Featuring Vista Series microscopes
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Application Note

Study of Organic/Inorganic Composite via PiFM

Block-selective infiltration with inorganics such as metal oxides on self-assembled block copolymer patterns should provide a robust mask for pattern transfer (via plasma etch, for example) for sub-15 nm lithography in wafer-scale processes. Although electron microscopy can generate high resolution and high contrast images of pre- and post-infiltration block copolymer patterns, it cannot unambiguously identify the chemical makeup of the observed features. PiFM, with its capability to image both topography and chemical makeup of the sample can provide valuable insight to the block-selective infiltration process. In this application note, we examine the sequential infiltration synthesis (SIS) of AlOx in PS-b-PMMA self-assembled fingerprint patterns via PiFM.

Sample Description

Exposure of self-assembled PS-b-PMMA block copolymer (BCP) thin films to a vapor of trimethyl aluminum (TMA) results in its incorporation into only the PMMA block (and not into the PS), due to a selective reaction between TMA and carbonyl groups in the PMMA [Fig. 1(b)]. The TMA is converted to aluminum oxide by subsequent exposure to water vapor (300 s) [Fig. 1(c)]. Larger amounts of aluminum oxide can be generated within PMMA domains by repeating the TMA/water exposure cycle [Figs. 1(b) and 1(c)]. In this work, block selective synthesis was performed in a commercial atomic layer deposition tool run in static mode (Fiji200, Cambridge Nanotech, no plasma applied). After synthesizing aluminum oxide within the polymer film by undergoing 3 SIS cycles at 90 C, the sample was analyzed by PiFM.

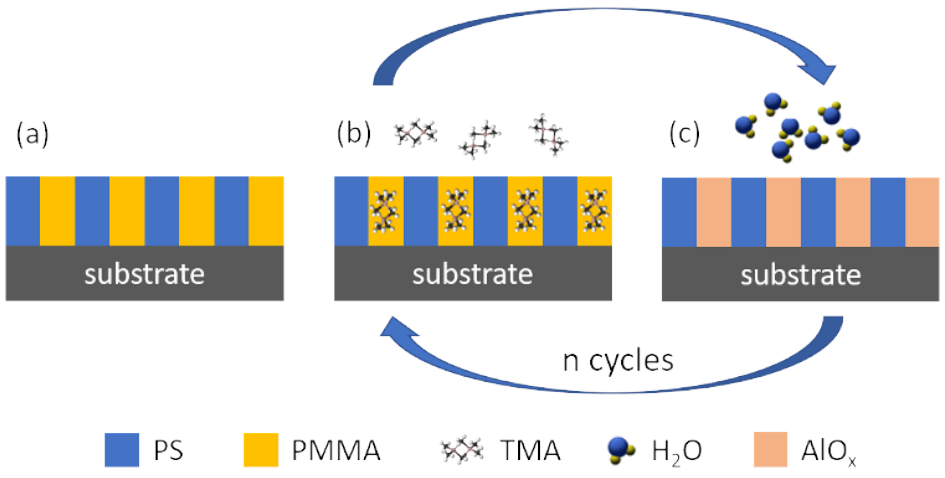

FIGURE 1: SIS of AlO_x in PS-b-PMMA BCP. (a) Prior to SIS processing; (b) During interaction with TMA vapor when TMA infiltrates PMMA selectively; (c) Exposure to water vapor converts TMA to aluminum oxide. Cycle is repeated n times.

PiFM Measurements

Figure 2 shows the topography and PiFM images of PS and PMMA blocks prior to the SIS processing. Note the prominent peaks associated with PMMA (PS) at 1727 cm^{-1} (1454 and 1495 cm^{-1}) in the PiFM spectrum. These bands are used to acquire the chemical map images of PS and PMMA molecules. As typical of PS-b-PMMA BCP, the PS and PMMA blocks appear equal in width before the SIS processing.

In Figure 3, we compare the PiFM spectra acquired after (red) and before (blue) the SIS processing. The red after-SIS spectrum shows a broad peak from about 800 to 1100 cm^{-1}, which can be ascribed to aluminum oxide. PiFM images of PS, PMMA, and AlO_x acquired at 1495, 1733, and 900 cm^{-1} respectively are shown in Figure 3 along with the topography. We can see that the PMMA block has swollen due to infiltration by AlOx. The PiFM images for PMMA and AlOx look well correlated confirming the selective infiltration into PMMA block. The cross-section profile of the PS chemical map image shows that the PS block measures about 9 nm in width compared to ~21 nm in the pre-SIS sample. The exceptional spatial resolution of PiFM is demonstrated by the sharp 10%-90% transition observed (~ 5 nm) in the same PS cross-section profile.

Figure 4 shows a hexagonal pattern of cylinder-forming PS-b-PMMA block copolymer that has undergone similar SIS processing. The PiFM images acquired at 1454 cm^{-1} and 1495 cm^{-1}, both of which correspond to PS molecules, highlight the PS block with small width while the PiFM images acquired at 1733 cm^{-1} and 1030 cm^{-1} highlight the PMMA and AlO_x molecules respectively, demonstrating excellent correlation from SIS processing.

We can see that PiFM images and spectra can be used to identify and study organic and inorganic molecular materials with sub-10nm lateral resolution and monolayer sensitivity (see our Application Note on Atomic Layer Processing where self-assembled monolayers utilized in area selective deposition (ASD) are mapped and analyzed).

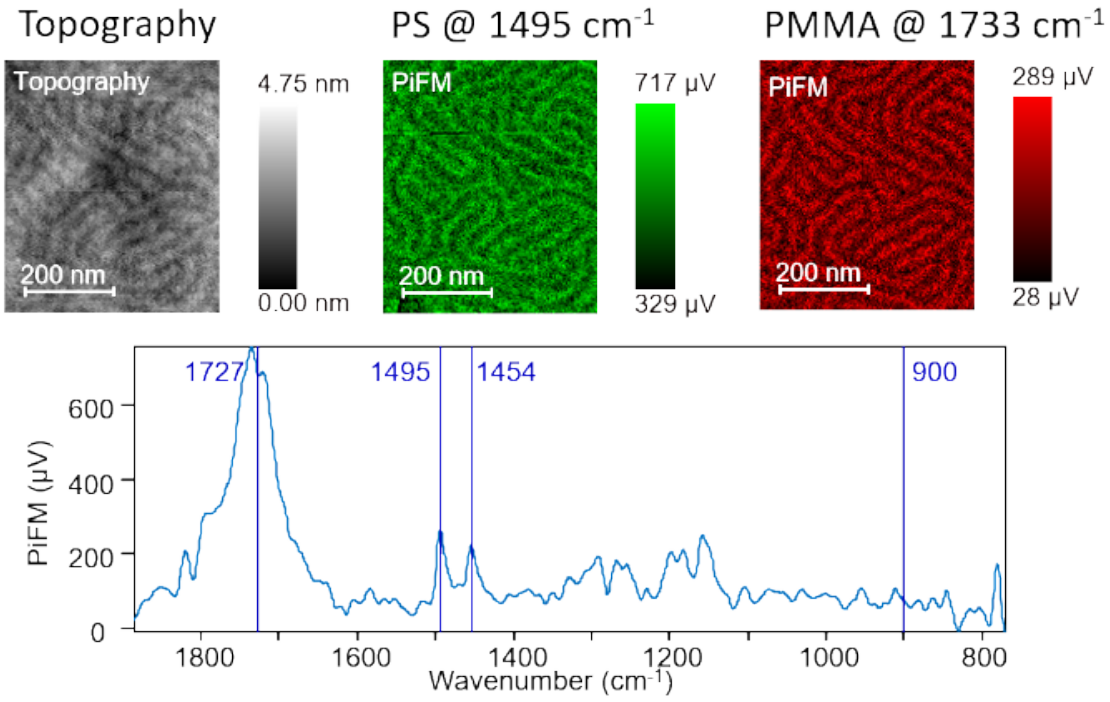

FIGURE 2: PiFM spectrum and images of PS and PMMA blocks in PS-b-PMMA BCP prior to SIS processing; note the equal block width of PS and PMMA molecules.

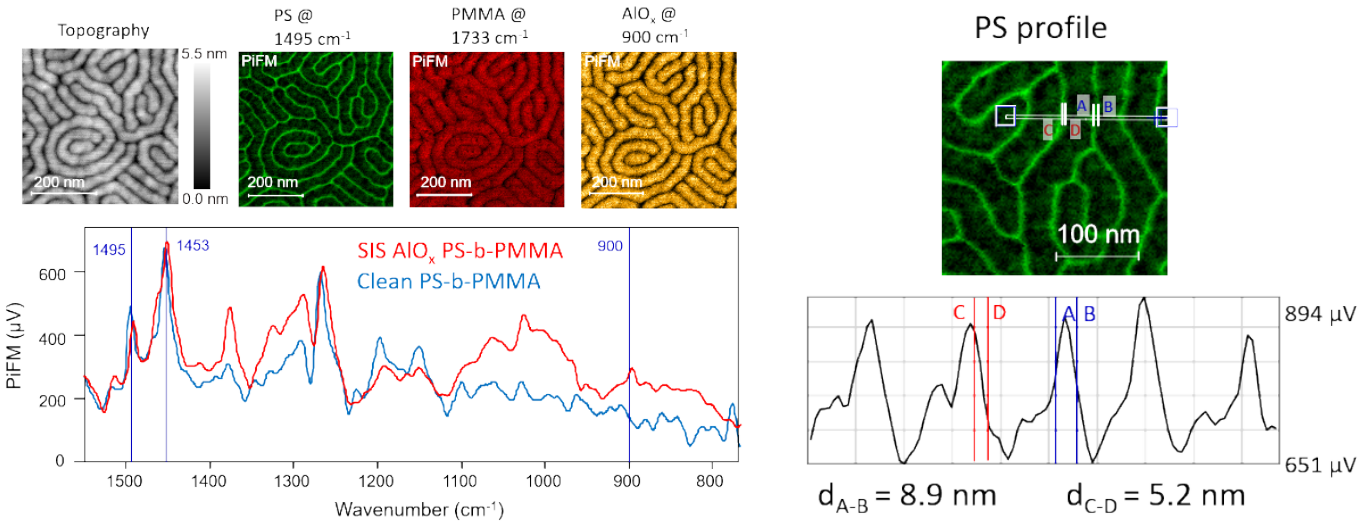

FIGURE 3: PiFM spectrum and images of PS-b-PMMA after the SIS processing. The region bounded by the white dotted square in the PS map is magnified for defining the PS cross-section profile; the PS width has shrunk to ~9 nm in width.

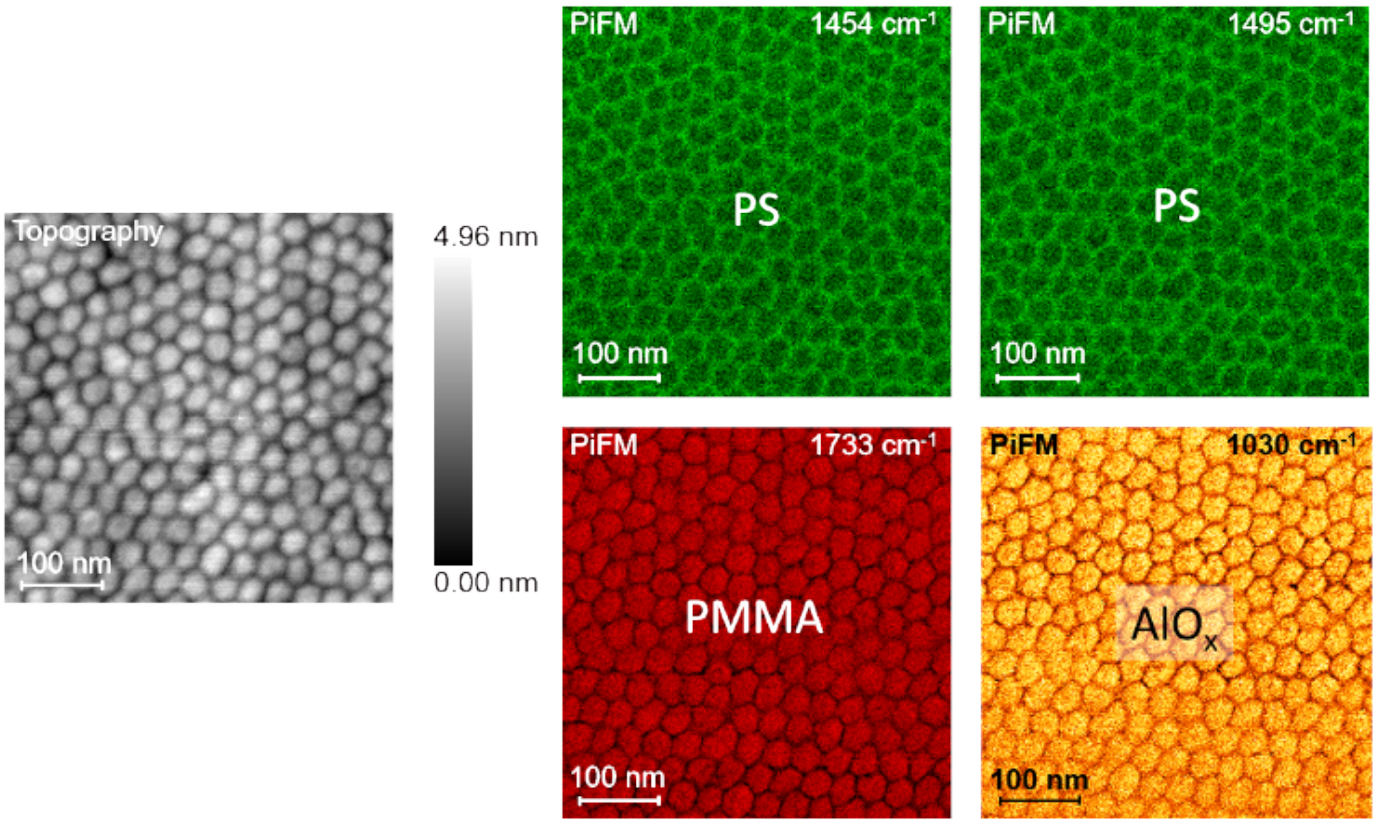

FIGURE 4: PiFM images and topography of hexagonal pattern of cylinder-forming PS-b-PMMA BCP after SIS processing.