Metal/semiconductor hybrid system with two magnetic terms dependent on the field region

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Abstract. A magnetic semiconductor/metal nanocomposite with a nanostructured silicon wafer as base material and precipitated metallic nanostructures (Ni, Co, Fe, NiCo) is fabricated by wet etching of a silicon wafer and subsequent electrodeposition of a metal. The achieved hybrid material exhibits an interesting two-fold magnetism, consisting of a ferromagnetic behaviour at low magnetic fields (below the saturation magnetization $M_S$ of the deposited metal) and a further non-saturating contribution at fields above $M_S$. In both cases a magnetic anisotropy is observed. The low-field behaviour is caused by the ferromagnetic properties of the metal-structures. With increasing magnetic field the enhancement of the non-saturating term above $M_S$ is nearly linear measured at temperatures above 80 K which opens the possibility to use this composite as magnetic high field sensor. The combination of silicon and a ferromagnetic metal renders this nanocomposite interesting for magneto-electronic devices.

1. Introduction

Ferromagnetic nanostructures are an important part in basic research but also in nanotechnological applications as magneto-optical devices, high density data storage and also in biomedicine such structures at the nanoscale are promising candidates for example in drug delivery, imaging or targeting of special cells. 3-dimensional arrays of nanostructures (nanowires, nanotubes) have been formed without prestructuring in using hexagonal arranged porous alumina as matrices [1] and magnetic properties of metal filled membranes (e.g. porous alumina, polycarbonate) are under extensive investigation [2]. Moreover magnetization reversal processes with the concomitant domain wall motion within the deposited metal nanostructures, the interactions among them [3], but also transport phenomena [4] like magnetoresistance in spin valves [5] are of great interest. Magnetic materials in the nanometer scale exhibit changed properties compared to bulk material and therefore offer great potential for nanotechnological applications. For applicability of the system the magnetic nanostructures need to be ferromagnetic at room temperature. In some cases a high anisotropy between the two magnetization directions, perpendicular and parallel to the surface, is of interest and thus needle-like structures are favourable due to their high demagnetizing field. One method to achieve low-dimensional structures is the deposition of metal nanostructures on patterned surfaces or into porous membranes with channels perpendicular to the surface and therefore the metal structures exhibit a high density with respect to the sample surface. Templates like porous alumina or polycarbonate foils are usually electrochemically fabricated and afterwards filled with a magnetic material by electrochemical deposition. In commercial microelectronics most devices are based on silicon technology and thus for compatibility a silicon substrate is a precondition for applicability. In
the present work a silicon wafer is porosified and the resulting nanostructured skeleton acts as template for incorporating the magnetic nanostructures.

2. Experiments
As template for the incorporation of ferromagnetic nanostructures porous silicon (PS) offering morphologies in the meso/macro porous regime is used. The incorporation of the nanostructures is performed by electrochemical deposition of a metal from a metal salt solution. The experimental setup and the used electrochemical parameters for the porosification of silicon as well as the subsequent metal incorporation can be found elsewhere [6]. For the presented investigations PS-matrices with pores grown perpendicular to the surface exhibiting an average pore-diameter of 80 nm and an interpore-spacing of about 40 nm are used. The metal deposition is carried out by pulsed deposition technique with frequencies between 0.025 Hz and 0.1 Hz. The applied current density has been varied between 10 mA/cm² and 25 mA/cm². The morphology and structure of the nanocomposite material is characterized by scanning electron microscopy (SEM). Magnetization measurements are performed by SQUID-magnetometry using samples with an area of 12 mm². The magnetic field is either applied perpendicular (easy axis) or parallel (hard axis) to the sample surface.

3. Results and Discussion
Considering magnetization measurements of a porous silicon/metal nanocomposite one sees that the magnetic behaviour is composed of two terms. A first one is observed at magnetic fields below the saturation magnetization of the incorporated metal. This behaviour is due to the spinmagnetism of the metal structures and strongly depends on the geometry of the precipitations. Comparing Ni and Co filled samples one can see that in both cases the dependence on the geometry is similar but in case of particles deposited within the pores, having a similar spatial distribution for both materials, different magnetic anisotropies are observed. In case of deposited Ni-particles the coercivity is about 50% higher for easy axis magnetization than for hard axis magnetization, whereas in case of Co-particles of similar size and density of the spatial distribution the anisotropy between the two magnetization directions is in the range of 10%. This indicates that the Ni-particles stronger interact along the pores than the Co-particles. Figure 1 shows the magnetization curves in both directions of magnetization (easy axis and hard axis) for Ni and Co filled specimens as well as the according SEM-images showing the Ni and Co distribution, respectively within the porous layer.

A further magnetic term is observed at magnetic fields greater than the saturation magnetization of the incorporated metal (Ni: \( \mu_0 M_S = 0.62 \) T, Co: \( \mu_0 M_S = 1.81 \) T). In this high field region far above 1 T the samples show an enhancement of the magnetization with increasing magnetic field without saturation up to an available field of 7 T. This non-saturating magnetization term is observed independent of the shape of the embedded metal-structures. Figure 2a shows the temperature dependence of the magnetization curves measured in a temperature range between 4.2 K and 310 K up to a magnetic field of 7 T. The magnetization measured at a certain field above the saturation magnetization of the incorporated metal decreases with increasing temperature. The temperature dependency of the high field term shows a paramagnetic behaviour and follows exactly the Curie Weiss law (Figure 2b). This unexpected non-saturating high-field term shows an enhancement with increasing magnetic field which is nearly linear, measured at temperatures above 80 K. Magnetization measurements of the bare silicon skeleton show a clear diamagnetic behavior. Thus the substrate can be excluded as reason for the peculiar non-saturating term. The occurrence of this additional high-field contribution is not completely clarified yet but there are hints to be caused by orbital currents in the silicon skeleton [7].

A new kind of magnetism is also observed by some groups in usually diamagnetic systems as thiol capped gold-nanoparticles or thin gold layers [8] caused by a strong spin-orbit coupling due to a broken symmetry at the surface. An enhancement of the orbital moment and the magnetic anisotropy by a tetragonal distortion of the lattice of FeCo-alloy films is demonstrated by [9]. Recently a unique kind of giant magnetic behaviour observed in organic monolayers is explained by bose condensation
of the electrons into a single low angular momentum quantum state caused by triplet pairing [10]. The occurring paramagnetism is explained by an internal angular momentum. Considering the PS/metal composite the occurrence of the non-saturating paramagnetic term could be explained by an interface magnetism caused by triplet-pairing of carriers injected into the Si-skeleton. The resulting orbital moment leads to the paramagnetic behaviour of the specimens.

Figure 1: a) Easy axis and hard axis magnetization of a porous silicon sample with deposited Ni-structures. b) Magnetization measurements (easy and hard axis) of a sample with precipitated Co-structures. c) Spatial distribution of the precipitated Ni-structures within the porous layer. d) Distribution of the Co-structures within the porous layer. c) and d) show a cross sectional view of the samples.

Figure 2: a) Magnetization curve of a porous silicon sample with deposited Ni-structures measured in the field range between 0 and 7 T. The temperature is varied between 4.2 K and 310 K. b) Temperature dependence of the magnetization curves which have been measured at 3 T (circles) and 7 T (squares). The experimental data follow exactly the Curie-Weiβ law.
4. Conclusions
The presented nanocomposite is fabricated during a low-cost two-step electrochemical process. Porous silicon, tunable in its morphology, acts as template for the incorporation of ferromagnetic nanostructures. Considering the magnetic behaviour of this system two characteristic terms are observed. A first one caused by the spinmagnetism of the embedded metal and a second one at higher fields showing a non-saturating behaviour up to 7 T (available magnetic field). Because the metal deposition can be strongly influenced by the process parameters, samples with desired ferromagnetic properties as magnetic anisotropy, remanence and coercivity can be fabricated. In this low field region the magnetic behaviour is strongly correlated with the structural and morphological features of the specimens and depends on the size, shape and spatial distribution of the deposited metal structures. The unexpected term at high magnetic fields is independent of the geometry of the metal precipitations. This non-saturating term shows a temperature dependence following a paramagnetic decrease of the magnetization with increasing magnetic field. All in all the presented nanocomposite material opens a broad variety of potential applications as magnetic sensors, magneto-optical devices and this combination of silicon with a ferromagnetic metal is a good candidate to detect spin-injection.

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.

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