Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ Thin Films as Perspective Material for Spintronics

A.V. Trukhanov$^1$, S.V. Trukhanov$^1$, A.N. Vasiliev$^2$

$^1$Scientific–Practical Materials Research Centre, Belarusian Academy of Sciences, Minsk, Belarus
$^2$Low temperatures physics and superconductivity department, MSU named after M.V. Lomonosov, Moscow, Russia

Abstract—Thin films Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ were obtained on Si substrates by ion-beam sputtering of Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ ceramic target. The thickness of the films was 200 and 400 nm. Optimal conditions for the transfer of the target material were determined. It was found that the composition of the films was close to the target composition. Optimal conditions for film crystallization in phase with spinel structure were determined. The crystal structure and magnetic properties of the films with different thicknesses (200 and 400 nm) were investigated. The films annealed at 900°C are characterized by maximum values of specific magnetization. Magnetotransport properties of the films with thicknesses 200 nm were investigated. Found that the negative coefficient of magnetoresistance increases from 1.33% (at 220 K) till 5.53% (at 180 K) with decreasing temperature.

Keywords—Thin Films; Ferrite Spinel Oxide; Ion-Beam Sputtering; Magnetic and Magnetotransport Properties

I. INTRODUCTION

A large number of publications indicate intensive processes of production and investigation of oxide materials in film form [1-4]. The high intensity of these studies is caused not only by the necessity of fundamental scientific concepts in chemistry and solid state physics, but also important scientific and applied aspects of the use of oxide materials in the modern fields of science and technology, such as microelectronics, energy, etc.

Currently, oxide films are part of the technology of digital and analog integrated circuits, memory modules, sensors, etc., which allows you to implement the miniaturization of devices. Despite the impressive progress in the development of microelectronics technology, physical and chemical processes accompanying the formation and study of oxide films aren’t studied enough. Relevance of scientific and applied research is defined oxides applied problems. For example, one of the major problems is the integration of magnetism in microelectronics, which is the basis of semiconductor materials. Successful implementation of this idea would create a computer on a single semiconductor device with a microchip recording, storing and reading of magnetic materials [5].

One approach of solving this problem is - the search for single-phase material that combines the properties of the semiconductor (SC) and ferromagnetic (FM). The second approach is - the formation of a hybrid (multilayer) film structure of the "ferromagnetic semiconductor". There are a number of requirements: 1) the Curie temperature ferromagnetic material should be above the working temperature ranges of microelectronic devices (> 150°C); 2) compatibility with standard semiconductor technology (based on Si, Ge, GaAs and GaN). The first approach is hampered by a number of objective factors: low-temperature magnetic phase transition [6]; bad compatibility with standard semiconductor technology; often high rates of chemical degradation of the surface during the transition in the multiphase state. Although it should be noted that the study of the ferromagnetic semiconductor synthesis with a high Curie point is very active carried out [7, 8]. The advantage of second approach is the possibility of an independent choice of the large number of ferromagnetic materials and standard microelectronic substrates. Film is two-dimensional object, and as a rule, the physical properties differ from the bulk analog, and are caused by the properties of the interface. Thus, if the interface is "ideal" (no impurity phases, defect-free) the quality of the hybrid structure will be better. Ferrites with the spinel structure - a unique class of materials, combining a wide variety of magnetic and electrical properties. It was shown earlier, it is advisable to use as a magnetically media materials in which the relaxation time of the magnetic moment (the magnetic moment of the return time to equilibrium) must be greater than the rotation of the magnetic moment vector at 180 degrees. The relaxation time in conventional metallic ferromagnets is small (about 1 ns [9]). For this purpose, suitable many compound oxides systems (for nickel ferrites relaxation time is about 100 ns [10]). Spinel ferrites are characterized by magnetoresistance effects and can be used as functional layers with controlled properties (spin filters and magnetic tunnel junctions, etc.) on semiconductor substrates. The problem of obtaining films of spinel ferrites on semiconductor substrates is relevant, since the solution involves a combination of two approaches: 1) search for single-phase magnetic semiconductor with controlled magnetic and electrical properties; 2) formation of a given composition of the magnetic film on semiconductor substrates. The study of dependencies changes the crystal structure and magnetic properties of spinel ferrite films on thickness and heat treatment of the films will make a significant contribution to the understanding of the nature of magnetic phenomena occurring in these compounds. It is known that the diamagnetic substitution in ferrites with spinel structure may induce changes in their magnetic structure. This can manifest itself in the form...
of deviation from strict collinearity of vectors in the directions of the magnetic moments - sperrimagnetizm (as in the case of Yafet-Kittel ferrites type) [11], as well as the formation of a frustrated magnetic structure [12]. The above factors lead to changes in magnetic properties and explain the nature of the magnetoresistance. Previously, it was found that the optimal composition for the preparation of thin films in the range of solid solutions of Mg(Fe$_{1-x}$Ga$_x$)$_2$O$_{4+δ}$ is the composition of 20% substitution by gallium ions [13, 14]. Exactly this compound Mg(Fe$_{0.8}$Ga$_{0.2}$)O$_{4+δ}$ is characterized by maximum values of conductivity ($\sim 10^{-9}$ S/m) and the specific magnetization ($\sim 28$ A*m$^2$*kg$^{-1}$) [13, 14]. The maximum values of the magnetization is indirect evidence of the maximum coefficient of spin polarization in the range Mg(Fe$_{1-x}$Ga$_x$)$_2$O$_{4+δ}$ of solid solutions.

II. EXPERIMENTAL

For obtaining films Mg(Fe$_{1-x}$Ga$_x$)$_2$O$_{4+δ}$ Ceramic target was used [15]. Films were grown by ion-beam sputtering (apparatus A 700Q by "Leybold-Heraeus GmbH"). The target was sputtered for 1.5 h in an oxygen atmosphere onto (100) single-crystal KBE silicon wafers 76 mm in diameter, maintained at 400 K. Angle of target slope concerning ion source was in the interval from 45° till 60°. Angle of slope between target and substrate surfaces was not exceeding 20°. Average speed of deposition of target material was $\sim$ 135 nm/h. The crystal structure was investigated on the complex Dron-3M diffractometer in CuKα-radiation and the range of angles 10°<2θ<40 deg. (at room temperature). X-ray diffraction analysis of the data was carried out using the program PowderCell. Phases were identified with the use of the JCPDS PDF2 database. The thickness of the films was evaluated according to the data of scanning electron microscopy - a cross-section (Focused Ion Beam, Helios NanoLab).

Auger analysis (Scanning Auger Multiprobe PHI – 660 ‘Perkin Elmer’) was used as to estimate the distribution of elements through the thickness of the film thickness and detection of the transition layer at the interface film-substrate interface. Magnetic properties (field dependences of magnetization were measured at 4.2 and 300 K) were carried out by Liquid Helium Free High Field Measurement System (vibration magnetometry). Temperature dependence of resistivity was investigated in the 180-300 K temperature range (and in presence magnetic field 14 T). Energy of activation was calculated using the expression:

$$E_{ac} = 2K_B \frac{\partial(\ln \rho)}{\partial(1/T)}$$

Where $\rho$ - resistivity; $E_{ac}$ - Energy of activation; $K_B$ - Boltzmann’s const, T – temperature.

Coefficient of negative magnetoresistive effect was calculated using the relation:

$$M_s = \frac{R_0 - R_1}{R_0} \cdot 100\%$$

Where $R_0$ – value of resistivity in magnetic field (14 T), $R_0$ – value of resistivity without magnetic field (Liquid Helium Free High Field Measurement System).

III. RESULTS AND DISCUSSION

A. Chemical Composition

As a result of ion-beam sputtering of ceramic target Mg(Fe$_{1-x}$Ga$_x$)$_2$O$_{4+δ}$ controlled film structures on silicon have been formed, where the film thickness was $\sim$ 200 and $\sim$ 400 nm (Fig. 1). The combined analysis of the results suggests that the formation on the surface of silicon products sputtering occurs in the form of agglomerates of MgO, GaOx, FeOx. This is the optimum condition for the formation of inhomogeneous structures on silicon in the form of a film with a composition close to stoichiometric composition of the target. It was noted [16], resulting in the transfer of products of the conformal sputtering on the substrate is not formed spinel-type structure. The method of layer-Auger spectroscopy has been established a uniform distribution of cations through the thickness of the films (Figs. 2-3). All samples with thickness $\sim$ 200 nm, are anion-deficient (deviation is about 7% of the calculated atomic concentration), as well as characterized by a uniform distribution of cations across the film thickness with a deviation from the desired cation stoichiometry of less than 5% (Fig. 2). This deviation from the cation stoichiometry (across the film thickness) hadn’t significant effect on the magnetic properties of the films. In this case the deviation in the cation stoichiometry (formation of vacancies) should increase the electrical conductivity. Significant deviation from cation stoichiometry on the film-substrate interface and increasing of the film-substrate interface thickness up to 60-100 nm (Fig. 2c) was detected in the sample annealed at 1000°C. This fact is due to chemical reactions of the material of the film and the silicon. Uniquely identifying the impurity phases according to Auger analysis is not possible. However, given the X-ray diffraction data from previous studies [16], we can assume that the silicate cations included in the film and the silicon oxide. The thickness of the transition layer for the film annealed at a temperature of 900°C was 30-40 nm. Minimum thickness of transition layer was sample annealed at 800°C. This confirms the assumption that the thickness of the transition layer and the formation of impurity phases, depends on two factors: 1). contribution from the target atoms, which penetrates a certain depth into the substrate during the ion-beam sputtering deposition and 2). contribution due to heat treatment of the film. The last factor is crucial. With increasing annealing temperature the thickness of the transition layer increases due to mutual diffusion of the ions of the film and the silicon atoms, which leads to the formation of impurity phases in the film-substrate interface.
Fig. 1 SEM images (cross section) of Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ films
   a – film thickness 200 nm; b - film thickness 400 nm

Fig. 2 Auger spectra of Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ films (films thickness ~200 nm)
a- Temperature of annealing is 800°C; b- Temperature of annealing is 900°C; c- Temperature of annealing is 1000°C
In the film (thickness ~ 400 nm) stoichiometric ratio over the entire thickness of the film was close to the composition of ceramic target (Fig. 3). Deviation from cation stoichiometry was not more than 5% of a given concentration. It was recorded a negative deviation from the oxygen stoichiometry (as in case with the samples of thickness ~ 200 nm). This fact can be explained in terms of processes of the features. Preparation of the films was carried out at low pressure of oxygen. The transfer of the material was not carried out in atomic, and in the form of agglomerates of oxides of non-stoichiometric composition. The most significant deviation from the cation stoichiometry was observed in the film-substrate interface.

We should note that the parameters of the deviations from oxygen stoichiometry ($\delta$) in films with different thickness were very close. Auger spectroscopy data show that the $\delta$ varies as a function of film thickness. The maximum deviation from the desired concentration in both cases (200 and 400 nm) was observed at the interface film-substrate. The minimum deviation was marked in both cases on the film surface. Definitely appreciate the value $\delta$ in films wasn’t possible (because it varies with the thickness). Therefore, based on Auger spectroscopy data, we calculated the average values $\delta$. The values $\delta$ for the films 200 and 400 nm were very close and didn’t exceed 5-7% of a given atomic concentration.

B. Crystal Structure and Microstructure

It was shown [16] that the optimal conditions for the formation of phases with the spinel structure in the films of this system are annealed in air at 900°C for 30 min. This allowed crystallizing the film material on the silicon substrates. In the diffraction patterns Figs. 4-5 clearly show two structural peaks (in 30.4 and 35.9 deg.), which are typical for the structure of the ceramic target. These peaks correspond to reflections from atomic planes (220) and (331) respectively. It should be noted that the diffraction peak of the impurity phase (polymorph of silica) is present - around 20 deg. Fig. 5 shows the X-ray diffraction of film Mg(Fe$_{0.8}$Ga$_{0.2}$O)$_4$ with thickness of ~ 400 nm. The average crystallite size calculated by Scherer formula was 50-80 nm (for films ~200 nm) and 120 nm (for films ~400 nm). After total X-ray diffraction analysis of the data we can conclude that increasing in film thickness leads to improved crystallinity of the structure with increasing size of the crystallites with respect to the films with smaller thickness. Improving the quality of the crystal structure is in the form of increasing in the ratio “signal to noise”. The films are characterized by the cubic symmetry of the unit cell of the type of space group $Fd\bar{3}m$. Unit cell parameters of the films are close in magnitude to the values of the lattice parameters of ceramic target Mg(Fe$_{0.8}$Ga$_{0.2}$O)$_4$ ($a = 0.838$ nm). The unit cell parameters for film with thickness 200 nm was $a = 0.834$ nm, and for films with thickness 400 nm was $a = 0.835$ nm. The negative deviation in the values of the parameters of the unit cell can be explained by two factors: 1). negative deviation from oxygen stoichiometry; 2). structural stress of the crystal lattice of the film at the film-substrate interface due to the significant mismatch of crystallographic parameters.

DOI: 10.5963/JBAP0202007
Fig. 4 X-ray diffraction pattern of Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ film (film thickness ~200 nm)
Temperature of annealing is 900°C
Black line – experimental data, red line – theoretically calculated data, green line - differences

Fig. 5 X-ray diffraction pattern of Mg(Fe$_{0.8}$Ga$_{0.2}$)$_2$O$_{4-\delta}$ film (film thickness ~400 nm)
Temperature of annealing is 900°C
Black line – experimental data, red line – theoretically calculated data, green line - differences

Fig. 6 shows images (obtained by scanning electron microscopy) of the surface film samples. The average crystallite size in films with a thickness of ~200 nm is 50-90 nm (Fig. 6a). The average crystallite size in films with a thickness of ~400 nm is
100-150 nm. These data agree well with values calculated from the data of X-ray diffraction. The increase in crystallite size at a relatively low intensity of chemical interaction between film and substrate material during annealing should lead to increased exchange interactions. This should lead to an increase in the values of specific magnetization of the film samples with increasing thickness.

Fig. 6 SEM images of film surface
Temperature of annealing is 900°C
(a- film thickness ~200 nm, b- film thickness ~400 nm)

C. Magnetic Properties

Results of measurements of the field dependences of the specific magnetization of film with thickness ~200 nm are shown in Fig. 7. Films which were annealed at 800°C are characterized by a weak magnetic signal and a minimum values of specific magnetization (M = 1.4 A*m^2*kg^-1 at 4.2 K and 0.7 A*m^2*kg^-1 at 300 K). Magnetization curves do not go into saturation even when the external magnetic field up to 3 Tesla. The coercive force (H_c) of the sample is about 40 Oe. Small values of the magnetization can be explained by the unformed of crystal structure. What can be expressed in the unformed-range magnetic order [18]. The behavior of the sample in an external magnetic field is described by a model of superparamagnetic. With increasing annealing temperature values of coercive force and the specific magnetization of the films increased. After annealing process at 900°C coercive force was ~ 210 Oe and M~ 6.8 A*m^2*kg^-1 at 4.2 K and ~ 4.5 A*m^2*kg^-1 at 300 K. Magnetization curve of the film annealed at 1000°C at room temperature does not go into saturation in fields up to 3 Tesla. At low temperatures the magnetization curve goes into saturation at low magnetic fields. After annealing at 900°C magnetization was ~ 2.8 A*m^2*kg^-1 at 4.2 K and ~ 1.8 A*m^2*kg^-1 at 300 K. The coercive force is increased by 5 times (H_c ~ 1050 Oe). These facts may indicate an inhomogeneous ferrimagnetic state. This may be due to the increasing degree of inhomogeneity of the distribution of cations and the formation of phases at the external interface of the film-substrate interface during heat treatment of the films. The value of the specific magnetization of the film sample (annealing temperature is 900°C) at room temperature is ~ 16% of the value of ceramic sample magnetization. Results of measurements of the field dependences of the specific magnetization of film with thickness ~400 nm (annealing temperature is 900°C) are shown in Fig. 8. Assumption that values of specific magnetization increases with increasing film thickness is confirmed by vibration magnetometry. The value of the specific magnetization of the film sample (thickness ~400 nm, annealing temperature is 900°C) at room temperature is ~ 52% of the value of ceramic sample magnetization. Film magnetization was ~ 17.7 A*m^2*kg^-1 at 4.2 K and ~ 14.6 A*m^2*kg^-1 at 300 K (after film annealing at 900°C). Magnetization curve as in the case of the ceramic target has a rectangular shape and goes into saturation already at low values of external magnetic fields (~ 0.3 T). The increase in the film thickness leads to decreasing the crystallinity parameters (crystallite size increases). The increase in values of the magnetization with increasing film thickness is the result of two factors: 1). decline in the proportion of thickness of the transition layer at the interface film-substrate relative to the total film thickness; 2). strengthening of long-range exchange interactions (due to the increase in crystallite size) [19].
Fig. 7 Field dependences of film magnetization (film thickness ~200 nm)
a- Temperature of annealing is 800°C, b- Temperature of annealing is 900°C, c- Temperature of annealing is 1000°C

Fig. 8 Field dependences of film magnetization (film thickness ~400 nm)
Temperature of annealing is 900°C
D. Magnetotransport Properties

Due to the high resistivity of the sample (at 300 K ~50 MΩ·cm) and the limitation of current source of the measuring system, resistivity was measured in the temperature range 300-180 K. Fig. 9 shows temperature dependence of resistivity of Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} film (thickness ~200 nm) which was annealed at 900°C. For linearization of resistivity exponential dependence we build the logarithm of resistivity in T^{-1} coordinates. As seen from Fig. 9 film was characterized by semiconducting type of conductivity. It was found that the resistivity increases (approximately on the 2 order of magnitude at temperature interval 300-180 K). Film resistivity increases from ~50 MΩ·cm (at room temperature) till ~3.1 GΩ·cm (at 200 K). It was determined that in this compound predominate impurity type of semiconducting conductivity. Energy of activation is 0.62 eV. This value is greatly differentiated from bulk sample energy of activation (0.89 eV). It can be explained by different nature of impurity in bulk and film materials. For example diffusion of Si atoms from substrate to film during annealing processes.

![Graph showing logarithm of resistivity vs. inverse temperature](image)

**Fig. 9** Logarithm of resistivity of Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} film (film thickness ~200 nm) annealed at 900°C (in T-1 coordinates)

- black dots – resistivity without magnetic field
- white dots - resistivity in magnetic field (14 T)

Behavior of Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} magnetoresistance (MR) in the presence of 14 T field and at different temperatures was investigated too. In our case we have intergranular contribution in MR (as in case of bulk sample) in Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} films. This contribution depends on spin-polarized carrier scattering on magnetic heterogeneity of granular boundary. This is due to multidirectional of crystallites magnetization vectors. For this sample 5.53% negative MR is observed at 180 K in the presence of 14 T field. Then MR coefficient is monotonic decreases with temperature increasing. At 200 K MR is 2.07% and at 220 K – 1.33%. Magnetoresistance effect wasn’t detected at temperatures higher 250 K. It can be explained by worsening of film crystalline parameters (decreasing of crystalline boundary quality). The nature of magnetoresistance effect in Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} can be explained by decreasing of spin polarization coefficient of magnetic heterogeneity local spins in granular boundary.

IV. CONCLUSIONS

We obtained Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} films (thickness ~200 and ~400 nm) on Si substrates by ion-beam sputtering of ceramic target Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ}. Film forming was made with significant mismatch crystallographic parameters of the substrate and film. The composition of the film is close to the composition of the ceramic target. It was shown that all the samples of the films are anion-deficient (deviation from the desired stoichiometry was no more than 5%). This fact can be explained by two factors: 1) process of obtaining the films was carried out at low pressure of oxygen; and 2) the transfer of the material was not carried out in atomic, and in the form of agglomerates of oxides of non-stoichiometric composition. Observed that single-phase Mg(Fe_{0.8}Ga_{0.2})_2O_{4-δ} films on Si substrates with highest values of magnetization were received by annealing film samples at
900°C (30 min.). Increasing the synthesis temperature leads to an increase in the formation of impurity phases silicides and silicates. As the film thickness increases the size of the crystallites and values of magnetization. The value of the specific magnetization of the film sample (annealing temperature is 900°C) at room temperature is ~ 16% (thickness ~ 200 nm) and 52% (thickness ~ 400 nm) of the value of ceramic sample magnetization. Difference between bulk sample and film magnetization can be explained by impurity phases at film-substrate interface and negative deviation from stoichiometric oxygen concentration. Last factor is limiting because of decreasing oxygen content is account for decreasing of exchange interaction parameter. The nature of negative MR in Mg(Fe_{0.8}Ga_{0.2})_2O_4 is caused by increasing spin polarization of local spins in the magnetic heterogeneity of granular boundary.

ACKNOWLEDGMENT

Work was supported by World Federation of Scientists (WFS Belarus National Scholarship Program) and by Russian foundation for basic research (Project 12-02-90904-mob_sng_st).

REFERENCES