Influence of a semiconducting matrix on the magnetic behaviour of iron oxide nanoparticles

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Abstract. To achieve a magnetic nanocomposite, iron oxide nanoparticles are prepared by high temperature decomposition of iron organic precursor and then they are infiltrated into oriented pores of a porous silicon (PS) matrix. The PS is fabricated by anodization of a n⁺ silicon wafer in aqueous HF solution. The magnetic behavior of this composite is determined by the morphology of the matrix as well as by the distribution of the particles within the individual pores. The composite offers FM/SPM switching due to dipolar coupling between the particles, whereas the transition temperature can be tuned in a broad range by the coating of the particles and the concentration of the particle solution. The anisotropy between two magnetization directions (magnetic field parallel and perpendicular to the pores) can be modified by varying the morphology of the PS matrix.

1. Introduction

The fabrication of nanostructured materials is important in many of today’s research areas not only because of the downscaling and miniaturization of devices but exceptionally also due to the modified and arising completely new physical properties compared to the bulk materials. Magnetic nanostructures such as nanowires, nanoparticles or nanodots are promising candidates for applications in magnetic data storage [1], electronic devices [2] as well as in biomedicine [3]. Often there is a high interest on metallic nanoparticles and their large magnetization but they are not stable in air and oxidize easily which leads to a loss of their magnetization [4]. Furthermore magnetic oxides, such as iron oxides are under extensive investigation, e.g. for magnetic recording [5], optical devices [6] and gas sensors [7]. They appear in various structures and hydration states and also their size and shape can be modified by the preparation conditions [8]. One of the most investigated iron oxides is Fe₃O₄
due to its inverse spinel structure, its ferromagnetic behaviour and its low toxicity which renders it a promising candidate for various biomedical applications as drug delivery or imaging. A hexane solution can be used to stabilize Fe3O4-particles and the treatment by oleic acid is widely spread [9]. In general quite monodisperse particles can be fabricated which is an important requirement because the physical properties strongly depend on the size. Particles in a size range between 5 nm and 20 nm are superparamagnetic but due to dipolar coupling a ferromagnetic behaviour can be observed. Furthermore the magnetic properties of magnetite particles are related with their surrounding, e.g. a non-magnetic material which is used as substrate or matrix. In this work magnetite nanoparticles of 5 and 8 nm in size are mixed with a hexane solution in the presence of oleic acid and infiltrated into a mesoporous silicon matrix to achieve a nanomaterial with specific magnetic properties which can be tuned by the morphology of the matrix as well as by the density distribution of the infiltrated particles.

2. Experiments

The formation of the porous silicon matrix is performed by anodization of an n⁺-silicon wafer in 10 wt% aqueous hydrofluoric acid solution [10]. All samples are produced under room temperature and the same electrolyte concentration and the pores exhibit a length of about 30 µm, grown in (100)-direction. The average pore-diameter of the investigated samples is 50 nm and 90 nm, respectively and the mean distance between the pores is in the range of 50 nm and 35 nm. In the fabricated diameter range the growth of side-pores in (111)-direction can not be suppressed completely but it is assured that the pores are separated from each other. The magnetite nanoparticles are produced by high temperature decomposition in the presence of an organic precursor following the procedure described in [11]. To prevent oxidation, the particles are mixed with hexane and oleic acid. The average size of the Fe3O4-particles is 5 nm (figure 1a) and 8 nm (figure 1b), respectively, whereas the size of the particles is varied by changing the organic solvent. An increase of the boiling temperature of the solvent results in an increase of the particle size.

![Figure 1](image_url)

**Figure 1**: Transmission electron microscopy images of magnetite nanoparticles covered with oleic acid a) particle-size 5 nm b) particle-size 8 nm.

A nanocomposite material is produced by infiltration of the Fe3O4-nanoparticles into the pores of the porous silicon matrix—and this procedure is carried out at room temperature for a time of about 30
minutes. To gain information about the nature of the particles infiltrated into the porous silicon matrix XRD-diffractograms were recorded by a Philips 1710 diffractometer using CuKα radiation. Evidence of the presence of iron oxide within the pores has been investigated by EDX-spectroscopy showing the distribution of the elements.

The magnetic behaviour of the fabricated nanocomposite has been investigated by SQUID-magnetometry in a temperature range between 4.2 K and 250 K whereas the transition between superparamagnetic and ferromagnetic behaviour has been figured out. Information about the anisotropy of the system has been elaborated by the magnetization versus magnetic field measured in two directions, namely with the external field applied normal and parallel to the sample surface.

3. Discussion

The utilized particle-sizes of 5 nm and 8 nm show a quite monodisperse distribution and XRD-diffractograms of the infiltrated particles correspond to an inverse spinel structure with a lattice parameter of 8.38 Å which correlates very well with the published magnetite pattern (JCPDS 19-629). The presence of the iron oxide particles inside the pores has been investigated by EDX-spectroscopy, whereas a line-scan at a cross-sectional region of the sample gives the intensities of the elements (Fe, O) along the pores which is shown in figure 2. One can see that the oxygen as well as the iron is slightly decreasing towards the pore-tips but nevertheless the pores are filled with magnetite till down to the tips.

![Figure 2: Line scan across a porous layer from the pore-tips to the pore-mouth (sample surface) filled with magnetite particles, showing the intensity of the various elements (carbon, oxide, iron and silicon).](image)

Individual particles could be resolved by scanning electron microscopy (SEM) along the whole pore-length, which verifies a more or less homogeneous filling of the entire porous layer (figure 3).

For the greater particles infiltrated into the matrix a size of about 8 nm has been identified which is in good agreement with the transmission electron microscopy (TEM) images of the pure magnetite particles (see figure 1a, b).

In the case of the smaller used particles the individual magnetite particles of 5 nm in size could not be resolved by SEM. TEM investigations of such porous silicon/magnetite samples is not an adequate method because the particles are adhered weakly to the pore-wall and thus they are released during the preparation of the sample by focused ion beam (FIB).
The magnetic behaviour of such nanocomposites consisting of porous silicon matrices with infiltrated magnetite particles of 8 nm in size and of 5 nm in size has been investigated by magnetization measurements performed in a broad temperature range between 4.2 K and 250 K. The temperature dependent magnetization gives information about the blocking temperature $T_B$ which indicates the transition between superparamagnetic and ferromagnetic behaviour. This transition can be influenced not only by the size [12] of the particles but also by changing their interaction in using different concentration of the Fe$_3$O$_4$ solution which is infiltrated into the pores. Magnetic field dependent measurements have been performed in two directions of magnetization, with an applied field perpendicular and parallel to the sample surface. The magnetic anisotropy varies with the morphology of the porous silicon template as well as with the particle size. Considering a matrix with an average pore-diameter of 90 nm and a mean distance between the pores of 35 nm the magnetization shows only a small anisotropy between the two magnetization directions. In the case of an average pore-diameter of 50 nm and a pore-distance of about 50 nm there is a clear anisotropy between easy axis (magnetic field along the pores) and hard axis (magnetic field normal to the pores) magnetization (table1).

| Particle-size (nm) | Pore-diameter (nm) | Pore-distance (nm) | $H_{C,II}$ (Oe) | $H_{C,\perp}$ (Oe) |
|-------------------|-------------------|-------------------|-----------------|--------------------|
| 8                 | 90                | 35                | 230             | 250                |
| 8                 | 50                | 50                | 275             | 370                |
| 5                 | 50                | 50                | 60              | 60                 |

This anisotropy is caused by dipolar coupling between the magnetite particles which arises differently in the two magnetization directions because the distance between the particles within individual pores is in minimum twice the thickness of the coating which is about 6 nm, whereas the minimum distance
between particles of adjacent pores is the thickness of the pore-walls which is in average 50 nm. Therefore the coupling between particles within the pores is stronger than between particles of neighbouring pores. In the case of larger pore-diameters and smaller pore-distances this behaviour becomes weaker which results in a diminished anisotropy of the magnetization between the two directions. Infiltration of magnetite nanoparticles of 5 nm in size shows an isotropic behaviour in both direction of magnetization. Furthermore the blocking temperature ($T_B$) which indicates the transition between superparamagnetic and ferromagnetic behaviour is around 10 K (figure 4). $T_B$ is significantly decreased compared to the one of specimens with infiltrated particles of 8 nm. In the latter case $T_B$ is around 135 K which indicated dipolar coupling between the particles. Both, the isotropic behaviour as well as the low blocking temperature reveals that the 5 nm particles are not interacting. The dipolar coupling of nanoparticles is strongly correlated to the size of the particles and decreases linearly with the size. The oleic acid coating is for both particle sizes around 3 nm, whereas in the case of the 5 nm particles this separation has a stronger influence due to a weaker dipolar coupling of the smaller particles.

![Figure 4: ZFC/FC measurements of 8 nm and 5 nm particles infiltrated within porous silicon. $T_B$ is shifted towards lower temperatures for smaller particles indicating less coupling between them.](image)

4. Conclusions

In this work the magnetic behaviour of porous silicon matrices with infiltrated Fe$_3$O$_4$-nanoparticles is presented. Magnetite particles of 5 nm and 8 nm in size which are quite monodisperse are incorporated into the oriented pores of a porous silicon matrix resulting in a composite material exhibiting magnetic anisotropy between applying a magnetic field parallel or perpendicular to the sample surface. The anisotropy depends on the structure of the porous silicon matrix (e.g. pore-diameter, pore-distance) and the dipolar coupling between the particles, respectively. In the case of densely packed particles within the pores the coupling is stronger within the pores than between adjacent pores resulting in various coercivities. The minimum distance between particles within one pore is determined by the thickness of the oleic acid coating whereas the distance between adjacent pores is assigned to the thickness of the pore-walls. If the relation between particle-size and distance between them becomes small enough by reducing the particle size (same coating) the interaction and the anisotropy, respectively is no longer observed.
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