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Short communication

Studies on the structure and gas sensing properties of nickel–cobalt ferrite thin films prepared by spin coating

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ABSTRACT

The influence of Co^{2+} ions content on structure and sensing properties of $Ni_{1-x}Co_xFe_2O_4$ ($x = 0.25$, 0.5, 0.75) thin films deposited on glass substrates by spin coating is presented. Structural characterization evidenced thin films with cubic spinel structures and morphologies dependent on cobalt content. Repartition of cations in spinel tetrahedral and octahedral sites was determined and was found that the presence of Co^{2+} ions in octahedral sites favor the formation of Fe^{2+} species. The sensitivity to some reducing vapor gases (acetone, liquefied petroleum gas LPG, ethyl alcohol and methyl alcohol) was investigated and was found that thin films with $x = 0.75$ exhibit high sensitivity to ethyl alcohol and thin films with $x = 0.25$ have high sensitivity to acetone. This sensitivity largely depends on the temperature and test gas concentration and was related to the Fe^{2+} species formed in octahedral sites.

1. Introduction

In the last years, a considerable attention was given to the low dimensional magnetic materials from both: experimental [1,2] and theoretical [3,4] perspectives. Semiconductor gas sensors like SnO_2, ZnO or Fe_2O_3 have been well studied to detect most of the reducing gases and they are considered interesting for their low cost and simple sensing method [5]. Nevertheless, there still exist some problems with them, for example, the poor selectivity of SnO_2 [6] or the high working temperature of ZnO (400–450 °C) [7]. Several new materials are also being tested. Transition metal ferrites are a family of oxides that play an important role in a wide variety of fields because of the variety of transition metal cations that can be incorporated into the lattice of the parent magnetite structure. For the use of ferrites in applications for gas sensor devices, lower density and higher surface area are generally required. It was also concluded that the gas response depends not only on morphology but also on annealing temperature, ferrite composition, gas concentration and gas type to be detected [8].

In order to make planar devices, several deposition methods were used for thin films preparation: sol–gel, co-precipitation, hydrothermal, spray pyrolysis, plasma spray or sputtering [9–16]. A simple technique such as spin coating can be also used for the thin film formation in the sol gel process [17,18].

There is a growing interest in ferrite thin films with controlled functionalities for advanced applications [19]. $Ni_{1-x}Co_xFe_2O_4$ thin films may exhibit magnetic, sensing and catalytic properties as a function of Ni and Co species formed into spinel type structures.

This paper relates on the preparation and characterization of some $Ni_{1-x}Co_xFe_2O_4$ thin films for gas sensor applications. The thin film sensor elements have been tested to four reducing vapor gases (acetone, LPG, ethyl alcohol and methyl alcohol).

2. Materials and characterization methods

As deposition method for $Ni_{1-x}Co_xFe_2O_4$ thin films we adopted the method we used for other metal oxide thin films by mixing certain contents of iron nitrate, nickel acetate and cobalt acetate solutions in N-N-dimethylformamide ($FeN_3O_9{\cdot}4H_2O$, $Ni(CH_3COO)_2{\cdot}4H_2O$; $Co(CH_3COO)_2{\cdot}4H_2O$, p.a.; 2 g metal acetate or nitrate in 10 ml DMF) in order to obtain $x = Co/(Ni + Co)$ ratios of 0.25, 0.50 and 0.75 and $Fe/(Ni + Co) = 2$. Ceramic slides (calcium titanium magnesium aluminum silicates) were used as substrates for thin film depositions. The deposition process involved depositing a small volume of a certain solution onto the center of a substrate and then spinning with a speed of 1500 rpm during 30 seconds. After spinning, thin films were annealed at 100 °C for 5 min and at 300 °C for 10 min. The procedure was repeated 8 times. Finally, the as-obtained spin-coated films were annealed at 800 °C for 1 h in order to obtain oxide nanocrystalline thin films. Thin film thicknesses were measured by using a DEKTAK profilometer and were found to be around 200 nm.

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Structural phase identification of the films was carried out by standard X-ray diffraction techniques with Cu Kα radiation (λ = 1.5418 Å, Shimadzu LabX XRD-6000, scan speed 2 deg/min). Compositional analysis of the thin film surface was conducted using X-ray photoelectron spectroscopy (XPS, PHY-ULVAC VersaProbe 5000, Al Kα source, 1486.6 eV). Charge neutralization was used for all samples. The binding energy scale was charge referenced to the C 1s at 284.6 eV. XPS spectra were analyzed using XPSPEAK41 software.

For the gas sensing measurements, silver electrodes were deposited by thermal evaporation technique in vacuum. The sensor element (thin film) was provided with a heater and a fan and was introduced in a glass chamber (with 2 dm^3 volume). The test gases were injected into the glass enclosure with a calibrated syringe. The measurements were performed in the temperature range from 100 °C to 400 °C, to avoid the effect of the surface adsorbed water [20].

The working temperature was measured with a Cromel–Alumel thermocouple located in the close proximity of the sensor element. The electric resistance of the thin film was recorded at fixed temperatures, both in air and in the presence of the test gas, using a digital LCR meter at 100 Hz. The sensitivity, S, was calculated using the relation:

$$S = \frac{\Delta R}{R_a} = \frac{R_a - R_g}{R_a} \quad (1)$$

where R_a is the thin film resistance in air and R_g is the thin film resistance after the exposure to the test gas, recorded at a given temperature.

After each change of the test gas, the sensor element was activated by submitting it to a heat treatment for 5 min in order to form the initial structure and to be thermodynamically stabilized. Heat cleaning of the samples was found to be necessary for a better and a reproducible sensitivity.

3. Results and discussion

3.1. Structural characterization

X-ray powder diffraction (XRD) patterns of $Ni_{1-x}Co_xFe_2O_4$ (with $x = 0.25, 0.50, 0.75$) are shown in Fig. 1a in comparison with diffraction patterns of substrate and pure $NiFe_2O_4$ (Crystallographica Search-Match, PDF No. 74-2081). XRD patterns show the reflection planes of the spinel cubic structure, (1 1 1), (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0), (2 0 0), (5 3 3), superimposed on the XRD peaks belonging to the oxide substrate.

The XRD patterns show changes in XRD peak intensities and positions suggesting different lattice sites for nickel and cobalt. The spinel unit cell parameter, a, was determined by using XLAT – Cell Parameter Refinement program (Table 1). The computed values of the lattice parameters showed an increase with cobalt content, in agreement with the Vegards's law observed by other authors for $x = 0$–1.0 [21,22].

The average crystallite sizes were estimated from the full-width at half maximum (FWHM) of the most intense XRD peak (3 1 1) using Scherrer formula:

$$D_{331} = \frac{0.9\lambda}{w \cos\theta} \quad (2)$$

where λ is the wavelength of Cu Kα, θ is the angle of Bragg diffraction, and w is the full width at half maximum (FWHM) [23,24]. The results shown in Table 1 evidence a monotonically decrease with the increase in cobalt content.Wide-scan XPS spectra of the $Ni_{1-x}Co_xFe_2O_4$ thin films evidenced Fe, Co, Ni and O elements, and no other impurity elements except carbon (Fig. 1b). Surface contaminants were removed through Ar^+ ion sputtering prior XPS

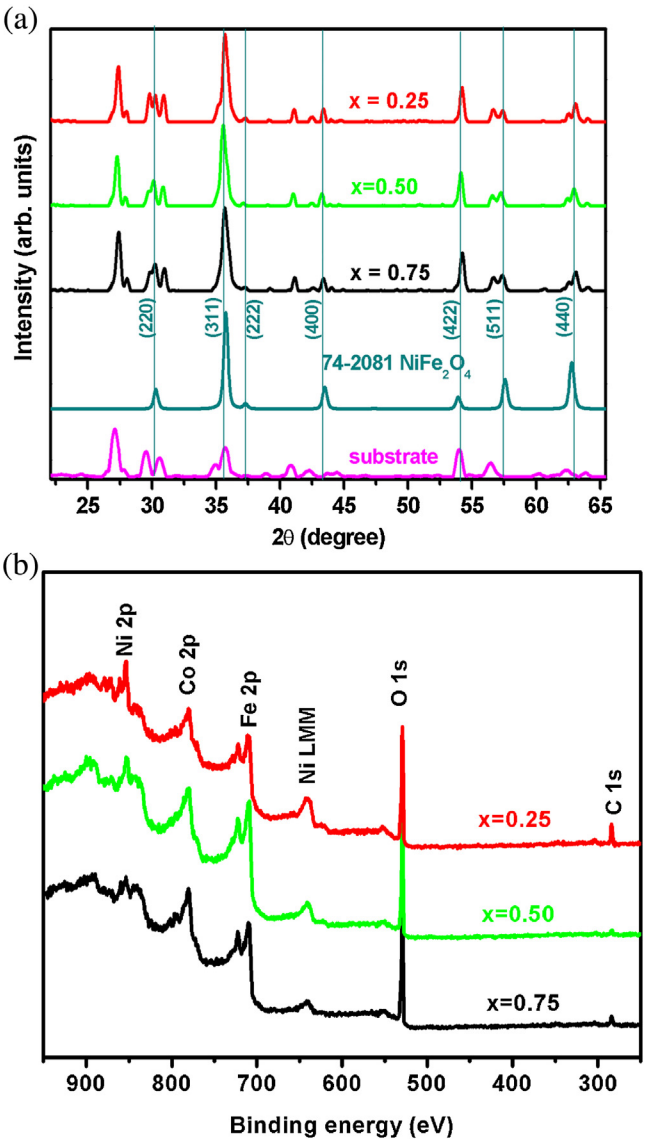

Fig. 1. Structural investigations of nickel–cobalt ferrite thin films: (a) XRD powder patterns; (b) wide-scan XPS spectra.

spectral acquisition.The high-resolution narrow-scan XPS spectra of Fe 2p, Co 2p, Ni 2p and O 1s peaks of thin films with $x = 0.75$ are shown in Fig. 2. The peak shapes for XPS spectra were fitted with XPSPEAK41 program, the fitting parameters being based on those presented in recent papers [25–29]. In Fig. 2a is shown a typical fitted Fe $2p_{3/2}$ XPS spectrum. The obtained Fe $2p_{3/2}$ binding energies, BE, for all the studied thin films are presented in Table 1. The presence of two nonequivalent bonds of Fe^{3+} ions, consistent with Fe^{3+} ions in octahedral sites (Fe_o^{3+} BE = 709.3 eV) and Fe^{3+} in tetrahedral sites (Fe_t^{3+}, BE = 712.3 eV) and the presence of Fe^{2+} ions in octahedral sites (BE = 707.7 eV) was revealed [25,26]. The relative contributions of Fe^{3+} ions in octahedral and tetrahedral sites were determined. It was found that 68.4% of Fe^{3+} ions are located in octahedral sites and 32.6% in tetrahedral sites.

It is known that in Fe_3O_4 the ratio of Fe^{2+}/Fe^{3+} was found to be about 0.5, and that by doping with Co^{2+} this ratio reduces, indicating that Co^{2+} ions substitute Fe^{2+} in octahedral sites [25]. A decrease in the Fe^{2+}/Fe^{3+} ratio by increasing cobalt content was established for the thin films (Table 2).

Co $2p_{3/2}$ XPS peaks were decomposed in two main XPS peaks located around 779 and 782 eV and attributed to Co^{2+} ions in