MICRO / NANO SELF-ASSEMBLED STRUCTURES FROM BLOCK COPOLYMERS / Fe, Fe-Sm NANOPARTICLES HYBRID MATERIALS INDUCED BY VUV LIGHT

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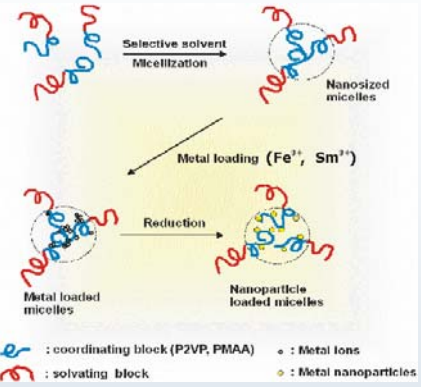
Abstract

Thin films of block copolymer/samarium-iron metal nanoparticles hybrid organic-inorganic materials were prepared either by combination of **wet chemistry**, involving metal nanoparticle formation in block copolymer micellar templates and physical processing via casting or by spin coating and **VUV laser illumination at 157nm.**

A variety of self-assembled structures in the nanometer to micrometer scale were observed by imaging techniques, including TEM, SEM and AFM. Investigations show a closely related hierarchy of the structures formed in the different length scales. Ferromagnetic response was observed forFe loading.

Experimental set up



Schematic lay out of the reduction process catalyzed by wet chemistry. The last step can be also realized by VUV light illumination at 157 nm of the preformed thin films.

X-Y-Z micro-illumination VUV stage-chamber

Synthesis of block copolymers:

The poly(styrene-b-2-vinylpyridine) (PS-P2VP) block copolymer utilized in this work was prepared by anionic polymerization high vacuum techniques. The block copolymer had the following characteristics: M_w=70,400, M_w/M_n=1.01 and 44 % by weight PS.

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:

1) Chemical reduction. Micelle preparation has taken place in toluene solutions.
The loading of the micellar cores was accomplished by addition of varying amounts of a salt precursors, $SmCl_3$ and $FeCl_3$.
After 24h, Fe^{3+}, Sm^{3+} cations are reduced by adding a small amount of hydrazine in the presence of air Thin films of the composite materials are obtained by spin coating of the final solutions on silicon wafers

2) VUV reduction. Thin films were fabricated prior to metal reduction. Reduction now is taking place after irradiation of the film at 157nm.

Experimental set up for VUV reduction:

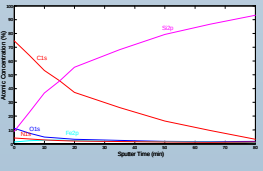
- Molecular F_2 laser
- XYZ micro translator stage

Micro / nano structures characterization:

- Atomic Force Microscopy
- Scanning Electron Microscopy
- Quantitative analysis of different sample's areas

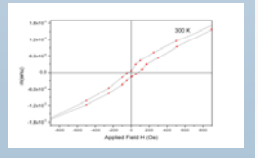
Results

PS-P2VP loaded with $FeCl_3$ precursors fabricated on Si / Ta substrates

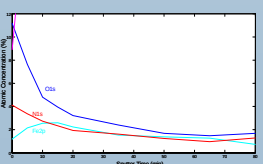


XPS depth profile obtained on the SVP sample.

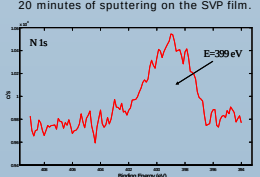
XPS spectrum of the Fe 2p peak obtained after 20 minutes of sputtering on the SVP film.



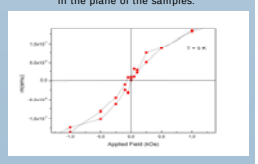
The magnetization curve versus applied field, of the VUV reduced S2VP/Fe films at room temperature. The applied magnetic field is lying in the plane of the samples.



XPS depth profile obtained on the SVP sample, only the range up to 12 at.% on the y-axis is shown.

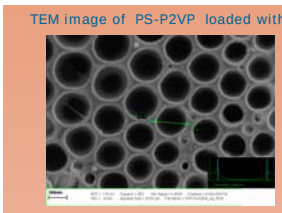


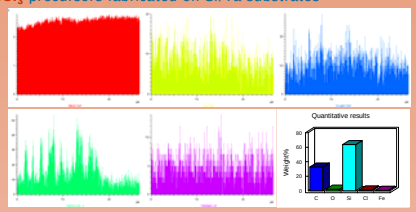
XPS spectrum of the N 1s peak obtained after 20 minutes of sputtering on the SVP film.

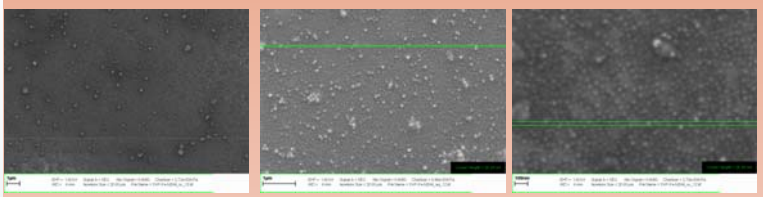


The magnetization curve versus applied field, of the VUV reduced S2VP/Fe films at at 5K. The applied magnetic field is lying in the plane of the samples.

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

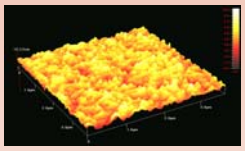




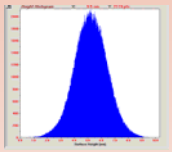


The average dimension of the micelle was ~100 nm and for thicker films start to aggregate forming larger structures. In the case of thinner films, the size of the micelle was scaled down to the average size of 30 nm, and in this case surface interaction and short range interactions manifest themselves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

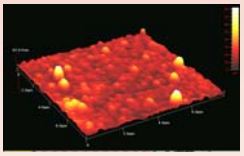
PS-P2VP loaded with $FeCl_3$ and $SmCl_3$ precursors fabricated on Si / Ta substrates



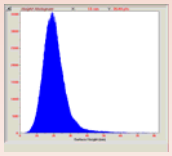
AFM image of the surface morphology of the S2VP film prior loading the precursors.



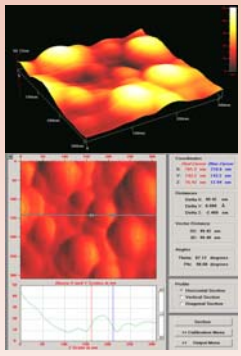
The height histogram (Z-direction) of the S2VP film prior loading the precursors.



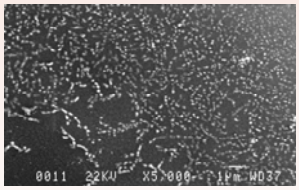
AFM image of the S2VP loaded with $FeCl_3$ and $SmCl_3$ precursors on Si/Ta substrates following chemical reduction.



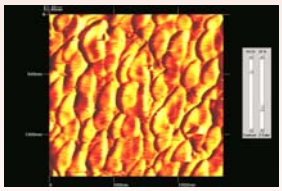
The height histogram of the S2VP film following loading of the $FeCl_3$ and $SmCl_3$.



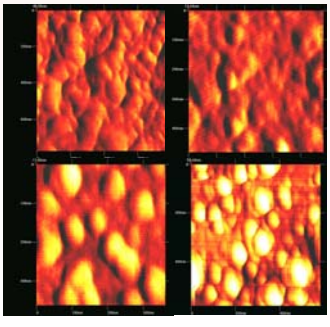
At higher magnification micelles with size scaled down to the ~ 50 nm can be seen.



SEM image of the S2VP loaded with $FeCl_3$ and $SmCl_3$ precursors on Si/Ta substrates following chemical reduction.



AFM image of the S2VP loaded with $FeCl_3$ and $SmCl_3$ precursors on Si/Ta substrates and following VUV laser reduction.



AFM images of the S2VP loaded with $FeCl_3$ and $SmCl_3$ precursors on Si/Ta substrates following VUV laser reduction.

Conclusion

Micro/nano self-assembled structures were induced on diblock copolymer hybrid materials by laser VUV irradiation. poly(styrene-b-2-vinylpyridine) (S2VP). The polymers were loaded with a) $FeCl_3$ and b) $FeCl_3$ and $SmCl_3$. The thin films of the hybrid materials after reduction, (either by wet chemistry **or VUV laser light at 157 nm**), were surface modified exhibiting different self-assembled micro/nano domains. Nano-domain structures for one of the diblock/hybrid material could be identified as self-assembled micellar or honeycomb–like structures. Structuring depends on the film thickness and the type of the diblock polymer. The concentration profile of iron, carbon and oxygen moieties in the chemically or light modified micro/nano-structured areas follows the periodicity and space distribution of the micro/nanostructures, a fact which verifies the different chemical composition of the nano-domains in the micro/nano-structured surfaces, as well as the role of the metal ions in the induction or modification of such micro/nano-structures. Ferromagnetic response was observed at low (5K) and room temperature for the S2VP/Fe hybrid material following 157nm laser exposure.