European School on Magnetism 2007, Cluj-Napoca

Deposition and growth methods of media films, nano-assembled and nano-organized objects, lithography methods

Julien Bachmann

Max Planck Institute of Microstructure Physics, Halle, Germany

Current magnetic recording platforms (computer hard drives) consist of ferromagnetic thin films. Each binary bit of information is stored by an area consisting of large numbers (≈20-1000) of magnetic grains. Within this framework, size reduction driven by the need to reach ever-increasing data storage densities will at some point reach a limit, set by superparamagnetism. Indeed, below a certain size limit (related to the volume of magnetic domains), the magnetic energy of a single magnetic particle is too small relative to thermal energy for magnetic ordering to occur — the tendency of neighboring spins to align is overcome thermally, and the bit of information is lost.[1] The development of future high-density data storage platforms thus requires the preparation and systematic investigation of magnetic nanoobjects susceptible to overcome the superparamagnetic limit. The requirements on the nanoobjects are stringent:

a. *Small lateral size*
b. *Ferromagnetism along a preferred axis*
c. *Two-dimensional organization*
d. *Homogeneous, tunable geometry and magnetic parameters*

Most current research towards the synthesis of objects meeting these goals *a-d* is based on a combination of some or all of the following approaches.

A. **Pseudo-1D magnetic objects.** A 1D geometry allows the lateral size of the object to be reduced almost arbitrarily (*a*), while the large shape anisotropy can overcome superparamagnetism and orient the ferromagnetic response along a single axis (*b*).
B. **Lithography.** Various lithographic methods are available to create a perfect pattern of micrometer period or below on large areas of substrate, and subsequently transfer the pattern to a magnetic material (*c*).
C. **Ordered porous templates.** Several materials can be prepared with a self-ordered or lithographically ordered porous structure, such that the geometry of the pores is determined by the experimental preparative parameters — deposition of magnetic material into the pores yields organized arrays of magnetic 1D nanostructures of tunable geometry (*c*, *d*).
D. **Electrodeposition.** When an electrode defined at the bottom of the template pores supplies electrons to an solution containing metal cations, precipitation of the ("reduced") solid metal occurs at the electrode and then progresses upwards into the pores, thus forming nanowires (**A**) inside the template matrix.

E. **Atomic layer deposition.** The pore walls of the template are covered conformally with solid material deposited layer by layer by a self-limiting chemical reaction occurring at the surface between two gaseous, thermally stable, precursors. ALD thus yields nanotubes (**A**) of accurately tunable thickness (*d*).

A. Pseudo-1D magnetic objects

In a ferromagnetic object of elongated, cylindrically symmetric (oblate) geometry, the *z* axis is the “easy” axis for magnetization. In the absence of an external field, the magnetic moment of the magnetized oblate will lie along +*z* or –*z*, and magnetizing the object in another direction costs an additional energy term.[1,2] The energy difference between states magnetized in the *z* and in the *x* (or *y*) direction furnishes a quantification of the shape anisotropy of the system. If the shape anisotropy is much larger than thermal energy, the ferromagnetic state is stable and superparamagnetism is overcome. In the case of large aspect ratios (wires), however, reversing the magnetization from +*z* to –*z* by application of an external magnetic field requires less energy than rotation of the overall magnetic moment into the *(x, y)* plane, because magnetization reversal is not homogeneous: instead, it occurs via an intermediary “curling” state which has no *(x, y)* component of the magnetic moment.[3] Magnetization reversal in nanowires of very small diameter may occur only via formation of a domain boundary at one extremity and its propagation along the wire,[4] a mechanism that usually results in larger coercive fields.

B. Lithography

Lithography is based on thin films of organic materials called “resists”, the chemical identity of which changes upon exposure to light or an electron beam. A pattern is “written” in the resist using a shadow mask, an interference figure, or the focused electron beam of an electron microscope, and then developed by chemical etching. The pattern in the resist can subsequently be transferred to the underlying substrate by further etching steps (dry or wet chemical), or to another substrate by physical contact.[1,5,6] Lithographic methods thus provide the ability to organize nanoobjects in perfect periodic (one- or two-dimensional) arrangements over macroscopic areas. Hexagonal and square arrays of quantum dots, disks, and pillars are achievable (Figure 1), as well as parallel alignments of wires lying “horizontally” on the substrate. However, to date lithographic techniques have not yielded arrays of wires or tubes of high aspect ratio standing “vertically” (*i. e.* with their long axis perpendicular to the substrate plane).

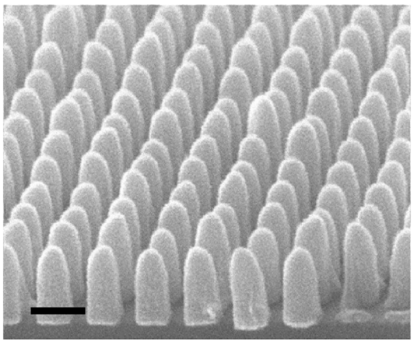

Figure 1. Array of Ni pillars obtained lithographically (scale bar: 100 nm; from Ross).[1]

C. Ordered porous templates

Some materials can be obtained as micrometer-thick membranes traversed with pores, the axis of which is perpendicular to the plane of the membrane. Even if the preparation technique is particular to a specific material system (such as Al_2O_3 or TiO_2), deposition into the pores may be general. It thus allows one to obtain wires or tubes of a desired material by using the porous membrane as a template. The ordering of the nanoobjects is determined by that of the template. Chemical dissolution of the template yields isolated nanoobjects.

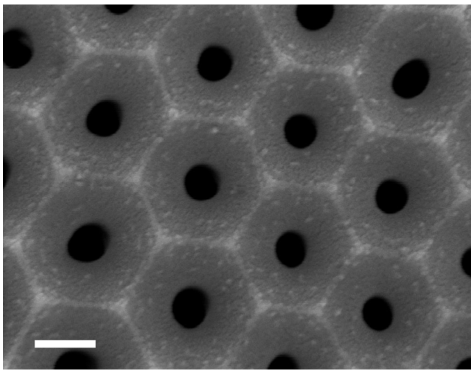

Figure 2. Top view of a sample of porous anodic alumina (scale bar: 200 nm).

Ion-track-etch polycarbonate membranes, available commercially as filters for use in chemistry and biology, have been used as templates, but their pores are randomly distributed and are not aligned parallel to one another.[7] In another approach, phase separation phenomena can be used, in particular in block copolymeric systems: selective etching of a columnar phase-separated structure yields vertical hollow cylinders.[8] So-called "macroporous silicon" is obtained by electrochemical oxidation of a doped and lithographically pre-patterned Si wafer under irradiation in solutions of hydrofluoric acid.[9] The pores are nearly perfect structurally and their geometry can be adjusted experimentally, however the diameters are rather large (≥ 200 nm). Finally, porous anodic alumina (Figure 2) results from the electro-chemical oxidation of aluminum in aqueous acidic solutions. Processes have been reported with and without lithographic pre-patterning that allow experimental access to pores of 20 to 400 nm diameter.[10-12]

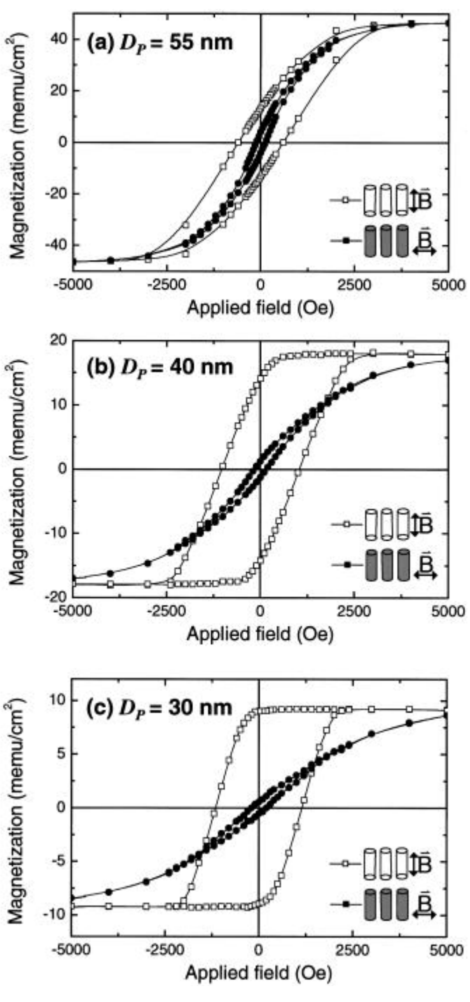

Figure 3. Magnetic characteristics of electro-deposited Ni nanowire arrays of three different outer diameters D_p (from Nielsch *et al.*).[14]

D. Electrodeposition

A thick layer of conducting material deposited onto one side of a porous membrane serves as an array of nanoelectrodes placed at the bottom of each pore. Application of a suitable potential to the electrodes in a solution containing redox-active species (molecules or ions susceptible of being oxidized or reduced) can result in the precipitation of the reduced or oxidized species at the bottom of the pores. If the solid thus obtained is a sufficient electrical conductor, electrodeposition is not limited by the thickness deposited and it results in the growth of nanowires in the pores, of diameter set by the geometry of the template and of length determined by the total amount of current passed.

Ordered arrays of Ni nanowires obtained in this manner yield a very anisotropic magnetic response, and the quality of the hysteresis curve (remanence) strongly depends upon the wire diameter (Figure 3).[13-15] Electrochemical techniques can be generalized to multisegmented wires, and such systems may give rise to interesting GMR effects.[16]

E. Atomic layer deposition

Alternated exposure of a surface to two gaseous reactants that are thermally stable at the reaction temperature but very reactive towards each other results in the chemisorption of successive monolayers of each reactant (independently of the excess amount of reactants in the gas phase), in a self-limited growth mode called atomic layer deposition (ALD). The thickness of a solid film deposited by ALD only depends on the number of reaction cycles performed, not on other experimental parameters such as the vapor pressure of precursors. Therefore, employing excess amounts of precursors allows one to coat substrates of arbitrarily complex geometry, in particular very porous ones. These characteristics make ALD the only gas-solid deposition technique not limited to a flat substrate geometry, and thereby able to grow nanotubes in porous templates (as opposed to CVD for example).[17,18]

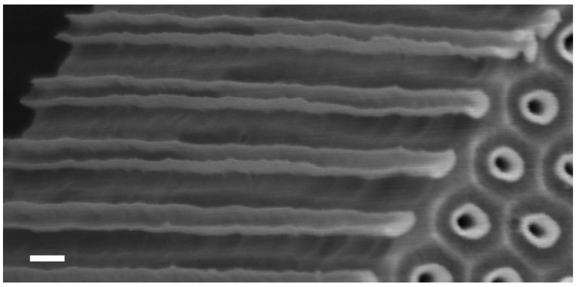

Figure 4. An array of Fe_2O_3 nanotubes in the porous anodic alumina matrix (scale bar: 200 nm; from Bachmann *et al.*).[20]

ALD combined with porous anodic alumina templates has allowed magnetic nanotubes of Co, Ni and Fe_3O_4 to be obtained in ordered arrays and with well-controlled geometry (Figure 4).[19,20] Systematic tuning of their geometric parameters reveals different magnetization reversal modes depending on geometry.[20,21]

References

1. C. A. Ross, *Annu. Rev. Mater. Res.* **2001**, *31*, 203-235.
2. K. Nielsch and B. J. H. Stadler, in *Handbook of Magnetism and Advanced Magnetic Materials*, Vol. 4; H. Kronmüller and S. Parkin, eds.: John Wiley and Sons, Ltd., Chichester, **2007**.
3. E. H. Frei, S. Shtrikman and D. Treves, *Phys. Rev.* **1957**, *106*, 446-454.
4. R. Hertel and J. Kirschner, *Physica B* **2004**, *343*, 206-210.
5. Y. N. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.* **1999**, *99*, 1823-1848.
6. Y. N. Xia and G. M. Whitesides, *Annu. Rev. Mat. Sci.* **1998**, *28*, 153-184.
7. M. Wirtz and C. R. Martin, *Adv. Mat.* **2003**, *15*, 455-458.
8. B. Smarsly and M. Antonietti, *Eur. J. Inorg. Chem.* **2006**, *6*, 1111-1119.
9. S. Ottow, V. Lehmann and H. Foll, *J. Electrochem. Soc.* **1996**, *143*, 385-390.
10. H. Masuda, F. Hasegwa and S. Ono, *J. Electrochem. Soc.* **1997**, *144*, L127-L130.
11. A. P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, *Adv. Mat.* **1999**, *11*, 483-487.
12. K. Nielsch, J. Choi, K. Schwirn, R. B. Wehrspohn and U. Gösele, *Nano Lett.* **2002**, *2*, 677-680.
13. K. Nielsch, F. Müller, A.-P. Li and U. Gösele, *Adv. Mater.* **2000**, *12*, 582-586.
14. K. Nielsch, R. B. Wehrspohn, J. Barthel, J. Kirschner, U. Gösele U, S. F. Fischer and H. Kronmüller, *Appl. Phys. Lett.* **2001**, *79*, 1360-1362.
15. K. Nielsch, R. B. Wehrspohn, J. Barthel, J. Kirschner, S. F. Fischer, H. Kronmüller, T. Schweinbock, D. Weiss and U. Gösele, *J. Magn. Magn. Mat.* **2002**, *249*, 234-240.
16. L. Piraux, J. M. George, J. F. Despres, C. Leroy, E. Ferain, R. Legras, K. Ounadjela and A. Fert, *Appl. Phys. Lett.* **1994**, *65*, 2484-2486.
17. M. Leskalä and M. Ritala, *Angew. Chem. Int. Ed.* **2003**, *42*, 5548-5554.

---

18. R. L. Puurunen*, J. Appl. Phys.* **2005**, *97*, 121301.
19. M. Daub, M. Knez, U. Gösele and K. Nielsch, *J. Appl. Phys.* **2007**, *101*, 09J111.
20. J. Bachmann, J. Jing, M. Knez, S. Barth, H. Shen, S. Mathur, U. Gösele and K. Nielsch, *submitted for publication*.
21. J. Bachmann, J. Escrig, J. Jing, D. Altbir, U. Gösele and K. Nielsch, *manuscript in preparation*.