Academic Science Journal

Effect of MnO_2 on Morphological and Electrical Properties for SnO_2 Nanostructure Thin Films

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Received: 6 June 2024 **Accepted: 28 July 2024**

Published: October 2025

DOI: https://dx.doi.org/10.24237/ASJ.03.04.915C

Abstract

Using the technique of chemical spray pyrolysis,(SnO_2) thin films doped with different ratios of (MnO_2) (2%, 4%, 6%, 8%) were prepared and deposited on glass substrates at (350 ºC). The spectral analysis of the prepared films was done using a field emission scanning electron microscope, and electrical measurements were carried out to verify the prepared samples. FE-SEM measurements revealed inhomogeneous granular structures, where these groups are large. The size of these groups' decreases with increasing doping ratio of (MnO_2), and the reason for this decrease is the dispersion of manganese oxide (MnO_2) particles within the crystal lattice of tin oxide (SnO_2). Electrical measurements were used to determine the type and concentration of charge carriers and the Hall coefficient, conductivity, resistance, and mobility. The prepared films showed (n-type) charge carriers according to the Hall coefficient values, and this is due to the effect of temperature and impurities. An increase in the Hall coefficient values was also observed with the increasing doping ratio of manganese oxide (MnO_2), reaching the highest value at a doping ratio of (6%), Conductivity also increased with increasing doping ratio, while mobility decreased with increasing doping ratio.

Keyword: SnO_2 film, Hall Effect, FE-SEM, doping effect.

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Introduction

$SnO2$, also known as tin (IV) oxide or stannic oxide, is a chemical compound composed of tin and oxygen [1]. It is a white or off-white crystalline solid and is commonly found in nature as the mineral cassiterite. SnO2 has a wide range of applications due to its properties. Structure, Electrical Conductivity, Optical Properties, Gas Sensing, Catalyst Support, Protective Coatings, Optoelectronics. Manganese chloride is a chemical compound composed of the elements manganese and chlorine [2]. Manganese (Mn) is a metallic element belonging to Group 7 in the periodic table of elements and is known for its distinctive mineral and chemical properties. Chlorine (Cl) is a gaseous element that belongs to Group 17 in the periodic table. Manganese chloride occurs naturally in the environment, but it can also be prepared in the laboratory or by industrial means. It is typically available as a white powder or crystalline crystals and is soluble in water. Thin films are thin layers of materials used in semiconductor technology and electronic devices [3]. The electrical properties of thin films vary depending on the material used in their fabrication and the atomic arrangement of that material. However, there are some basic electrical properties that can be common among thin films, including: Electrical resistance, Capacitance, Trans conductance, Barrier properties, Sensitivity. Due to the advancement of science and technology and the wide and significant applications in the field of thin films, methods for preparing thin films have been developed [4]. The selection of the appropriate method depends on several factors, including the type of material used, the intended application, and the cost of preparation. One of the most common chemical methods for preparing thin films is the chemical vapor deposition (CVD) technique [5]. This method involves spraying a solution onto hot substrates made of glass or quartz at a specific temperature depending on the type of material used [6]. As a result of the thermal chemical reaction between the material atoms and the hot substrates [7], a thin film is formed, thin films is typically achieved using techniques such as thermal evaporation [8], sputtering [9], chemical vapor deposition [10], atomic layer deposition [11] , and solution deposition[12].

The current study aims to prepare doped (SnO2) thin films with different percentages of (MnO2) (2, 4, 6, 8%) using the Chemical spray pyrolysis technique, to obtain films with good specifications and high homogeneity, and to study the effect of (MnO_2) doping on the structural and electrical properties of the prepared films.

After this introduction, it is necessary to refer to some previous studies related to this topic:

In 2015 researchers (Selma.A and A) conducted a study on doped and undoped thin films of (SnO_2) using chemical thermal decomposition technique. The prepared films had a thickness of 300 nm and were annealed at a temperature of 500°C for one hour. Scanning electron microscopy (SEM) examinations showed that the average grain size decreased with increasing doping concentration [13]

In 2017 Researchers (Othman. A and M.H.S) conducted a study on CdO/SnO_2 thin films prepared using chemical deposition on glass substrates at a temperature of 300 degrees Celsius. The Hall Effect study demonstrated that all the films had negative charge carriers. Furthermore, the gas sensitivity study revealed that the highest sensitivity to nitrogen oxide gas was observed at a 10% cadmium oxide ratio and a temperature of 200 degrees Celsius, with a response time of 14.6 seconds and a recovery time of 57 sec [14]

In 2019 Researchers (A.G.H) conducted a study on thin films (SnO_2/TiO_2, CuO/TiO_2). The samples were prepared using techniques such as high-angle X-ray diffraction, X-ray reflectivity, and scanning electron microscopy. It was found that the surface of SnO_2 and CuO exhibited well-developed structures with uniform distribution of TiO_2 particles [15].

In 2019 Researchers (Asil.A and K.E) conducted a study to prepare thin Al/Cdo/Mn films using the sol-gel technique. Scanning electron microscopy (SEM) images showed cubic structures of cadmium and manganese, indicating frequency differences at 499. Additionally [16].

In 2020 Researchers (Kiruba and H) conducted a study on the preparation of $NioSnO_2$ membranes and the fabrication of porous thin-film devices using the n-SnO_2/p-NiO spray technique. The electrical characterization of the bilayer devices across the interface confirmed response values (SnO_2) ranging from (144% to 157%) for a concentration range of (2-10) parts per million [17].

Experimental

The chemical spray pyrolysis (CSP) technique was used to obtain thin films of Tin Dioxide (SnO_2) doped with Manganese Dioxide (MnO_2). The fabrication process of the prepared thin films was carried out on glass substrates with dimensions of (2.5x2.5) cm^2, at (350 °C). The solution was subjected to ultrasonic treatment for (15 min) to achieve a clean surface. The effect of Hall measurements was studied to determine the efficiency of the semiconductor using an (HMS 300) device, This device operates based on the (Van Der Pauw) method and is connected to a computer equipped with software that displays the important parameters of the sample under examination, such as the type of semiconductor, carrier concentration, mobility, and Hall coefficient, The surface morphology of the prepared films was also studied using a Field Emission Scanning Electron Microscope (FE-SEM) of the (MIRA3, Model-TE-SCAN) type, located at the University of Tehran, Islamic Republic of Iran. The (FE-SEM) device enables the determination of particle shape, homogeneity, as well as the detection of crystalline structure defects.

Results and Discussion

A morphological study was conducted on the surfaces of all Thin Films prepared using Field Emission Scanning Electron Microscopy (FE-SEM), which provides high-resolution and high-magnification surface images. Figures (1-a-b-c) an illustrate (FE-SEM) images showing a non-homogeneous granular morphology with clusters of SnO_2 prepared on glass substrates, with the clusters being large [18]. The particle cluster size decreases with increasing manganese oxide (MnO_2) doping ratio [19]. The reason for this decrease is the dispersion of manganese oxide (MnO_2) particles within the crystalline lattice of tin oxide (SnO_2) [20]. This is agreement with the results conducted by the (Selma.A and A at el) [13]. The largest particle clusters were observed in the pure SnO_2 Thin Film, while the lowest value for cluster size was found in the thin Film doped with an 8% ratio of manganese oxide, The thickness of the formed film layer is approximately 243.63 nm as shown in fig.(1-D) , Despite the films being formed in three layers, no boundaries were observed in the FE-SEM images. This indicates the possibility of controlling the thickness of tin oxide (SnO_2) and manganese oxide (MnO_2) Thin Films by depositing a layer in the range of (200-30) nm.

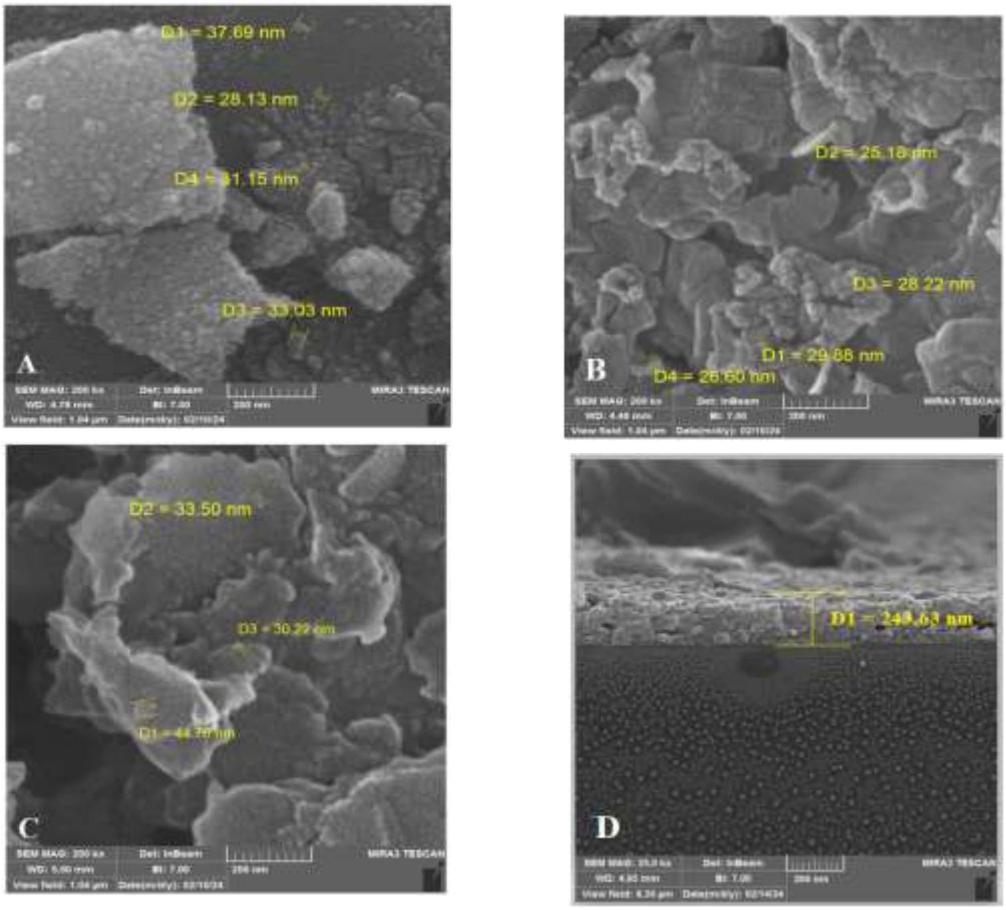

Figure 1: FE-SEM Images of : A- (SnO_2 Pure), B ($SnO_{2(0.98)}$: $MnO_{2\ (0.02)}$) , C- ($SnO_{2(0.92)}$: $MnO_{2\ (0.08)}$) , and D- thickness for the prepare film

A study was conducted to investigate the effect of doping pure tin dioxide (SnO_2) thin films with manganese dioxide (MnO_2)[21,22].Table(1) shows the thin films were doped with different doping ratios (2%, 4%, 6%, 8%) in order to determine the concentration and type of charge carriers, as well as the Hall coefficient, electrical conductivity, resistivity, and mobility at room temperature. It was found that both pure tin dioxide (SnO_2) films and those doped with manganese dioxide (MnO_2) exhibited negative (n-type) charge carriers, as indicated by the Hall coefficient values [23]. This is agreement with the results conducted by the (Othman. A and

M.H.S at el) [14]. This can be attributed to the influence of temperature and impurities present in the environment during the preparation process [24]. The table (1) shows the measurement results of the Hall effect, where an increase in the Hall coefficient values with increasing manganese dioxide (MnO_2) doping ratio is observed, reaching a maximum value at a doping ratio of 6%. On the other hand, the resistivity values indicate that the highest value was obtained for the film doped with 2% manganese dioxide (MnO_2), while the conductivity values were low and increased with increasing doping ratio reaching the highest value at a ratio of 8% manganese dioxide (MnO_2). As for the mobility, its value decreases with increasing manganese dioxide doping ratio, with the lowest value recorded for the film doped with 8% manganese dioxide (MnO2)[25,26],The figures(2,3,4) illustrate the Hall coefficient, resistivity, and charge carrier concentration as functions of the doping ratio for all prepared films This is agreement with the [27]. Previous study (Kiruba and Hmm)[17].

Table 1: Hall Effect measurements for the prepared thin films.

Sample	Concentration $(cm)^{-3}$	Hall Coefficient RH (m^2/C)	Conductivity $(\Omega.cm)^{-1}$	Resistivity (Ω.cm)	Mobility (cm^2/v.s)
SnO_2	-8.487×10^{11}	-7.355×10^{7}	1.718×10^{6}	5.822×10^{5}	1.263×10^{3}
$(SnO_2)_{0.98}(MnO_2)_{0.02}$	-2.059×10^{11}	-3.031×10^{7}	1.114×10^{6}	8.975×10^{5}	3.377×10^{3}
$(SnO_2)_{0.96}(MnO_2)_{0.04}$	-2.368×10^{11}	-2.636×10^{7}	1.885×10^{6}	5.305×10^{5}	4.970×10^{3}
$(SnO_2)_{0.94}(MnO_2)_{0.06}$	-4.787×10^{11}	-1.304×10^{7}	1.129×10^{6}	8.861×10^{5}	1.472×10^{3}
$(SnO_2)_{0.92}(MnO_2)_{0.08}$	-1.909×10^{11}	-3.269×10^{7}	3.970×10^{6}	2.519×10^{5}	1.298×10^{3}

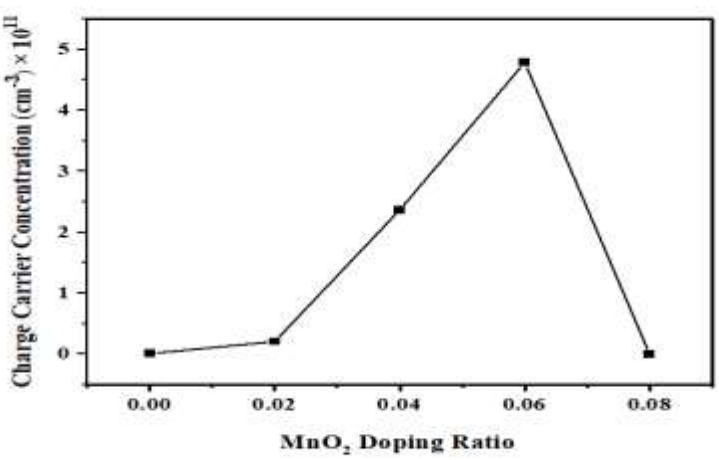

Figure 2: Concentration of charge carriers for the prepared films

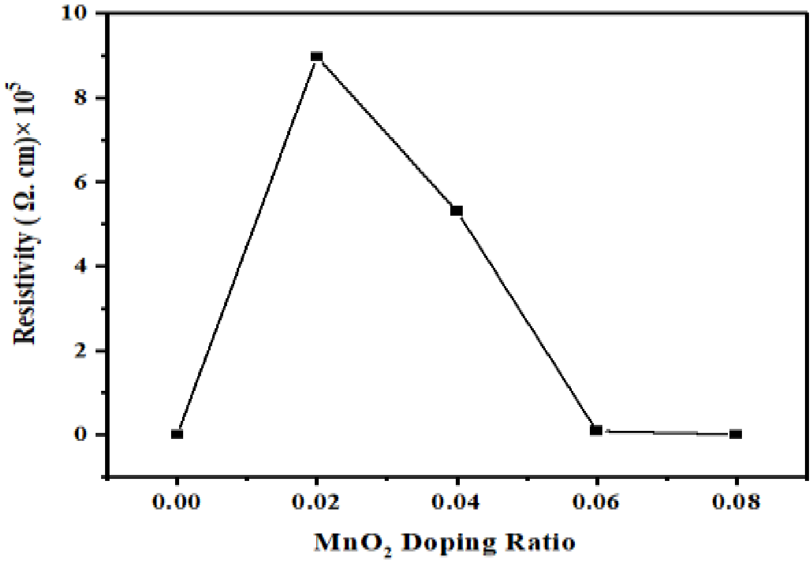

Figure 3: The resistivity for the prepared films

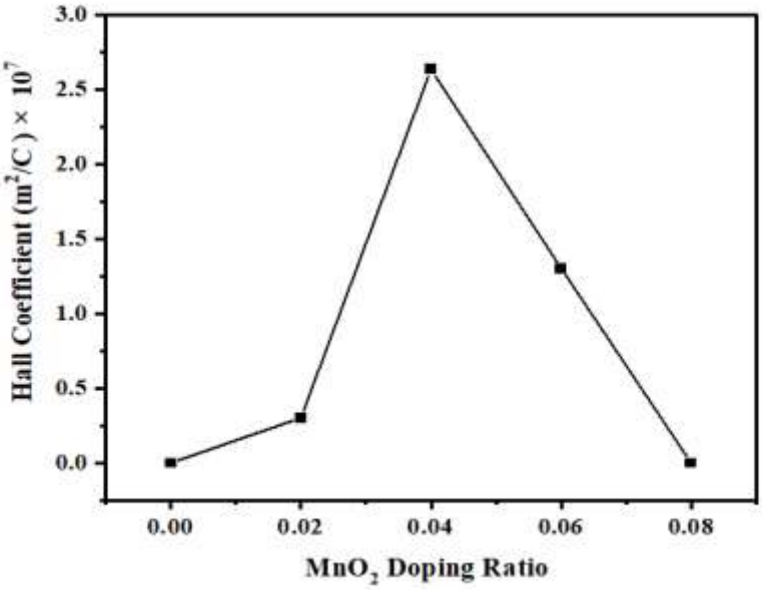

Figure 4: The Hall coefficient for the prepared films

Conclusions

In this research, the technique of chemical spray pyrolysis was used to prepare tin oxide (SnO_2) membranes doped with manganese oxide (MnO_2) at different ratios (2%, 4%, 6%, 8%), deposited on glass substrates at high temperatures. FE-SEM was used for spectral analysis and electrical measurements to verify the prepared samples. It was observed that the SEM measurement shows inhomogeneous granular structures, where they are in the form of large groups, and the size of these groups decreases with the increase in the doping ratio of manganese oxide (MnO_2). As for the electrical measurements, they were used to determine the type and concentration of charge carriers, as well as the Hall coefficient, electrical conductivity, resistivity, and mobility. The prepared membranes showed that the charge carriers are of type (n) according to the Hall coefficient, and the reason for this is the effect of temperature and impurities, where the Hall coefficient is observed to increase with the increase in the doping ratio of manganese oxide (MnO_2).

Source of funding: This research received no funding.

Conflict of interest: The authors declare that there is no conflict of interest.

Ethical clearance: Ethical approval was not required for this study.

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