Magnetic nanoparticles in “amorphous ferromagnetic metal-insulator” nanogranular thin films

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Abstract

A lot of factors limit possible applications of magnetic nanoparticles in medicine for drug delivery and magnetic hyperthermia therefore it is of primary importance to understand influence of classical and quantum-size effects, surface layers, interparticle distance, shape of nanoparticles on their magnetic properties. Magnetic nanogranular thin films, known also as nanocomposites, can be considered as a convenient model for such investigations as it is possible to tune easily many of mentioned above parameters by varying of the fabrication conditions. The ion-beam sputtering technique has been developed to prepare “amorphous ferromagnetic metal-insulator” nanocomposites with different concentration and parameters simultaneously in one technological cycle. This feature is achieved by using of a composite target (consisting of a metal and dielectric parts) with an asymmetric arrangement of the dielectric parts on the metal base. Influence of sputtering conditions and post-fabrication treatment on structural, magnetic, electrical and magnetotransport properties of magnetic nanocomposites in a wide range of metal volume fraction and distance between magnetic nanoparticles is being discussed.

Keywords: Magnetic and electrical properties, nanocomposites, magnetoresistance

Introduction

In this century an investigation of physical phenomena in nanostructured materials are rapidly evolving. It is obvious that a new scientific direction has been formed and one of the objects is being considered is a heterogeneous media with inhomogeneous structure at a nanoscale. Devices of electronic engineering made of nanomaterials have several advantages: small size, low control voltage and operating currents, high response speed or switch. A special place among these systems is being occupied by magnetic nanostructures and magnetic nanoparticles. For such systems the manifestations of nonlinear properties in extremely small external fields, the changing of the phase...
transformation temperature, the manifestation of new mechanisms of electron transport (conductivity, thermopower, magnetoresistance, magnetic thermopower), the emergence of large magnetoelectric effect, giant Hall effect as well as manifestations of new physical phenomena, not observed in homogeneous bulk materials, are characteristic. On the other hand very promising application of magnetic nanoparticles is possible in medicine sphere for example for drug delivery and magnetic hyperthermia. Unfortunately, a lot of factors limit these applications therefore the understanding of mechanisms which govern the physical properties of the nanoparticles is really necessary. Magnetic nanogranular thin films can be considered as a very convenient model for investigations of the particle properties because it is possible to tune easily many of their parameters by varying of the fabrication conditions.

Using of the nanotechnology has allowed to expand opportunities of preparation of the solid-state structures with fundamentally new properties or significant expansion of existing performance range. In particular it allows changing the magnetic properties due to the controlled changes of material micro- and nanostructure by means of changing the chemical composition and topology arrangement of atoms or molecular clusters on the distance of a few nanometers. The physical basis of such effects and phenomena is a manifestation of quantum-dimensional laws and the dominant influence of the surface on the properties of nanoparticles and nanostructured materials. On the other hand, knowledge of these mechanisms will deliberately create nanostructures with new functional properties. The objective of the present work is the investigation of magnetic, electrical, magnetotransport properties of magnetic nanocomposites in a wide range of volume fraction of metal nanoparticles in nonmetallic media.

1. Preparation of metal-dielectric nanogranular composites

Preparation of nanocomposite structures is not a simple trivial task. The size of the metal granules must be at the level of several nanometers (3-6) and dielectric matrix must divide them by distances of 0.5-2 nm. A special equipment was designed and created for these purposes in the Voronezh State Technical University. The equipment makes it possible to obtain nanogranular structures in the form of thin films with practically any concentration of metal in dielectric matrix [Gridnev et. al (2012)].

In order to obtain metal-dielectric composite it is necessary to sputter the target consisting from corresponding materials (metal and dielectric) to the level of atoms and deposit these atoms on the substrate where the required nanostructure will be formed. The sputtering of the target material is accomplished with the aid of the ion sources which form the beam of high-energy ions directed by the anode electric field to the sputtered target (see Fig. 1). Two sources (4) serve for sputtering each target to obtain homogenous atomic flow. One additional source (5) serves for cleaning the substrates (2). Perimeter of the vacuum chamber is mounted by the holder support (7) which can rotate with a speed up to 2 rev/min. The special source of intensive electronic emission, so-called, compensator (6) is used to neutralize the positive potential, which appears on dielectric parts of the target of substrate.

![Fig. 1. The scheme of equipment (vacuum chamber, view from above) for ion-beam sputtering: (1) vacuum chamber; (2) substrate; (3) water-cooled target; (4) ion-beam sputtering source; (5) ionic etching source; (6) compensator; (7) rotating support holder for substrates.](image_url)
Nanocomposites are made by using of a composite target, which consists from several plates of quartz (SiO$_2$) or alumoxide (Al$_2$O$_3$) fixed on metal base surface. The distance between the dielectric plates is changing from 3 mm on one edge of the target to 24 mm on the other end (see Fig. 2).

3. Experiment

Electrical properties of the granular nanocomposites radically depend on the ratio of the metallic and dielectric phases in the material. There are two fundamentally different conduction regimes in composites defined by volumetric ratio of the dielectric and metallic phases and by the structure of the material: metal and non-metallic regime [Gridnev et. al (2012)]. Non-metallic conduction regime realizes when the volume fraction of the metallic phase in the composite is less than the percolation threshold. The structure of this material consists of the metallic nanogranules electrically isolated from each other by the dielectric interlayers. Non-metallic regime is characterized by high values of resistivity increasing by several orders with reduction of the metal concentration in the composite. The electrical resistance of the composites increases with temperature reduction and in the temperature range of 4.2 - 300 K the change is up to several orders.

Metallic conduction regime is realized when the volume fraction of the metallic phase exceeds the percolation threshold. In such a case sizes and number of the granules per unit volume increases so much that the metal clusters begin to form and therefore the conductive continuous metal channel (chains of mutually contacting with each other granules) penetrate the entire material and provide the metallic conductivity. On the other hand the dielectric areas exist between the channels. These areas increase the overall level of the electrical resistivity of the material but do not extremely affect on the conduction mechanism. In this regime the material behaves like a metal conductor although those properties which depend on the mean free path of electrons are significantly altered because of the strong scattering on grain boundaries. For example, the electrical conductivity of such composites is several times less than its usual values for the pure metals or metal alloys [Beloborodov et. al (2007)].

Investigations of the magnetic properties of a wide class of the nanocomposite materials has shown that the concentration of the phases and structure of ferromagnetic nanogrannular clusters formed during film growth process has a decisive influence on the formation of their parameters [Denisova et. al (2007), Ohnuma et. al (2000)]. Usually, transition metals Co, Fe, Ni or their alloys are used as a ferromagnetic phase in the composites. Oxides of Si, Al, Zr, Cr, Hf, etc., or fluorides such as MgF$_2$ are often used as the dielectric matrix. A number of publications have reported good high-frequency properties of such composites. If the metallic granule net is isotropic a good soft magnetic composite structure with high permeability in the RF and microwave frequency bands is formed when concentration of the metal phase is larger than the percolation threshold. If the granules form a columnar structure, the magnetization vector is orientated perpendicular to the film plane and the permeability has a low value. Prior to the percolation threshold the ferromagnet-insulator composites are in a superparamagnetic state.

Electron microscopic investigations of composite structures also revealed the existence of concentration fluctuations of metal granules in the sample volume and these areas are distributed like a fractal and have characteristic dimensions of a few tens of nanometers. In addition, if the dielectric or metallic granules are in a crystalline state, they create a group with close reflection position.

Magnetoresistance (MR) in usual conductors or magnetoresistive effect in ferromagnetic materials is an effect where electrical resistance of the material is changed under the action of external magnetic field. In common
materials (metals, metallic alloys, homogeneous semiconductors) the reason of the magnetoresistance is a Lorentz effect (the change of electron trajectories in the external magnetic field). For homogeneous conductors MR acquires a measurable value, when charge carriers move perpendicularly to magnetic field. The concept of "relative magnetoresistance" is

\[
\frac{\Delta R}{R_0} = \left[ \frac{R(H) - R(0)}{R(0)} \right] \cdot 100\% ,
\]

here \( R(H) \) is electrical resistance in fixed magnetic field; \( R(0) \) is electrical resistance in zero magnetic field. In metals and alloys relative magnetoresistance at room temperature is very small, being 0.01-0.1% in fields of the order of 10 kOe. As a rule, this magnetoresistance is positive, i.e., increase of magnetic field leads to the increase of electrical resistance.

In granular ferromagnetic - dielectric nanocomposites the action of magnetic field leads to completely opposite results. With increasing of the magnetic field strength the resistivity of the material decreases. Moreover, in contrast to homogeneous systems, decrease reaches several percents (up to 10-12%) in fields of ~10 kOe. Because of these great values the effect was called "Giant Magnetoresistance", however, recently the term "Tunnel Magnetoresistance" is frequently used because it reflects the physical mechanism of negative magnetoresistance.

Investigation of MR in many ferromagnetic - dielectric systems showed that at room temperature the concentration dependence of MR is identical for all such systems. When the metallic phase concentration increases the MR changes nonmonotonically, reaching the maximum value near the percolation threshold and decreasing to zero above the threshold (Fig. 3). Maximum of MR is caused by special topological features of composites near the percolation threshold – the lowest thickness of dielectric barrier, through which polarized electrons tunnel from one ferromagnetic granule to another ones. In the vicinity of the percolating threshold one can observe the abnormal positive magnetoresistance in the ferromagnetic - dielectric composites. The positive effect is due to complicated structure of the composites where clusters as well as separated granules simultaneously present in the material [Stognie et. al (2007)].

Characteristic feature of the concentration dependences of MR values (fig.3) is the relationship between the maximum value of magnetoresistance and the density of states at the Fermi level \( g(E_F) \). The maximum of the MR is higher in those composites, which have higher \( g(E_F) \) value. Similar correlation is also observed for the maximum values of magnetoresistance and saturation magnetostriction of the metallic phase as well as maximum values of the Kerr effect [Buravtsvo et. al (2003)]. When Kerr effect values as well as the saturation magnetostriction of the composite ferromagnetic phase increase according to the order: CoNbTa to CoFeB and further to CoFeZr the MR values of the composites also increases in the same sequence. The observed correlations between saturation magnetostriction of ferromagnetic phase and the maximum values of the magnetoresistance seem to be related with increasing contribution of d- electrons to the spin- dependent tunneling which follows to the
same sequence of nanocomposites: CoNbTa $\rightarrow$ CoFeB $\rightarrow$ CoFeZr.

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References