FORMATION OF Bi-SUBSTITUTED YTTRIUM IRON GARNET NANOSIZED FILMS

L. I. GURSKII, E. V. TELESH
Belarusian State University of Informatics and Radioelectronics
P. Brovka 6, 220013 Minsk, Belarus

M. A. KALANDA, A. A. PAULENKA
Scientific-Practical Materials Research Center NASB
P. Brovka 19, 220072 Minsk, Belarus
Kalanda@physics.by

V. A. UKHOV
Scientific-Industrial Enterprise "BELMIKROSISTEMY"
Korzhenevski 12, 220108 Minsk, Belarus

The staging realization of structural transformations in $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films during heating with various oxygen pressures (pO_2) is revealed at the analysis of oxygen exchange processes between the film and gas environment. It is established that the films annealed at 680 ºC and $pO_2=10^5$ Pa during 30 min show improved structural, optical and magnetooptical characteristics. This is caused by a crystallization of the amorphous film, a decrease of anionic vacancies and a compression of the charge disproportionation process $Fe^{3+} \leftrightarrow Fe^{4+} + Fe^{2+}$.

1. Introduction

The $Y_{3-x}Bi_xFe_5O_{12-\delta}$ (Bi:YIG) films have a number of substantial advantages: high transparency, a broad range of operating frequencies, giant Faraday rotation ($\Theta_F \sim (10\text{-}20)\times10^4$ deg/cm), good temperature and mechanical stability, high polarization twisting angle of electromagnetic reflection (~1.2 deg at λ=465 nm) *etc*. [1-3]. Nevertheless, these materials have not got a wide application in the electronic industry due to the technological problems of their acquisition. As the ion radius bismuth {$r(Bi^{3+})$ = 1.132 nm} is substantially larger than that of yttrium {$r(Y^{3+})$=1.017 nm}, the synthesis of $Y_{3-x}Bi_xFe_5O_{12-\delta}$ compound is problematic because it is not a thermodynamically stable phase at Bi concentrations higher than 60% [4]. The above problems bear witness of the expedience of a search for new approaches for the development of Bi:YIG films containing nanocrystallites. This is caused by the fact that the nanometric grain size expands a thermodynamic stability of the Bi:YIG films by formation point defects in the anion and cation sublattices [5]. In this concern a considerable interest is provoked by an investigation of the effect of gas-thermal conditions on

the film structure formation and creation of point defects which determine optical and magnetooptical properties of the films. This is important for the optimization of the conditions of an acquisition of nanosized films with the predetermined properties.

2. Experimental procedure

Oxygen sorption-desorption processes and calculations of the oxygen nonstoichiometry parameter (δ) in $Y_3Fe_5O_{12-\delta}$ single crystals and $Bi_xY_{3-x}Fe_5O_{12}$ films were investigated by means of the coulometric measuring complex "OXYLIT". X-ray diffraction investigations of the experimental samples have been carried out with the "DRON-3" setup with copper K_α-irradiation. Deposition of the $Bi_xY_{3-x}Fe_5O_{12-\delta}$ was carried out using a vacuum setup of "Z-400" (Leybold-Heraeus), equipped with the oil-free pumping system. For studies of the Faraday rotation in $Bi_xY_{3-x}Fe_5O_{12-\delta}$ films a modified version of the heterodyne interferometry has been used.

3. Results and discussion

The $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films were deposited at the rate of 6-9 nm/min on gallium-gadolinium garnet single-crystal substrates with (111) orientation. It was found that the films deposited at a substrate temperature of 120-150 ºC was amorphous. The additional gas-thermal treatment of the films was made with a goal of the garnet structure formation. Investigations of the oxygen exchange between the film and gas environment at various oxygen partial pressures (pO_2) were carried out for the optimization of annealing conditions. The coulometric titration data recorded in polythermal modes at 27-1097 ºC and pO_2 = 400 Pa, have shown the existence of 4 extrema of the oxygen precipitation rate at 370, 680, 910 and 1000 ºC. This points out the staging realization of structural transformations in the $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films (Fig. 1a). It was supposed that the first spike of oxygen desorption is caused by the oxygen diffusion on grain boundaries. This fact is confirmed by a consistence of transmission coefficient (***t***) values after the $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ film annealing at 370 ºC and pO_2=400 Pa during 15, 30 and 45 min. The emergence of a cubic structure corresponding to the *Ia3d* space group was observed after annealing at 680 ºC and pO_2=400 Pa for 15 min. During the study of the dispersion dependence of annealing time it was found that the films annealed for 30 min had a maximal transmission at λ = 800-1000 nm (Fig. 2).

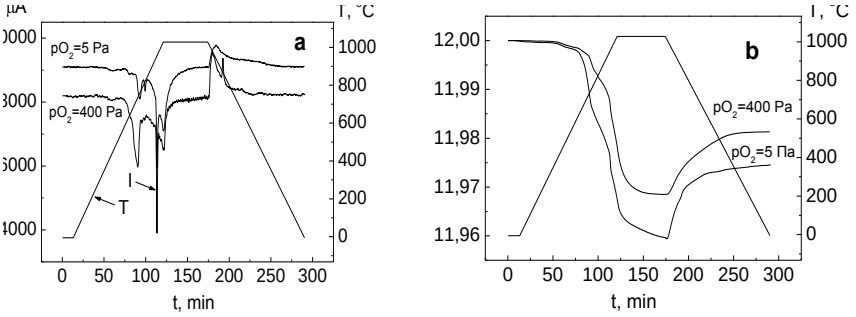

Figure 1. Time dependences of titration current (a) and oxygen index (b) of the $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films.

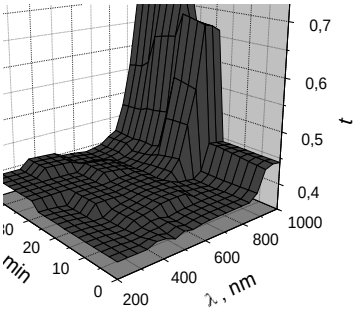

Figure 2. Dispersion dependence of the $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films transmission coefficient (*t*) in the wavelength range 300-1000 nm.

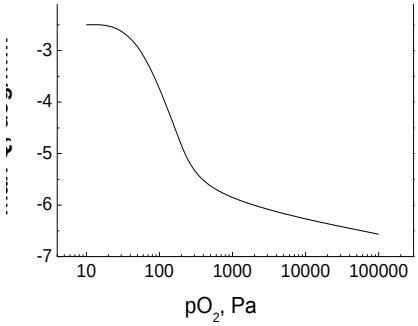

Figure 3. The influence of oxygen partial pressure on the Faraday rotation values ($max\Theta_F$) of polarization plane of electromagnetic wave passing through the $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films.

One can suppose that during film annealing at 680 ºC and pO_2=400 Pa, the anion vacancies [V_o] formation takes place within the first 30 min. This promotes redistribution of electron density with a decrease of [Fe^{4+}] cations concentration which stimulates the increase of ***t*** value. During further annealing up to 45 min accumulation of [Fe^{2+}] cations occurs which leads to an increase of optical absorption of the film which is confirmed by the following experimental results.

At the consideration of the oxygen desorption spectra of the films annealed at pO_2=5 Pa in the polythermal mode the fourth extreme value of the oxygen desorption at 810 ºC appears and the amount of precipitated oxygen increases (Fig. 1). An accumulation of Fe^{2+}cations is expected. Due to their large ion

radius they are located only in the octahedron positions of the garnet crystal lattice and stimulate disproportionation of the charge passing according to the scheme $Fe^{3+} \leftrightarrow Fe^{4+} + Fe^{2+}$. This mixed state should promote thermodynamically stable coexistence of the aggregates, and the increase of the optical absorption of the film, which is actually observed. In that case the process of film recovery is presented by a quasi-chemical reaction of the following form: $\{Y_{3-x}^{3+}Bi_x^{3+}\}[Fe^{3+}_2](Fe^{3+}_3)O_{12}^{2-} \leftrightarrow \{Y_{3-x}^{3+}Bi_x^{3+}\}[Fe^{2+}_{2\delta}Fe^{3+}_{2-2\delta}Fe^{4+}_{\delta}](Fe^{3+}_{3-3\delta}Fe^{4+}_{\delta})(V_O^{\bullet}V_O^{\bullet\bullet})_{\delta}O_{12}^{2-} + \delta/2O_2\uparrow$. During the oxidation of $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films at 680 ºC and $pO_2=10^5$ Pa for 15, 30 and 45 min, according to the data of $\boldsymbol{t} = f(\lambda, t)$ and $\Theta_F = f(t)$ a decrease of Fe^{2+} concentration was observed (Fig. 3). A sharp increase of the optical transmission starting at 800 nm corresponds to the electron transitions of Fe^{+3} cations which locate in octahedron positions of the garnet crystal lattice after Fe^{2+} cations oxidation according to the scheme $Fe^{2+} \leftrightarrow Fe^{3+} + e$. One should suppose that the suppression of optical absorption in the red range of the spectrum is caused by the sharp decrease of a number of point defects responsible for the broad absorption bands.

4. Conclusions

It is established that $Bi_{1.8}Y_{1.2}Fe_5O_{12-\delta}$ films annealed at 680 ºC and $pO_2=10^5$ Pa for 30 min show improved structural, optical and magnetooptical characteristics. This is caused by a chemical process of the formation of the crystal film from the amorphous one, a decrease of anionic vacancies with various effective charge values, and a compression of the charge disproportionation process, which considerably lowers the optical transmission.

References

1. T. Okuda, T. Katayama, H. Kobayashi, N. Kobayashi, *J. Appl. Phys*. **67**, 4944 (1990).
2. T. Okuda, N. Koshizuka, K. Hayashi *et al.*, *IEEE Trans. Magn.* **MAG-23**, 3491 (1987).
3. M.-Y. Chern, F-.Y. Lo, D.-R. Liu *et al.*, *Jpn. J. Appl. Phys.* **38**, 6687 (1999).
4. M. Gomi, K. Satoh, M. Abe, *Proceedings ICF* (*India)* 919 (1989).
5. M. Inoue, T. Fujii, *J. Appl. Phys.* **81**, 5659 (1997).

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