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The role of solvents on the physical properties of sprayed iron oxide films

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ABSTRACT

Iron oxide thin films were prepared by the spray pyrolysis technique using different solvents such as water, ethylene glycol/water, and ethanol/water. The properties of the films were studied by Raman spectroscopy, X-ray diffraction (XRD), atomic force microscopy and magnetometry. New results of the role of solvent on the growth and crystal structure of iron oxide films are presented. It was found that the solvent type affects the growth of iron oxide films, such as the deposition rate and the crystalline phase of the films. Additionally, it was revealed that the crystalline phase of the films depends strongly on the film thickness. Metastable phases such as oxyhydroxides and maghemite were found in thinner films while pure hematite was obtained in thicker films. It was detected that metastable phases can be stabilized in thinner films if organic solvents are used; particularly, single phase maghemite thin films can be obtained if ethylene glycol is used. The crystalline structure determined by Raman and XRD correlates very well with the magnetic properties of the iron oxide films; i.e., the canted ferromagnetic in hematite films and the ferrimagnetic character of maghemite were detected.

1. Introduction

Iron oxides are very important materials in science and technology, their applications range from pigments to high tech applications such as photoelectrochemical cells [1–4], spintronic devices [2], supercapacitors [5], thermo-sensor applications [6] and biomedical sciences as drug delivery [7]. The construction of different devices requires the preparation of thin films with controlled morphology, particle size, thickness, and crystalline phase. There are many thin film preparation techniques and among the chemical routes, spray pyrolysis is a practical one because the physical and chemical properties of the films could be controlled and the cost of equipment and chemicals are affordable [1,8]. It has been reported that as-deposited iron oxide thin films prepared by spray pyrolysis can exhibit the hematite phase [8,9], maghemite [10], mixtures of hematite-maghemite [11], mixtures of hematite-magnetite [8], magnetite [10], amorphous films [12], and oxyhydroxides [9,12,13]. A careful analysis of these studies reveals that it is complex to distinguish different iron oxide polymorphs in thin film configuration; e.g., due to textural properties.

In thin films prepared by spray pyrolysis using aqueous solutions, it has been demonstrated that single-phase iron oxide films are very hard to prepare [9]. Additionally, different characterization techniques have to be used for assuring the presence of a specific phase in the films [3,9]. The growth of a specific crystalline phase is a critical characteristic for a particular application, because impurity phases are detrimental to the performance of devices [14]. In order to prepare different iron oxide polymorphs, electrochemical cycling has been used to induce phase transformations [3]. However, in the specialized literature, very little attention has been paid to the relation of phase evolution within the thickness [3,13].

This paper reports the role of different solvents on the crystal structure of iron oxide thin films prepared by spray pyrolysis. To the best of our knowledge, the effect of the solvent on the physical properties of sprayed iron oxide films has not been studied. It has

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been found that the type of solvent has a critical role on the crystalline phase and the magnetic properties of the films.

2. Experimental details

2.1. Preparation of iron oxide thin films

Iron oxide thin films were prepared by pneumatic spray pyrolysis using three different solvents; namely, water, ethylene glycol (EtGly), and ethanol (EtOH). The organic solvents were used in mixture with water because the high viscosity of EtGly (14.78 cp [15]) does not allow the generation of a spray with moderate pressures (2 bar). In contrast, the lower surface tension (22.1 mN/m) and the high volatility of EtOH do not allow the synthesis of iron oxide films with desired optical properties. Water with a surface tension of 72.8 mN/m [16] and a viscosity of 0.89 cp [15] helps to decrease the viscosity of EtGly mixtures and increase the surface tension of EtOH mixtures [15]. It will promote the generation of a spray with optimal characteristics for the pyrolytic process.

Multiple mixtures were used for the spray deposition; however, the following solvents are analyzed in this work: pure water, a mixture of EtGly/water 10 v/v%, and a mixture of EtOH/water (1:1). The precursor solutions were prepared by dissolving $FeCl_3 \cdot 6H_2O$ in the three different solvents in order to get a concentration of 0.1 M. For the spraying process, the nozzle (Quikmist, Spraying Systems Co.) to substrate distance was fixed at 30 cm, and compressed air was used as carrier gas at 2 bar. The precursor solutions were sprayed for 1 s onto glass substrates of 7.5×7.5 cm^2 (Corning 2947) heated at 350 or 450 °C; after the spraying process, intervals with no spray of 10 s were employed. The deposition temperature of the films prepared with ethanol solvent was of 350 °C because the low boiling point of ethanol. When iron oxide films are intended to be deposited at 450 °C using ethanol, the resulting material is a powdery film with non-uniform properties. In order to evaluate thin films with different thickness, 5, 20 and 40 mL of the precursor solutions were sprayed. The deposition time was different for each solvent and depended on the respective solution flow rate; namely, 13.4 mL/min for water, 11.8 mL/min for EtGly/water 10 v/v%, and 12.6 for EtOH/water (1:1). Table 1 indicates the series of samples analyzed in this work.

2.2. Characterization of iron oxide thin films

The structure of the films was studied by X-ray diffraction (XRD) and Raman spectroscopy. For the XRD measurements, a Philips X'Pert diffractometer was used. Raman spectroscopy studies were performed in a Witec-Alpha 300 micro-Raman confocal microscope. A $\lambda = 633$ nm of HeNe laser beam was focused on the sample surface by 10, 20 and 100× objectives; for preventing possible phase transformations, the power of the excitation light was below 1 mW [17,18]. The surface of the films was studied by atomic force microscopy (AFM) using a Witec-Mercury 100 microscope with silicon nitride tips. Furthermore, the surface of the thin films were characterized by scanning electron microscopy (SEM) using an Auriga Karl Zeiss microscope. The thickness of the thin films was determined in a Vecco Dektak-8 Stylus profiler. For the thickness measurements, the steps were prepared by both, masking one part of the film during the deposition and by etching the films with 0.1 M hydrochloric acid. Similarly to other static spray pyrolysis deposition apparatuses, the used one in this work gives a thickness profile, with a greater thickness in the center of the spray. For all the thickness measurements, the central part of the coated substrate was measured. Additionally, magnetic properties of the films were measured at room temperature with parallel to magnetic field silica probes, using an alternating gradient magnetometer AGM Micromag-2900 by Princeton-measurements. For magnetic measurements, the samples were cut with 4×4 mm^2 dimensions.

Table 1
Series of iron oxide thin film samples prepared at different deposition conditions.

Sample	Solvent	mL of sprayed solution	Deposition time (min)	Deposition temperature (°C)	Thickness (nm)	Particle size (nm)	RMS Roughness (nm)
W5	Water	5	4.1	450	38	50	20.7
W20		20	16.4	450	150	140	66.2
W40		40	32.8	450	258	250	74.8
E5	EtGly[a]	5	4.6	450	22	150	4.77
E20		20	18.6	450	88	155	28.3
E40		40	37.2	450	152	155	21.6
A5	EtOH[a]	5	4.3	350	47	200	21.8
A20		20	17.5	350	224	200	38.2
A40		40	34.9	350	473	195	44.7

[a] In mixture with water, see text.

3. Results

3.1. Structural characterization

In order to evaluate the effects of both the nature of solvent and the volume of the precursor solution on the structure of the films, the prepared samples were characterized by Raman spectroscopy and XRD. In all the Raman scans, it was assured that the structure of the films is not converted into hematite by the laser beam [17]. Fig. 1 shows Raman spectra of the prepared iron oxide thin films with different solvents, the first column corresponds to water, the second to EtGly/water and the third to EtOH/water; the rows correspond to different volumes of starting solution used. It can be observed in Fig. 1 that the effect of the solvent on the structure of the films plays a key role when low volumes are used. For higher volumes, upper row in Fig. 1, hematite is found in the films as a unique phase, although the films were prepared at different temperatures. It is because hematite is thermodynamically the most stable iron oxide phase [9,19]. The exception is for the sample prepared with the mixture of EtGly/water (E40), where still maghemite phase is found in combination with hematite. The transition to hematite takes place due to longer permanence of the films on the hot plate; it is because thicker films require longer deposition times. Similar results are observed in the XRD patterns shown in Fig. 2, where hematite diffractions dominate when higher volumes were used. A more detailed description of the role of the solvents will be discussed in the next paragraphs.

Water is an excellent solvent for thin film preparation by spray pyrolysis because it is cheap, non-dangerous, and dissolves multiple metal salts. However, water has a high surface tension, it promotes the generation of greater droplets which may cool down the surface substrate during the spraying process. Low substrate temperatures may promote the generation of iron oxide thin films with poor crystallinity and the growth of oxyhydroxide phases, such as ferrihydrite [9]. Fig. 1(a) shows the evolution of the structure of the films prepared at 450 °C with different volumes of starting solution using water as solvent. For the films prepared with 5 mL, different low intensity bands can be observed, the sharp bands are assigned to hematite (see the vertical lines in the graph), and the broad band located at 695 cm^{-1} and the bands located at 325, 372 and 383 cm^{-1} are assigned to oxyhydroxides such as goethite, akaganeite and ferrihydrite, see the dashed arrows [13,18,20]. Otherwise, when 20 mL of the starting solution were sprayed, the structure of the films exhibits more intense hematite bands and the bands corresponding to oxyhydroxides are even present, except the broad one which corresponds to ferrihydrite, see dashed arrows in the spectrum. For the films prepared with 40 mL, all the exhibited