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B.K. Ostafiychuk[1], I.P. Yaremiy[1], S.I. Yaremiy[2], M.M. Povkh[1], L.S. Yablon[1], I.M. Budzulyak[1]

Aging Processes in Implanted Fluorine Ions and Laser Irradiated Films of LaGa:YIG

[1]Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, 76018, Ukraine, yarimiyip@gmail.com
[2]Ivano-Frankivsk National Medical University, Ivano-Frankivsk, 76000, Ukraine, Yaremiy.S.I@gmail.com

Based on the results of X-ray structural analysis, changes in the crystalline structure during natural aging and laser annealing, which occurred in near-surface layers of epitaxial films of LaGa-substituted Iron-Yttrium Garnet, implanted by F^+ ions, were studied. The processes that occur during the ion implantation by F^+ in ferrite-garnet films, and the processes that accompany the low-temperature aging of ion-implanted films are considered. From the experimental rocking curves, obtained immediately after ion implantation, after the laser irradiation and after several years, strain profiles were determined. Two stages in the changes of the crystalline structure of the near-surface disturbed layer over time are revealed. During the first of them, the maximum deformation in the ion-implanted layer increased slightly, and on the second it decreased. It was established that the results of laser annealing and natural aging of near-surface layers implanted by F^+ ions and laser irradiated LaGa:YIG films depend on the direction from which laser irradiation occurred. However, the result of their total exposure does not depend on the side of laser irradiation.

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

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Introduction

Ion implantation leads to defects in the near-surface layer and, accordingly, change in the interplanar distance in it, and also to changes in all properties of the materials [1]. The change over the time of physical properties is typical for all the materials [2], including radiation resistant as ferrite garnets, and the restructuring and migration of defects in the crystal lattice during the exploitation are the main factors that lead to changes in the exploitative characteristics of devices with implanted epitaxial ferrite-garnet films. Therefore, it is important to study the time stability of the structural parameters of the modified layer, establish the regularities of the restructuring of their crystalline structure during aging at room temperatures and predict their behavior during the process of exploitation.

The purpose of this work was to study the time stability of structural parameters of near-surface layers of epitaxial films of ferrite garnets implanted by F^+ ions and establish the regularities of their crystalline structure rearrangement during aging at room temperatures and similar aging after laser annealing.

I. Objects and methods of research

The films of lanthanum-gallium substituted yttrium iron garnets (LaGa:YIG) were studied. They were grown by the method of liquid-phase epitaxy on the substrates of gadolinium-gallium garnet (GGG) with a plane (111). Implantation of ions F^+ was carried out with an energy of 90 keV in the range of doses $1\cdot10^{13}$ cm^{-2} – $2\cdot10^{14}$ cm^{-2}.

X-ray structural investigations were carried out by methods two-crystal diffractometry at the DRON-3 (monochromator GGG or two-crystal monochromator *Ge* (in mutually dispersed positions)) using CuK_{a1} radiation.

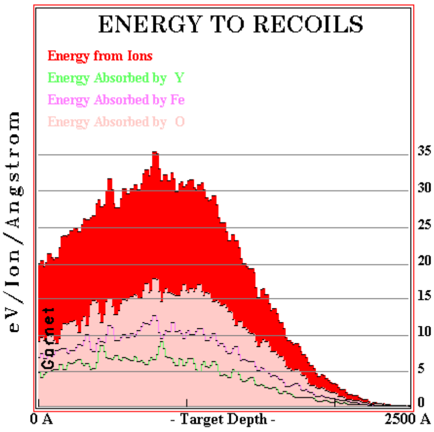
Strain profiles $Dd/d(z)$ and defect parameters obtained from the experimentally rocking curves were calculated. These calculations were made by simulating the propagation of X-rays in a nonideal crystal by means of the statistical dynamic theory of scattering of X-rays. The method which was used to analyze the rocking curves is described in detail in [3].

II. Crystal structure of the films of LaGa:YIG impaled by F^+ ions

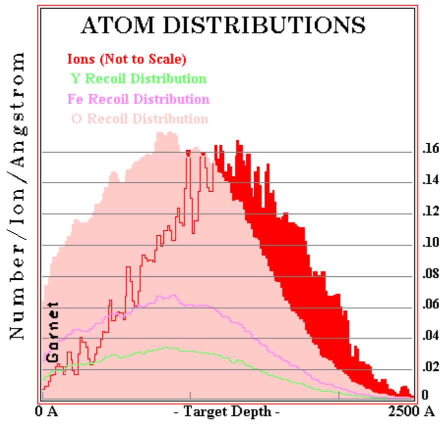
To analyze the processes that occur during ion implantation and subsequent deformation of the near-surface layer, we will use the approaches that were used in our article [4] while studying the aging processes in implanted by B^+ ions yttrium iron garnet films.

With the help of the SRIM [5] program profiles of losses of ions energy in nuclear subsystem were calculated (Fig. 1, a) and the distribution of implanted fluorine ions and displaced ion matrices (Fig. 1, b). From Fig. 1, b it is seen that the maximum of implanted fluorine ions is at a depth of ~ 1200 Å, the maxima of the displaced ion of the matrix and the maxima of the profiles of losses of ions energy in nuclear subsystem coincide and equal to ~ 800 Å.

The statistical analysis of the results simulation of a full cascade of collisions on the basis of the theory of elastic collisions using the SRIM program showed that the energy transmitted by the ion to the nuclear subsystem of the matrix throughout the length of the track in many cases reaches the values necessary for the development of the secondary displacement cascade (Fig. 2). It has been established that for fluorine ion implants with the energy of 90 keV the process of generating Frenkel pair (one displaced atom) is the most probable (≈ 46%). The probability of the development of cascade from two recoil atoms is ≈15%, from three ≈8%. It turns out that there are cascades which consist of 20 or more displaced atoms of the matrix (6.5%). There are also cascades containing more than 160 decayed atoms (0.18%). Radiation clusters and dislocation loops formed from large cascades are taken into account in the diffraction model while determining the parameters of



a



b

Fig. 1. Profiles of losses of ions energy in nuclear subsystem (a) and profiles implanted fluorine ions and displaced ions of the main components of the matrix (b). Implantation by F^+ ions, E = 90 keV.

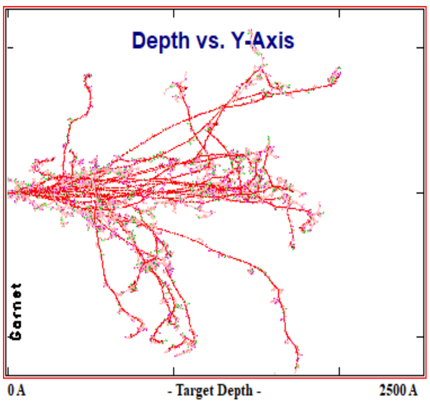


Fig. 2. Simulation tracks of Fluor ions in LaGa:YIG. Implantation by F^+ ions, E = 90 keV.

Fig. 3. Growing clusters in the structure of LaGa:YIG films.

the structure of the disturbed layer.

Not only do the nuclear energy losses (interaction of the implant with the nuclei of the ions of the matrix) occur, but also an inelastic interaction of the ion-implant with electrons during the motion of an ion-implant in a crystal. As shown in [6], this interaction may also lead to the formation of radiation defects. Therefore, while analyzing experimental rocking curves, the strain profile was considered to be proportional to the defect profile (which is valid for irradiation doses in which the amorphization of the structure is insignificant) and was given as a sum of asymmetric Gaussian (describes defect formation due to nuclear losses of ions energy) and downward Gaussian (describes defect formation due to electronic losses of ions energy). According to the results of ion implantation simulation, it can also be assumed that the strain profiles will extend to a depth of 2500 Å and have maximums in the region of ≈ 800-900 Å.

Using optical microscopy, it was found that triangular and hexagonal clusters of size 8-40 mkm in the studied films (Fig. 3). These may be clusters of technological impurity, such as platinum or iridium. These clusters are located in the plane of growth (111) of garnet films, and for their inclusion in the diffraction model it is necessary to take into account the anisotropy in their orientation. To do this, corresponding functional dependences were obtained using the statistical dynamic theory of diffraction [7, 8]. Authors of this article have taken into account both the orientation of the cluster and the shape of the field of mechanical stress created by it. Also, used diffraction model takes into account the anisotropy in the orientation of the dislocation loops in the ion-implanted layer. Defects in the crystalline structure of the substrate, film and disturbed layer were taken into account for analysis of structure of disturbed layers [9].

In [10] was described the strain profiles we have defined for implanted by F^+ ions LaGa:YIG films. Although there they were calculated in the form of only one asymmetric Gaussian, they express all basic characteristics of the distribution of deformation in the ion-implanted layer. For this reason, they are not given in this paper, but we will provide only their general characteristics. The deformation maximum in that profiles is situated on a depth of 500-600 Å and the deformation extends to a depth of 2500 Å. At low doses of implantation, the profiles are monotonically decreasing, and with large nonmonotonic ones. Dependence of the magnitude of the maximum relative deformation of the lattice on the dose of implantation in the studied dose interval is linear. The thickness of the deformed layer at all doses is the same. Maximum deformations at the implantation dose of $1\cdot10^{13}$-$2\cdot10^{13}$cm^{-2} are on the surface; with increasing dose they are shifted to the depth of the film.

III. Structural transformations in ion-implanted La, Ga: YIG during the natural aging

Over time, even at room temperatures there are intense diffusion processes in the ion-implanted layer [11, 12]. The study of changes in the structure of ion-implanted layers over time was carried out on LaGa:YIG films implanted by F^+ ions with energy 90 keV and doses $4\cdot10^{13}$ cm^{-2}, $8\cdot10^{13}$ cm^{-2} $2\cdot10^{14}$ cm^{-2}. The rocking curves were obtained in 4, 11 and 14 years after ion implantation and storage of ion-implanted films at room temperature. Changes can be seen on the experimental rocking curves obtained at certain intervals (Fig. 4, a). First of all, this is manifested in the region of an additional oscillatory structure. The angular length of the additional oscillatory structure over time initially increases slightly, and then decreases, which is evidence of a nonmonotonic change in the maximum deformation of the ion-implanted layer.

Calculated strain profiles for LaGa:YIG film implanted dose of $8\cdot10^{13}$ cm^{-2}are shown in Fig. 4, b. As we see, there is a slight increase in the maximum deformation with the simultaneous displacement of the profile to the surface. After this stage of aging there is a decrease in the maximum deformation. A diffusion model describing such behavior of strain profiles is considered in [13]. It is worth noting that the changes in

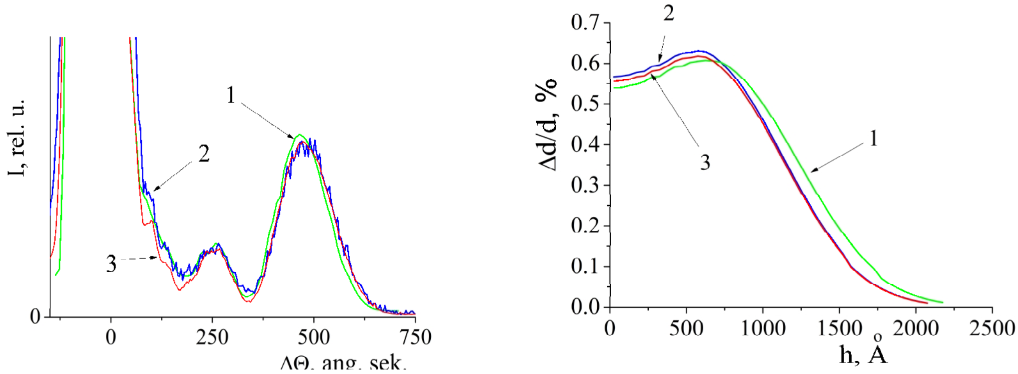


Fig. 4. Experimental rocking curves (444) (a) and corresponding strain profiles (b), obtained from films LaGa:YIG implanted by F^+ ions immediately after implantation (1), after 11 years(2) and after 14 years (3) (irradiation dose was $8\cdot10^{13}$ cm^{-2}).

near-surface ion-implanted layers described in [13] were much larger, which is due to a much larger diffusion mobility of helium in the ion-implanted layer.

IV. Structural transformations in ion-implanted and laser irradiated La, Ga:YIG during the natural aging

In order to eliminate the radiation defects formed as a result of ion irradiation, increase the thermostability of the structure, and partial removal of mechanical stresses [14, 15], laser irradiation of the films was performed. A pulse laser YAG: Nd^{3+} with pulse E = 0.04 J, pulse duration τ = 15 ns, and pulse follower frequency f = 56 Hz were used. The irradiation duration varies within 25-35 s. The films were irradiated with a laser both from implanted and from nonimplanted side (from the side of the substrate). The rocking curves was obtained immediately after ion implantation and laser irradiation, and 7 years after storage of ion-implanted films at room temperature.

Given that for the films under $hc/\lambda < E_g$ (λ = 1,06 mkm – wavelength of laser radiation, E_g = 2,8 eV – width of the band gap), the energy of laser radiation is absorbed mainly by the imperfections of the crystalline structure formed both in the process of growth of ferrite-garnet films and by generated ion implantation. Obviously, the concentration of defects in the ion-implanted layer of the garnet film is several orders of magnitude larger than that of the non-implanted one, and consequently, the effect of the laser irradiation is most fully manifested in this layer.

Laser irradiation stimulates diffusion and recombination processes, and thus partial or complete elimination of radiation defects created by ion irradiation proceeds [2, 14]. This is possible both as a result of the recombination of neighboring Frenkel pairs (most likely oxygen-anion vacancy) and the movement of defects to the surface of the runoff (dislocation loops, surface). In case of laser annealing, deformation gradient and temperature gradient are one of the determining factors of the motion of defects [16, 17].

Rocking curves from samples after ion implantation, annealing and natural aging are shown in Fig. 5.

As can be seen from the length of the additional oscillatory structure of the rocking curves (Fig. 5), after the laser annealing, the maximum deformation slightly decreased. Reducing the maximum deformation is more in the sample implanted from the side of the substrate. The effect of further natural aging for 7 years manifests itself in the redistribution of deformation in the thickness of the disturbed layer. The natural aging of the sample irradiated by the laser from the side of the substrate does not lead to a noticeable change of the maximum deformation. The natural aging of the sample irradiated by the laser from the side of the disturbed layer is manifested in a slight decrease of the maximum deformation.

The difference between the rocking curves and, accordingly, the difference between the strain profiles of samples irradiated from different sides (from the side of the implanted layer and from the side opposite to the implanted layer), indicates that changes in the strain profile after laser irradiation are influenced by both factors − deformation gradient and temperature gradient. In particular, in [18] it is shown that irradiation of ion-implanted ferrite garnet films from the side opposite to the implanted layer is more effective (the strain profiles were defined in the form of only one asymmetric Gaussian). This is due to the lower concentration of radiation defects, which absorb the energy of the laser beam on its path to the layer with maximum deformation. It is worth paying attention that after laser annealing and natural aging, the rocking curves from films with laser irradiated of different sides do not differ in accuracy, and, therefore, the strain profiles are the same. Thus, the difference in the influence of laser irradiation was compensated by the difference in diffusion processes during natural aging.

It is worth noting that some questions to the accuracy

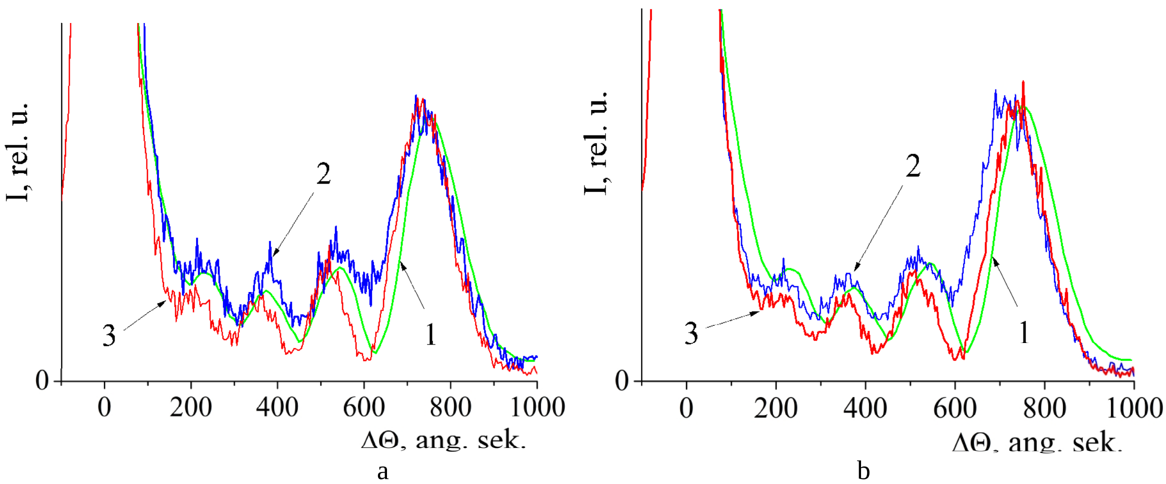


Fig. 5. Rocking curves from films after ion implantation – 1, laser annealing – 2, and natural aging for 7 years – 3: a – films were irradiated by a laser from the implanted side, b – the films were irradiated by the laser from the side of the substrate.

of the obtained rocking curves arise due to small changes in the rocking curves during the natural aging at room temperature. Therefore, we would like to note that an X-ray diffractometer automatic control system was developed. Automatic control of goniometer, reading and saving of diffractograms were performed using software through a personal computer. A special system of photophixation with the corresponding software has been developed in order to improve the accuracy and control of the angular position of the sample and the counter, which makes it possible to significantly increase the accuracy of the definition of diffraction data. Also, control of diffractometric data was obtained by obtaining control diffractograms using other modern X-ray diffractometers.

Conclusions

1. During the natural aging of films LaGa:YIG implanted by F^+ ions in the disturbed layer there are two consecutive processes:

- a slight increase of maximum deformation with the simultaneous displacement of the strain profiles to the surface;
- decrease of deformation throughout the thickness of the disturbed layer.

2. Results of laser annealing and natural aging of near-surface layers implanted by F+ ions and laser irradiated, depend on the direction from which laser irradiation occurred. They are manifested in the redistribution of deformation in the thickness of the disturbed layer.

3. After laser annealing and natural aging for 7 years irrespective of the direction from which laser irradiation occurred, the strain profiles within the limits of accuracy are the same, that is, the difference in the influence of laser irradiation was compensated by the difference in diffusion processes during natural aging.

Ostafiychuk B.K. - corporation member NAS of Ukraine, Doctor of Sciences (Physics and Mathematics), Professor of the Department of Materials Science and New Technologies.
Yaremiy I.P. - Doctor of Physical and Mathematical Sciences, Professor of Department of Materials Science and New Technologies;
Yaremiy S.I. - PhD, Assistant of Department of Medical Informatics, Medical and Biological Physics;
Povkh M.M. - postgraduate student;
Yablon L.S. - Doctor of Physical and Mathematical Sciences, Associate Professor, Department of Theoretical and Experimental Physics
Budzulyak I.M. - Doctor of Physical and Mathematical Sciences, Professor of Department of Materials Science and New Technologies..

[1] Ion beam applications in surface and bulk modification of insulators (International Atomic Energy Agency, Vienna, 2008).
[2] V.S. Vavilov, A.E. Kiv, O.R. Niyazova, Mekhanizmy obrazovaniya i migratsii defektov v poluprovodnikakh (Nauka, Moskva, 1981).
[3] I. Yaremiy, S. Yaremiy, M. Povkh, O. Vlasii, V. Fedoriv, A. Lucas, Eastern-European Journal of Enterprise Technologies, 6(12 (96)), (2018) (doi: 10.15587/1729-4061.2018.151806).
[4] I.P. Yaremiy, M.M. Povkh, V.O. Kotsyubynsky, V.D. Fedoriv, S.I. Yaremiy, R.I. Pashkovska, Physics and Chemistry of Solid State, 20(1), (2019) (doi: 10.15330/pcss.20.1.56-62).
[5] J.F. Ziegler, J.P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids (Pergamon Press, New York, 1985).
[6] B.K. Ostafiychuk, V.D. Fedoriv, I.P. Yaremiy et al., Phys. Status Solidi A 208(9), (2011) (doi: 10.1002/pssa.201026749).
[7] V.B. Molodkin, S.I. Olikhovskii, E.N. Kislovskii et al., Phys. Status Solidi A 227(2), (2001).
[8] S.I. Olikhovskii, V.B. Molodkin, E.N. Kislovskii et al., Phys. Status Solidi A 231(1), (2002).
[9] V.M. Pylypiv, O.S. Skakunova, T.P. Vladimirova et al., Metallofizika i Noveishie Tekhnologii 34(11) (2013).
[10] B.K. Ostafiychuk, V.D. Fedoriv, L.S. Yablon et al., Physics and Chemistry of Solid State, 3(4), (2002).
[11] I. Izhnin, V. Bogoboyashchyy, F. Sizov, Proc. SPIE 5957, 595713 (2005).
[12] I.I. Izhnin, E.I. Fitsych, A.Yu. Bonchik, G.V. Savitskiy i.dr., Izvestiya vysshikh uchebnykh zavedeniy. Fizika 55 (8/2) 150 (2012).
[13] B.K. Ostafiychuk, I.P. Yaremiy, S.I. Yaremiy et al., Metallofizika i Noveishie Tekhnologii 35(10) (2012).
[14] A.V. Dvurechenskiy, G.A. Kachurin, E.V. Nidaev, L.S. Smirnov, Impul'snyy otzhig poluprovodnikovykh materialov (Nauka, Moskva, 1982).
[15] R.I. Batalov, V.V. Vorobev, V.I. Nuzhdin et al., Opt. Spectrosc. 125, 571 (2018). (doi: 10.1134/S0030400X18100065).
[16] V.P. Voronkov, G.A. Gurchenok, Fizika i tekhnika poluprovodnikov (10), 1831 (1990).
[17] V.V. Titov, Rol' mekhanicheskikh napryazheniy pri legirovanii materialov s pomoshch'yu ionnykh puchkov (Preprint IAE-3774/11, Moskva, 1983).
[18] B.K. Ostafiychuk, I.M.Budzulyak, I.P. Yaremiy et al., Physics and Chemistry of Solid State, 9(1), (2008).

Б.К. Остафійчук[1], І. П. Яремій[1], С. І. Яремій[2], М. М. Повх[1],
Л. С. Яблонь[1], І. М. Будзуляк[1]

Процеси старіння в імплантованих іонами фтору та лазерно опромінених плівках LaGa:ЗІГ

[1]ДВНЗ «Прикарпатський національний університет імені Василя Стефаника», м. Івано-Франківськ, 76018, Україна,
yarimiyip@gmail.com
[2]ДВНЗ «Івано-Франківський національний медичний університет», м. Івано-Франківськ, 76000, Україна,
Yaremiy.S.I@gmail.com

На основі результатів Х-променевого структурного аналізу вивчено зміни кристалічної структури під час природного старіння та лазерного відпалу, які відбувалися в приповерхневих шарах епітаксійних плівок LaGa-заміщеного залізо-ітрієвого гранату, імплантованого іонами F^+. Розглянуто процеси, що відбуваються під час імплантації іонами F^+ ферит-гранатових плівок, та процеси, які супроводжують низькотемпературне старіння іонно імплантованих плівок. З експериментальних кривих дифракційного відбивання, отриманих відразу після іонної імплантації, після лазерного опромінення та через кілька років, визначено профілі деформації. Виявлено два етапи в змінах кристалічної структури приповерхневого порушеного шару з часом. На протязі першого з них максимальна деформація в іонно імплантованому шарі незначно зростала, а на другому зменшувалася. Встановлено, що результати лазерного відпалу та природного старіння приповерхневих шарів імплантованих іонами F^+ та лазерно опромінених плівок LaGa:ЗІГ залежать від того, з якої сторони відбувалося опромінення лазером. Однак, результат їх сумарного впливу не залежить від сторони лазерного опромінення.

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