Experimental report

12/02/2021

Proposal: CRG-2597 **Council:** 4/2019

Title: Neutron Scattering Study of Selective Infiltration Synthesis into Block Copolymer for Sub-10 nm Nanolithography Applications

Research area: Engineering

This proposal is a new proposal

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Samples:
Polystyrene-block-Maltoheptaose and 1 cycle of Alumina on Silicon
Polystyrene-block-Maltoheptaose and 2 cycles of Alumina on Silicon
Polystyrene-block-Maltoheptaose and 4 cycles of Alumina on Silicon
Polystyrene-block-Maltoheptaose and 8 cycles of Alumina on Silicon
Polystyrene-block-Maltoheptaose and 12 cycles of Alumina on Silicon
Polystyrene-block-Maltoheptaose on Silicon
Polystyrene on Silicon
Polystyrene and 1 cycle of Alumina on Silicon
Polystyrene and 4 cycles of Alumina on Silicon
Polystyrene and 12 cycles of Alumina on Silicon
Maltoheptaose on Silicon
Maltoheptaose and 1 cycle of Alumina on Silicon
Maltoheptaose and 2 cycles of Alumina on Silicon
Maltoheptaose and 4 cycles of Alumina on Silicon
Maltoheptaose and 8 cycles of Alumina on Silicon
Maltoheptaose and 12 cycles of Alumina on Silicon

Instrument	Requested days	Allocated days	From	To
SUPERADAM	5	3	10/02/2020	13/02/2020

Abstract:

Block copolymer (BCP) lithography addresses some issues high-lighted for next generation lithography - high pattern density over large areas. The self-assembled BCP Polystyrene-block-Maltoheptaose (PS4.5k-b-MH1.2k) has a bulk periodicity of 10 nm. Challenges in the sub-10 nm regime is achieving an etch mask to enable pattern transfer. By selectively infiltrating the Maltoheptaose part of the BCP with Alumina, a higher etch selectivity between blocks can be achieved. Investigation of the effect of number of sequential infiltration synthesis (SIS) cycles into PS-b-MH showed that the Alumina feature diameter increases with number of cycles. However, neither the infiltration mechanism nor the self-assembly type is clear. Therefore, a study of the infiltration process into PS-b-MH, as well as into Polystyrene and Maltoheptaose, using neutron reflectivity in air is proposed. The aim is to describe the Alumina growth, to determine if surface deposition or full infiltration is occurring, and to verify the selectivity between blocks. Furthermore, to identify any polymer wetting layer on top of the substrate. The results will contribute to development of next generation lithography.

CRG-2597 Experimental Report

Neutron scattering study of selective infiltration synthesis into block copolymer for sub-10 nm nanolithography applications

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Background

Block copolymer (BCP) Poly(styrene)-*block*-Maltoheptaose (PS-*b*-MH) of molecular weight 4.5 kg/mol and 1.2 kg/mol, respectively, were infiltrated with Trimethyl Aluminium (TMA) and water in an atomic layer deposition (ALD) chamber, in a process known as sequential infiltration synthesis (SIS). The BCP had a pattern periodicity of 12 nm after self-assembly into horizontal MH cylinder orientation. Aiming for a quantitative characterization of the resulting Alumina inclusion in respective block, thin film samples of homopolymer Maltoheptaose (MH, 1.2 kg/mol), homopolymer Hydroxyl terminated Poly(styrene) (PS-OH, 4.5 kg/mol), and self-assembled PS-*b*-MH were investigated, for varying number of infiltration cycles, in specular neutron reflectivity (NR) measurements in air at 5.12 Å wavelength, for incident angle 0-4°, at Super-ADAM neutron beamline, Institute Laue-Langevin (ILL), Grenoble, France, on February 10-13, 2020.[1] Also, experiments exploring any differences in Alumina content in the polymer films after using two different SIS methods, dynamic and static infiltration, were initiated. Furthermore, aiming for information on lateral periodicity in BCP samples,[2] off-specular small-angle neutron scattering (SANS) in air was performed on BCP samples.

Preliminary results

Table 1 shows samples measured in specular NR, whereas samples measured in SANS are shown in Table *2*, including their corresponding scan numbers.[1] The BCP samples were made in two batches, here called batch H, and batch V, respectively, slightly differently processed (hotplate dehydration, or UV-Ozone treatment, respectively) prior to spin-coating of the polymer.

Table 1. Sample material measured in specular NR, and their corresponding scan numbers.

SIS method	Number of SIS cycles	Si substrate	Alumina	MH	PS-OH	PS-*b*-MH (H)	PS-*b*-MH (V)
N/A	0	802	777	813	825	775	807
Dynamic	1	N/A	N/A	856		850	854
	2	N/A	N/A	829	835	781	811
	4	N/A	N/A	831		779	809
	8	N/A	N/A	815	827	772+773	805
Static	2	N/A	N/A	839	814	833	
	4	N/A	N/A			837	

N/A Not applicable.

Table 2. Sample material, and direct beam, measured in SANS, and their corresponding scan file numbers.

Number of dynamic SIS cycles	PS-*b*-MH (H)	PS-*b*-MH (V)
0	789	820
2	790	821
8	791	822
Direct beam	792	823

Analysis of MH samples showed an increase in neutron scattering length density (SLD) with increasing number of infiltration cycles, which can be seen in Figure 1.[3] The corresponding Al_2O_3 content after eight dynamic infiltration cycles was 23 vol% in the topmost 2.5 nm of the MH film. Eight dynamic infiltration cycles into PS-OH resulted in a slight increase in SLD, corresponding to 0.8 vol% inclusion of Al_2O_3 throughout the full 17 nm thickness of the PS-OH film (see Figure 2). A comparison shows similar performance between the static and the dynamic infiltration methods for two cycles, where the static method shows a slightly lower SLD of MH, but also 0.3 nm thicker infiltrated layer (see Figure 3).[3]

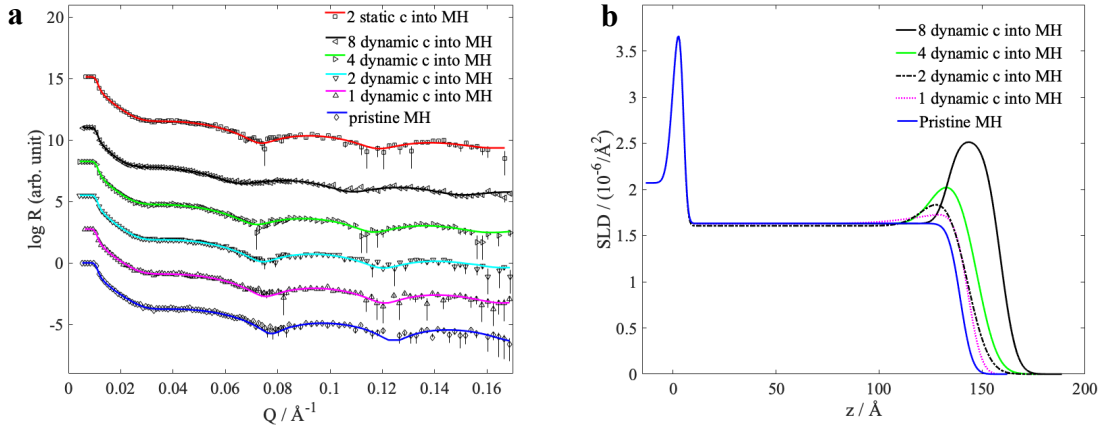

Figure 1. a) Measured MH specular neutron reflectivity R with error bars as a function of neutron momentum transfer perpendicular to substrate surface Q, and fitted models, and b) fitted scattering length density (SLD) as a function of perpendicular distance from substrate surface z.[3]

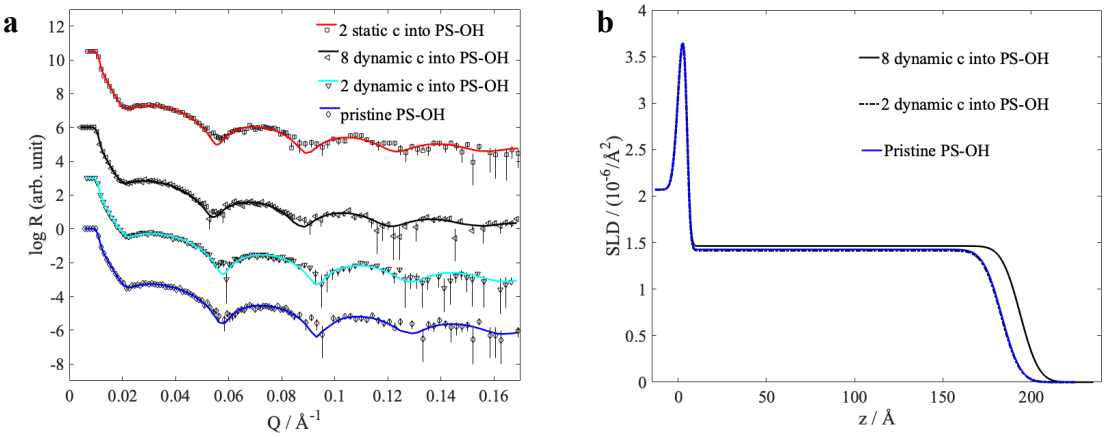

Figure 2. a) Measured PS-OH specular neutron reflectivity R with error bars as a function of neutron momentum transfer perpendicular to substrate surface Q, and fitted models, and b) fitted scattering length density (SLD) as a function of perpendicular distance from substrate surface z.[3]

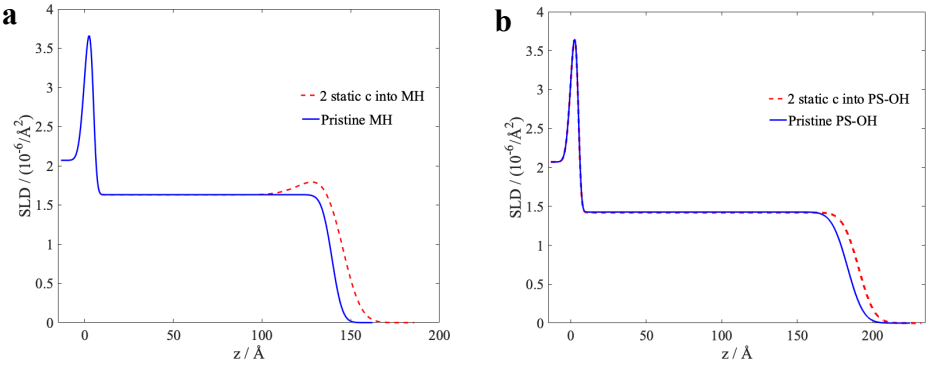

Figure 3. Fitted scattering length density (SLD) as a function of perpendicular distance from substrate surface z, a) for MH, and b) for PS-OH.[3]

Analysis of PS-*b*-MH (batch V) samples is presented in Figure 4, showing an increase in SLD in the lower BCP layer with increasing number of dynamic infiltration cycles, corresponding to 2.4 vol% of Al_2O_3 inclusion after 4 cycles.[4] The upper layer consists of a mixture of BCP and air and is therefore less straight forward to draw conclusions from. It is likely that the 2 cycles sample had a smaller percentage of BCP prior to infiltration.

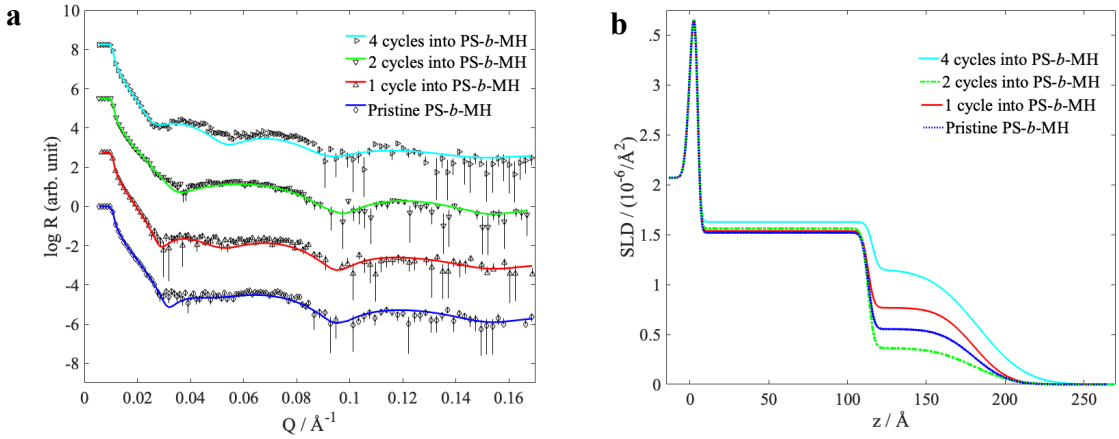

Figure 4. a) Measured PS-b-MH specular neutron reflectivity R with error bars as a function of neutron momentum transfer perpendicular to substrate surface Q, and fitted models, and b) fitted scattering length density (SLD) as a function of perpendicular distance from substrate surface z.[4]

No preliminary conclusions have been drawn from the SANS measurements.

Acknowledgements

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References

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