene)
PS-PEO	Polystyrene-*b*-poly(ethylene oxide)
PS-PFS	Polystyrene-*b*-poly(ferrocenylsilane)
PS-PLLA	Polystyrene-*b*-poly(L-lactide)
PS-PMMA	Polystyrene-*b*-polymethyl methacrylaye
PS-PTMSS	Polystyrene-*b*-poly(trimethylstyrene)
PS-PVP	Polystyrene-*b*-polyvinylpyridine
PTFE	Poly(tetrafluoroethylene)
PVC	Poly(vinyl cyclohexane)
QPL	Quadratically perforated lamellae
Rg	Radius of gyration of copolymer film
S	Spheres
SAMs	Self-assembled monolayers
SCFT	Self-consistent field theory
t	Film thickness
TDGL	Time-dependent ginzburg-Landau theory
T_{odt}	Order-disorder transition temperature
XPS	X-ray photoelectron spectroscopy
ZA	Zone annealing
γ	Interfacial energy
ε	Effective interaction parameter
λ	Average surface pattern size
ϕ	Polymer volume fraction for solutions
Φ_P	Shrinkage ratio of the film thickness during drying
χ	Flory-Huggins interaction parameter
$\Delta\gamma$	Interfacial energy difference
∇T	Temperature gradient

1. Introduction

Historically, the development of microelectronics has been following Moore's law (the linewidth of the pattern has approximately halved every 18 months) to satisfy the growing demands for higher speed and lower energy consumption per computing unit. When the feature size reduces below the sub–22 nm size, the "top-down" photolithography method will become prohibitively expensive, and approach its physical limit. Directed self-assembly (DSA) of block copolymers (BCPs) combining the advantage of traditional "top-down" lithography and thermodynamics-governed "bottom-up" self-assembly for spontaneously forming sub–22 nm nanostructures with high degrees of perfection, accuracy, registration and complexity is an appealing approach. There are some review articles on recent progress toward techniques that achieve controlled orientation of BCP thin films through DSA using chemical or topographical guiding patterns [1–5].

Block copolymers (BCPs) composed of two or more chemically distinct, incompatible blocks are well-known to self-assemble into various ordered nanostructures resulting from a balance between