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Physical and ethanol sensing properties of sprayed $Fe_2(MoO_4)_3$ thin films

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ABSTRACT

Monoclinic $Fe_2(MoO_4)_3$ thin films have been prepared by chemical spray technique deposited on glass substrates and investigated their physical properties. The obtained thin films were characterized by X-rays diffraction (XRD) using Rietveld's method which confirm the appearance of pure monoclinic $Fe_2(MoO_4)_3$ thin films. Moreover, the surface morphological was investigated using scanning electron microscope (SEM), which showed the formation of porous microstructures with rough surfaces and spherical nanoparticles.

The spectrophotometer UV–Vis–NIR reveals that the sample presents an optical gap equal to 2.0 eV. Electrical properties dependence on both temperature and frequency of the $Fe_2(MoO_4)_3$ thin films have been reported. The ac conductivity plot showed a universal power law according to the Jonscher model. Activation energy values deduced from the relaxation frequency is of the order of 0.71 eV. Finally, $Fe_2(MoO_4)_3$ thin films have been tested as sensitive films against ethanol vapor at different operating temperatures and gas concentrations. The films showed promising ethanol sensing behavior with good reproducibility and especially an excellent sensing performance at 275 °C.

1. Introduction

Semiconductor such as the binary metal oxides like MoO_3, ZnO, Mn_3O_4 and WO_3 which are the most extensively studied are considered to be potential materials for electrochemical applications [1], lithium ion batteries [2] and sensors [3–5] because of their feasible oxidation state and high electrical conductivity. Multi-component oxide thin films have found a large variety of uses in optics and electronics as a direct result of their ability to achieve properties unattainable in binary metal oxide films. On the other hand, mixed metal oxides are interesting for various applications while the combination of two metals in oxide-matrices produces the materials with new structure and chemical properties compared to that of binary oxides.

Recent literature survey indicates the projection of several ternary metal oxides that include $ZnWO_4$, $BiVO_4$, $Bi_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, $NiMoO_4$, and $CoMoO_4$ as potential visible light active photocatalysts [6]. Among them, ferric molybdate is prospective materials and it has recently been referred as good heterogenous catalysts for oxidation of methanol to formaldehyde [7] and a good photocatalytic activity under UV irradiation. However, in general, the crystal structure of monoclinic $Fe_2Mo_3O_{12}$ always appears to be the most thermodynamically stable product [8].

Therefore, ferric molybdate is one of the most important metal molybdates materials and is expected to offer richer redox chemistry compared to single component oxides due to its combined contributions from both iron and molybdenum ions. These materials have attracted tremendous research and have been widely applied in various fields such as optical fibers, magnetic materials and catalysts [9]. An excellent review covering various aspect of methanol oxidation on ferric molybdates was recently published; A. M. Beale et al. [10] proved that ferric molybdate catalysts have high activity and selectivity for the oxidation of methanol to formaldehyde and this ternary material was more active than molybdenite alone.

According to previous studies, very few reports are available on ethanol sensor using $Fe_2Mo_3O_{12}$ thin films. Joseph E. Gatt et al. [11] prepared $Fe_2(MoO_4)_3$–MoO_3 catalysts as selective sensors substrates by sol-gel technique for thermal microsensor detection of

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ethanol in automotive fuel. They observed that these catalysts provide excellent reaction selectivity towards all classes of hydrocarbon present in automotive fuels. Previously, J. Liang et al. [12] synthesized $Fe_2(MoO_4)_3$ by a rapid and environment friendly microwave irradiation method to detect H_2S gas. The results showed that ferric molybdate oxide nanoparticles exhibited excellent gas sensing properties in which response value reached 13.5 for 50 ppm H_2S gas.

There are many publications focused on the synthesis of ferric molybdate oxide $Fe_2Mo_3O_{12}$ including hydrothermal [13], sol-gel [14], RF magnetron, atomic layer deposition (ALD) and spray pyrolysis, etc. Among these various deposition techniques, spray pyrolysis is one of the best techniques as it is simple, cost effective and useful for large area thin films. Additionally, because in many cases the bimetallic oxides can form different crystal structures or phases depending on the synthetic conditions and compositions, a large variety of systems could be modeled and tested.

For several years great effort has been devoted to the study of $Fe_2(MoO_4)_3$ thin films using spray pyrolysis method and as observed from the literature no research are available on the synthesis of these thin films for detection of ethanol gas. The aim of our study is to report the application of spray method to prepare crystalline $Fe_2(MoO_4)_3$ thin film. Furthermore, this phase was then characterized using physical techniques such as X-Ray diffraction (XRD), scanning electron microscope (SEM), UV-VIS spectroscopy and impedance spectroscopic measurements. Rietveld refinement analysis was used to characterize the structural parameters of obtained thin films such as crystallite size, microstrain and lattice constant. The gas sensing properties such as, gas response, gas concentration, reproducibility and selectivity of $Fe_2(MoO_4)_3$ films based sensor is also studied as an application in this paper.

2. Experimental details

2.1. Films preparation

Based on previous work in our group on the optimization of the deposition parameters of the molybdenum oxide MoO_3 deposited by the chemical spray technique [15], we adopted for the deposition of $Fe_2(MoO_4)_3$ on the glass substrates the same technique with the value of 460 °C as substrate temperature and an equimolar concentrations ratio of the iron and molybdenum elements [Mo]/[Fe] = 1. The obtained precursor solution is then sprayed at the rate of 4 ml/min through a 0.5 mm-diameter nozzle. The nozzle-to-substrate plane distance was fixed at the optimal values of 27 cm [16].

2.2. Characterization techniques

In order to optimize sample's quality, the structural analysis of obtained thin films was reached by means of X-ray using CuKα monochromatic radiation (λ = 1.5418 A). The structural parameters were obtained from the Rietveld refinement of the XRD patterns by using MAUD program [17,18]. It is based on the Rietveld method combined with Fourier analysis, well adapted for broadened diffraction Bragg peaks. This program thus allows the refinement of the structural and microstructural parameters such as the lattice parameters, the size and the microstrain of crystalline domains.

In addition, the morphology of thin films was examined by a JOEL-JSM 5400 model scanning electron microscope SEM. The optical measurements were carried out using a Shimadzu UV 3100 double-beam spectrophotometer in the wavelength range of 300–1800 nm.

The impedance measurements of films were recorded out in the frequency range 1 Hz–13 kHz at various temperatures (593–653 K), using an impedancemeter (Hewlett- Packard 4192 analyzer). The electrical measurements of real and imaginary components of impedance parameters (Z′ and Z.) have been obtained by means of a symmetrical cell Ag/$Fe_2(MoO_4)_3$/Ag type. Metallic electrodes were pointed on the two extremities of the sample using silver paste. AC conductivity was obtained from $\sigma_{AC} = \frac{\ell}{Z'A}$, where Z′ is the real component of complex impedance, ℓ is the distance between electrodes and A is the cross-sectional area.

The sensing properties of $Fe_2(MoO_3)_4$ thin films based sensors under ethanol vapor were investigated according to the experimental protocol described in our work elsewhere [19].

The ethanol concentration ranges from 0.1 to 0.5% at an operating temperature of 225, 250 and 275 °C in order to determine the optimal working temperature of this film.

The response time is defined as the time taken by the sensor element to acquire the 90% of its maximum resistance value in the presence of gas. Once the maximum resistance value is attained, the gas was flushed out of the chamber and sensor element was allowed to regain its initial resistance value in atmospheric air keeping the sensor at the same temperature. The recovery time is the time taken by the sensor to reacquire 10% greater than its initial resistance value in the presence of atmospheric air.

3. Results and discussion

3.1. Structural properties

Firstly, the crystal structure of $Fe_2(MoO_4)_3$ is built up from [FeO_6] octahedra and [MoO_4] tetrahedra which all octahedra are only linked to tetrahedral by common corners and each oxygen being bound to one iron and one molybdenum atom.

Second, the X-ray diffraction was employed to characterize the crystal phases of $Fe_2(MoO_4)_3$ thin films in the 2θ range from 10° to 50°, the typical XRD spectrum of the sample is shown in Fig. 1.

All peaks can be well indexed to the monoclinic $Fe_2(MoO_4)_3$ with no other impurities, confirming that $Fe_2(MoO_4)_3$ have high phases purity. In addition, the purity of the monoclinic phases is also analyzed by Rietveld method of the structural refinement observed in Fig. 2. The lattice parameters are a = 15.7 nm, b = 9.23 nm, c = 18.20 nm and β = 125.25° which is match well with the standard XRD pattern for monoclinic $Fe_2(MoO_4)_3$ (JCPDS 83-1701) [20,21].

The structural refinement has confirmed the phase purity of the

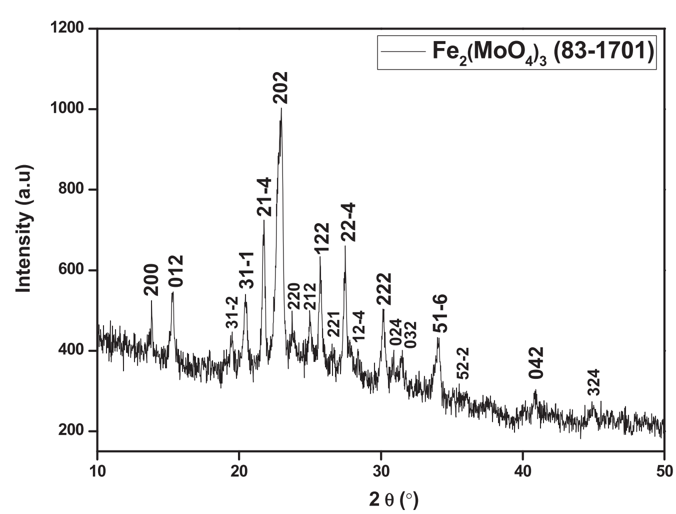

Fig. 1. XRD patters of $Fe_2(MoO_4)_3$ thin film.