Ferromagnetic nanostructure arrays self-assembled in mesoporous silicon

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Abstract. The investigated nanocomposite system is composed of a porosified silicon wafer and embedded ferromagnetic nanostructures. Porous silicon achieved by anodization of a highly doped (100) silicon wafer offers straight pores grown in (001)-direction which are clearly separated from each other. Within the pores of the porous silicon matrix ferromagnetic nanostructures are precipitated. The obtained self-assembled hybrid system combines the electronic properties of silicon with the magnetic properties of the incorporated ferromagnetic metal. Such a magnetic system can be achieved by electrochemical deposition of a transition metal from a metal salt solution into the pores of the nanostructured silicon skeleton. The porous silicon/metal nanocomposites are characterized by electron microscopy (SEM, TEM) to get information about the interior interface and SQUID-magnetometry. Furthermore the structural analyzed regions are investigated by MFM to gain more local information about the magnetic state of the embedded nanostructures.

1. Introduction
Nanostructured magnetic materials are of great interest in today’s basic research but the downscaling of systems opens also a broad avenue for applications. The improvement of high density magnetic data storage is one aim whereas the overcome of the superparamagnetic limit plays a key role. A further topic for extensive research is diluted magnetic semiconductors which are intended to be used to merge conventional electronics with the spin properties of the electrons, the so called spintronics [1]. Traditional electronic devices will be replaced by applications which exploit the electron spin to perform their functions. One crucial point is the operation at room temperature and has to be reached to be adequate for the implementation in microelectronics. The advantage to use silicon as semiconducting material is the long spin lifetime, inversion symmetry of the crystal lattice and the low spin orbit interaction [2]. The presented system, consisting of a silicon base material with embedded ferromagnetic nanostructures is not a usual ferromagnetic semiconductor but it also merges semiconducting and ferromagnetic properties within one system. The silicon substrate is nanostructured by wet etching, offering straight pores and the ferromagnetic metal is deposited within these pores during a further electrochemical step. The embedded metal structures are variable in size, shape and their spatial distribution within the pores. In the following the structural characteristics of the composite material are investigated and correlated with the magnetic ones.
2. Experiments
The porous silicon (PS) template is formed by anodization of a (100) n-type silicon wafer. Using appropriate parameters of the applied current and the electrolyte concentration, which has been described in detail elsewhere [3], results in straight pores which are separated from each other. Thus an interconnecting network of pores can be excluded.

Within these pores metal nanostructures are deposited by a galvanic process. Favorable ferromagnetic metals as Ni and Co are precipitated to get a semiconducting/ferromagnetic composite material. The deposition process is performed in a pulsed way. The average current density of the deposition current is about 50 mA/cm², whereas the frequency of the pulses varies between 0.025 Hz and 0.2 Hz. Considering the deposition of Ni an increase of the frequency from 0.025 Hz to 0.2 Hz leads to an elongation of the embedded Ni-structures from sphere-like particles up to needle-like structures which reach a length of a few microns (almost an aspect ratio of 100). Also the spatial distribution of the metal within the pores can be influenced by the deposition parameters [4] and thus samples with desired properties can be fabricated.

The metal/silicon composite is analyzed by scanning electron microscopy (SEM) to get information about the structure of the template and the geometry of the metal structures (figure 1). In the latter case the back scattered electrons (BSE) are used to figure out the different elements. From transmission electron microscopy (TEM) investigations details about the interface between silicon and metal as well as between the ferromagnetic nanostructures are gained but it has to be considered that the preparation by focused ion beam (FIB) can modify the sample [5]. The interior surfaces play a key role for the magnetic behaviour of the system.

Magnetization measurements are used to get a correlation between the structure of the nanocomposite and the magnetic properties. Magnetic force microscopy (MFM) as a local method shows the magnetic state of the deposited Ni-structures. First principle measurements are gained from a cleaved edge of a cross section of the sample.

![Figure 1: a) Plan view of a self-assembled porous silicon sample exhibiting pore diameters of about 80 nm and mean pore distances of 40 nm. b) Cross sectional view showing Ni needles precipitated within the pores of the porous silicon template.](image)

3. Discussion
The achieved nanocomposite system offers specific properties which are due to the nanostructuring of both, the silicon template as well as the deposited metal. By tuning the electrochemical parameters samples with desired properties can be fabricated. The geometry of the metal precipitates can be adjusted by tuning especially the pulse duration of the deposition current. By analyzing the structural features of the specimens as pore diameter, pore distance and shape of the deposited metal structures together with their magnetic behaviour a correlation between magnetism and morphology can be figured out [6]. The elongation of the metal deposits is a key factor for the magnetic properties due to the demagnetizing effects. With the spatial distribution within the pores the magnetic interactions
between the particles can be influenced which also leads to different magnetic characteristics as coercivity, squareness and anisotropy.

TEM-investigations of the PS-structure show the oxidation of the pore walls of the template. A native oxide layer of about 5 nm is obtained by storing the samples in air (figure 2a) which favours the deposition of elongated metal structures resulting in a higher magnetic anisotropy above 50%. In figure 2b the TEM image of a PS/Ni-nanocomposite shows the Ni-particles within the pores of the matrix. The fact that not every pore of the membrane is filled with Ni at the shown level is because the metal is not continuously deposited along one pore but nanostructures, tunable in their geometry and distribution, are precipitated depending on the electrochemical parameters in each pore. Pores without precipitations in figure 2b contain also Ni-particles but at another cutting plane. Furthermore the preparation of the membrane by FIB can lead to the loosening of particles.

Energy electron loss spectroscopy (EELS) performed by a line scan across an individual Ni-particle (not shown here) shows not only Ni but also oxygen whereas field cooled magnetization measurements show that the Ni-structures are not covered by an antiferromagnetic Ni-oxide shell. The missing exchange bias effect indicates that no antiferromagnetic contribution is present but some sort of oxidation of the metal structures cannot be excluded due to the presence of oxygen.

![Figure 2: a) TEM image of a porous silicon template showing a native oxide layer of about 5 nm covering a pore wall. b) Ni-particles within the pores of the porous silicon membrane.](image)

MFM-measurements of the cross section of a sample filled with Ni-particles show the magnetic signal arising at the transition between the porous silicon layer and bulk silicon (figure 3).

![Figure 3: a) MFM image showing the transition between bulk silicon and Ni-filled porous silicon. b) Corresponding magnetic phase of figure 3a shows an enhancement of the magnetic signal at the transition region.](image)

The MFM measurements show that the precipitated particles are magnetically aligned along the pores whereas the direction of magnetization, parallel or antiparallel to the pores, cannot be seen in
case of scanning a cross sectional region. The magnetic alignment of the particles within the pores is in good agreement with SQUID-measurements. Magnetization measurements of the considered sample (figure 4) in two directions, with the magnetic field applied parallel and perpendicular to the pores, respectively show a magnetic anisotropy caused by the coupling of the particles resulting in a “magnetic chain”. Due to the fact that the magnetocrystalline anisotropy of Ni ($K_1 = -0.005$ MJm$^{-3}$) is small the observed anisotropy has to be caused by interactions between the particles within the individual pores leading to quasi-elongated structures of the adjacent particles along the pores which behave wire-like. Considering the investigated sample the distance between the particles is less than 20 nm gained from SEM images. An interaction between different pores is weak due to the pore-distance of about 40 nm [8].

![Figure 4: Hystereses loops measured in two directions of magnetization, perpendicular (easy axis) and parallel (hard axis) to the surface showing an anisotropy caused by the shape and interaction of Ni-structures along the pores.](image)

### 4. Conclusions

The present work introduces a magnetic nanocomposite material which combines a semiconductor and a ferromagnet within one system. Morphology and internal interface information is figured out by SEM and TEM. Magnetic measurements performed by SQUID-magnetometry and MFM give information about the correlation between structural characteristics and magnetic behaviour. Due to this correlation and the tunable morphology of the specimens by the process parameters a broad avenue of desired magnetic properties of the nanocomposite is offered. The hybrid system is not only a versatile material for basic research but also a promising candidate to detect spin-injection due to the silicon base substrate.

### Acknowledgements

This work is supported by the Austrian Science Fund FWF under project P21155. The authors thank Prof. H. Krenn from the Institute of Physics at the Karl Franzens University Graz for making available the SQUID-magnetometer and furthermore the authors are grateful to Martina Dienstleder from the Institute for Electron Microscopy at the University of Technology Graz for FIB-preparation of the samples.

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