A self-assembled nanoporous magnetic sensor*

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Abstract

Recently we have synthesized highly monodispersed nanoporous silica fibers with the pores running along the axis of symmetry of the fibers. Pore size is unusually uniform, and has size of ca. 3nm. Each fiber has a hexagonal cross-section of ca. 2 µm and the length of ca. 5 µm, i.e., contains hundreds of thousands parallel pores. Filling such pores with metal can create a unique system of nanowires. Each of nanowires is capable to detect magnetic field via the effect of magnetoresistance. We show that the parallel array of the wires can amplify the magnetoresistance up to 30 times due to cross-talking between the wires, because of the classical Hall effect. We estimate the effect for the case of a conductor which demonstrates quantum behavior of the conductance charge carries (dynamic scattering). The latter case is realistic even for room temperatures for such material as bismuth.

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1 Introduction

Importance of magnetic sensors in modern technology is hard to overestimate. Going to smaller and smaller scales can open new properties, which

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finally may result in higher signal/noise ratio for the sensors. Arrays of nanowires are a new type of nanostructures that exhibit quasi-1D characteristics. Such arrays have already exhibited a rich variety of novel properties, including localization of charge carries, perpendicular magnetic anisotropy, enhanced coercivity, and magneto-resistance compared with gigantic one (GMR). At the same time fabrication of templates for nanowires is a non-trivial problem. A creative combination of self-assembly and microfabrication may provide the way to future nanotechnology because of its inherent simplicity, high reliability and low cost of production. The liquid crystal templating of hexagonal, cubic and lamellar nanostructured silica of complex forms was reported [1-3]. It becomes possible to synthesize inorganics with highly uniform pores of a few nanometers and architectures over such large length scales, up to hundreds of microns. Synthesis of mesoporous thin films [4-9], spheres [10-12], curved shaped solids [13,14], tubes [15], rods and fibers [14-16], membranes [17], and other monoliths [18] has been reported recently. The fibers look to be the most interesting for the application described in the present work. Each fiber has parallel channels, pores running along the fibers [14-16]. Despite demonstrated success of this approach, there are two problems that have prevented broader use of the assembled porous shapes: 1. Self-assembly process brings too large variety of the assembled shapes, 2. The yield of the desired shapes is far from being the hundred percent. These factors make it difficult to extract, and subsequently, to use the desired shapes. Recently we have reported [19] a new synthesis of nanoporous silica fibers that is free of the aforementioned problems. We synthesized highly monodispersed nanoporous silica fibers, Fig. 1. Pore size is unusually uniform, and has size of ca. 3nm [19]. Each fiber has a hexagonal cross-section of ca. 2 µm and the length of ca. 5 µm. The reported synthesis showed surprisingly high yield (virtually 100%) of nanoporous fibers. In the present work, we will describe a possible magnetic sensor, which can be built based on these templates.

Unique properties of bismuth [20-24] make this material very attractive for manufacturing magnetic sensors. Bismuth has a rather low Fermi energy, the Fermi wavelength can be within 10-100 nm range (depending on the crystallographic direction) vs. a few angstroms for most metals. In combination with a long mean-free electron path of even in room temperatures, this set of properties attracts researchers to build magnetic sensors [25-33]. Nanowires of bismuth is of particular interest because the electron density is $\sim 10^5$ times smaller (liquid helium temperatures) than in typical metal, which results in a rather high resistivity, while having the long mean-free path. This enhances such resistance anomalies as localization effects [34].
Furthermore, as was predicted [35] and confirmed [23], bismuth nanowires have a very much enhanced thermoelectric figure of merit.

Advantage of having a parallel array created of magnetoresistant wires was noticed in [36]. Such an array of Ni$_80$Fe$_{20}$ ca. 700nm wires was manufactured by standard optical lithography. One of the first arrays of submicron bismuth wires was electrodeposited and studied in [31]. Positive magnetoresistance (MR) was demonstrated as high as 300% at low temperatures and 70% at room temperature, with a quasilinear field dependence. It is worthy noting that it is a highest MR in room temperature (compare with gigantic MR of ca. 50%; colossal MR is low in room temperature).

Figure 1: SEM image of self-assembled nanoporous silica fibers. The bar size is 3 µm.

In the present work, we suggest architecture as well as describe the manufacturing steps to build a magnetoresistive sensor based on a parallel array of bismuth nanowires embedded inside a self-assembled silica fiber. We first describe the proposed sensor architecture to create a magnetic sensor of high sensitivity. After that, we analyze feasibility of manufacturing such a sensor.
2 The sensor architecture

Each fiber described above has hundreds of thousands parallel pores. Filling such pores with metal will create a unique system of parallel nanowires, each within a nanometer from the other. Feasibility of filling pores of a few nanometers in diameter with metals has been already demonstrated in the literature, see, e.g., [31, 32]. Each of nanowires is capable to detect magnetic field via the effect of magnetoresistance. Therefore, each measurement is effectively equivalent to hundreds of thousands simultaneous measurements. This will increase decrease any stochastic, random noise, and therefore can increase the signal/noise ratio, i.e., increase sensitivity. Furthermore, the parallel array of the wires can amplify the magnetoresistance due to cross-talking between the wires. Let us show it. For the magnetic field less than some threshold, the electrons inside a nanowire move on trajectories that close to arcs of circumference, which is terminated on the wire interfaces. If the electron mean-free pass is larger than the length of such arc, the electron scatters mostly from the interface. This phenomenon called dynamic electron scattering is the major contributor to the magnetic resistance. The more magnetic field, the shorter the length of the arc, and consequently, the electrons collide with the interface more frequently. This leads to the increase of resistance, and therefore, called positive magnetic resistance. If the magnetic field exceeds some threshold, the electrons start moving along the helical trajectories, avoiding frequent collisions with the interface. This leads to the decrease of resistance, and consequently, called negative magnetic resistance. Because as was shown, bismuth wires demonstrate a high positive magnetic resistance, we will focus on the advantages of having parallel array of nanowires for the case of positive MR. Fig.2 shows a sensor based one fiber (SEM image on the left). The right part of Fig.2 demonstrates a “zoomed” scheme of nanowires running in parallel inside the fiber. Assuming that the pores are filled with metal, we can apply voltage between the opposite ends of the fiber, i.e., between all nanowires in the fiber. In presence of magnetic field, for example, perpendicular to the image plane as shown in Fig.2, the electrons will be deflected down. This will result in appearance of excessive negative charge of the bottom and positive on the top slide of each wire. This is well known classical Hall effect.

It should be noted here that the scheme sketched in Fig.2 is an approximation, presented to demonstrate the physics of the proposed nanowires geometry. As was shown [23,37,38], when bismuth has a sufficiently small dimension, it demonstrates semiconductor behavior. This implies that one should take into account additional hole conductivity. It was studied in de-
tail for bismuth films. As was shown in [23], measurements on 200-nm think films show a difference between electron and hole densities on the order of 3.8x10^{17} \text{cm}^{-3} that is at least 10% of the total concentration [37]. For thinner films the hole concentration gradually increases. When Bi film thickness was of the order of 20nm, the electron density was at least 5 times lower than the hole concentration even for the room temperatures. Because we consider bismuth wires of even smaller size, we will assume that bismuth wires of a few nanometers in diameter have one concentration of charge carrier, holes, considerably larger than the other, the electron one.

Presence of the excessive charges on the neighbor wires shown in Fig. 2 will also affect charges inside of each wire. As one can easily see in Fig. 2, the charges in each wire will be pushed towards the bottom not only by the magnetic field but also by the additional electric field, $\Delta E$. Here an important note should be done. The amount of charge carriers is very small in nanosize bismuth. Although, it is not a dielectric (conductivity of 7 nm wires was measured in [39]), it is not enough to create normal shielding as in the case of good conductors. Taking concentrations of holes for the case of 20-nm film [23] to be $\sim 5 \times 10^8 \text{cm}^{-3}$, and using this number for the case of 3nm Bi wire, one can see that the above concentration corresponds to an average distance between the nearest holes of the order of 7 nm. Obviously such rare charges can not provide the shielding of the electric field for nanosize wires. As was shown in [40], one can effectively estimate some decrease of the filed inside the nanowired bismuth by means of effective “dielectric” constant. The amount of electrical field penetrating inside the material is then $\Delta E/\varepsilon$, where $\varepsilon$ is such a “dielectric” constant of the material. For a nanosize bismuth this number is a relatively small, and was estimated in [40] as $\varepsilon \sim 4$.

The Hall equation for an charge $e$ balanced by the magnetic field $B$ and the Hall potential $U_{Hall}$ will be modified as follows:

$$\frac{U_{Hall}}{D_{wire}}e = F_{Hall} + e\Delta E,$$

(1)

where $D_{wire}$ is the nanowire diameter, $e$ is the electron charge, $F_{Hall}$ is the force that compensates the classical Hall potential $U_{Hall}$ (when $\Delta E=0$). Such a force depends on the applied magnetic field, charge carrier density, etc. (is equal to $eBv$ for a single carrier case, where $v$ is the carrier speed). Specific dependence of $F_{Hall}$ on those parameters is not important in this work.

To find exact value of $\Delta E$, one would need to take into account all wires around each wire, and find the electric field inside the composite structure
Figure 2: A diagram showing electron, magnetic field, electrodes, (right part of the image) and their position in a real fiber (SEM image, the left part of the diagram).

shown in Fig. 2. To demonstrate the effect, here we will just estimate $\Delta E$ due to the closest neighbors. As we obtain from low angle X-ray analysis [19], the average pore periodicity is ca. 3.8 nm. Average diameter of the pores was found by the gas absorption isotherms method (unpublished) to be 3.0 nm. Therefore, one can estimate the wall between the future bismuth wires as 0.8 nm, which is noticeably smaller than the wire diameter of 3.0 nm. We will assume that the Hall potential is created by two linear distributions of charges, along the top and bottom of each wire. These are denoted as “+” and “−” in Fig. 2.

Using the fact that the electrical field of a line of charges decreases reversely proportional to the distance, one can find the contribution, $\Delta E$ from two nearest wires as follows:

$$\Delta E = \frac{U_{Hall}}{D_{wire} + 4\Delta},$$

where $2\Delta$ is the thickness of the silica wall between the wires.

Taking into account this field, and using eq. (1), one can find a new value for the Hall potential, $U_{Hall}^{new}$. It is interesting to compare that value with the initial Hall potential, $U_{Hall}^{init}$. One can derive from Eq. 1 that

$$\frac{U_{Hall}}{U_{Hall}^{init}} = \frac{1}{1 - D_{wire}\Delta E/U_{Hall}} = 1 + \frac{D_{wire}}{4\Delta}.$$  

For the values of $D_{wire} = 3\text{ nm}$ and $2\Delta = 0.8\text{ nm}$ corresponding to the synthesized fibers, one can calculate that the Hall potential increases by a factor
ca. 3. Therefore, one can say that the effect of the magnetic field on each charge carrier increased by that factor of 3. As was shown in [31,33], positive MR depends approximately linear on the applied magnetic field. Because positive MR occurs due to the same deflection of electrons (and/or holes) by magnetic field as in the Hall effect, one can anticipate that the Hall effect should bring about 3 times increase in MR in the case of closely packed array of wires.

Let us see what effect it can result in for the case of bismuth nanowires. The smallest bismuth nanowire reported [39] has a diameter of 7 nm. The MR reported for such wires was \( \sim 3\% \) for temperature \( T=60^\circ K \) and \( \sim 15\% \) for \( T=1.39^\circ K \) (\( B=5T \)). Taking the value of amplification discussed above, one can get \( \sim 10\% \) and 50\% respectively.

Playing with conditions of the synthesis, it is unrealistic to get \( \Delta < 0.3-0.4 \text{nm} \) (close to a monolayer of silica). At the same time, it is possible to increase the pore diameter, and consequently, \( D_{wire} \) close to 10 nm by using different length of templating molecules [41]. Therefore, the maximum amplification of the proposed effect for the reported self-assembled fibers is unlikely to be higher than 30 times. This, however, would allow us attaining MR at the level of from \( \sim 100\% \) (up to 1400\% for lower temperatures), which is higher than the gigantic MR (GMR). Certainly, going to the bigger pore sizes seems to be advantageous according to eq. (3). We will study possibility of assembling the structures with such pores in the future.

3 The steps to manufacture the sensor

From engineering point of view, it is important to analyze feasibility of fabricating the sensor described above. There are three methods to deposit bismuth inside the pores, electroless, electrochemical, and plasma deposition. While electroless method could bring simplicity, it is not really well developed for bismuth. Therefore, we envision electrochemical or plasma deposition as the most prospective way to fill the pores. From industrial point of view, plasma deposition is less attractive due to its high cost. Below we consider the steps that are suitable for both plasma and electrochemical depositions.
The major problem in both methods is to place the fiber on the electrode or provide a stream of plasma through the pores, while the area around the fiber must be sealed. It looks unrealistically to make such a positioning for a single fiber. Instead of that way, we propose to utilize the following method. The fibers will be randomly mixed in electrically insulating matrix, for example, epoxy. After fast curing the epoxy, a thin film of epoxy together with the fibers inside will be cut using a microtome device. The obtained in this way film is shown in Fig. 3.

The layer of bismuth will be deposited on the resultant thin film, for example by plasma vapor deposition. Such a film can be directly used for electro-deposition of bismuth, which is known. Putting the electrode now on the other side of the film, Fig. 3, one obtains a film of sensors that can be directly used as a MR sensor. The film can further be cut into smaller pieces to get smaller sensors.

Therefore, we speculate that the suggested architecture is capable of mass production.

4 Conclusion

A possibility of creation of a parallel array of nanowires for magnetic sensing is described. Such array of the wires will amplify the magnetoresistance due to cross-talking between the wires via classical Hall effect. We estimated the effect for the case of a conductor which demonstrates ballistic behavior of the conductance charge carries (dynamic scattering). For an example of bismuth nanowires and already synthesized templates, the effect of amplification can be as high as \(\sim 10\%\) at high temperature (liquid nitrogen range), and 50\% at low temperatures (single units of Kelvin). Potentially, the MR based on the suggested architecture can reach 100\% at the high temperature and 1400\% at the low temperature. This is higher that gigantic MR (GMR).
effect, which is currently utilized in magnetic recording sensors. From fundamental point of view, creation of the nanowire array will bring more understanding of fundamental nanoscale magnetoresistance phenomena. Finally, it should be noted that the proposed sensor may have considerably improved signal to noise ratio (due to having hundreds of thousands parallel sensor wires), as well as faster response time (due to its nanosize). The latter two characteristics are equally important for building a good sensor.

References


