Rare Earth Doped Gallium Gadolinium Orthogallate Films Prepared by Pulsed Laser Deposition

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Abstract. The decomposition of Gd3Ga5O12 single crystal target induced by a KrF excimer laser pulse during the deposition process was observed. This phenomenon was studied ex situ by EDX analysis of ablated target and in situ by Optical Emission Spectroscopy of the laser plasma. The decomposition process depends mainly on the absorption coefficient of the target on the corresponding laser wavelength and oxygen partial pressure in the deposition chamber during laser ablation. Taking into account the differences between absorption coefficients of Pr:Gd3Ga5O12 and Yb:Gd3Ga5O12 targets the Pr:GdGaO3 and Yb:GdGaO3 thin films were successfully fabricated at different oxygen pressures of 1 Pa and 2.5 Pa, respectively. The structural properties of the fabricated films were studied by RBS and XRD.

1. Introduction

The rare-earth orthogallates (ReGaO3) are the most intriguing among the perovskite-like ABO3 compounds. They normally must be synthesized under conditions which differ from those used for the other ReBO3 perovskite compound (B=Fe, Al, Cr etc.) [1]. ReGaO3 crystal has the same perovskite structure as the very well known YAlO3 (YAP) crystal. It potentially can be an interesting material for laser techniques. However the growing of the rare-earth orthogallate (ReGaO3) is very difficult due to the fact that in oxide compounds the Ga3+ cation has a strong preference for tetrahedral coordination and in the perovskite structure they are all octahedral. The perovskite GdGaO3 have been obtained either by decomposition of the Gd3Ga5O12 (GGG) garnet at high pressure (45 kbars) and at high temperature around 1000°C in presence of flux [2] or by overheating of the 0.5 Gd2O3-0.5 Ga2O3 liquid mixture to 1900°C by using a CO2 laser [3,4]. Because of the perovskite phase being difficult to obtain, only a few works have been presented about the preparation and properties of GdGaO3 crystal, see e.g. [1-5]. Moreover the doping of this crystal by rare-earth and thin film fabrication up to now have not been presented.

Pulsed Laser Deposition (PLD) is a very powerful technique to grow crystalline complex-oxide waveguides especially because of the possibility to transfer materials from the target to the film keeping the stoichiometry [6]. However due to some processes occurring during film elaboration the films can have also composition significantly different from that of the bulk. In our previous study concerning deposition of waveguiding Pr:Gd3Ga5O12 (Pr:GGG) films from single crystalline target, a strong dependence of the Ga content in the film on oxygen ambient pressure was found [7]. Moreover for the first time, the epitaxial (110) Pr:GdGaO3 films were deposited on (010) YAP substrates from Pr:GGG target [8]. Unfortunately after successfully repeated experiments with Pr:GdGaO3 thin films,
the fabrication of Yb doped GdGaO$_3$ thin films from the Yb:GGG target by the same way was unsuccessful.

In this contribution we report on a study of decomposition of the GGG target induced by excimer laser radiation during the ablation process in oxygen ambient. Successful fabrication of epitaxial GdGaO$_3$ films doped by Pr and Yb on YAP substrate is presented.

2. Experimental

The Pr:GGG and Yb:GGG targets were cut from single crystals grown by the Czochralski method [9] with mean Pr and Yb concentration 1 at.% and 5 at.%, respectively. An excimer KrF laser was focused on the rotating target on a rectangular spot of 2.5x4 mm$^2$ area. The laser energy density (E) was modified by variation of the laser output in the range 0.5-6 J/cm$^2$. The (010) YAP substrates were positioned 45 mm away from the target. The depositions were carried out either at substrate temperature (T$_s$) equal of 800°C or at room temperature with a purpose to exclude the possibility that the decomposition of the target can be caused by the additional target heating from a massive holder during the deposition. The oxygen pressure (p$_O$) varied from 10$^{-2}$ Pa to 10 Pa.

In order to study more in detail the effect of GGG single crystal target decomposition, the laser plasma was monitored in situ by time-and spatially resolved Optical Emission Spectroscopy (OES). After each deposition the target composition was analyzed by spatially resolved Energy Dispersion X-Ray analyses (EDX). After EDX measurements the target was optically polish for next deposition. The structural properties and composition of the films were examined by conventional X-ray diffraction (XRD) and Rutherford backscattering spectroscopy (RBS), respectively.

3. Results and Discussion

In our previous works [7,8] concerning Pr:GGG we proved that the decreasing of the Ga content in the deposited film is caused by the decomposition of the Ga$_2$O$_3$ in GGG target induced by laser pulses to very volatile Ga$_2$O during the deposition, which is promoted at lower p$_O$. Fig. 1 compares the evolution of the [Ga]:[Gd] atomic ratio with oxygen partial pressure for films deposited from Pr:GGG (dots) and from Yb:GGG (cross) single crystals targets, respectively on YAP substrates at constant T$_s$=800°C. In this graph the point at 0 Pa of oxygen represents the film grown in pure argon ambient at pressure of 10 Pa. As p$_O$ decreases, the films become strongly Ga deficient, but the decreasing of the Ga content in the fabricated film depends not only on oxygen pressure, but also on nature of the target. This phenomenon has to be caused by different optical properties of the Pr:GGG and Yb:GGG targets. Due to this the optical characterizations of the single crystal targets were performed. While the equal reflectivity around 15.5% was measured for 4 mm thick Pr:GGG and Yb:GGG single crystals, the large difference were noticed for absorption coefficients $\alpha$ determined by ellipsometry at 248 nm wavelength: 35800 cm$^{-1}$ and 87400 cm$^{-1}$ for Yb:GGG and Pr:GGG, respectively. Due to different $\alpha$, the decomposition of the GGG target is significantly different and due to this feat we observed unequal modification of the target composition at especially at low p$_O$ during deposition (Fig.2).

The [Ga]:[Gd] ratio, measured in the center of the target by EDX after deposition (Fig.2), shows a same dependences as in the film for both crystal targets, but it is slightly higher than those observed in the film (Fig.1). This differences can be explained by the higher penetration depth of the electron beam during the EDX analyses (for 10 kV it could be estimated around 500 nm) compare to absorption depth of the laser beam in the target, which is approximately 1/$\alpha$ (115 nm and 280 nm for Pr:GGG and Yb:GGG), thus the non-decomposed GGG deeper in the target increases the amount of Ga measured by EDX in the centre of the target.

Fig. 3a shows an emission spectrum of laser plasma generated from a Pr:GGG target at oxygen pressure 10 Pa. The peaks associated to emission from Gd II and oxygen [10] are in this range. The emission from O and Gd or Ga could be easily determinate by time resolve spectra-see inserted graphs in Fig. 3a,b. From measurements at different p$_O$ from both targets no evidence of the changing of the emission spectra was observed in the regions of 415-420 nm as well as 430-435 nm. Contrary to this behavior, the emission spectra in region 636-643 nm, where the strongest emission lines of Ga atoms
Fig. 1. [Ga]:[Gd] atomic ratio in films deposited form Pr:GGG target (circle) and Yb:GGG target (cross) as a function of $p_0$. The films deposited at $p_0=0$ Pa denotes the film fabricated at 10 Pa of argon ambient. The dashed lines corresponding with [Ga]:[Gd] in GGG and GGP single crystals.

are located, strongly depend on $p_0$ and target nature—see Fig. 3b. The emission spectra observed from Yb:GGG target at delay time 1 μs are very weak in comparison to the same plasma generated from Pr:GGG target at constant $p_0$ equal of 1 Pa. The emission intensities associated to the Ga atoms increases with an increasing $p_0$. To estimate the Gd and Ga atoms ration in the plasma plume the ratio of areas of peaks corresponding to Gd at 416.6 and 418.5 nm and Ga at 640.2, 641.1 and 641.8 nm were plotted as a function of $p_0$—Fig. 2.

Fig. 4 shows the XRD pattern of the films grown from Pr:GGG (black line) and Yb:GGG (grey line) targets at $p_0=1$ Pa and $p_0=2.5$ Pa, respectively on YAP substrate. On the patterns of both films are presented three narrow and strong diffraction peaks located at around 23.2°, 47.4° and 74°. In respect to the films composition (see Fig.1), these peaks can be associated to the three orders of reflections from (110) planes of GGP crystals—PDF-19-0469. The diffraction peaks are slightly displaced to smaller d spacing according to the database, which can be explained by the presence of the compression stress and also by the differences of the ion radius of Gd$^{3+}$ and dopands ions (Gd$^{3+}$=107.8 pm, Pr$^{3+}$=113 pm and Yb$^{3+}$=100.8 pm in octahedral positions [11]). For example the d

Fig. 3a OES of laser plasma plume generated from Pr:GGG target, $E= 2$ J/cm$^2$, $p_0=10$ Pa, measured with time delay 0.4 and 1 μs. In the inserted figure the time evolution of the signals are plotted for different wavelengths.

Fig. 3b OES of laser plasma plume generated from Yb:GGG at $p_0=1$ Pa a), Pr:GGG at $p_0=1$ Pa b) and Yb:GGG at at $p_0=10$ Pa c). In the inserted figure the time evolution of signals associated to emission from atomic O and Ga are plotted.
spacing of (330) reflection (see detail in inserted figure) is shifted to 1.280 Å and 1.275 Å for Pr:GGP and Yb:GGP, respectively. The main difference between the Pr and Yb doped GGP films are also more evident on the third order of reflection (330). The diffraction peaks are broader in case of Yb doping, which is caused firstly by the higher doping level and secondly by the larger differences between the ions radiuses. These induced higher number of defects in the crystalline structure of the film. The growing regime, for which the (110) plane of the GGP film is parallel to the (010) YAP surface, can be simply explained by the minimizing of the lattice mismatch between the growing films and substrate and was already explained in our previous work [8].

![XRD patterns of Pr:GGP and Yb:GGP films deposited at oxygen pressure 1 Pa and 2.5 Pa, respectively. The third order of reflection (330) is showing more in detail in insert figure.](image)

4. Conclusion
The preparation of the gadolinium orthogallates single crystal is very difficult. However, PLD crystalline epitaxial (110) orientated Pr:GGP as well as Yb:GGP films were prepared from corresponding optically polished single GGG doped crystal targets on (010) YAP single crystal substrates using a KrF laser. Films were deposited at a relatively low substrate temperature equal of 800°C and oxygen pressure 1 Pa and 2.5 Pa in case of Pr:GGP and Yb:GGP, respectively. According to EDX and OES measurements the decomposition of the GGG target during the ablation process and formation of GGP crystalline films depend on the oxygen partial pressure and absorption coefficient of crystalline target. The small effect of the laser energy density on the composition and crystalline structure was also observed. The fabrication of GGP single crystal doped thin films clearly demonstrates the availability of PLD technique for a materials science.

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