SURFACE PHASE SEPARATION AND SELF-ORGANIZED 2D STRUCTURES OF BLOCK COPOLYMER /Fe HYBRIDS

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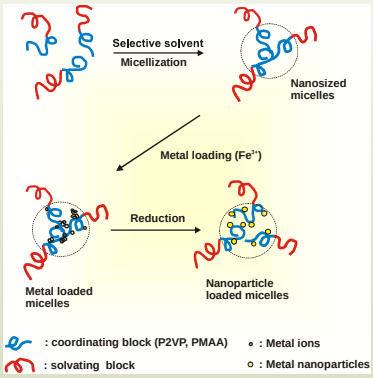
Abstract

Hierarchical micro/nano self–assembled 2D structures on thin films of block copolymers/Fe hybrid materials were induced on Si/Ta substrates, either by wet chemistry or by laser vacuum ultraviolet (VUV) light at 157 nm. Formation of either lamellas or micelle depends on the symmetric diblock copolymer composition and the volume fraction of the solutions. Honey comb-like nano-self-assembled cylindrical structures were formed for one of the diblock copolymer hybrid material. The honey comb-like structures have a different chemical composition than the rest areas of the film and they are rich in iron concentration. VUV irradiation is altering the surface morphology, and under certain illumination conditions semi regular micro ordering on the film surface was induced. Inside the micro-structured domains nano-structured aggregations were formed rich in iron concentration.

Experimental set up



A schematic representation of the micelle preparation protocol

VUV Exposure chamber

Synthesis of block copolymers:
Diblock copolymers poly(styrene-b-2-vinylpyridine) (PS-P2VP) precursors were synthesized by anionic polymerization high vacuum techniques.
•Styrene was polymerized first in THF, using n-BuLi as the initiator, followed by the addition of tert-butylmethacrylate or 2-vinylpyridine. Living anions were terminated by degassed methanol.
•The polymers were isolated after precipitation in hexane or methanol/water mixture. The poly(tert-butylmethacrylate) blocks of the PS-PtBMA were transformed to poly(methacrylic acid) blocks by post polymerization hydrolysis in dioxane.

Characterization Methods:
•Molecular weights and molecular weight distributions of the precursor block copolymers were determined by size exclusion chromatography .
•Composition of the precursor diblocks were determined by 1H-NMR spectroscopy.
•Infra-red spectra of the precursors and the final amphiphilic block copolymers confirmed the conversion of the tert-butylmethacrylate units to methacrylic acid segments.

Micelle and nanocomposite preparation:
•Micelle preparation has taken place in toluene solutions. The loading of the micellar cores was accomplished by addition of varying amounts of a salt precursor, $FeCl_3$.
•After 24h, Fe^{3+} cations are reduced by adding a small amount of hydrazine2 in the presence of air **(chemical method)**.
•Thin films of the composite materials are obtained by spin coating of the final solutions on silicon wafers.

•**Alternatively**, thin films are formed before reduction of the metal and reduction in this case takes place after exposure of the film to **VUV radiation** at 157nm.

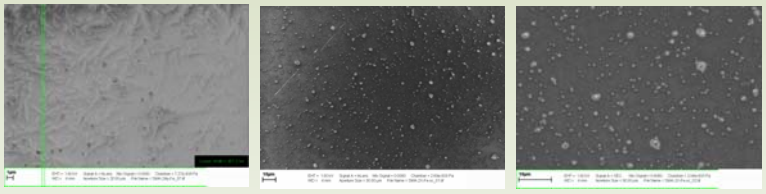
Experimental set up for VUV exposure:
• Molecular F_2 laser
•XYZ micro translator stage

Micro / nano structures characterization:
•Atomic Force Microscopy
•Scanning Electron Microscopy
•Quantitative analysis of different sample's areas

Results

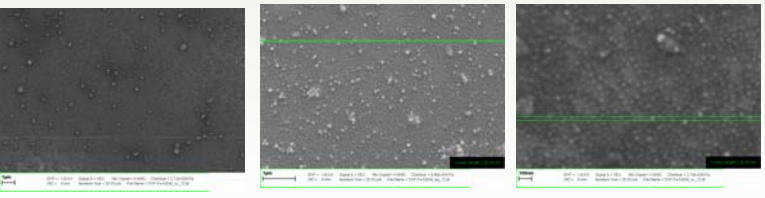
NON EXPOSED

TEM image of PS PMAA loaded with $FeCl_3$ precursor was first spin coated on a Si wafer coated with Ta thin film,

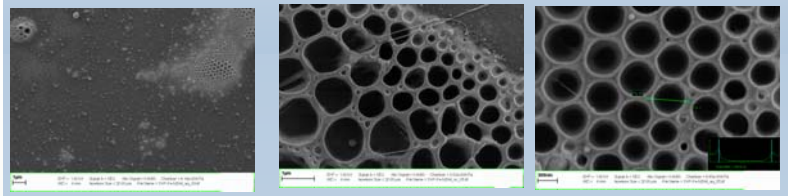


The film morphology and phase separation structures strongly depended on the film thickness. For thicker films, elongated star like shape lamellas, 5 μm long and 1 μm wide on the average were formed and randomly distributed on the polymer surface, while for thinner films oval/elongated micelle like shapes, 200 nm long on the average were formed and non uniformly distributed on the surface of the film.

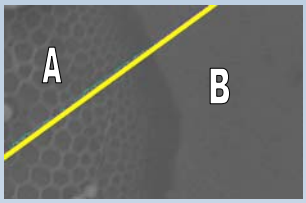
TEM image of PS P2VP loaded with $FeCl_3$ precursors fabricated on Si/Ta substrates

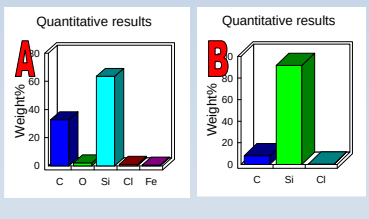


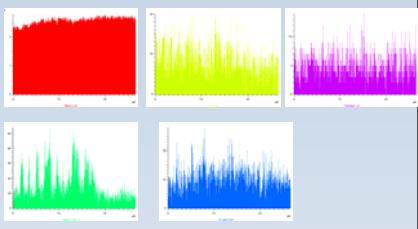
The average dimension of the micelle was ~100 nm and for thicker films start to aggregate forming larger structures. In the case of thinner films, the size of the micelle was scaled down to the average size of 30 nm, and in this case surface interaction and short range interactions manifest themselves with self ordered structures.



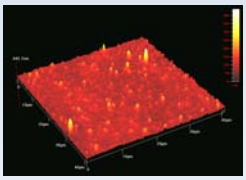
For even thinner films ~20 nm, irregularly spaced islands with well defined self organized structures of circular/oval honey comb like shapes randomly distributed on the surface with 500 nm average distance between them were formed on the surface .



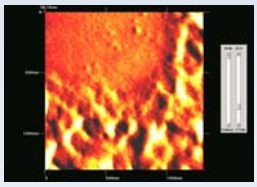




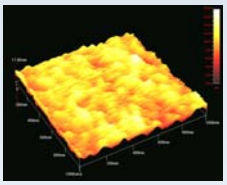
X–ray microanalysis of the TEM image of the honey comb like structure and the substrate across the yellow line, reveals the excess amount of iron and oxygen in the honey comb like self assembled nano structures in comparison to the remaining substrate and the micelle. The analyses were performed in repetive rounds for 12 islands and all of them were found to have an excess amount of iron and oxygen in comparison to the remaining substrate



AFM surface image of a thin film of SVP+ Fe diblock copolymer. The surface of the polymer exhibits micelle like structures 40 50nm long.

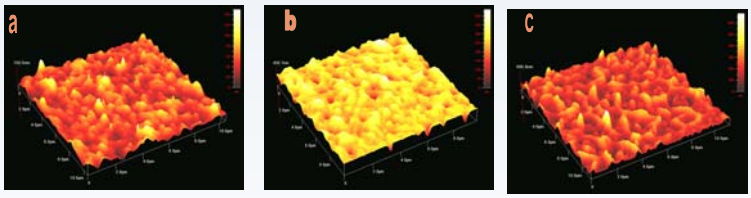


AFM surface image of a thin film of SVP+ Fe diblock copolymer where circular/oval honey comb like shapes can be seen

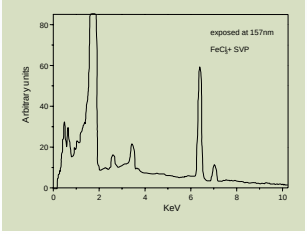


AFM image of the SVP 70 in toluane. No iron is present that is catalyzing the formation of self assembled nano domains in one of the diblock copolymer containing the PVP group

EXPOSED AT 157nm



Following laser illumination at 157nm with 100 nm laser pulses at 1mJ/cm^2 per laser pulse, the ordering on the film surface is enhanced (a). Further increasing the laser energy (b) and (c) , the surface roughness of the film is changing with the appearance of holes ~1μm wide, increasing ordering in the micro scale. In addition inside the holes additional nanostructures are formed a aggregation like structures (c).



X ray microanalyses of the holes with SEM suggests that the concentration of iron in this case is enhanced in comparison to the concentration of the iron outside the holes of the illuminated areas.

Conclusions

•Micro and nano self assembled structures and phase separation was induced on diblock copolymer hybrid materials.
•Two types of polymers were used as initial matrixes: poly(styrene-b-tert-butylmethacrylate) (PS-PtBMA) precursors and poly(styrene-b-2-vinylpyridine) (PS-P2VP) were synthesized by anionic polymerization high vacuum techniques using the sequential monomer addition technique. The polymers were loaded with $FeCl_3$, and the hybrid material after reduction either by wet chemistry or VUV laser light at 157 nm was surface modified to phase separated micro and nano nomains.
• Nano domain structures were self-assembled to micellia or honey comb –like structures.
•Structuring depended on the film thickness and the type of the matrix polymer.
•The concentration of iron carbon and oxygen in the chemically or light modified areas nano-structured areas was different than in the micro-phase domains, a fact which verifies different chemical composition catalyzed by iron.

TNT2006 "Trends in Nanotechnology"
04-08 September, 2006 Grenoble