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Top-coats for scalable Nano-manufacturing with High- χ Block Copolymers in Lithographic Applications

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Abstract

Results for the self-assembly of lamellar silicon-containing high- χ BCPs with innovative neutral top-coat design are presented. We demonstrate that these materials and associated processes are compatible with a standard lithographic process, and oriented toward a potential HVM. We show that this dedicated technology is able to guarantee the stability and planarity of the stack even at elevated self-assembly bake temperatures, and opens new opportunity in the fields of 3D BCPs stacks. Finally, we show interesting results for the etch-transfer of a lamellar BCP in silicon.

Introduction

The directed self-assembly (DSA) of block-copolymers (BCPs) is a powerful method for the manufacturing of high-resolution features in lithographic applications. Studies performed over recent years have demonstrated impressive potential in terms of integration capabilities and defect levels with the well-known PS-*b*-PMMA system enabling its use within standard lithographic processes at an industrial level. However, this particular system is limited to dimensions above ~20 nm in period, due to a rather weak segregation strength (measured by the Flory-Huggins parameter χ) between both blocks, and new challenges have arisen with the use of high- χ systems. Among them, rapid self-assembly capabilities, etch performances, integration flows, coatings uniformity, etc... are still major concerns and hardly addressed topics in existing literature, even though of crucial importance for nanomanufacturing with DSA. Early works on high- χ systems demonstrated some interesting potential with the use of top-coats (TC) to drive the perpendicular orientation of the BCP domains,^{1,2} but improvements are still needed for a realistic industrial implementation. For instance, wet-removal of TC in (1)

may lead to defects and inhomogeneities across the wafer, and the TC coating may not be homogeneous either as the water-based solvent may not wet properly the BCP film due to surface tension mismatch. In (2), the TC process followed is appealing, but necessitates a PECVD-dedicated tool and an extended deposition time (>75 minutes) for the TC. Additionally, in this specific publication, the BCP cannot be transferred directly into the substrate and necessitate an additional time-consuming sequential infiltration process, precluding thus high-throughput of wafers.

In the present communication, we highlight our recent achievements on the design of specific top-coat materials used here with a silicon-containing high- χ BCPs systems based on poly(1,1-dimethyl silacyclobutane)-*block*-poly(styrene) (abbreviated PDMSB-*b*-PS), tackling successfully the aforementioned bottlenecks.

Experimental

Synthesis of TC material: the synthesis of the TC material was performed by radical polymerization in solution with AIBN as initiator. All the methacrylic monomers, solvent, initiator and terminating agent were used as received.

*Synthesis of PDMSB-*b*-PS BCP:* the synthesis of the BCP material was performed as previously reported.³

Preparation of thin films: NL material is dissolved into MIBK at 2%, spin-coated onto Si monitor samples at 1500 rpm, grafted at 200°C during 75 sec, and then the samples are rinsed into MIBK. The 0.9 wt% PDMSB-*b*-PS solutions in MIBK were spin-coated (2 krpm) on immobilized NLs followed by a soft-bake at 60°C for 1 min to produce BCP layers with approximatively 30 nm thickness. The TC material, previously dissolved into absolute ethanol at 2 wt%, is spin-coated on the BCP thin film at 1500 rpm. The stack is baked at 90°C for 3 minutes, and the BCP is self-assembled at 240°C for 5 minutes.

Ellipsometry: The coating uniformity of the various polymeric layers was probed using spectroscopic ellipsometry with a phase modulated spectroscopic ellipsometer (UVISEL, from Horiba Scientific) on the spectral range 200-800 nm.

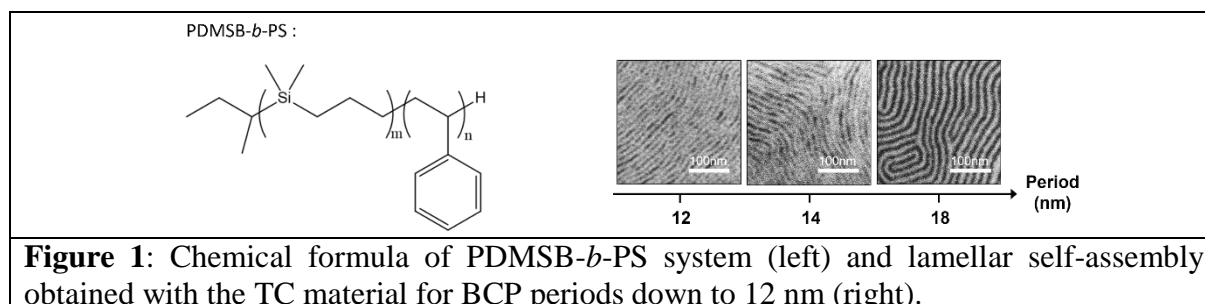
Scanning electron microscopy and scanning transmission electron microscopy: Top-view SEM images were acquired on a Hitachi CD-SEM H-9300 microscope with 0.5 kV electron acceleration voltage and a 6 μ A current. STEM cross-sections were prepared and obtained with a Helios 450S-FEI dual-beam microscope.

Plasma etching: Etching experiments were performed in a 300 mm AdvantEdge™ MESA™ from Applied Materials. In this inductively coupled plasma (ICP) etch tool the chamber walls are made of yttrium oxide. BCP samples were patched on 300 mm Si wafers. The chamber was first cleaned using a three-step plasma: NF₃/Cl₂ for 45 s, Cl₂/O₂/Ar for 45 s, and finally O₂ for 30 s, to allow a good process reproducibility.

Results and discussion

The PDMSB-*b*-PS BCP system chosen here is depicted on the Figure 1. This system enables the formation of very high-resolution dimensions, as highlighted by the captured CD-SEM images of lamellar systems shown in the Figure 1 presenting periods from 12 to 18 nm.

We note that further lowering of the dimensions could be still possible for the PDMSB-*b*-PS system, as the smallest lamellar morphology is well phase-separated even at the annealing temperature used here (240°C). Such high- χ system is therefore quite appealing in the context of lithography with DSA. Moreover, the silicon-containing PDMSB block provides an additional etch-resistance for the resulting features, and thus avoid the use of time-consuming processes like sequential infiltration, to optimize the throughput of future related devices.



The whole set of materials used in the framework of the self-assembly is available in large amounts, as shown in Figure 2 where 1L bottles at 2 wt% of both the neutral layer (NL) and the TC, and 0.5L for the BCP, are displayed. The NL and TC materials are both based on a methacrylate chemical platform, and thus can be synthesized through a simple classical radical polymerization in high yields and purity over a wide range of compositions, and more importantly, on a scale of several 10th of kg per batch if necessary. It can be noted that the TC itself can be used as a NL, as it contains chemical functions to enable the grafting of the material onto a variety of surfaces. These materials are not developed especially for the PDMSB-*b*-PS system, as they do not contain any of the BCP monomers in their formula, their respective composition is just easily adapted to this system to obtain a neutral material for the BCP. Therefore, these NL and TC materials can fit other BCP systems by a simple compositional adjustment if necessary while keeping intact their own intrinsic characteristics. The three materials involved in the self-assembly (NL, BCP, TC) are all able to be readily spin coated from the initial solution. The TC material is designed on purpose to be entirely soluble into eco-friendly solvents like alcohols (ethanol, IPA...), so as not to dissolve the BCP film during the spin-coating step. The respective process of the three materials, of a few minutes each before being entirely functional, is especially designed to favor a high throughput of wafer in the view of a potential HVM (Figure 2).


	Neutral underlayer	BCP	Neutral TC	
Film Thickness	~2-5nm	30nm (std) 1-many L ₀	50nm (std) 15-200nm	
Solvent	MIBK/PGMEA	MIBK	Alcohol (EtOH-IPA)	
Coating	Spin-coating	Spin-coating	Spin-coating	
Processing Time	75s/2mins	30s-hours	3min (std) 1-10mins	

Figure 2: Details of process parameters for the various materials involved in the self-assembly, showing compatibility with standard techniques and devices of lithography industry (left). Commercial bottles of 1L, 0.5L and 1L for the NL, BCP and TC reported in this communication (right).

A special attention has been paid to the thickness uniformity for each layer involved in the final stack, as important variations are precluding any use of the materials into a potential application. The measurement reported here is performed on 4 inches wafers, with hand-dispensed materials for the corresponding spin-coated layers. A first visual inspection enables to confirm an excellent coating quality without any noticeable comet or other coating-related defects. Thicknesses variations were estimated through ellipsometry for each layer, from a series of automated measurements involving 31 independent points for each layer. The results reported in the Figure 3 further confirmed the excellent coating quality for each layer, with a 3σ variation of 0.2, 0.5 and 2.4 nm for NL, BCP and TC materials, respectively. It is noteworthy that the TC uniformity of 2.4 nm is still less than 5% of the corresponding thickness across the whole wafer and cumulates the variation of the two other buried layers (NL and BCP). Therefore, the actual thickness variation of the TC layer itself is below this overestimated value, even after the self-assembly step performed at 240°C during 5 minutes.

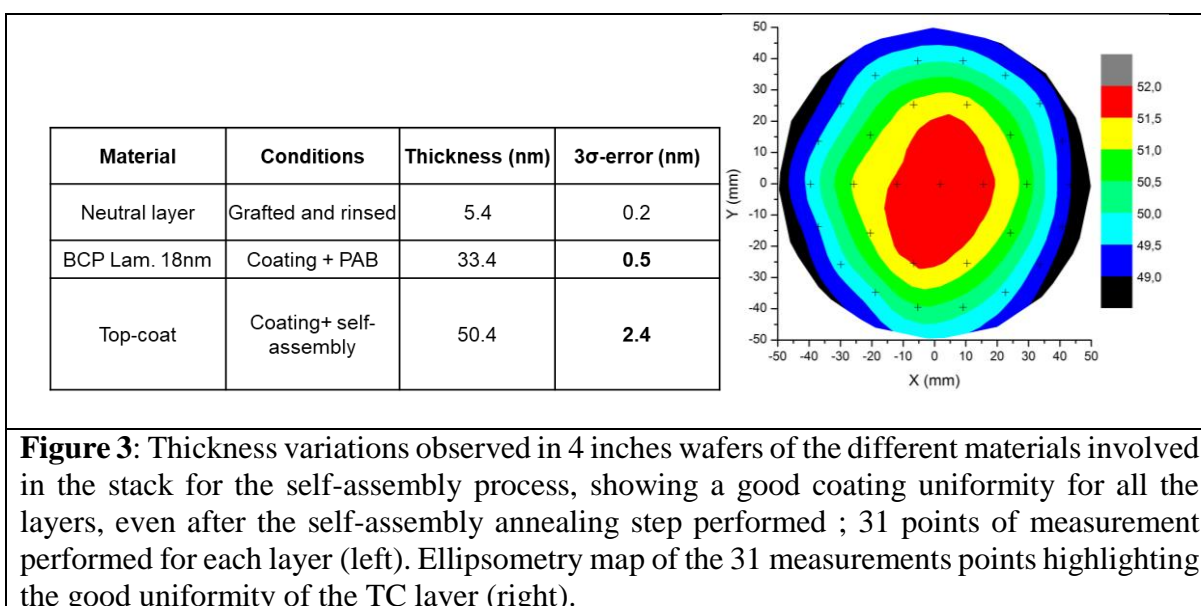
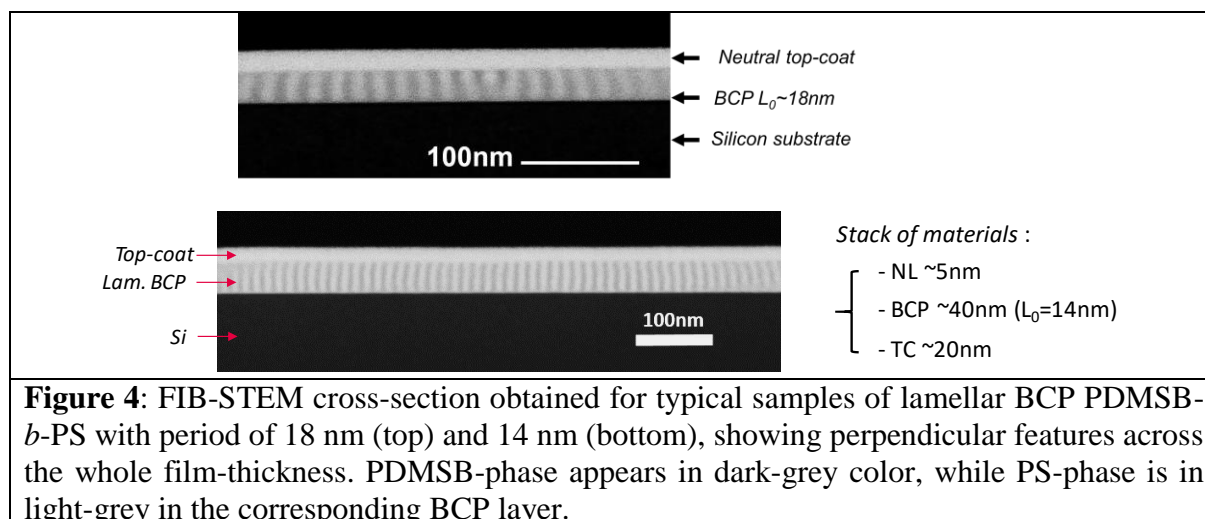


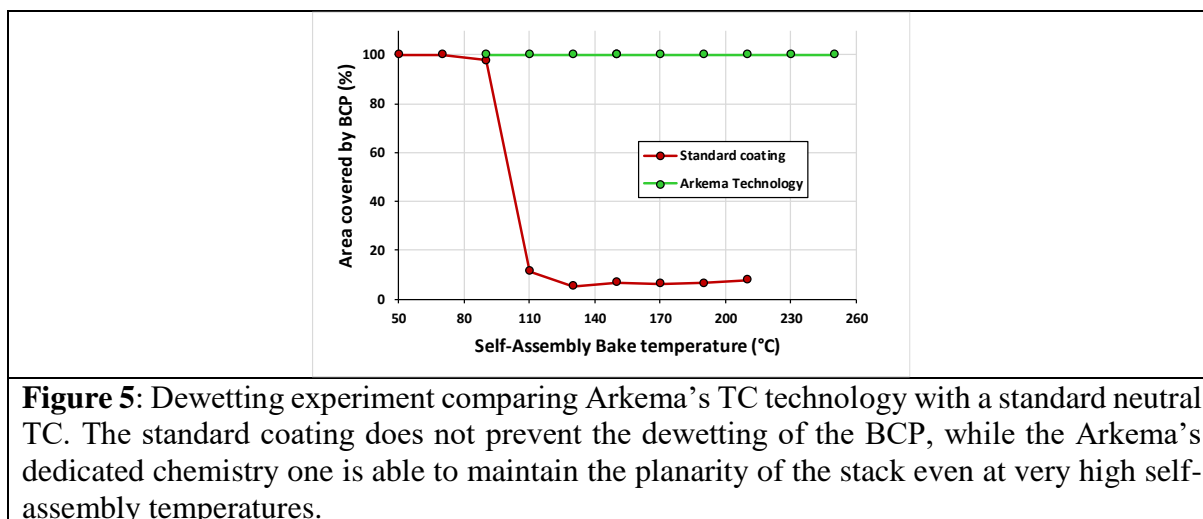
Figure 3: Thickness variations observed in 4 inches wafers of the different materials involved in the stack for the self-assembly process, showing a good coating uniformity for all the layers, even after the self-assembly annealing step performed ; 31 points of measurement performed for each layer (left). Ellipsometry map of the 31 measurements points highlighting the good uniformity of the TC layer (right).

The top-view SEM pictures for the various lamellar BCPs presented in the Figure 1 are already providing a good insight into the good quality of the self-assembly for each system. Indeed, upon selective removal of the TC through dry etch after the annealing step, well defined lamellar morphologies were observed on each random location probed by SEM. To gain further insights on the quality of the self-assembly, a series of FIB-STEM experiments were performed on the lamellar self-assembled films of 18nm and 14nm period, without the TC-etch step. The cross-sections obtained for these samples are presented in the Figure 4. For both systems, the STEM images show that the out-of-plane lamellar features are spanning the whole BCP film thickness (30 nm for the 18 nm period and 40 nm for the 14 nm period, respectively), leading to high aspect-ratio features ($AR \sim 6$ in the case of the BCP with 14 nm period). It confirms thus the well-balanced interfacial interactions for both blocks of the BCP with the TC and NL

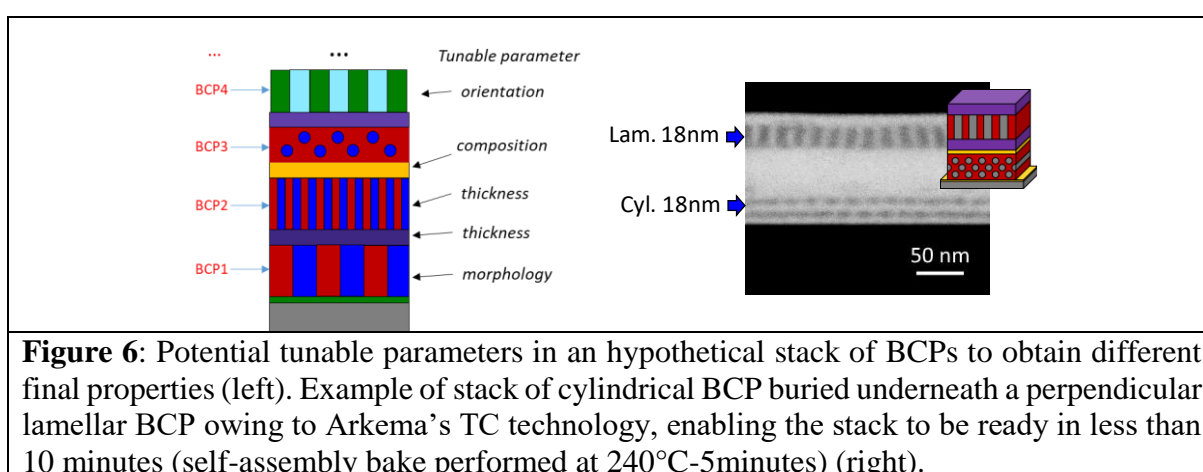
materials. We can note also that each interfaces involved in the system is well identified and separated from each other, confirming the absence of intermixing of the TC material inside the BCP layer.



A unique aspect of these TC material is their propensity to guarantee the initial flatness of the stack despite of the various annealing treatments. Indeed, due to the particular configuration of DSA-usable materials (thin film, neutral interfaces), the well-known issue of dewetting is often present in BCP self-assembly, especially in the case of high- χ BCPs where the low molecular-weight and the large surface-energy difference between the blocks of the BCP favor dewetted configurations. The TC material designed in this study enables the circumvention of this critical issue owing to its particular macromolecular design. This exceptional propriety is demonstrated in the Figure 5, where the mean-area covered by the BCP layer (18 nm period) for the inspected surfaces is plotted versus the self-assembly temperature of the system. One point on the graph correspond to one-dedicated sample made at the specified self-assembly temperature. From this graph, it is clearly observed that the dewetting start to proceed at 90°C for the standard neutral coating, leading quickly to an entirely dewetted configuration corresponding to a low BCP-covered area (~10% only of the total inspected surface is covered by the BCP in the final state). Conversely, the BCP film coated by Arkema's neutral TC keeps its integrity and flatness even for high self-assembly temperatures (250°C), as 100% of the inspected area is covered by the BCP. This technology not only ensures a fully functional self-assembled BCP thin film, but also enables to tremendously increase the thermal annealing budget for the self-assembly process in order to kinetically favor a potential defect-free configuration for a given BCP system.

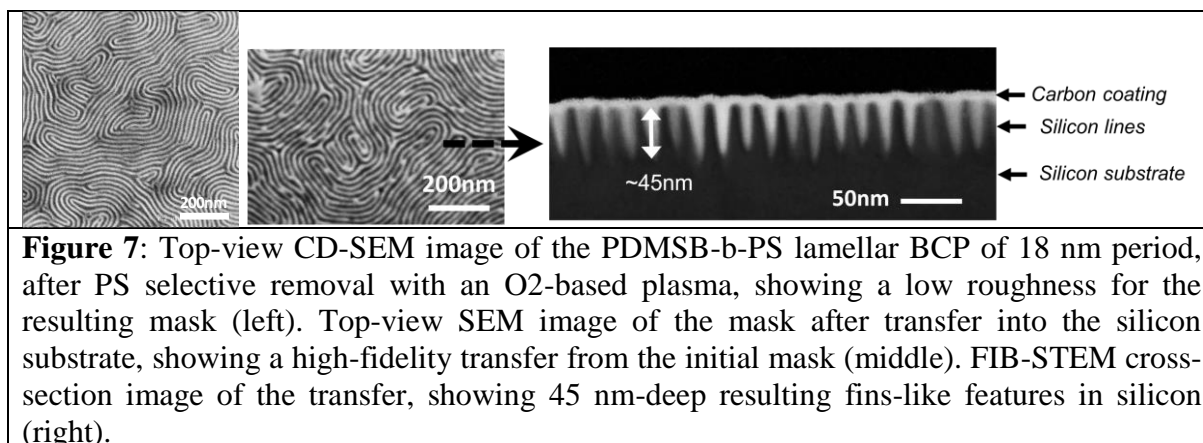


Another unique property of our TC technology dedicated to BCP self-assembly lies in the possibility of stacking various self-assembled BCP layers directly on top of each other. Such 3D-multilayered structures are potentially valuable in cutting-edge technologies as photonics, metamaterials and microelectronics through the extension of non-natural features obtained by BCP self-assembly. Although already reported in the literature, these multilayers stacks often necessitate additional processing steps to reinforce the buried layers as regards to a potential re-solubilization along with the coating of new layers. These additional processes are somehow time-consuming, and lead to a significant decrease of throughput for the overall process. In the case of Arkema's technology, such additional processing steps are not necessary owing to the well-chosen constituents of the TC material itself. It results in a very swift process, as an entirely functional bilayer of BCPs such as the one depicted in the Figure 6 can be realized within less than 10 minutes (including a self-assembly bake of 5 minutes). Such a quick process, together with the multiple possible combinations to tune the final properties of the stack (orientation, morphologies, compositions, etc... see left panel of Figure 6), and the intrinsic readiness for the preparation of the stack, render these TC materials extremely appealing in view of such applications.



The demonstration of the designed TC material as an optimal neutral layer for a silicon-containing BCP is further corroborated through etch results. Indeed, the TC material can be readily removed with an O₂-based plasma, owing to its fully organic nature, while the BCP

layer behaves as an etch-stop layer for the very same plasma chemistry. The end of the TC-etch step is therefore quite straightforward with such materials combination. Afterwards, the PS phase can be removed selectively as regard to the PDMSB one, once again with an O₂-based plasma, leaving at the end of the process low roughness silica-like perpendicular lamellae (Figure 7, left panel). A common patterning strategy is to then transfer the DSA patterns into a thin (5-10 nm, usually) amorphous Silicon hard mask⁸ to be used for further patterning steps, depending of the considered stack. Using synchronously-pulsed HBr/O₂ plasma, we demonstrate here that such oxidized PDMSB masks are resilient enough to pattern up to 45 nm-deep features of CD <9 nm in mono-crystalline Silicon and would therefore not be limiting in terms of hard-mask strategies (thickness, etc.) for any application.



Conclusions

We have presented here the results relative to newly designed TC materials for BCP self-assembly with high- χ copolymers, taking into account well-known issues in DSA, and enabling a potential HVM for such processes. The optimized combination of these materials with a silicon-containing BCP enables the formation of high aspect-ratio perpendicular features, while allowing one to design functional stacks of BCP materials for advanced applications.

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- (8) Insert one of the IMEC’s papers from Pathangi or from PESM, showing the stack used.