Magneto-optical properties of epitaxial strained ferrite films grown by MOCVD method

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Abstract. CoFe₂O₄ (111) epitaxial films on a single crystalline (100) ZrO₂(Y₂O₃) substrates and non-oriented CoFe₂O₄ films on a metal tape were grown by the metalloorganic chemical vapour deposition (MOCVD) method. The CoFe₂O₄/ZrO₂(Y₂O₃) films contain the coherent high-angle boundaries between variant domains due to the complex epitaxial distortions compared to polycrystalline state of the CoFe₂O₄/(metal tape) film. The structural peculiarities of films with variant structure lead to the strong anisotropy of its magnetooptical properties. Moreover a significant magnetorefractive effect, up to 1 % at 6 kOe, is revealed in both the polycrystalline and epitaxial films with variant structure in the near infrared spectral range.

1 Introduction

Thin films of ferrites possessing strong magnetic coupling, high-permeability and magnetization, high resistivity and low loss characteristics at high frequencies are the potential material as for perpendicular recording as creation magnetostatic wave devices [1,2]. The major interest is that the high magnetocrystalline anisotropy field reduces the external field required for resonance processes in ferrites [3]. It is worth to notice that magnetic properties of films of ferrites are usually different from those typically known in the bulk phase. It remains a challenge for developing efficient synthetic techniques to fabricate epitaxial ferrite films with artificially created microstructure and excellent magnetic properties close to a bulk.

Chemical vapour deposition (CVD) is one of the attractive method for the fabrication of multi-component stoichiometric films [4]. This deposition method also has the advantages of relatively low cost, high deposition rates, industrial compatibility and the flexibility to fabricate composite structures over conventional thin film processes. In the area of targeted thin-film design the special attention is paid for nanostructured materials possessing unusual magnetic and structural anisotropy [5-7]. One of the perspective ways of tuning the magnetic properties of thin films is an epitaxial strain-engineering involving large lattice mismatch at a substrate – film interface. For example, it was shown the appearance of nanostructured (variant) domain structure in MnFe₂O₄ films grown on ZrO₂(Y₂O₃) substrates [8]. Large perpendicular magnetic anisotropy was also achieved for these ferrite films [4,8]. However, the variant epitaxial structures have not yet received adequate attention. Little attention has been paid for structural peculiarities and magnetooptical (MO) properties of such structures.
Meanwhile it is well known that MO effects are very suitable contactless methods for studying the evolution of nanostructured materials.

As one of the promising candidates for studying the variant epitaxial structures can be considered CoFe$_2$O$_4$ ferrite that besides the strong coercive force and high MO effects possesses the highest magnetostriction values for a semiconductor [9].

Only recently, the magnetooptical properties of CoFe$_2$O$_4$ were carefully considered in the near- and middle-infrared (IR) range. It is important that the new IR magnetooptical phenomena associated with magnetoelastic interactions was revealed in CoFe$_2$O$_4$ single crystal [10,11]. The maximum of MO response to magnetostriction up to 10 % was achieved in CoFe$_2$O$_4$ crystal on transmission mode in the low-energy region below the fundamental absorption band. In reflection mode this response is quite less (∼1 %) pronounced [12]. An interesting emerging question is the existence of such the phenomena in epitaxial films of CoFe$_2$O$_4$.

In this work, we present the new results on magnetooptical properties of CoFe$_2$O$_4$ epitaxial and non-oriented films grown by CVD method. Moreover, we demonstrate that the optimized deposition parameters are suitable for the growth of thin CoFe$_2$O$_4$ films on a metal tape substrate with sufficient MO quality. Finally yet importantly, the noticeable magnetorefractive effect is observed in the CoFe$_2$O$_4$ films near the absorption edge.

2 Methods and samples

2.1 Samples

CoFe$_2$O$_4$ (CFO) ~300 nm thick epitaxial films were grown by metalloorganic chemical vapour deposition (MOCVD) on a hastelloy (corrosion and chemically resistive Ni-based alloy C276 tape) and single crystalline (100)-oriented ZrO$_2$(Y$_2$O$_3$) – YSZ substrate in one procedure. The deposition temperature was 700°C, the precursor evaporation temperature – 170°C, the oxygen partial pressure - 4 mbar and the total gas pressure – 10 mbar (the deposition rate was about 10 nm/min). According to the x-ray diffraction measurements (XRD), performed by the Rigaku D/Max-2500 diffractometer, the CFO films on YSZ (100) substrates are a (111) epitaxially grown single-phase spinel structure ferrite (Figure 1).

![Figure 1. XRD Cu-Kα 0–2θ scan for the 300 nm-thick CoFe$_2$O$_4$ film grown on the ZrO$_2$(Y$_2$O$_3$) (100) substrate.](image)

θ-2θ XRD patterns demonstrates only (200) and (400) reflections of the YSZ single-crystal substrate, as well as (222), (333) and (444) reflections from the CFO film. It indicates a high degree of orientation of the film, with the series (hhh) planes parallel to the substrate surface, i.e. crystallographic direction [111] of the spinel lattice is perpendicular to the surface plane of the YSZ (100) substrate. Thus, on the substrate/film interface, the hexagonal grid of film atoms is
superimposed on the square grid of substrate atoms. Since the hexagonal and square grids are not geometrically combined completely, symmetrically located and locally ordered variant structures of limited size should occur in the CFO/YSZ film [13]. Each variant is characterized by the alignment of the volume diagonal of the perovskite cube along the face diagonal of the fluorite structure cube. Earlier it was shown that the orientation relations of such variants as well as their ratio are fixed and almost do not vary through the film thickness [8,13]. Moreover, the domain boundaries are structurally coherent along the normal to the film plane. This is the main distinction of the variant CFO/YSZ films from the polycrystalline CFO/tape ones. That is why, no strong peak broadening is observed in 0-20 XRD patterns that are sensitive to the crystallite size in the films in the normal direction but not in the lateral direction. CFO/hastelloy film is polycrystalline non-oriented and its diffraction pattern corresponds to that of CoFe$_2$O$_4$ powder from the database (not shown).

2.2 Magnetooptical set-up
Spectral dependences of the magnetorefractive (MRE) and transversal (TKE) Kerr effects were recorded in 0.5-4 eV energy range with the help of grating monochromator equipped by a halogen source of light. Spectral resolution was about 1 meV. Modulation of the in-plane-applied magnetic field was in the range (-8, +8) kOe with the speed ~ 2 Hz. The complex Kerr rotation spectra were then calculated as half of the difference of the two spectra. The angle between polarizer and analyzer was set 45 deg and the light incidence angle 0 ~ 70 deg for TKE and 30 deg for MRE measurements, respectively. In the experiments we separately measured the relative change of $p$-polarized (TKE) and $s$-polarized light intensity (MRE) reflected from the sample: $\delta = \frac{[I(H) - I(0)]}{I(0)} \times 100 \%$, where $I(H)$ and $I(0)$ – intensity of the reflected light with and without a magnetic field, respectively. All measurements of TKE and MRE were carried out ex-situ under ambient conditions and at room temperature with the accuracy about 5 %. As a reference for magnetooptical studies a single crystal of CFO were used. Before starting the MO experiments, the samples were demagnetized with a variable magnetic field.

3 Results
3.1 Transversal Kerr effect
The Kerr effect is the most convenient method of investigation of magnetic properties of thin films but compared to bulk samples it is complicated by a significant contribution from the diamagnetic opaque substrate placed on a copper holder. The TKE spectra for CFO films are close to those of CFO single crystals and other ferrites [14].

Spectral dependences of TKE (Figure 2) have S-shaped anomaly at E~0.85, 1.5 and 2.6 eV. The feature at E=2.6 eV is attributed to inter-sublattice charge transfer electronic transition (Fe$^{3+}$)$_2$→[Fe$^{3+}$]$_{2e}$ [15] that confirms the presence of the inversed spinel structure. Therefore, the decrease in the intensity of the positive extremum at ~2.6 eV as compared to the data for single crystal are related to the magnetic inhomogeneity of the films. This conclusion is supported by the changes in the intensity of this peak for nanostructured CFO/YSZ film after it was rotated on 90 degrees in the plane of magnetic field application (Figure 2). The rest low-energy pronounced transitions (0.85 and 1.5 eV) are assigned to 4A$_2$-4T$_1$(4F) and 4A$_2$-4T$_1$(4P) crystal field transitions, respectively, from the 3d$^7$ configuration of the Co$^{3+}$ ions occupying the tetrahedral sites of the ferrite [16]. The rotating of the CFO sample leads to significant enhancing of the peaks at 0.85 eV and 2.6 eV while the intensity of the peak at 1.5 eV has not been changed. It can be associated with the strong influence of magnetocrystalline anisotropy of the variant film on both the hybridization between cobalt and oxygen ions [16] and the magnitude of an effective internal magnetic field.
Figure 2. Spectra of TKE of CFO films on different substrates and CFO single crystal (dashed line) taken at room temperature and in-plane magnetic field $H=2.2$ kOe. The TKE spectrum for the CFO/YSZ film rotated on 90 deg. is labeled with -r.

Field dependences of the relative magnetization of the films $M/M_s = I(H)/I_{sp}(H)$ (where $I_{sp}(H)$ is the value of the Kerr effect at $H=6$ kOe and $E=2.5$ eV; see Figure 3) show a typical for magnetic materials behavior with an enough high coercive force due to the existence of out-of-plane magnetization component, delayed increase in the magnetization and magnetization saturation at fields $H>4$ kOe. The same behavior of $M/M_s(H)$ is for CFO single crystal (Figure 3). For arbitrary chosen orientations of the film with variant structure the magnetization dependence has an asymmetry (not shown) indicating the contribution of quadratic in magnetization components and strong magnetocrystalline anisotropy. In our opinion, the magnetocrystalline anisotropy as well as deviation in cations and anions distribution in ferrites can explain the observed peculiarities in $M/M_s(H)$ behavior for variant and polycrystalline films. The detailed angle dependences of Kerr effect in the variant CFO films are pretty time consuming and are going to be the subject of future research.

Figure 3. Field dependences of the relative magnetization $M/M_s$ of the CFO films on different substrates and CFO single crystal (dashed line) taken at room temperature and $E\sim 2.5$ eV.

The observed spectral features of the Kerr effect in the studied films as compared to the data of the single crystal are most probably due to magnetic and charge inhomogeneity caused by growth conditions, epitaxial strains and/or nonstoichiometric composition of sublattices.
It is also worth to mention the unusual photomagnetic behavior of the CFO films detected during the MO measurements (not shown). We observed the dramatic change in the intensity of Kerr effect depending on the exciting wavelength and light intensity fluence similar due to the light-induced demagnetization. The single crystal was less sensitive to variation of light beam intensity. The results are similar to those obtained for cobalt ferrite nanoparticles [17] but the possible origin of this phenomenon in the CFO films is a subject of future researches.

3.2 Magnetorefractive effect
The application of an external magnetic field weakly changes the reflectivity of the CFO films in the spectral range 1-4 eV (insert on Figure 4). The magnitude of MRE in the films reaches about $10^{-4}$ that coincides well with the data for CFO single crystal [12]. Unfortunately, there is no reference date for CFO single crystal because of fracture failure during the magnetic field multi-cycling.

![Figure 4](image-url). A part of the spectral dependences of MRE in CFO films on different substrates for s-polarized light at room temperature and at in-plane magnetic field $H=4.4$ kOe. The MRE spectrum for the CFO/YSZ film rotated on 90 deg. is labeled as – r. On insert - the typical MRE spectrum for the CFO/YSZ film.

It is interesting that a strong S-like feature was in the area of crystal field transitions, slightly below the absorption band, (Figure 4) detected in CFO films for the first time. Out of this area the MRE tends to minimal values. The MRE reaches the maximum about 0.6 % at $H=4$ kOe. The close values of MRE were earlier obtained for magnetic spinel [18].

Compared to TKE, the MRE for the CFO films have linear field dependence up to 7 kOe (Figure 5) and reaches unprecedented 1 % in magnitude like as for semiconducting manganites films [18].

![Figure 5](image-url). Field dependences of MRE for CFO films on different substrates taken at room temperature at the positive maximum of the effects (0.74 eV for CFO/tape and 0.77 eV for CFO/YSZ sample).

The spectral and field behavior of MRE depends on the angle orientation of CFO/YSZ film as well as in case of TKE. However, the highest value of MRE was observed for polycrystalline CFO/tape film. The MRE in CFO films can be regarded as being due to the change in intensity and position of...
the peak responsible for $4A_{2}-4T_{1}(4F)$ in Co$^{2+}$ ions under the influence of magnetic field. Previously the similar feature was for manganites films observed [19], but the origin of high magnetic field sensitivity of reflectivity in CFO can be different.

Earlier it was shown the existence of giant magnetotransmission and magnetoreflection effect for magnetostrictive CFO single crystal in the unpolarized light [10-12]. The effects reached about few percent in the IR spectral range, changed its sign depending on the wavelengths and magnetic field and were connected with the indirect influence of an external magnetic field on crystal sublattice and electronic structure of the CFO single crystal [10]. One has to notice that magnetostrictive properties are saved in thin films that are widely used in microsystem applications [20]. Therefore, it would be a significant achievement to observe the magnetoptical response on magnetostriction in thin films by analogy with aforementioned results for CFO single crystal [10-12]. The possible contribution of magneto-elastic coupling to MRE in CFO films should manifest themselves in a correlation between the field dependences of MRE and saturation magnetostriction value $\lambda_s$ that is enhanced in magnetic fields above 3-4 kOe depending on the orientation of a magnetic field [9]. By other words, MRE in CFO films should also demonstrate saturation at the field above 4 kOe [10-12]. Figure 5 shows that MRE almost linearly increases with an increase of the magnetic field and there is no clear saturation trend, regardless of the crystal quality of the films. The slightly nonlinear field dependence as well as higher magnitude of MRE for the CFO/tape film can be also attributed to a contribution of interference processes. It is known that the multiple reflection of light at a film/substrate interface can increase the MO response in thin films [21]. However, this feature should also be valid for TKE measurements but it is not the case: TKE is maximal for CFO/YSZ films. It illustrates the challenge of the problem of finding the correlation between the magnetostriction and MRE in thin ferrite films and demands for further researches.

The understanding of the nature of the MRE in CFO films will allow one to use this phenomenon to produce sufficient stress- or interface-induced anisotropy to make these materials suitable for magnetooptical information storage, reconfigurable spin-wave routing etc.

4. Conclusion

In summary the highly-oriented epitaxial and polycrystalline films of CoFe$_2$O$_4$ have been synthesized by metalloorganic chemical vapour depositions on single crystalline ZrO$_2$($Y_2$O$_3$) and hastelloy substrates. The magnetooptical properties of the obtained films are coincide well with the CoFe$_2$O$_4$ single crystal and previously published data. It is shown the ability to modulate the Kerr effect magnitude in the wide spectral range by conscious selection of the angle of application magnetic field due to the substantial contribution of internal interfaces for the variant film. It represents the achievements made owing to the targeted design of the epitaxial variant structures.

The high potential of thin CoFe$_2$O$_4$ film for studying the magnetorefractive effect was also demonstrated for the first time. The observed effect reaches its maximum about 1 % at 6 kOe for polycrystalline film. One of the possible explanation of this phenomenon is connected with the indirect influence of magnetic field on the intensity of crystal field transitions of the Co$^{2+}$ ions due to strong magneto-elastic properties of magnetostrictive CoFe$_2$O$_4$ compound but the multiple reflections at the film/metal substrate interface should be also taking into account. Finally, though the understanding of the nature of the IR magnetorefractive effect in CoFe$_2$O$_4$ films is still open the further researches can soundly be expected to be a success.

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