Physical Properties and Behaviour of Highly Bi-Substituted Magneto-Optic Garnets for Applications in Integrated Optics and Photonics

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1. Introduction

It is now more than 40 years since the giant magneto-optical effects in bismuth-substituted iron garnets (Bi:IG) were reported first in 1969 and used extensively for fabricating various magnetic recording media. But the synthesis efforts aimed at controlling the properties of Bi:IG compounds containing various metal dopants have started back in 1960s, and different methods were used, including Pulsed Laser Deposition (PLD), Liquid Phase Epitaxy (LPE), Ion Beam Sputtering (IBS), Reactive Ion Beam Sputtering (RIBS), Sol-gel process, and RF magnetron sputtering [1–9]. Bi:IGs are still considered to be the best magneto-optic (MO) material type among all known semitransparent materials and are therefore of interest for various optical, MO, and other applications. The extraordinary MO properties of highly Bi-substituted iron garnet materials allow the modulation of the polarisation state and intensity of polarized light by means of applying external magnetic fields on a nanosecond time scale. Highly bismuth-substituted iron garnets are becoming more and more attractive nowadays for various application fields ranging from magnetic data recovery to quantum optical information processing [10–19]. Extensive studies have been conducted by multiple groups working world-wide to synthesize new garnet materials with properties suitable for various emerging technologies and having a high Bi content and also other metal-atom dopants like Ga or Al within the garnet structure. The physical properties (optical, magnetic, and MO) of all garnet materials depend significantly not only on the Bi content and the substitution of other extra atoms and dopants within the sublattices of the garnet structure, but also on the multiple process parameters relevant to the synthesis of Bi:IGs [3]. The synthesis of high-quality Bi:IG thin film materials is usually a very complex and multi-step process sequence which also requires complex multiparameter process optimizations applied at both the deposition
and annealing stages. RF magnetron sputtering using low-pressure (1–5 mTorr) argon (Ar) plasma is one of the most flexible approaches to deposit MO garnet materials. The ability to vary the substrate temperature during the deposition and also the possibility of growing the films on relatively cold substrates are very important for the integration of Bi:IG films into optical devices. We prepare highly Bi-substituted dysprosium (or lutetium) iron garnet thin films using RF sputtering followed by the conventional (postdeposition) oven annealing in air atmosphere. Our MO garnet thin film materials are highly competitive (in terms of MO figure of merit) with all other garnet materials synthesized to date by using various modern microfabrication technologies.

In this paper, we report on the physical properties and behaviour (especially the magnetic switching behaviour) of several RF-sputtered high-performance, highly bismuth-substituted ferrimagnetic garnet materials which are suitable for integration into various photonic devices and for many magneto-optic applications.

2. Experimental

2.1. RF Sputtering Processes and Thin Film Growth. Highly bismuth-substituted garnet films and also various cosputtered nanocomposite garnet-bismuth oxide thin films were fabricated by using RF magnetron sputtering system (Korea Vacuum Technology Ltd KVS-T 4065). The garnet and composite garnet-oxide thin films of different thicknesses (up to 1500 nm) were prepared in a high-vacuum chamber using low-pressure argon (Ar) plasma at different substrate temperatures ranging between 250–680 °C during the deposition. We prepared several batches of garnet thin films and also garnet-bismuth oxide composite films having different volumetric contents of Bi2O3 added by cosputtering from a separate target. The nominal stoichiometries of the sputtering targets Bi<sub>m</sub>Dy<sub>3−m</sub>Fe<sub>5−m</sub>Ga<sub>n</sub>O<sub>12</sub> (where m = 2 and n = 1 and 0.7) and Bi<sub>a</sub>Lu<sub>b</sub>−aFe<sub>5−b</sub>Al<sub>b</sub>O<sub>12</sub> (where a = 1.2 and b = 1.4) based on high-purity (99.99%) oxide material mixes were selected to experiment with different levels of magnetostriction-induced uniaxial magnetic anisotropy. A separate Bi2O3 target was used as an external source of Bi oxide (and also Bi) content for incorporation into the nanocomposite materials during cosputtering processes. A schematic diagram of our cosputtering geometry is shown in Figure 1 (up to two guns were used concurrently in our experiments). The target materials (garnet and oxide) of 3” diameter were placed at three RF guns of the down-sputtering system having about 18 cm of source-to-substrate separation. All the guns with independently activated shutters are placed at the corners of the equilateral triangle and tilted towards the substrates. The substrates’ stage rotation was adjusted to be near 40–50 rpm during the deposition processes to provide a good deposition thickness/composition uniformity of sputtered films on all substrates. The film thicknesses were always measured in two ways; thicknesses were monitored during the deposition and also remeasured after deposition using the spectrally best-fitted transmission spectra and also their measured refractive index and absorption spectra.

2.2. Oven Annealing Heat Treatment. The as-deposited films (amorphous-phase layers) were placed into a conventional box-furnace-type oven annealing system to anneal them in air atmosphere using the appropriate composition-dependent optimized isothermal crystallization regimes. The annealing processes were run to crystallize the sputtered thin films inside the oven with temperature ramp rates (up and down) in between 3–5 °C/min, for a number of different annealing durations. We used low rates of temperature ramping during the annealing processes for our garnet-oxide composite materials to avoid the film surface degradation and microcrack formation in samples. We found that the optimization of annealing regimes (both temperature and annealing process durations were optimized) for our highly Bi-substituted garnet materials was strongly dependent on the composition of films. Figure 2 shows a photograph of (150 W Bi<sub>3</sub>Dy<sub>3</sub>Fe<sub>5</sub>Ga<sub>0.7</sub>O<sub>12</sub> + 30 W Bi<sub>2</sub>O<sub>3</sub>, or having 37 vol.% of excess Bi<sub>2</sub>O<sub>3</sub>) composite films on Corning 1737 glass (larger sample) and on a GGG (smaller sample) substrate having hazy and optically damaged (scatterer-type) surfaces due to over-annealing. These films were annealed in air atmosphere for only 30 minutes at 520 °C, with a temperature ramp (up/down) rate of 5 °C/min. However, this amount of thermal exposure was already excessive, due to the rather high bismuth content of the deposited layers. It is evident that either the annealing temperature or the annealing duration or both were not optimized to form optically flat nanocrystalline layers from the amorphous phase of these garnet-oxide composites. So it is one of the important factors of garnet thin films synthesis to find an optimized annealing regimes as the optical and MO properties are vitally related to the optimization of the annealing regimes. Even though these films were optically spoiled, they still did demonstrate some useful MO properties in terms of Faraday rotation per unit film thickness as reported in a previous publication [10].

2.3. Thin-Film Materials Characterization. The structural, optical, magnetic, and MO properties of high-quality annealed garnet thin films were subjected to characterization using a number of characterization techniques. The crystal structure and impurity phases of garnet and garnet-bismuth oxide thin films of type (BiDy)<sub>3</sub>(Fe,Ga)<sub>5</sub>O<sub>12</sub> have been analyzed using X-ray diffractometry (XRD) data generated by Panalytical X’Pert Pro X-ray diffractometer configured for near-grazing-incidence powder diffraction measurements using the CuKα1 (λ = 0.15406 nm) radiation. The optical properties of garnet films were investigated by variable-angle spectroscopic ellipsometry and also by deriving the absorption coefficient spectra, while the measurements of Faraday rotation hysteresis loops revealed the most important magnetic and MO properties of the garnet films. The specific Faraday rotation measurements were performed almost across the entire visible spectral region by using several laser light sources, a Thorlabs PAX polarimeter and an electromagnet. A transmission-mode polarizing microscope (Leitz Orthoplan) was used to observe the magnetic domain patterns of garnet films.
3. Results and Discussion

The correctly annealed highly Bi-substituted magneto-optic doped-iron-garnet thin films demonstrated excellent optical properties across the visible and near-infrared spectral range. We observed very similar behaviours of the optical absorption spectra in both types of our sputtered garnet films (dysprosium iron garnets and lutetium iron garnets). It is important to note that lower absorption coefficients were always observed (as was expected) in the cosputtered garnet-bismuth oxide composite thin films compared to the absorption of typical (stoichiometrically deposited) garnet layers. Figure 3 shows the absorption coefficient spectra measured in typical (Bi, Dy)₃(Fe, Ga)₅O₁₂ garnet layers and also those measured in the best-performing cosputtered garnet-oxide (Bi, Dy, Lu)₃(Fe, Ga, Al)₅O₁₂:B₃O₃ composite layers sputtered onto GGG (111) substrates. Similar trends in the absorption coefficient spectra were also observed in the films sputtered onto the glass (Corning 1737) substrates.

We have previously not only reported on the optical and magneto-optical properties of the sputtered (Bi, Dy)₃(Fe, Ga)₅O₁₂ material type and its nanocomposite derivatives of type (Bi, Dy)₃(Fe, Ga, Al)₅O₁₂:B₃O₃ but also documented their annealing behaviour and the effects of thermal exposure on the resulting optical and MO properties [10, 16]. We have also reported on the synthesis of RF-sputtered garnet materials of composition type Bi₁₈Lu₁₂Fe₆Al₄O₁₂ for the first time, and we believe that no physical vapour deposition methods have so far been used previously to synthesize this material type with a high Bi-content (near two formula units) [17]. The codeposited nanocomposite derivatives of type (Bi, Lu)₃(Fe, Al)₅O₁₂:B₃O₃ have been under investigation, and the detailed results will be reported elsewhere soon. The addition of excess B₃O₃ to the base garnet composition of type Bi₁₈Lu₁₂Fe₆Al₄O₁₂ during cosputtering did not have much influence on the Faraday rotation of the garnet layers but significantly reduced the optical absorption. The garnet-oxide composite films of type (Bi, Lu)₃(Fe, Al)₅O₁₂:B₃O₃ (4.5 vol.% extra bismuth oxide) possessed extremely large MO figure of merit (more than 50° at 635 nm), which was more than three times higher than that of the typical garnet layer (Figure 4). Figure 4. shows the values of the specific Faraday rotation achieved and MO figures of merit measured using 532 nm and 635 nm light.

The X-ray diffraction patterns of Bi₂Dy₁Fe₄Ga₆O₁₂ and (BiDy)₃(FeGa)₅O₁₂:B₃O₃ layers synthesized on glass substrates are presented in Figure 5. The data reveals the nano-crystalline microstructure of the annealed garnet materials and the body-centered cubic lattice structure type, as well as only one identifiable impurity phase (Fe₃O₄) being present. The addition of extra B₃O₃ always reduced the relative intensities of the iron-oxide diffraction peaks, as witnessed by the diffraction datasets of the films synthesized by cosputtering. This indicates the presence of less iron oxide outside
Advances in Optical Technologies

Figure 3: Derived absorption coefficient spectra of the best-performing garnet layer types and these of the garnet-oxide composite (having different vol.% content of excess Bi$_2$O$_3$) films deposited onto GGG (111) substrates.

Figure 4: Summary of the measured specific Faraday rotation data (dashed lines) and MO figures of merit (bar diagrams) of different garnet and garnet-oxide composite layer types; the highest values (of the specific Faraday rotation and MO figure of merit) achieved in our experiments so far are indicated.

The effects of extra bismuth oxide incorporation on the MO properties were investigated, and also the influence of the volumetric content of extra bismuth oxide was observed (Figure 6(a)). Our experimental results revealed that by controlling the volumetric content of extra Bi$_2$O$_3$ it was possible to control (to some degree) the magnetic switching behaviour and the coercive force value of garnet-oxide nanocomposite media. This type of control over the garnet nanocrystallites. No diffraction peaks characteristic of Bi$_2$O$_3$ have been observed since the bismuth oxide remained in its amorphous phase even after the annealing treatments.

Figure 6 shows the hysteresis loops of specific Faraday rotation at 532 nm measured in several best-performing garnet-bismuth oxide nanocomposite films, which had different coercive force, saturation field, and switching field values.
magnetic properties can lead towards achieving tunability in magneto-photonic crystals, which is very essential for different types of applications including the optical isolators and optical polarization controllers. The experimental setup for characterization of magneto-optic switching response as well as magnetization dynamics has been described in [20]. Nanosecond-range switching response times of below 20 ns were measured previously in 1–2 μm thick highly Bi-substituted iron garnet films of composition type (Bi, Dy)3(Fe, Ga)5O12. Note that the high-speed switching time constant of 2.4 ns has also been measured in Bi3Fe4Ga1O12 garnet films of 1 mm aperture size at 532 nm [13]. On the other hand, rather low coercive force values were measured in the second type of thin film materials studied (bismuth-substituted lutetium iron garnets doped with aluminium) sputtered onto GGG (111) substrates. The measured coercive force for the films on GGG substrates was about 45 Oe, whereas the addition of extra bismuth oxide into the films reduced the coercivity of the films as indicated in the inset (Figure 6(b)). We measured a high Faraday-effect magnetic field sensitivity within the linear range of magnetizations of up to 42.8°/(cm·Oe) at 635 nm, which was higher than that obtained previously in epitaxial (BiLu)3(FeGa)5O12 films prepared by LPE [18].

Figure 5: X-ray diffraction patterns of several sputtered Bi-substituted thin-film garnet materials deposited onto glass substrates.
6 Advances in Optical Technologies

Figure 7: Magnetic domain patterns obtained in two different garnet-bismuth oxide composite thin films (a) Bi$_2$Dy$_3$Fe$_5$Ga$_4$O$_{12}$:Bi$_2$O$_3$, with an est. 23% of excess oxide, and (b) Bi$_{1.8}$Lu$_{1.2}$Fe$_{3.4}$Al$_4$O$_{12}$:Bi$_2$O$_3$, with an est. 4.5% of excess bismuth oxide sputtered onto GGG (111) substrates.

Figure 8: The existing and potential new application areas of MO garnet materials.

We also measured even lower coercive force values of less than 20 Oe in thin films sputtered onto GGG at high substrate temperatures near 680°C.

The magnetic domain structures observed in our two different types of garnet-bismuth oxide composite thin films in the absence of externally applied magnetic fields are shown in Figure 7. The domain patterns were observed using a transmission-mode polarizing microscope.

The combination of physical properties of the highly Bi-substituted iron garnets of both types shows a great promise for the future development of different emerging types of integrated and reconfigurable nanophotonic devices. Garnet thin films of type (BiDy)$_3$(FeGa)$_5$O$_{12}$ demonstrated simultaneously a record high MO quality, and strong uniaxial magnetic anisotropy will be attractive for visible-range and near-infrared applications, including the development of high-performance magnetic field visualizers and integrated optical polarization controllers. The garnet films of type (BiLu)$_3$(FeAl)$_5$O$_{12}$ feature magnetically soft behaviour and possess a significant in-plane magnetization component which will be especially suitable for the development of garnet waveguides, nonreciprocal integrated optics components as well as the magnetic field imaging and sensing devices.

4. Applications of RF-Sputtered Garnet Materials

Modern civilization demands superior technologies and high-speed communication systems for achieving a better lifestyle. It is the challenge for modern science and technology to serve the requirements of society by providing all required technological facilities through new research, inventions, and reconfiguration of the existing devices and technologies. Materials science is one of the branches of science that can achieve rapid progress in research and applications for many new and existing technologies. A wide and growing range of applications require the design and development of new photonic materials (including MO garnet materials) which can enable control over the interaction of light with matter. MO garnet materials, especially the Bi-substituted iron garnet compounds are very suitable for various applications (Figure 8) including lightwave polarization controllers, MO flaw detection, high-density magnetic recording and MO data recovery, high-speed spatial and temporal light modulators, magnetic nanostructures for ultracold atoms trapping, and the development of magnetic photonic crystals (MPCs). The combination of the remarkable properties of magnetic garnet materials shows great promise for applications in next-generation integrated optics, nanophotonics, and also in reconfigurable photonics. The development of new garnet-type materials by synthesizing Bi-substituted iron garnets and their codeposited nanocomposite garnet-oxide derivatives will not only allow the integration of garnet-based components into existing integrated-optics manufacturing processes, but will also help achieve cost efficiency by providing the functional materials which are technologically compatible with the presently used material combinations. That will have influence on numerous communities, because most of the innovative technologies using these advanced materials will be easy to implement and less
costly.

5. Conclusions
We have synthesized a range of bismuth-substituted iron garnet thin-film materials having different bismuth substitution levels and metal dopants using the RF magnetron sputtering technique, which is one of the most common physical vapour deposition methods. We have characterized the nanocrystalline thin-film garnet materials crystallized using high-temperature oven processing and found the ways of achieving low optical absorption losses, relatively high specific Faraday rotation, and also some control over the magnetic switching behaviour. Our newly synthesized MO materials of two different composition types possess record high MO figures of merit in conjunction with other excellent physical properties which are attractive for use in various integrated-optics and photonics applications.

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