Magneto-Optical Behavior of Fe_3O_4 Films Obtained by Modified Ferrite Plating

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Abstract-The paper presents studies on the composition, structure, and the optical and magnetic properties of Fe_3O_4 films prepared by means of a modified technique that combines spray-pyrolysis from aqueous solutions at low temperatures (proposed by M. Abe and Y. Tamaura) with co-precipitation. This method enabled us to obtain films with Fe_3O_4 content of more than 99% with reproducible magneto-optical properties. The films are investigated by X-ray diffraction, scanning electron microscopy, Moessbauer spectroscopy, optical spectroscopy and vibrating sample magnetometer.

I. INTRODUCTION

The optical transmittance phenomena taking place in the visible range make Fe_3O_4 a very promising compound in the development of a new generation of materials for magneto-optical media. This fact has lately stimulated the search for novel technological procedures for deposition of thin magnetic films. The ferrite plating technique (proposed by M. Abe and Y. Tamaura [1]) for oxide ferromagnetic films preparation from an aqueous solution (FPAS) at temperatures lower than 100°C is of particular interest, as it allows one to use non-heat-resistant substrates. On the other hand, co-precipitation of Fe^{2+} and Fe^{3+} , studied in detail in [2], can be used as a separate stage in the process of Fe_3O_4 films preparation from aqueous solutions. The conditions for carrying out these two types of chemical processes open up not only the magneto-optical applications but the possibility of their integration into the microwave circuit technologies for fabrication of passive elements for microwave integral circuits.

The paper presents an attempt to combine the FPAS technique with elements of the co-precipitation method with the aim of obtaining high-quality Fe_3O_4 films.

II. EXPERIMENT

Fe_3O_4 films were deposited on glass and woven glass-teflon (PTFE) substrates from 0.03M solutions of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (pH = 5 - 6) and 0.02M solutions of NaNO_2 (pH = 6 - 7). The equipment

used was similar to that described in article [3]. The process temperature ($T = 97^\circ\text{C}$) was monitored by means of two thermocouples: one placed under the substrate holder, the other, on its surface. The solutions were introduced in the reaction chamber as aerosol with nitrogen (purity 5N) as carrier.

The films were deposited following the spray-pyrolysis technique, with the use of different initial solutions, as described below:

- (FPAS1) - Successive spraying of the main solution and the oxidant with pH = 7;
- (FPAS2) - Spraying of a mixed solution with pH = 7. In both cases, the ratio of the constituents solutions is strictly maintained; the pH correction is performed using 0.1 M KOH;
- (Modified FPAS) - The procedure combines spray-pyrolysis with co-precipitation: the two solutions are mixed in the ratio required without pH correction; KOH is then added until a black precipitate is formed (pH = 13). Precipitate was washed several times with distilled water to reach pH=7. The spraying is carried out with a strongly diluted dispersed solution.

III. RESULTS AND DISCUSSION

The X-ray diffraction patterns demonstrated that the films prepared following procedures FPAS1 and MFPAS were polycrystalline with single-phase Fe_3O_4 spinel structure without preferred crystallographical orientation. The films obtained by FPAS2

contained a large amount of Fe_2O_3 (mixed phase). The most probable reason for the latter fact is the initiation of intensive oxidation in the solution before it is fed in the reaction chamber.

We did not observe differences in the crystallochemical properties of the film depending on the type of substrate used.

Fig. 1. Optical transmittance spectra of films plated by:
a) FPAS1-thickness = $0.8\mu\text{m}$; b) FPAS2- thickness = $3\mu\text{m}$; c) MFPAS- thickness = $3\mu\text{m}$.

Using a CARY-5 spectrophotometer both in polarized and non-polarized beam modes, we obtained transmission spectra of the samples in the visible and near infrared spectral ranges (Fig.1). The spectra of the films deposited following the FPAS1 and MFPAS techniques present a transmission curve with Fe^{3+} and Fe^{2+} absorption peaks that is typical of a magnetite. The curves taken with beam-polarization normal and parallel to the surface are identical, showing that the films are isotropic.

There are, however, some problems in the control of iron valancy when the ferrite plating metod is applied. The transmission spectra of the films prepared by FPAS2 is different from the previous two. The probable reason is its different composition ($\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio) and roughness.

The films were subjected to a photolithographical treatment and their thickness was measured with TALYSTEP equipment.

The mechanism of ferrite deposition from

aqueous solutions at low temperature was proposed by M. Abe and Y. Tamaura [1] and that of co-precipitation was investigated in details by P. Jolivet et al. [2].

The composition of the films deposited by ferrite plating depends on the $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio, pH of the solutions, the type of oxidant and the process temperature. $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio, pH of the media and the aging time of the precipitate are very important for the process of co-precipitation. These special features of the two processes have been taken into account in the modified ferrite deposition method.

Further, the microprobe analysis revealed that the films produced by MFPAS had Fe_3O_4 content exceeding 99.27% (Fig.2).

Fig.2. X-Ray SEM analysis of film plated by MFPAS.

A vibration sample magnetometer (VSM) was used to measure the M-H hysteresis loops. Reproducible values of about 70 Oe (see Fig.3a) were obtained for coercive force H_c , with rectangularity of the curve $S_q = 0.22$. The samples were studied in two perpendicular directions in the film surface - the films magnetization exhibited no definite anisotropy in this respect.

Fig.3b, presenting Moessbauer spectra of the films, showed the site assignments of iron ions typical for Fe_3O_4 .

Fig.3 a)

b)

Fig.3. a) VSM measurement of Fe_3O_4 film plated by MFPAS on glass-teflone substrate. The sample size is 6mm x 6mm x 0.25mm. $S_q=0.225$. and b) Moessbauer spectra of film.

The optical spectrum (Fig.4) of the MFPAS film presents a transmission curve with Fe^{3+} and Fe^{2+} absorption peaks that are typical for magnetite. The curves taken with beam-polarization normal and parallel to the surface are identical, showing that the films are isotropic.

Fig.4. Optical transmittance spectra of Fe_3O_4 film deposited by modified ferrite plating and glass substrate.

IV. CONCLUSION

Our studies demonstrated that films prepared following the MFPAS are polycrystalline with the single-phase spinel structure of a magnetite without preferred orientation. This technique enables one to produce isotropic polycrystalline Fe_3O_4 films content of more than 99% with H_c of about 70 Oe and rectangularity of the hysteresis loops of about 0.22. An absorption peak typical for magnetite was observed in the visible range of the optical transmittance spectrum.

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