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STRUCTURAL INHOMOGENEITY OF A GARNET'S THIN FILMS

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The results of study of yttrium – iron garnet (YIG) thin films structure after ion-beam deposition on gadolinium gallium garnet substrate are presented. According to the data of Rutherford backscattering spectrometry of the gadolinium gallium garnet substrate structure and films layer-by-layer analysis leads us to the conclusion about variable elemental composition of substrate and YIG films. The amorphous paramagnetic films of YIG are formed on substrate surface. The iron and yttrium content is increased on the depth of films.
KEY WORDS: iron-yttrium garnet, thin films, element and phase composition, amorphization, crystallization, magnetically phase.

СТРУКТУРНЫЕ НЕОДНОРОДНОСТИ ТОНКИХ ПЛЕНОК ГРАНАТА
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Представлены результаты исследования процессов формирования пленок железо-иттриевого граната (ЖИГ) методами ионно-лучевого распыления на подложках галлий - гадолиниевого граната. Послойный анализ пленок по данным спектрометрии резерфордовского обратного рассеяния приводит к выводу о переменном элементном составе подложки и пленок ЖИГ. На поверхности подложки образуются аморфные парамагнитные пленки ЖИГ. Содержание железа и иттрия увеличивается по глубине пленок.
КЛЮЧЕВЫЕ СЛОВА: железо-иттриевый гранат, тонкие пленки, элементный и фазовый состав, аморфизация, кристаллизация, магнитоупорядоченная фаза.

СТРУКТУРНА НЕОДНОРІДНІСТЬ ТОНКИХ ПЛІВОК ГРАНАТУ
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Представлені результати дослідження процесів формування плівок залізо - ітрієвого граната (ЗІГ) методами іонно-променевого розпилення на підкладках галлій-гадолінієвого граната. Пошаровий аналіз плівок за даними спектрометрії резерфордовського зворотного розсіяння приводить до виводу про змінний елементний склад підкладки і плівок ЗІГ. На поверхні підкладки утворюються аморфні парамагнітні плівки ЗІГ. Вміст заліза і іттрію збільшується по глубені плівок.
КЛЮЧОВІ СЛОВА: залізо-іттрієвий гранат, тонкі плівки, елементний і фазовий склад, аморфізація, кристалізація, магнітовпорядкована фаза.

During the process of formation of magneto optic layers of yttrium iron garnet (YIG) on gadolinium gallium garnet (GGG) substrate the role of transition layer between the substrate and the film layer increases when film thickness decreases up to 1 μm and less. Transition layer thickness should be rather small in comparison with film thickness. Micro defects of GGG substrate near-surface layer worsen the properties of film layers. For example, on the surface of GGG in the process of epitaxial growth of yttrium iron garnet (YIG) film dendrite crystallites appear which then penetrate into the film [1]. Single-crystal garnet ferrites (GF) are used as materials in the devices at cylindrical magnetic domains [1-3]. Nowadays ion-beam implanted GF films on gallium-gadolinium garnet (GGG) substrates are used to create devices with high data density. Garnet ferrites $Y_3Fe_5O_{12}$ [$Y_3Fe_2(FeO_4)_3$] structure consists of FeO_4 tetrahedrons and FeO_6 octahedrons with YO_8 polyhedrons in their cavities. The degree of GGG films perfection is determined by the way of their obtaining, by the purity of source materials and the degree of crystalline perfection of single-crystal GGG plates [4]. Ion-beam approach is widely used for yttrium – iron garnet (YIG) thin films obtaining [5]. Films formation with the aid of high-energy particles (their energy is tree-four orders greater than that one of particles taking part in thermal deposition processes) allows growing single-crystal ferrite films of nanosize structures with small transition layers, with widened boundaries of cation replacement in garnet composition and with widened boundaries of lattice parameters discrepancy of substrate and film.

Ion beam implantation (IBI) is one of the efficient processing methods of epitaxial garnet ferrite films [6]. This approach is a universal method for conversion of domain boundaries structure of cylindrical magnetic domains (CMD) and for suppression of rough CMD. Ion beam implantation efficiency is defined by the value of magnetic anisotropy change $\Delta K_и$ in the garnet ferrite film [7] due to the appearance of sufficient concentration of radioactive damages causing compressive stress action. Magnetostriction mechanism initiated by compressive stress action is responsible for the anisotropy energy change under IBI. Complex correlation between magnetic anisotropy change and IBI structure of the layer isn't completely studied. In [8] there was experimentally determined the correlation between the change of struc-

ture and magnetic properties of $(EuSmLuCa)_3(FeGe)_5O_{12}$ garnet ferrite surface layer exposed to IBI. Using X-ray double-crystal diffractometry and conversion electrons Mossbauer spectroscopy (CEMS) it was shown that dose $D = 6 \cdot 10^{13}$ cm^{-2} is the optimal one with Ne ions with energy E = 350 кeV. However the ion-implanted layer obtained under these conditions has rather insufficient stability of obtained magnetic properties and damages input while implantation [9].

In general to obtain YIG films with required performance attributes it's necessary to find the efficient combination of film deposition methods and to obtain data about elemental composition, structure-phase and magnetic states at different stages of magnetic structure formation.

When forming films by means of such methods as ion-beam, laser, and magnetron sputtering of spread material target, films can be amorphous and high temperature annealing is needed for their crystallization. At that in amorphous film as well as in substrate amorphous layer the occurrence of diffusion processes is inevitable which in turn can lead to transition layer thickness increase or to sufficient inhomogeneity of film's chemical and phase composition.

This work was aimed at study of structure and phase composition of surface layer of YIG on GGG substrates with different structural perfection. The aim of this work was to study structural-phase state, elemental and phase composition of thin film structures by means of nuclear physics methods of analysis and control. In particular, there were studied yttrium-iron garnet nanofilms after they were synthesized using ion beam deposition with the following thermal annealing and ion beam implantation.

THE EXPERIMENTAL STUDY TECHNIQUE

YIG films were deposited on GGG substrate with (111) orientation during ion-beam sputtering (IBS) of the corresponding target enriched with ^{57}Fe isotope up to 25%. IBS approach was performed through formation of argon ions beam with current density up to 10 mA/cm^2 and energy about 1-3 keV in vacuum chamber and the beam was directed on the target made of material being sputtered.

There were used GGG substrates in form of monocrystal plates obtained by means of blank diamond cutting with (111) orientation. Chemical composition of GGG plate volume was determined by means of neutron activation analysis using NG-150M neutron generator. Structural perfection of GGG substrates surface layer has been studied using double-crystal spectrometer according to Berg-Barrett method as well as by means of X-ray analysis. Before depositing YIG film on GGG plates the substrates were exposed to ion- thermal processing that consisted of substrate irradiation with oxygen ions.

There were used several modes of film deposition and ion-thermal processing of the substrate O^{2+}; E=0.3keV; T=570K; 30 min. The first mode was in depositing film on the substrate right after ITP. During the second one after ITP the stuttering was performed for 30 minutes and only after that film was deposited on GGG substrate. In the third mode we used the ion source with cold cathode for sputtering. In the 4-th mode of deposition there was also ion source with cold cathode and target sputtering was performed in higher vacuum. Ions H^+ were implanted with energy E=1.5 MeV and fluence 10^{17}cm^{-2}.

Elemental analysis of GG films near-surface layers was performed using Rutherford backscattering spectrometry (RBS). There were used proton bunches with energy (E=1 MeV) or α - particles (E=2.2 MeV) accelerated by means of Van de Graaff generator. Spectrometer energy resolution isn't less than 20 KeV. The depth of the layer being analyzed was about 3 μm.

Phase composition of thin films surface layers was defined by means of Mössbauer spectroscopy on ^{57}Fe nuclei in backscattering geometry with registration of internal conversion electrons. The target was enriched with ^{57}Fe on 25%. Registration efficiency was close to 100%. Depth of layer analyzed with CEMS was about 0.3 μm.

RESULTS AND DISCUSSION

According to the data obtained by means of Berg-Barrett approach for GGG substrates with different structural perfection, values of their rocking curve width vary, and they're correspondingly equal to 5′ and 1′. In the first case this corresponds to the presence of blocks 5-10 mm in size and to their misalignment about 2-3′ . In the second case blocks don't show up that indicates higher structural perfection of GGG substrates. Ion-thermal GGG surface treatment with argon ions under the temperature equal to 573K during 30 min hasn't led to amorphous stage elimination. Open air annealing under the temperature equal to 1070K during 1 hour has led to amorphous stage elimination. There is a correlation between amorphous content in the layer with change of stoichiometric content (Gd:Ga:O=0.15:0.25:0.60). Elemental composition of near-surface layer with depth up to 500 Å changes along the depth (Gd:Ga:O=0.20:0.32:0.48) and depends on GGG substrate treatment method (Fig. 1).

Ion-thermal treatment and annealing have lead to the sufficient decrease of gadolinium concentration. Besides according to RBS data in initial state oxygen content is reduced up to (47±10)% in comparison with stoichiometric one (60%). Also gallium content as well as gadolinium content is raised (35±5)% and (19±5)% in comparison with stoichiometric values 25% and 15%, oxygen content is up to (67±10)% with small increase (24±5)%, and, as it was said earlier, gadolinium content deceased up to (9±5)%. Substrate annealing during amorphous stage elimination leads to oxygen content increase up to (76±10)% and to sufficient decrease of gallium (16±5)% and gadolinium (7±5)% content on the surface.

In Fig.2 there are given RBS spectrum of YIG film on GGG substrate. The analysis of RBS spectra leads to the inhomogeneous distributions of Y and Fe on depth of YIG film (Fig. 3). Our attention was turned by the difference in Fe and other YIG components content in the initial state of garnet ferrite films just after obtaining. Maybe it's connected with penetration of GGG substrate elements into YIG layer and with film components replacement. Iron segregation along the YIG layer depth can be the other reason for this. Indeed, iron atoms segregation is observed along the YIG film layer depth range 400-600Å. RBS data are proved by the results of selective CEMS along the layer depth.

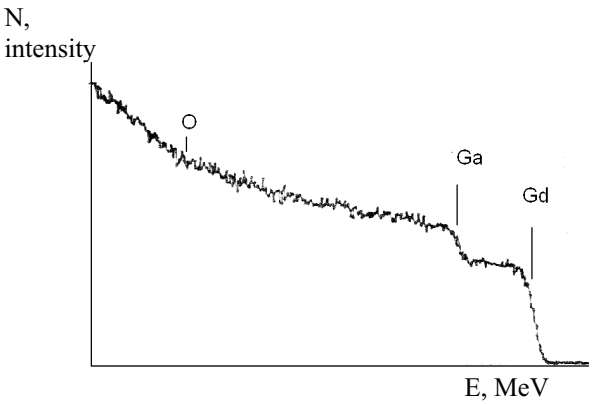

Fig.1. RBS spectrum of unannealing GGG substrate

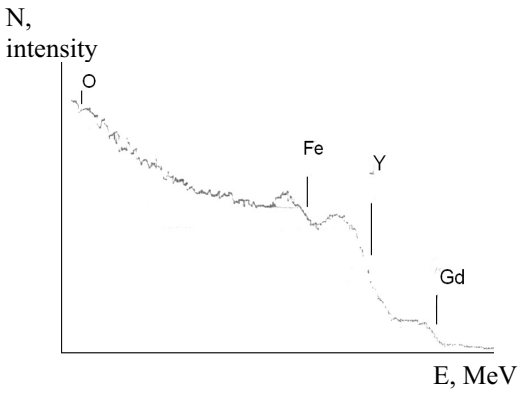

Fig.2. RBS spectrum of YIG film on GGG substrate

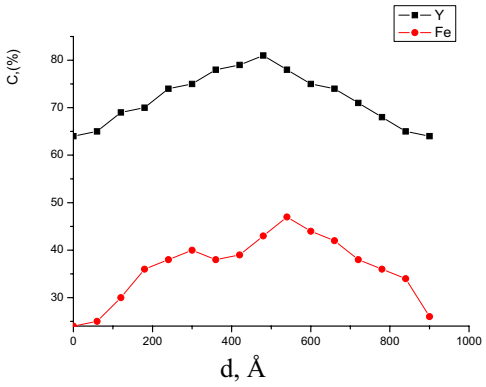

Fig.3. Distributions of Y and Fe on depth of YIG film by RBS data

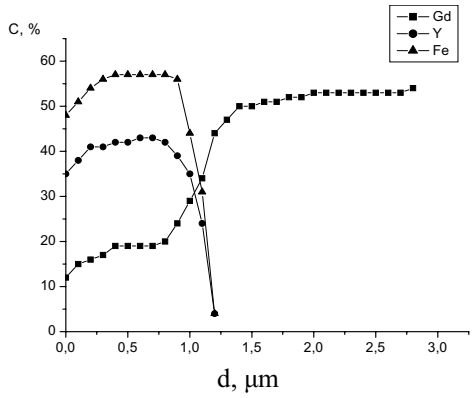

Fig.4. Distribution of components (mass.%) of substrate and YIG film obtained using mode 4.

Elemental composition of YIG films according to RBS data is inhomogeneous along films width (Fig. 4, 5). Almost in all cases in upper surface layers (up to 0.2 – 0.4 μm) concentration of iron and yttrium is decreased. Concentration of iron and yttrium decreases on substrate boundary. Note that when using the shutter the heterogeneity along film thickness decreases sufficiently in comparison with mode 1. Moreover gadolinium diffuses to YIG films surface when they are being formed. Gadolinium comes out on YIG film surface in some cases during deposition process and annealing. Mention that gadolinium presence in near-surface layer didn't prevent amorphous (in its initial state) film from transition to magnetically ordered state during annealing process.

Mössbauer scattering spectra for these films in their initial state occur to be stretched doublet and they're typical for fine-dispersed amorphous paramagnetic state (Fig. 6). This happens both when films annealing and using mode 4 without gadolinium segregation in films. According to CEMS data garnet ferrite films obtained using different deposition modes are in paramagnetic state just after their formation. CEMS spectra are presented by widened doublets with little different doublet parameters for different samples.

In our case selectivity of analysis along the layer depth is achieved by using CEMS. The yield of conversion electrons is equal to the square under CEMS spectrum for the given incidence which corresponds to relative Fe atoms content in the layer being analyzed. In Fig.7 such a dependency is given for reference sample where Fe atoms segregation in surface layer is prevented beforehand. One can see the abrupt lowering of reference curve in the thickness range 0.1-0.05 μm being observed. Such a dependency has completely different behavior for YIG film; it doesn't show the abrupt lowering typical for distribution of iron homogenous along the layer length. From these differences in dependencies behavior along the layer depth in thickness range 1000 - 500 Å one can find the confirmation of RBS data as for non-monotony of iron atoms concentration on YIG film surface (with thickness up to 3 μm) after its obtaining.

Isochronal annealing in temperature range 500 – 900 K has led to the change of amorphous phase parameters but lines of magnetic ordered YIG phase hasn't appeared. Values of resonance effect of scattering change non-

monotonically. First the scattering effect intensity rises and then in temperature range 570-670 K it decreases and after that a slight rise follows. One of the possible processes responsible for this can be gas release which leads to pores formation. Decrease of relative fraction of iron atoms on external and internal surface must lead to spectra intensity decrease. Also less value of Debye-Waller factor (DWF) on the surface can lead to such decrease of spectra intensity. Pores size increase under the annealing temperature change leads to decrease of surface area due to small pores disappearance and causes spectra intensity rise.

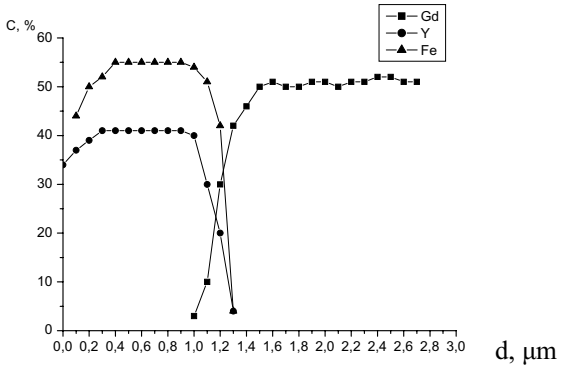

Fig.5. CEMS spectra of YIG amorphous film scattering after its deposition on GGG film in mode 2

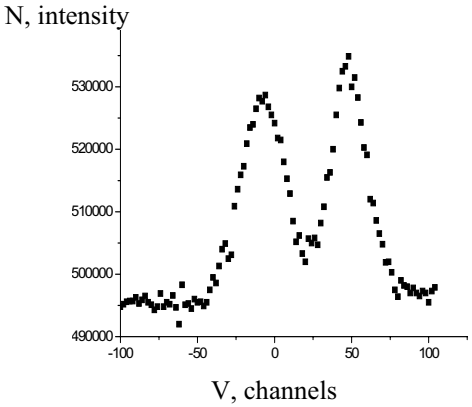

Fig.6. Distribution of components (mass. %) of substrate and YIG film obtained using mode 2

After annealing of specimens the magnetic-ordered phases were formed (Fig. 8). Crystallization process is accompanied by gas emission which leads to pores formation. The other reason for YIG intensity decrease is the appearance of gadolinium or gallium (according to RBS data) on YIG surface.

From the ratio of spectral lines intensity of magnetic-ordered phase there were estimated averages values of the angle θ between film surface normal and iron atoms magnetic moment direction that corresponds with the direction of easy magnetization axis. Preliminary substrate annealing doesn't influence θ value within experimental error.

Magnetic hyperfine splitting of CEMS spectra of YIG thin films just after their obtaining isn't observed so it can be concluded that the spectrum can be the one of paramagnetic amorphous phase where then garnet ferrite layers are formed after deposition. Scattering spectrum for paramagnetic garnet ferrites can be represented as superposition of two doublets corresponding to Fe^{3+} ions positions in tetrahedron and octahedron nodes. Quadrupole spectra splitting Δ for ion atoms in octa – sites are 1 mm/s, for tetra-nodes it's 0.3 – 0.5 mm/s. As Δ_{exp} value is close to the one of tetrahedron position the conclusion can be made that in case of amorphous state octahedrons are distorted much more than tetrahedrons because spectral lines for octahedron positions have low intensity. Iron concentration values in thin near-surface YIG layer obtained from comparison of scattering effect values are maximal for mode 1 and minimal for mode 3. As scattering effect values are proportional to iron content in near-surface layer with 0.1 μm therefore YIG films differ in iron content. Storage in mode 2 decreases scattering effect value at 11%, and when spraying using mode 3 - at 70%. This decrease can be connected with formation of the layer which doesn't content Fe atoms on YIG film surface. According to RBS data when using spraying mode 3 there was thin layer of gadolinium on YIG film surface which could diffuse to the surface through the amorphous YIG film during the spraying process (up to 6 hours), which is longer than in case 1 and 2 (2 hours). But still one can see some features of CEMS spectra parameters behavior depending on films thickness. Spectra splitting decreases as film thickness decreases which indicates the change of film imperfection along its thickness. Isomer shift doesn't change along film thickness. Ratio of spectral lines intensity to half-width of scattering spectrum doublet lines changes like quadrupole scattering spectra does. I.e. some nonmonotony of film properties is observed according to layer-be-layer CEMS analysis.

Thermal annealing of obtained YIG films in the range 970 – 1070 K leads to the crystallization of amorphous layers and to YIG transition to magnetic ordered state at that films are polycrystalline ones (Fig.8).

The crystallization of amorphous YIG films already takes place at T = 970 K [10]. In such a way fine-dispersed amorphous YIG particles obtained by the chemical salt-gel approach about 200 Å size when heating transferred to crystalline state at temperature range 920 – 970 K. In YIG films obtained by means of plasma spray process the amorphous phase disappeared after the annealing at 1470 K during 24 h widened doublet spectra consists of the doublets corresponding to Fe^{2+} and Fe^{3+} (in tetra- and octahedron positions). Slowing down of crystallization process can be connected with film imperfection. More continuous annealing or annealing temperature increase is needed to remove the faults. At that diffusion of substrates components to the film will show up more clearly which can worsen its properties. It's necessary to define the reasons of stability of YIG film amorphous state during annealing; what influences substrate-film boundary and external film surface stability in the first place.

The nonlinearity response of spin system on external high- frequency electromagnetic field can lead to chaotic modulation of the spin oscillations and waves. These effects were discovered and well studied in bulk samples of ferrites. In this report presented study of the relationship between structure of nanolayers and chaotic high-

frequency response in thin films of yttrium iron garnet. As in the work [11] measuring of transmission high-frequency waves was held. The results of theoretical calculations based on transfer matrix method and simulation based on finite elements method satisfactory agreement with experimental data. From the ratio of spectral lines intensity of magnetic-ordered phase $Y_3Fe_5O_{12}$ there were estimated average values of the angle between film surface normal and the direction of iron atoms magnetic moment that corresponds with the direction of easy magnetization axis.

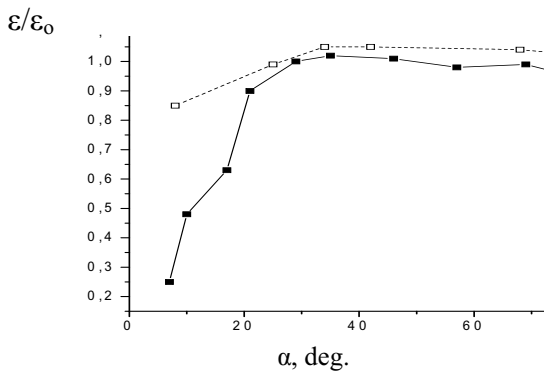

Fig.7. Dependencies of scattering effect relative value $\varepsilon/\varepsilon_O$ for YIG film spectra (□) and α-Fe reference spectra (■) on γ-quant incidence

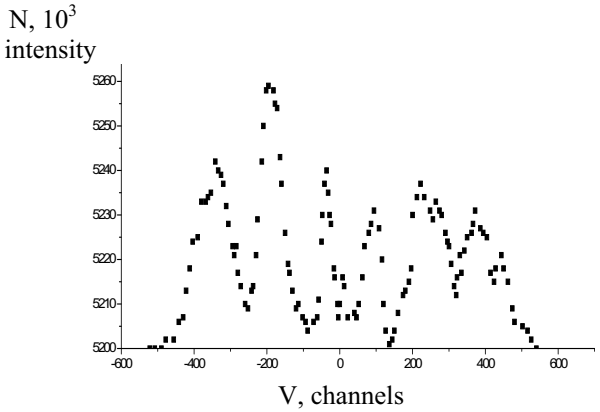

Fig. 8. CEMS spectra of magnetically ordered YIG film scattering after annealing at 970 K

From ratio of spectral lines intensities of magnetically ordered phase there were estimated the average values of angle Θ between the normal to film surface and magnetic moment of iron atoms which coincides with easy axis direction. Angle Θ is defined by the formula $\theta = \arccos\sqrt{(4-3\beta)/(4+3\beta)}$, where $\beta = J_2+J_5/J_1+J_6$; J_1, J_2, J_5, J_6 - are correspondingly the intensities of 1-st, 2-nd, 5-th and 6-th spectral lines from left to right of Mosbauer six line scattering spectrum of YIG film (Fig. 8). Preliminary substrate annealing doesn't influence value Θ within the experimental error. Value of angle between normal to film surface and EA direction for $Y_3Fe_5O_{12}$ film after irradiation with protons is equal to 60^0.

CONCLUSIONS

During ion beam deposition the inhomogeneity of amorphous paramagnetic films of iron-yttrium garnet on single-crystal surfaces of gadolinium-gallium garnet is due to rather high level of structure imperfection of GGG substrate surface. Amorphous films of garnet ferrites are transferred to crystalline magnetically ordered layers during the annealing at 900K. Besides, gadolinium diffuses to YIG films surface during their formation. When analyzing of annealed YIG films it was found that iron and yttrium segregate to near surface layer to the depth about 500 Å. Such inhomogeneity of films phase composition can influence their magnetooptical parameters.

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