Synthesis and characterization of a self-assembled nanostructured silicon/metal composite

P. Granitzer 1, K. Rumpf 1, P. Poelt 2, S. Šimić 2, H. Krenn 1

1 Institute of Physics, Karl Franzens University Graz, Universitaetsplatz 5, 8010 Graz, Austria
2 Institute for Electron Microscopy, University of Technology Graz, Steyrergasse 17, 8010 Graz, Austria
petra.granitzer@uni-graz.at

Abstract. A silicon/metal nanocomposite is fabricated by electrochemical deposition of a metal (Ni, Co) into the pores of mesoporous silicon prepared from n⁺-silicon consisting of highly oriented channels which are tunable in a range between 40 nm and 100 nm in their diameter and a concomitant interpore spacing. Fourier transform infrared (FTIR) measurements give details about the top surface as well as the interior surface of the pore walls. IR optical investigations are used to determine the optical parameters like the refractive index, depending on the porosity of the porous silicon (PS) layer. Porosities between 25% and 80% exhibit an estimated refractive index between 3 and 1.7. The channels of the obtained nanostructured semiconductor are galvanically loaded with a metal of a metal-salt solution. The selective precipitation of metal-nanostructures is performed by pulsed deposition technique with varying electrochemical parameters depending on the deposited metal (Ni, Co). Metal loaded PS specimens show significant different transmission compared to bare PS. Additional absorbance peaks appear in the spectra which are due to the deposition process leading to a modification of the Si/SiOx/metal-interface. Magnetic characterization of the samples has been performed by SQUID-magnetometry.

1. Introduction
Nanostructured magnetic materials are of extensive interest in today’s research and technology especially dimensions approaching the length scale of a few nanometers. Not only pre-patterning of templates by lithography but also self-organization of particles on surfaces or of porous media during a formation process acting as matrix for metallic particles are commonly used methods to achieve magnetic nanoarrays due to the low cost and time consuming processing. Utilized matrix materials are porous anodized aluminium [1] and block copolymer films [2]. An important property of the fabrication is the ability to adjust the size, shape and composition of the magnetic nanostructures to obtain a desired magnetic behavior offering certain magnetic characteristics like coercivity, squareness and magnetic anisotropy. In this work we employ self-assembled porous silicon templates to produce samples with magnetic properties tuneable by the fabrication process. A further applicability of metallic nanostructures is the field of magneto-optics and spintronics [3] whereas a metallic/silicon hybrid system is promising to be successful in such experiments.
2. Experiments

To achieve an array of metal-nanostructures an n⁺-silicon wafer is used as starting material to fabricate a porous silicon template with oriented pores. The PS membrane is obtained by electrochemically etching without pre-patterning of the substrate. The self-formation process leads to quasi-regular structures with a noticeable fourfold symmetry which can be obtained in a diameter regime between 40 nm and 100 nm (pore-length up to 50 µm). The adjustable morphology of the PS is self-assembled with a rather regular arrangement confirmed by optical diffraction of the top-view pattern [4]. The pore-distance is determined concomitant to the pore-diameter in using a certain electrolyte composition (10 wt% aqueous HF-solution). To achieve oriented pores with sufficient smooth pore walls the distance between two pores has to be smaller than twice the space charge region.

Metal nanostructures are deposited into the channels of the membrane by a galvanic process. As electrolyte an adequate metal-salt solution like NiCl₂, NiSO₄ or CoSO₄ is used. The electrolyte consists of 0.2 M NiCl₂, 0.1 M NiSO₄ or 0.2 M CoSO₄ and 0.1 M H₃BO₃. Utilizing pulsed deposition technique leads either to metal-nanowires reaching an elongation of several micrometers or to particles with a maximum length of a few hundred nanometers. An additional metal layer covering the porous silicon can also be obtained by shorter pulse durations. The metal top-layer is needed for planned contacting the sample due to the inconvenience of evaporating a metal layer on the nanocomposite due to the rather rough surface.

The semiconductor/metal hybrid system is investigated optically by FTIR-measurements, magnetically by SQUID-magnetometry and the structure is figured out by scanning electron microscopy.

3. Results and discussion

The structure of the PS templates as well as of the deposited metal is figured out by scanning electron microscopy (SEM). To identify the metal particles within the channels the back scattered electrons which allow element specific monitoring. Figure 1 shows SEM-images of a Ni-loaded sample exhibiting nanowires with an elongation of about 2 µm near the pore tips, a PS-template loaded with Ni-particles with a maximum length of 500 nm and a Ni-layer of about 1 µm thickness deposited on top of the PS-sample. These different results have been achieved by varying the current density and the pulse duration of the deposition current.

![SEM-images of Ni-loaded samples](image)

Figure 1: a) Precipitated Ni-wires with a diameter of about 50 nm and a length of a few micrometers near the pore-tips (current density: 40 mA/cm², pulse duration: 5 s). b) Ni-particles with a length up to 500 nm deposited within the channels (current density: 40 mA/cm², pulse duration: 20 s). c) Ni-layer on top of the porous silicon template (current density: 20 mA/cm², pulse duration: 10 s). In this case the sample is tilted 45°.

Optical investigations carried out by FTIR-spectroscopy give details about the composition of the samples, especially about the interior surface and interface. Due to occurring interference fringes the
refractive index of the PS-samples can be determined. Porous silicon templates which exhibit various porosities between 25% (pore diameter of about 40 nm) and 80% (pore diameter about 95 nm) yield a refractive index between 1.7 and 3. A PS-sample of 40% porosity (pore diameter about 60 nm) and a porous layer thickness of 35 µm offers a refractive index of 2.7 which corresponds quite well with values known from literature [5]. Transmission spectra of a porous silicon sample recorded in the mid-IR range show three absorption peaks around 2100 cm⁻¹ (2094 cm⁻¹, 2107 cm⁻¹, 2145 cm⁻¹) which are due to Si-Hx stretching modes, two further peaks at 2341 cm⁻¹ and 2359 cm⁻¹ could not be identified yet. The Ni-filled sample shows a lower transmittance (~2%) with absorption peaks at 1368 cm⁻¹ (due to SiO₃), 1635 cm⁻¹ (Si-OH bending modes) and 2250 cm⁻¹ (O-Si-H modes). These transmission curves are shown in figure 2. The occurrence of oxygen in the Ni-loaded specimen is caused by the oxidation of the H-terminated as-etched sample during the deposition process.

![Figure 2: FTIR-transmission spectra of a bare PS-template and a Ni-loaded PS-sample showing absorption peaks due to the internal surface of the PS-sample and the metal/silicon interface of the PS/Ni-system, respectively.](image)

Magnetic measurements of the differently loaded PS/Ni-samples have been performed by SQUID-magnetometry in a temperature range between 4.2 K and 250 K. The magnetic field has been applied perpendicular to the sample surface (⊥) and parallel to the surface (∥), respectively in a broad field regime of ±7 T. The samples prepared under various loading conditions (described above) exhibiting precipitated a) nanowires, b) nanoparticles and c) a Ni-layer covering the PS-template show different coercivities in both magnetization directions (figure 3).

![Figure 3: Hystereses loops measured at 4.2 K for easy axis and hard axis magnetization showing different coercivities. a) \(H_{C\perp} = 270\) Oe, \(H_{C\parallel} = 180\) Oe. b) \(H_{C\perp} = 380\) Oe, \(H_{C\parallel} = 190\) Oe. c) \(H_{C\perp} = 150\) Oe, \(H_{C\parallel} = 300\) Oe.](image)
The specimen with the additional Ni-toplayer of about 1 µm thickness shows mainly the contribution of the layer recognizable from the magnetization measurements which are comparable to such metal layers. Considering the hysteresis loops of the two samples with deposited Ni-wires and particles, respectively a similar anisotropic behavior can be recognized although mainly caused by shape anisotropy whereas the geometry of wires and particles is drastically different. Due to the high magnetic anisotropy which is mainly caused by the shape of the Ni-structures it can be assumed that the Ni-particles are not insolated within the channels but be connected to each other within one channel. In contrast a PS-template filled with deposited Co-particles of comparable size show a very small magnetic anisotropy (figure 4) which is in addition to the shape anisotropy also caused by the magnetocrystalline anisotropy being higher for Co than for Ni [6]. Consequently the Co-particles have to be more or less insolated deposited within the template which differs from the Ni-deposition process.

Figure 4: Left: SEM-image showing the precipitated Co-particles within the PS-matrix. Right: corresponding magnetization measurements for easy axis and hard axis, respectively.

4. Summary and conclusion
The self-assembled nanostructured hybrid system composed of silicon and an embedded ferromagnetic metal offers an interesting magnetic system with magnetic characteristics tunable by the fabrication parameters. Optical investigations give information about the surface and interface especially about the modification of the interface during the deposition. Magnetic properties depending on size, shape and composition of the precipitated nanostructures as well as on their mutual arrangement provide the opportunity of adjustability. Therefore the magnetic and optical behavior of the silicon based specimens can be tailored by varying the morphology of the PS-template as well as by the experimental parameters of the metal deposition. The obtained silicon/Ni (Co) nanoscopic system is planned to be used for spin-injection experiments and detection of the spin-polarized electrons in silicon.

References
[1] A. P. Li, F. Müller, A. Birner, K. Nielsch, U. Gösele, J. Appl. Phys. 84 (1998) 6023.
[2] T. Thurn-Albrecht, J. Schotter, G. A. Guarini, C. T. Black, M. T. Tuominen, T. P. Russel, Science 290 (2000) 2126.
[3] A. Fert, H. Jaffres, Phys. Rev. B 64 (2001) 184420.
[4] K. Rumpf, P. Granitzer, P. Pölß, A. Reichmann, H. Krenn, Thin Solid Films, 512 (2006) 716.
[5] H. S. Kim, Y. H. Xie, M. DeVincentis, T. Itoh, K. A. Jenkins, J. Appl. Phys. 93 (2003) 4226.
[6] R. Skomski, J. Phys. : Condens. Matter 15 (2003) R841.