Spinel oxides thin films for write-once optical recording with blue laser sources

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Non-stoichiometric spinel ferrite films are proposed in this work as write-once recording layers for high density optical storage with blue laser sources. Two types of ferrite films has been studied: mixed Co-Cu ferrites and γ -Fe₂O₃ which are anionic deficient and cationic deficient phases respectively. For Co-Cu ferrites films, the minimal writing powers leading to “readable” bits were 15 and 4 mW for red and blue laser spots respectively. Writing is realized by local oxidation of the film by laser heating. The readout signal takes benefit of the resulting changes in optical properties and bump formation on media surface. γ -Fe₂O₃ films can be locally transformed into α -Fe₂O₃ by blue spot irradiation without any topographical modification of the film surface. The transformed domains can be optically read because of different optical indices for γ and α phases in the blue spectral region. Writing sensitivity of γ -Fe₂O₃ film can be improved by adding 10 nm thick absorptive Ti layer. 5 mW is then enough to write bits at 488 nm. For this type of structure, small bumps are however formed on the written domains.

Key words: optical recording, spinel ferrite, write-once media, oxide, thin film, non-stoichiometry.

1. Introduction

A general formula such as $M_x\text{Fe}_{3-x}\text{O}_4$ is generally used to describe the chemical composition of spinel ferrites. Non-stoichiometric spinel ferrites can however be encountered, specially in the form of fine powders or thin films.

Some of them, mainly copper substituted ferrites, have a low excess of cations (i.e. metallic cations / oxygen anions $> 3/4$). They can then be described by a general formula such as: $M_x\text{Fe}_{3-x}\text{O}_{4+\delta}$ ($\delta > 0$, M: metallic cations). For such ferrites, non-stoichiometry occurs due to excess of low valence state cations, which are located in oxygen interstices, normally free of cations in the spinel structure. “Interstitial” cuprous ions surrounded by six oxygen anions were thus revealed in copper substituted ferrites¹⁻²⁾. It was also demonstrated that

$\text{Cu}_x\text{Fe}_{3-x}\text{O}_{4+\delta}$ fine powders could be oxidized into $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ stoichiometric ferrites at moderate temperatures³⁾ ($< 400^\circ\text{C}$).

Other non-stoichiometric ferrites display cation deficiency (i.e. metallic cations / oxygen anions $< 3/4$). In fact, fine powders or thin films of $M_x\text{Fe}_{3-x}\text{O}_4$ or $M_x\text{Fe}_{3-x}\text{O}_{4+\delta}$ ferrites containing oxidizable cations such as Cu^+ , Fe^{2+} , Mn^{2+} , Mn^{3+} , Mo^{3+} , Mo^{4+} ...⁴⁾ can be oxidized to make cation deficient spinels which can be roughly written $M_x\text{Fe}_{3-x}\text{O}_{4+\delta}$ ($\delta > 0$, M: metallic cations).

These phases are generally metastable phases and are transformed into one or two more stable phases when treated in air at temperatures higher than about 300°C . This transformation temperature depends on the surface / volume ratio of the ferrite and on the nature and concentration of the substitute cations.

Following the previously described processes, the magnetite Fe_3O_4 can be oxidized in air into maghemite⁵⁻⁶⁾ which could be written $\text{Fe}_3\text{O}_{4.5}$, but which is generally known as γ -Fe₂O₃. This latter can be transformed at higher temperature into α -Fe₂O₃ called hematite.

Oxidation and crystallographic transformation modify electronic exchange between cations and cations surroundings respectively. Thus, they can both involve some changes in ferrites optical properties. Local oxidations or transformations carried out by laser spot could then be used to write irreversible bits which can be optically read. These ferrite modifications are studied in this paper with the aim in view to make write-once optical media mainly working with blue laser sources.

2. Preparation of samples

The thin films were prepared by radio-frequency sputtering of spinel oxide targets made of $\text{Co}_{0.15}\text{Cu}_{0.85}\text{Fe}_2\text{O}_4$ for the first series of samples and Fe_3O_4 for the second one. The targets were sputtered by argon plasma. The argon pressure was kept at 0.5 Pa. The films were deposited on 5”1/4 glass discs of 1.2 mm thick. They displayed the same cationic composition as the targets. Fe_3O_4 films were oxidized at 300°C to get γ -Fe₂O₃ phases.

Fig. 1 Servo-tracking marks written in ferrite film (image square side 20 μm).

Fig. 2 AFM images of Co-Cu ferrite films written at different powers. (image square side 5 μm).

Optical sampled format was directly written inside the ferrite films using a mastering machine. The irradiated regions by the laser beam were partly melted making optically readable marks for servo-tracking, thanks to their well defined shape (Fig. 1).

3. Mixed cobalt-copper ferrites

3.1 Samples characteristics

– Writing and reading experiments

Films deposited are poorly crystallized. X-ray diffraction patterns show broad peaks attributed to the spinel structure. Atomic force microscopy (AFM) reveals that these films are made of small crystallites. The mean crystallite size is about 25 nm and Ra surface roughness is close to 1 nm for 70 nm thick films.

The formatted discs were written by red (780 nm) and blue (488 nm) laser sources on an optical drive working at a rotation speed of 1150 rpm. The minimal writing powers leading to “readable” bits were 15 and 4 mW for red and blue laser spots respectively when the laser pulse duration is 100 nanoseconds. The written bits can be revealed by AFM observations. In fact, bumps are created in each small regions irradiated by sufficient high power laser spots (Fig. 2). The diameter and height of

the bump depend on laser power but are lower than 1 μm and 50 nm respectively, for power spread out from 5 to 15 mW. The bumps, which corresponds to the bits, are very regular in diameter, size and shape (Fig. 2 and 3). Due to this topographical homogeneity revealed by AFM, it could be expected that chemical modifications involved by laser heating are also reproducible from one bit to another one. This interpretation is in agreement with the reading tests, which reveal very steady readout signals (Fig. 4)

Fig. 3 Cross-section of AFM image of bits written at 7.5 mW in Co-Cu ferrite film.

Fig. 4 Readout signal for Co-Cu ferrite films ($\lambda = 488 \text{ nm}$, bit size 0.5 μm , writing power 5 mW).

3.2 Physico-chemical phenomena related to the writing process

To understand the physico-chemical phenomena involved during the writing operation, Co-Cu ferrite films were annealed in different atmospheres. It has been demonstrated that spinel structure is retained after heating up to 450°C in air or in inert gas. Heat treatments at higher temperatures were not carried out because of low thermal stability of glass substrates. The improvement of film crystallization was however observed by both AFM and X-ray measurements, despite the relatively low annealing temperature carried out. Magneto-optical properties were also drastically changed. As-deposited films coercive force and remnant Faraday rotation at 440 nm are nearly equal to zero. But, after

annealing they become higher than 7 000 Oe and 1 deg/ μm respectively.

Even if spinel structure is preserved, ferrite films annealed in air, cannot be written by red or blue laser spots when their power lies from 15 to 30 mW or 5 to 15 mW respectively. It has then been concluded that oxidation phenomena are responsible of writing process. Cuprous ions, which appear in $\text{Cu}_x\text{Fe}_{3-x}\text{O}_{4-\delta}$ ($\delta > 0$) non-stoichiometric ferrite thin films or fine powders^(3,7), seems to be the single oxidizable cationic specie in Co-Cu ferrite film studied. Oxidation reaction could then be written in a first approximation:

Films annealed in inert gas can however be only written when higher laser powers than those required before heat treatment, are used. This can be due to the increase in crystallite size, which induces lower reactivity to oxygen. Modification of in-plane stress could also play an important role. In fact, from X-ray measurements it can be deduced that the as-deposited film is submitted to an in-plane compression but, after annealing in inert gas, stress is reduced. The in-plane compression in as-deposited film could then bring the required energy for the bump formation during laser heating. This potential energy is lowered after heating in inert gas.

The previous assumption is confirmed by other writing experiments carried out on films with in-plane tension. In these ferrite layers deposited by sputtering under 2 Pa argon pressure, writing process involves bits with crater-like shape. In fact, the in-plane tension tends to make a hole during laser heating. Optical contrast detected during the readout process could be due, at least, to the topographical modifications of ferrite surface in the written domains.

It was however observed that as-deposited films have different optical properties compared to annealed films in air, for both red and blue wavelengths. For instance, the refractive (n) and absorptive (k) indices of the as-deposited oxide are 2.5 and 0.9 at 488 nm, but after annealing at 450°C, they become 2.6 and 0.1 respectively. Laser heating can then induce important changes in optical properties of ferrite films. Consequently, readout signal can be assumed to be due to the combination of topographical modification and optical property change.

4. $\gamma\text{-Fe}_2\text{O}_3$ films

4.1 Samples characteristics

Twenty nanometers thick $\gamma\text{-Fe}_2\text{O}_3$ films were used for the experiments. These oxide layers are made of randomly oriented crystallites of about 15 nm and display Ra roughness of about 1 nm. Some samples were covered by 10 nm thick titanium film to improve writing sensitivity of ferrite layer. Titanium was chosen because of its quite low reflectivity (35%), moderate heat capacity ($2.8 \cdot 10^{-6} \text{ J.m}^{-3}$) and small thermal conductivity ($15 \text{ W.m}^{-1}\text{K}^{-1}$).

Fig. 5 AFM and MFM images of $\alpha\text{-Fe}_2\text{O}_3$ domains written in $\gamma\text{-Fe}_2\text{O}_3$ films (square side 5 μm).

4.2 Writing and reading experiments

First writing experiments were carried out with a mastering machine. The wavelength of the laser was 476 nm, the speed rotation of the disc was 600 rpm. Bits were then recorded on very simple media since only $\gamma\text{-Fe}_2\text{O}_3$ is deposited on glass substrate. Laser source was placed on the side of the ferrite film.

Laser power higher than about 10 mW has involved topographical modifications of $\gamma\text{-Fe}_2\text{O}_3$ films. From 7.5 to 10 mW no crater or bump are observed in irradiated regions but a local transformation of $\gamma\text{-Fe}_2\text{O}_3$ into $\alpha\text{-Fe}_2\text{O}_3$ occurs. This can be demonstrated by X-ray diffraction on samples in which many tracks were entirely written. X-ray patterns then display $\gamma\text{-Fe}_2\text{O}_3$ diffraction peaks, corresponding to the regions between the tracks, and $\alpha\text{-Fe}_2\text{O}_3$ peaks related to the tracks themselves. Because of magnetic transitions between ferrimagnetic $\gamma\text{-Fe}_2\text{O}_3$ zones, and antiferromagnetic $\alpha\text{-Fe}_2\text{O}_3$ domains, magnetic force microscopy (MFM) reveals written bits. Isolated bits display a regular circular shape and their size, determined by MFM, is close to 0.5 μm . It is interesting to remark that continuous writing without special writing strategy, gives well-shaped lines without enlargement of the end of the lines (Fig. 5). Bit can be read thanks to different n and k indices for γ and α phases in the blue spectral region⁽⁸⁾.

Other writing experiments were carried out with an optical drive ($\lambda = 488 \text{ nm}$). The rotation speed of the disc was 1150 rpm. Laser source was placed on the side of the glass substrate. At least 14 mW laser power was necessary to write homogeneous bits on simple glass substrate/ferrite film structures. This low writing sensitivity, which is a drawback for practical applications, can be improved when titanium layer is deposited on the backside of the recording film. Experiments show that 10 nm thick titanium layer lowers minimal writing power from 14 to 5 mW. Moreover, there is a sharp transition around the critical writing power: 4 mW is too low to write, but 6 mW is high enough to record bits for which associated readout signal is close to saturation value (Fig. 6). Written bits in glass substrate/ferrite/Ti structures are however revealed by small bumps in AFM images (Fig. 7).

Fig. 6 Readout signal for glass substrate/ γ -Fe₂O₃/titanium media written at a) 6 mW, b) 5 mW and c) 4 mW.

5. Conclusion

Spinel ferrites are well-known for their magnetic or magneto-optical properties. But, when they display non-stoichiometry, because of oxygen or cation deficiency, optical information can be recorded on these ferrimagnetic materials.

Bits can be written in Co_{0.15}Cu_{0.85}Fe₂O_{4-δ} films by red or blue laser spots heating. The writing process is related to ferrite oxidation that involves local topographical modifications and change in optical properties. These homogeneous and reproducible modifications are easily read with red or blue laser sources.

Fig 7 AFM image of γ -Fe₂O₃ film covered by 10 nm of titanium layer, written by 488 nm laser spot.

Optical information can also be written and read by blue laser spots, using the local crystallographic transformation of γ -Fe₂O₃ films into α -Fe₂O₃. Bits can be written without any topographical transformation. To improve writing sensitivity, γ -Fe₂O₃ films have to be covered by a very thin titanium layer, but low topographical modifications are then observed in insulated domains.

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