Magneto-optical studies of BaFe$_{12}$O$_{19}$ films grown by metallo-organic decomposition

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Abstract: M-type barium hexagonal ferrites BaFe$_{12}$O$_{19}$ (BaM) films considered for new devices that operate in the 40-70 GHz range with small or zero applied magnetic fields were characterized by magneto-optical (MO) complex polar “Kerr” effect (PKE) spectroscopy, MO magnetometry, and spectral ellipsometry (SE). The textured polycrystalline films were grown on Pt(111)/TiO$_2$ template on Si wafer using metallo-organic decomposition technique (MOD) followed by rapid thermal annealing. In the films grown in one, two and three MOD iterations, the thickness was evaluated by SE and transmission electron microscopy. The film thickness ranged from 30 nm to 50 nm per MOD iteration. The best films display out-of-plane effective magnetic anisotropy field of 13 kOe, high perpendicular remanent magnetization and ferromagnetic resonance linewidth of 340 Oe at 60 GHz. The coercivity deduced from the MO hysteresis loops ranged between 0.25 kOe and 0.52 kOe. The SE and PKE spectra were taken at photon energies from 0.7 eV to 6.4 eV and from 1.2 eV to 4.8 eV, respectively. The PKE spectra display the structure observed on BaM single crystal natural faces normal to the c-axis. They are consistent with magnetoplumbite structure, with high degree of grain c-axis ordering, absence of foreign phases and Fe valence-exchange mechanism. Single phase nature of the films was further confirmed by grazing incidence X-ray diffraction and $^{57}$Fe nuclear magnetic resonance at 4.2 K.

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References and links

I. Introduction

M-type barium hexagonal ferrites $\text{BaFe}_{12}\text{O}_{19}$ (BaM) are important for microwave, millimeter and sub-millimeter wave devices. Several deposition techniques were investigated with the aim to grow BaM films on semiconductor substrates with desirable physical properties, in particular, low ferromagnetic resonance (FMR) linewidth, $\Delta H$, and high effective magnetic anisotropy field, $H_A$. In addition, high hysteresis loop squareness would enable device operation with small or zero applied magnetic fields [1–5]. The present study is focused on textured polycrystalline BaM films grown on Pt/Si substrates using repeated cycles of metallo-organic decomposition technique (MOD) followed by rapid thermal annealing [6,7]. The best films prepared so far display out-of-plane uniaxial effective magnetic anisotropy field, $H_A = 13$ kOe, $\Delta H = 340$ Oe at 60 GHz, and high hysteresis loop squareness [7,8]. The properties of the films depend on several growth and post deposition thermal treatment parameters. Consequently, the film optimization requires extensive investigations.

The BaM films display smooth surface and offer the possibility to routinely evaluate their physical properties quality in large series using optical techniques. Here, magneto-optical (MO) complex polar “Kerr” effect (PKE) spectroscopy is most convenient as it can detect BaM structure on thinnest films at first or second MOD iteration where other techniques lack sufficient sensitivity. There is a strong correlation between PKE spectra and microwave properties. The desirable low FMR linewidth in BaM films requires small dispersion of the hexagonal $c$-axis orientation (perpendicular to the surface), low porosity, absence of foreign phases, low surface roughness, etc. PKE spectra in best BaM films will approach that observed in BaM single crystals. The correspondence in BaM spectral details will confirm BaM structure in the films, absence of foreign phases and absence of Fe valence-exchange mechanism. The dispersion of the $c$-axis and porosity will reduce the PKE spectral amplitudes. Surface roughness in the BaM films will also reduce the amplitudes with a stronger effect at the higher photon energy end of PKE spectra.
The present work investigates BaM films grown by MOD using MO complex PKE spectroscopy, spectral ellipsometry (SE) and MO hysteresis loop magnetometry. Selected films were also characterized by grazing incidence X-ray diffraction (GIXRD), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR).

II. Results

MOD technique used to prepare the BaM thin films was already described by Nie et al. [6] and Harward et al. [7]. The films were grown onto Si wafers with 500 nm thick SiO₂ surface covered by 50 nm thick TiO₂ adhesion layer followed by 300 nm thick Pt template using a repeated deposition steps (producing 30-50 nm BaM per iteration) [7]. The precursor for the hexagonal ferrite film was spun on at a spin speed ranging from 1500 to 5000 rpm for 30 s. The organic solvents were removed by annealing in air at three different temperatures (hot plates), i.e., 150 °C, 250 °C, and 350 °C. Two stepped Rapid Thermal Annealing (RTA) was carried out, first in N₂ for 30 sec at 950 °C and then in O₂ for 5 minutes at 1035 °C. Annealing in N₂ leads to polycrystalline films with most grains oriented with their hexagonal \( c \)-axis along the surface normal. Subsequent O₂ annealing removes defects caused by oxygen deficient during the N₂ annealing. The MOD iteration process is outlined in Fig. 1. Table 1 summarizes the growth conditions for the samples studied.

![Fig. 1. The MOD iteration process.](image-url)

### Table 1. Growth conditions for hexagonal ferrite BaFe₁₂O₁₉ films. The application or skipping of the rapid thermal anneal (RTA) performed in N₂ and then in O₂ is indicated by Yes or No

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOD cycles</th>
<th>Spin speed [rpm]</th>
<th>Hot plate anneal time [min]</th>
<th>RTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1st layer / 2nd layer / 3rd layer</td>
<td>150°C-250°C-350°C</td>
<td>950°C N₂ / 1035°C O₂</td>
</tr>
<tr>
<td>1a</td>
<td>1</td>
<td>1,500</td>
<td>1-4-4</td>
<td>Yes</td>
</tr>
<tr>
<td>1b</td>
<td>1</td>
<td>3,000</td>
<td>1-4-4</td>
<td>Yes</td>
</tr>
<tr>
<td>1c</td>
<td>1</td>
<td>5,000</td>
<td>1-4-4</td>
<td>Yes</td>
</tr>
<tr>
<td>1d</td>
<td>1</td>
<td>3,000</td>
<td>1-4-4</td>
<td>Yes</td>
</tr>
<tr>
<td>2a</td>
<td>2</td>
<td>1,500 / 1,500</td>
<td>1-4-4 / 1-4-4</td>
<td>No / Yes</td>
</tr>
<tr>
<td>2b</td>
<td>2</td>
<td>1,500 / 3,000</td>
<td>1-4-4 / 1-4-4</td>
<td>Yes / Yes</td>
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<tr>
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<td>1,500 / 5,000</td>
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<td>2</td>
<td>5,000 / 1,500</td>
<td>1-4-4 / 1-4-4</td>
<td>Yes / Yes</td>
</tr>
<tr>
<td>3a</td>
<td>3</td>
<td>1,500 / 5,000 / 1,500</td>
<td>1-4-10 / 1-4-4 / 1-4-4</td>
<td>Yes / Yes / Yes</td>
</tr>
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</table>
The PKE spectra and SE were taken at photon energy, $E$, ranges 1.2-4.8 eV and 0.7-6.4 eV, respectively using previously described techniques capable to determine the MO ellipsometric angles with the accuracy better than $10^{-3}$ deg [8]. Complementary characteristics on selected samples were extracted from cross-sectional TEM pictures, high resolution TEM patterns, GIXRD, NMR, and MO hysteresis loop magnetometry with the magnetic field applied parallel to the easy axis (perpendicular to the film surface).

Table 2. Thicknesses of hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$ films grown using a single iteration process determined by spectral ellipsometry. The void fraction in the surface layers was 0.32.

<table>
<thead>
<tr>
<th>Sample</th>
<th>1a</th>
<th>1b</th>
<th>1c</th>
<th>1d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface layer [nm]</td>
<td>4.4</td>
<td>5.7</td>
<td>5.1</td>
<td>5.5</td>
</tr>
<tr>
<td>Total thickness [nm]</td>
<td>32.8</td>
<td>27.1</td>
<td>26.2</td>
<td>31.5</td>
</tr>
</tbody>
</table>

Table 3. Thicknesses of hexagonal ferrite $\text{BaFe}_{12}\text{O}_{19}$ films grown using a two iteration process determined by spectral ellipsometry. The void fraction in the surface layers was 0.29.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2a</th>
<th>2b</th>
<th>2c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface layer [nm]</td>
<td>23.4</td>
<td>23.4</td>
<td>14.3</td>
</tr>
<tr>
<td>Total thickness [nm]</td>
<td>71.3</td>
<td>64.1</td>
<td>62.3</td>
</tr>
</tbody>
</table>

Fig. 2. Cross-sectional transmission electron micrographs taken in four different positions in Sample 3a grown using a three iteration process. The scale bars represent 0.2 μm, 100nm, 100nm, and 200 nm in (a), (b), (c), and (d), respectively. Average thicknesses of $\text{BaFe}_{12}\text{O}_{19}$, Pt and $\text{TiO}_2$ layers (from top to bottom) were estimated to be 145 nm, 340 nm and 50 nm, respectively.
The thicknesses of BaM films produced by MOD using one, two, and three iterations were
determined by SE and independently estimated using MO spectroscopy in the transparency
region at E<3 eV. The thicknesses of Samples 1b and 3a were also evaluated from cross-
sectional TEM (Fig. 2). Both SE and TEM indicated surface roughness of the order of 10 nm.
In the thickness evaluation, the film surface layer was modeled as an effective medium
composed of hexaferrite and voids. The thicknesses of the films grown in one and two
iterations are collected in Table 2 and Table 3, respectively. Cross-sectional TEM micrograph
of BaM film Sample 3a (Fig. 2) grown using a three iteration process shows columnar growth
across the whole layer thickness. SE on this sample gave the total BaM film thickness of 116
nm including the surface layer of 20 nm containing the void fraction of 0.3.

GIXRD analysis was carried out using Bruker D8 DISCOVER diffractometer equipped
with X-ray tube with rotating Cu anode operating at 12 kW. All measurements were
performed in parallel beam geometry with parabolic Goebel mirror in the primary beam.
GIXRD on the 3a film confirmed magnetoplumbite structure (space group Pb3/mmc) with the
lattice parameters $a = 0.5832$ nm and $c = 2.3198$ nm. This should be compared with the
values of $a = 0.5892$ nm and $c = 2.3183$ nm reported by Nie et al. [6]. The X-ray diffraction
pattern on sample 1b is shown in Fig. 3.

Fig. 3. X-ray diffraction pattern of hexagonal ferrite BaFe$_{12}$O$_{19}$ film recorded in grazing
incidence set-up. Only diffraction maxima of BaM phase and of Pt template are visible. The
angle of incidence was set to 0.4° in order to suppress the contribution of Pt phase.

Fig. 4. $^{57}$Fe NMR spectra of 1a (top) and 3a (middle) samples and their decompositions into
contributions of the four M-type hexaferrite sublattices. Bottom graph shows the spectrum of
the bulk single crystal BaM hexaferrite.
$^{57}$Fe NMR spectra were measured at 4.2 K in zero external magnetic field. The frequency region 70 – 77 MHz that covers NMR resonances of four from the five magnetic sublattices of the M type hexaferrite [9], was analyzed to confirm the M-type structure. Similar to the spectra of submicron barium hexaferrite particles [10], the NMR spectral lines were broadened and shifted with respect to those of the bulk single crystal due to demagnetizing fields and their distributions. For all measured samples it was possible to decompose satisfactorily the NMR spectra into contributions of particular magnetic sublattices of the M-type structure keeping the ratios of their integral intensities as well as (for a given sample) the uniform lineshape (Fig. 4). Weak variations in spectral shifts of individual lines are probably due to slight changes in lattice parameters in the films [11].

In the investigated films, the coercivity, $H_c$, was determined using the MO easy axis hysteresis loops (taken in the fields up to ± 10 kOe normal to the film plane). $H_c$ varied between 0.25 kOe and 0.5 kOe consistent with the measurement on Alternating Gradient Magnetometer [6]. The MO hysteresis loop of Sample 3a is shown in Fig. 5.

Fig. 5. The normalized polar Kerr rotation loop measured at 670 nm of M-type hexagonal ferrite film, Sample 3a, grown using a three iteration process.

The PKE spectra in the samples prepared by one and two MOD iterations are displayed in Figs. 6 and 7, respectively. They were taken in the applied magnetic field of 5.4 kOe. The inspection of the corresponding MO hysteresis loops measured in magnetic fields ($H_{appl}$), $-10$ kOe $\leq H_{appl} \leq +10$ kOe, showed that in $H_{appl} = 5.4$ kOe the PKE amplitudes in the samples approached the saturation above 90%. Figure 8 shows the PKE spectra in Sample 3a grown by three iterations measured in the field of 11.4 kOe, more than sufficient for the saturation.

Fig. 6. Polar Kerr rotation (a) and ellipticity (b) in hexagonal ferrite BaFe$_{12}$O$_{19}$ films grown by a single iteration process.
III. Discussion

The optical penetration depth, $\delta$, in BaM decreases monotonously with $E$. According to Atkinson et al. [12] $\delta(2\text{ eV}) = 200 \text{ nm}$, $\delta(3.5\text{ eV}) = 25 \text{ nm}$ with $\delta(2.5\text{ eV}) = 60 \text{ nm}$. In the low absorption region at $E < 2.8 \text{ eV}$, $\delta$ becomes close to the doubled thickness of the BaM layers and the MO spectra are combined Kerr (reflection) and Faraday (propagation) effects [13,14]. The MO contribution from the propagation effect depends on the thickness and absorption in the BaM films. At $E > 2.6 \text{ eV}$, the MO PKE spectra of films grown by three iterations show correspondence in structural details with the spectra of PbFe$_{12}$O$_{19}$ single-crystals [15,16]. In particular, single-crystalline PbFe$_{12}$O$_{19}$ shows peaks in PKE azimuth rotation centered near 2.75 eV, 3.15 eV, and 4.3 eV and a shoulder near 4.0 eV. The corresponding peaks in the MOD BaFe$_{12}$O$_{19}$, Sample 3a in Fig. 8, occur near 2.75 eV, 3.15 eV, and 4.25 eV and a shoulder near 3.7 eV. This structure appears also in the spectra measured after the first and second iterations (Figs. 6 and 7) with the exemption of the peak centered near 4.3 eV (in PbFe$_{12}$O$_{19}$) which shift toward 4.5 eV. Note that this structure was also observed in sputtered SrFe$_{12}$O$_{19}$ [17]. At $E > 2.6 \text{ eV}$, where the interference effects are negligible, the MO PKE spectra of the MOD BaFe$_{12}$O$_{19}$ display the spectral features found in bulk PbFe$_{12}$O$_{19}$ single crystals and SrFe$_{12}$O$_{19}$ and support the single phase nature of the films. The amplitudes in the MOD films are lower due to the partial misorientation of grains and due to the presence of voids.

Of the four films grown by a single iteration two, Sample 1b and Sample 1d, were grown at the same spin speed of 3,000 rpm (Table 1) and their PKE rotation spectra in Fig. 6 are practically identical. Sample 1c grown at 5,000 rpm displays largest amplitudes in this set while Sample 1a grown at 1,500 rpm displays the lowest amplitudes.

In the set of the films grown by a two iteration, Fig. 7, the highest amplitudes in the PKE rotation were found in Sample 2c grown first at 1,500 rpm and, in the second iteration at 5,000 rpm and then only RTA annealed. Sample 2b and Sample 2d, RTA annealed already
after the first iteration, display reduced amplitudes. In the films grown by one and two iteration, the lattice mismatch at Pt and BaM film interface may induce increased surface roughness (suggested by surface TEM). This is probably the mechanism which shifts the peak at the highest \(E\) to 4.5 eV. At the third iteration, the roughness becomes reduced, as indicated by AFM images [6] and the peak returns to the position observed in hexaferrite single crystals. The best resolved PKE spectra with the highest amplitudes are achieved in films grown by three iterations. This indicates low porosity, smooth surface and optimal ordering along \(c\)-axis with the magnetization perpendicular to the film surface.

To confirm the consistency between PKE spectra in hexagonal ferrite single crystals and MOD films, in Fig. 8 the MO spectra of Sample 3a are modeled using a transfer matrix formalism and the optical and MO spectra in bulk BaM [12,18]. Because of the optically thick Pt layer of 350 nm, the effect on the reflection characteristics of lower layers TiO\(_2\) and SiO\(_2\) and that of Si substrate is negligible. The sample is modeled as a magnetic layer capped by a surface layer on a thick Pt substrate [19]. For simplicity, the surface layer is assumed nonmagnetic effective medium 20 nm thick with the void fraction 0.3 deduced from SE [20]. The columnar growth of BaM films makes the magnetization as well as the optical and MO constants reduced with respect to BaM single crystal. In the model for the magnetic BaM layer, the optical constants published by Atkinson et al. [12] were therefore reduced by a factor of 0.9 deduced from SE. The MO constants, linear in magnetization, were reduced by the factor of 0.8 found for the reduction of magnetization [8]. At \(E<3\) eV, the model reasonably explains the observed trends. The deviations at \(E>3\) eV might be due to reduced precision of the employed MO spectra of ref [12], where they depart from the trends observed in PbFe\(_{12}\)O\(_{19}\) and SrFe\(_{12}\)O\(_{19}\) [15–17].

Low absorption manifested by the development of the propagation MO effect and the presence of spectral details typical for hexaferrite single crystals show that the films are free of foreign phases and contain trivalent iron cations, only, starting from the first MO iteration. The presence of Fe\(^{3+}\) or Fe\(^{4+}\) (due to the oxygen excess or deficiency), known to contribute to FMR damping, would induce the undesirable mechanism of valence-exchange between Fe cations contributing to line broadening in the PKE spectra, and to increased absorption at low \(E\).

**IV. Conclusions**

The observed agreement between the measured PKE spectra with those on the hexagonal ferrite single crystal natural faces normal to the \(c\)-axis, both in structural details and also in amplitudes, is consistent with the single phase nature confirmed by GIXRD, TEM and NMR and a high degree of grain \(c\)-axis ordering of the films. The presence of MO effects in transmission below 2.8 eV along with the well resolved structure above 2.8 eV are typical for the MO spectra originating exclusively from the exchange coupled ferric ions. This behavior of MO spectra is a necessary condition for observed relatively low FMR damping in MOD grown BaM films [6,7]. The MO measurement confirmed the square hysteresis loops and the coercivity in the range 0.25 kOe and 0.5 kOe, i.e., higher than in M-type bulk barium hexagonal ferrites. This may be exploited for self-biased or low bias operation of microwave and mm wave devices.

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