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Aging Processes in Films of Iron-Yttrium Garnet Implanted by Boron Ions

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Based on the results of X-ray structural analysis, changes in the crystalline structure that occurred during 15 years in surface layers of epitaxial films of iron-yttrium garnet implanted by B+ ions were studied. The processes that occur during the B+ ion implantation of in ferrite-garnet films, and the processes that accompany the low-temperature aging of ion-implanted films are considered. Strain profiles were determined from the experimental rocking curves, obtained immediately after ion implantation and after 15 years. It was found that the value of relative maximum deformation of surface layers decreases at constant thickness of the disturbed layer.

Keywords: natural aging, strain profile, X-ray diffraction, ion implantation, defects of structure.

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Introduction

The development of durable and reliable instruments made on the basis of epitaxial heterostructures is one of the most problems of semiconductor technology. The technical characteristics of the device to a large extent are determined by the profiles of the concentration of implanted impurities and radiation defects and, accordingly, the strain profile. The restructuring and migration of defects in the crystalline lattice during the operation and storage of ion-implanted ferrite-pomegranate films are the main factors that lead to changes in the operational characteristics of the devices where they are used. Thus, studying the time stability of the structural parameters of the disturbed layer, establishing the regularities of the restructuring of the crystalline structure at room temperatures and predicting their behavior in the process of exploitation is an important theoretical and practical task.

The aim of this work is to establish the patterns of aging processes at room temperatures in films of iron-yttrium garnet implanted by boron ions.

For the analysis of the processes that occur during the natural aging of ion-implanted layers of iron-yttrium garnet films, it is necessary to consider processes that occur during ion implantation, and processes that accompany low-temperature aging after ion implantation. Therefore, the structure of this article includes both parts of the research in these areas.

I. Methodology of the experiment

In order to study the processes of low-temperature relaxation (aging) of the implanted layer, films of iron-yttrium garnet (YIG) with a thickness of 5.11 mkm were irradiated with B^+ ions of 80 keV energy and doses of $3{\cdot}10^{14}$ and $1{\cdot}10^{15}$ cm^{-2}.

Films of YIG were grown by the method of liquid phase epitaxy on the substrates of gadolinium-galium garnet (GGG) monocrystals with a cut plane (111). Ion implantation was performed on the implantator MPB-202 of the company "Balzers" in the mode, which excludes channeling.

X-ray structural investigations were carried out using two-crystal diffractometry at the DRON-3 (monochromator GGG or two-crystal monochromator Ge (in mutually dispersed positions)) using CuKα_1 radiation.

From the experimentally obtained rocking curves, strain profiles $Dd/d(z)$ and defect parameters were calculated. These calculations were made by simulating X-ray diffraction in a nonideal crystal by means of the statistical dynamical theory of scattering of X-rays. The method used to analyze the rocking curves is described in detail in [1].

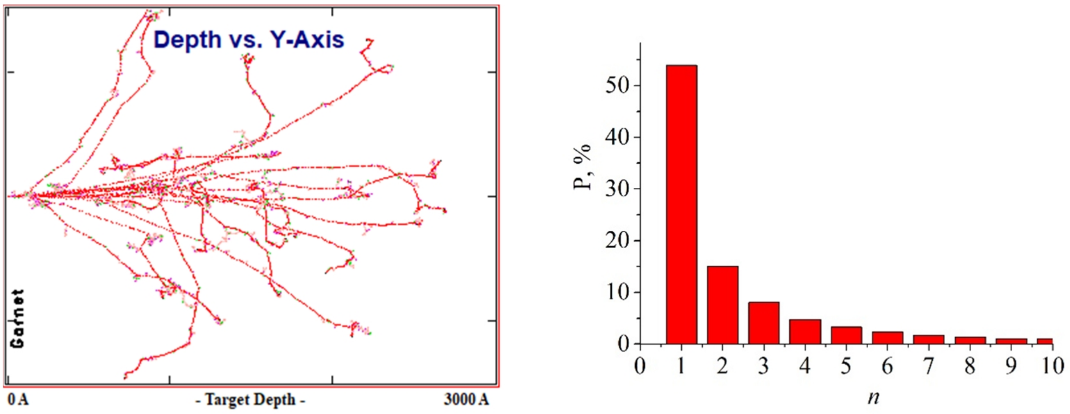
II. The processes that occur during ion implantation

During ion implantation an important role is associated with elastic collisions of ion implantant with the nuclei of the target and inelastic collisions with free and bound electrons. Experimental confirmation of defect formation by electron energy loss in materials with garnet structure is shown in [2]. It is described in this paper that in the films of ferrite garnets, which were implanted with ions with an energy of 80 keV, two disordering centers were observed in the disturbed layer: on the surface and inside the disturbed layer. Disordering inside the disturbed layer is associated with elastic ion-atomic interaction (nuclear energy losses of the ion-implant). Near-surface disorder is the result of inelastic collisions of an ion implant with matrix ions (electronic energy losses).

For a detailed study of the processes that occur during the implantation of B^+ ions in the garnet lattice, the SRIM program was used. Radiation defect occurs when the energy of displacement ions from their positions in the matrix exceeds the value E_d. For the single crystal YIG the value energy of displacement E_d according to [3] is: for ions O – 30 eV, for Fe ions – 56 eV, for Y ions – 66 eV.

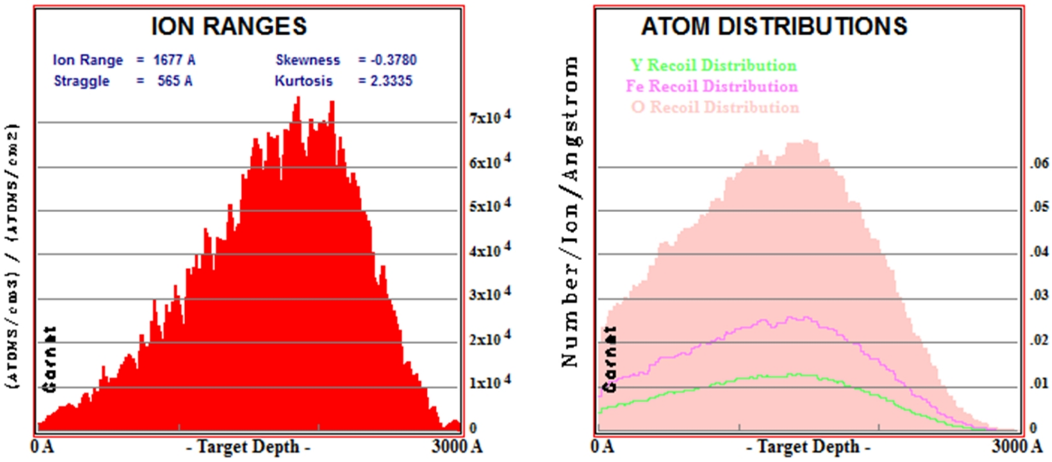
On the basis of the theory of elastic collisions using the SRIM program, the processes of interaction of boron ions with YIG atoms were investigated. In fig. 1, and shows 20 tracks calculated by simulating a complete cascade of collisions. From the type of tracks, we can conclude that the energy transferred by the ion-implant to the nuclear subsystem of the YIG in many cases reaches the values necessary for the development of the cascade of secondary displacements.

The statistical processing of the simulation results of the complete cascade of collisions showed that, with an energy of 80 keV for boron, the most probable (≈ 54 %) is the process of generating Frenkel couple (one displaced atom). The probability of developing a cascade of two recoil atoms is ≈ 15 %, of three ≈ 8 % (Fig. 1, b). It turns out that there are cascades that consist of 20 or more displaced atoms of the matrix (3.5 %). There are



a b

Fig. 1. Simulate tracks of ions B^+ implanting in the YIG (E = 80 keV) (a) and the probability (P,%) of the formation of cascades of secondary displacements of atoms matrix with different number of displaced atoms n (b).



a b

Fig. 2. Profiles of the distribution ion-implants (a) and displaced ions of the matrix O, Fe, Y (b) versus depth when implanted by B^+ ions in the YIG, E = 80 keV.

also cascades containing more than 160 knocked out atoms (0.04 %).

In the simulation of the ion implantation process, distributions of implanted ions and displaced atoms of the matrix in depth were obtained (Fig. 2).

As can be seen from Fig. 2 a, b, the maximum of the profile of the introduced boron ions is shifted to a depth relative to the position of the maximum of the profile of the displaced atoms of the matrix. This is due to the fact that ion implants in the final stages of motion have not sufficient energy to generate defects, and their collisions with the atoms of the matrix result only in the increase of oscillations of the atoms.

In the SRIM program, electronic energy losses are taken into account, but they determine the process of continuous slowdown of the ion implant and do not affect the direction of movement of the incident particle (ie, electrons form a "free electron gas") and do not created defects. However, as already mentioned, generation of radiation defects may occur due to electronic losses of ions energy. Using the approaches described in [4], calculations of distributions of defects formed during implantation of boron ions in YIG were performed (Fig. 3). As can be seen from the figure, the defects concentration formed due to nuclear and electronic losses of ions energy is commensurable; therefore, in calculating the strain profiles, it is necessary to take into account both methods of generating defects.

Generalized picture of the processes taking place in the ferrite garnet films describes the dynamic model implanted layer [2]. According this model, in smaller doses $9 \cdot 10^{14}$cm^{-2} amorphization of disturbed layer from the surface of the films starts and spreads in depth. At doses greater than $9 \cdot 10^{14}$cm^{-2}, the second amorphous layer emerges in the region of maximum nuclear energy losses. At a dose of ~ $3 \cdot 10^{15}$см$^{-2}$, both amorphous layers merge into one. With further increase in the dose of implanted ions occurs increase the amount of the amorphous phase. The maximum thickness of the amorphous phase is determined by countervailing factors: the propagation of the amorphous phase in the depth of the film and spraying the film surface.

At low doses the strain profile proportional to profile defects, which, according to a dynamic model of the ion-implanted layer is the sum of two components: the defects that are formed due to nuclear losses of ions energy and defects that are formed due to electronic losses of ions energy. As the calculations showed [4, 5], profile of defects (and therefore strain profile) has a complex dependence on depth, so to obtain a simple analytical formula without loss of accuracy, it can be written as the sum of asymmetric and decreasing Gaussians:

$$D = \begin{cases} D_{\max}^{N} \exp\left[-(h-R_p^N)^2 \Big/ \left(s_1^N\right)^2\right], & \text{if } h < R_p^N \\ D_{\max}^{N} \exp\left[-(h-R_p^N)^2 \Big/ \left(s_2^N\right)^2\right], & \text{if } h < R_p^N \end{cases} + D_{\max}^{N} \exp[-(h-R_p^E)^2 \Big/ \left(s^E\right)^2]$$

$D = \dfrac{\Delta d}{d}$, h – is the distance from the surface, R_P^N – is the merging point of two Gaussian curves, and σ_1^N, σ_2^N and σ^E – are parameters that describe the Gaussian curve's width at half maximum. The upper indices N and E mean, that these parameters characterize the components of the profile associated with nuclear and electronic losses of ions energy, respectively.

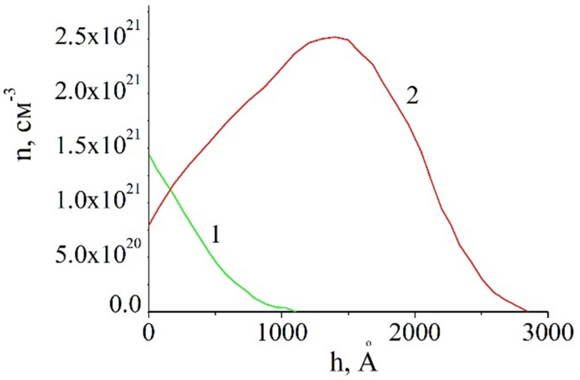
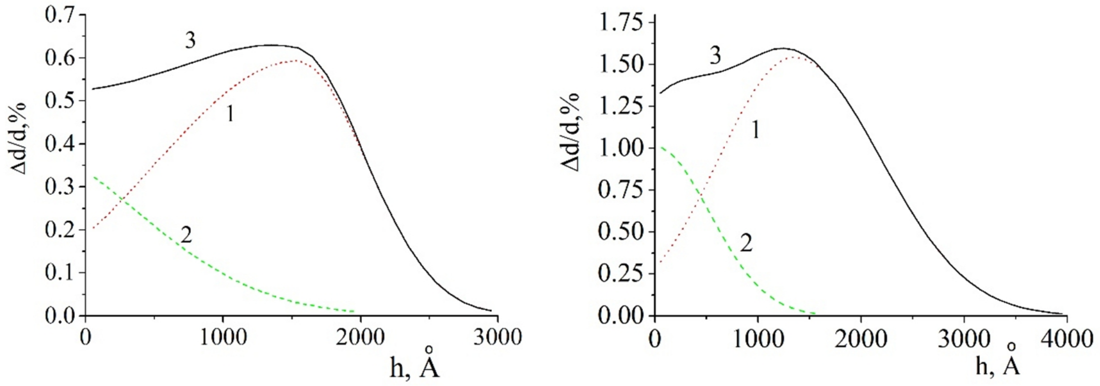


Fig. 3. Theoretical calculations distributions of the concentrations of defects formed as a result of electronic losses of ions energy (1) and nuclear losses of ions energy (2) (B^+ ions in the YIG, E = 80 keV, $D = 8 \cdot 10^{14}$ см$^{-2}$).

The strain profiles were determined taking into account the defects of the crystalline structure in the substrate, the film, and the disturbed layer [6]. Calculated from experimental rocking curves strain profiles for irradiation doses of $3 \cdot 10^{14}$ cm^{-2} and $1 \cdot 10^{15}$ cm^{-2} are shown in Fig. 4

An example of experimental and theoretical rocking curves from implanted B^+ ions with an energy of 80 keV and a dose of $1 \cdot 10^{15}$ см$^{-2}$ of the film YIG is presented in Fig. 5. A good match between the theoretically calculated and experimental rocking curves is a confirmation of the correctness of the chosen model of the defective system of the ion-implanted layer.

As can be seen from Fig. 4, the characteristic form of strain profiles for doses of $3 \cdot 10^{14}$ cm^{-2} and $1 \cdot 10^{15}$ cm^{-2} is different. At a dose of $3 \cdot 10^{14}$ cm^{-2} the strain profile is proportional to the defect profile and the elastically deformed intermediate layer, which is located outside the layer with radiation defects, is not formed. In the film implanted with a dose of $1 \cdot 10^{15}$cm^{-2}, an elastically



a b

Fig. 4. The strain profiles in films of YIG, implanted with B^+ ions with energy of 80 keV and doses of $3\cdot10^{14}$ cm^{-2} (a) and $1\cdot10^{15}$ cm^{-2} (b) (1, 2 – components of the profile associated with nuclear and electronic energy losses respectively, 3 – the total profile).

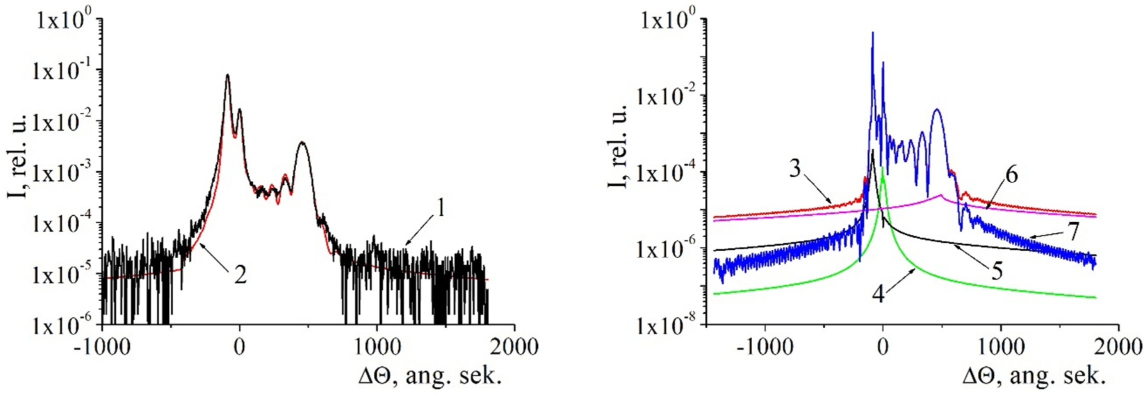


Fig. 5. Rocking curves for reflex (444) from implanted B^+ ions with energy of 80 keV and a dose of $1\cdot10^{15}$ cm^{-2} film YIG (1 – experimental, 2 – theoretically calculated rocking curve with taking into account spectrometer broadening, 3 – theoretical rocking curve and its components: diffuse from the film (4), diffuse from the substrate (5), diffuse from the disturbed layer (6) and coherent (7)).

deformed intermediate layer is formed at a thickness of about 1000 Å, which is located outside the layer with radiation defects. This is due to significantly greater deformation at higher doses of implantation and the spread of radiation-induced mechanical stresses in the depth of film.

The maximum deformation (Fig. 4) is the result of the total effect of both defects formed due to elastic nuclear collisions and defects formed due to electronic energy losses. Dependence of deformation on the dose of implantation is well described by the classical dependence of the accumulation of radiation defects within the framework of the model, which takes into account their annihilation due to the possible occurrence of this defect in the zone of instability of an already existing defect (Fig. 6).

For the quantitative description of the process of accumulation of structural disordering of the near-surface layer of the ferrite-garnet films, experimental data $\left(\Delta d/d\right)_{\max}(D)$ were approximated by the dependence of the species [7]:

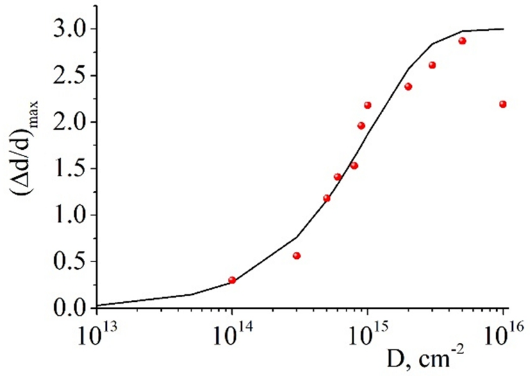
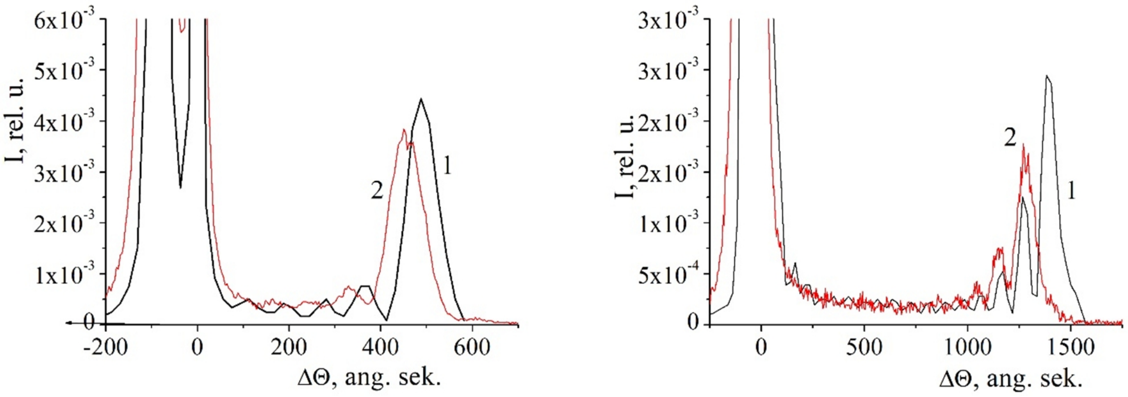
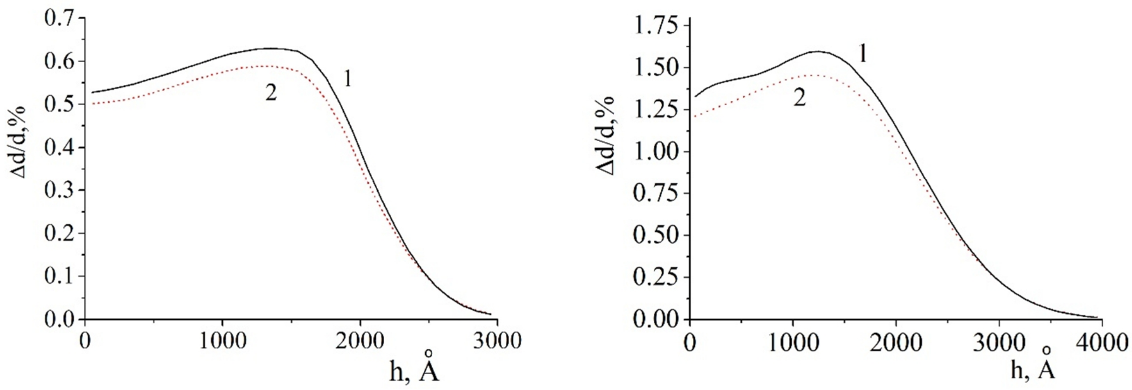


Fig. 6. The dose dependence of the maximum relative deformation $\left(\Delta d/d\right)_{\max}(D)$ (points) and $\omega(D)$ (line) for YIG films implanted by B^+ ions, E = 80 keV.



a b

Fig. 7. Experimental rocking curves (reflex (444)) which are obtained immediately after implantation (1) and after 15 years (2) from YIG films implanted by B^+ ions (E = 80 keV): a - radiation dose of $3{\cdot}10^{14}$ cm^{-2} , b – $1{\cdot}10^{15}$ cm^{-2}.



a b

Fig. 8. Strain profiles calculated from experimental rocking curves, which are obtained immediately after implantation (1) and after 15 years (2) from YIG films implanted by B^+ ions (E = 80 keV): a - radiation dose of $3{\cdot}10^{14}$ cm^{-2} , b – $1{\cdot}10^{15}$ cm^{-2}.

$$w(D) = 1 - \exp\left(-{N_k}/{N_{kr}}\right), \quad N_k = s_n N_0 D,$$

where $s_n(x)$ – the differential cross section of elastic defect formation, D – the dose of irradiation, N_0 – the average number of atoms per unit volume of the target (for YIG $N_0 = 8{,}4{\cdot}10^{22}$ cm^{-3}), N_{kr} – critical value of the concentration of defects at which the amorphization of the structure begins. According to the calculations, N_{kr} is $\approx 0{,}65{\cdot}10^{22}$ cm^{-3}, which corresponds to the radiation dose $\approx 2{\cdot}10^{15}$ cm^{-2}.

On the curve ω(D) there are three areas that can be interpreted in the following way. In the area of low doses, ionic tracks do not overlap, the defect structure is minimal. At intermediate doses, the rapid accumulation of point defects begins, which is confirmed by the experimental fact of the sharp increase in deformation. A further increase in the dose leads to overlapping of ionic tracks. Diffusion of defects causes the formation of disordered amorphous zones, which leads to the gradual exit of the dependence ω(D) on the plateau.

At doses larger than $1{\cdot}10^{16}$ см$^{-2}$, the crystal lattice is so much damaged that it is impossible to estimate the maximum deformation according to the X-ray diffractometry.

III. Processes that accompany the low temperature aging of the ion-implanted layer

A comparison was made between X-ray structural analysis results obtained for these films at intervals of 15 years after storage at room temperature. Over time, the parameters of the disturbed layers undergo changes that can be traced already from the experimental rocking curves obtained at certain intervals. In the first place, this is manifested in the region of an additional oscillatory structure. The angular length of additional oscillating structure decreases with time, which is a testament to decrease with time of maximum deformation ion implanted layer.

At relatively low doses of implantation to $1{\cdot}10^{14}$ cm^{-2} the maximum value of deformation does not change much, but there is a general smoothing of strain profile.

The thickness of the disturbed layer remains unchanged.

According to the research of implanted films of YIG by Rutherford's inverse scattering method, mainly anionic sublattice is destroyed at low doses of irradiation with B^+ ions (E = 80 keV), and significant disordering of cation lattice was observed at doses $\geq 8\cdot10^{14}$ $см^{-2}$ [8]. Thus, recorded after aging structural change probably conditioned by the redistribution of anionic defects with minimal energy of migration and migration of boron atoms in anionic vacancies. The tendency to occupy anionic vacancies by boron has been proven by method of nuclear reactions $^{11}B(p,\alpha)^{8}Be$ [9]. Probably, the restoration of the structure does not occur, and observed changes in the structure of the near surface layer due to migration of radiation defects and their disappearance by joining to the dislocation loops. However, for low doses of boron implantation, the maximum relative deformation of the lattice does not exceed 0,3%, and on rocking curves it manifests itself as an additional peak or an influx. Therefore, the resulting changes in the form of a strain profile during aging can only be perceived in a qualitative plan.

More detailed information can be obtained at higher doses of irradiation. Doses of irradiation up to $1\cdot10^{14}$ cm^{-2} are on the flat section of the dependence of the structural disordering of ferrite-garnet films on the radiation dose $\omega(D)$, therefore, the dose increasing does not lead to significant deformations of the crystalline lattice. In the case of higher doses of implantation, a sharply increase in the disordering curve begins, and therefore an increase in the dose of implantation by half the order leads to quick increase in relative deformation. On the rocking curves there is a complex oscillatory structure.

Fig. 7 shows the rocking curves which are obtained immediately after implantation and 15 years after implantation.

According to experimental rocking curves, strain profiles were calculated (Fig. 8). As we can see, deformation with natural aging in all samples decreases, and the thickness of the disturbed layer is practically unchanged. In the maximum deformed layer the relative deformation is reduced by 7-8 %.

The explanation of the indicated changes in the near-surface layer of YIG films in accordance with modern ideas about the process of implantation of ions in the crystal is as follows. Radiation defects immediately after emergence migrate, annihilate one with one, form complexes of different types or remain unitary and stable. Complexes of interstitial atoms pass into dislocation loops of interstitial type, and vacancy clusters – in dislocation loops or vacancy pores [10]. Proceeding from the fact that the energy of the migration of interstitial atoms is less than the energy of the migration of vacancies, during the cooling period, the interstitial atom formed in the cascade may away from the place of its formation for a greater distance than the vacancy [11].

In the aging of films implanted with boron ions, the process of the disappearance of point defects predominates over the processes of diffusion, which leads to a decrease in the value of deformation and almost does not affect the thickness of the disturbed layer. At the same time, some vacancies annihilate with interstitial atoms, and the remaining point defects annihilate on the dislocation loops.

Conclusions

1. Parameters and characteristic features of strain profiles obtained during implantation of YIG films by medium-energy boron ions depend on the implantation dose. In particular, the strain profile is proportional to the defect one at implantation dose of $3\cdot10^{14}$ cm^{-2}, and the elastically deformed intermediate layer outside the layer with radiation defects is not formed. Implantation of boron ions (dose of $1\cdot10^{15}$ cm^{-2}) leads to the formation of an elastically deformed intermediate layer outside the layer with radiation defects about 1000 Å in thickness.
2. The value of deformation along the entire thickness of the ion-implanted layer decreases with time at the natural aging of YIG films implanted by medium-energy boron ions. The relative deformation is reduced to 7-8 % in the maximum deformed layer. The thickness of the disturbed layer thus remains unchanged.

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Процеси старіння в плівках залізо-ітрієвого гранату, імплантованих іонами бору

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На основі результатів Х-променевого структурного аналізу вивчено зміни кристалічної структури, які відбувалися на протязі 15 років в приповерхневих шарах епітаксійних плівок залізо-ітрієвого гранату, імплантованих іонами B^+. Розглянуто процеси, що відбуваються під час іонної імплантації B^+ у ферит-гранатові плівки, та процеси, які супроводжують низькотемпературне старіння іонно імплантованих плівок. З експериментальних кривих дифракційного відбивання, отриманих відразу після іонної імплантації та через 15 років, визначено профілі деформації. Виявлено, що значення відносної максимальної деформації приповерхневих шарів зменшується при незмінній товщині порушеного шару.

Ключові слова: природне старіння, профіль деформації, Х-променева дифракція, іонна імплантація, дефекти структури.