

Synthesis and Characterization of Ferrite Thin Films Obtained by Soft Chemical Methods

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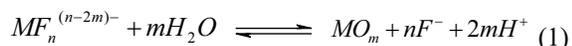
ABSTRACT

This paper reports on the synthesis of single phase uniform zinc ferrite thin films prepared the liquid phase deposition (LPD) method. The films with adjustable chemical compositions are identified with a crystal structure as spinel-type and present a spherical/rod-like microstructure. The magnetic films present a superparamagnetic behavior above blocking temperatures which decrease with increasing the Zn content.

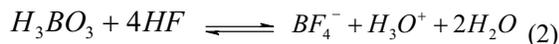
KEYWORDS: ferrite thin films, liquid phase deposition, soft solution processing, superparamagnetism

1. INTRODUCTION

With the burst of miniaturization of electronic components, the development of new synthetic strategies for the selective deposition of transition metal ferrites MFe_2O_4 films is critical for the future of microelectronic circuitry. Consequently, a myriad of synthetic strategies which differ in the manufacturability, cost, complexity and environmental hazard have been developed in the last decade [1-5]. The liquid phase deposition (LPD), proposed by Nagayama et al. [6] for the synthesis of dielectric films consists of the direct precipitation of homogenous metal oxide films via the controlled hydrolysis of the corresponding solutions of transition metal-fluoro complexes in presence of a F-scavenger.



Boric acid or aluminum are suitable as fluoride scavengers by virtue of forming stable soluble complexes which cause the shift of the equilibrium reaction with formation of the metal oxide.



However, considerably less is known on using the liquid phase deposition method to synthesize single phase multicomponent oxide films. Gao and coworkers deposited polycrystalline perovskite-type ABO_3 (A=Sr, Ba) thin films with a columnar morphology [7], whereas Deki *et al.* reported the formation of iron-nickel binary oxide films [8]. The present investigation aims at developing the liquid phase deposition method for the synthesis of zinc ferrite films with different chemical compositions.

2. EXPERIMENTAL

The experiments were performed in open atmosphere using a magnetic hotplate with an external temperature controller. Source chemicals were reagent grade purity and used as received from Alfa Aesar. Prior to deposition, the substrates were degreased by washing repeatedly with acetone and then sonicated in MilliQ water. The parent solution was obtained by dissolving 0.3g of $FeO(OH)$ in a 1M NH_4F -HF aqueous solution. $FeOOH$ was precipitated from an aqueous solution of $Fe(NO_3)_3 \cdot 7H_2O$ upon addition of a diluted solution of ammonia. Then, a separate aqueous solution of Zn^{2+} with a concentration of 2M was prepared by dissolving the corresponding amount of zinc nitrate $Zn(NO_3)_2 \cdot 4H_2O$ in distilled water. Zinc ferrite thin films were deposited on non-alkali glass plates (Corning no. 7059) substrates and p-type {111} single crystal Si wafers, respectively. Three separate solutions of iron hydroxides, $Zn(NO_3)_2$ and boric acid (aqueous solution $c=0.5M$) were mixed in different proportions to obtain a final solution with fixed concentrations of iron and H_3BO_3 , whereas the concentration of Zn^{2+} was varied in the range 0.1-0.6M. Substrates were suspended vertically and soaked in the reaction solution at different temperatures ranging between 25°C and 65°C for different periods of time, typically ranging between 3 and 24 hours. To ensure complete crystallization of the zinc ferrite films, samples were subjected to a heat treatment in open air at 600°C followed by a natural cooling to room atmosphere. Surface morphology and microstructure of the films was studied by using a JEOL-JSM 5410 scanning electron microscope, whereas their thicknesses were measured by a surface profile

measuring system Dektak-IIA. Identification of the crystalline phases, crystallite size and the phase purity of the films were examined by X-Ray diffraction using a Philips X'Pert System equipped with a curved graphite single-crystal monochromator (Cu K_{α} radiation).

The metal contents of the deposited zinc ferrite films were determined by inductive coupled plasma (ICP) spectroscopy, using a Varian FT220s flame absorption spectrometer.

Thermal behavior of the as grown films was studied using a TA Instrument TGA 2950. Infrared spectra were collected with a Nicolet Magna 750 FTIR instrument in the range of $\nu = 4000$ to 500 cm^{-1} with a resolution of 5 cm^{-1} .

3. RESULTS AND DISCUSSION

A low temperature, single step deposition of solutions of transition metal salts in NH_4FHF leads to uniform, well adherent zinc ferrite films with thickness which can be easily controlled by varying the deposition time. The slow hydrolysis of transition metal oxy-fluoro-anions leads to supersaturated solutions of oxides/hydroxides which further precipitate onto the substrate to produce a high quality film. For a given deposition time, the increase of the reaction temperature accelerates the chemical deposition which, in turn results in thicker films. The film thickness varies roughly linearly with the deposition time and was found to range typically between 50 and 960nm for a deposition time of 2-24h. In Fig. 1 is represented the variation of the relative amounts of Zn in the deposited ferrite films vs. the concentration of Zn^{2+} ions in the reaction solution. Thus, this variation clearly shows that the composition of the film can be strictly controlled by varying the transition metal concentration in the reaction solution. The X-Ray diffraction patterns of the as deposited ferrite films show that they are composed by well crystallized $\text{FeO}(\text{OH})$.

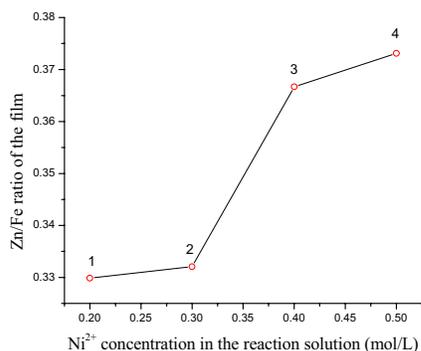


Fig. 1 Variation of the Zn/Fe ratio of the film with the Ni^{2+} concentration of the reaction solution

Although $\text{Zn}(\text{OH})_2$ is not detectable by X-Ray diffraction, EDX and TGA experiments revealed that the as prepared films have a Fe/Zn ratio in good agreement with the results

obtained from ICP spectroscopy, suggesting that the $\text{Zn}(\text{OH})_2$ is amorphous in the as grown films. Fig. 2 displays the TG thermogram of the sample with the composition $\text{Zn}_{0.82}\text{Fe}_{2.18}\text{O}_4$ at a heating rate of $1^\circ\text{C}/\text{min}$ under flowing air. The mass loss profile exhibits a very well defined decrease over the temperature range of $25\text{-}600^\circ\text{C}$, which corresponds to the conversion of the intermediate into the final products achieved in three steps. The first inflection point observed at $T \approx 150^\circ\text{C}$ (weight loss = 5.11%) is associated with the loss of the hydrated and lattice water, whereas the second one observed at $T \approx 460^\circ\text{C}$ (weight loss of 15.21%) corresponds to the dehydroxylation reaction of the transition metal hydroxides: $2\text{OH}^- \rightarrow \text{O}^{2-} + \text{H}_2\text{O}$ and a supplementary loss of water. The third plateau (weight loss of 5.32%) corresponds to the partial reduction of the Fe^{3+} ions to Fe^{2+} with formation of the zinc ferrite spinel structure. Such a large amount of retained water is not surprising, since the films are obtained from aqueous solutions and Zn containing ferrite intermediates are known to retain an unusually amount of associated water [9].

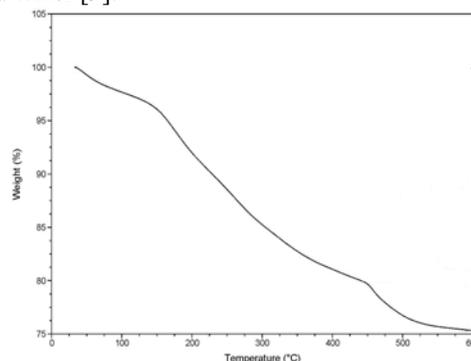


Fig. 2 Thermogravimetric analysis (TG) of hydroxide intermediates with a heating rate of $1^\circ\text{C}/\text{min}$

As shown in Fig. 3, all the experimental diffraction peaks observed in addition to the broad pattern originating from the glass substrate can be assigned to those of the standard polycrystalline ZnFe_2O_4 (franklinite, JCPDS 22-1012), which indicates the formation of a spinel-type structure.

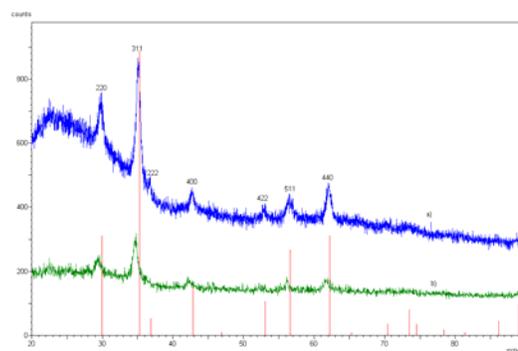


Fig. 3 X-Ray diffraction pattern of the annealed film obtained from the reaction solution with initial Zn^{2+} concentration of 0.2M(a), and 0.3M

The refined value of the cell parameter was $a=8.449(3)\text{\AA}$, which is in a good agreement with that of the standard bulk zinc ferrite ($a=8.4411\text{\AA}$) [10]. The crystallite size of the film was further determined from the modified Scherrer's formula [11], and found to be close to 20nm. In Fig. 4 are shown typical SEM micrographs the films corresponding to starting solutions whose concentrations of Zn^{2+} ions range from 0 to 0.5M. Highly homogeneous films with a columnar architecture are observed in all cases (Fig. 4b), except the reaction solution whose zinc concentration is 0 and 0.1M where the particles forming the film retain the spherical shape (Fig. 5a) similar to that observed in the case of the $\alpha\text{-Fe}_2\text{O}_3$ film [12]. In most of cases films are scratch-resistant and free of cracks. Although the role of Zn^{2+} ions in the treatment solution on the morphology of the ferrite films remains unclear, the experimental data shows that the increase of the Zn^{2+} concentration is accompanied by a change of the morphology of the deposited films from spherical to rod-like type. Additionally, the microstructure of the films doesn't vary noticeably with the thermal treatment.

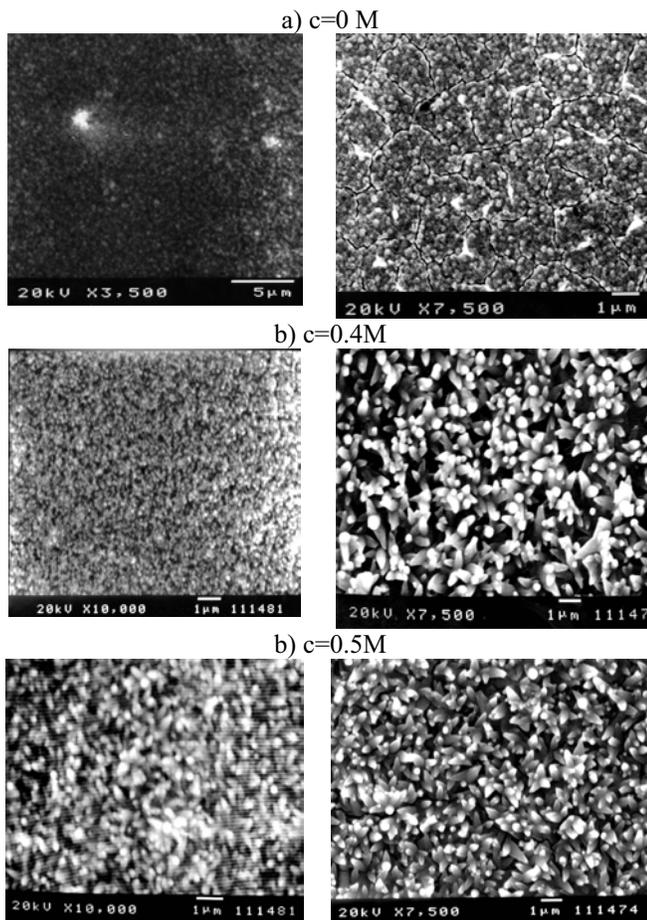


Fig. 5 Top-down SEM micrographs of zinc ferrite films deposited onto a Corning glass substrate from starting solutions with different Zn^{2+} concentrations

Zinc ferrite films were characterized by using standard zero-field-cooling (ZFC) and field-cooling (FC)

procedures. The temperature dependence of the magnetization was measured between 5K and 300K under an external static magnetic field of 100Oe, as shown in Fig. 6. We observe that the ZFC and FC data diverge at low temperature, which is indicative of a superparamagnetic behavior of the zinc ferrite films. The blocking temperature and saturation magnetization roughly decreases with increasing the zinc composition of the sample. Below the critical temperature T_c , the samples exhibit a ferrimagnetic behavior, which is related to the cationic disorder of the two sublattices (denoted by A for tetrahedral and B for octahedral, respectively) of the spinel structure.

The coercivity is found to increase with increasing the Zn content of the films, whereas the values of the magnetization saturation fall within the range reported in literature for zinc ferrites [13].

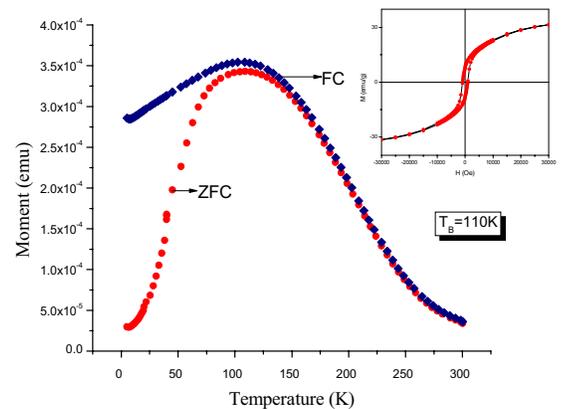


Fig.6 ZFC and FC curves of $\text{Zn}_{0.74}\text{Fe}_{2.26}\text{O}_4$ film. The inset represents the hysteresis loop recorded at 5K

However, the maximum saturation magnetization of 32.11emu/g observed for a Zn/Fe ratio of 0.327 is much lower than is the case of ZnFe_2O_4 films obtained by rf sputtering, whose magnetization at 5K was reported to be 90 emu/g for a cation distribution given by the formula $(\text{Zn}_{0.4}\text{Fe}_{0.6})^{\text{tet}}(\text{Zn}_{0.6}\text{Fe}_{1.4})^{\text{oct}}\text{O}_4$ [14]. Such a lower value of the saturation magnetization originates from a much smaller fraction of Fe^{2+} ions distributed over the tetrahedral sites which gives rise to a net magnetic moment of the tetrahedral sublattice and, in turn, enhances the A-B interactions at the expense of the B-B ones.

3. CONCLUSIONS

Highly homogenous monophase zinc ferrite thin films can be produced by a simple and flexible soft processing technique, the so-called the liquid phase deposition (LPD) method. Films with a controllable chemical composition present a complex morphology, being constructed by particles with spherical or rod-like shapes.

The dependence with temperature of the magnetic properties of Zn ferrite films with different chemical compositions evidences a superparamagnetic behavior with blocking temperatures ranging between 88 and 108K. The low temperature magnetic properties are closely related to the cationic distribution of Fe²⁺ ions over the two crystallographic sites.

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