Two kinds of magnetism observed in a semiconductor/metal nanocomposite

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Abstract. A ferromagnetic nanocomposite consisting of metal-structures enclosed in a porous silicon skeleton is investigated magnetically by SQUID-magnetometry and the structural examination is performed by SEM. The ferromagnetic nanostructures are achieved by chemical deposition of Ni or Co from an adequate metal-salt electrolyte. The deposited Ni-nanostructures are restricted to the highly oriented pores of an aspect ratio up to 1000 and therefore the samples show a strong magnetic anisotropy between easy axis and hard axis magnetization, respectively. In the field range below 1 T the observed anisotropy is mainly caused by shape anisotropy of the Ni-nanostructures (spheres and elongated particles). It enhances with the amount of needle-like shaped nanoparticles exhibiting a length of a few micrometers which fill the pores successively over the entire depth of the porous layer of about 30 µm. Magnetization measurements exhibit strong temperature dependence between 4.2 K and 300 K. At low temperatures the samples do not get saturated with the available magnetic fields of 7 T but give rise to a paramagnetic behavior due to orbital magnetism. This additional magnetic behavior to the known ferromagnetic property is due to the enhanced orbital magnetic moment at surfaces compared to the spin moment. The orbital moment can be associated to the spin polarized states at the surface of the metal-particles which are less bound due to a reduced exchange interaction. The change in the magnetic behavior between the usual mere ferromagnetic character and the supplementary paramagnetic behavior is only observed for magnetic fields perpendicular to the sample surface.

1. Introduction
Magnetic materials in the nanometer scale exhibit unusual properties compared to bulk material and therefore offer great potential for applications e.g. in high density data storage [1], functionalization in nanobiology [2] or sensors [3]. The nanoscopic systems consist either of particles or wires with magnetic properties due to their geometry and arrangement. For applicability of the system the magnetic nanostructures need to be ferromagnetic at room temperature. Furthermore a high anisotropy between easy axis and hard axis magnetization is of interest and thus needle-like structures are favourable due to their high demagnetizing field. A well working method is the deposition of metal nanostructures into porous membranes with channels perpendicular to the surface and therefore the metal structures exhibit a high density with respect to the sample surface. The templates like porous alumina or polycarbonate foils are usually electrochemically fabricated and afterwards filled with a
magnetic material by a galvanic process. In commercial microelectronics most devices are based on silicon technology and thus for compatibility a silicon substrate acting as skeleton to embed the magnetic nanowires is suitable.

2. Experimental details
Metallic nanostructures with geometries of spheres, ellipsoids and wires are deposited into an anodized n+-silicon template offering oriented pores of high aspect ratio (~ 1000). The diameter of the pores is adjustable between 40 nm and 100 nm with a concomitant diameter of the metal precipitations. The pore-distance arises from the self-formation process depending on the electrolyte concentration which has to be kept constant during the anodization process in the range of about 10 wt%. The detailed fabrication process of the porous silicon matrix can be taken from references [4, 5]. Electrochemical metal (Ni, Co) deposition from a NiSO₄ or CoSO₄ solution leads to a distribution of metallic nanoparticles and nanowires within the channels of the matrix. The diameter of the metal structures is constrained by the pore diameter and the length depends on the deposition parameters especially the applied deposition current density and the pulse duration of the current. A maximum length of several micrometers of the metal precipitations is achieved. The characterization of the nanocomposite system is carried out on the one hand structurally by scanning electron microscopy [6], especially in using the back scattered electrons to distinguish between deposited metal and substrate and on the other hand magnetically by SQUID-measurements in a temperature range from 4.2 K up to 300 K and a magnetic field adjustable between ± 7 T.

3. Discussion
The achieved (metal/semiconductor) nanocomposite system shows an extraordinary magnetic behavior which is composed of two terms. On the one hand a ferromagnetic property due to the spin-magnetism of the deposited metal within the channels of the porous silicon template appearing at magnetic fields below the saturation magnetization of the precipitations. On the other hand a second paramagnetic-like term which occurs at higher magnetic fields and does not saturate up to 7 T. The non-saturating behavior is dominant at low temperatures and decreases with increasing temperature (figure 1).

![Figure 1: Non-saturating paramagnetic-like behavior of the specimens occurring simultaneously with the ferromagnetic property but dominating at high magnetic fields and low temperatures.](image)
In the low field region the hysteresis loops measured in easy axis as well as hard axis magnetization which means parallel and perpendicular to the channels, respectively show a distinct magnetic shape anisotropy. Typical values for the coercivity $H_C$ at a temperature of 4.2 K are $H_C = 280$ Oe for easy axis and $H_C = 160$ Oe for hard axis magnetization. The corresponding squareness $M_R/M_S$ for the two magnetization directions is 41% and 19%, respectively.

Concerning the non-saturating term in the high field region figure 2 shows the decrease of the magnetization with the temperature for applied magnetic fields between 1 T and 7 T.

![Figure 2: Temperature dependency of the maximum magnetization for a magnetic field range from 1 T to 7 T. In the inset a Curie Weiss-fit performed at 7 T is shown.](image)

The decay of the magnetization follows approximately the Curie Weiss law, especially at higher temperatures (> 50 K) the fit suits quite well with the experimental data. Furthermore the paramagnetic-like behavior is less distinctive for hard axis magnetization which means the magnetic field applied parallel to the sample surface (figure 3). The described magnetic behavior of the samples is not fully clarified yet but the appearance of the paramagnetic-like behavior can be explained by the occurrence of orbital magnetism due to persistent currents in silicon between the channels of the PS-template. This assumption also elucidates the anisotropy between the two magnetization directions. The enhancement of orbital moments is in first principle attributed to the nanoscale nature of the investigated system [6] concerning the incorporated metal nanostructures as well as the nano-patterned template.

Recently in literature has been reported about orbital magnetism observed in nanostructures thin films as well as in particles [7, 8] caused by the spin-orbit coupling. It is a well known fact [9] that the orbital moment is enhanced between magnetic and non-magnetic interfaces and the investigated PS/metal hybrid system offers internal interfaces between the ferromagnetic Ni-nanostructures and the non-magnetic silicon skeleton. The saturating behavior of the nanocomposite system can not be understood in terms of spin-magnetism but only by taking into account the orbital moments associated to the spin-polarized states at the surface of the metal precipitations.
Figure 3: Orbital magnetism occurring at high magnetic fields (above the saturation magnetization of the metal) additionally to the spin-magnetism which occurs at low magnetic fields. Also a wide difference of about 50% between the two magnetization directions is observed.

4. Conclusion
The fabricated nanoscopic system exhibits simultaneously two kinds of magnetism. Additional to the ferromagnetic spin-magnetism dominant at low magnetic fields a paramagnetic-like behavior is observed above the saturation magnetization of the ferromagnetism of the specimens. The paramagnetic term shows a strong temperature dependency and the magnetization follows a Curie-Weiss law for temperatures greater than 50 K. The non-saturating characteristic of the magnetization curve even far above the saturation magnetization of the used metals exhibits also an anisotropy due to the magnetization direction perpendicular and parallel to the metal-loaded channels.

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