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## Silicon/metal hybrid system offering specific magnetic properties in two different field regions

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**Abstract :** A magnetic semiconductor/metal nanocomposite with a nanostructured silicon wafer as base material and electrochemically deposited metallic nanostructures (Ni, Co, NiCo) is fabricated in two steps. First the silicon template is etched in an HF-electrolyte to obtain a porous structure with oriented pores grown perpendicular to the surface. Second this matrix is used for metal deposition. 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  $M_S$ . The low-field behaviour which is due to the spin-magnetism of the ferromagnetic metal-structures depends on geometrical characteristics of the precipitates and can be tuned by the deposition process whereas the non-saturating term is independent of the geometry of the incorporated metal structures but is influenced by the kind of deposited metal. With increasing magnetic field the enhancement of this novel non-saturating term above  $M_S$  is nearly linear for both metals measured at temperatures above 80 K which opens the possibility to use this composite as magnetic high field sensor. The occurrence of this additional high-field contribution is not completely clarified yet. In the low field region where the ferromagnetic spin-magnetism is dominant the geometrical features and the spatial distribution of the precipitated metal-structures as well as the morphology of the PS-templates determine the magnetic characteristics of the nanocomposite. Accurate control of the process parameters enables low-cost fabrication of samples with tailored ferromagnetic properties compatible with today's microtechnology because of the silicon base material.

### Introduction :

Nanostructured and low dimensional materials play a decisive role in basic research and applications because of the drastic change of the physical properties compared to the bulk-materials. The fabrication of nanopatterned materials is widely spread in physics, chemistry and also in biology. A common technique to produce nanometric structures is lithography but also self-assembled and self-organized structures are of great interest due to the elementary fabrication processes. Quite often nanoparticles are grown on a substrate by self-assembly [1] and also 3-dimensional arrays of nanowires [2] or nanotubes have been produced without pre-structuring, whereas porous alumina templates, growing in a hexagonal arrangement are widely-used matrices [3]. Magnetic properties of metal filled membranes (e.g. porous

alumina, polycarbonate) are under extensive investigation [4, 5]. Magnetization reversal processes with the concomitant domain wall motions within the deposited metal-nanostructures, the interaction mechanisms between them [6], but also transport phenomena [7] like magnetoresistance in spin valves [8] are of great interest.

Porous silicon (PS) is already successfully fabricated and investigated by various groups since the beginning of the 1990s [9, 10, 11]. A very new research topic is concerned with magnetic functionalization of porous silicon after filling the channels with a ferromagnetic metal which is promising because of the semiconducting base-material which is applicable in today's microelectronics. Merging the electronic properties of a semiconductor with nanomagnetism of the embedded metal structures results in a hybrid system offering ferromagnetic properties at room temperature. The introduced system, a nanocomposite of metal particles/wires embedded in a silicon matrix, offers a quasi-regular pore arrangement obtained by self-assembly with metal precipitations quite homogeneously distributed over the entire porous layer. This novel composite material at the nanoscale exhibits new magnetic properties which are not only of great interest in basic research but the system is also a promising candidate for future applications.

### **Experiments :**

The nanocomposite material is fabricated in a two-step procedure. First the porous silicon matrix is formed by wet etching of a silicon wafer in aqueous hydrofluoric acid solution. Then the obtained porous silicon is dried in air. During this storage a native oxide layer covering the pore-walls is formed. Subsequently the PS-matrix is filled with a ferromagnetic metal during an electrochemical deposition process.

The PS/metal hybrid material is investigated magnetically by SQUID-magnetometry, whereas the magnetic field is applied perpendicular and parallel to the sample surface, respectively. A maximum field of  $\pm 7$  T can be reached and the temperature has been varied between 4.2 K and 360 K.

### **Results and discussion :**

Magnetization measurements are firstly performed dependent on the applied magnetic field. In doing so, two occurring characteristic field regions are of importance. A first one at low magnetic fields, below the saturation magnetization ( $M_S$ ) of the deposited metal and a second one at higher fields, above  $M_S$  are investigated in detail. At low magnetic fields the ferromagnetic properties of the semiconductor/metal hybrid system as coercivity, remanence and magnetic anisotropy depend on the geometry of the deposited metal nanostructures but also on their mutual arrangement within the pores. Due to the spatial distribution of the metal structures within the pores the magnetic interaction can be influenced. Between the pores dipolar coupling takes place, whereas exchange interaction can be excluded because of the pore-distances being greater than 10 nm. Figure 1 shows magnetization measurements in dependence on the geometry of the deposited metal structures.

Magnetization measurements performed at magnetic fields far above the saturation magnetization of the deposited metals show a non-saturating term which strongly depends on the temperature. But this additional non-saturating term does not depend on the shape of the metal precipitates. Figure 2 shows the dependence of the magnetization on the temperature. The magnetic moment measured at a certain field decreases with increasing temperature. The

characteristic can be fitted quite well by the Curie Weiss law which means that the magnetization at high fields seems to be a paramagnetic contribution.

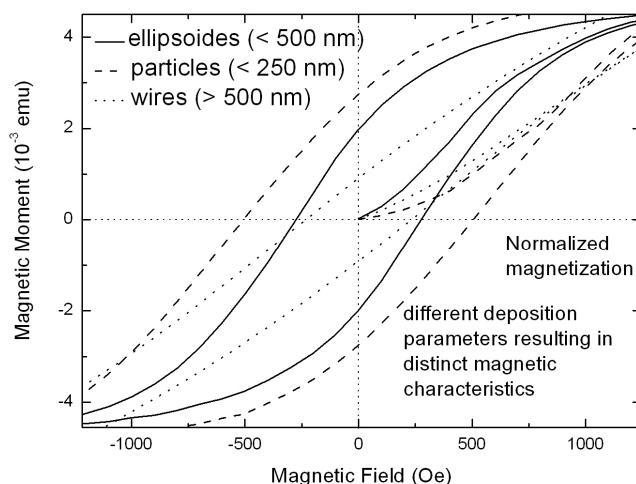


Figure 1: Hysteresis curves of PS/Ni-nanocomposites containing precipitates of varying geometry.

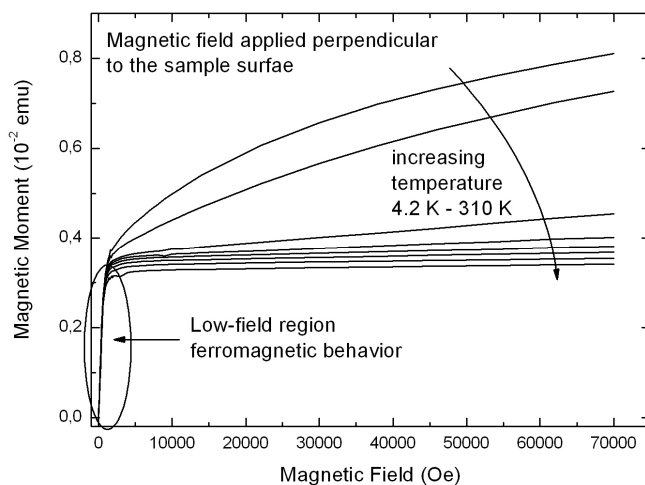


Figure 2: Magnetization in dependence on the magnetic field measured at different temperatures between 4.2 K and 310 K.

This non-saturating magnetization follows a nearly linear course measured at temperatures above 80 K (figure 3) and thus this behaviour is interesting for magnetic sensor technology. The linearity at room temperature renders this nanocomposite system a potential candidate for magnetic field sensors. Because of the silicon base material it could play a crucial role in integrated technology.

The interpretation of this non-saturating magnetic term at high fields is not completely clarified yet but also in literature peculiar magnetic behaviour caused by nanostructured materials has been observed. A new kind of magnetism is observed by some groups in generally diamagnetic materials as thiol capped gold-nanoparticles or thin gold layers [12]

caused by strong spin-orbit coupling due to a broken symmetry at the surface. 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 [13]. 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.

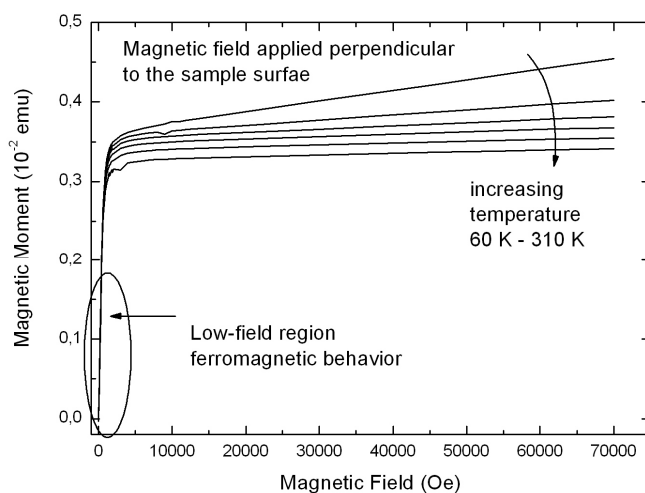


Figure (3) : Linear enhancement of the magnetization with increasing magnetic field for temperatures higher than 80 K.

### Conclusion :

The presented nanocomposite consists of a semiconductor base material with embedded magnetic nanostructures. Considering the magnetic behaviour of this system two distinct magnetic terms are observed. A first one caused by the ferromagnetism of the embedded metal and a second one at higher fields showing a non-saturating behaviour which could be observed up to 7 T (available magnetic field). Samples with desired ferromagnetic properties as magnetic anisotropy, remanence and coercivity can be fabricated due to the adjustability of the process parameters. 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 peculiar term at high magnetic fields is independent of the shape of the metal precipitates. This non-saturating term shows a temperature dependence following a paramagnetic decrease of the magnetization with increasing magnetic field. Because of the linear enhancement of the magnetization with increasing magnetic field for temperatures greater than 80 K the system offers high potential for high field magnetic field sensors.

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