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A study of optothermal and AC impedance properties of Cr-doped Mn_3O_4 sprayed thin films

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ABSTRACT

Chrome-doped Mn_3O_4 thin films were grown on the glass substrates by the spray pyrolysis technique at 350 °C. XRD diffraction and Raman spectroscopy analysis revealed that all samples have tetragonal spinel structure with a preferred orientation along the direction (101). Absorption coefficient has been measured using both transmission and mirage effect. The band gap energy decreases from 2.2 to 1.9 eV with Cr content while Urbach energy value increases from 354 to 473 meV. Also, thermal conductivity was evaluated. Finally, physical properties have been evaluated and discussed in terms of alteration of the band gap edges, electrical patterns and mirage effect.

1. Introduction

Recently, transparent conductive transition metal oxides are highly attractive materials in many fields. Because of the outstanding optical transmittance (>80%) and metal-type conductivity, these materials have been proved to be an appropriate candidates for many applications in different technological areas, such as chemical applications, catalysis, electrochemical sensor and lithium batteries [1–4]. Among a variety of materials, the manganese oxides are of great potential due to various valence states, crystalline structures, low manufacture cost and non-toxicity [5–7]. In particular, Mn_3O_4 is multivalent oxide that forms the tetragonal spinel structure with Mn^{3+} in the octahedral sites and Mn^{2+} in the tetrahedral ones, respectively. The octahedral symmetry is tetragonally distorted due to Jahn–Teller effect on Mn^{3+} ions ($3d^4$) causing structural defects [8]. Because of this duality among the tetrahedral and octahedral sites, electrical conduction is believed to take place by the jumping of charge carriers between these two oxidation states. In addition, the study of frequency and temperature dependence of AC conductivity leads usually to characterize the mechanisms of conduction. To date, one of the challenges in the Mn_3O_4 related research field is improving properties through controlling the optical, morphological, thermal and electrical properties. Thus, doping Mn_3O_4 with transition metal ion can be a reliable approach to adjust conductivity and band gap of these oxides for potential applications, such as sensing devices. As previously reported, Jha et al. found that the energy band gap of Mn_3O_4 nanorod increased continuously with the increase of Zn doping concentration [9]. Moreover, Zhao et al. prepared Sn-doped Mn_3O_4/C nanocomposites as a supercapacitor electrode with higher capacitance [10]. Also, Spinel-type Cu-doped Mn_3O_4 microcrystal shows that Mn_3O_4 is an effective reagent for the degradation of organic contaminants in water [11]. In addition, chromium is efficient donor specie which can take a mixed valence state used for enhancing many features of transition metal oxide in a wide area of applications. For instance, doping ZnO with chromium was shown to reduce the sensor's operating temperature and enhance its response [12]. It is also proved that by chromium doping ferromagnetism properties of husmannite Mn_3O_4 nanowires are largely enhanced [13]. Supercapacitor performance of Mn_3O_4 nanocrystals is improved through Cr doping was also pointed out [14]. So far, some research have been reported on the effects of doping Cr content on the structural and electrical properties of transition metal oxides by substitute a small amount of dopant ions at the transition metal sites [15,16]. The aim of this work is to investigate the influence of Cr-doping on the optical, thermal and electrical properties of Mn_3O_4 sprayed thin films. The variation in Cr content allowed controlling band gap and thermal conductivity in the obtained Cr-doped films. Indeed, experimental results on AC conductivity over range of temperature 603–643 K and frequency 100 Hz–5 MHz have been provided that these physical properties can be tuned by varying Cr content. Also, we study the band gap alteration and their effect on the physical properties of pure and Cr-doped Mn_3O_4 thin films synthesized

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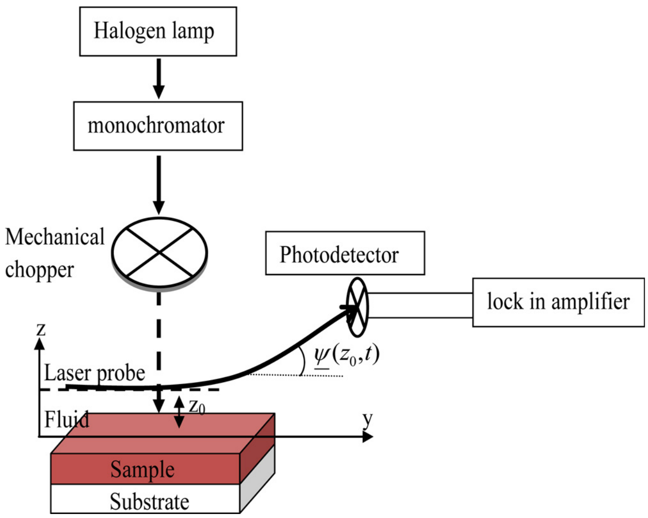

Fig. 1. The 'Mirage Effect' set-up.

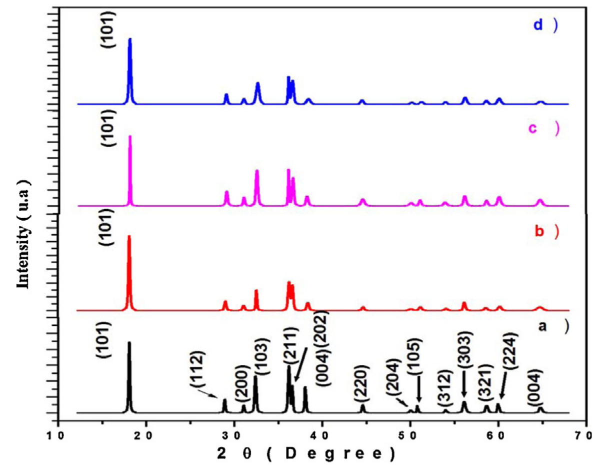

Fig. 2. XRD pattern of (a) Mn_3O_4 pure, (b) Mn_3O_4:Cr 1%, (c) Mn_3O_4:Cr 2% and (d) Mn_3O_4:Cr 3% thin films.

using this cost-effective process. Finally, the interest of studying this compound from the point of view of several detailed and relevant experiences in order to establish any eventual correlation that can lead to the development of interesting optoelectronic components.

2. Experimental procedure

2.1. Experimental setup

Cr-doped manganese oxide thin films with varying Cr content were grown on glass substrates at 350 °C using the spray pyrolysis technique. For preparation of Cr-doped Mn_3O_4 films, the initial solution was prepared by dissolving manganese chloride ($Mncl_2 \cdot 6H_2O$) 0.1 M in 100 ml deionized water. Chromium chloride ($CrCl_3 \cdot 6H_2O$) is added to the starting solution as doping agent at various [Cr]/[Mn] concentration ratios: 1, 2 and 3 at%. The substrate temperature was maintained using a temperature controller. The starting solution was sprayed at rate of 6 ml/min through a fine glass nozzle. The distance between nozzle and substrate was about 20 cm. Nitrogen gas was used as a carrier gas.

2.2. Characterization techniques

The phase and crystallinity of the as-obtained films were characterized using a Siemens D500 X-ray diffractometer with CuKα radiation (λ = 1.54056 Å). The micro-Raman spectra were recorded at room temperature with a Horiba Jobin HR 800 system at a spatial resolution of 2 μm in a backscattering configuration. A 632.8 nm line of a He–Ne laser was used for off-resonance excitation. The surface morphology was studied by an atomic force microscopy at taping mode (AFM, VEECO digital instrument 3A). The optical reflectance and transmittance spectra of the samples were carried out by UV–vis–NI spectrophotometer (Shimadzu, UV-1601) in the wavelength range of 250–2500 nm. The thermal behavior was performed by the mirage effect using the photothermal deflection PTD spectroscopy technique in which the sample is heated using a 250 W halogen lamp placed behind the slot of a monochromator. The light coming out of the monochromator is modulated with a mechanical chopper. When the sample absorbs this monochromatic light, it gets heated in a periodic manner then it acts as a source of thermal wave that propagates into surrounding ambient fluid creating refractive-index gradient. This causes indeed a periodic deflection of the laser probe beam skimming the sample surface which is detected with a four quadrant photodetector related to a lock in amplifier for measuring the amplitude and phase of the photothermal signal (Fig. 1). On the other hand, the electrical conductivity of the samples is measured using an impedance meter (Hewlett-Packard 4192 analyzer) at various temperatures (603–703 K) in the frequency range 5 Hz–13 MHz. The experimental data are obtained by means of two shaped electrodes of band painted on either end of the sample by using the silver paste. AC conductivity is provided via $\sigma_{AC} = \ell / Z'A$ calculation, where Z' is the real components of complex impedance, ℓ is the distance between electrodes and A is the cross-sectional area. These measurements were performed by varying the Cr content.

3. Results and discussion

3.1. Structural and morphological characteristic

The XRD patterns of the Cr-doped Mn_3O_4 are depicted in Fig. 2. The obtained diffraction peak positions are compared with the standard value and are found to be in agreement with JCPDS-01-075-1560, confirming the formation of tetragonal single phase Mn_3O_4 (space group I41/amd). No other impurities related with the

Table 1
Summary of the lattice parameters, unit cell volumes and structural results of Cr-doped Mn_3O_4 thin films.

Sample	Cell parameters				D (nm)	Dislocation density δ	Microstrain
	a (Å)	c (Å)	c/a ratio	Cell volume (Å^3)		(10^{14}lines/m^2)	(ε)
Mn_3O_4	5.75	9.45	1.64	312.67	56.5	3.18	3.23×10^{-3}
Mn_3O_4:Cr 1%	5.75	9.34	1.62	309.31	34	3.4	3.4×10^{-3}
Mn_3O_4:Cr 2%	5.74	9.51	1.67	309.18	48	4.32	4.57×10^{-3}
Mn_3O_4:Cr 3%	5.73	9.30	1.61	309.93	96	1.08	2.29×10^{-3}