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High Zr doping effects on the microstructural and optical properties of Mn_3O_4 thin films along with ethanol sensing

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ABSTRACT

Transition metal oxides as transparent conducting oxides (TCOs) films, with high optical transparency (≥82%), various valence states and p-type conductivity are used in a several physical domains. This work covers the physical study of Zr doped Mn_3O_4 semiconductor thin films using a spray pyrolysis method where Zr content varies in starting solutions from 0 to 20 at.%. The impact of this work is to offer some understanding of microscopic effects of relatively high doping Zr and then correlate these effects with the macroscopic properties for interesting applications especially gas sensor. In fact, the addition of Zr ions pointed out the reduction of crystallite size (24.1 (nm)) with 20 at.% doping allowing a better adsorption of gas molecules. In addition, it promotes the increase of optical gap (2.92 eV) with 6 at.% doping which is a useful parameter for some optical devices. X-ray diffraction (XRD), Raman spectroscopy, FTIR spectroscopy, atomic force microscopy (AFM) and EDAX techniques were used. It is found that these films crystallized in spinel type tetragonal hausmmanite structure. The gas sensing activity of these thin films (0, 6, 12 and 20 at.% Zr) was examined with Ethanol. The performances of these last four sensing layers were compared. All the tests were performed at different working temperatures $T_{work} = 125, 150, 175$ and 225 °C and under two gas concentrations: 0.1% and 0.5% ethanol using dry air as carrier gas. The films exhibited noticeably ethanol sensing especially the sample doped with 6% of zirconium exhibits the most excellent sensing performance since it showed a clear response already at a low ethanol concentration of 0.1%.

1. Introduction

During the last two decades, nanocrystalline thin films of transition-metal oxides have attracted growing attention owing to their exceptional structural diversity linked to novel physical and chemical properties [1,2]. Therein, manganese oxides have a fantastic potential because of their aptitude to adopt several oxidation states such as MnO, MnO_2, Mn_2O_3, Mn_3O_4 and Mn_5O_8 which are of special interest in various technological applications such as catalysts [3], dry cells, solar energy conversion and molecular adsoption [4]. Among the various forms of manganese oxides, mixed-valent spinel Mn_3O_4 is the most stable one and it has attracted significant interest because of its potential applications in rechargeable lithium-ion batteries, gas sensing, supercapacitors and catalysis [5–8]. Moreover, the valence degree, the abundance, and hence low cost of the major constituents, makes it more attractive. Until now, a number of synthesis procedures have been used to obtain different Mn_3O_4 nanostructures such as the pulsed laser ablation process, chemical bath deposition technique and (SILAR) method [9–11].

In this work, the spray pyrolysis technique is selected because it is a versatile deposition method allowing a good control of layer stoichiometry by varying the concentration of precursors in the starting solutions and most importantly-large-area coatings can be obtained by using cost-effective equipments, in relatively low energy consuming conditions. In spray pyrolysis the deposition rate, the thickness and the uniformity of prepared sprayed films are the consequence of nucleation and crystal growth processes which are mainly influenced by the deposition temperature, the substrate nature, the solution and the gas flow rates and so on. On the other hand, inspecting the microstructure and the morphology of nano-forms is crucial in the context of Mn_3O_4 because every structure has its own value when used in a potential application. Recently, many research results showed that electronic, optical and catalytic properties of Mn_3O_4 nanostructures are highly dependent on their dimensionality, size, morphologies and the crystalline forms [12–16]. So, doping with transition-metal ions is another alternative to control the properties of these functional materials. Characteristically, doping with low valence cations may induce new phenomena not found in bulk materials which may be to the confinement of electronic states and the tendency to occupy the sites in the crystalline structure.

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Dopants such as Ni, Cr, Co, Cu, Zn, Li, Fe, S and Sn have been studied [17–28]. However, poor numbers of reports have been published concerning Zr as transition-metal doping into Mn_3O_4.

In this work, Zirconium was chosen as the doping element due to its abundance, low cost and because it can potentially acts as double donor providing up to two extra free electrons per ion when substituted for Mn^{2+}, an important factor in electronic applications. Besides, the wide band gap of ZrO_2 is beneficial to widen the band gap between Mn_{3d} and O_{2p} states thereby it will have a potential to increase transparency in the visible range [29]. In the present work, a strong correlation between XRD, EDAX, Raman and FTIR investigations as a function of Zr concentration is revealed. As well as, an examination of how Zr doping can lead to an enhancement of the sensitivity of Mn_3O_4 against ethanol gas is carried out.

2. Experimental section

2.1. Preparation of Zr doped Mn_3O_4 thin films

The deposition of both undoped and Zr doped Mn_3O_4 films was carried out using spray pyrolysis method. In a typical procedure, 1.97 g of $MnCl_2$_$4H_2O$ (0.1 M) and $ZrCl_4$, added as doping agent in a distilled water (100 ml). The ratio of [Zr]/[Mn] is varying in the starting solution as: 3, 6, 12 and 20 at.%. The solution is then sprayed on glass substrates at optimized substrate temperature ($T_s = 350$ °C). The substrates were first cleaned with a water bath, followed by acetone and ethanol successively. Finally the substrates were rinsed with deionised water and then dried in air. The deposition parameters like solution flow rate, and nozzle to substrate distance were kept as 4 ml/min and 27 cm, respectively. The total deposition time was maintained at 20 min. Nitrogen air was used as a gas carrier. After the deposition, the films were allowed to cool slowly to room temperature.

2.2. Characterization techniques

The structural characterizations of the films were analyzed by X-ray diffraction (XRD) using a Siemens D500 diffractometer with monochromatic CuKa radiation (l = 1.5406 Å) in the span of the angle between 10° and 70° with the steps of 0.05° at room temperature. Raman experiments were carried out at room temperature recorded by means of were obtained with a Fourier transform infrared spectrometer (genesis II DTGS). The scanning wavelength of infrared was 4000–400 cm^{-1}. The surface morphology of all the samples was performed by an atomic force microscopy at taping mode (AFM, VEECO digital instrument 3A). The films were excited with the He—Ne 632 nm laser source. Optical absorption spectrum was carried out in the wavelength range 250–2500 nm using SHUMATZU UV 3100 UV–vis spectrophotometer. PL spectra were performed at room temperature using a Perkin-ElmerLS55 Fluorescence spectrometer with an excitation wavelength of 275 nm. The thickness of the sample (3 at.%) as well as the different element analysis were measured using environmental scanning electron microscope FEI Quanta 200 model coupled to a spectrometer analysis by energy dispersive X-ray (EDAX).

2.3. Sensing test

The sensing properties of Zr doped Mn_3O_4 under ethanol vapor were investigated using the experimental set-up described previously [30]. First, the dilution of ethanol as vapor in dry air is achieved using a two-arm gas-flow device. These two mass flow controllers allowed

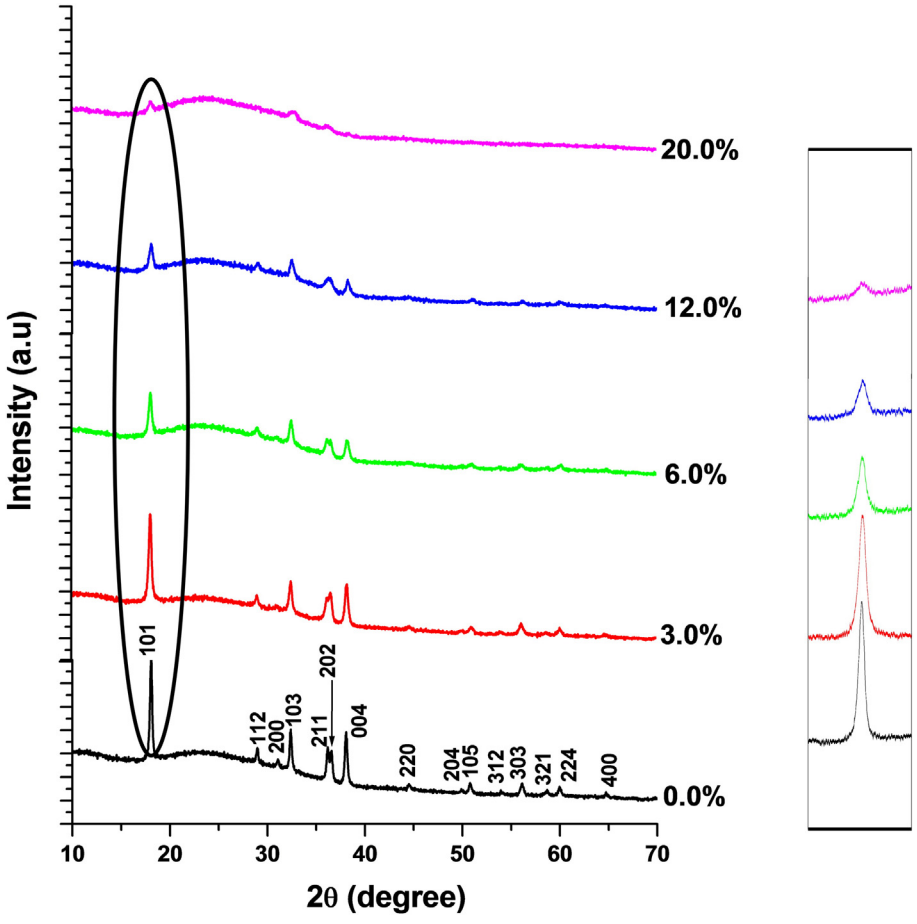

Fig. 1. X-ray diffraction (XRD) patterns of Zr doped Mn_3O_4 films.