Controlling domain orientation in self-assembled block copolymer thin films for lithographic application

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Manufacturing strategies based on directed self-assembly of block copolymer (BCP) thin films have been the subject of an intense research activity over the last decades. The propensity of BCP to self-assemble in a variety of periodic morphologies, with characteristic dimensions spanning from 5 nm to 50 nm, has been exploited to produce templates that are subsequently transferred to the underlying substrates by additive or subtractive approaches. In this respect, nanostructured BCP thin films are commonly considered suitable candidates to integrate and extend conventional photolithographic techniques, enabling the fabrication of next generations of microelectronic devices.

The orientation control of BCP morphologies with respect to the substrate represents a key success factor, with the perpendicular orientation being preferred because of the sharp side walls and the high aspect ratio achievable for the resulting template. Domain orientation is mainly controlled by the interaction of each block with the substrate and the free surface through wetting energetics and polymer confinement, eventually including commensurability effects that result from the (mis)matching of the BCP periodicity with the film thickness. Preferential wetting of one block of the BCP to the substrate drives the BCP domains to be oriented parallel to the plane of the substrate. The most robust strategy for promoting the perpendicular orientation in BCP thin films relies on the surface modification using poly(A-r-B) random copolymers (RCP) chemically grafted to the substrate via the "grafting to" approach. In particular, the use of functional hydroxyl-terminated poly(styrene-r-methyl methacrylate) [P(S-r-MMA)] RCP is a well-studied approach to inducing the perpendicular orientation in polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) BCPs. For this class of polymers, at 225 °C, the interfacial interactions at the free surface are balanced, thus allowing the perpendicular orientation of domains to be obtained when they are annealed on a neutral substrate surface. Interestingly, the use of hydroxyl terminated P(S-r-MMA) RCP brush layers has been recently extended to mixtures of low molar mass PS-b-PMMA and ionic liquids as well as to high-x polystyrene-b-poly(propylene carbonate)s (PS-b-PPC) BCP. An accurate tuning of the P(S-r-MMA) composition allows the substrate surface to be made neutral for both systems leading to the perpendicular orientation of BCP domains. These results clearly indicate that functional P(S-r-MMA) can be employed to control the substrate wetting characteristics for different BCP systems, extending the range of applicability towards systems with smaller and smaller characteristic dimensions.

In this study, we review recent results in the field investigating the role of the RCP brush layers in the selfassembly of BCP thin films. Important relations between the characteristics of the RCP brush layer and the kinetics of the self-assembly process are highlighted, elucidating the effective role of the RCP in the evolution of the BCP system towards its final equilibrium state.

Biography

Michele Perego received the Degree in Physics from Università degli Studi dell'Insubria in 1999. In February 2004, he obtained his PhD in Physics, applied Physics and Astrophysics from Università degli Studi di Milano for his work on the ToF-SIMS characterization of silicon nanocrystals embedded in thin oxide films. In the period 2004-2007 he has been Post-Doctoral Fellow at the MDM Laboratory in Agrate Brianza where he has been working as research scientist since 2007. He is currently the coordinator of a research group working on the development of new bottom-up approaches for the synthesis of functional nanostructured materials with typical feature dimension below 20 nm. The focus of his research activity is on one side the investigation of fundamental issues related to the self-assembly processes in polymeric films and on the other side the use of these macromolecules to synthesize and manipulate functional nanostructures for microelectronics, optoelectronics and photovoltaic applications.