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STRUCTURAL AND MAGNETO-OPTICAL PROPERTIES OF PULSED LASER DEPOSITED Bi SUBSTITUTED IRON GARNET FILMS

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Abstract- Oriented, highly Bi substituted Dy iron garnet films with perpendicular magnetic anisotropy have been grown by pulsed laser deposition on (111) $Ga_3Gd_5O_{12}$, single crystal substrates. The effect of substrate temperature and oxygen pressure on the structure and magneto-optical properties of the films has been investigated. The Bi stoichiometry was found to be sensitive to both substrate temperature and oxygen pressure. The results suggest that at elevated temperatures required to nucleate the garnet phase, the oxygen background pressure must be sufficiently high to incorporate the volatile Bi atoms into the film. Reduced oxygen pressures negatively affect the perpendicular anisotropy.
KEYWORDS: PULSED LASER DEPOSITION, LASER ABLATION, BI - SUBSTITUTED IRON GARNETS, GARNET FILMS

INTRODUCTION

Bi substituted rare earth iron garnets (Bi: RIG) thin films are the subject of considerable research interest because of their potential applications in short-wavelength magneto-optical (MO) recording and non-reciprocal waveguide devices such as optical isolators and circulators. The technological interest in these materials is mainly driven from their intrinsic large MO activity and low optical absorption in the visible to near IR region. Necessary condition for the implementation of devices that exploit optical waveguides is long range structural coherence, in order to reduce propagation losses associated with scattering from structural defects. The requirement for structural perfection in the case of MO recording application is not so stringent, since the film should have large coercivity to ensure magnetic stability of the thermo-magnetically written domains. However, randomly oriented, polycrystalline Bi based garnet films tend to have large readback-noise due to a large number of grain boundaries, the related domain irregularity and scattering of the incident polarised light.

$Dy_{3-x}Bi_xFe_{5-y}(Ga, Al)_yO_{12}$, is ideally suited for the development of Bi based MO recording media. The uniaxial anisotropy is controlled through the magnetostrictive effects of Dy and the collective demagnetisation effects of Ga and Al. Moreover, the MO activitity is enhanced by the Bi content. This derives from the increase of spin orbit interaction of the iron ions through mixing of the bismuth and oxygen wavefunctions.

It is generally accepted that in-situ films are superior to those requiring a post-deposition anneal since post-processing of amorphously deposited material requires high substrate temperatures and routinely leads to the production of granular films with random orientations, impurity phases and reduced Bi content [1]. The growth of Bi substituted garnets is especially challenging because of the volatile Bi atom and the multi-element composition. Among the large variety of physical vapour deposition techniques, pulsed laser deposition (PLD) has been shown to be well suited for growth of high quality complex multi-component materials. There have only been a few attempts to deposit Bi based garnets by PLD [2, 3] due in part, to the relatively recent development of the technique.

The physical properties of garnet films depend both on their chemical composition and their microstructure which are influenced by deposition parameters. Control over the deposition parameters is required to preclude loss of the volatile components and formation of non garnet phases.

In this work we give a detailed account on the influence of substrate temperature and oxygen pressure on the structural and MO characteristics of $(Bi, Dy)_3(Fe, Ga)_5O_{12}$ films grown by laser ablation on single crystals (111) of Gallium Gadolinium Garnet (GGG). The main objective was to find the conditions that yield superior quality thin films with perpendicular anisotropy and large magneto-optical effects as well as to understand why these conditions induce the appropriate crystal quality and phase.

EXPERIMENTAL

The laser ablation target was a ceramic disc of highly Bi substituted Dy Iron garnet with average composition $Bi_{1.5}Dy_{1.5}Fe_4Ga_1O_{12}$. The basic PLD apparatus has been described previously [4]. Briefly, the output from a KrF excimer laser was focused onto the rotating target at an angle of incidence of 45 deg, to an energy density of ~2 J/cm^2. The laser ablated material was deposited onto a substrate positioned ~3 cm away parallel to the target. GGG (111) wafers were cemented with silver paint to a substrate stage which was heated by a pair of silicon nitride heaters. The substrate temperature was monitored with a chromel-alumen thermocouple embedded in the heated substrate block. The measured temperature, as reported in this paper, represents the block temperature, which is higher than the actual substrate surface temperature. Films were grown at various substrate temperatures and oxygen pressures ranging from 400 to 670 °C and 0.01 to 0.3 mbar respectively.

Crystal phase and orientations were determined by X-ray diffraction. Spectroscopic Kerr polarimetry was used to determine the MO spectra of the saturated films in the wavelength range 300-900 nm. The magnetic characteristics were investigated by means of a polar Kerr hysteresis looper.

RESULTS AND DISCUSSION

The first studies conducted, had as an objective the determination of the optimum growth temperature range. Figure 1 shows a series of three x-ray spectra of the (444) reflection, generated by BiGa: DyIG films, about 300 nm thick, grown at 500, 590, 670 °C respectively in a background oxygen pressure of 0.1 mbar. The Θ-2Θ large angle scans (10-110 deg) consistently contained only two peaks: the (444) garnet film reflection and adjacent to it, the (444) garnet substrate reflection. This means that the films had a single garnet phase with preferred [111] orientation perpendicular to the film plane.

As a measure of crystallinity we used the film garnet (444) peak splitting due to the $K\alpha_1$ (λ = 1.54056 A°) and $K\alpha_2$ (λ = 1.54439 A°) lines of the incident Cu radiation. A well equilibrated and relaxed crystal matrix should be accompanied by clear doublet $K\alpha_1$ and $K\alpha_2$ components. The three spectra were normalised to the $K\alpha_1$ film peak intensities in order to facilitate comparisons of the films since the substrates did not have exactly the same area.

A comparison of the three cases shows superior crystalline quality for the (111) films grown in the temperature range 500-590 °C as is evidenced by the splitting of the $K\alpha_{1,2}$ doublet in these cases. For temperatures lower than 500 °C or higher than 590 °C the garnet film peak became progressively broad, weak and shallow indicating inferior crystalline quality.

Along with the broadening and reduction in intensity of the (444) peak at the increased substrate temperature of 670 °C, the peak shifted to a higher 2Θ angle corresponding to a decrease in the lattice parameter. The contraction in the lattice parameter (a_f) at elevated temperatures was suspected to originate from a Bi deficiency, whose large ionic size is a major contributor to a_f. This is entirely to be expected since Bi is the most volatile of the four elements (Bi, Dy, Fe, Ga) present in the BiGa: DyIG compound. At high temperatures the Bi and Bi_2O_3 ablated species may not adhere to the substrate surface due to a reduction in the sticking coefficients and/or may re-evaporate after incorporation into film due to their high volatility. The deficiency in Bi was further supported by composition analysis. Bearing in mind, that reduction of dodecahedral site substituents such as Bi, raises the compensation temperature, an increase in coercivity is expected for films grown at high temperatures.

There appear to be limits in the useful substrate

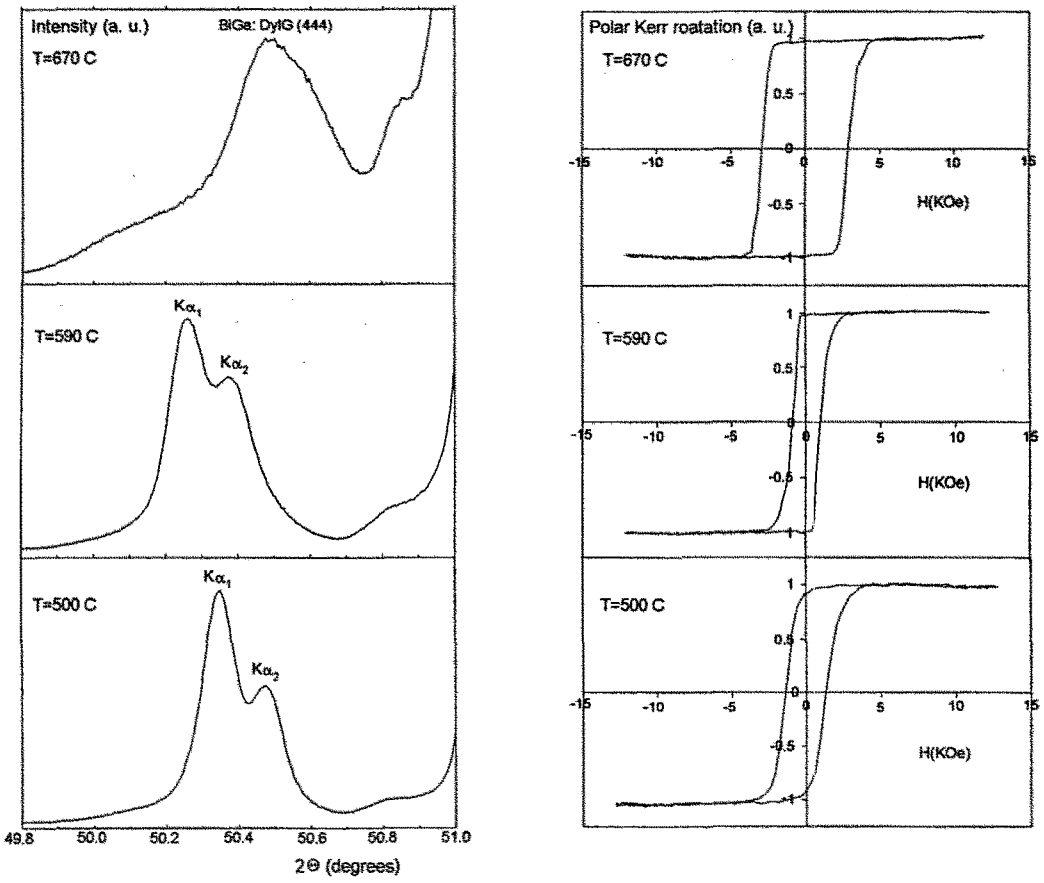

Fig.1 XRD patterns of the (444) garnet film reflection and polar Kerr effect loops for BiGa: DyIG grown at an oxygen pressure of 0.1 mbar and substarte temperature of 670, 590 and 500 °C respectively.

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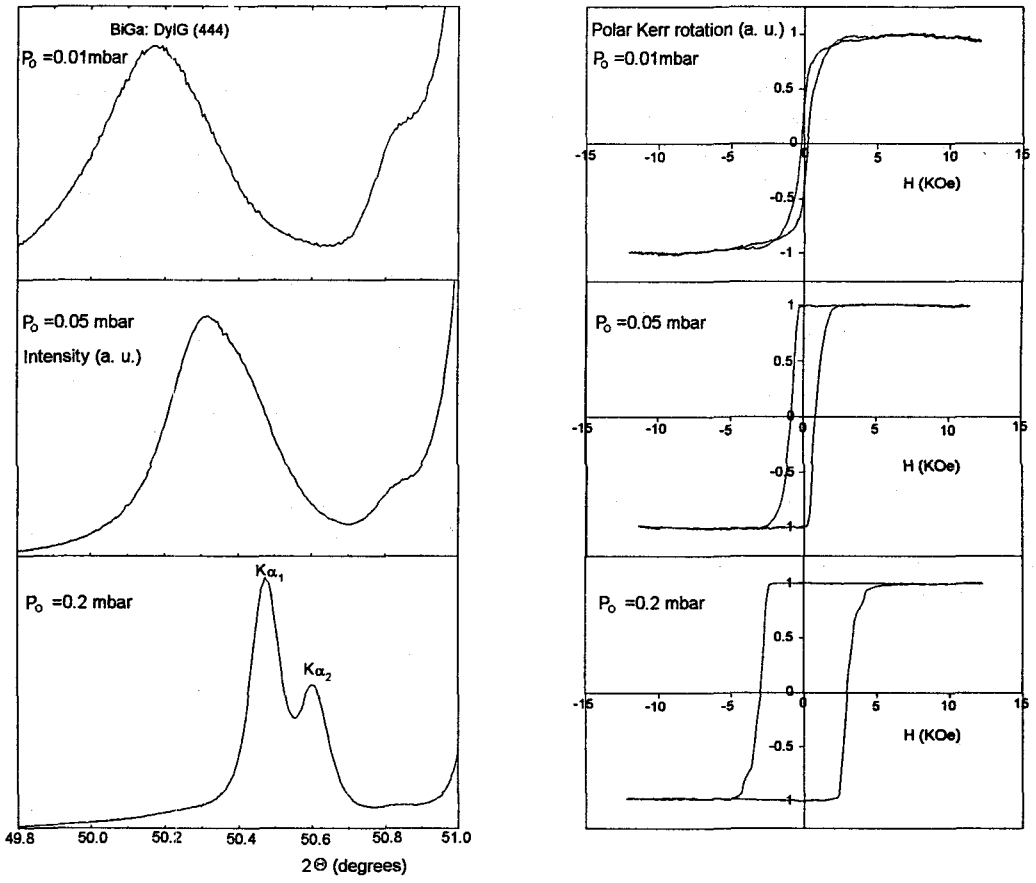

Fig.2 XRD patterns of the (444) garnet film reflection and polar Kerr effect loops for BiGa: DyIG grown at a substrate temperature of 590 °C and oxygen pressure of 0.01, 0.05, and 0.2 mbar respectively.

temperature: a lower limit defined by the ability to form the desired crystalline quality and an upper limit beyond which excessive vaporisation of the volatile film constituent takes place and deleterious reactions/interdiffusions occur at the film substrate interface.

The thermal energy that the condensing species attain on the heated substrate surface allows for increased surface mobility and energy for nucleation and growth of the films. Relatively high substrate temperatures promote long range surface mobility and improved crystalline quality. However, as the substrate temperature continues to increase the associated effects of chemical interactions and Bi re-evaporation result in the formation of a worse quality film.

The above results were also reflected in the MO behaviour of the films. The hysteresis loops of all the samples were determined by a MO Kerr plotter operating at 633 nm. Films grown at 590 °C exhibited perpendicular magnetic anisotropy as is evident by the square hysteresis loop of figure 1. They displayed low coercivity and a shoulder in the loop, characteristic of magnetisation reversal proceeding by stripe domains in thin films with perpendicular anisotropy. The shoulder disappeared as the substrate temperature was reduced to 500 °C. Variations in the temperature away from 590 °C did not affect the squareness considerably, however, they resulted in reduced MO Kerr rotation in the blue and near-UV wavelength region. It should be noted that in this wavelength region the films were much thicker than the optical skin depth, hence complications arising from the details of the underlying substrate were unimportant.

At the highest deposition temperature of 670 °C the MO signal decreased and the coercivity increased considerably which is consistent with the reduction in Bi content and the broad x-ray peak observed in figure 1.

The study of the temperature effects was followed by the investigation of the oxygen pressure on the film quality. Figure 2 shows how the (444) peak changes with a change in oxygen partial pressure between 0.01 and 0.2 mbar, when the substrate is kept constant at 590 °C. The results for films grown at 0.1 mbar have already been presented in fig.1.

The main characteristics of this series are the reduction in the perpendicular lattice constant, the decreasing basal width and the increasing separation of the $K\alpha_1$, $K\alpha_2$ peaks with increasing oxygen pressure. The broadening of the diffraction peak at the reduced oxygen pressure of 0.01 mbar indicates an imperfection in crystal structure such as strain,

deformation or compositional inhomogeneity. Furthermore, the low pressure film is characterised by a large lattice spacing. The expansion of the lattice spacing appears to be a general feature of oxide films prepared at reduced oxygen pressure and is believed to originate from oxygen deficiency and/or crystal disorder. The higher pressure film peaks are gradually shifted to lower lattice spacings, producing a smaller mismatch with the substrate and a relaxed crystal network structure as illustrated by the clear splitting in the (444) peaks.

These conclusions were supported by the MO hysteresis loops presented in figure 2. The low pressure film displayed a narrow-shaped hysteresis loop with low remanence and MO signal. It is evident that low ambient pressure negatively affects the perpendicular anisotropy of the films. All films grown at pressures equal to or higher than 0.05 mbar were characterised by square hysteresis loops and increased coercivity. The increased H_c values may be related to a difference in composition, but may also reflect the material's microstructure. A background pressure of 0.3 mbar resulted in reduced squareness and rough surfaces.

Polar Kerr rotations in the blue region were significantly lower for the 0.01 mbar sample, in agreement with the poor structural quality of the film. For films grown at higher oxygen pressures, the magnitude of Kerr rotation increased progressively, reaching its maximum value at 0.2 mbar, which upon further increase of oxygen started to decrease again. This trend, suggests a dependence of Bi content on the oxygen background pressure. It is presumed that a) the Bi volatility from the deposited film is reduced by high background pressures of O_2 and/or b) the sticking coefficients of Bi-oxygen co-ordinated species is greater.

The observed improvement in Bi incorporation into the film is mainly ascribed to the fact that the re-evaporation of volatile Bi atoms is suppressed at high background pressures of oxygen, by the formation of Bi oxides with a lower vapour pressure than that of Bi. This result suggest that the concentration of Bi oxides in the plume plays a critical role in the incorporation of Bi in the film.

It should be pointed out that diatomic oxygen has a low chemical activity due to the large energy barrier to dissociation and it is most probable that the Bi does not react easily with oxygen. This general unreactivity of oxygen towards Bi can be compensated by either increased oxygen pressures, as in our case, or through more reactive oxygen ambients (N_2O background gas [5] or anion assisted PLD technique [6]). Such energetic approaches have lead to the production of reactive O radicals/anions which react more easily with the plume species or the growing film and increase the probability of volatile incorporation into the film as well as lower processing temperatures.

Furthermore, the increase of Kerr rotation with oxygen pressure may as well be linked with the improvement of crystalline structure due to reduction of strains. The dramatic rise in Kerr rotation was followed by a fall at 0.3 mbar. This decrease is related with an energy reduction of the ablated particles, typically observed at high ambient pressures after collisional thermalisation of the plume.

CONCLUSIONS

Highly Bi substituted iron garnet films were grown at various substrate temperatures and oxygen pressures on (111) GGG single crystal substrates using the PLD technique, in order to evaluate the structural and MO properties of the films and to determine the best deposition conditions.

There appeared to be two limits to the useful temperature: a lower limit defined by the ability to nucleate the garnet phase and an upper limit beyond which deleterious reactions/interdiffusions occur at the film substrate interface and excessive vaporisation of the volatile film constituent takes place. It was found, that the Bi volatilisation problem could be relieved by depositing at high ambient pressure of oxygen. The observed improvement in Bi content at high oxygen pressures is most likely related to the low vapour pressure of Bi oxides.

The results demonstrated that highly [111] oriented garnet films with large magneto-optical effects and square hysteresis loops could be obtained when the temperature was kept in the region of 550-590 °C and the oxygen pressure in the neighbourhood of 0.2 mbar.

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