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Ultra high density nanopore arrays using self assembled diblock copolymer

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Processing conditions for high density nanoporous templates using self assembled morphology of asymmetric diblock copolymers with pore lengths stretching the entire thickness of the polymer films are investigated. Poly styrene (PS) and poly methylmethacrylate (PMMA) are used as polymer blocks for fabrication of diblock copolymer film. Polymer solution of 1% (w/w) in toluene was spin coated on gold coated silicon substrate to obtain polymer film of varied thickness ranging from 72.4 nm to 2631.57 nm. Upon annealing the film under the influence of electric field and etching by UV radiation followed by rinsing in sonicated acetic acid, highly dense hexagonally ordered pores perpendicular to the substrate over the entire film thickness with average pore diameters from 13.7 nm onwards were obtained. The spin speed and polymer concentration account for thickness of the film, while the molecular weights of the polymer blocks, annealing time and etching time determine the pore formation and density in the resulting template. The resulting ultrahigh density nanoporous templates were used for growth of Co nanowires using electrodeposition in three electrode configuration. The morphological features of the polymer film, nanoporous template and the nanowires were investigated using SEM and AFM techniques.

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1. Introduction

Continued shrinking of device dimensions demand for fabrication of magnetic nanostructures with feature sizes much lesser than that are commonly obtained by standard semiconductor photolithography and electron beam lithography [1]. Self assembly in diblock copolymers provides a simple, inexpensive and yet efficient means of producing ordered nanoporous templates for fabrication of nanostructures that overcome the size scale limitations of lithographic techniques [2].

Template based synthesis of ordered magnetic nanowire arrays has been a subject of great interest both from academic and technical fronts as these systems provide scope for understanding one-dimensional physics as well as find relevance to increased aerial density magnetic storage media [3]. Several kinds of templates are available, such as track-etched membranes [4], anodized aluminum [5] and diblock copolymer [6]. Track etched membranes display lower pore densities and poor ordering. Anodized aluminum templates possess high density, highly ordered pore arrays but they require special etching procedures involving strong acids. In comparison, diblock copolymer template forms a simple route to generate periodic structures with well defined size and periodicity that can be easily tunable from a few nanometers to several tens of nanometers.

However, there is a scope for preferential interfacial interaction of one of these two polymer blocks with the substrate which prevents from required cylindrical orientation of the minority polymer block perpendicular to the film plane. There were some attempts using random copolymer brushes to overcome this problem by controlling the polymer surface interactions [7]. Also, another method was reported by applying sufficiently strong electric fields parallel to the diblock copolymer film so that reorientation of heterogeneous dielectric media based on the dielectric mechanism would take place to facilitate cylindrical orientation [8]. In both the approaches, special etching procedures involving exposure to ultraviolet light and rinsing in acetic acid are required to convert the ordered minority polymer cylinders into pores. Nevertheless, this latter approach well suits, particularly when the work involves electrodeposition of magnetic component into the ordered pores as it requires electrodes for deposition.

Thus, in the present work, we investigate processing conditions for electric field assisted fabrication of nanoporous templates, and verify their suitability for subsequent deposition of cobalt nanowires. The conditions for bringing modifications in polymer film thickness, pore size, size distribution and their morphologies are discussed. In the end, fabrication of nanoporous templates and electrodeposition of cobalt nanowires into the pores are successfully reported.

2. Experimental procedure

The substrate used in the experiment is a gold coated silicon wafer, which acts as bottom electrode for application of electric field and also for electrodeposition. PS-PMMA films of different thickness were spin coated onto silicon wafers by adjusting both the spin speed and

solvent (toluene) concentration for these experiments. Commercially available PS-PMMA diblock copolymers with molecular weights of PS and PMMA as 30,400 and 14,100 g/mol, respectively were employed. After successful coating, the films were annealed in vacuum at 180 ^{o}C starting from 48 hours to 72 hours by applying an electric field of 400 V/µm. The electric field was kept applied for more than 5hours even after the temperature controller was switched off to obtain complete orientation of the polymer blocks in the direction of the electric field. Then, the films were exposed to intense UV radiation to remove the PMMA block. However, complete removal of the PMMA block was successfully done only after rinsing the film in acetic acid for few minutes which is supposed to degrade the remaining PMMA in the film. This completes the formation of the nanoporous templates, and the same were subsequently used for morphological characterizations using scanning electron microscope (SEM) and atomic force microscope (AFM). The templates were also used for successful verification of electrodeposition of cobalt nanowires in standard three electrode potentiostatic cell configuration.

3. Results and discussion

Fig.1 shows the SEM images of PS-PMMA diblock copolymer films prepared under different processing conditions. Variations in spin speed, coating time and polymer concentration have resulted in varied thicknesses. The thickness varies from 72.4 nm for the synthesis condition of 3000 rpm spin speed and 30 sec coating time of 1% polymer solution to 2631.6 nm for the condition of 4000 rpm spin speed and 150 sec coating time of the same 1% polymer solution in toluene. The film thickness was observed to increase either with the increase in spin coating time or the polymer concentration. The increase in spin speed, however, increased the uniformity of the film surface.

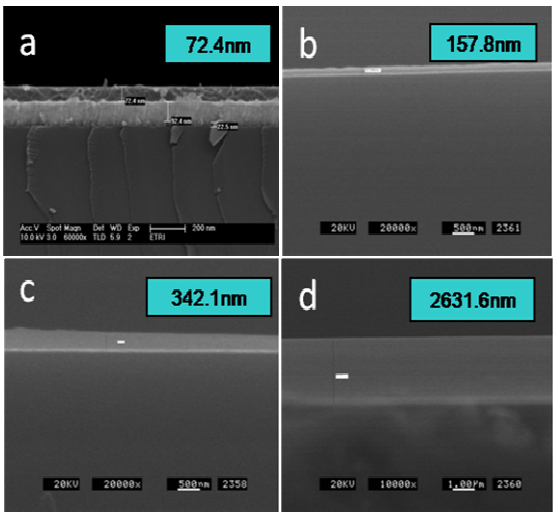

Fig. 1. SEM images of different thickness ranging from 72.4 nm to 2631.6 nm a) with thickness of 72.4 nm, b) with thickness of 157.8 nm, c) with thickness of 342.10 nm, d) with thickness of 2631.6 nm

The process of spin coating time was increased by performing the experiment repeatedly while dropping the polymer solution on the spinning substrate.

Fig.2 shows typical AFM images of the nanoporous template and poly styrene posts after successful etching of PMMA from the polymer film. The PMMA cylinders were observed to extend through the full thickness of the polymer film. It can be seen that the height of the PS posts was little varied in the observed area indicating that the film surface is uniform all along the investigated structures.

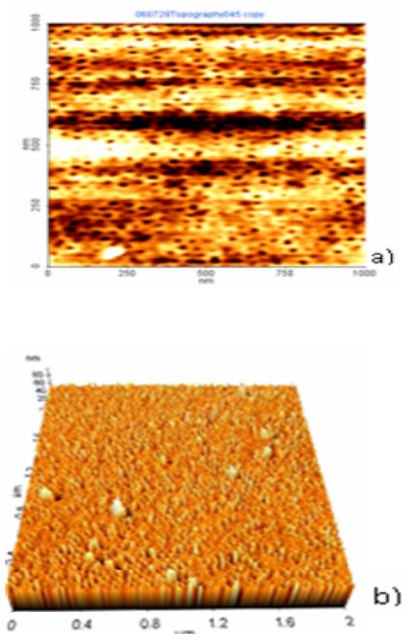

Fig.2. a) Top view AFM image of the nanoporous template and b) AFM height image of the PS posts

Fig.3 shows typical SEM images of hexagonally ordered nanoporous templates annealed under different durations. The dark regions are areas where the PMMA cylinders were removed by UV exposure and developing process. It is clearly evident that the hexagonal order is of short range leaving some areas without pores. As the time of annealing increases, there observed to be developing more pores resulting in higher density. Exception to the density of 69 h duration which may be caused by rather slow development of the pores. From these images, the mean pore diameter was calculated in each case and the best obtained pores due to in homogeneities within the investigated regions of polymer film.

The formation of the ordered diblock copolymer template depends on many factors, including substrate material, polymer film thickness, annealing conditions, and copolymer molecular weights. Among all, the degree of ordering depends critically on the polymer film thickness and the strength of the electric field. Thurn-Albrecht et al [9] have successfully demonstrated that it is

possible to produce perpendicularly oriented smaller diameter cylinders in thicker films even by applying an external electric field of approximately >30V/μm. In this work, we could not, however, obtain successful orientation of cylindrical PMMA structures for electric fields less than 400 V/μm. It is further observed that if the applied electric field is less than the required to microphase separate the immiscible polymer blocks for the entire thickness of the film, PMMA cylinders were oriented only for part of the film up to some thickness and for the remaining film thickness the PMMA was observed to align with PS without any order. This could perhaps be one of the reasons for structural in homogeneity discussed above resulting in lower pore density for the annealing of 69 h duration sample.

However, among all the nanoporous templates explored, the smallest pore diameter obtained was found to be 13.7 nm with the center to center spacing of the pores in the hexagonal array by about 44 nm. With the obtained parameters of pore diameter and center to center spacing of pores, the best obtained density of pores was estimated to be in excess of 0.94 tera bits per square inch, which is reported elsewhere [10] and is characterized as a highly promising route for subsequent electrodeposition of metal nanowires for information storage.

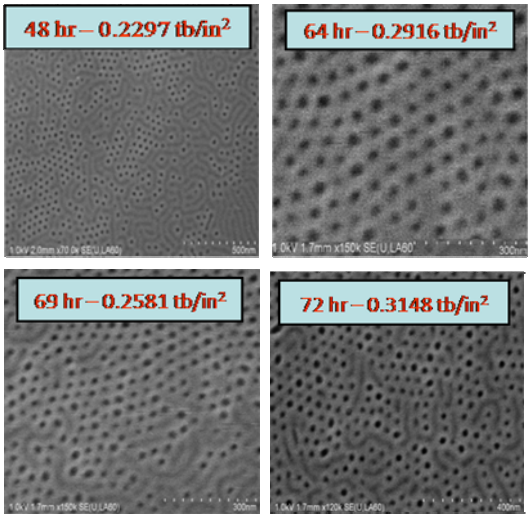

Fig. 3. SEM images of different nanoporous templates as a result of different annealing times.

In order to verify whether the obtained nanotemplates could be used for fabrication of nanowires, we have conducted experiments of electrodeposition in a 3-electrode potentiostatic configuration on these samples. It has been successfully established that the cobalt sulphate electrolyte bath containing 20% methanol by volume and a buffering boric acid with a pH of more than 3 could result in deposition of cobalt nanowires. Fig. 4 shows the SEM image of the electrodeposited cobalt nanowires after heat treatment. It can be seen that the nanowires are randomly aligned due to the thermal energy assisted mobility of the polymer domains out of heat treatment with their bases still linked with the polymer heaps.

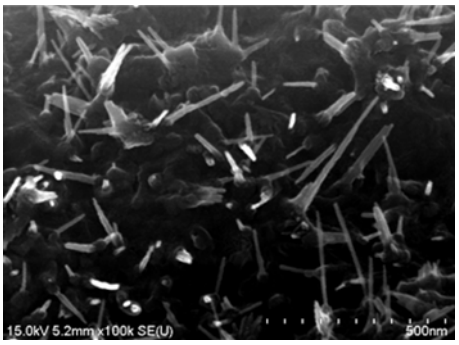

Fig. 4. SEM images of electrodeposited cobalt nanowires after heat treatment

Investigations related to magnetic behaviour of fabricated nanowires are underway and will be reported elsewhere. However, the elegance of the spontaneous self assembly in diblock copolymer structures with fully controllable pore diameter and lattice periodicity of the present study clearly makes this process more attractive as it is practical and compatible for generating nanostructures meant for many applications including information storage and sensing geometries.

4. Conclusion

In summary, processing conditions for fabrication of high density nanoporous templates using self assembled morphology of asymmetric diblock copolymers were thoroughly investigated. 1% (w/w) solution of PS-PMMA in toluene was used for fabrication of polymer film. Electric field assisted annealing was done for cylindrical orientation PMMA, and UV light exposure and acetic acid rinsing were used for removal of PMMA and formation of nanopores. Annealing time and strength of the electric field are found to be playing crucial role in determining the order and pore density. Pore diameters as low as 13.7 nm and pore densities as high as 0.94 tb/in^2 were obtained from the study. The fabricated nanoporous templates could be successfully used for electrodeposition of metallic nanowires.

Acknowledgements

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References

[1] T. Ishikawa, S. Kohmoto, K. Asakawa, Appl. Phys. Lett. **73**, 1712 (1998).

[2] M. Park, C. Harrison, P.M. Chaikin, R.A. Register, D. H. Adamson, Science **276**, 1401 (1997).
[3] J.I. Martin, J. Nogues, Kai Liu, J.L. Vincent, I.K. Schuller, J. Magn. Magn. Mater. **256**, 449 (2003).
[4] J.C. Hulteen, C.R. Martin, J. Mater. Chem. **7**, 1075 (1997).
[5] A. Huczko, Appl. Phys. A Mater. Sci. Proc. **70**, 365 (2000).
[6] K. Shin, K. Amanda Leach, J.T. Goldbach, D.H. Kim, Lett. **9**, 933 (2002).
[7] P. mansky, Y. Liu, E. Huang, T.P. Russell, C. Hawker, Science **275**, 1458 (1997).
[8] Y. Tsori, F. Tournilhac, D. Andelman, and L. Leiber, Phys. Rev. Lett. **90**, 145504-1 (2003).
[9] T. Thurn-Albrecht, J. Schotter, G.A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C.T. Black, M.T. Tuominen and T.P. Russell, Science **290**, 2126 (2000).
[10] V. Sudha Rani, S.S. Yoon, C.O. Kim, B. Parvatheeswara Rao, and CheolGi Kim, Sensors lett. **5**, 39 (2007).

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