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Edge Absorption of $(Y_{0.06}Ga_{0.94})_2O_3$ Thin Films

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Fundamental absorption edge of $(Y_{0,06}Ga_{0,94})_2O_3$ thin films, obtained by radio-frequency ion-plasmous sputtering, was investigated using the method of optical spectroscopy. It was established that these films are formed in the monoclinic structure of β-Ga_2O_3. The optical band gap of these films is greater than β-Ga_2O_3 films and is 4.66 eB for films annealed in oxygen atmosphere, 4.77 eV for the films annealed in argon atmosphere and 4.87 eV for the films, restored in a hydrogen atmosphere. Consolidated effective mass of free charge carriers in $(Y_{0,06}Ga_{0,94})_2O_3$ films after annealing and after reconstitution in hydrogen was estimated. It was found that the concentration of charge carriers after annealing in oxygen atmosphere is 1.32×10^{18} cm^{-3}, after annealing in argon atmosphere - 3.41×10^{18} cm^{-3} and after reconstitution in hydrogen is 5.20×10^{18} cm^{-3}, which is typical for degenerated semiconductors. It was shown that the shift of fundamental absorption edge in $(Y_{0,06}Ga_{0,94})_2O_3$ thin films is caused by Burstein-Moss effect.

Key words: gallium and yttrium oxide, thin films, fundamental absorption edge.

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Introduction

Recently, the metal oxide materials are attracting much attention through wide possibilities of their use in modern optoelectronics and instrument engineering. A large band gap, high values of dielectric permeability make them promising the development of full-color screens, reflective coatings, gas sensors, UV detectors. Among these compounds, recent investigations have revealed a number of interesting properties of Ga_2O_3 films, obtained by different methods [1 – 4]. The pure or doped Ga_2O_3 thin films are widely applied as transparent conductive electrodes [5], phosphors [6, 7], cathode phosphors or electroluminescent phosphors [8 – 10] depending on the method of preparation and dopant. The Ga_2O_3 thin films can be dielectrics or semiconductors according to the conditions of preparation. The films obtained in oxygen atmosphere exhibit dielectric properties [11]. The films that are grown in a reducing environment exhibit semiconductor properties (n-type) [12]. In general, the optical and electrical properties of Ga_2O_3 films are determined by the methods of manufacture, regimes of coating and the following technological methods as well as introduction of impurities which can purposefully change the properties of thin layers of oxides. Therefore, we have investigated $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, where part of Ga^{3+} ions has been replaced by of Y^{3+} ions, it hasn't required local compensation of electric charge. It is because the Y_2O_3 films are also quite promising in terms of their use in optoelectronics and luminescent technique [13 – 16]. The investigation of optical properties of thin films, including edge absorption, seems quite actually as it gives important information about their energy structure. Therefore, in this paper we investigated the optical absorption edge of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, obtained by radio-frequency ion-plasmous sputtering, which is optimal to obtain semiconductor and dielectric films.

I. Experimental

Thin films of $(Y_{0.06}Ga_{0.94})_2O_3$ were obtained by radio-frequency ion-plasmous sputtering. The films were deposited on fused quartz υ-SiO_2 substrates. The thickness of the deposited films ranged between 0.2 μm and 1.0 μm. After deposition, thin films were subjected to heat treatment in oxygen atmosphere or in argon atmosphere at 1000–1100°C as well as reconstitution in hydrogen atmosphere at 600–650°C. X-ray diffraction investigations showed the presence polycrystalline structure which is slightly different depending on the method of heat treatment films. The typical X-ray diffraction patterns of the obtained films are shown in Fig. 1. Their analysis shows that the structure of these films corresponds monoclinic crystal structure β–Ga_2O_3.

The results indicate that in the thin films after annealing in oxygen atmosphere have observed preferred orientation in (110) (002) (111) and (512) planes. In the thin films after annealing in argon atmosphere observed predominant orientation in (002) and (111) planes and we can see a relative decrease orientation in (110) and (512) planes. For films, annealed in hydrogen atmosphere, observed redistribution of received reflexes and for these films the orientation prevails in (201), $(31\bar{1})$, $(40\bar{3})$ and $(31\bar{3})$ planes. Except the appearance of the most intense reflex from (201) plane which is a characteristic for structure β–Ga_2O_3, on X-ray diffraction pattern observed the reflex from (321) plane which is typical for $Y_3Ga_5O_{12}$ [17]. This indicates that in the $(Y_{0.06}Ga_{0.94})_2O_3$ thin films,

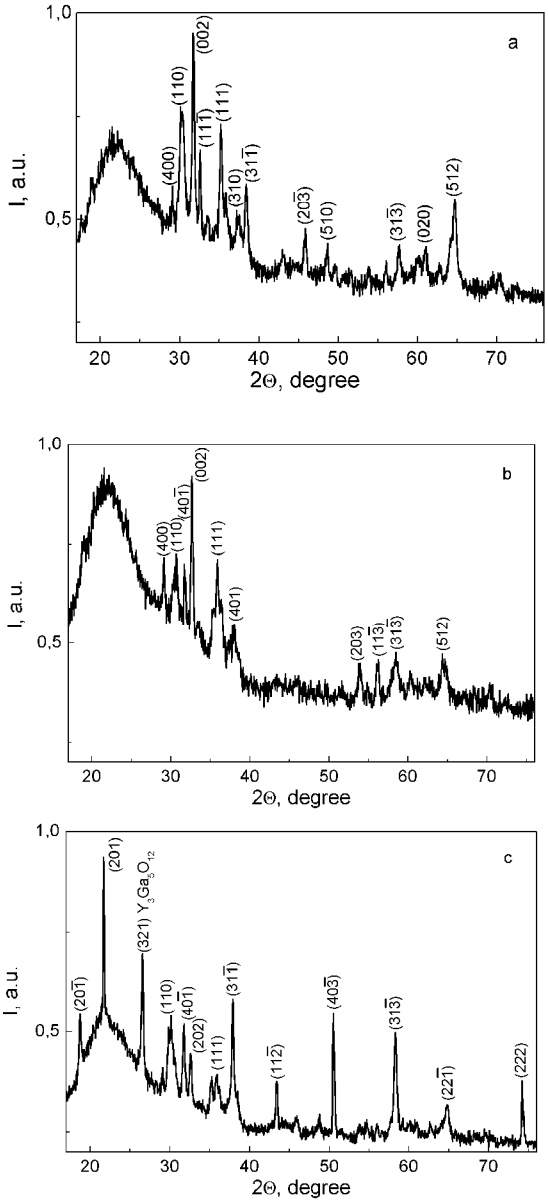

Fig. 1. The X-ray diffraction pattern (at Cu K_α - radiation) of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, obtained by radio-frequency ion-plasmous sputtering, after heat treatment in oxygen atmosphere (a), in argon atmosphere (b) and after reconstitution in hydrogen atmosphere (c).

except the main structural phase of β–Ga_2O_3, can be observed the presence of $Y_3Ga_5O_{12}$ yttrium-gallium garnet phase after annealing in hydrogen atmosphere. It quite good consistent with the results of investigation diagram state of Y_2O_3 – Ga_2O_3 system [18], where found that in such system at the contents of Ga_2O_3 more than 65 ml. % formed a complex of Ga_2O_3 and $Y_3Ga_5O_{12}$. In the same paper [18] found that in such a system if the content of Y_2O_3 to at least to 1.8 ml. % observed only the structure of Ga_2O_3. Changes in the structure was revealed at the presence of Y_2O_3 more than 23.6 ml. %. Thus, obtained results make it possible to assert that the structure of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films after annealing in oxygen atmosphere and in argon atmosphere is responsible the structure of β–Ga_2O_3 and in these thin films after reconstruction in hydrogen atmosphere observed the presence of $Y_3Ga_5O_{12}$ phase.

The theoretical analysis of experimental diffraction patterns makes it possible to establish such an important parameter of thin films as the size of crystallites. Using approximation the method of least squares individual reflexes from analytical dependence pseudo-Voigt determined integrated half-width reflexes, which subsequently used in finding the physical expansion of diffraction profiles. From these data, using the Scherrer equation, the size of crystallites (*D*) was calculated. In Table 1 are reported the results obtained for different types of $(Y_{0.06}Ga_{0.94})_2O_3$ films. It can be seen that the calculated values D indicate that the composition of the annealing atmosphere in this temperature range don't significantly influence on the size of crystallites.

Using energy dispersive spectrometer OXFORD INCA Energy 350 was executed elemental analysis of samples at several points on the surface of films. The calculations confirmed the correspondence percentage contents of components in received films to their percentage contents in $(Y_{0.06}Ga_{0.94})_2O_3$ compound.

Table 1

The sizes of crystallites of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films

The annealing atmosphere	The size of crystallites *D*, Å
Oxygen	342 ± 32
Argon	307 ± 32
Hydrogen	306 ± 32

II. Results and discussion

Figure 2 shows the typical transmission spectra $T(\lambda)$ for β–Ga_2O_3 thin films annealed in oxygen atmosphere and for $(Y_{0.06}Ga_{0.94})_2O_3$ thin films annealed in oxygen atmosphere (I), in argon atmosphere (II) as well as after the reconstruction in hydrogen atmosphere (III). These spectra in the wavelength region which are commensurate with the thickness of the films, due to the effect of interference have oscillating nature. Inasmuch, in the strong (interband) absorption region at T (λ) <0.3 we almost do not observe the interference therefore to determine the absorption coefficient of thin films $\alpha(h\nu)$ using the ratio [19]:

$$a(hn) = -\frac{1}{d}\cdot\ln\left[\frac{(n(hn)+1)^3\left(n(hn)+n_n^2\right)\cdot T}{16n_n\cdot(n(hn))^2}\right], \qquad (1)$$

where d is the thickness of the thin film; T is the relative

value of transmission; n and n_n is the refractive index of the film and the substrate, respectively. In order to calculate $\alpha(h\nu)$ was used the required quantities $n(h\nu)$ in the strong absorption region which determined by extrapolation dependence $n(h\nu)$ in this frequency region. The dependence $n(h\nu)$ found for the transparency region and weak absorption. The definition of such dependence and method of finding thickness of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films were based on the interference Valeev methods [20] and the example of β–Ga_2O_3 films that in detail described by us in [21].

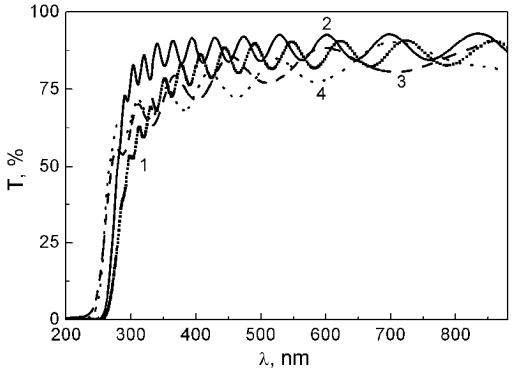

Fig. 2. The transmission spectra of β–Ga_2O_3 thin films annealed in oxygen atmosphere (1) and of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, I (2), II (3) and III (4).

As a result of our investigation has found that regardless of the atmosphere heat treatment the absorption coefficient $\alpha(h\nu)$ of thin films in the region fundamental absorption edge is described power function

$$a(hn) = \frac{A(hn - E_g)^{1/2}}{hn} \qquad (2)$$

from which we can determine the band gap E_g (Fig. 3). Such a course of the absorption edge is characteristic for the permitted direct photo transitions [22].

The analysis of the fundamental absorption edge by using equation (2) shows that the optical band gap in $(Y_{0.06}Ga_{0.94})_2O_3$ thin films is greater than β–Ga_2O_3 films and it increases at the replacement oxygen atmosphere annealing on the argon atmosphere annealing and especially after the subsequent reconstruction in hydrogen atmosphere. Meanwhile, it is also observed the increasing of coefficient A in the equation (2). In Table 2 are shown the typical values that we was obtained for E_g and A for the investigated thin films.

The annealing films in inert argon atmosphere relatively annealing in oxygen atmosphere leads to a relative increase the concentration of oxygen vacancies, scilicet to the increase number of structural defects.

If one takes into account that after re-annealing of thin films in hydrogen atmosphere at 600–650°C, that to were previously annealed in oxygen atmosphere or in argon atmosphere, the elemental composition of the films is practically unchanged (except hydrogen), it can be assumed that the change the optical band gap at the annealing is not associated with a change in stoichiometry of thin films. Probably, the one of the factors that determines the E_g at the annealing is to change the amount and nature of the hydrogen bonds due to the formation of structural defects.

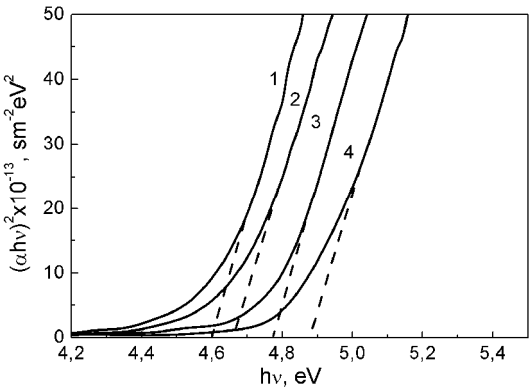

Fig. 3. The spectra of fundamental absorption in the coordinates $(\alpha \times h\nu)^2 = f(h\nu)$ for β–Ga_2O_3 thin films annealed in oxygen atmosphere (1) and $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, I (2), II (3) and III (4), respectively.

The increasing energy band gap by changing the amount of structural defects that leads to changes in the concentration of current carriers can be explained on the basis Burstein-Moss effect [23]. According to this effect, the absorption spectrum of heavily doped or strongly defective (degenerate) semiconductors similar to the absorption spectrum of non-degenerated semiconductor, but its edge is shifted towards the region of bigger energies. This situation, as seen on Fig. 3, is realized in $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, which can be regarded as strongly of Y_2O_3 doped β–Ga_2O_3 thin films and the increase defectiveness these thin films is achieved after annealing in argon atmosphere or especially after the reconstruction in hydrogen atmosphere.

For parabolic the conduction band and valence band at the direct-band transitions can be written:

$$E_g = E_{g0} + \Delta E_g^{B-M}, \qquad (3)$$

where E_{g0} is the own band gap, and ΔE_g^{B-M} is the the Burstein-Moss shift due to the filling the lower energy levels in the conduction band [24]. The magnitude of this shift is expressed as follows:

$$\Delta E_g^{B-M} = (h^2/8p^2m)(3p^2N)^{2/3}, \qquad (4)$$

where N is the concentration of free charge carriers, and μ is the their consolidated effective mass. This ratio shows that the value of the Burstein-Moss shift is proportional to the concentration of free charge carriers. We estimate the value of the concentration of free charge carriers in β–Ga_2O_3 films using previously determined value consolidated effective mass of free charge carriers based on the edge spectra absorption.

As we know from [25], in the direct band gap compounds in the case of an electronic transition between the valence band and the conduction band the spectral motion the absorption coefficient that describes the single-photon absorption edge, is defined as:

$$a(hn) = \frac{2e^2(2m)^{3/2}}{m^2 c\mathbf{h}^2 n}\left|P_m\right|^2 \frac{(hn - E_g)^{1/2}}{hn}, \qquad (5)$$

where μ is the consolidated effective mass ; $|P_\mu|^2$ is the square matrix element of the dipole transition; n is the refractive index in the region absorption edge.

If express the $|P_\mu|^2$ through the oscillator strength f_μ interband transition:

Table 2

The band gap Eg, the coefficient A in ratio (2), the consolidated effective mass *m* and the concentration of free charge carriers *N* in β–Ga_2O_3 and $(Y_{0.06}Ga_{0.94})_2O_3$ thin films

Film	E_g, eV	A, $sm^{-1}\times eV^{-1/2}$	m	N, sm^{-3}
Ga_2O_3	4.60	1.35×10^7	$0.281m$	
$(Y_{0.06}Ga_{0.94})_2O_3$ (I)	4.66	2.40×10^8	$0.349m$	1.32×10^{18}
$(Y_{0.06}Ga_{0.94})_2O_3$ (II)	4.77	2.49×10^8	$0.416m$	3.41×10^{18}
$(Y_{0.06}Ga_{0.94})_2O_3$ (III)	4.87	3.63×10^8	$0.641m$	5.20×10^{18}

$$\left|P_m\right|^2 = \frac{mhn}{2} f_m \qquad (6)$$

as well as if apply for the allowed transitions $f_\mu \approx 1$, we are obtain:

$$a \approx \frac{(2m)^{3/2} e^2}{mc\mathbf{h}^2 n}\left(hn - E_g\right)^{1/2}. \qquad (7)$$

Substituting numerical values using the straight sections of $(\alpha\times h\nu)^2=f(h\nu)$ (Fig. 3), we estimated the consolidated effective mass of free charge carriers in thin films. As a result, $\mu\approx0.281\ m$ for β–Ga_2O_3 films annealed in oxygen atmosphere, $\mu\approx0.349\ m$ for $(Y_{0.06}Ga_{0.94})_2O_3$ films annealed in oxygen atmosphere, $\mu\approx0.416\ m$ for films annealed in argon atmosphere and after reconstitution in hydrogen is $\mu\approx0.641\ m$ for $(Y_{0.06}Ga_{0.94})_2O_3$ films. The some increase the value of the consolidated effective mass the Y_2O_3-doped β–Ga_2O_3 films and especially after their annealing in argon atmosphere or after reconstruction in hydrogen atmosphere can be explained by increasing concentration of impurities or defects whereon can be localized the free charge carriers. The typical values of the consolidated effective mass of free charge carriers for the investigated films are shown in Table 2.

Using the defined value of the consolidated effective mass of free charge carriers of $(Y_{0.06}Ga_{0.94})_2O_3$ thin films and the obtained value of shift the band gap by Burstein-Moss effect ΔE_g^{B-M} based on the ratio (4) we can estimate the concentration of free charge carriers *N*. Based on the calculations obtain that the $N\approx1.32\times10^{18}$ см$^{-3}$ for $(Y_{0.06}Ga_{0.94})_2O_3$ thin films annealed in oxygen atmosphere, $N\approx3.41\times10^{18}$ см$^{-3}$ for thin films annealed in argon atmosphere and $N\approx5.20\times10^{18}$ см$^{-3}$ for films after reconstruction in hydrogen atmosphere. According to literature reports [26] in strongly doped, degenerate semiconductor the concentration of the charge carrier is from 10^{16} sm^{-3} to 10^{18} sm^{-3}. Sometimes the concentration to 10^{20} sm^{-3} was observed. Note also that the evidence of Burstein-Moss effect was found in β–Ga_2O_3 single crystals [27] as well as in the slightly related GaInZnO films [28] and ZnO:Ga films [29]. Thus, based on the investigation of the electrical conductivity in β–Ga_2O_3 single crystals were found that the concentration of charge carrier is $N\approx5.2\times10^{18}$ см$^{-3}$. Depending on the different number of structural defects the concentration of free charge carriers of GaInZnO thin films changed from 2×10^{19} to 6×10^{19} sm^{-3} [28], for ZnO:Ga thin films changed from 5.43×10^{18} to 2.48×10^{19} sm^{-3} [29]. Obtained by us the *N* values show that the determined quantity the concentrations of free charge carriers for the investigated films are characteristic of degenerate semiconductors and for them are inherent the Burstein-Moss effect. This confirms the existence of this effect in $(Y_{0.06}Ga_{0.94})_2O_3$ thin films after replacement in *b*–Ga_2O_3 thin films of Ga^{3+} ions on the Y^{3+} ions and after their annealing in argon atmosphere as well as after the reconstruction in hydrogen atmosphere when the fundamental absorption edge shifts to the high-energy region.

Conclusions

The investigation has shown that in the $(Y_{0.06}Ga_{0.94})_2O_3$ thin films, obtained by radio-frequency ion-plasmous sputtering, the fundamental absorption edge is formed by direct allowed phototransitions of electrons and regardless of the atmosphere heat treatment. Although the optical band gap Eg increases from 4.66 eV for films annealed in oxygen atmosphere to 4.77 eV for films annealed in argon atmosphere and to 4.87 eV for the annealed films after reconstruction in hydrogen atmosphere. The concentration of free charge carriers was estimated. It was shown that for $(Y_{0.06}Ga_{0.94})_2O_3$ thin films the shift of fundamental absorption edge is due to the Burstein-Moss effect.

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О.М. Бордун, І.Й. Кухарський, І.І. Медвідь, Ж.Я. Цаповська

Крайове поглинання тонких плівок $(Y_{0.06}Ga_{0.94})_2O_3$

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Методом оптичної спектроскопії досліджено область фундаментального поглинання тонких плівок $(Y_{0.06}Ga_{0.94})_2O_3$, отриманих методом високочастотного іонно-плазмового розпилення. Встановлено, що дані плівки формуються у моноклінній структурі β–Ga_2O_3. Оптична ширина забороненої зони даних плівок є більшою ніж у плівках β–Ga_2O_3 і становить 4,66 еВ для плівок, відпалених у кисні, 4,77 еВ для плівок, відпалених у аргоні і 4,87 еВ для плівок, відновлених у атмосфері водню. Оцінено зведену ефективну масу вільних носіїв заряду у плівках $(Y_{0.06}Ga_{0.94})_2O_3$ після відпалу плівок та після відновлення у водні. Встановлено, що концентрація носіїв заряду після відпалу у кисні становить 1.32×10^{18} $см^{-3}$, після відпалу в аргоні – 3.41×10^{18} $см^{-3}$, та після відновлення у водні – 5.20×10^{18} $см^{-3}$, що характерне для вироджених напівпровідників. Показано, що зсув краю фундаментального поглинання в тонких плівках $(Y_{0.06}Ga_{0.94})_2O_3$ зумовлений ефектом Бурштейна-Мосса.

Ключові слова: оксид ітрію і галію, тонка плівка, край фундаментального поглинання.