Interacting low dimensional nanostructures within a porous silicon template

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Abstract. Ni nanostructures of different geometries as spheres, ellipsoids or wires, as well as with various spatial distributions are deposited electrochemically within the pores of porous silicon (PS). The hybrid material offers magnetic properties which depend on the morphology of the composite and the interactions between the metal precipitates, respectively. So the magnetic behavior can be correlated with the process parameters. On the one hand the morphology of the PS template determines the coupling of the metal structures located within adjacent pores and on the other hand the spatial distribution and geometry of the deposits influences the interaction of nanostructures within one pore. Thus also the anisotropy of the nanocomposite can be modified not only by the shape of the ferromagnetic nanostructures but also by their spatial density within the oriented pores of the porous matrix.

1. Introduction

The fabrication of materials having their characteristic length scale in the nanometer regime are of great interest due to their specific properties. Top-down or bottom-up processes in using lithographic or self-organizing methods are widely spread to achieve such nanosized objects whereas self-organization is of special interest especially to obtain large area samples of nanostructures and nanoparticles on surfaces and in 3-dim arrays. A lot of works report on metal or oxide particles dispersed in a host material as another metal [1] or a nonmagnetic matrix [2]. Polymers are often utilized as matrix to investigate the properties of the obtained composite as well as the interaction between the magnetic particles [3] within the investigated system. Furthermore there are reports on the formation of mixed metal complexes leading to a phase-homogeneous product at low temperatures which is obtained by dispersing magnetic particles within silica [4]. Silicon oxide is also used as host for the fabrication of a superparamagnetic composite material with particle-size dependent properties [5]. The presented work reports on a magnetic/semiconducting nanocomposite material which is achieved by electrodeposition of ferromagnetic metal nanostructures into the pores of the silicon template.
matrix whereas the self-organized pores are grown straight and normal to the silicon surface. The shape and size of the deposits as well as their spatial distribution within the pores can be controlled by the electrochemical process parameters and thus samples with desired magnetic properties can be achieved. Semiconductor and ferromagnetic materials combined in one system join the electronic properties of the semiconductor and the ferromagnetic behaviour of the Ni nanostructures.

2. Experiments

A wet etching process of a highly n-doped silicon wafer under certain conditions leads to porous silicon in the mesoporous regime which is acting as template material. The formation of straight grown pores with an average pore-diameter of 55 nm is achieved by anodization in an 8 wt% aqueous hydrofluoric acid solution in applying a constant current density of 80 mA/cm$^2$. The pores are oriented perpendicular to the surface and clearly separated from each other. The pore-arrangement is self-assembled but nevertheless offers a four-fold symmetry of domains in the micrometer regime under certain conditions. Such a quasi regular morphology is obtained by applying a constant current density between 75 mA/cm$^2$ and 100 mA/cm$^2$ [6]. For higher current densities the critical current density $J_{PS}$ is reached and instead of pore formation electropolishing at the porous silicon/silicon border takes place [7], whereas in the case of lower current densities the pore-diameter becomes smaller and less regular. In the case of smaller pore-diameters ($< 40$ nm) the distance between the pores is enhanced and exceeds twice the thickness of the space charge region and thus nucleation of pores in the remaining silicon walls is possible.

Within the fabricated highly oriented pores a ferromagnetic metal e.g. Ni is electrochemically deposited resulting in a nanocomposite material consisting of a silicon matrix and precipitated Ni nanostructures. The deposition is performed in a pulsed way under cathodic conditions. As electrolyte an adequate metal salt solution is used whereas in the case of Ni-deposition the so called Watts electrolyte ($\text{NiCl}_2$, $\text{NiSO}_4$) with boric acid as buffer is utilized. A variation of the pulse frequencies and the current density leads to modifications of the geometry of the metal deposits [8]. The shape of the metal deposits can be controlled by varying the pulse-frequency of the applied current density between 0.025 Hz and 0.2 Hz which results in a modification from spheres to wires of an aspect ratio of 100 (ratio of length to diameter). The spatial distribution of the precipitates can be adjusted by varying the current density between 5 mA/cm$^2$ and 25 mA/cm$^2$ whereas the distance between precipitated particles within the pores is modified by the time between the pulses. In the case of densely packed particles (mean distance about 10 nm) the time between the pulses is 5 s and for loosely packed particles (mean distance about 200 nm) it is 20 s. This opens a broad avenue to achieve desired magnetic properties of the specimens but requires accurate control of the deposition parameters. The temperature of the electrolyte during deposition is also an important factor but it has been kept constant at room temperature during the presented experiments.

Magnetic measurements are carried out by SQUID-magnetometry (SQUID magnetometer Cryogenics) up to a magnetic field of 6 T and in a temperature range between 4 and 250 K. The structure and composition of the nanocomposite is investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Especially the shape of the metal deposits and their average size is gained from many successively recorded back scattered electron (BSE) images over a broad cross-sectional region of the samples and using image processing.

3. Discussion

In order to investigate the correlation between magnetic characteristics and structure of the nanocomposite we deposit different metal nanostructures within a silicon matrix. The porous silicon structure offers pores which are arranged in a quasi regular way depending on the anodization conditions and the deposited metal structures are distributed randomly within these pores. The morphology of the porous silicon matrices can be varied in pore-diameter, pore-distance and pore-
length as discussed in the experimental section. To assure a clear separation of the channels the
distance between the pores must not exceed twice the thickness of the space charge region of the
substrate which is around 10 nm for highly doped silicon. In this investigated morphology regime
always a dendritic growth of pores is observed which means that small side-pores (length smaller than
the pore-radius) grow in (111)-direction additionally to the main-pores [9]. Pulsed electrodeposition is
employed to deposit Ni structures within mesoporous silicon whereas this technique allows to vary the
pulse frequency of the applied current and the time between the pulses. The precipitated Ni structures
within the pores are also self-assembled which results in a randomly arranged but more or less
homogeneously over the entire porous matrix distributed metal nanostructure array. The cross-
sectional image of a specimen gained by scanning electron microscopy in figure 1 shows a
homogeneous distribution of sphere-like Ni structures within the pores whereas the distance between
the particles is small enough for dipolar coupling.

Temperature dependent magnetization measurements show that the coercivity ($H_C$) of porous silicon
matrices with precipitated Ni-particles (figure 2a) is always higher than $H_C$ of samples with deposited
elongated Ni-structures (figure 2b) due to the higher demagnetizing field of the latter ones which
exhibit an average elongation of 1 µm. $H_C$ varies in the case of Ni-particles between 580 Oe ($T = 4$ K)
and 410 Oe ($T = 250$ K), if the magnetic field is applied perpendicular to the sample surface meaning
parallel to the pores. In the case of elongated structures $H_C$ decreases to values between 330 Oe ($T = 4$
K) and 200 Oe ($T = 250$ K). If the magnetic field is applied parallel to the sample surface a further
decrease of the coercivity is always observed (figure 2 a, b) which is mainly caused by the shape-
anisotropy of the precipitates in case of elongated metal-structures. In the case of Ni particles the
observed magnetic anisotropy is also a quasi shape effect because sufficient densely packed Ni
particles interact dipolar within one pore (average distance about 10 nm) but the coupling of particles
between adjacent pores (distance between the pores around 50 nm) is neglectable which leads to quasi
elongated magnetic structures within the oriented pores.

Figure 1: Ni particles with a diameter of about 55 nm (equal to the pore-diameter) and an average
length of 70 nm (maximum 100 nm) within the pores of a porous silicon matrix. The SEM-image
(back scattered electrons) shows a cross-sectional region of the sample.
Figure 2 a: Decrease of the coercivity $H_C$ with increasing temperature measured on porous silicon with embedded Ni-particles. The curves show an exponential behaviour which is up to now an experimental result. The measurements are performed with a magnetic Field applied perpendicular to the surface (squares) as well as parallel to the surface (triangles). The magnetic field has been varied between ±1Tesla.

The magnetic anisotropy can be modified by varying the geometry of the precipitated metal structures or by changing the spatial distribution of the deposits within the pores. Densely distributed particles meaning a distance between them in the range of their size or smaller interact magnetically within the pores and thus show a higher anisotropy between the two magnetization directions than loosely packed particles.

Figure 2 b: Temperature dependency of porous silicon with incorporated elongated Ni structures. The experiments show that $H_C$ decreases with increasing temperature in an exponential way for both magnetization directions, magnetic field perpendicular to the surface (squares) and parallel to the surface (triangles).
The deposited particles corresponding to figure 2a show a value of the coercivity $H_c$ for a magnetic field applied parallel to the surface which is about 23% less than for a field applied normal to the surface. In the case of the elongated Ni structures corresponding to figure 2b the anisotropy is in the same range (~ 27%). The elongated structures are packed less densely than in the case of particles but the anisotropy is caused by the shape. The packing density of the Ni structures is obtained by image processing using BSE images of the samples. Estimations of elongated Ni-structures with an aspect ratio of about 20 (ratio of length to diameter) are in good agreement with the literature [10]. If the particles interact within the pores they form a magnetic quasi chain also resulting in a quasi shape anisotropy. Particles (average diameter 55 nm) deposited within the pores with a distance between them much greater than their size (by adequate control of the deposition parameters as mentioned above) offer a weak dipolar coupling and therefore no significant magnetic anisotropy between the two magnetization directions can be observed (figure 3).

Considering the anisotropy between easy axis (magnetic field perpendicular to the surface) and hard axis (magnetic field parallel to the surface) magnetization the differences of the coercivities at each temperature of the whole temperature range (between 4 K and 250 K) are in the same range for any morphology which can be seen in figure 2a and figure 2b. Phenomenologically it is found from the experimental data that both curves follow an exponential law.

The presented nanocomposite system offers ferromagnetic properties whereas the magnetic characteristics as coercivity, remanence and magnetic anisotropy can be tuned by the fabrication parameters (e.g. the pulse-frequency of the current, current density and electrolyte concentration).

Figure 3: Hystereses curves of porous silicon with precipitated Ni particles (average diameter 55 nm) whereas the distance between them is much greater than their size offering weak interactions (interparticle distance > 200 nm). Measurements are carried out at $T = 250$ K in two directions of magnetization exhibiting coercivities which are nearly equal (Magnetic field perpendicular to the surface: $H_{c\perp} = 160$ Oe; magnetic field parallel to the surface: $H_{c\parallel} = 150$ Oe).

4. Conclusions

The fabrication of a nanocomposite system consisting of a semiconducting matrix and embedded ferromagnetic nanostructures has been presented. The ferromagnetic properties of the system can be
controlled by the electrochemical process parameters. On the one hand various geometries of the metal structures can be precipitated leading to different magnetic characteristics as coercivity, remanence and shape anisotropy. On the other hand the density of the spatial distribution of the deposits within the pores can be modified which influences the magnetic interactions between the particles. In the case of densely packed particles within the pores dipolar coupling between them occurs and results in quasi magnetic chains which offer a much larger magnetic anisotropy than non-interacting particles. The investigated nanocomposite offers the possibility to vary its magnetic properties in a broad range and therefore it is adequate for magnetic applications e. g. sensors, whereas it is due to the silicon based host-material proper for the integration in existing process technology.

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