MAGNETIC PROPERTIES OF CRYSTALLINE COBALT FERRITE FILMS

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RESUMEN

Películas delgadas (PD) de la ferrita ($CoFe_2O_4$) han sido preparadas por el método sol – gel sobre sustratos de vidrio. El sol de $CoFe_2O_4$ fue preparado de la disolución de $Fe(NO_2)_3{\cdot}9H_2O$ y $Co(NO_3)_2{\cdot}6H2O$ en agua de coco procesada. La solución depositada en el sustrato de vidrio fue spin coated, luego las películas precursoras resultantes se cocieron a 673K durante 15 minutos, acto seguido se sometieron a tratamiento térmico a 773K durante 4 h. Dos muestras de diferente espesor se prepararon. La muestra A1 es una película con un espesor de 60 nm; se coció a 673K por 4 h. La muestra A2 tiene un espesor de aproximadamente tres veces el respectivo de A1. El tratamiento térmico fue el mismo para ambas muestras. La microestructura de las películas fue estudiada por medio de difracción de rayos X (DRX), espectroscopia de fotoelectrones generados por rayos X (EFX) y la microscopía de fuerza atómica (MFA). Las imágenes MFA se obtuvieron en el modo intermitente a temperatura ambiente. Las raíces cuadráticas medias (rcm) de los valores de la rugosidad de las imágenes de MFA se determinaron empleando el programa Nanoscope. La MFA facilitó el estudio de la morfología, nucleación y desarrollo de la rugosidad de las PD de $CoFe_2O_4$. El análisis de EFX estableció que para las películas A1 y A2 se tiene $Fe/Co \approx 2$. Las propiedades magnéticas fueron investigadas por la espectroscopia Mössbauer de transmisión. Los espectros Mössbauer entre 4,2 – 300K se registraron por medio de un espectrómetro de aceleración constante y una fuente Mössbauer $^{57}Co/Rh$. Los espectros a temperatura ambiente para A1 y A2 muestran un doblete atribuido a un comportamiento superparamagnético. A 4.2K las muestras tienen parámetros hiperfinos que corresponden a una distribución del Fe en un sitio tetraédrico y en un sitio octaédrico.

Palabras claves: CoFe2O4, XRD, XPS, XPS, mediciones Mössbauer

ABSTRACT

Thin films of cobalt ferrite ($CoFe_2O_4$) by a sol-gel process on glass substrates have been prepared. A $CoFe_2O_4$ sol from dissolution of $Fe(NO_2)_3{\cdot}9H_2O$ and $Co(NO_3)_2{\cdot}6H2O$ in processed coconut water was prepared. The coating solution onto the glass substrates was spin coated, and then the resulting precursor films at 673K during 15 min were annealed and subsequently at 773K during 4 hours heat treated. Two samples with different thicknesses were prepared. The first sample (A1-sample) consisting of a film with a layer thickness of 60 nm at 673 K for 4 hours was annealed. Sample A2 has thickness of approximately threefold the thickness of A1. The heat treatment of A2 was the same as for A1. The microstructure of the films by means of X - ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) was investigated. AFM images at room temperature in the tapping mode were acquired. Root mean square (rms) roughness values from AFM images using the Nanoscope software were determined. The AFM to study the morfology, nucleation and the development of the roughness of $CoFe_2O_4$ thin films was utilized. Analysis XPS indicated that A1 and A2 films have $Fe/Co \approx 2$. The magnetic properties by transmission Mössbauer spectroscopy were investigated. ^{57}Fe Mössbauer spectra between 4.2-300 K by means of a standard constant acceleration spectrometer and Mössbauer sources of $^{57}Co/Rh$ were recorded. The spectra at room temperature for two films showed a doublet attributed to the superparamagnetic behavior. At 4.2K, the samples have hyperfine parameters corresponding to distribution of Fe in site tetrahedral and site octahedral.

Keywords: $CoFe_2O_4$, XRD, XPS, XPS, Mössbauer measurements.

1. Introduction

Cobalt ferrite films, prepared in different ways, have attracted considerable attention because of

their wide application in technological fields including permanent magnets, microwave devices, recording media [1-2]. Spinel ferrites have a spinel-like structure with the molecular formula $A^{2+}B_2^{3+}O_4^{-2}$, where A^{2+} and B^{3+} are the divalent and trivalent cations occupying tetrahedral (A) and octahedral (B) interstitial positions of the fcc lattice formed by O^{2-} ions. The magnetic properties of these oxides depend on the type of cations and their distribution between the two interstitial positions. $CoFe_2O_4$ is a well-known inverse spinel with Co^{2+} ions on B sites and Fe^{3+} ions distributed equally among A and B sites. Many physical techniques, including pulsed laser deposition and sputtering have been applied to prepare cobalt ferrite thin films [3-4]. The sol-gel route can provide multicomponent oxides with homogenous composition and lower processing temperature and shorter annealing time owing to the metal ions dispersed primarily and uniformly with the required stoichiometry [5-6]. Of other great importance is the easy creation of the films consisting of nanocrystalline grains with near single-domain dimension by this approach, which has great technological interests. In this work, we show an original method to prepare cobalt ferrite films by the sol-gel method, using coconut water that provides precursor organic chains [7-8]. Their microstructure and magnetic properties as a function of annealing temperature using atom AFM, XPS, and Mössbauer spectroscopy are investigated.

2. Experimental

Thin films of cobalt ferrite ($CoFe_2O_4$) by a sol-gel process on glass substrates have been prepared. A $CoFe_2O_4$ sol from dissolution of $Fe(NO_2)_3{\cdot}9H_2O$ and $Co(NO_2)_3{\cdot}6H2O$ in processed coconut water was prepared. The coating solution onto the glass substrates was spin coated and the resulting precursor films at 673K during 15 min were annealed and subsequently at 773K during 4 hours heat treated. Two samples were prepared with different thicknesses. The sample A1 consists of a film with a layer thickness of 60 nm annealed at 673 K for 4 hours. Sample A2 has thickness of approximately threefold the thickness of A1. The heat treatment of A2 was the same as for A1.

AFM images at room temperature in the tapping mode (silicon cantilevers) were acquired, using a Digital Instruments Multimode microscope with a Nanoscope IV controller and using commercial Si_3N_4 cantilevers with a spring 0.7 Nm^{-1}. Root mean square roughness (Ra) values from AFM images using the Nanoscope software were determined. The AFM to study the nucleation and the development of the roughness in the growing of the $CoFe_2O_4$ films was utilized. X-ray photoelectron spectroscopy on an ESCALAB 220I-XL (VG Instruments) with a base pressure of 2×10^{-10} mbar was carried out. All XPS spectra using non-monochromatic Al-K_a source anode (1486.6 eV) operated at 15 kV, 10 mA were collected. The magnetic properties by transmission Mössbauer spectroscopy were investigated. ^{57}Fe Mössbauer spectra between 4.2 and 300K by means of a standard constant acceleration spectrometer and radiation sources of ^{57}Co/Rh were recorded. The velocity with an α-Fe foil (25μm) was calibrated.

Results and discussion

The crystal structure and orientation of the prepared films were investigated by analyzing the X-ray diffraction pattern. Fig. 1 plots the obtained patterns of the sample prepared at different layer thickness. The ability of AFM to create three-dimensional micrograph with resolution down to the nanometer and Angstrom scales had made the instrument an essential tool for imaging surfaces and microstructure [6]. Fig. 2 shows a $CoFe_2O_4$ crystal surface imaged with the AFM in air to atomic resolution. AFM images with scan sizes of 1x1 μm of A1 and 1.5 x 1.5 μm of A2 samples, respectively, are showed in Fig. 2. The samples appeared to consist of regular grains with a narrow distribution of grains size. The films are composed of granular

shape grain with an average size of 10 - 40 nm, which is in the range used for electronic devices and their Ra roughness is about 4.9 nm and 5.2 nm, respectively. When the thickness films are increased, the surface roughness increases due to increases of the grain size. In the three-dimensional plot (Fig. 3b); atomic corrugations are visible. We can see grains on the thin films, where a relatively smooth surface for, the 50 and 120 nm thick are seen. A grain size analysis of the film gives an average diameter of 20 and 27 nm for A1 and A2 - samples, respectively. Surface profiles and roughness are quality features of thin films, which can be investigated as mentioned. The roughness analysis and the cross-section profile shown in Fig. 3a give an impressive insight of the capability of the method to measure surface topography. The surface roughness – Ra - is the mean roughness that is the mean value of the surface relative to the center plane of the glass substrate, in the range of Ra = 0.5-1.5 nm. The thicker film has a greater roughness than the thinner one. In our case the roughness are 4.9 nm and 5.2 nm, for the A1- and A2-samples.

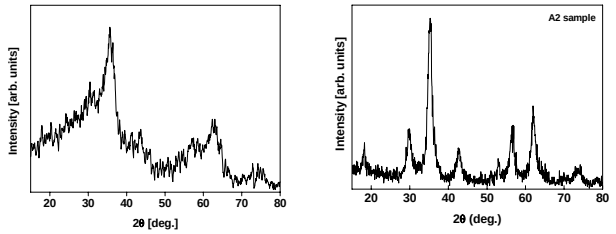
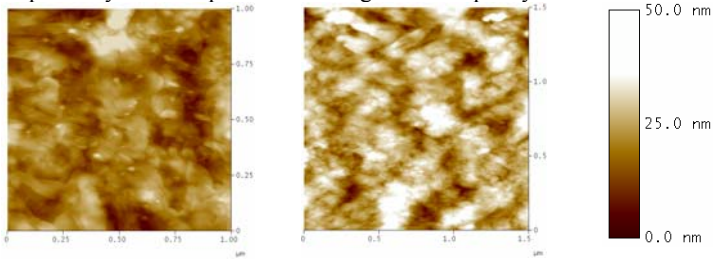


Fig. 1 X-ray diffractograms of $CoFe_2O_4$ film at different layer thickness.



(a) (b)

Fig.2 AFM images of cobalt ferrite crystalline films: a) A1-, b) A2-samples

Analysis by XPS of the Fe $2p_{3/2}$ and $Co2p_{3/2}$ peak intensities indicated that all the films have Fe/Ni ≈ 2.

The room temperature Mössbauer spectra of the cobalt ferrite films in fig. 4a were fitted with Lorentzian - shaped lines. The Mössbauer spectra for the A1- and A2-samples consisted of a single doublet with a broadened line width. The broadening may hide some complex effects in A2-samples (sextet with hyperfine field of 406.1 kOe). The structural disorder and paramagnetic relaxation-related phenomena can cause broadening of the absorption width. The Mössbauer parameters resulting from the least squares fitting at room temperature and 4.2 K, in Tables 1 and 2 are given. At 4.2K, the weighted average hyperfine field decreases from 529 kOe for the A2-sample to 522 kOe for the A1-sample. These hyperfine fields are different the bulk $CoFe_2O_4$-values (506 kOe for the A site and 548 kOe for the B site) at room temperature and can be due to the existence of superparamagnetic particles or increase in the roughness of the films. The superparamagnetic doublet at room temperature disappears when the samples are cooled to 4.2 K and can be as seen from the Mössbauer spectra shown in Fig. 4b. As the films thickness is decreased, a gradual collapse of the magnetically split component to a doublet occurs, which is the dominant feature at 300 K for the A1- and A2-samples, respectively. This is most probable due to superparamagnetic relaxation caused by the smaller grain size in which result in a blocking below room temperature.

There are only slight increases in the grain sizes with increasing film thickness. This suggest that the nucleation of the spinel phase takes place inside the amorphous-like grains in the precursor films so that the crystallization process is not necessarily accompanied by grain

growth. The nucleation inside the grains leads to growth only through the rearrangement and short-distance diffusion of atoms nearby which requires energy. Thus, the grains should have the core shell structure as previously suggested [5].

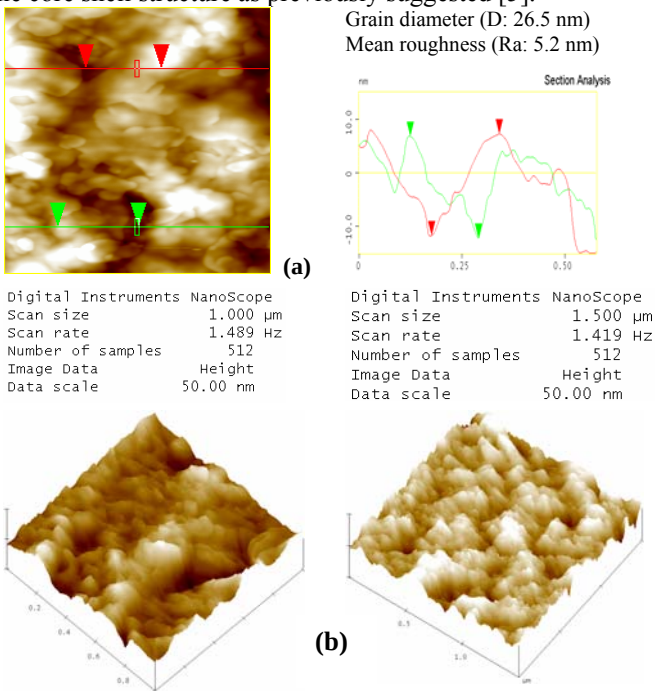


Fig. 3. (a) Atomic cross-section analysis of a $CoFe_2O_4$ films (A2 sample) and (b) three-dimensional AFM image of atomic resolution of the $CoFe_2O_4$ film (A1 and A2 samples).

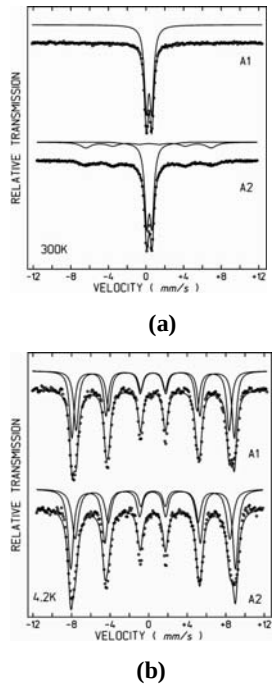


Fig. 4. Mössbauer spectra of thin films of $CoFe_2O_4$, a) room temperature, b) 4.2 K

Table 1. Hyperfine parameters for $CoFe_2O_4$ films at room temperature.

Sample	IS(mm/s)	QS(mm/s)	H_{hf}
A1	0.33	0.58	
A2	0.34	0.59	
	0.34	0.05	406.1

Table 2. Hyperfine parameters for $CoFe_2O_4$ films at 4.2K.

Sample	Site	IS(mm/s)	QS(mm/s)	H_{hf} (kOe)
A1	(A)	0,43	- 0,02	491,8
	(B)	0,46	0,02	522,2
A2	(A)	0,43	- 0,06	501,8
	(B)	0,51	- 0,02	529,5

4. Conclusions

We propose a chemical synthesis route for magnetic nanocrystalline thin films of cobalt spinel ferrite by the sol-gel from dissolution of $Fe(NO_2)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ in processed coconut water that is used as a complexing agent.

The experimental results suggest that the cobalt ferrite films grown by our sol-gel method have a great potential as a technological applications at a low cost.

The Mössbauer spectra of the films change from superparamagnetic to a ferrimagnetic patterns with increase of the film thickness. The thermal treatment during 15 min with post annealing during 4 hours at 773K are key parameters to the film quality.

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