Synthesis and Characterization of Nanostructured SnO_2 doped MnO_2 thick films for Sensing Applications

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Abstract : Nanostructured MnO_2 powders were synthesized by the hydrolysis of AR grade manganese chloride in aqueous-alcohol solution with bismuth chloride (dopant in the proportion 1, 3, 5 and 7 wt %) to get fine powder. Thick films of SnO_2-doped MnO_2 powders were prepared by screen printing technique. The structural properties of Nanostructured SnO_2 doped MnO_2 thick films were studied by X-ray diffraction technique. The XRD spectrum revels that the films are polycrystalline in nature and tetragonal in structure. The unit cell volume was evaluated as 71.81. The SEM micrographs show a number of spherical and granular particles of Sn-species distributed uniformly with smaller size and shape among the MnO2 grains. The average particle size ranges from 40 nm to 114 nm. It is clear that the numbers of Sn-species are distributed among MnO2 grains in larger amount than in others decreasing the porosity which in turn decreased the adsorption of the gas molecules inside the pores, leading to decrease in the effective surface area or surface to volume ratio.

The symmetrical I-V characteristics suggest that the contacts fabricated on the films were ohmic in nature and the p-n junctions were randomly distributed on the surface of the film. The increase in conductivity with increasing temperature (above 1000C) could be attributed to negative temperature coefficient and semiconducting nature of the SnO2 activated MnO2 samples. The SnO2 activated films showed very high electrical resistance of the order of 107 Ω in air.

Keywords: SnO_2-doped,MnO_2, XRD, SEM, conductivity.

1. Introduction

a significant change in the electrical resistance of the material can be obtained by adsorption of gas molecules on a metal-oxide semiconductor surface [1]. Their surface properties are sensitive to changes in the gas atmosphere, especially on small amounts of hydrocarbons and hydrogen [2]. Tin oxide (SnO_2), which is an n-type semiconductor material, is one of the most investigated materials [3]. The gas-sensing mechanism depends on chemical and electronic properties and on the three-dimensional ordering of both the bulk and the surface material, and is mainly influenced by the surface region of the grains/particles. Gopel *et. al.* emphasized that the development and improvement of a chemical sensor requires a balance between empirical knowledge and systematic research as long as the basic processes involved are unknown [4]. Accordingly, studying the structure as well as the volume and surface chemical composition, is of great importance to better understand the gas-sensing mechanism [5].

Generally, under stoichiometric tin oxide (SnO_{2-x}) is used as sensing material because oxygen vacancies are necessary for the gas-sensing mechanism. Consequently, the chemical composition during synthesis needs to be optimized and a stable crystallographic structure and stoichiometry must be formed for best sensor operations. In spite of many studies concerning the oxidation of SnO_x thin films prepared from Sn or SnO_2 precursors [6], only a little amount of work on the oxidation process of SnO nano particles can be found in literature. Nevertheless, it is known that annealing treatments and structure influence the sensitivity of SnO_2 thin film gas sensors [7].

Nanostructured materials for gas-sensing applications are of great interest due to their higher surface/volume ratio compared to that of bulk material leading to a larger reactive surface. Additionally, microelectronic circuitry provides the means of achieving low fabrication cost and ease of miniaturization of nanostructured gas-sensing devices [8]. SnO_2 gas sensors are one of the examples of functional materials where the use of nano particles was shown to lead to improved sensor properties due to the higher surface to volume ratio [9]; nano particles build porous films, thus increasing the reactive surface in relation to the whole material volume of the dense film.

over the past few years, the tin oxide based films are widely used in a gas sensing device due to their high sensitivity. Because of its simple design, robustness, fast response and the possibility of miniaturization of the devices [10]. When a SnO_2 semiconductor film is exposed to air, physisorbed oxygen molecules receive electrons from the conduction band of the film and change to O^- ads or O^{2-} ads species. These adsorbed molecules form an electron depletion layer just below the surface of SnO_2 particles and forms a potential barrier between particles; consequently the SnO_2 film becomes highly resistive [11– 13]. The lowering of the potential barrier takes place when the adsorbed oxygen species are exposed to the reducing gases, resulting in the increased conductance of the sensitive film. The variation of the conductance measured under specific gases depends on many parameters such as intrinsic resistance, grain size [14], grain boundary barriers, detection temperature etc. Tin oxide films have been prepared by a number of techniques including spray pyrolysis [15, 16], sputtering [17, 18], chemical vapour deposition (CVD) [19] and evaporation [20].

In this paper we report the synthesis, structural and electrical properties of SnO_2-modified MnO_2 thick film for the sensing application.

2. Experimental

2.1 Preparation of material powder

The nanostructure MnO_2 powder was synthesized by the hydrolysis of AR grade manganese chloride (99.9 % pure) in aqueous-alcohol solution. distilled water and propylene glycol is used to prepare aqueous alcohol solution. This solution was mixed with aqueous solution of tin chloride in ratio such that the manganese concentration was 0.01M and the alcohol to water ratio was 1:1. The special arrangement was made to add drop wise aqueous ammonia (0.1ml / min.) with constant stirring till the pH of solution becomes 8.3. The hydroxides were washed by distilled water until chloride ions were not detected by $AgNO_3$ solution after complete precipitation. Then the hydroxide in a glass beaker was placed in a microwave oven (input power 600W) for 15 minutes with on-off cycle. The dried precipitate was ground by using agate pestle mortar and annealed in a muffle furnace at 550°C for 30 min.

2.1.2 Fabrication of thick films

The fine powder was calcinated at 800^0C for 24 h in air and reground to ensure sufficiently fine particle size. The paste of inorganic to organic i.e thixotropic paste by mixing nanostructured MnO_2 with a solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellulose, butyl carbitol acetate and turpineol in ratio 80: 20 was formed. The thixotropic paste was screen printed on the glass substrate in desired patterns. Films prepared were fired at 550°C for 30 min.

3. Results and Discussions.

3.1 X-ray diffraction studies

X ray diffraction study of SnO_2 doped MnO_2 thick films was carried out using BRUKER AXSD8 (Germany) advance model X ray diffraction with $CuK\alpha_1$ (λ=1.54056 Å) radiation in the 2θ range 20^0- 80^0. Figure 1 shows the XRD pattern of SnO_2 doped MnO_2 thick films. The 2θ peak observed at 26.19, 34.53, 37.62, 41.2, 42, 43.5, 45.32, 54.13, 61.04, 64.56, 71.3, 74 which correspond to the (200), (211), (220), (310), (220), (222), (321), (301), (112), (400), (510) and (420) planes of reflections. The XRD spectrum reveals that the films are polycrystalline in nature and tetragonal in structure. There are no prominent peaks of SnO_2 associated in XRD pattern of MnO_2 due to smaller wt % of SnO_2 in comparison with MnO_2. The lattice parameters were found to be a = 4.7365 and c = 3.2010. The unit cell volume was evaluated as 71.81. (JCPDS data card no. for Mn – 89 - 4836 and for Sn – 89 - 2761).

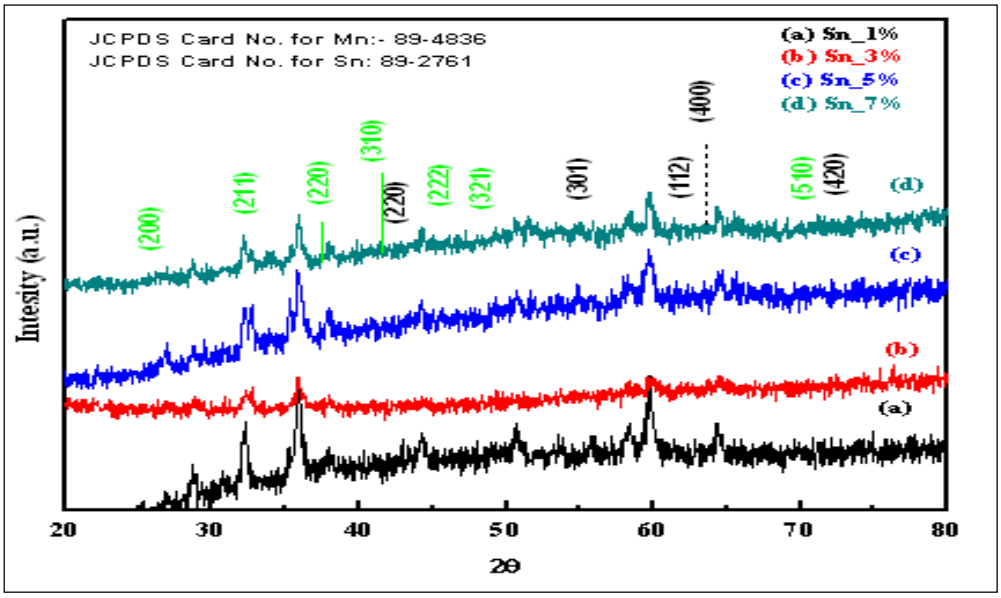
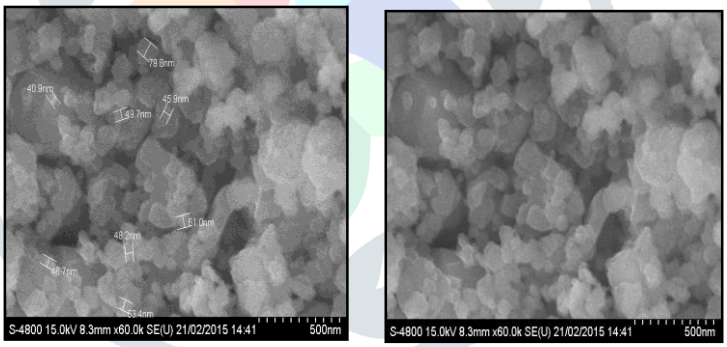


Fig. 1: XRD of SnO_2 doped MnO_2

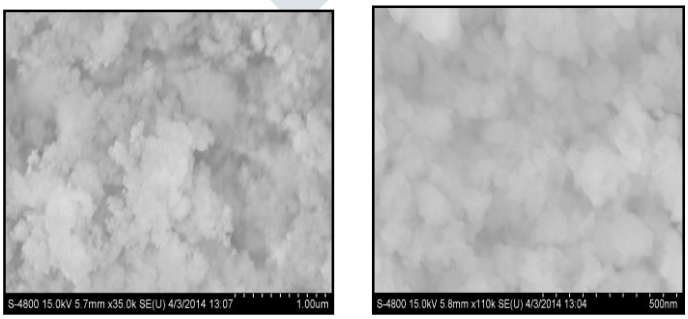
3.2 Morphological study of SnO_2 doped MnO_2

Fig. 2 (a - h) depicts the SEM images of SnO_2 doped MnO_2 thick films fired at 550^0C. The micrographs show a number of spherical and granular particles of Sn-species distributed uniformly with smaller size and shape among the MnO_2 grains. The average particle size ranges from 40 nm to 114 nm. It is clear from the micrograph that the numbers of Sn-species are distributed among MnO_2 grains so that the porosity of the film is largest than others. It is clear from the micrograph (3 wt % and 5 wt %) that the numbers of Sn-species are distributed among MnO_2 grains in larger amount than in others decreasing the porosity which in turn decreased the adsorption of the gas molecules inside the pores, leading to decrease in the effective surface area or surface to volume ratio.



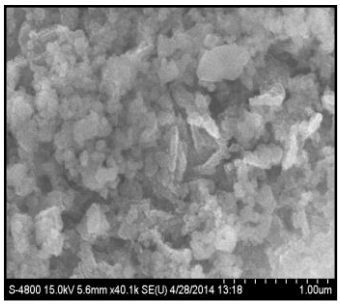
(a) **(b)**

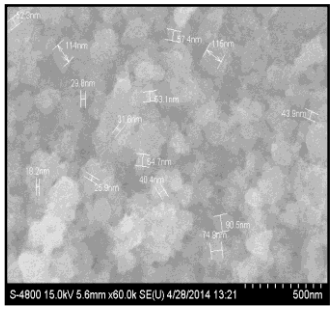
SnO_2 doped MnO_2 (1 wt %)



(c) **(d)**

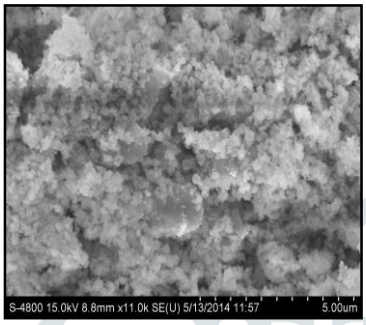
SnO_2 doped MnO_2 (3 wt %)

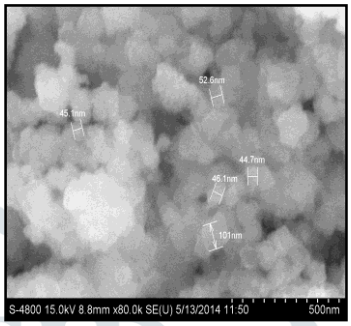




(e) **(f)**

SnO_2 doped MnO_2 (5 wt %)





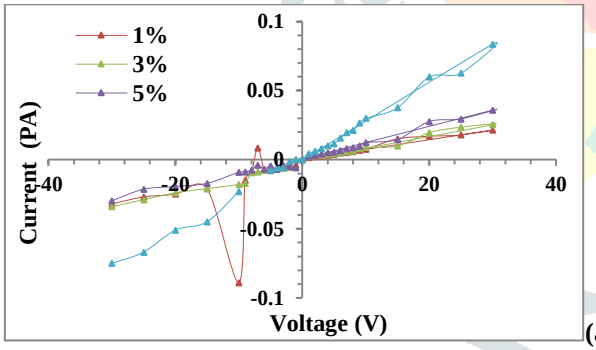
(g) **(h)**

SnO_2 doped MnO_2 (7 wt %)

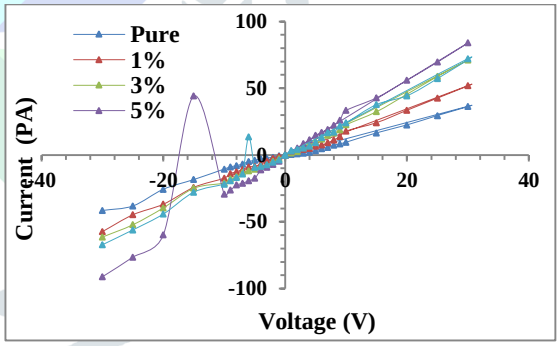
3.3 Electrical properties

3.3.1 I-V characteristics

Fig. 3 (a, b) represents I-V characteristics of the SnO_2 doped MnO_2 films at room temperature and at high temperature.



(a)



(b)

Fig. 3 (a, b) I-V characteristics at RT and at High Temperature

It is clear from the symmetrical I-V characteristics that the contacts fabricated on the films were ohmic in nature and the p-n junctions were randomly distributed on the surface of the film.

3.3.2 Electrical conductivity

Fig. 4 depicts the variation of log (conductivity) with operating temperature of SnO_2 activated MnO_2 thick films. The semiconducting nature of MnO_2 is observed from the measurement of conductivity with temperature. The conductivity values of all samples were larger at room temperature than at higher temperature. It may be due to air humidity associated with the films at room temperature. The increase in conductivity with increasing temperature (above 100^0C) could be attributed to negative temperature coefficient and semiconducting nature of the SnO_2 activated MnO_2 samples. The SnO_2 activated films showed very high electrical resistance of the order of 10^7 Ω in air.

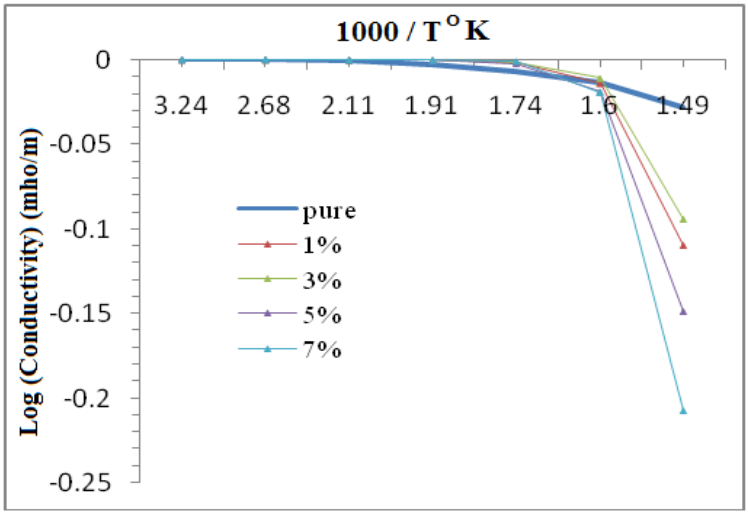


Fig. 4 Variation of log (conductivity) with operating temperature

From figure, it is clear that the conductivity of the sensor increases with an increase in operating temperature, indicating a negative temperature coefficient of resistance. This behavior confirmed the semiconducting nature of the undoped and doped MnO_2.

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