The growth of iron-yttrium garnet Y₃Fe₅O₁₂ (YIG) films with of 1...15 μm thicknesses on single-crystal substrates of gallium-gadolinium garnet Gd₃Ga₅O₁₂ (GGG) was carried out using the method of liquid phase epitaxy (LPE).

The influence of the composition and mass of the charge, the temperature regimes, the rates of movement and the substrate rotation on the films parameters were studied. The layered structure caused by the heterogeneity of the chemical composition in the film thickness was determined and studied. The dependence of the degree impurity of Pb²⁺ and Pt⁴⁺ ions in YIG films and their influence on the ferromagnetic resonance (FMR) line width ∆H on the films growth conditions was investigated. It’s shown that in order to obtain by the LPE method the series of defect-free films with low magnetic losses and reproducible parameters, it’s necessary to use melt-solutions of large mass (6...12 kg) and apply their additional mixing during the growth process.

Keywords: iron-yttrium garnet, ferrite-garnet films, liquid phase epitaxy, ferromagnetic resonance.

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I. Experimental techniques

Currently the method of liquid-phase epitaxy is the most recognized for obtaining the monocristalline YIG films.

YIG films were grown by isothermal dipping of GGG single crystalline substrates of (111) orientation in the oversaturated melt-solution (MS) of ferrite charge using...
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\[ R_1 = \frac{\text{Fe}_2\text{O}_3}{\text{Y}_2\text{O}_3}; \]
\[ R_3 = \frac{\text{PbO}}{\text{B}_2\text{O}_3}; \quad (1) \]
\[ R_4 = \frac{\text{Fe}_2\text{O}_3 + \text{Y}_2\text{O}_3}{\Sigma \text{oxides}}. \]

Melting of the charge, its homogenization and films growth were carried out in platinum crucibles. The saturation temperature \( T_s \) of the melt-solution was determined as the temperature of the beginning of film growth on the substrate.

The substrates with a diameter of 50.8 mm were cut from the GGG single crystal of cylindrical form. It’s known that the GGG crystal lattice parameter \( a = 12.382 \) Å and for YIG \( a = 12.376 \) Å. The thickness of the substrates was 0.5 mm, and the density of defects on their area did not exceed 0.5 cm\(^2\). The substrates were mechanically ground and polished to 14- purity class. Such treatment does not completely eliminate the defects of the substrate surface layer. The defects appear after their etching in hot orthophosphoric acid. The presence of defects in the substrate leads to the increase \( \Delta H \) parameter of YIG films to 8.2…8.9 Oe.

Therefore the substrates else were subjected to chemical-mechanical polishing using the colloidal suspension. After that, the substrates were chemically polished in orthophosphoric acid at the temperature of 438 K.

An automated installation was used for epitaxial growth. The temperature in the furnace zones was maintained with an accuracy of ±0.1 K. The thickness of the grown films was 1…15 μm. Optical interference method was used to measure their thickness. The interference pattern is formed by measuring the transmission spectra when a light stream is incident on the sample in a direction close to normal. The measurement error of the film thickness did not exceed 2 %.

The transmission spectra of FES were obtained using Specord M-40 and Specord 75 IR spectrophotometers. The line width \( \Delta H \) of films was measured by the “magnetic gap” method [7] in which the area of localization of measurements is 0.4 mm. The saturation magnetization \( 4\pi M_s \) of films was measured using a vibrating magnetometer [8]. The structure and composition of epitaxial films were studied using an electron microscope with a Comebax X-ray microanalyzer.

II. Results of experiments and their discussion

The purpose of the technology of growing monocrystalline YIG films is to minimize to the acceptable level from the numbers of negative factors, which influence on the \( \Delta H \) value, the homogeneity of \( \Delta H \) over the film area, the repeatability of the main films parameters during the growth of the series films. Therefore, to obtain high-quality films suitable for practical use, it’s necessary to control the composition and weight of the starting charge and the technological conditions of their growth.

For the small thicknesses of ferrite film (1...15 μm), the influence of the film-substrate (FS) transition layer and the film-air (FA) surface layer on its main parameters becomes significant. These layers have a defective structure compared to the film itself [9-11] and obviously contribute to the anisotropic properties of the film [12-16].

In the process of forming a ferro-garnet film the transition FS layer grows on the boundary between the YIG layer and the GGG substrate enriched with Ga\(^{3+}\) and Gd\(^{3+}\) ions.

These ions migrate into the melt-solution. As the result, the acid of the Gd\(_{2}\)Ga\(_{3}\)O\(_{12}\) substrate in the PbO-B\(_{2}\)O\(_{3}\) solvent at the beginning growth stage. The FS transition layer is a solid solution of YIG and nonmagnetic GGG. The Gd\(^{3+}\) and Ga\(^{3+}\) ions in this solid solution are introduced into the dodecahedral and tetrahedral positions of the ferro-garnet film, respectively. This transition layer has a lower saturation magnetization and a higher \( \Delta H \) value than the YIG. Since Gd\(^{3+}\) ions contribute to the increase of the \( \Delta H \) value through the mechanism of ionic relaxation. Consequently, the heterogeneity of the YIG film composition in the FS layer leads to the increase of the \( \Delta H \) parameter.

The decrease in the FS layer of Gd\(^{3+}\) and Ga\(^{3+}\) ions carried out by means of the selected molar ratio \( R_2 \) in the charge. The experiments with the PbO-B\(_{2}\)O\(_{3}\) solvent for value \( R_2 = 12.4; 14; 15.6; 16 \) showed that the degree of solubility of GGG substrates linearly increases with increasing concentration of B\(_{2}\)O\(_{3}\) in the solvent. It is necessary to use solvents with the lower content of B\(_{2}\)O\(_{3}\). During the films growth from the different charge compositions it was found that the most optimal for decreasing of Gd\(^{3+}\) and Ga\(^{3+}\) ions in the FS layer are MS with \( R_2 = 15.6 \).

The select of the \( R_2 \) ratio (1) was based on the need to decrease the quantity of Pb\(^{2+}\) and Pt\(^{4+}\) ions in the structure of the YIG films. The Pb\(^{2+}\) ions are introduced into the YIG film from the PbO-B\(_{2}\)O\(_{3}\) solvent and Pt\(^{4+}\) ions - from the crucible material [17]. The quantity of Pb\(^{2+}\) and Pt\(^{4+}\) ions is increases with the increase of the film growth rate, which is proportional to the overcooling degree \( \Delta T \) of the MS. The \( \Delta T \) is equal to the difference between the saturation temperature \( T_s \) and the film growth temperature \( T_f \), which is lower than \( T_s \): \( \Delta T = T_s - T_f \). For each MS composition there is a growth rate at which the film has a minimum value of the \( \Delta H \) parameter. The appearance of these minimums is explained by the same content of Pb\(^{2+}\) and Pt\(^{4+}\) ions in the YIG films. With equal in ratio of the Pb\(^{2+}\) and Pt\(^{4+}\) ions in the film, the charge compensation is realized. That eliminating is causes of the appearance of Fe\(^{3+}\) and Fe\(^{3+}\) ions in the films. The exchange of electrons between Fe\(^{3+}\) and Fe\(^{3+}\) ions leads to the increase of \( \Delta H \) parameter.

The coefficient \( R_1 \) (1) should be such that only the garnet phase crystallizes from the melt - solution. From the results of phase analysis of charges it was obtained that this requirement realized when \( R_1 = 11...30 \).

The Table 1 shows the growth technological
parameters for two FES with a thickness of 5 μm and different values of ΔH.

Table 1 shows that the minimum value of ΔH = 0.22 Oe has film No. 2 with almost the same contents of lead (0.23 mass. %) and platinum (0.21 mass. %). According to the data of Table 1, it can also be observed that with the increase the growth rate to 0.54 μm/min, the concentration of lead in the YIG film increases more quickly than the concentration of platinum. As the result, the also increases the ΔH to ΔH = 0.61 Oe.

Consequently, to obtain YIG films with minimal values of ΔH, it's necessary to set the rate of their growth at which the same concentrations of Pb⁵⁺ and Pt⁴⁺ ions are generated in the films, i.e. charge compensation is created. This growth rate must be supported constant when growing a series of films.

We have found that at the substrate rotation rate with ω =100 rpm/min the impurity of Pt⁴⁺ ions into the film structure increases with the increase of the overcooling degree of the MS. The concentration of Pb⁵⁺ ions in the YIG films also increases with increasing growth rate and decreases with decreasing of the MS overcooling degree. This means that it’s possible to create such technological regimes when the platinum and lead ions in the film have certain ratio concentrations. This way it is possible to influence on the ΔH line width.

At the first moment when the substrate is introduced into the melt-solution of the liquid phase epitaxy process the diffusion border layer is formed near the substrate. Further growth of the film is caused by mass transport of garnet-forming components through this layer [18]. The thickness δ of the diffusion layer depends on the growth parameters. With a stationary substrate this layer has a maximum thickness. When the substrate rotates, its thickness decreases with increasing rotation rate:

\[ \delta = 1.58 \frac{D^{1/3}}{\gamma^{1/6}} \omega^{1/2}, \]

D – diffusion coefficient; γ – kinematic viscosity; ω – the angular rotation rate.

This equation is valid if the laminar flows, arising due to convection, forms the homogeneous in thickness the flat diffusion layer along the crystallization front. The heterogeneity of the film thickness over its area influences on magnetic properties [19] and degree of practical use of the growing film.

At the growth of YIG films with the thickness of 1...15 μm using one-sided horizontal rotation of the substrate, the heterogeneity of the film thickness equal to 30...50 % and the FMR line width ΔH = > 100 % are observed (Table 2).

This heterogeneity is due to the formation of a convex diffusion layer at the crystallization front. The thickness of the diffusion layer increases to the center of the substrate. As can be seen from the Table 2 the ΔH increases with increase of the diffusion layer thickness. During reverse rotation, the shape and thickness of the diffusion layer change periodically. In this case, the heterogeneity of the film thickness over the area equal to 20...30 %, the ΔH ~ 50 %. The such periodic change is formed of a layered film structure with different lead content in the layers. Therefore, one-sided and reversed rotation of the substrate does not form a flat diffusion layer, which is necessary for growing YIG films with homogeneous parameters in over the area of film.

To include the total bulk of the melt-solution in the

<table>
<thead>
<tr>
<th>№ of the sample</th>
<th>Molar coefficients</th>
<th>Overcooling degree ΔT, K</th>
<th>Growth rate fg., μm/min</th>
<th>Content of Pb, mass. %</th>
<th>Content of Pt, mass. %</th>
<th>FMR line width ΔH, Oe</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>11.698</td>
<td>0.08</td>
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<td>0.54</td>
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<tr>
<td>2</td>
<td>25.0</td>
<td>0.13</td>
<td>10</td>
<td>0.35</td>
<td>0.23</td>
<td>0.34</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>№ of the sample</th>
<th>Thickness of the YIG film, μm at the distance from the edge, cm</th>
<th>FMR line width ΔH, Oe at the distance from the edge, cm</th>
</tr>
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<tbody>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
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<td>6.1</td>
<td>5.5</td>
</tr>
<tr>
<td>2</td>
<td>8.8</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>14.6</td>
<td>12.4</td>
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</table>

<table>
<thead>
<tr>
<th>№ of the sample</th>
<th>One-sided rotation of the substrate</th>
<th>Reverse rotation of the substrate</th>
<th>One-sided rotation of the substrate with mixer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.9</td>
<td>5.1</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>8.7</td>
<td>7.3</td>
<td>7.2</td>
</tr>
<tr>
<td>3</td>
<td>14.3</td>
<td>12.4</td>
<td>11.3</td>
</tr>
</tbody>
</table>
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Film growth process and to form a flat diffusion layer the method of additional mixing of the melt-solution with a special mixer was used. The mixer was attached to the holder substrate and rotates with substrate [20]. The mixer grips fresher liquid from the depths of the crucible and moves it to the surface of the grown film. At the same time, removes the used melt-solution, which is degraded on ferro-garnet components. Table 2 shows that when using a mixer the difference of the thickness over the films area does not exceed of 4% and the value of ΔH ~ 8 %.

Fig. 1 shows the FMR spectra of the YIG films grown by reverse rotation (1) of the substrate and by one-sided rotation (2) of the substrate together with the mixer. From Fig. 1 we can see that the FMR spectrum of the YIG film grown using reverse rotation has a distorted shape. The FMR resonance curve (2) for the YIG film grown with the use of a mixer has good resolution.

Using the method of X-ray spectral electron microanalysis, we studied the layered structure of YIG films of (111) orientation with thicknesses up to 5 μm. To investigate the FS and FA transition layers and their influence on the magnetic properties of the epitaxial ferrite films structures were subjected these structures to layered structure in relation to the values of ΔH and 4πMs parameters. This layered film structure is forms during the growth process. These layers have different thicknesses, are characterized by lower or higher saturation magnetization compared to YIG (for the YIG 4πMs = 1750 Gs) and much higher values of the ΔH parameters. For example, films 1 and 3 had a magnetization of 1780 Gs. After two etchings, their magnetization decreased to 1700 Gs. The increased magnetization of the FA layer of these films is due to the presence of a large number of Pb2+ ions in this layer, which displace Fe3+ ions from the octahedral positions of the garnet. In the transition FS layers with the thickness of 0.2 μm, there are large number of Ga3+ ions that displace Fe3+ ions from the tetrahedral positions of the garnet, decreasing the magnetization to 1470 and 1510 Gs, respectively (Table 3).

As noted above, in order to decrease the etching of the Gd3Ga5O12 substrate in the MS and, consequently, the decrease of Gd3+ and Ga3+ ions content in the MS, it’s necessary to decrease the boron oxide content in the solvent. However, a decrease of boron oxide content in the MS, along with positive factors also has negative ones - the compositional stability of the garnet phase is decreased and the volatility of lead oxide is increases. The highly volatility of PbO also leads to significant etching of substrates and films as they are lowering or lifting out of the growth furnace. Fig. 2 shows the surface of the YIG film etched by PbO vapor. To minimize of substrates and film etching the platinum screen should be attached below the substrate to the substrate holder. In our experiments the platinum mixer served as a screen.

The dependence of the thickness of the transition layers on the technological regimes was investigated. The thicknesses of the FS and FA layers are decreased if the substrate holder together with the mixer rotates at a frequency of ~ 50 rpm/min during the dipping of the substrate into the MS and the FES drawing from the MS after the end of the growing process. This can be explained by the removal of Gd3+, Ga3+ and Pb2+ ions from the substrate by the upward flow of fresh MS and supply the YIG components to the substrate.

The thickness of the FA layer also dependent on the rate of vertical movement of the substrate during its dipping and post growth removal from the melt-solution. Experiments have shown that the removal of FES from the

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### Table 3.

Thicknesses and magnetic parameters of three samples of YIG films during the etching process

<table>
<thead>
<tr>
<th>№</th>
<th>d, μm</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
<th>4πMs, Gs</th>
<th>ΔH, Oe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.1</td>
<td>1780</td>
<td>0.9</td>
<td>1780</td>
<td>0.8</td>
<td>1700</td>
<td>0.8</td>
<td>1710</td>
<td>0.7</td>
<td>1650</td>
<td>0.7</td>
<td>1600</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
<td>1780</td>
<td>0.83</td>
<td>1700</td>
<td>0.80</td>
<td>1710</td>
<td>0.64</td>
<td>1650</td>
<td>0.73</td>
<td>1600</td>
<td>0.7</td>
<td>1470</td>
<td>1.40</td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>1780</td>
<td>0.8</td>
<td>1700</td>
<td>0.71</td>
<td>1680</td>
<td>0.71</td>
<td>1590</td>
<td>0.7</td>
<td>1530</td>
<td>0.7</td>
<td>1460</td>
<td>1.34</td>
</tr>
<tr>
<td>4</td>
<td>3.8</td>
<td>1780</td>
<td>0.8</td>
<td>1700</td>
<td>0.71</td>
<td>1680</td>
<td>0.71</td>
<td>1590</td>
<td>0.7</td>
<td>1530</td>
<td>0.7</td>
<td>1460</td>
<td>1.34</td>
</tr>
</tbody>
</table>

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MS at a rate of ~ 20 cm/min minimizes the thickness of the surface layer of the FA and the change in the parameter \( \Delta H \).

When growing the series of films from the one MS the following reasons cause the depletion of the MS:

a) lead evaporation during homogenization and growth processes;

b) depletion of the MS into garnet-forming components during of the film growth process;

c) reducing of MS quantity due to the formation of droplets and small melt marks on the FES and equipment.

Based on our research, it was concluded that when growing YIG films it’s necessary to use a large mass of MS to minimize the change in the saturation temperature. This makes it possible to grow a larger number of films with identical parameters from one MS.

**Fig. 2.** The surface of the YIG film etchedby PbO vapor, zoom: x200.

Fig. 3 shows the influence of MS depletion on the \( \Delta H \) of YIG films grown from the melt-solution of 6 kg. It can be seen that the \( \Delta H \) increases with the number N of grown films. This increase of \( \Delta H \) is associated with a change in the starting ratio between the quantities of Fe, YG, and Pt ions in the film structure. The greater of the MS mass the greater the numbers N of films with similar parameters can be grown. The research results showed that the most favorable charge for growing the YIG films with a thickness of 1...10 \( \mu \)m and a diameter of 50.8 mm is a charge with the mass of 12.0 kg.

As the result of the research, the optimal weight composition of the melt-solution in which the solubility of GGG at growing temperatures is insignificant: PbO – 90.34 %; B_2O_3 – 1.81 %; Fe_2O_3 – 7.13 %; Y_2O_3 – 0.72 %. The YIG films with a thickness of 1...10 \( \mu \)m grown from this melt-solution on GGG substrates with a diameter of 50.8 mm have a FMR line width \( \Delta H = 0.3...0.5 \) Oe and are suitable for use in microwave devices.

**Fig. 3.** The dependence of the \( \Delta H \) FMR line width on the number N of grown films.

**Conclusions**

The optimal composition of the charge for growing YIG films by liquid-phase epitaxy is determined by the molar coefficients \( R_1, R_3 \) and \( R_4 \) which must have values: 11 \( \leq R_1 \leq 30 \); \( R_3 = 15.6 \) and \( R_4 = 0.13 \).

When growing a series of YIG films with similar parameters, it’s necessary to use melt solution of large mass (6...12 kg) with a high content of garnet-forming oxides and the use additional mixing.

To decrease the concentration of lead in the YIG films it’s necessary to grow the films at small overcooling.

The film-substrate layer is enriched with Ga\(^{3+}\) and Gd\(^{3+}\) ions and the surface layer of the YIG film is enriched with Pb\(^{2+}\) ions. Transition layers have different magnetizations from the main YIG film and have a higher FMR line width \( \Delta H \).

To obtain YIG films with narrow values of \( \Delta H \) it is necessary to set the growth rate at which similar concentrations of Pb\(^{2+}\) and Pt\(^{4+}\) ions are formed in the films.

The use of additional mixing of the melt-solution during the growing process decrease the thickness heterogeneity to 4 % and the \( \Delta H \) to 8 %.

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The epitaxial iron-yttrium garnet films with homogeneous properties…


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Епітаксійні плівки залізо-ітрієвого гранату з однорідними властивостями та вузькою шириною лінії ФМР

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Методом рідкофазної епітаксії (РФЕ) проведено вирощування плівок залізо-ітрієвого гранату Y3Fe5O12 (YIG) товщиною 1...15 мкм на монокристалічних підкладках галій-гадолінієвого гранату Gd3Ga5O12 (GGG). Досліджено вплив складу та маси шихти, температурних режимів, швидкостей руху та обертання підкладки на параметри плівок. Визначено та досліджено шарувату структуру, зумовлену неоднорідністю хімічного складу в товщині плівки. Досліджено залежність ступеня забруднення іонів Pb2+ та Pt4+ у плівках YIG та їх вплив на ширину лінії феромагнітного резонансу (ФМР) ΔH від умов росту плівок. Показано, що для отримання методом РФЕ серії бездефектних плівок з малими магнітними втратами та відтворюваними параметрами необхідно використовувати розчини-розплави великої маси (6...12 кг) та застосовувати їх додаткове змішування під час процесу росту.

Ключові слова: залізо-ітрієвий гранат, ферит-гранатові плівки, рідкофазна епітаксія, феромагнітний резонанс.