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THE STRUCTURE OF NANOMETRIC FERRITE'S FILMS AFTER ION IMPLANTATION

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The results of study of hexaferrite Ba and Bi-Gd garnet films on gadolinium gallium garnet substrates are presented. In the result of ion-beam induced deposition the amorphous paramagnetic films of Ba-hexaferrite and Bismuth gadolinium garnet film are formed on substrate surface and then under the thermal annealing they transform their state into magnetically ordered one. For the easy magnetization axis to turn into the film plane the most efficient makes is ion beam implantation of He^+ ions.
KEY WORDS: thin films, element and phase composition, hexaferrite Ba, Bi-Gd garnet, spectroscopy.

СТРУКТУРА НАНОМЕТРИЧЕСКИХ ПЛЕНОК ФЕРРИТОВ ПОСЛЕ ИОННОЙ ИМПЛАНТАЦИИ

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Представлены результаты исследования процессов формирования пленок гексаферрита Ba и Bi-Gd граната на подложках галлий - гадолиниевого граната. В результате ионно-лучевого осаждения на поверхности подложек образуются аморфные парамагнитные пленки гексаферрита Ba и висмут - гадолиниевого граната с последующей кристаллизацией магнитоупорядоченных пленок при термическом отжиге и ионной имплантации. Для поворота оси легкого намагничивания в плоскость пленки наиболее эффективна ионная имплантация ионов He^+.
КЛЮЧЕВЫЕ СЛОВА: тонкие пленки, элементный и фазовый состав, гексаферрит Ba, Bi-Gd гранат, спектроскопия.

СТРУКТУРА НАНОМЕТРІЧНИХ ПЛІВОК ФЕРРИТІВ ПІСЛЯ ІОННОЙ ІМПЛАНТАЦІЇ

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Представлені результати дослідження процесів формування плівок гексаферриту Ba і Bi-Gd гранату на підкладках галлійгадолінієвого граната. В результаті іонно-променевого осадження на поверхні підкладок утворюються аморфні парамагнітні плівки гексаферриту Ba та плівки вісмут- гадолиниевого граната з формуванням магнітовпорядкованих плівок при термічному відпалі й іонної імплантації. Для повороту осі легкого намагнічування у площину плівки найбільш ефективна іонна імплантація іонів He+.
КЛЮЧОВІ СЛОВА: тонкі плівки, елементний і фазовий склад, гексаферрит Ba, Bi-Gd гранат, спектроскопія.

YIG (yttrium iron garnet) is actually a synthetic form of garnet. It has interesting magnetic properties which allow it to perform as a tunable microwave filter for example [1]. Also, because of their uniaxial crystalline magnetic anisotropy, high value of magnetic anisotropy constant and chemical inertness strontium and barium-M hard-magnetic hexaferrites are prospective materials for creation of constant magnets and magnetic carriers with high data density [2, 3]. Replacement of iron and strontium atoms by other cations in hexaferrites also allows wide range variation of the substance magnetic properties. To obtain hexaferrites and other types of garnet ferrites (e.g. bismuth gadolinium garnets) with the required performance attributes it's necessary to search for the efficient combination of film deposition techniques and to obtain the information about their elemental composition, structural-phase and magnetic states at different stages of magnetic structure formation. Ion beam technique allows creating new approach to the problem of condensation of composite garnet ferrites films on substrates with noncoincident lattice parameters. By means of Mössbauer spectroscopy there were studied both Ba and Sr hexaferrites, iron oxides and Ba hexaferrite thin films (as well as Sr ones) [4, 5]. It's rather promising to use garnets for immobilization of radioactive wastes with high specific activity [6]. At that, garnets and garnet ferrites elemental composition in particular and structural-phase state are rather important parameters.

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 Ba-hexaferrite thin films and bismuth-gadolinium garnet after they were synthesized using ion beam deposition with the following thermal annealing and ion beam implantation.

THE EXPERIMENTAL STUDY TECHNIQUE

Ba-hexaferrite and bismuth-gadolinium ferrite films $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ were deposited on gadolinium gallium garnet (GGG) substrate with (111) orientation using vacuum deposition approach 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. Before film deposition on GGG plates the substrates were exposed to ion-beam and thermal processing that consisted of substrate irradiation with oxygen ions.

Phase composition of thin films surface layers was defined by means of Mössbauer spectroscopy on ^{57}Fe nuclei in backscattering geometry with the registration of conversion electrons. Depth of layer analyzed with CEMS was about 0.3 μm. Structural perfection of GGG substrate surface layer was defined both by using double-crystal spectrometer according to Berg-Barrett method and by X-ray up to 3 μm. Elemental analysis of ferrite films surface layers was performed using Rutherford backscattering spectrometry (RBS) up to depth selectivity 3 μm. He$^+$ ions implantation was performed with energy 26 keV and fluence up to $\Phi=2\cdot10^{14}$ cm^{-2}.

RESULTS AND DISCUSSION

On the first stage the simulation of He$^+$ ion irradiation of YIG by SRIM-2011 was performed (Fig. 1 – 9).

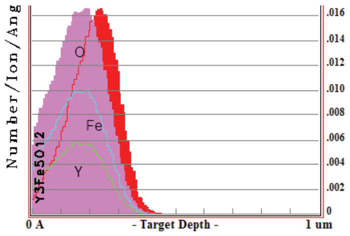

Fig. 1. Atom distributions

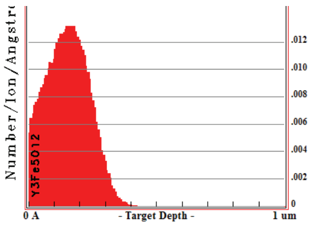

Fig. 2. Collision events. Vacancies produced

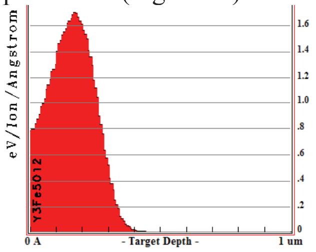

Fig. 3. Energy to recoils

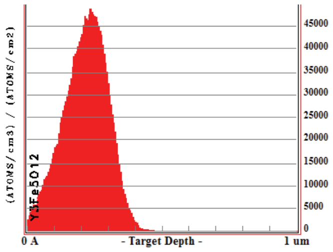

Fig. 4. Ion ranges.
Ion Range = 2154 Å, Straggle = 798 Å,
Skewness = 0.2463 Å, Kurtosis = 2.6832 Å

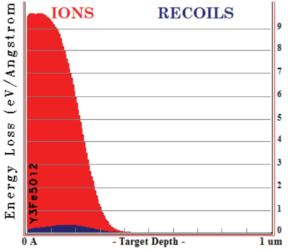

Fig. 5. Ionization of ions and recoils

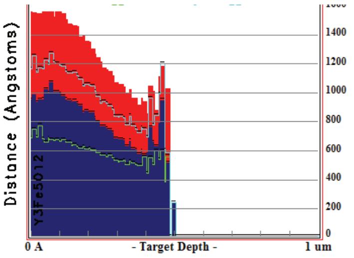

Fig. 6. Lateral distribution

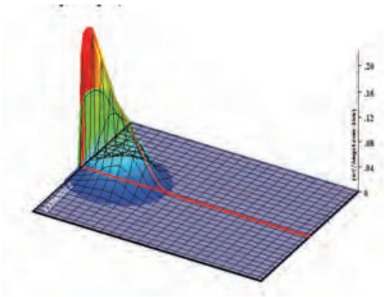

Fig. 7. Target phonons.
Total ionization = 21.7 keV/Ion/,
tonal phonons =4.1 keV/Ion,
total target damage =0.22 keV/Ion

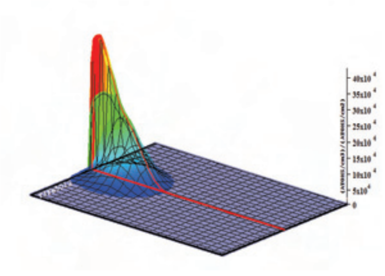

Fig. 8. Recoil distribution.
Ion Range = 2141 Å, Straggle = 799 Å,
Skewness = 0.281 Å, Kurtosis = 2.629 Å

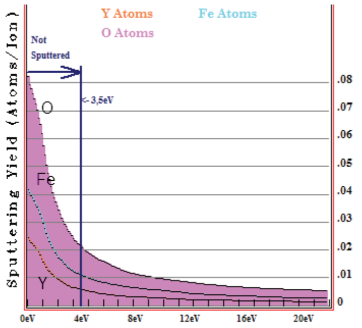

Fig. 9. Atoms reaching surface with energy normal to surface

The results of simulation demonstrate character features of two peaks atom distributions on target depth which connect with various parameters of He$^+$ implantation into multi element YIG target.

In these calculations do not take into account the penetration of the gadolinium from the GGG substrate into the YIG film (Fig. 10). To determine the thickness of transition layer between the film and substrate RBS method was used. Transition layer thickness didn't exceed 0.1 μm. This parameter is important when forming structures of submicron sizes by means of solution-melt deposition of films which thickness is commensurable with transition layer thickness.

There were given the CEMS spectra of $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ films after sputtering (Fig. 11). Films $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ after processing using IBS approach are presented by widened doublet scattering spectra which indicates the amorphous state of the films. Comparison of quadruple splitting ΔE of garnets allows supposing that there's some contribution of sputtering in form of clusters. These are several Angstrom size clusters and they can be formed when recombination of sputtered ions (Fig. 9). There by at different ways of garnet ferrite thin films deposition the common thing is the formation of amorphous layers at the first stage of films deposition.

This is also proved by the experimental data as for hexaferrite films formation. The shape of doublet scattering spectra shows that first the amorphous film appears in paramagnetic state. Parameters of doublet scattering spectra on (isomeric annealing δ=0.35 mm/s relative to α-Fe and quadrupole splitting Δ=1.05 mm/s) correspond to Fe^{+3} ion state. Half-width values of doublet lines $\Gamma_1=\Gamma_2=0.7$ mm/s indicate that Fe^{+3} ions in Ba-hexaferrite are characterized by wide set of inequivalent positions.

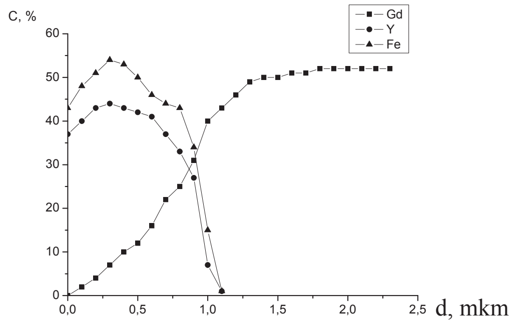

Fig. 10. Distribution of elements on film depth

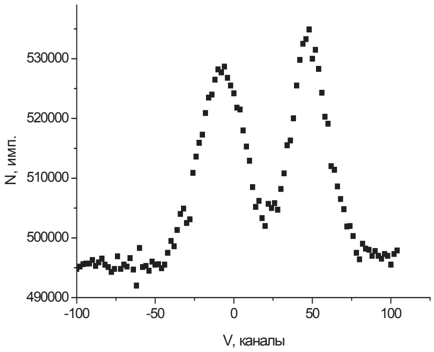

Fig. 11. CEMS spectra of $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ films after sputtering

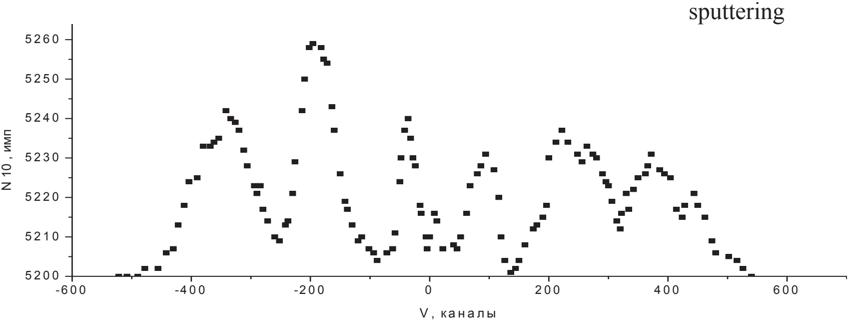

Fig. 12. CEMS spectra of $Bi_{2.2}Gd_{0.8}Fe_{4.4}Ga_{0.6}O_{12}$ films after and annealing at 1070 K; 2.5 h

Annealing of bismuth containing films was performed at 1070 K in time range from 10 min to 10 hours. In 10 minutes after the annealing was started the doublet in scattering spectra was replaced with magnetically ordered phase spectrum (Fig. 12). This spectrum corresponds to the presence of at least two nonequivalent ^{57}Fe atoms in the lattice, which are characterized by average values of nuclei magnetic fields H_1=(460+10) kOe and H_2=(460+10) kOe. These fields can be considered as those in tetra- and octahedron positions correspondingly. Increase of annealing time up to 10 hours leads to the appearance of three nonequivalent Fe atoms positions in the film lattice.

From the ratio of spectral line intensities ***I*** for magnetically ordered phase there were estimated the average values of the angle θ between normal to the film surface and iron ions magnetic moment direction matching with easy axis direction. Using CEMS spectra lines ratio for magnetically ordered film there can be estimated the average value of angle $\overline{\theta}$ between the normal to the film surface and iron ions magnetic moment direction matching with easy axis direction.

The angle $\overline{\theta}$ is defined using known formulae (1):

$$\overline{\theta} = \arccos\sqrt{(4-3\beta)/(4+3\beta)}\,,$$

where $\beta = \frac{I_2+I_5}{I_1+I_6}$, I_1,I_2,I_5,I_6 – 1-st, 2-nd, 5-th and 6-th spectral lines intensities correspondingly.

So, for the sample obtained in mode 1 and annealed at 1060 K during 0.5 hours the $\overline{\theta}$ angle value was about 60°. Angle $\overline{\theta}$ has tendency to decrease when increasing the annealing time. It's known that according to CEMS data for garnet ferrites Fe magnetic moment deflection from the normal to the surface decreases along near-surface layer depth and it's a natural sequence of surface imperfection.

In Table the θ angle values are given for different magnetically ordered films of garnet ferrites on GGG substrate.

Implantation with H+, He+, Ne+ ions of single-crystal films of magnetooptical structures leads to the whole bunch of sequences. Single-crystal films after annealing are characterized by the slope angle between easy axis (EA) and normal to film plane, which is equal to ≈ 0º. The main task of implantation is to turn EA into the film plane in near-surface layer for suppression of rough magnetic bubble domains (MBD). At that θ angle value varies from 0º to 90º.

Table

Calculated using experimental data $\overline{\theta}$ angle values for different garnet ferrites

№	Sample	$\overline{\theta}$, degrees
1	Initial sample $Y_3Fe_5O_{12}$	69
2	YIG, irradiation He^+, E=26 кeV, $\Phi=1.5\cdot10^{14}$cm^{-2}	78
3	Hexaferrite annealing 1070 K, t=1 h	56
4	$Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$. annealed substrate, annealing 1070 K, 2.5 h non-annealed substrate, annealing 1070 K, irradiation He^+, E= 0.6 MeV, $\Phi=3\cdot10^{13}$ cm^{-2}	42 48
5	$Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$., annealing 1070 K, 10 m + He^+ , E=26 кeV, $\Phi=1.5\cdot10^{14}$ cm^{-2} annealing 1070K, 10 m + He^+ , E=26 кeV, $\Phi=2.25\cdot10^{14}$ cm^{-2}	90 90

In our case films are amorphous after processing and the annealing leads to their crystallization into polycrystalline fine-dispersed structures with high number of imperfections. Substrates preliminary annealing almost doesn't affect $\overline{\theta}$ value for $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ films. But this value is essentially lower then the one obtained for YIG after proton irradiation and annealing. Angle θ value has a tendency to decrease with increase of annealing time for Bi-Gd-Fe-Ga-O films.

According to RBS data the implantation with He^+ ions with E=0.6 MeV leads to BS spectra blur and as a result to the problem of elemental composition distribution along the film thickness. According to CEMS data the irradiation with He^+ ions with E_1=0.6 MeV leads to small increase of $\overline{\theta}$ value, but at that spectra blur isn't observed. Irradiation with He^+ ions with E_2=26 кeV leads to CEMS spectra blur for $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ films and to the turn of EA into the film plane ($\overline{\theta}$=90º). In addition, the weak lines of amorphous phase are observed for dose $\Phi=2.25\cdot10^{14}$ cm^{-2}. Irradiation of YIG with He^+ ions with E=26 кeV (previous proton irradiation E =1 MeV, $\Phi=10^{17}$cm^{-2}, annealing 1060 K, 1 h) leads to angle $\overline{\theta}$ increase up to 78°, but the EA vector doesn't fit into the plane. Thereby $Bi_{2,2}Gd_{0,8}Fe_{4,4}Ga_{0,6}O_{12}$ irradiation with He ions leads to abrupt change of EA orientation (angle value $\overline{\theta}$=90º*)* (Table).

Surface amorphization occurs again when irradiation of $BaFe_{12}O_{19}$ hexaferrite with high-energy heavy ions of Ar and Cr [7,8]. This is what happens when heavy ions, e.g. Ne^+, are implanted into garnet ferrites. Near-surface layer amorphization increases with the dose. According to CEMS data implantation of H_2^+ ions to garnet ferrites doesn't lead to amorphization. However implanted hydrogen forms chemical connections with some elements present in garnet composition. That's why it again proves the expedience of He^+ ions choice as ions being implanted.

CONCLUSIONS

Ion beam deposition of Ba-hexaferrite films leads to the formation of amorphous paramagnetic films which are transferred into magnetically ordered state under thermal annealing. The results of simulation demonstrate character features of two peaks atom distributions on target depth which connect with various parameters of He^+ implantation into multi element target. Films layer-by-layer analysis according to the RBS data lets us come to the conclusion about variable elemental composition of ferrite films. Phase composition is inhomogeneous along the film thickness. Gadolinium diffuses from the substrate to the films surface when they are formed. Deposition of bismuth-gadolinium garnet is also connected with amorphous paramagnetic films formation and with further crystallization of magnetically ordered films under thermal annealing and ion implantation. Implantation of He^+ ions is the most efficient procedure, which leads to easy axis turn into the film plane.

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