SELF-ASSEMBLED MAGNETIC STRUCTURES OF Fe POLYMERS

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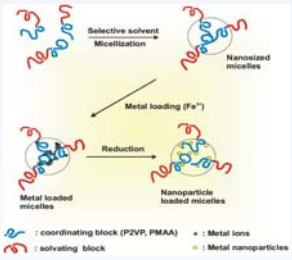
Abstract

Self-assembled 2D structures on thin films of block copolymers/Fe hybrid materials were fabricated on Si/Ta substrates, either by wet chemistry or laser irradiation at 157 nm. The polymer exhibits micelle-like structures with average dimensions of 5-10 and 30-50nm for light and chemically reducted films respectively. SQUID measurements reveal ferromagnetic response at 5K for the laser processed films and 100 Oe coersivity was obtained for 2:1 iron concentration. On the contrary, superparamagnetic response with near zero coersivity at 5K was obtained for chemically reduced films.

Experimental

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.



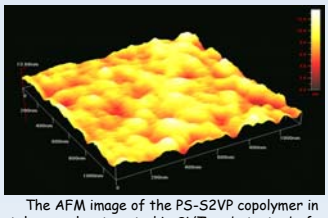
Micelle and nanocomposite preparation:
1) Chemical reduction. Micelle preparation has taken place in toluene solutions.
The loading of the micellar cores was accomplished by addition of varying amounts of a salt precursors, $FeCl_3$.
After 24h, Fe^{3+}, cations are reduced by adding a small amount of 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.

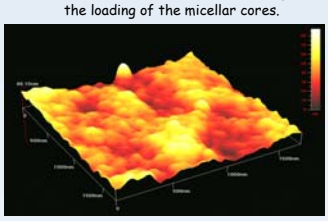

X-Y-Z micro-illumination VUV stage-chamber

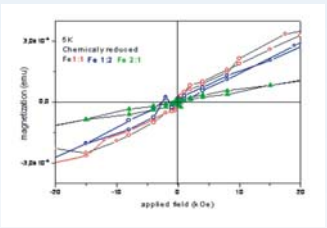
Experimental set up for VUV reduction:
Molecular F2 laser
XYZ micro translator stage

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

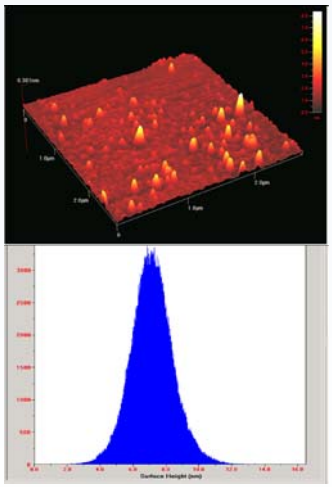
Results and Discussion


The AFM image of the PS-S2VP copolymer in toluene solvent coated in Si/Ta substrate, before the loading of the micellar cores.

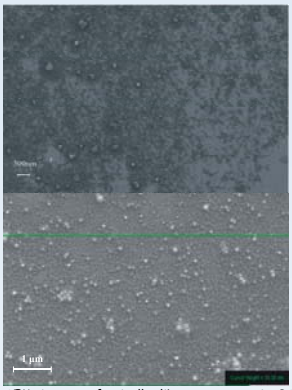

AFM image of the PS-S2VP/$FeCl_3$ hybrid film. The typical surface roughness is~30nm for 1.7μmX1.7μm.



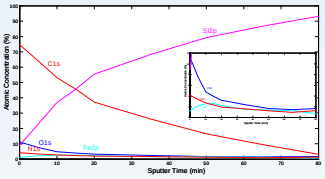
Superparamagnetic response of the chemically reduced films at 5K and 300K. The applied magnetic field is lying in the plane of the samples


The magnetization curve versus applied field, of the VUV reduced films at 5K and 300K. The applied magnetic field is lying in the plane of the samples.

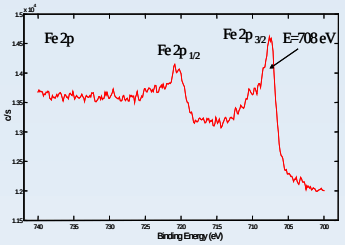
Chemical Reduction



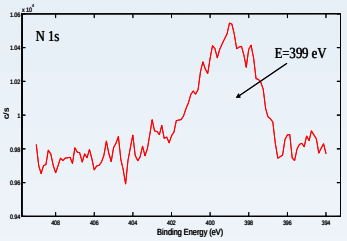
SEM images of micelle like structures in PS-P2VP/$FeCl_3$ hybrid film following chemical reduction. The average dimension of nano particles is 30nm.



XPS depth profile of the S2VP film after chemical reduction. In the inset the depth profile is shown with magnification of y-axis. C, O, Fe and N elements were found in the film surface.

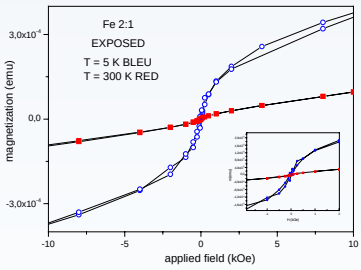


The XPS analysis of Fe2p peak performed on the samples produced by chemical reduction after 20min of sputtering

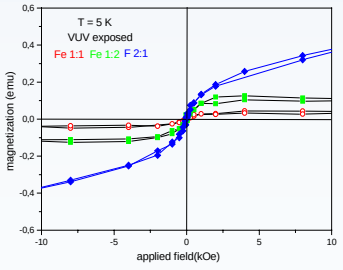


The XPS spectrum of Nitrogen 1s peak carried out on the samples produced by chemical reduction after 20minutes of sputtering.

VUV Reduction



Ferromagnetic response of the irradiated films at 5K, at different iron concentrations for fields up to 20KOe. The coersivities up to 1200kOe are 99, 74, 60Oe for iron concentrations Fe 2:1, 1:1 and 1:2 respectively.



AFM image of the VUV light reduced films. The edge between light exposed and non-exposed areas is indicated. The exposed area surface in the microscale is rougher than of the non-exposed ones, however molecular photo-dissociation and rearrangement on the processed areas limits the size of the iron nanostructures to 10 nm.

Conclusion

- **Self-assembled** magnetic structures on thin films of block copolymer/Fe hybrid materials were fabricated on Si/Ta substrates, either by wet chemistry or laser vacuum ultraviolet light processing at 157 nm.
- **XPS analysis** reveals the presence of metallic-like iron in the 2p state. In addition depth profile XPS spectra reveal metallic iron and FeII bonding.
- **The 157nm-reduced films** indicate ferromagnetic response at 5K and superparamegnetic at room temperature, while the chemically reduced films were superparamagnetic for both temperatures.
- The ferromagnetic response of the VUV light reduced films is attributed to the formation of 5-10nm metallic iron nanostructures