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Magnetization of self-organized Ni-nanowires with peculiar magnetic anisotropy

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Abstract

Porous silicon (PS) offering a quasi-regular pore arrangement in the meso-/macroporous regime acts as a matrix for incorporating ferromagnetic nanostructures. The electrochemically fabricated structures are self-assembled and exhibit pores with a diameter tunable between 30 and 100 nm. The subsequent electrodeposition of Ni into these pores leads to a Ni/Si-nanocomposite consisting of Ni-particles and Ni-wires, respectively. The ratio of particles and wires depends on the electrochemical deposition conditions like current density as well as current pulse duration. The different distributions cause a variation of the magnetization curves. Especially in the high field regime a negative magnetization branch occurs and decreases with increasing amount of particles. This peculiar high field magnetic behavior appears if the external magnetic field is applied perpendicular to the sample surface and is due to antiferromagnetic coupling between the Ni-nanostructures.

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1. Introduction

Nanostructured magnetic materials are of great interest nowadays because of their applicability for magnetic data storage technology, spintronic as well as sensor devices [1]. One's attention is mainly turned on highly ordered arrays of nanowires and nanoparticles [2]. The fabrication of such arrangements has been investigated since the last two decades and still goes on. The magnetic behavior of nanoscopic systems differs from those of bulk material and therefore they are of great interest to be investigated experimentally [3] as well as theoretically [4].

Nanomagnetic patterns can be obtained either by pre-structuring of the substrate using lithography or by self-assembling of the structures. A well known self-organized template for nanowires is porous alumina [5] exhibiting a honeycomb-like hexagonal arrangement of the pores.

In this work we use porous silicon (PS) as matrix in which ferromagnetic nanowires are incorporated [6] and we show that the magnetic behavior of this nanocomposite system differs strongly from the known hystereses loops [7]. In the described Si/Ni-nanocomposite system two regions of an applied external magnetic field can be distinguished. The behavior in the low field regime is comparable with that of other metal-incorporated systems [8]. But there exists a peculiar magnetic behavior in the high field region around a few Tesla which can be controlled by the deposition parameters like current density and current pulse duration. This system is interesting not only because of silicon as basic material but also because of the low-cost fabrication and the extraordinary magnetic properties.

2. Experimental details and structural investigations

The PS matrix is fabricated during an anodization process using aqueous hydrofluoric acid solution as electrolyte. The electrochemical parameters as well as the doping density of the silicon wafer are correspondingly

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chosen [9,12] to achieve pores in the meso-/macroporous regime. The fabricated PS system exhibits highly oriented pores perpendicular to the surface and a sharp termination between porous layer and crystalline silicon (Fig. 1). A quite homogeneous pore distribution is obtained without any pre-structuring. The self-assembled pore-arrangement shows a quadratic-like ordering which is found by Fourier transform image processing [12].

The pore diameter of a typical sample like that in Fig. 1 is about 50 nm and thus lies in the transition region between mesopores and macropores [10]. A subsequent electrochemical procedure is used for metal-deposition into the template. In this work the channels are filled with Ni employing pulsed deposition technique [11]. As electrolyte a $NiCl_2$ (185 g/l), H_3BO_3 (45 g/l) solution and a Watts electrolyte ($NiCl_2$ 45 g/l, $NiSO_4$ 300 g/l, H_3BO_3 45 g/l) are used, respectively. Depending on the electrochemical deposition conditions (see Table 1) the filling of the pores varies and leads to distinct magnetic behavior due to the depth and width of the depression in the magnetization curve at high fields (see Fig. 3). The Ni-content within the channel-layer is demonstrated by EDX-mapping. Some examples are presented in Fig. 2.

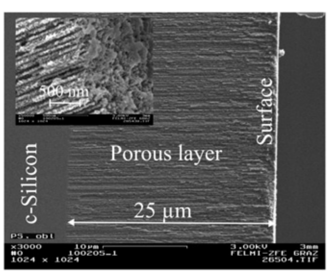

Fig. 1. Cleaved edge of a porous silicon layer of 25 µm. In the inset a tilted view of the porous sample is displayed showing the oriented pores.

Table 1
Electrochemical deposition parameters associated with the EDX-images in Fig. 2

Sample	Current density j(mA/cm^2)	Pulse duration t_{pulse} (s)
a	10	20
b	20	10
c	50	10

The EDX-maps in Fig. 2 are a rough survey and do not resolve individual pores but the altered distribution of nickel within the porous layer is sufficiently proved.

3. Magnetization and anisotropy of the PS/Ni-nanocomposite

Magnetization measurements have been carried out by a SQUID-magnetometer (Quantum Design MPMS XL7) in the field range of ± 7 T and a temperature variation between 4.2 and 300 K. Considering the hysteresis loops in the low field regime (below 1 T) the magnetic behavior is comparable with conventional nanocomposite systems like metal filled porous alumina [8], which are mostly governed by dipolar interwire interaction.

Structural investigations of the fabricated PS/Ni-nanocomposite using SEM and EDX as well as magnetization measurements lead to the assumption that the metallic Ni phases within the pores consist of Ni-particles and Ni-wires. The Ni-particles are smaller than 150 nm in length [12] and offer a spherical or ellipsoidal shape. Calculating the critical radius r_C of Ni-single-domain particles after reference [13] yields to $r_C \approx 50$ nm. Most of the particles found are below 50 nm in diameter and thus they are single domain. Determining the coercive field of a particle with a diameter of 60 nm after Ref. [13], a value of 450 Oe is achieved which is in good accordance with the measurements. Table 2 gives a summary of different PS/Ni-samples with coercivity H_C, squareness M_R/M_S and an estimate of the Ni-volume in cm^3. The given low field hystereses properties and the Ni-contents are related to the incorporated Ni-particles.

Table 2
H_C, squareness and Ni-content of investigated Ni-filled PS samples for H-field parallel ($\|$) and normal ($\perp$) to the pores (wires)

$H_C,\|$ (Oe)	$H_C,\perp$ (Oe)	$M_R,\|/M_S$ (%)	$M_R,\perp/M_S$ (%)	Ni (10^{-6} cm^3)
350	190	50	22	3.813
280	160	39	19	2.859
260	170	52	26	1.9
220	150	45	31	1.9

The Ni-content is derived from the first saturated magnetization plateau at low fields.

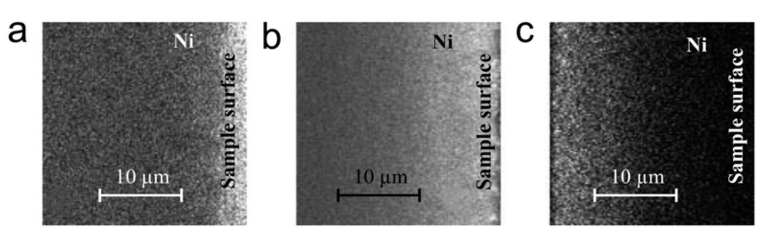

Fig. 2. X-ray maps over the cleaved edge of the samples showing different Ni-distributions. (a) Accumulation of Ni near the surface region, (b) nearly homogeneous distribution within the porous layer and (c) the pore-tips are preferentially filled with Ni. Higher brightness of the pixels means higher Ni-content.

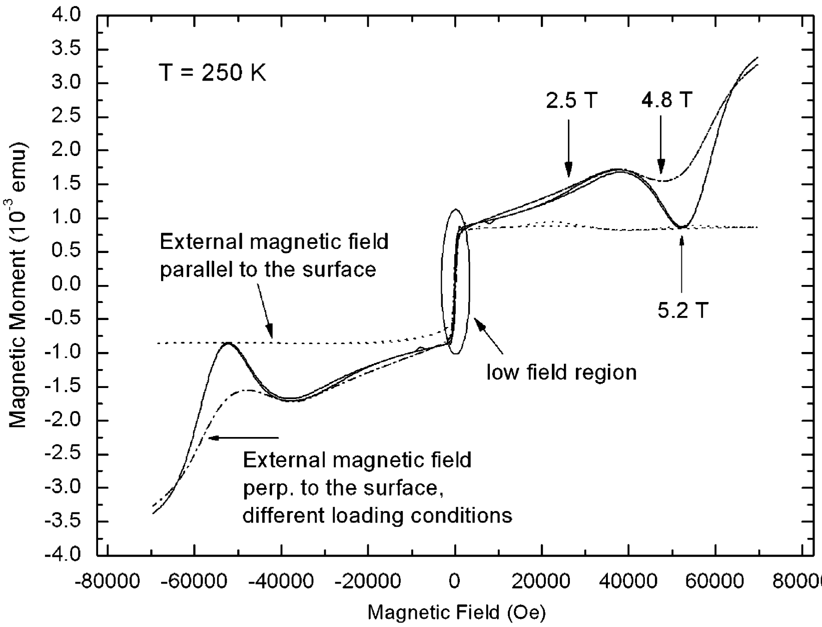

Fig. 3. The solid curve and the dashed line show the magnetization for an external magnetic field normal to the surface but of two samples Ni-loaded with different electrochemical parameters (solid: $j = 50\,\mathrm{mA/cm^2}$, pulse duration $= 10\,\mathrm{s}$, dashed: $j = 50\,\mathrm{mA/cm^2}$, pulse duration $= 5\,\mathrm{s}$). Both samples show a depression of the magnetization of different depth at 4.8 and 5.2 T, respectively. The dotted curve corresponds to the sample represented by the solid line but for a magnetic field parallel to the surface. In this magnetization direction the investigated samples do not show a depression.

In the high field region of a few Tesla a peculiar magnetic behavior is found, showing a deep depression in the magnetization signal (Fig. 3). This "negative peak" of the magnetization curve at 5.2 T is due to an antiferromagnetic interaction between the Ni-wires. Regarding dipolar coupling between neighboring wires with an interpore distance equal to the pore diameter leads to a sum of the stray fields of nearest and next nearest wires of about 2.5 T under the assumption of a quadratic array and a saturation magnetization for each contributing wire of 0.6 T. This value is too small to characterize the depression but it is near the beginning of the negative slope of the magnetization curve for some other samples.

In accordance with structural investigations and magnetization measurements the incorporated Ni is assumed to consist of particles and wires like previously pointed out. The low magnetic field behavior is due to the particles, whereas the one at high magnetic fields corresponds to the high aspect ratio Ni-wires. This conception of a bimodal PS/Ni-composite is additionally endorsed by measurements of samples prepared using different electrochemical filling parameters leading to changed Ni-distributions. The corresponding magnetization curves show different "negative peaks" in the high field range. If the Ni-filling of the PS-template becomes stronger towards the pore-tips, the depression of the magnetization curve increases in depth. At last the magnetization increases up to full saturation. Samples with Ni accumulated near the surface region are missing this peculiar behavior. If the external magnetic field is applied parallel to the sample surface the nanocomposite system is not fully saturated due to the high demagnetizing field perpendicular to the Ni-wires. In this case saturation magnetization is given by the Ni-particles and no longer an up-turn of the magnetization signal is observed up to an available field of 7 T.

4. Conclusion

A quasi one-dimensional PS/Ni-nanocomposite system has been fabricated during a two-step electrochemical process for (i) forming the PS template and (ii) for filling this silicon matrix with nickel. The ferromagnetic precipitations consist of Ni-particles as well as Ni-wires whereas the latter ones cause strong anisotropic magnetic responses. The particles offer a "soft" hysteresis in the low field regime below 0.1 T whereas an antiferromagnetic coupling of the wires leads to a "negative magnetization slope" at magnetic fields of a few Tesla. This depression of the magnetization curve can be influenced in depth, width and slightly in the magnetic field signature (between 4.5 and 5.4 T) by various electrochemical filling parameters like current density, current pulse duration and (not shown) by temperature. The physical nature of negative magnetization due to antiferromagnetic interwire exchange is not yet clear but has been already reported in literature [14].

Acknowledgments

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